

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JANUARY, 1930.

### General, Physical, and Inorganic Chemistry.

**Dissymmetry of emission of series lines.** J. STARK (Nature, 1929, 124, 946).—Of the hydrogen series lines  $3p^2H_\alpha \pm 1$ ,  $4p^2H_\beta \pm 6$ ,  $5p^2H_\gamma \pm 13$  ( $2s - mp^2$ ),  $4d^3, f^3H_\beta \pm 4$ ,  $5d^3, f^3H_\gamma \pm 10$  ( $2p^2 - md^3, f^3$ ),  $4p^4H_\beta \mp 2$ ,  $5p^4H_\gamma \pm 3$  ( $2s - mp^4$ ),  $6d^5, f^5H_\beta \pm 6$  ( $2p^2 - md^5, f^5$ ), and  $6p^6H_\beta \mp 2$  ( $2s - mp^6$ ) those which are displaced by an electric field towards the red or violet are, respectively, more intense opposite to or along the direction of the field. Similar regularities were observed with helium lines. A. A. ELDRIDGE.

**Band spectrum of helium.** W. E. CURTIS (Trans. Faraday Soc., 1929, 25, 694—707).—The present position is summarised. A strong triplet and a weaker singlet system exist. The structure of successive bands in a sequence shows a progressive change due to a change of coupling, the transition giving rise to anomalies of structure and intensity. The values of the electronic terms, the vibration frequencies, and the rotation term differences for the first and last members of each sequence are tabulated. The structure of a number of bands is shown graphically to illustrate the effects of the uncoupling process, and the second differences of the rotation terms are plotted. The correlation between electronic terms for coupling to the nuclear and to the rotation axis, respectively, is shown.

N. M. BLIGH.

**The rotation structure of the bluish-green lithium bands.** K. WURM (Z. Physik, 1929, 58, 562—569).—An analysis of the fine structure of two bands of the bluish-green band system of the lithium molecule is made and the molecular constants are calculated. The occurrence of the intensity variation within the single branches is investigated.

A. J. MEE.

**Spectrum of oxygen under different conditions of excitation.** D. B. DEODHAR and S. K. DUTT (Phil. Mag., 1929, [vii], 8, 617—625).—At a pressure of 0.2—0.3 mm. the spectrum of oxygen in a Geissler tube has been compared with that obtained in a "field-free discharge" in a special type of quartz discharge tube. Striking differences between the two spectra have been observed. In addition, a new band head has been seen in the neighbourhood of  $\lambda$  4500 and is being investigated. M. S. BURR.

**"Flash" in the after-glow of the electrodeless discharge with change of pressure.** C. T. KNIPP and L. N. SCHEUERMAN (Phil. Mag., 1929, [vii], 8, 684—689).—An apparatus by which a sudden increase

of pressure may be produced in an electrodeless discharge tube is described. By means of this it has been shown that, during the after-glow which follows the electrodeless discharge in oxygen or nitrogen with traces of another gas, a flash is observed when the pressure is suddenly increased. The flash has the form of a flat disc which travels onward from the initial point of compression, and seems to accompany a pressure pulse. In air and oxygen the flash can be obtained, during the time of the after-glow only, over the whole range of pressures for which the after-glow is visible. The after-glow in nitrogen is very bright at first and diminishes gradually, having a maximum life of 125 sec., according to Thomson. The flash can be obtained during the whole time the after-glow is visible, the brilliancy of the former being, apparently, in direct proportion to that of the latter. Following the flash the after-glow is still visible, and continues to die out gradually, instead of disappearing completely with the flash as in oxygen. It seems likely that a real flash is obtained, and not merely a compression of the after-glow. If the after-glow is due to illumination which accompanies recombination in an ionised gas the flash may be explained by supposing that, on compression, the ions are pushed closer together, facilitating recombination. No flash should be obtained, therefore, on sudden expansion of the excited gas. Preliminary experiments favour this view. Newall (Proc. Camb. Phil. Soc., 1897, 9, 295) observed that, in a mixture of oxygen and nitrogen, the phosphorescence reaches a maximum at about 0.4 mm. and fades away as the pressure is either increased or decreased. If the initial pressure is higher than that for maximum phosphorescence, and the pressure is suddenly reduced during the after-glow, a wave of increased brightness travels along the tube towards the end remote from the pump.

M. S. BURR.

**Isotopes in band spectra.** R. T. BIRGE (Trans. Faraday Soc., 1929, 25, 718—725).—From an analysis of band spectra isotopes of oxygen of mass 17 and 18 (cf. Giauque and Johnston, A., 1929, 369, 736) and a carbon isotope of mass 13 in the spectrum of  $C_2$ , CO, and CN (cf. King and Birge, *ibid.*, 970) have been discovered. The analysis and theoretical calculations are described. The moment of inertia and frequency of vibration of two isotopes differ. The quantitative difference in any molecular constant for two isotope molecules can be calculated from the dependence of the various band spectra on mass.

N. M. BLIGH.

**New terms in the oxygen arc spectrum.** R. FRERICHS (Physical Rev., 1929, [ii], 34, 1239—1246).—The oxygen arc spectrum, in absence of bands, was excited in large-diameter heavy-current discharge tubes and in narrow capillary quartz discharge tubes, and grating spectrograms with large dispersion were made. The green auroral line 5577.35 Å. appeared strongly in both tubes. Fifty new lines are tabulated and classified, involving six new triplet terms and one new singlet term based on the  $2s^2 2p^3(^2D)$  and  $2s^2 2p^3(^2P)$  configurations. A comparison is made with the terms to be expected on the Hund theory and an energy level diagram is given and discussed in detail. N. M. BLIGH.

**Low atomic energy levels for elements of the oxygen group.** J. C. McLENNAN and M. F. CRAWFORD (Nature, 1929, 124, 874).—The energy levels  $^3P_{0,1,2}$ ,  $^1D_2$ , and  $^1S_0$  for neutral oxygen, sulphur, selenium, and tellurium are tabulated. It is shown that close triplets in the neighbourhood of 9530 and 3520 Å. would be expected in the spectrum of the polar aurora and in that of the night sky. Lines analogous to the auroral green line of oxygen are: sulphur, 6300 Å.; selenium, 7247.5 Å.; tellurium, 7909.2 Å. A. A. ELDRIDGE.

**High-intensity non-reversed sodium arc.** C. J. CHRISTENSEN and G. K. ROLLEFSON (Physical Rev., 1929, [ii], 34, 1154—1156).—An improved high-intensity sodium arc on the Cario-Lochte-Holtgreven principle (cf. A., 1927, 489), for exciting the fluorescence radiation of sodium vapour by the 3303 Å. resonance radiation, is described. N. M. BLIGH.

**Influence of the method of excitation on transition probabilities in sodium vapour.** C. J. CHRISTENSEN and G. K. ROLLEFSON (Physical Rev., 1929, [ii], 34, 1157—1166).—Using an improved source of excitation (cf. preceding abstract) the fluorescence spectrum of sodium vapour was excited at 180° by the second member of the principal series, 3303 Å., and the transitions from the 3P level were studied. The transition probabilities  $3P \rightarrow 2S$  and  $3P \rightarrow 1S$  were found to be approximately equal, whereas for the low-voltage arc excitation, Weiss (cf. Ann. Physik, 1929, [v], 1, 565) reported a value of 25:1 for this ratio. The difference is concluded to indicate that, contrary to the accepted view, the transition probabilities are not independent of the method of excitation. N. M. BLIGH.

**Excitation of the Mg II spectrum by impacts of the second kind with metastable atoms and ions of the rare gases.** O. S. DUFFENDACK, C. L. HENSHAW, and (Miss) M. GOYER (Physical Rev., 1929, [ii], 34, 1132—1137).—The Mg II spectrum was excited in normal low-voltage arcs in mixtures of magnesium vapour with hydrogen, argon, neon, and helium, respectively, in a tungsten furnace apparatus, and the densities of the spectral lines were measured with a Moll microphotometer. Wave-lengths, classifications, excitation potentials, and relative densities are tabulated. The mechanism of the excitation is discussed. N. M. BLIGH.

**Recombination spectra of halogens and the probability of molecular formation from the**

**atoms.** V. KONDRATJEV and A. LEIPUNSKY (Trans. Faraday Soc., 1929, 25, 736—737).—The thermoluminescence spectrum of various halogen vapours at 1000° corresponds with the respective absorption spectrum, and consists of bands in the long-wave region followed by a continuum in the short-wave region. The bands are considered to arise from simple thermal collisions between molecules, and the continuum from the recombination of atoms proceeding according to the scheme  $X + X' \rightarrow X_2 + h\nu$ , where X is a halogen atom and X' an excited atom. The probability of such a process is determined for bromine and shown to be rare. N. M. BLIGH.

**Wave-lengths and atomic levels in the spectrum of the vacuum iron arc.** K. BURNS and F. M. WALTERS, jun. (Pub. Allegheny Obs., 1929, 6, 159—211).—Wave-lengths of about 600 lines of Fe I between 2800 and 8800 Å. emitted by a vacuum arc have been measured with a median accuracy of 1 in  $5 \times 10^3$ , and the results have been used to compute the wave-lengths of about 1200 Fe I lines between 2100 and 9000 Å. CHEMICAL ABSTRACTS.

**Spark spectrum of copper, Cu II.** G. KRUGER (Physical Rev., 1929, [ii], 34, 1122—1131; cf. Shentstone, A., 1927, 389).—Using a Schüler lamp of the hollow-cathode type as a source, the spectrum of copper for the region 0—2600 Å. was photographed on a single plate by means of a specially designed vacuum spectrograph. Complete terms and term values and all classified lines and the assigned term combinations from which the line arises are tabulated. Two higher members of the  $3d^9 ns^1 D^3 D$  series were found, and the limits of the series were calculated, showing that the  $3d^{10} ^1S_0$  level lies 163634.2 cm.<sup>-1</sup> below the  $3d^9 ^2D_{5/2}$  of Cu III, from which the ionisation potential of Cu II is 20.2 volts, placing the first members of the  $3d^9 ns^3 D_{3,2,1}$  series at 141709.2, 140790.7, and 139639.5 cm.<sup>-1</sup>, respectively. Higher members of the  $3d^9 np^1 (P^0 D^0 F^0)^3 (P^0 D^0 F^0)$  series were identified, and Hund's predictions on series limits (cf. A., 1929, 363) were confirmed. The revised notation (cf. *ibid.*, 967) is used. N. M. BLIGH.

**Influence of argon and of hydrogen on the spectra of zinc vapour.** J. G. BLACK, W. G. NASH, and C. A. POOLE (Physical Rev., 1929, [ii], 34, 1138—1141; cf. Crew, A., 1929, 366).—The low-voltage arc spectrum of zinc in pure zinc vapour, alone and with hydrogen or argon, was photographed and the relative intensity decreases and increases for a number of lines under the three conditions are tabulated. The strong resonance line 3075 Å. was strong in the zinc-argon mixture, but was not found in the zinc-hydrogen mixture. N. M. BLIGH.

**Fine structure of spectral lines.** J. C. McLENNAN and (Miss) E. J. ALLIN (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 7—11).—Using a Paschen electrode in a quartz tube the lines in the visible region of the lead spark spectrum were analysed with high resolution. It is concluded that the levels  $^2S_{1/2}$ ,  $^2D_{3/2}$  are simple,  $^2P_{1/2}$ ,  $^2P_{3/2}$  are each double with different separations, and  $^2D_{5/2}$  is complex. Results are compared with those for the fine structure of the lines of the



thallium arc. The origin of the hyperfine structure of many lines in the spectra of atoms is discussed.

N. M. BLIGH.

**Fine structure of spectral lines.** J. C. MCLENAN and (Miss) E. J. ALLIN (Phil. Mag., 1929, [vii], 8, 515—520).—A continuation of previous work (cf. preceding abstract). The fine structure was investigated of the spectra of Zn II and Cd II, using the hollow cathode discharge, and of Ba I and La II, using a salt of the metal in a carbon electrode. Results are tabulated and an energy level diagram is given for the lines of Ba I. It is concluded that there is no similarity between the structure of a line in an arc spectrum and the structure of a line in the homologous series of the corresponding first spark spectrum, a result in agreement with the theoretical origin of the fine structure of a spectral line in the spin of the nuclei of the atoms giving rise to it.

N. M. BLIGH.

**Magnetic analysis of a spectrum by means of the unresolved Zeeman patterns and its application to Ag II.** A. G. SIENSTONE and H. A. BLAIR (Phil. Mag., 1929, [vii], 8, 765—771).—To obtain a complete magnetic analysis of a spectrum, the Landé magnetic factors "*g*" are required. A method for determining these from the unresolved Zeeman patterns of weak lines is discussed, and applied to the silver spark spectrum obtained by an experimental arrangement which is described. A Hilger E1 quartz spectrograph, with a resolving power at  $\lambda$  2500 of approximately 40,000, is used. The *g*-values of most of the terms are reasonably near the Landé values, with the following exceptions: (a) terms of the structure  $4d^25p$  and  $J=2$ ; (b) terms of the structure  $4d^25d$ ,  $J=2$  and  $J=1$ . The marked departure of these measured values from the theoretical involves the question of the relative importance which is to be assigned to the *g*-values and to the intensities of combinations, respectively, in the designation of the levels of the spectrum.

M. S. BURR.

**Intensity relationships in the principal series of caesium.** C. FÜCHTBAUER and H. W. WOLFF (Ann. Physik, 1929, [v], 3, 359—372).—The intensity ratios for the doublet components  $1s-3p_1=4593 \text{ \AA.}$ ,  $1s-3p_2=4555 \text{ \AA.}$ ;  $1s-4p_1=3889 \text{ \AA.}$ ,  $1s-4p_2=3877 \text{ \AA.}$  in the caesium emission spectrum have been measured by means of photographic photometry. The caesium was vaporised in a high vacuum in a glow cathode tube without addition of foreign gases. Improvements in photometric technique are recorded. The second member of the principal series (4555) shows a small change in the intensity ratio from 3.12 to 2.90 with changing vapour pressure, the effect being due to self-absorption. When this effect is eliminated (extrapolating to zero self-absorption) the ratio is 1:3.3. For the other doublet (3877) the measurements were carried out over the temperature range 112—130°, corresponding with a vapour pressure change of 1:2.7, and the intensity ratio was found to be constant at 1:4.6 within the limits of error (extreme values 1:4.24, 1:4.91).

R. A. MORTON.

**M-Series absorption spectra of metallic platinum and gold.** A. J. M. JOHNSON (Physical

Rev., 1929, [ii], 34, 1106—1114).—Discrepancies between the experimentally observed and theoretically deduced positions of the discontinuities in the *M*-absorption spectra of osmium, iridium, and platinum reported by Rogers (cf. A., 1928, 101) were attributed partly to a "chemical effect." Employing a vacuum spectrograph the *M*-absorption spectra of platinum and gold were investigated, using absorption screens of the pure elements. Discontinuities were found for platinum at 5.711 ( $M_1$ ), 5.506 ( $M_2$ ), 4.677 ( $M_3$ ), 4.085 ( $M_4$ , very faint), and 3.742  $\text{\AA.}$  ( $M_5$ ), and for gold at 5.506 ( $M_1$ ), 5.315 ( $M_2$ ), 4.501 ( $M_3$ ), and 3.603  $\text{\AA.}$  ( $M_5$ ). Values of  $(\nu/R)^{1/2}$ , found experimentally and theoretically, are plotted against atomic numbers, and discrepancies in the case of  $M_1$  and  $M_2$  are confirmed (cf. also Lindberg, A., 1929, 746).

N. M. BLIGH.

**Spectrum of the neutral mercury atom in the wave-length range from 1 to 2  $\mu$ .** E. D. MCALISTER (Physical Rev., 1929, [ii], 34, 1142—1147).—Using a special thermocouple and an automatic recording spectrograph, the near infra-red spectrum of mercury was investigated. Wave-lengths, relative intensities, classifications, and frequencies for 45 lines are tabulated; 14 new lines predicted by the combination principle and 8 unclassified lines were found. Relative intensities in the principal triplet  $1^3S_1-2^3P_{0,1,2}$  are given.

N. M. BLIGH.

**Normal quadratic Zeeman effect.** E. GUTH (Z. Physik, 1929, 58, 368—372).—From wave-mechanical considerations an approximate expression is deduced for calculating the maximum extent of the Zeeman separation towards the violet conditioned by the quadratic Zeeman effect. Calculations of the shift for the thirteenth Balmer line in a magnetic field of 30,000 gauss lead to figures in good agreement with experiment. The method is unsuited to a differentiation between the older and newer quantum theories.

J. W. SMITH.

**Theory of normal Zeeman effect.** O. HALPERN and T. SEXL (Ann. Physik, 1929, [v], 3, 565—574).—Mathematical. The expression derived by the use of wave mechanics does not agree completely with that obtained from the old quantum theory.

A. J. MEE.

**Determination of heats of dissociation by means of band spectra.** R. T. BIRGE (Trans. Faraday Soc., 1929, 25, 707—716).—Previous methods of calculation (cf. A., 1926, 993) are amplified, and a new method of plotting vibration frequencies leading to more accurate values of heats of dissociation *D* is described, and illustrated in the case of the  $O_2$  and  $H_2$  molecules, the values of *D* being calculated by extrapolation. The curve for the *B* level of  $H_2$  indicates a transition from ionic to atomic binding. For the neutral  $N_2$  molecule *D* is found to lie between 8.84 and 9.24 volts, the most probable value being 9.1 volts. *D* is given for  $O_2$  6, for NO 6.6, and for CO 10.3 volts.

N. M. BLIGH.

**Band spectra and electronic states of some metal hydrides.** E. BENGTSSON and E. HULTHÉN (Trans. Faraday Soc., 1929, 25, 751—757).—The spectra of the neutral or ionised metal hydrides of the first, second, and third groups of the periodic

table were studied in the light of the theory of electronic states in diatomic molecules, and a simple treatment of the stability problems of the hydrides is obtained. Data and quantum assignments for the band spectra of the hydrides of copper, silver, gold, zinc, cadmium, mercury, magnesium, and aluminium are tabulated and discussed. The view is supported that an intermediate molecular state of some stability is formed when the adiabatic transition between the states of the separate atoms into those of the combined atoms involves a large energy drop and *vice versa*, and that a corresponding state of the combined atoms of the hydride generally forms the origin to a molecular state in the succeeding hydride.

N. M. BLIGH.

**Spectra of metal molecules.** S. BARRATT (Trans. Faraday Soc., 1929, 25, 758—762).—The presence of bands in the absorption spectra of the vapours of some metals and alloys indicates the presence of di- or poly-atomic molecules. The spectra of vapours of mixtures of cadmium, zinc, and mercury with those of the alkali metals were examined, and the relationships between the band spectra and the atomic line absorption spectra and their explanation in terms of molecular structure were studied. Electronic band systems showing fine structure, and isolated diffuse bands with no fine structure were found. The positions of the heads of the diffuse bands corresponding with the different molecules are tabulated. The most important characteristic of this group of spectra is the uniform presence of the diffuse band, which is suggested as representing the dissociation spectra of the corresponding molecules (cf. A., 1928, 812). The calculation of the heat of formation of the molecules from the position of the bands is discussed.

N. M. BLIGH.

**Determination of work of dissociation of molecules from band spectra.** J. FRANCK and H. SPONER (Nachr. Ges. Wiss. Göttingen, 1928, 241—253; Chem. Zentr., 1929, ii, 132—133).—Theoretical.

A. A. ELDRIDGE.

**Origin of the spark lines in X-ray spectra.** B. B. RAY (Phil. Mag., 1929, [vii], 8, 772—778).—The characteristics of the so-called "spark" lines in X-ray spectra are described. The explanations offered as to their origin are discussed, and another interpretation is suggested on the basis of the supposition that, during excitation, two electrons are ejected simultaneously, one from  $K_1$  and the other from  $L_1$ , resulting in a rearrangement by which one electron passes from  $L_2$  to  $K_1$ .

M. S. BURR.

**Wave-length determinations in the  $L$  series of the elements from copper to calcium with the plane-grating spectrograph.** G. KELLSTRÖM (Z. Physik, 1929, 58, 511—518).—The  $L$  spectra of the elements from copper to iron, chromium, and titanium to calcium, comprising the elements of atomic numbers 29 to 26, 24, and 22 to 20, were measured relative to the aluminium  $K\alpha$  line. An optical plane glass grating with 591 lines per mm. was used. For each element (except nickel, where only a weak plate was obtained) two lines were obtained which correspond with the doublets  $\alpha\beta$  and  $l\eta$ . These doublets are not separated, but a comparison with the values obtained by Thoræus

shows that the weaker components  $\beta$  and  $\eta$  exert no noticeable effect on the results. The wave-lengths extend from copper,  $L\alpha$  (13.32 Å.), to calcium  $Ll$  (40.90 Å.). The intensities of the  $L\alpha$  lines decrease with the atomic numbers, so that for calcium  $l\eta$  is much stronger than  $\alpha\beta$ .

A. J. MEE.

**$K$ -Series of the elements 48 Cd and 49 In.** J. VALASEK (Physical Rev., 1929, [ii], 34, 1231—1233).—Using a precision spectrograph (cf. Larsson, A., 1927, 603) the wave-lengths of the  $\alpha_2$ ,  $\alpha_1$ ,  $\beta_3$ ,  $\beta_1$ , and  $\beta_2$  lines in the  $K$ -series of cadmium and indium were re-measured.

N. M. BLIGH.

**Intensity of reflexion of X-rays from diamond.** (Miss) A. H. ARMSTRONG (Physical Rev., 1929, [ii], 34, 1115—1121; cf. Ponte, A., 1927, 191).—Ionisation spectrometer measurements of the intensity of reflexion of the  $K\alpha$  doublet of molybdenum by fine diamond powder were made by the transmission method. Primary extinction is discussed; secondary extinction was probably negligible. From the peaks obtained by the ionisation method the relative intensities of the radiation reflected from different planes of the diamond were determined, and from them the relative atomic scattering factors were calculated by a modified Compton formula and placed on an absolute scale by comparison of the intensity of the (220) reflexion of diamond with that of the (220) reflexion of sodium chloride. The origin of the observed (222) reflexion is discussed.

N. M. BLIGH.

**Angular intensity distribution of continuous X-ray spectrum.** Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 11, 251—290).—Mathematical. The method of quantum mechanics is applied to the intensity of the continuous X-ray spectrum emitted from a thin target bombarded by cathode rays with a definite direction. Expressions connecting the angle between the directions of the cathode rays and emitted radiation and the intensity and polarisation are obtained which are in satisfactory agreement with experimental results (cf. Kuhlenskampff, A., 1929, 14).

N. M. BLIGH.

**Effect of filtration of general radiation on the X-ray diagrams of liquids. Coefficients of absorption.** J. THIBAUD and J. J. TRILLAT (Compt. rend., 1929, 189, 907—909).—To verify the theory (this vol., 19) explaining the secondary diffraction ring the coefficients of absorption ( $\mu_1$  and  $\mu_2$ ) have been determined for the monochromatic radiations  $\lambda = 0.707$  and  $1.54$  Å. ( $K\alpha$  of copper and molybdenum) by measurements with thicknesses of 4 and 8 mm. of acetic acid ( $\mu_1 = 0.73$ ,  $\mu_2 = 7.9$ ), heptioic acid ( $\mu_1 = 0.65$ ), nonoic acid ( $\mu_1 = 0.5$ ,  $\mu_2 = 4.95$ ), and molten stearic acid ( $\mu_1 = 0.5$ ,  $\mu_2 = 3.72$ ). Curves and tables show the relation between intensity and wave-length for unfiltered general radiation and for the same filtered through 8 mm. of nonoic acid, whence the dimensions of the secondary ring are calculated. The results agree well with those of experiment. The importance of eliminating this secondary ring in investigations of molecular structure is stressed.

C. A. SILBERRAD.

**Recoil in the Compton effect with hydrogen atoms.** G. WENTZEL (Z. Physik, 1929, 58, 348—

367).—Mathematical. The directional distribution of the recoil electrons produced by the scattering of hydrogen atoms is calculated according to Dirac's theory of radiation. J. W. SMITH.

**Relative intensities of nebular lines.** J. H. BARTLETT, jun. (Physical Rev., 1929, [ii], 34, 1247—1262).—Theoretical. The idea that quadrupole radiation is the important factor in causing the emission of nebular lines (forbidden for dipole radiation) is tested. The theoretically and experimentally strongest lines are in agreement, but not the weaker lines. The relative intensities of the lines of the multiplet  $2P \rightarrow 2D$  are found to be in the ratio  $3/2 \rightarrow 5/2 : 1/2 \rightarrow 3/2 : 3/2 \rightarrow 3/2 : 1/2 \rightarrow 5/2 = 10 : 5 : 2 : 1$ . In the multiplet  $1D \rightarrow 3P$  the line  $1D_2 \rightarrow 3P_2$  is strongest,  $1D_2 \rightarrow 3P_1$  is about half as strong, and  $1D_2 \rightarrow 3P_0$  varies from zero to a value of the order of that of  $1D_2 \rightarrow 3P_1$ . Bowen's hypothesis (cf. A., 1929, 536) attributing the emission of the "forbidden" nebular lines to quadrupole radiation is to some extent substantiated. N. M. BLIGH.

**Spectrographic investigation of the corona effect.** S. P. ŻEBROWSKI (Physikal. Z., 1929, 30, 687—692).—The ratio  $d_{\text{ultra-violet}}/d_{\text{visible}}$  for the corona,  $d$  being the diameter measured photographically using glass and quartz lenses, is 1.85. The corona spectrum consists of seven principal groups between about 297 and 434  $\mu$ , only one of which lies in the visible region. There are 42 lines mostly agreeing in wave-length with air lines, the intensity distribution being quite different in the two cases. The corona spectrum in neon also shows seven groups. Microspectrophotometric curves are recorded, and calculation of the energy distribution indicates for the corona in air that 16.75% of the whole optical energy refers to rays longer than 400  $\mu$ , whilst in neon the corresponding figure is 23.6%. R. A. MORTON.

**Variations of intensity distribution of the auroral spectrum and the possible influence of sunlight.** L. VEGARD (Nature, 1929, 124, 947—948).

**Filter radiometry.** D. C. STOCKBARGER and L. BURNS (Physical Rev., 1929, [ii], 34, 1263—1270).—It is shown that in order to avoid the error due to assuming the cut-off of a filter to be where the transmission of the filter becomes zero, the effective cut-off should be located at such a wave-length that the energy transmitted by the filter below this is equal to that selectively absorbed by it above the cut-off. This, in effect, compensates for the departure of the transmission curve from rectangular shape. This conclusion is illustrated by an application to two analyses of water-filtered quartz mercury arc radiation made by two glass filters. N. M. BLIGH.

**Measurement of spectral light intensities by photography.** G. R. HARRISON (J. Opt. Soc. Amer., 1929, 19, 267—316).—The general principles, apparatus, and methods, and some special methods of photographic spectro-photometry, are reviewed and compared critically in detail. Methods suitable for special spectral regions are also examined. N. M. BLIGH.

**Photo-electric thresholds of alkali metals.** N. R. CAMPBELL (Phil. Mag., 1929, [vii], 8, 667—

668).—The conclusions of Ives and Olpin (A., 1929, 968) that the photo-electric thresholds of thin films of the alkali metals are identical with the resonance potentials of their neutral atoms have a more limited application than these authors suppose. They may be true when the film is deposited on gas-free platinum or silver, or even when deposited on any surface which is gas-free, although experiment seems to show that this is probably not true for a deposit on gold. When, however, thin films of potassium are deposited on oxidised surfaces of copper (A., 1928, 1297), they have threshold potentials on the long wave-length side of 0.85  $\mu$ , whilst films of caesium, deposited on oxidised silver (Koller, Gen. Elec. Rev., 1928, 31, 476), have thresholds on the long wave-length side of 1  $\mu$ . The resonance potentials of potassium and caesium are 0.79  $\mu$  and 0.89  $\mu$ , respectively (Ives and Olpin, *loc. cit.*). M. S. BURR.

**A new form of quantised energy in the mercury atom. Possibility of a rotation.** R. G. LOYARTE (Physikal. Z., 1929, 30, 678—687).—All the well-established potentials recorded by various authors and not corresponding with quantum jumps between optical levels in the arc series of mercury are shown to be arrived at by addition or subtraction of 1.4 volts (or a multiple thereof) to or from such differences between levels. The new potential corresponds with an energy occasioned by a single act occurring once, when two elementary acts coincide, because a large number of optical lines are shown in which the wave numbers are reproduced accurately by adding or subtracting 11,316 (1.39 volts), or a multiple thereof, to or from the wave-numbers of the series lines. This result is ascribed to a quantised rotation of the mercury atom, corresponding in discrete energy with a free-axial rotator of wave mechanics. This rotation does not influence the theoretical value (5/3) of the specific heat of the mercury atom, and it is shown that mercury vapour is "degenerate" at the ordinary temperature and also at 2500° Abs. The mechanism of energy interchange during the collision of an electron with an atom conceived as a rotator is discussed together with the origin of the quantised rotation shown to exist for mercury. R. A. MORTON.

**Ionisation of air by cathode rays of 10—60 kilovolts.** A. EISEL (Ann. Physik, 1929, [v], 3, 277—313).—From the total ionisation of air by means of cathode rays of various velocities, the amount of energy  $\epsilon$  necessary for the formation of an ion pair is found to be independent of electron velocity and equal to  $32.2 \pm 0.5$  volts. This applies to electrons having velocities within the limits of 9—59 kilovolts, perpendicular magnetic deflexion being used for separating out the various velocity ranges. R. A. MORTON.

**Ionisation of halogens (except fluorine) and their methyl compounds by means of X-rays.** O. GAERTNER (Ann. Physik, 1929, [v], 3, 325—332).—For filtered copper radiation of mean wave-length 1.38 Å., the following values in volts per ion pair were obtained: chlorine 23.6, bromine 27.9, iodine 28.8, methyl chloride 26.0, methyl bromide 28.7, methyl iodide 29.8. The influence of the thickness of absorbing layer has been investigated (cf. A., 1929, 868). R. A. MORTON.

**Regulation of thermionic-electric current from oxide-covered metallic foils by irradiation with ultra-violet light.** E. BODEMANN (Ann. Physik, 1929, [v], 3, 614—628).—The properties of the photo-electronic emission from a heated oxide-covered platinum surface were investigated. The additional current produced with the photo-electric current on irradiation can be reduced to zero by out-gassing the foil. After the admission of dry air, and keeping the foil for some days, the additional current is restored to its original value after pumping out the air. The experiments lead to the conclusion that by irradiation during the giving up of gas by the foil the negative space charge becomes more active than without irradiation, and causes a checking of the photo-electric current.

A. J. MEE.

**Electron scattering in mercury vapour.** F. L. ARNOT (Proc. Roy. Soc., 1929, A, 125, 660—669).—A study has been made of the scattering of electrons of about 80 volts energy from an oxide-coated platinum filament by mercury vapour (pressure  $10^{-3}$  mm.), with the object of determining how the intensities of the elastic and the inelastic groups vary with the angle through which the electrons are scattered. There are three main groups: (1) those which have been elastically scattered; (2) those which have, in the process of being reflected by the atom, excited it to the resonance or some higher level; (3) those which on being scattered have ionised the atom. The data also show that when an 80-volt electron, on being scattered through  $10^\circ$ , ionises a mercury atom practically no energy is carried away by the ejected electron. The number of electrons scattered at an angle  $\theta$  decreases rapidly as  $\theta$  is increased. The elastic scattering curve falls off more sharply than it does in helium, for the same velocity of the primary beam (cf. Dymond and Watson, A., 1929, 368). Electrons that have made inelastic collisions fall off more sharply than the others, the curves crossing each other at  $\theta=15^\circ$ ; below this value there are more inelastically scattered electrons, above it, fewer. At angles greater than  $55^\circ$  there appear to be equal numbers of elastically and inelastically scattered electrons. The mean free path of an electron in mercury vapour at a pressure of 0.0012 mm. of mercury is about 40 cm.

L. L. BIRCUMSHAW.

**Electron scattering and high-frequency radiation.** J. A. C. TEEGAN (Phil. Mag., 1929, [vii], 8, 664—667).—Theoretical. Electrons, or de Broglie's electron waves, corresponding with  $940 \times 10^6$  volts, are calculated to have practically the same coefficient of absorption by matter as a  $\gamma$ -radiation of corresponding wave-length ( $0.013 \times 10^{-11}$  cm.). Thus it seems impossible to predict, from a study of its absorption, whether the most penetrating of Millikan's cosmic radiation is of a corpuscular or of a  $\gamma$ -ray nature.

M. S. BURR.

**Test for polarisation in a beam of electrons by scattering.** C. T. CHASE (Physical Rev., 1929, [ii], 34, 1069—1074; cf. Myers and Cox, this vol., 8).—High-speed  $\beta$ -particles from radium impinging on lead targets were twice scattered at right angles, and the number, counted at various azimuthal angles by a

point-discharge counter, was studied as the radium and upper target were rotated with respect to the counter and lower target. Counts taken at four azimuthal angles at  $90^\circ$  intervals showed no indication of polarisation, nor of the analogous effect found by Barkla for X-rays.

N. M. BLIGH.

**Emission of electrons from metals covered by thin films in intense electric fields.** T. E. STERN (Proc. Camb. Phil. Soc., 1929, 25, 454—460).—Mainly mathematical. The results of Fowler and Nordheim on the auto-electronic discharge (cf. A., 1928, 681) are extended to take into account the effect of thin films on the cathode. The films have a lower thermionic work function than the clean metal and greatly increase the electronic emission for any given intensities of the electric field; an emission formula for the case in which the electrons leaving the metal must penetrate a thin film is derived.

N. M. BLIGH.

**Production of high-speed electrons by indirect means.** E. T. S. WALTON (Proc. Camb. Phil. Soc., 1929, 25, 469—481).—An unsuccessful attempt was made to produce high-speed electrons by an arrangement similar to that employed in experiments on the electrodeless discharge in gases. Assuming the electrons to be thrown into circular paths by the magnetic field, the corresponding conditions for stability were calculated and a new apparatus was designed to comply with these conditions, but no definite results were obtained. The failure is attributed to stray fields sending the electrons to the walls of the vessel.

N. M. BLIGH.

**Refraction of electrons by ionic crystals.** E. RUPP (Ann. Physik, 1929, [v], 3, 497—506).—Electron deflexion experiments have been carried out on the ionic crystals of sodium and potassium chlorides and potassium bromide, using the method of electron reflexion with a constant angle of incidence and varying the velocity of the electrons. The curves showing reflected electron intensity against velocity in volts have the following maxima: sodium chloride (opposed field 15 volts) 18, 32, 42, 56, and 76 volts; potassium chloride 16, 29, 34 volts; potassium bromide 27, 40 volts, and 14 volts with an opposed field of 4.5 volts. These results conform to the de Broglie relation  $\lambda = (150/V_m)^{1/2} \times 10^{-8}$  cm.,  $\lambda$  agreeing well with the values given by  $n\lambda = 2d \sin \phi$ ,  $d$  being the value obtained from crystal analysis. The refractive index for electrons using ionic crystals differs little from unity, so that the inner lattice potential  $E_0$  [ $\mu = (V + E_0/V)^{1/2}$  for metallic crystals] is zero within the limits of error. The velocity distribution of the reflected electrons differs markedly from that obtained with metallic crystals. No effect traceable to the heavy metal in alkali halide phosphors can be detected.

R. A. MORTON.

**Ranges of ionising electrons in helium.** T. H. OSGOOD (Physical Rev., 1929, [ii], 34, 1234—1238).—Theoretical. The fourth-power law for the absorption of ionising electrons in helium is shown to agree with experiment only for initial energies greater than 250 electron volts. A relation is deduced between the range of an electron and its initial energy, which agrees with available data, and appears to be applic-

able, with suitable changes of constants, to other gases. N. M. BLIGH.

**Ionising action of fast electrons.** H. KÜLENKAMPFF (Physikal. Z., 1929, 30, 777—780).—The total ionisation in air produced by cathode rays of 9–60 kilovolts follows a strictly linear course, the mean energy required for an ion pair being 32.2 volts. Since this value is considerably greater than the (lowest) ionisation potentials for molecular nitrogen or oxygen, the integral ionisation effect must be a complicated process. The intensities of *K*-lines in relation to cathode-ray velocity have been studied for copper, the results being presented as the variation of  $S_K$  (number of atoms showing *K*-ionisation) with  $U = V/V_K$  (ratio of cathode-ray energy  $V$  to excitation energy  $V_K$ ). The interpretation of the results is discussed. R. A. MORTON.

**Disordered movement of electrons in gases.** R. SEELIGER and T. HANDT (Ann. Physik, 1929, [v], 3, 575—584).—Light emission excited by electron impacts is partly linearly polarised in a certain direction, which is oriented with respect to the direction of the collision. From the amount of polarisation it is possible to reach conclusions regarding the direction of electron impact. An apparatus is described for finding the polarisation of the mercury 4347 line, the emission of which was caused by electron collisions. The degree of polarisation was found under varying conditions. In the first cathode layer there was a considerable degree of polarisation amounting to more than 0.25. In other regions the degree of polarisation was zero or negligible. In these parts the slower electrons at least must be quite disordered in their motion. A. J. MEE.

**Method of measuring the polarisation of electronic collision glow.** J. LASS (Ann. Physik, 1929, [v], 3, 701—720).—The polarisation was investigated with reference to the velocity of the colliding electrons. The degree of polarisation shows, within the range examined, no discontinuity. A. J. MEE.

**Examination of field changes in respect of the *K*-shell by means of *H*-particles.** C. GERTHSEN (Ann. Physik, 1929, [v], 3, 373—408).—The scattering of *H*-canal rays by manganese agrees to within about 10% with Rutherford's theory. The deviations have been traced to the action of *K*-electrons, the screening effect of which has been estimated. Penetration of the *K*-shell is not accompanied by a constant increase in the scattered intensity (for larger angles and proportional to the square of the effective nuclear charge), the higher effective nuclear charge merely effecting a change in the normal angular distribution. R. A. MORTON.

**Recent investigations on canal rays.** H. R. VON TRAUBENBERG (Physikal. Z., 1929, 30, 750—758).—A lecture in which various investigations depending on the use of canal rays are reviewed. R. A. MORTON.

**Detection of atomic disintegration in aluminium by measuring the ionisation of a single *H*-ray.** H. POSE (Physikal. Z., 1929, 30, 780—782; cf. A., 1929, 963, 971).—A more detailed account of earlier work. R. A. MORTON.

**Effective cross-section of inert-gas molecules towards electrons below 1 volt.** C. RAMSAUER and R. KOLLATH (Ann. Physik, 1929, [v], 3, 536—564, and Physikal. Z., 1929, 30, 760—766; cf. A., 1929, 1123).—The curve, electron velocity in volts/effective cross-section (in cm.<sup>2</sup>/cm.<sup>3</sup> at 0° and 1 mm. Hg), for helium is approximately horizontal between 0.16 and 2 volts, two ill-defined minima and one maximum, however, being indicated. For neon, the curve shows a very slow increase in cross-section with increasing velocity over the same range. For argon, krypton, and xenon minima are shown at 0.3<sub>7</sub>, 0.6<sub>0</sub>, and 0.6<sub>5</sub> volt, respectively, whilst the maxima are at 13.<sub>2</sub>, 11.<sub>3</sub>, 6.<sub>4</sub> volts. The curves increase in steepness in the order argon, krypton, xenon. Quantitative data indicate considerable errors in earlier work. The principal results for helium, neon, and xenon are supported by a qualitative method depending on the change in shape and location of the magnetic velocity distribution curve in vacuum and in the gas. R. A. MORTON.

**Is there an isotope displacement in the spectrum of cadmium?** S. GOUDSMIT (Naturwiss., 1929, 17, 805—806; cf. Schüller and Brück, A., 1929, 967).—Theoretical. The isotope effect with cadmium would be very small, and within the limits of accuracy of the instruments used. A. J. MEE.

**Rate of emission of  $\alpha$ -particles from radium.** F. A. B. WARD, C. E. WYNN-WILLIAMS, and H. M. CAVE (Proc. Roy. Soc., 1929, A, 125, 713—730).—A determination has been made of  $Z$ , the number of  $\alpha$ -particles from disintegrations taking place in 1 g. of radium per sec., by directly counting the number of particles emitted within a known very small solid angle. A new type of electrical counter, due to Greinacher (A., 1926, 553; 1927, 915), is employed. The ionisation produced by a single  $\alpha$ -particle is linearly amplified by triode valves, there being no ionisation by collision. The final deflexion of the recording instrument is proportional to the initial ionisation, and the counting of  $\alpha$ -rays, which can be carried out accurately at a high rate (i.e., about 500 particles per minute), is undisturbed by the presence of  $\beta$ -rays. As a mean of several determinations, the value  $Z = 3.66 \times 10^{10}$   $\alpha$ -particles per sec. per g. of radium is obtained. This can be directly compared with the value  $3.69 \times 10^{10}$  recently found by the "total charge" method by Braddick and Cave (A., 1929, 6), since the same radium standard was used in both experiments and the type of source and method of  $\gamma$ -ray comparison was the same. The probable error in the value of  $Z$  is estimated at about 0.5%, assuming the value of the standard to be accurately known. L. L. BIRCUMSHAW.

**Quantum mechanics of  $\alpha$ -rays.** R. D'E. ATKINSON and F. G. HOUTERMANS (Z. Physik, 1929, 56, 478—496).—Theoretical. A. J. MEE.

**Collision between free and combined  $\alpha$ -particles.** J. KUDAR (Z. Physik, 1929, 58, 129—133).—According to wave mechanics it would appear possible that by bombardment of radioactive atomic nuclei by  $\alpha$ -particles, collisions would occur between free and combined  $\alpha$ -particles such that the impinging

$\alpha$ -particle does not enter the inner nucleus of the atom. The probability of such collisions is calculated.

J. W. SMITH.

**Transmission of  $\beta$ -rays through magnetised iron foil: an attempt to polarise a beam of electrons.** F. E. MYERS and R. T. COX (Physical Rev., 1929, [ii], **34**, 1067—1068; cf. Cox and others, A., 1928, 1169).—A beam of  $\beta$ -rays from radium was transmitted through two magnetised iron foils, and a Geiger counter was used to find the number penetrating both foils with varying angles between their directions of magnetisation. No evidence of polarisation of the beam was obtained.

N. M. BUGH.

**Emission of  $\beta$ -rays in radioactive change.** L. B. LOEB (Physical Rev., 1929, [ii], **34**, 1212—1216).—Theoretical. The relations between  $\beta$ -rays and  $\gamma$ -rays in radioactive disintegration are summarised. The mechanism of the emissions and the theoretical difficulties of simultaneous escape of  $\beta$ -rays with varying velocities and of  $\alpha$ -rays of constant energy are discussed.

N. M. BUGH.

**Upper limits of energy in the  $\beta$ -ray spectra of actinium-*B* and actinium-*C''*.** B. W. SARGENT (Proc. Camb. Phil. Soc., 1929, **25**, 514—521).—The absorption in paper was measured for the  $\beta$ -rays of actinium-*(B+C)* and actinium-*C''*. Values found for the mass-ranges of the  $\beta$ -rays of actinium-*B* and -*C''* were 0.24 and 0.62 g./cm.<sup>2</sup>, corresponding with maximum velocities of 3430 and 6140 gauss cm. The  $\gamma$ -ray ionisations of actinium-*(B+C)* and -*C''* are respectively about one third and one sixth % of the initial  $\beta$ -ray ionisation of actinium-*C''*.

N. M. BUGH.

**$\beta$ -Particles of very small energy emitted during radioactive transformation.** N. FEATHER (Proc. Camb. Phil. Soc., 1929, **25**, 522—529).—A new type of gold leaf source is described, suitable for use with an expansion chamber for the detailed examination of  $\beta$ -particles of energy less than 50,000 electron volts. Some results obtained with sources of radium-*D* and thorium-*(B+C)* of this type are outlined.

N. M. BUGH.

**Spectral distribution and mean wave-length of Ra- $\gamma$ -rays.** D. SKOBELEZYN (Z. Physik, 1929, **58**, 595—612).—The distribution of the  $H_{\rho_{\max}}$  values for 567 Compton electrons in a Wilson chamber was observed. It is found that the scattering coefficient calculated on the statistical distribution according to the theory of Klein and Nishina (cf. A., 1929, 373) agrees within experimental error with that observed. On the other hand, the values of the coefficient calculated by the use of Dirac and Gordon's theory and Compton's theory differ by 34% and 39%, respectively. The spectral distribution, effective wave-length, and mean energy of the quanta of radium-*B* and -*C*, and the radium-*C*  $\gamma$ -radiation were derived using Klein and Nishina's theory. The spectral distribution is compared with that of the spectrum produced photo-electrically. The distribution obtained with stronger filtration was compared with that calculated and found to be in good agreement.

A. J. MEE.

**Scattering of thorium-*C''*  $\gamma$ -radiation by radium-*G* and ordinary lead.** W. KUHN (Phil.

Mag., 1929, [vii], **8**, 625—636).—It might be expected that, analogous with the absorption of the *D*-lines by non-luminous sodium vapour, there should be a selective absorption of monochromatic  $\gamma$ -rays by atomic nuclei, corresponding with an emission of the same radiation. To test this possibility the scattering of thorium-*C''*  $\gamma$ -radiation by the lead isotope radium-*G* and by ordinary lead has been compared. Ordinary lead contains about 50% of thorium-*D* and it might be possible to observe a nuclear resonance of thorium-*D* nuclei for some  $\gamma$ -lines of thorium-*C''*. The experimental arrangement is described. The result showed that any nuclear effect produced must be no more than 0.05 of the electronic scattering. This negative result cannot be explained by assuming that the  $\gamma$ -rays are emitted by electrons or protons. The expected result would, however, fall within the limits of the experimental error if the following assumptions were made: (1) The  $\gamma$ -rays are emitted by helium nuclei. (2) A time interval of about 10<sup>-10</sup> sec. or more elapses between the emission of the  $\beta$ -rays and that of the  $\gamma$ -rays. There is some evidence of the existence of such a time interval (cf. Jacobsen, A., 1928, 104). (3) The resonance line must, in the case of thorium-*D*, have a rather short wavelength (10 X. or less). (4) The movements of the  $\alpha$ -particle cause the residual nucleus to move in such a way that the centre of gravity is at rest.

M. S. BURR.

**Decay of radium-*D*.** MME. P. CURIE and (MME.) I. CURIE (J. Phys. Radium, 1929, [vi], **10**, 385—387).—The decay of radium-*D* in a specimen of active lead chloride purified from radium-*E* and polonium was studied over a period of 16 years in an ionisation chamber. From the corrected ionisation current-time curve it is concluded that the life period usually accepted from measurements of the growth of polonium is too short. The value found is 19.5 years.

N. M. BUGH.

**Quantity of polonium accumulated in tubes of radon, and the period of radium-*D*.** (MME.) I. CURIE (J. Phys. Radium, 1929, [vi], **10**, 388—391).—The life period of radium-*D* was evaluated from measurements of the quantity of polonium, estimated by different methods, resulting from the destruction of a known quantity of radon over periods of 2—4 years. The value obtained, 23 years, shows an unexplained divergence from that given by the decay of radium-*D* (cf. preceding abstract). The value 21 years and radioactive constant 0.033 year<sup>-1</sup> is provisionally adopted.

N. M. BUGH.

**Pendulum orbit of the normal hydrogen molecule ( $H_2$ ).** D. BUCHANAN (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 125—131).—Mathematical. Assuming that the two electrons oscillate along the right bisector of the line joining the nuclei and are always equidistant from the join of the nuclei, the periodic solutions are considered by classical mechanics. The case of the  $H_2^+$  ion, where one electron is lacking, is also considered.

N. M. BUGH.

**Interaction of excited helium and hydrogen atoms.** H. JONES (Proc. Camb. Phil. Soc., 1929, **25**, 445—453).—Mainly mathematical. By the method



of wave mechanics the interaction of a hydrogen atom in its normal state and a helium atom in either the  $2^3S$  or  $2^1S$  state is investigated. The first case is found to give the condition for the formation of a loosely-bound molecule and the second to lead to elastic reflexion.

N. M. BLIGH.

Rotating electron in a beam of light. B. M. SEN (Phil. Mag., 1929, [vii], 8, 690—697).—Mathematical. A solution of the wave equation of a rotating electron under a plane polarised beam of light is considered, and some of the consequences are indicated.

M. S. BURR.

Possible form of metallic nitrogen. G. HOROWITZ (Z. Physik, 1929, 58, 710—717).—Theoretical. An approximate calculation indicating the possibility of the existence of a metallic form of excited active nitrogen is given. This possibility rests on the basis of a similarity between carbon and the  $N^+$  ion which has a homopolar arrangement. This may also be the origin of the abnormally large heat of dissociation of the nitrogen molecule. A complete calculation of the case is impossible; only an approximate derivation of the properties of the lattice is possible. The stability of the metallic form is considered in comparison with organic explosives.

A. J. MEE.

Heitler-London theory of homopolar molecules. J. FRENKEL (Physikal. Z., 1929, 30, 716—717).—Preliminary. The Heitler-London wave-mechanical treatment of homopolar molecules is criticised on the ground that the application of the Pauli principle, in the sense of symmetry of functions restricted to single electron pairs, is invalid.

R. A. MORTON.

Structure of atomic nucleus. G. GAMOW (Physikal. Z., 1929, 30, 717—720).—The large mass defect of the  $\alpha$ -particle (stability) indicates that in atomic nuclei the individuality of the  $\alpha$ -particle is not lost. Only those protons which are not sufficient in number for the formation of new  $\alpha$ -particles can be described as free within the nucleus. The principal constituent of the nucleus is a conglomerate of  $\alpha$ -particles around which a certain number of electrons can be grouped. The number of stable electron levels is determined by the  $\alpha$ -conglomerate and each level has two electrons with different directions of spin (Pauli principle). The energy of the nucleus is expressed as  $E = N_\alpha \cdot \epsilon_\alpha + E_\alpha + E_p + E_e$ , where  $\epsilon_\alpha$  is the mass defect of a single  $\alpha$ -particle and  $E_\alpha$ ,  $E_p$ , and  $E_e$  are the binding energies of the  $\alpha$ -conglomerate, the free protons, and the nuclear electron shells, respectively. The stability of nuclei in relation to the number of  $\alpha$ -particles and protons is investigated theoretically from this point of view.

R. A. MORTON.

Explanation of the absorption spectrum of the solar atmosphere. L. A. SOMMER (Z. Physik, 1929, 58, 573—576).—Spectral lines in the absorption spectrum of the solar atmosphere can be explained on the quantum theory as being due to transitions between deep-lying metastable terms of the atomic spectra of nitrogen and oxygen.

A. J. MEE.

Theory of nuclear disintegration. M. BORN (Z. Physik, 1929, 58, 306—321).—It is shown that

the disintegration-probability of nuclei may be treated according to the conception of quantum mechanical transition probability. For two different nuclear models the disintegration probability is calculated as a function of the  $\alpha$ -ray energy.

J. W. SMITH.

Dynamic atom model of the first eleven elements of the periodic table. J. G. BLACK (J. Opt. Soc. Amer., 1929, 19, 317—319).—A dynamic model of the Bohr atom is described, capable of representing all the normal and many excited configurations of the first eleven elements. The nucleus and electrons are supported in space on jets of air and move in appropriate paths. Among the fourteen concepts illustrated are the electron grouping, the progression of perihelion, and, by inclining the model, the spinning electron and the quantisation of the spin axis in space.

N. M. BLIGH.

Repulsion of atomic kernels as a factor in organic rearrangements. W. M. LATIMER (J. Amer. Chem. Soc., 1929, 51, 3185—3190).—A review of available data shows that most molecular rearrangements occur with a decrease of the inter-kernel repulsion energy; increase in the repulsion energy is rare and is always accompanied by redistribution of the electrons in the molecule. Sometimes the repulsion energy remains unchanged. The following general principle is enunciated. If there are a number of possible arrangements of the atoms in a molecule which have the same number of electrons per atom and satisfy equally well the tendencies of the more electronegative elements to complete their octets of electrons, that form will be the most stable which gives a minimum of repulsion between the atomic kernels.

S. K. TWEEDY.

Probability law for the disintegration of radioactive substances at very small concentrations. G. I. POKROWSKI (Z. Physik, 1929, 58, 706—709).—Large deviations from the ordinary probability law have been observed under certain conditions for the disintegration of radioactive substances; previously relatively strong sources were used. An experiment is described in which the source was comparatively weak and the aperture large. It was found that regular deviations from the probability law occurred in this case. This points to the fact that the disintegration of one atom is not independent of the disintegration of neighbouring ones. The activation of radioactive substances by radiation of short wave-length is considered.

A. J. MEE.

Scattering of short-wave radiation by atoms according to Dirac's theory of radiation. I. WALLER (Z. Physik, 1929, 58, 75—94).—Mathematical.

J. W. SMITH.

Atomic frequencies in solids. R. DE MALLERMANN (Compt. rend., 1929, 189, 736—738).—From the principle that in a discontinuous medium the half-wave-length of stationary vibrations cannot be less than the shortest equilibrium distance between the constituent particles is deduced the relation  $v_m = V/2a$ , where  $v_m$  is the maximum frequency, i.e., that of the residual ray,  $a$  the distance between the particles, and  $V$  the velocity of sound. Satisfactory agreement between observed and calculated values of



$v_m$  deduced from  $a$  and  $V$ , and of  $a$  from  $v_m$  and  $V$  is shown.

C. A. SILBERRAD.

**Charge of an electron.** A. S. EDDINGTON (*Nature*, 1929, **124**, 840).—Further mathematical consideration affords the value  $hc/2\pi e^2=137$  (cf. A., 1929, 117).

A. A. ELDRIDGE.

**Alteration of the absorption spectra of maltose, lævulose, and dextrose under the influence of hydrogen and hydroxyl ions.** L. KWIECINSKI and L. MARCHLEWSKI (*Bull. Acad. Polonaise*, 1929, **A**, 317—330).—The absorption spectra produced by mixing  $N$ - or  $0.5N$ -solutions of maltose, lævulose, and dextrose with  $N$ - or  $0.5N$ -solutions of hydrochloric acid have been measured at intervals of 6, 24, 72, 120, and, in some cases, 240 hrs. after mixing the solutions. Maltose and hydrochloric acid give an increase of the absorbing power but no distinct absorption bands. There is also very little change in the optical rotation even at  $100^\circ$ . With dextrose and hydrochloric acid the solution remains unchanged even after 240 hrs., but with sodium hydroxide selective absorption progressively increases owing to the formation of decomposition products. Lævulose and hydrochloric acid show a slight shifting of the absorption maximum, towards shorter wave-lengths, whereas with sodium hydroxide there is a gradual shift of the band to the red.

A. I. VOGEL.

**Absorption of ultra-violet light by xylenes.** B. CHARLAMPOWICZOWNA and L. MARCHLEWSKI (*Bull. Acad. Polonaise*, 1929, **A**, 335—339).—An investigation of the absorption spectra in alcoholic solution of the three xylenes is described and it is shown that all follow Beer's law. *o*-Xylene gives two bands with maxima at 2708 and 2624 Å., *m*-xylene two bands with maxima at 2724 and 2644 Å., and *p*-xylene two bands with maxima at 2744 and 2670 Å. The *p*-compound absorbs ultra-violet light much more strongly than the other two isomerides.

A. I. VOGEL.

**Absorption of ultra-violet light by cinnamic and hydrocinnamic acids.** L. MARCHLEWSKI and O. WYROBEK (*Bull. Acad. Polonaise*, 1929, **A**, 331—334).—Hydrocinnamic acid, *m. p.*  $49^\circ$ , in aqueous solution yields two bands with maxima at 2670 and 2580 Å., whilst cinnamic acid, *m. p.*  $134^\circ$ , in alcoholic solution gives only one band with a maximum at 2710 Å.; the latter is considerably more absorbent.

A. I. VOGEL.

**Absorption of aqueous solutions of tartaric acid and of alkali tartrates.** G. BRUHAT and R. LEGRIS (*Compt. rend.*, 1929, **189**, 745—747).—The absorption of solutions of tartaric acid and sodium and potassium tartrates has been measured, and the results are shown by  $\log y : \log \lambda$  curves, where  $y$  is the optical density per cm. of solution. For tartaric acid for values of  $\lambda$  from 2460 Å. to the beginning of the visible spectrum, and for the tartrates from 2378 to 2536 Å., the relations  $\lambda/\sqrt{y}=a(\lambda^2-\lambda_0^2)$ , and  $\kappa/\lambda=a'\lambda^2/(\lambda^2-\lambda_0^2)^2$ , where  $\kappa$  is the extinction and  $a$  and  $a'$  are constants, hold,  $\lambda_0$  being approximately 2330 Å. for all.

C. A. SILBERRAD.

**Absorption spectra of dibasic aliphatic acids in the ultra-violet.** (MME.) RAMART-LUCAS and

F. SALMON-LEGAGNEUR (*Compt. rend.*, 1929, **189**, 915—917).—To test the validity of the theory (A., 1929, 1447) that absorption spectra depend on intramolecular attractions and so rather on the distance in space between the interacting groups than on the number of carbon atoms separating them, the absorption curves have been examined for the normal dibasic aliphatic acids containing from 2 to 18 carbon atoms. The curves are more or less similar in shape, but show no regular connexion with the number of carbon atoms; to that extent the theory is supported.

C. A. SILBERRAD.

**Comparative stability of isomerides according to their absorption spectra. Relation between absorption in the ultra-violet region and structure of diaryl derivatives of ethylene and ethane.** (MME.) RAMART-LUCAS (*Compt. rend.*, 1929, **189**, 802—804).—The ascending branch of the absorption curve in the ultra-violet region of the symmetrical compound lies nearer to the visible region than does that of the unsymmetrical isomeride in a series of isomeric diaryl derivatives of ethylene and isomerides of the type  $\text{CArR}_2\cdot\text{CO}\cdot\text{Ar}$  and  $\text{CAr}_2\text{R}\cdot\text{CO}\cdot\text{R}$ . With isomeric diaryl derivatives of ethane the reverse is the case.

A. A. GOLDBERG.

**Absorption spectra of methyl halides and some other methyl compounds in the ultra-violet and in the Schumann region.** G. HERZBERG and G. SCHEIBE (*Trans. Faraday Soc.*, 1929, **25**, 716—717).—Measurements were made at vapour pressures between 100 and 0.01 mm. Methyl iodide, bromide, and chloride showed continuous absorption bands, with maxima at 2500, 2000, and 1750 Å., and discontinuous absorption beginning at 2010, 1785, and 1600 Å., respectively, and of increasing broadness. The absorption spectra of methyl alcohol and acetonitrile are similar to that of methyl chloride, and completely continuous to 1600 Å. Bands reported by Leifson (*Astrophys. J.*, 1927, 63) for ethyl alcohol were not found and are attributed to impurity.

N. M. BLIGH.

**Spectrographic investigations of cellulose derivatives.** B. RASSOW and W. AEHNELT (*Cellulosechem.*, 1929, **10**, 169—195).—Curves for the ultra-violet absorption of the xanthate, nitrate, acetate, and ethyl ether of cellulose have been obtained between 4000 and 2200 Å. by the Baly-Hartley method. The lack of a suitable solvent prevents similar observations with cellulose. Cellulose nitrate shows only a general absorption. Cellulose triacetate gives a curve similar in form to that of a diacetate (cellite), and to triethyl-cellulose. Cellulose xanthate (viscose) has a strong band at 3000 Å. Since this persists after purification it cannot be due to impurities such as ethyl xanthate or sodium trithiocarbonate, which have bands in the same position.

The influence of cations on the ageing and precipitation of viscose has been investigated, and it is shown that the hydrogen-ion concentration of the medium is an important factor.

T. H. MORTON.

**Absorption spectrum of cobalt chloride and its variation.** P. VALLANT (*Compt. rend.*, 1929, **189**, 747—749).—Six solutions of cobalt chloride were examined: three in water, and three in aqueous

alcohol of  $d$  0.91, 20% sodium chloride, and 68% zinc chloride solutions, respectively.  $\beta$  in the absorption formula,  $i = I \times e^{-n\beta}$  ( $n$  = concentration,  $l$  = thickness of solution), was determined for eleven values of  $\lambda$  between 5000 and 6000 Å. The  $\beta$ - $\lambda$  curves thus obtained, although showing maxima for varying values of  $\lambda$ , are all superposable. They consist of two approximately linear branches. It is concluded that in all six solutions the only absorbent is the  $\text{Co}^{++}$  ion, the activity of which varies with its concentration and that of the other ions in the solution. C. A. SILBERRAD.

**Certain electronic bands of carbon dioxide.** J. F. DUNCAN (Physical Rev., 1929, [ii], 34, 1148—1153).—Using a low-voltage arc discharge as source in a stream of carbon dioxide the electronic bands near 2880 and 2895 Å. reported by Fox (cf. A., 1927, 916) were photographed under very high dispersion and examined with a comparator and a Moll microphotometer. Wave-numbers of lines and estimated intensities are tabulated. The fine structure, the probable emitter of the bands, and their relation to other bands of the spectrum are discussed.

N. M. BLIGH.

**High-temperature absorption spectra of alkali halide phosphors.** (FRL.) M. FORRÓ (Z. Physik, 1929, 56, 534—543).—The temperature variation of the absorption of natural rock-salt, of synthetic crystals of sodium chloride, potassium chloride and bromide, and of these substances containing from 0.001 to 0.01% of thallium, lead, and silver, has been examined in the ranges  $-183^\circ$  to  $550^\circ$  and from 1800 to 3600 Å. The absorption of the chloride phosphors is relatively small, and changes slowly in character or amount with temperature, silver producing the greatest effect; that of the bromide phosphors is more complex and is characterised by a greater temperature coefficient.

R. W. LUNT.

**Absorption spectra of six new alkali halide phosphors with the addition of thallium.** (FRL.) M. FORRÓ (Z. Physik, 1929, 58, 613—618).—The absorption spectra of six new alkali halide phosphors were determined and compared with those of six previously investigated. With the exception of the absorption spectrum of caesium iodide all the others have a similar structure. In all, the different effects of the lattice anions is noticeable. The absorption spectrum of pure caesium iodide is also given and there is a discussion of the advantages and disadvantages of the use of thin phosphor crystal layers prepared by melting the substances between quartz plates. (Cf. preceding abstract.)

A. J. MEE.

**Isotope effect in the absorption spectrum of iodine monochloride.** J. PATKOWSKI and W. E. CURTIS (Trans. Faraday Soc., 1929, 25, 725—736).—The isotope effect in band spectra where relatively large changes of vibrational quantum number occur should differ markedly from that in band systems involving relatively small changes. The isotopic separation of band heads should reach a maximum for a particular value of  $n'$ , which is the same for all values of  $n''$ , and the true  $n'$  values may be derived from the position of this maximum if accurately located, or may be calculated from individual separations if the  $n''$  numeration is known. New measure-

ments of a number of  $\text{ICl}^{35}$  and  $\text{ICl}^{37}$  heads are given, and used with existing data to verify these conclusions and to obtain the true vibrational quantum numbers. The correction to the  $n'$  values of Wilson (cf. A., 1928, 1306) is  $+6\frac{1}{2}$ . The  $n''$  value for the first progression is probably  $\frac{1}{2}$ . The values of the fundamental vibration frequencies of  $\text{ICl}$  are 382 for the normal and 224  $\text{cm}^{-1}$  for the excited molecule. The corresponding decrease in the binding force (2.9 : 1) is approximately the same as for the  $\text{Cl}_2$  (3.2 : 1) and  $\text{I}_2$  (2.8 : 1) molecules. The electronic frequency associated with this band system is 13,674  $\text{cm}^{-1}$  (1.69 volts).

N. M. BLIGH.

**Absorption spectrum of chlorine dioxide.** C. F. GOODVEY and C. P. STEIN (Trans. Faraday Soc., 1929, 25, 733—751).—Investigation of the visible, near ultra-violet, and ultra-violet spectrum was made over a wide range of pressures; these consist of regular sequences of bands degraded towards the red, each sequence being made up of four principal bands decreasing in intensity with rise of frequency. The bands form series the members of which have a common frequency difference. The wave-numbers corresponding with the positions of the heads of the members of the principal series are tabulated, and a number of heads of weak bands are arranged as sub-series. Deslandres' law is applied to the interpretation of the series spectrum, which is discussed theoretically, and a proposed assignment of vibrational quantum numbers and doublet structure is tabulated. The double band-heads in relation to the isotope effect and the rotational fine structure are considered. It is suggested that the molecule acts as a diatomic molecule, the oxygen atoms being close together and acting as a unit.

N. M. BLIGH.

**Visible absorption spectra in some crystalline salts of the rare earths.** F. I. G. RAWLINS (Trans. Faraday Soc., 1929, 25, 762—765; cf. Ephraim and Bloch, A., 1928, 217).—The visible absorption spectra of the crystalline nitrates and sulphates of praseodymium, neodymium, and samarium are ascribed to the ions  $\text{Pr}^{+++}$ ,  $\text{Nd}^{+++}$ , and  $\text{Sm}^{+++}$  as carriers. The sharpness of many of the lines is due to the shielding of the  $4f$  electrons by the  $5s$  and  $5p$  shells. These spectra are peculiar to the rare earths on account of the incomplete nature of their inner electronic shells. From a consideration of the ground states of the ions  $\text{R}^{+++}$ , no obvious relation with the spectra of the neutral metal atoms is expected.

N. M. BLIGH.

**Ultra-violet lead oxide band system.** S. BLOOMENTHAL (Science, 1929, 69, 677).—Bands attributed to lead monoxide have been observed with heads at 3209.2, 3264.4, 3320.7, 3341.8, 3401.9, 3485.7, and 3594.2 Å., together with many weaker bands. The isotope effect calculated from the formula for the lead monoxide system is 0.033 Å., in agreement with the value 0.037 Å. given by measurements of the bands obtained using  $\text{Pb}^{206}$  and then  $\text{Pb}^{208}$ , 207, 206 in the light source.

L. S. THEOBALD.

**Mechanism of homogeneous gas reactions.** II. **Absorption spectrum of nitrogen pentoxide and its method of decomposition.** H. C. UREY, L. H. DAWSEY, and F. O. RICE (J. Amer. Chem. Soc., 1929, 51, 3190—3194).—The ultra-violet absorption

spectrum of nitrogen pentoxide is continuous, the absorption commencing at about 3050 Å. and extending into the Schumann region. The upper absorption limit corresponds with a reaction energy of 93.2 kg.-cal., thus indicating that the primary reaction  $\text{N}_2\text{O}_5 = 2\text{NO}_2 + \text{O}$ , which has an energy of 96 kg.-cal., takes place. Evidence is cited in favour of this conclusion and it is suggested that the mechanism of the reaction is analogous to that suggested by Gurney and Condon (A., 1928, 1170) for radioactive decomposition, or to the spontaneous dissociation of the excited hydrogen molecule (Blackett and Franck, A., 1925, ii, 1097).

S. K. TWEEDY.

**Infra-red spectra of certain rare earths and other elements.** H. J. C. IRETON and (Miss) A. M. KEAST (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 13—18).—The spark spectra of ruthenium, rhodium, palladium, osmium, iridium, and platinum and the arc spectra of ytterbium, praseodymium, and tantalum were photographed and wave-lengths measured and tabulated. No definite spark lines were found for ruthenium and osmium.

N. M. BLIGH.

**Infra-red spectra of solid bodies.** C. SCHAEFER (Trans. Faraday Soc., 1929, 25, 841—855).—A general survey is given of work on the infra-red spectra of solids with special reference to its bearing on molecular structure. The theory of vibrations in solids and methods of observation by reflexion, absorption, and dispersion are reviewed. A review is given of measurements of the infra-red spectrum of solids through refractive indices, of the longer wave-lengths by the method of residual rays, illustrated for diatomic crystals, of work on the fundamental internal vibration frequencies of chemical radicals in more complex crystals, on the weaker combination frequencies found by the more sensitive methods of absorption, and on "external" vibrations for polyatomic crystals.

N. M. BLIGH.

**Infra-red absorption spectra of salts containing the group  $\text{AX}_4$ .** A. M. TAYLOR (Trans. Faraday Soc., 1929, 25, 856—860).—The absorption spectra of the sulphate, chromate, perchlorate, and permanganate of potassium were measured, using a modified form of Tolksdorf's method (A., 1928, 565). Results are plotted for the four salts and all show intense absorption near 10  $\mu$ . This frequency is due to the oscillation of the oxygen atom along the median of the tetrahedral group, and tends to be slowed down with increasing distance from the central atom, and to be made more rapid as the charge on the latter increases. Another frequency is due to the oscillation of the central atom. Results are discussed in relation to earlier measurements of the reflexion spectra.

N. M. BLIGH.

**Band spectrum of potassium permanganate in the crystalline state and in solution.** A. M. TAYLOR (Trans. Faraday Soc., 1929, 25, 860—863).—Reasons are given for expecting the absorption spectrum of potassium permanganate in the visible region to be banded. Such a band spectrum is found; the frequency difference between the bands is the frequency of oscillation of the manganese atom as determined from the infra-red spectrum of the salt which gives a band at 12.7  $\mu$ . The spectra of the

crystalline salt in aqueous and in ethyl acetate solution were photographed and compared. Differences in band spacing are attributed to the influence of solvation on the  $\text{MnO}_4$  ion.

N. M. BLIGH.

**Infra-red spectra of liquids.** J. LECOMTE (Trans. Faraday Soc., 1929, 25, 864—876).—A general survey is given of work on the infra-red absorption, reflexion, and magnetic rotation spectra of liquids; the results obtained are summarised and correlated with chemical constitution. The origin of and calculations on the spectra are discussed and their connexion with the visible and ultra-violet spectra is examined. Some physico-chemical applications, calculations of heats of vaporisation, heats of combination, and activation energy of molecules are illustrated. The principal unsolved problems are enumerated.

N. M. BLIGH.

**Infra-red bands of hydrogen combined with carbon in the molecule of organic compounds.** G. B. BONINO (Trans. Faraday Soc., 1929, 25, 876—888).—The infra-red bands of hydrogen combined in the organic molecule, and particularly the band at 3.4  $\mu$  found in compounds containing the CH linking, are discussed. The deduction of structure from the position of the various bands and evidence on chemical properties from a study of the fine structure of the bands is indicated. From the intensity of absorption evidence can be obtained as to the probability that a given band may change its proper energy level, thus giving rise to certain chemical consequences. Infra-red spectrometry data can be applied to the study of the energy and kinetics of molecules.

N. M. BLIGH.

**Molecular absorption spectra of liquids below 3  $\mu$ .** J. W. ELLIS (Trans. Faraday Soc., 1929, 25, 888—898).—The absorption spectra of organic liquids show numerous bands in the region below 3  $\mu$ , and certain features among the spectra of chemically related compounds recur regularly. The frequency ratio of eight experimentally observed bands was found to be given by a simple relation and an equation for the frequencies was deduced, which is discussed with special reference to the bands of benzene, and is analysed on a quantum basis. The series is attributed to the CH linking, and the evaluation of the heat of linking of this linking is treated theoretically and compared with experimental data. The doubling of certain absorption bands and its explanation are discussed. Most or all of the fundamental absorption bands of hydrocarbons which are associated with the fundamental vibration rates of the molecule probably occur in the spectrum with wave-lengths greater than 3  $\mu$ ; hence bands below 3  $\mu$  must be interpreted as overtone and combination frequencies. The benzene bands in this region are investigated. The occurrence of bands for other compounds which can be associated with linkings other than CH is examined, and is supported by NH bands at 1.5 and 1  $\mu$ .

N. M. BLIGH.

**Infra-red spectra of gases.** (Sir) R. ROBERTSON (Trans. Faraday Soc., 1929, 25, 899—912).—A summary of the history and development of work in the infra-red, chiefly as applied to the investigation of gases, with special reference to its bearing on chemical

problems, and its relation to other physical properties of gases. N. M. BLIGH.

**Chemical structure and infra-red analysis.** E. K. RIDEAL (Trans. Faraday Soc., 1929, 25, 921—925).—Data on the convergence point of the vibrational spectrum can be applied to the interpretation of the mechanism of photo-chemical dissociation and to the evaluation of the dissociation energy effected by oscillation. Information can be obtained from the fundamental frequency on the existence of tautomeric modifications, and probably on the rate of attainment of equilibrium in tautomeric systems, and on the distribution of isotopic forms. The determination of the stability of the more complex molecular systems and a comparison with that determined from the potential functions of resulting binary systems are discussed. From the calculated moments of inertia the angle of the symmetrical system can be determined, and will probably permit the evaluation of the alteration of the tetrahedral angles for carbon-hydrogen in the XMe group as alterations are made in the group X, thus leading to a quantitative study of polarity. Identifications of certain linkings have been made from the characteristic infra-red absorption spectra of certain organic compounds; further information can be obtained from the fundamental and overtone vibration frequencies. A dipole system, as a function of two terms only, for an attractive and a repulsive force is investigated. N. M. BLIGH.

**Infra-red spectra of gases under high dispersion.** E. F. BARKER and C. F. MEYER (Trans. Faraday Soc., 1929, 25, 912—921).—Experimental methods of investigation using a diffraction grating and a monochromator to limit the spectral range, and various modifications which have contributed to refinements of measurement are described. Typical gases for which vibration bands have been resolved are tabulated in four groups according to the order of complexity of rotation: diatomic molecules for which the rotating nuclei move only in a plane; methane, which may rotate about any axis without precession; molecules which rotate with a simple precession, and those with three unequal moments of inertia. The character of the absorption bands as influenced by the nature of the rotation and the direction within the vibrating molecule of the change in electric moment is discussed, and illustrated in particular for ammonia and hydrogen chloride. N. M. BLIGH.

**Probable infra-red spectrum of sulphur vapour.** A. M. TAYLOR (Trans. Faraday Soc., 1929, 25, 929—930; cf. A., 1927, 925).—An apparatus is described by means of which attempts were made to measure the absorption of sulphur vapour. It was found possible only to locate the positions of the maxima of absorption which were shifted towards higher frequencies, the shift being opposite to that observed in raising the temperature of the solid or liquid states, the form of the spectra being otherwise mainly unchanged. N. M. BLIGH.

**Vibration-rotation spectra of diatomic molecules.** C. P. SNOW (Trans. Faraday Soc., 1929, 25, 930—936).—Vibration bands are discussed and the known band systems for a number of diatomic mole-

cules are tabulated. The rotational fine structure of vibration bands is treated mathematically. Deductions made for diatomic molecules from vibration-rotation spectra are tabulated and compared with those made from electronic band spectra.

N. M. BLIGH.

**Absorption spectrum of ammonia gas in the near infra-red.** R. MECKE and R. M. BADGER (Trans. Faraday Soc., 1929, 25, 936—938).—Under high dispersion, three separate bands of the oscillation-rotation type with centres at about 8810, 7920, and 6450 Å., respectively, were for the first time photographed. The 7920, or most intense, band resembles the 3  $\mu$  ammonia band, of which it is apparently the third harmonic, and is of high complexity. The weak 6450 band appears to be the fourth harmonic. The 8810 band is similar to that at 2  $\mu$ , and consists of two series of lines displaced with respect to each other, and each having the same spacing. With the new data the known ammonia bands are classified and explained as combinations of three fundamental frequencies.

N. M. BLIGH.

**Raman effect in the X-ray region.** W. KAST (Z. Physik, 1929, 58, 519—522).—If X-rays are scattered at aluminium the  $K$  ionisation corresponds with an energy loss of 1550 volts. This means for a line of wave-length 612 X. (the rhodium  $K\alpha$  line) a displacement of 50 X. towards the long waves. An exposure of 36 hrs. was given, this being about twenty times the length of exposure required to photograph the Compton line, but there was not the slightest appearance of the displaced line. The possibility of the occurrence of Raman lines in the X-ray range is discussed.

A. J. MEE.

**Molecular light scattering in solid bodies. III. Intensity of the light scattered by crystalline quartz.** G. LANDSBERG and K. WULFSOLM (Z. Physik, 1929, 58, 95—103; cf. *ibid.*, 1927, 43, 773; 45, 442).—The intensity of the light scattered by crystalline quartz has been compared with that scattered by carbon dioxide. The results obtained are in agreement with the values deduced on Gans' theory, but not with those from the Einstein-Smoluchowski formula. Calculation of the Avogadro number from the data gives a value of  $6.9 \times 10^{23}$ . J. W. SMITH.

**Raman effect and the hydrogen spectrum.** W. FINKELNBURG (Z. Physik, 1929, 58, 425—428).—Reasons are given to show that the suggestions made by Allen (A., 1929, 363) and Deodhar (*ibid.*, 1361) concerning the origin of the Raman effect in hydrogen are highly improbable. W. R. ANGUS.

**Investigation of molecular structure by light scattering.** (SIR) C. V. RAMAN (Trans. Faraday Soc., 1929, 25, 781—792).—The investigations on light scattering leading up to the discovery of the Raman effect are described. The nature of the effect and the studies made of it in gases, liquids, mixtures and solutions, crystals and amorphous solids, and of the intensity and polarisation of the scattered radiation are outlined. The relationship of the effect with ultra-violet and infra-red spectra, the theory of the effect, and its relation to molecular structure are discussed. N. M. BLIGH.

**Methods of excitation of Raman spectra.** R. W. WOOD (Trans. Faraday Soc., 1929, 25, 792—796).—A general summary of the methods employed in the study of the Raman effect is given. The most suitable wave-lengths of the exciting radiation, from a mercury arc or a helium tube, in relation to the substance to be investigated and the technique developed, are described and discussed. N. M. BLIGH.

**Raman effect with liquid hydrogen.** J. C. McLENNAN and J. H. McLEOD (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 19—20).—The spectrum of the light from the mercury arc scattered by liquid hydrogen contained the lines 4426.8, 4472.1, and 4863.5 Å., which were shown by a comparison with band spectra data to be due to the rotational  $0 \rightarrow 2$ ,  $1 \rightarrow 3$ , and the vibrational  $0 \rightarrow 1$  transitions, apparently contrary to the usual selection rules, and supporting the view that hydrogen at low temperatures is a mixture of symmetrical and anti-symmetrical molecules. N. M. BLIGH.

**Raman effect in the neighbourhood of the critical point.** S. L. ZIEMECKI and K. NARKIEWICZ-JODKO (Naturwiss., 1929, 17, 876).—The intensity of the Raman effect does not appear to change suddenly in the neighbourhood of the critical point. The critical temperature of an isobutyric acid-water mixture is near  $24^\circ$ , and although the classical scattering increases enormously with the appearance of opalescence, the Raman lines do not increase in intensity by more than 30%, even this small change being perhaps apparent only as the continuous background is also increased in intensity. Opalescence results in more efficient scattering of the weaker lines in the spectrum of the exciting light.

R. A. MORTON.

**Raman effect. I. Spectra of some halogenated hydrocarbons. II. Saturated and olefinic hydrocarbons. III. Aniline and dimethylaniline. IV. Pyridine and piperidine.** G. B. BONINO and L. BRÜLL (Gazzetta, 1929, 59, 643—660, 660—667, 668—675, 675—680).—I. The substitution of chlorine atoms for hydrogen atoms in the ethane molecule displaces the maximum at  $3.39 \mu$  in the infra-red absorption band characteristic of the CH group in ethane to shorter wave-lengths. From measurements of the Raman spectra of chloroethanes the following values were found: dichloroethane  $3.38$ , tetrachloroethane  $3.35$ , pentachloroethane  $3.345 \mu$ ; hexachloroethane gave no band. The corresponding maximum absorption band at  $3.28 \mu$  in the ethylene molecule is similarly displaced: *cis*- and *trans*-dichloroethylenes  $3.25$ , trichloroethylene  $3.24 \mu$ ; tetrachloroethylene, no band. The infra-red spectra of the above compounds between 2 and  $60 \mu$  deduced from the Raman spectra are given.

II. The Raman spectra of pentane, heptane, octane, decane, and amylene have been measured and the infra-red spectra calculated. All these hydrocarbons give the characteristic CH band at  $3.4 \mu$ , and a second CH band at  $3.49$ — $3.50 \mu$ . Amylene gives a third band at  $3.365 \mu$ .

III. From Raman spectrum measurements the presence of the  $3.28 \mu$  unsaturated CH band is confirmed in the infra-red absorption spectra of aniline

and of dimethylaniline. The NH band at  $2.98$ — $3.0 \mu$  is present in the aniline spectrum, but not in that of the dimethyl compound.

IV. The aromatic CH band at  $3.27 \mu$  is present in the infra-red spectrum of pyridine, whereas with piperidine the characteristic aliphatic CH bands (cf. II) at  $3.4$  and  $3.51 \mu$  are obtained. The piperidine spectrum also gives the characteristic NH band at  $3.01 \mu$ , which is absent in the pyridine spectrum.

O. J. WALKER.

**Raman effect in some liquefied gases.** P. DAURE (Trans. Faraday Soc., 1929, 25, 825—828).—The negative secondary lines are more intense than the corresponding positive lines, and more readily allow the determination of the characteristic frequencies. Experiments were made on liquefied gases in a small tube placed in a non-silvered Dewar flask illuminated with a mercury-vapour lamp, and the Raman spectra were photographed. Characteristic frequencies are tabulated for the liquefied gases hydrogen chloride, ammonia, methane, ethane, propane, ethylene, and acetylene dissolved in acetone, and their interpretation is discussed. N. M. BLIGH.

**Raman spectra in atmospheres surrounding metallic arcs.** B. VENKATESACHAR and L. SIBAIYA (Nature, 1929, 124, 838).—The spectrum of the mercury arc in carbon dioxide at 60 mm. contains two faint lines coinciding in position with the two Raman lines recorded by Rasetti (A., 1929, 241). Raman lines of carbon tetrachloride were not, however, observed with a mercury arc in an atmosphere of that substance. Some of the faint lines in other spectra may be Raman lines. A. A. ELDRIDGE.

**Raman effect. IV. Raman spectrum of organic substances (benzene derivatives).** A. DADIEU and K. W. F. KOHLRAUSCH (Monatsh., 1929, 53 and 54, 282—298; cf. A., 1929, 976).—Data concerning the Raman spectra of benzene, benzyl alcohol, dimethylaniline, ethylbenzene, benzonitrile, benzyl chloride, benzoyl chloride, benzophenone, acetophenone, and acetaldehyde are tabulated. Benzene shows the Raman line  $\nu = 2945 \text{ cm}^{-1}$  hitherto associated with the aliphatic C-H linking. This disappears in mono-substituted derivatives of benzene when the substituent contains no C-H linking. The results are discussed in terms of a theory of coupled vibrations and as to their significance in indicating an unsymmetrical structure for the benzene molecule.

L. S. THEOBALD.

**Raman effect. II. Raman spectrum of organic substances (benzene derivatives). III. Attempted interpretation of Raman spectra.** A. DADIEU and K. W. F. KOHLRAUSCH (Monatsh., 1929, 52, 379—407; cf. A., 1929, 1127).—II. The Raman spectra of benzene, chloro-, bromo-, and iodo-benzene, phenol, anisole, benzaldehyde, aniline, acetophenone, nitrobenzene, *o*- and *p*-dichlorobenzene, *o*-, *m*-, and *p*-xylene, methyl ethyl ketone, naphthalene dissolved in carbon tetrachloride, and a mixture of xylenes have been investigated. The results obtained are classified in tables and discussed. Between the Raman lines 1800 and 2800 none of the substances examined shows any lines. The most prominent benzene lines are reproduced in all the mono-derivatives and, with

slight deviation, in the di-derivatives; five of these have been termed "characteristic" benzene lines. The frequency of another line appearing in the Raman spectrum of benzene (2947) is attributed to an aliphatic CH group. Characteristic frequencies are assigned to the CO and NO<sub>2</sub> groups.

III. From the results obtained the authors have been led to the conclusion that at least some of the lines appearing in Raman spectra are due to certain parts of the irradiated molecules oscillating against one another. Although they do not offer this as a full interpretation of existing results, they show that a qualitative and partly quantitative relationship holds. "Inner" and "outer" oscillations are postulated and groups are classified under these heads. With the help of a formula connecting frequency with the binding force and the masses of constituent atoms, an approximate systematisation of the Raman spectra of liquids is given. Application of the theory (*e.g.*, to CO and NO<sub>2</sub> groups) shows that the values obtained are influenced in a constitutive manner.

W. R. ANGUS.

**Theory of the Raman effect.** G. PLACZEK (*Z. Physik*, 1929, 58, 585—594).—Theoretical. The explanation of the scattering process as a consequence of two processes, *viz.*, the absorption of a quant  $h\nu$ , and the emission of a quant  $h\nu'$ , is further considered. It is emphasised that the processes which give rise to the emission of Stokes and anti-Stokes lines do not compensate in their effect on the heat equilibrium. The intensities of the lines are dependent not only on the number of molecules in the initial and final states, as was formerly supposed, but also on the excitation frequency and the value of the characteristic frequency of the molecule.

A. J. MEE.

**Raman effect of AX<sub>4</sub> groups.** A. M. TAYLOR (*Trans. Faraday Soc.*, 1929, 25, 830—835).—The Raman spectra of sulphuric and perchloric acids and of the alkali sulphates were photographed, measured, and compared with infra-red spectra. The energy diagram of the AX<sub>4</sub> is indicated. The frequency of vibration of the AX<sub>4</sub> is found to be diminished on destruction of the crystal lattice and hydration of the group, and in the case of SO<sub>4</sub> to be still further diminished by the removal of the water and addition of H<sup>+</sup> ions to form molecular H<sub>2</sub>SO<sub>4</sub>. It is concluded that the hydrogen ions have penetrated the SO<sub>4</sub> ion, and it is suggested that H<sub>2</sub>SO<sub>4</sub> must crystallise with a molecular lattice.

N. M. BLIGH.

**Raman lines in the spectrum of the electric discharge.** H. S. ALLEN (*Trans. Faraday Soc.*, 1929, 25, 829—830; *cf. A.*, 1929, 363).—When hydrogen is subjected to an electric discharge the Balmer lines should be accompanied by a system of fainter lines or Raman companions arising from bombardment of molecules by light quanta. This view is supported by the results of Deodhar (*A.*, 1929, 1361).

N. M. BLIGH.

**Polarisation of Raman radiations in liquids and crystals.** J. CABANNES (*Trans. Faraday Soc.*, 1929, 25, 813—825).—In diffusion spectra all the secondary radiations characterised by the same change of frequency are in the same state of polarisation, whatever the frequency of the exciting radiation;

this state varies over wide limits according to the pair of secondary radiations. The measurement of depolarisation of the Raman radiations in liquids is described and results for benzene are given. Raman's depolarisation theory is shown to be disproved experimentally; a comparison is made of the depolarisation of secondary radiations in liquids and the depolarisation of the fundamental radiation in vapours, and an explanation based on the hypothesis of a virtual oscillator permanently associated with the molecule is proposed. Investigations of the dependence of depolarisation on the orientation of the molecule by a study of the effect in quartz and Iceland spar are described.

N. M. BLIGH.

**Plane-polarisation of the Raman spectra and on Raman lines scattered from coarsely powdered crystals.** A. C. MENZIES (*Trans. Faraday Soc.*, 1929, 25, 836—839).—No explanation in accordance with the Kramers-Heisenberg dispersion theory has been given for the polarisation of the Raman lines. Experiments were made on the polarisation of the lines for liquids and for quartz (*cf. Cabannes, A.*, 1929, 378). An explanation of some results is proposed by considering the initial and final directions of vibration in the molecule parallel for polarised lines, perpendicular for unpolarised lines, and oblique for partly polarised lines.

N. M. BLIGH.

**Degradation of light frequencies by molecular scattering.** J. CABANNES (*Trans. Faraday Soc.*, 1929, 25, 800—813).—The wave theory of diffusion spectra and of optical pulsations is described and its inadequacy in the interpretation of observations of the Raman effect is shown. Certain relationships are, however, found to be verified experimentally when the negative bands alone are considered. The necessity for an explanation through the quantum theory is shown. The different phenomena giving rise to, and the experimental results relative to, the degradation of frequencies in the molecular diffusion of light are enumerated. The theory of the ratio of intensities of the positive and negative lines is traced and is compared with experimental results. The non-symmetry between the positions of these lines resulting in a further frequency degradation or displacement towards the red was verified in accordance with theory. Experimental work on the continuous spectrum on both sides of the fundamental line and on the unsymmetrical broadening of the incident radiation by molecular diffusion at the middle of a gas or liquid is described.

N. M. BLIGH.

**Phosphorescence of solid argon irradiated with cathode rays.** J. C. MCLENNAN, E. W. SAMSON, and H. J. C. IRETTON (*Trans. Roy. Soc. Canada*, 1929, [iii], 23, III, 25—34).—Experiments on solid nitrogen (*cf. A.*, 1928, 1171) were applied to solid argon for evidence of the view that the phosphorescence may be due to an active centre of hydrogen in a diluting medium. A spectrogram of the cathodoluminescence spectrum was obtained and measurements are tabulated. Two strong bands were found, similar to the N<sub>1</sub> and N<sub>2</sub> bands of solid nitrogen. The B series of solid nitrogen bands was found with equal intensity for argon, but shifted towards the



longer wave-lengths. The diffuse *C* series of nitrogen bands is replaced for argon by a number of narrower bands. The general similarity for solid nitrogen and argon favours the hypothesis of ordinary luminescence, with hydrogen as an active centre in solid nitrogen and argon as diluents. N. M. BLIGH.

**Polarisation of thallium vapour fluorescence.** R. GÜLKE (Z. Physik, 1929, 56, 524—533).—An examination has been made of the polarisation of the lines 2768 and 3530 Å., arising from the same excitation level  $3d_{5/2}$ , which occur in the fluorescence spectrum of thallium vapour when excited by plane polarised light of the thallium line 2768 Å. These lines are polarised in directions at right angles, the direction for the line 2768 Å. being parallel to that of the exciting radiation. This result confirms predictions of Heisenberg's theory.

A satisfactory form of lamp constructed of hard glass or silica is described by means of which intense thallium radiation of 2768 Å. may be produced; self-reversal and fogging of the quartz window due to deposition of thallium are avoided by a rapid stream of a neon-helium mixture flowing between the thallium discharge and the window. R. W. LUNT.

**Magnetic quenching of iodine vapour fluorescence.** O. OLDENBERG (Z. Physik, 1929, 57, 186—191).—From observations of the quenching of the fluorescence of iodine vapour at 0.09 and 2.0 mm. by a field of 17 kilogauss it is concluded that the time during which the quenching occurs is of the same order as that of the half-life period of the excited atoms.

R. W. LUNT.

**New properties of the polarised fluorescence of liquids.** S. I. VAVILOV (Z. Physik, 1929, 58, 447—448).—Mathematical (cf. *ibid.*, 55, 690).

J. W. SMITH.

**Effect of temperature on the fluorescence of some organic solutions.** J. R. JENNESS (Physical Rev., 1929, [ii], 34, 1275—1285).—Alcoholic solutions of rhodamine-*B*, eosin, tetrachlorofluorescein, and sulphonefluorescein were studied spectrographically, and fluorescein by means of a spectrometer; the effect of concentration also was studied for the two first mentioned. Results are compared with those of Speas for absorption spectra (cf. A., 1928, 571). The temperature shift of the peak of the fluorescence band is proportional to the temperature change, and the shift due to concentration change is proportional to the logarithm of the concentration; in each case the shift is in the same direction as for absorption. For eosin and fluorescein a fall in temperature causes the peaks of the bands to shift to shorter wave-lengths, and for rhodamine-*B* to longer wave-lengths, with a similar effect in the case of this substance for increase in concentration. Changes in the width of the fluorescence bands do not follow the same law as for absorption; otherwise results are similar to those for absorption. N. M. BLIGH.

**Tesla-luminescence spectra. VIII. Some halogen-substituted derivatives of benzene.** A. RUSSELL and A. W. STEWART (J.C.S., 1929, 2432—2436; cf. A., 1929, 1364).—Contrary to a previous report (cf. J.C.S., 1923, 123, 2155) the vapour of chlorobenzene gives a feeble emission of 12 bands between  $\lambda$  2745

and 2955. Fluorobenzene gives at least 45 bands from  $\lambda$  3425 to 2578; no emission was found for bromo- and iodo-benzene. Both *o*- and *p*-dichlorobenzene gave spectra in the green and in the ultra-violet; *m*-dichlorobenzene gave a feeble emission in the green; the chlorotoluenes and *p*-fluorotoluene gave ultra-violet and green spectra. In the chlorophenols and chloroanilines where the halogen atom forms a second substituted group the spectrum is that of the parent substance weakened, except in the case of phenol and *o*-chlorophenol. The former gives 6 bands, the latter 14 bands; *p*-chlorophenol gives a continuation towards the visible of the phenol spectrum. Where bands are found the series of bands divides into groups, the members of which differ from the corresponding bands in the adjacent groups by a constant wave-number difference which is either 80  $\nu$  or 100  $\nu$ .

N. M. BLIGH.

**Fluorescence spectra of the vapours of fluorobenzene and *p*-fluorotoluene.** (Miss) W. MONYPENY and A. RUSSELL (J.C.S., 1929, 2436—2438; cf. preceding abstract).—The vapours of fluorobenzene and *p*-fluorotoluene when irradiated by the short waves from a mercury vapour lamp gave spectra identical with those given under the Tesla discharge, but containing fewer bands. Fluorobenzene gave 22 bands and *p*-fluorotoluene 18 bands in the ultra-violet, falling into groups which obey the wave-number relation found for the Tesla spectrum. No part of the fluorescence spectrum could be identified with the visible green bands in the Tesla spectrum.

N. M. BLIGH.

**Uranium as an activator. II.** (Miss) M. K. SLATTERY (J. Opt. Soc. Amer., 1929, 19, 175—186; cf. A., 1926, 659).—Solid solutions of uranium compounds in certain fluxes which are transparent in the ultra-violet showed, when irradiated with ultra-violet light, a fluorescent emission which for the fluorides gave bands which satisfied a "principle of essential identity," being capable of arrangement in three sets with a constant frequency interval of 18. It is suggested that the radical  $\text{UO}_2$  is broken down by the molten fluoride, giving a uranium ion, the fluorescence being due to uranium as an activator as distinct from the fluorescence of uranyl salts. A number of solvents was investigated to determine whether the bands would be members of the same three sets. The fluorides gave the brightest spectra and the best defined lines. Spectrographic measurements are tabulated for sodium and lithium fluorides, and the lines are found to fall into four sets of different frequency intervals, but one band is common.

N. M. BLIGH.

**Ionisation and dissociation processes in nitrogen, oxygen, carbon monoxide, and dioxide.** H. KALLMANN and B. ROSEN (Z. Physik, 1929, 58, 52—58).—The interpretation advanced by Hogness and Lunn (A., 1926, 104) for the high ratio of  $\text{N}^+$  to  $\text{N}_2^+$  ions ( $\text{N}^+$  70% of the total) in nitrogen subjected to 40-volt electrons, namely, that the  $\text{N}^+$  ions are formed as a result of secondary collisions between excited molecular ions and neutral molecules,  $\text{N}_2^+ + \text{N}_2 \rightleftharpoons \text{N}_2 + \text{N} + \text{N}^+$ , is unsatisfactory, since it is necessary to postulate that  $\text{N}_2^+$  ions exist with at least 8 volts energy and that the secondary process takes



place with an efficiency of 70%. Since the efficiency of the direct formation of ions in all known cases is much lower than this, a high value is improbable in a secondary process. The problem has been re-examined using the Smyth technique for the magnetic resolution of a sample of the ionised gas. Preliminary experiments indicated that the intensities of the various kinds of ions were determined by the gas pressure in this chamber; in particular molecular ions, *e.g.*,  $N_2^+$ , were preferentially strongly absorbed. This observation affords a simple explanation of the high ratio of  $N^+/N_2^+$  referred to above. Confirmatory evidence was obtained by measuring this ratio as a function of the gas pressure in the deflexion chamber under conditions such that the pressure in the ionisation chamber,  $3 \times 10^{-3}$  mm., and the electron velocity, 50 volts, remained constant. The absorption in the ionisation chamber was rendered negligible by providing that the ion path in this chamber was only 1/15 of that in the deflexion chamber. It was then observed that the ratio  $N^+/N_2^+$  varied from  $<0.058$  to 1.1 as the pressure in the deflexion chamber was increased from  $5 \times 10^{-5}$  mm. to  $2 \times 10^{-3}$  mm. It is concluded, therefore, that both ions originate in primary collisions between electrons and molecules.

In confirmation of Hogness' earlier work in oxygen, the formation of  $O_2^+$  and  $O^+$  ions was detected at 13.5 and 20 volts, respectively; the absorption of the molecular ion is much less marked than in the case of nitrogen.

In carbon monoxide at  $2 \times 10^{-3}$  mm. with 50-volt electrons the relative intensities of  $CO^+$ ,  $C^+$ , and  $O^+$  ions were measured as a function of the gas pressure in the deflexion chamber; the ratio  $CO^+/C^+$  varies from 25 to 0.6, and the ratio  $O^+/C^+$  from 0.2 to 0.0 as the deflexion chamber pressure was increased from  $3 \times 10^{-5}$  to  $10^{-3}$  mm. These results are held to establish that all these ions are formed by primary collisions.

With relatively low electron energies the four ions  $CO_2^+$ ,  $CO^+$ ,  $O^+$ , and  $C^+$  are formed in carbon dioxide, but no evidence was obtained for the processes  $CO_2 \rightarrow C + O_2$ , 2.4 volts, or  $CO_2 \rightarrow C^+ + O_2$ , 22 volts. With higher electron energies traces of  $O_2^+$  and  $C_2^+$  ions were found.

The results are held to show that the vast majority of dissociation processes in gases subjected to slow-moving electrons are primary, the only secondary processes of consequence being those concerned with the clustering and discharging of ions.

R. W. LUNT.

**Photo-electric investigations with solid dielectrics.** P. TARTAKOWSKY (Z. Physik, 1929, 58, 394—401).—By electronic bombardment of rock-salt, mica, and sulphur crystals a surface charge is produced on these dielectrics which can be removed by the action of light. The long-wave limit of the light effective in this respect has been determined approximately for these three materials. As was anticipated, a negative result was obtained in the case of diamond. From the data obtained the energy of evaporation of electrons from the surfaces could be calculated.

J. W. SMITH.

**in general.** E. WARBURG and W. RUMP (Z. Physik, 1929, 58, 291—305).—Unlike the hydrogen iodide solutions previously investigated (A., 1928, 490) the electrolytic dissociation of the photolyte cannot be neglected in the case of hydrogen sulphide solutions. Solutions of this compound in hexane follow the equivalent law, but not solutions in water. This difference is attributed to the fact that hydrogen sulphide does not react with hexane, but does so with water.

J. W. SMITH.

**Electron theory of metals.** J. FRENKEL (Physikal. Z., 1929, 30, 713).—The mobility of electrons in an external field can be represented, not only as a consequence of a supplementary velocity proportional to the field strength, but also equally well as a sequel to a different probability of displacement in different directions (with unchanged velocity), or a different free path somewhat greater in the direction of the field than in the contrary direction. These results are adaptable to the Fermi statistics. Bloch's theory of electrical conductivity in metals employs transition probabilities which can be considered in terms of the work of Dirac. The relations between metallic conduction and external magnetic fields and the Hall effect are discussed.

R. A. MORTON.

**Change in electrical conductivity in strong magnetic fields.** O. VON AUWERS (Naturwiss., 1929, 17, 867—873).—Mainly an exposition of the work of Kapitza (A., 1928, 825; 1929, 632).

R. A. MORTON.

**Conductivity of solid salts at high temperatures.** I. JOLLAND (Compt. rend., 1929, 189, 743—745; cf. Phipps, A., 1926, 231).—The conductivities ( $C$ ) of several alkali and alkaline-earth halides, carbonates, and sulphates have been determined at various temperatures up to  $1040^\circ$ . Two straight-line equations express the  $\log C - 1/T$  curves. The temperature at which the change from one to the other equation occurs appears to depend solely on the anion, being  $530$ — $540^\circ$  for chlorides,  $520$ — $525^\circ$  for bromides,  $407$ — $424^\circ$  for iodides,  $600$ — $640^\circ$  for fluorides,  $543$ — $567^\circ$  for sulphates, and  $416$ — $428^\circ$  for carbonates. The slope of the line for higher temperatures for sodium, potassium, and calcium is approximately double that of that for lower, whilst the reverse is the case for barium and strontium, which is inconsistent with Phipps' theory (*loc. cit.*).

C. A. SILBERRAD.

**Interpretation of the electrical nature of the linkings between carbon and hydrogen or other elements.** Z. WOJNICZ-SIANOŹECKI (Rocz. Chem., 1929, 9, 628—639).—The author's theory connecting the periodic law with atomic structure (*ibid.*, 1923, 3, 52) is applied to the structure and properties of organic compounds. Atomic stability is attained by atoms possessing 2, 8, 18, or 32 electrons; hydrogen possesses one electron, whilst carbon has one doublet and one quadruplet. Stability is achievable either by the loss of all valency electrons, or by the doubling of their number. Various apparently anomalous properties, such as the periodicity of m. p. of homologous aliphatic compounds, the molecular volumes of ethane, ethylene, and acetylene, etc., are explained on the basis of the above theory, and the molecular structures following from it are identical with the

**Photolysis of solutions of hydrogen sulphide in hexane and in water and photolysis of solutions**

stereochemical formulæ usually given in organic chemistry. Bivalent carbon is explained by the halving of the quadruplet of electrons to form a stable doublet. The toxic properties of carbon monoxide, acetylene chloride, and hydrogen cyanide (which is supposed to tautomerise thus:  $\text{H}\cdot\text{C}\cdot\text{N}\rightarrow\text{H}\cdot\text{N}\cdot\text{C}$ ) are ascribed to such bivalent carbon. Finally, the characteristic difference between the action of water on calcium carbide and on cuprous and silver acetylides is explained. R. TRUSZKOWSKI.

Effect of a magnetic field on the dielectric constants of gases. A. PÜTZER (Ann. Physik, 1929, [v], 3, 333—358).—With an apparatus capable of detecting small changes ( $\epsilon$ ,  $1\times 10^{-7}$ ,  $\epsilon-1$ ,  $2\times 10^{-4}$ ,  $(\epsilon-1)/4\pi$ ,  $2\times 10^{-3}$ ) in dielectric properties, it is found that a magnetic field of 8000 gauss has no measurable effect on oxygen, hydrogen, carbon dioxide, and nitrogen. R. A. MORTON.

Metallic reflexion. III. Optics of alkali halide deposits on glass. I. I. EBELING (Z. Physik, 1929, 58, 333—344; cf. A., 1925, ii, 643).—Absorption bands have been discovered and measured in the near infra-red region of the spectrum transmitted by thin films of potassium and rubidium. The significance of these bands is discussed. J. W. SMITH.

Dispersion of the electro-optical Kerr effect in the ultra-violet. G. SZIVESSY and A. DIERKES-MANN (Ann. Physik, 1929, [v], 3, 507—535).—Havelock's formula  $B=h(n^2-1)^2/n\lambda$  ( $B$  being the Kerr constant,  $n$  the refractive index for wave-length  $\lambda$ , and  $h$  a constant independent of wave-length) does not agree quantitatively with the data for the following liquids: chlorobenzene, hexane, carbon tetrachloride, toluene, and *m*-xylene. The Kerr constants have been determined for mercury lines in the visible and ultra-violet as far as the transparency of the liquids will allow, whilst the refractive indices in the ultra-violet were in most cases derived by interpolation from published data (cf. Voellmy, A., 1927, 812). The departures from the Havelock relation are considerable, but not always in the same sense.

R. A. MORTON.

Rotatory dispersion of tartaric acid and alkali tartrates in aqueous solution. G. BRUHAT and R. LEGRIS (Compt. rend., 1929, 189, 904—907).—The specific rotations of solutions of tartaric acid have been calculated from the formula  $[\alpha]=A/(\lambda^2-\lambda_1^2)-B/(\lambda_2-\lambda_0^2)$ , putting  $\lambda_0=2330\text{ \AA}$ , the value deduced from absorption determinations (cf. this vol., 10), and  $\lambda_1=1749\text{ \AA}$ . The results agree within 2% with experimental values of  $\lambda$  from 6438 to 2804  $\text{\AA}$ , but for  $\lambda=2652$  the discrepancy is 9%. For the neutral tartrates of potassium and sodium,  $\lambda_0$  remaining unchanged,  $\lambda_1=1670\text{ \AA}$ . The constants  $A$  and  $B$  vary but little with concentration, whence it is concluded that, as in the sugars, the rotatory powers of the two groups of electrons in the molecule vary but little. For tartaric acid  $B$  is approximately double its value for the tartrates. C. A. SILBERRAD.

Optical activity and the polarity of substituent groups. XII. Direct space effects of *m*- and *o*-*p*-directive substituents. 1-Menthyl esters of substituted naphthoic acids. H. G. RULE, J.

SPENCE, and E. BRETSCHER. XIII. Direct space effect in *d*-amyl derivatives. H. G. RULE (J.C.S., 1929, 2516—2524, 2524—2526).—The 1-menthyl esters of 2-methyl, 8-chloro-, and 4-, 5-, and 8-nitro-1-naphthoic acids, and of 3-chloro- and 1- and 3-hydroxy-2-naphthoic acids have been prepared and examined (cf. A., 1928, 884). The 8-nitro-acid is difficult to esterify; using thionyl chloride a 25% yield of 8-chloro-ester was obtained; treatment with dry hydrogen chloride for 120 hrs. at 140° gave only a small yield of impure nitro-ester. The 8-chloro-ester was not attacked by boiling alcoholic potassium hydroxide but was hydrolysed by fusion with the solid alkali at 180° for 2 hrs. The introduction of the *m*-directive nitro-group into the *peri*-position raises, whereas the *o*-*p*-directive chlorine and OMe lower the rotatory power. The groups Cl, Me, or OMe in an *o*-position to the ester group lower the rotation. The relative effect of different substituents is the same as for the benzoic esters. In the 4- and 5-positions the substituent has little or no influence. An *o*-hydroxyl group raises the rotation as in the salicylic ester, the value being diminished on ionisation. These esters are probably of chelate type. The substituent influence is probably propagated directly through space and is of electrostatic nature.

XIII. The changes in rotatory power due to variations in  $X$  in *d*-amyl derivatives of the type  $\text{C}_5\text{H}_{11}\text{X}$  are, in magnitude and direction, in agreement with the supposition of a direct space influence of the substituent. N. M. BLIGH.

Chemical combination as an electrostatic phenomenon. XIV. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 530—534).—The volatility of various compounds is discussed in relationship to the ease of polarisation: the volatility of the alkali metal halides is demonstrated to be a function of the size of the ions and of the ease of polarisation of the molecule. The polarisation theory is supported by consideration of the variations of the b. p. of the halides of a number of the elements, taken in order from the fluoride to the iodide, and also of the changes of b. p. which are observed when the hydrogen atoms of methane are successively replaced by halogen atoms. H. F. GILLBE.

Chemical combination as an electrostatic phenomenon. XV. A. E. VAN ARKEL and J. H. DE BOER (Chem. Weekblad, 1929, 26, 554—559).—Various types of complex compounds are considered, and a *résumé* is given of the whole series of papers. S. I. LEVY.

Quantum theory of valency. W. HEITLER (Physikal. Z., 1929, 30, 713—716).—The conception of monovalency for hydrogen implies the tendency of two atoms to form a molecule without the possibility of union with a third atom of hydrogen. Quantum mechanical methods are shown to provide an explanation of this result. The chemical inertness of the rare gases is considered in terms of spin-vectors. Electron pairs, especially for complete shells, cause repulsion, but free "light" electrons under suitable conditions cause attraction. The Lewis electron pair is regarded as a pair of electrons with antiparallel spin directions and arising from two different atoms, thus

bringing into being an interchange linking  $E_Q$ , interpreted in terms of the Schrödinger theory. When each of the electrons has linked up with an electron from another atom, forming pairs, a third atom is repelled, a pair acting as a closed shell. The conception of spin-coupling forces is applied to oxygen, halogens, and polyatomic molecules, the arguments throughout being given in outline only pending full publication.  
R. A. MORTON.

**Tetrahedral carbon atom.** R. HÖNIG (Z. Elektrochem., 1929, 35, 847—851).—The space formulæ for cyclic organic compounds are discussed with special reference to the views of Loewen (A., 1929, 54) and Bergmann and Mark (*ibid.*, 689).

R. CUTHILL.

**Form of the molecule of carbon dioxide.** F. I. G. RAWLINS (Trans. Faraday Soc., 1929, 25, 925—929).—Three models are possible for the carbon dioxide molecule: an isosceles triangular, a symmetrical linear, and an unsymmetrical linear model; the last-named, being unstable, is eliminated, and the evidence, especially that of the infra-red band spectra, on these forms is considered. The three regions of selective absorption in the infra-red are in favour of the first-named model; molecular heat data favour the second. The electric moment is investigated theoretically, and on comparison with experiment is conclusively in favour of the linear symmetrical model.

N. M. BLIGH.

**Simple possibility for the clear representation of X-ray levels by means of a face-centred cubic space lattice scheme.** R. REINICKE (Physikal. Z., 1929, 30, 693—697).—By the use of models built up from cubes in certain ways the representation and recognition of X-ray levels is facilitated.

R. A. MORTON.

**Diffraction of X-rays in various substances.** J. THIBAUD and J. J. TRILLAT (Compt. rend., 1929, 189, 751—753; cf. this vol., 4).—When X-rays are passed through a thick layer of liquid, in addition to the fundamental ring due to the mean distance between the molecules a secondary ring is observed. A layer of nonoic acid 4 mm. thick exposed to K-radiation from a copper anticathode shows this secondary ring, which is shown to be formed by radiation more penetrating than that forming the fundamental ring, as this latter alone disappears when a plate of aluminium 0.4 mm. thick is interposed. On increasing the voltage the diameter of the secondary ring decreases and its width increases, the ring becoming more diffuse. With a molybdenum anticathode the secondary ring tends with increasing voltage to merge into the fundamental. These effects have been observed in many liquids and are attributed to a filtration of the heterogeneous radiation by the increased thickness of the liquid.

C. A. SILBERRAD.

**X-Ray detection of the electrical polarisation of a crystal lattice.** J. HENGSTENBERG (Z. Physik, 1929, 58, 345—347).—The ionic displacement produced in a crystal by the application of an electric field has been observed by accurate X-ray intensity measurements. Observations on the intensity of the tenth order reflexions of the cubic plane of potassium

chloride gave results in agreement, within experimental error, with the theoretically predicted changes.

J. W. SMITH.

**Determination of the position of the axis of symmetry of a crystal by means of X-rays.** W. LENNIK (Nature, 1929, 124, 946).

**Determination of the orientation of crystals by means of the Laue diagram and stereographic projection.** B. SCHMIDT (Z. Physik, 1929, 58, 577—584).—A series of determinations using Schiebold and Sachs' method is described in which the method is extended and its accuracy increased. The stereographic projection of the Laue diagram is made and the crystallographic elements of symmetry are marked. The method is applicable to all crystallographic systems, including the monoclinic and triclinic, if the direction of the axes is otherwise known.

A. J. MEE.

**Quantitative chemical analysis by means of X-ray emission spectra.** H. SCHREIBER (Z. Physik, 1929, 58, 619—650).—Two processes of emission analysis using cathode-ray excitation are first compared as regards experimental errors. In one the determination of concentration is made by comparing corresponding lines of neighbouring elements. The other is the method of mixing used by von Hevesy and Coster. By the examination of Debye photographs it can be shown that in consequence of the high temperature of the anticathode, chemical decomposition can take place, which causes a change in the original concentration in the surface layer of the preparation. This accounts for the effect of mixing foreign substances first noticed by Coster and Nishina. In order to overcome the considerable heating of the test substance when the cathode-ray method is used, a new and general method of X-ray emission analysis is described in which the excitation of the characteristic radiation is brought about by primary X-rays. A complete elimination of the diffuse reflexion of electrons at the anticathode is unnecessary, for the amount of heating due to this is very small, as may be shown experimentally. Photographing the emission spectrum of a solution is possible. The new fluorescence method was tested on a number of mixtures with satisfactory results. Tin-antimony mixtures, with the addition of gypsum, a titanium-vanadium mixture, vanadium steel, a mixture of rare earths, and platinum metals were used. The effect of the admixture of foreign substances is in this method negligible. The sources of error are examined. The possible total error in the estimation of the concentration of an element is 7%.

A. J. MEE.

**Structure of the form of solid nitrogen stable below 35.5° Abs.** L. VEGARD (Z. Physik, 1929, 58, 497—510).—Debye-Scherrer photographs were obtained for the solid form of nitrogen stable below 35.5° Abs. It was found to crystallise in the cubic system. The elementary cell has a side of length 5.66 Å. and contains 8 atoms. A systematic discussion of the intensity distribution in the X-ray spectrum shows that the  $T^4$  space-group only is involved. The distance between atoms of two neighbouring molecules is much larger than the

central distance between two atoms in the molecule. The molecular axes coincide with the trigonal axes. The distance between two atoms in the molecule is 1.065 Å. The distance calculated from the Raman effect for the normal nitrogen molecule is 1.10 Å. The structure of this form of nitrogen resembles that of sodium chlorate and bromate and of nitrous oxide and carbon dioxide. The central distances between the atoms in the nitrogen molecule in the crystalline and gaseous states are the same within the experimental error. The separation energy calculated from the fundamental term of the  $\epsilon$  system is 11.2 volts. The value for the normal gas derived from the gas spectrum is 11.6 volts. The two are therefore identical within the experimental error.

A. J. MEE.

**Difference in space-lattice disturbance and texture between surface and nuclear zones of drawn single- and multi-crystal tungsten wire.** W. G. BURGERS (Z. Physik, 1929, 58, 11—38).—The difference in the disturbance of the space lattice in different zones of drawn tungsten single- and multi-crystal wire has been investigated by the determination of the change in the broadening of the Debye-Scherrer lines in X-ray spectrograms of the wires before and after etching away the surface layers. In all cases the lattice disturbance was found to be greater in the surface layers than in the zone lying immediately below them, but in the case of very strongly drawn wires this increased again towards the centre of the wire. The differences, however, are very small compared with the lattice disturbance in the wires as a whole.

J. W. SMITH.

**Crystal structure of ice between 0° and -183°.** W. H. BARNES (Proc. Roy. Soc., 1929, A, 125, 670—693).—Previous work on the crystal structure and crystallography of ice is critically reviewed, and possible causes for the conflicting nature of the data available are considered. A complete structure is proposed on the basis of results obtained from single-crystal rotation photographs about the principal crystallographic axes, oscillation photographs, and Laue photographs. Samples of naturally frozen ice, kept at -78.5°, were used for the last-named, whilst for the rotation and oscillation photographs (obtained at -20° with a Müller spectrograph and circular camera, specially adapted for use at temperatures below zero), prisms occurring in artificially frozen ice were employed. It is found that the unit cell contains 4 mols., and has  $a$  4.53,  $c$  7.41 Å.;  $c:a=1.634$ . The space-group is either  $D_{3h}^2$  (dihexagonal bipyramidal) or  $D_{3d}^2$  (ditrigonal bipyramidal), probably the former. The geometrical structure factor for two sets of possible equivalent points is given, one set being shown to be incompatible with the observed halvings. The equivalent points for the diffracting centres in the unit cell are found to be 1/3, 2/3, 1/6; 1/3, 2/3, 7/16; 2/3, 1/3, 9/16; 2/3, 1/3, -1/16. Arguments are advanced in an attempt to show that the structure is probably ionic in nature, and the most probable relative arrangement of hydrogen and oxygen ions is that in which one hydrogen is placed on the line joining each pair of oxygen centres and half-way between them.

A description is given of the apparatus used for taking powder photographs of ice at -9°, -13°, -78°, and -183°. The results indicate that no change occurs in the structure between 0° and -183°.

L. L. BIRCUMSHAW.

**Crystal structure of ammonium cupric chloride,  $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ .** L. CHROBAK (Bull. Acad. Polonaise, 1929, A, 361—389).—The crystal structure of the double salt,  $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$  ( $d$  2.007), prepared by the slow evaporation of aqueous solutions of cupric chloride (1 mol.) and ammonium chloride (2 mols.), belonging to the tetragonal rhombododecahedral system, has been investigated by the Laue and the rotating crystal methods. The basic cell contains two  $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$  molecules; the spatial orientation of the  $\text{NH}_4^+$ ,  $\text{Cu}^{++}$ , and  $\text{Cl}^-$  ions and of the  $\text{H}_2\text{O}$  molecules is deduced.

A. I. VOGEL.

**Crystal structure of potassium per-rhenate.** E. BROCH (Z. physikal. Chem., 1929, B, 6, 22—26).—Potassium per-rhenate ( $\text{KReO}_4$ ) is isomorphous with scheelite. Measurements of powder diagrams give the following constants:  $a$  5.615,  $c$  12.50 Å.,  $d$  (calc.) 4.887.

F. L. USHER.

**Crystal structure of wurtzite.** M. L. FULLER (Phil. Mag., 1929, [vii], 8, 658—664).—Wurtzite has been prepared free from cubic zinc sulphide or sphalerite by heating the latter with 10% of sodium chloride at 1100° in an atmosphere of hydrogen, cooling to the ordinary temperature in about 10 min., and screening on a 325-mesh screen without submitting the sample to any mechanical strain. The observed intensities on powder patterns are in good agreement with those calculated for space-group  $Ge-4$  with  $V=5/8$ , the zinc oxide type of structure as predicted by Bragg (A., 1920, ii, 433). The unit-cell dimensions are  $a_0$  3.811±0.004,  $c_0$  6.234±0.006 Å., and  $c/a=1.636$ ;  $d$  (X-ray) is 4.10±0.01, whilst the pyknometer  $d$  of the naturally occurring mineral is 3.98 and of the artificially prepared wurtzite 4.087. The different intensities obtained by other investigators are probably to be explained by the inclusion of varying quantities of sphalerite in the wurtzite.

M. S. BURR.

**Constitution of Rinmann's green, Thénard's blue, and other coloured solid derivatives of the oxides of cobalt.** G. NATTA and L. PASSERINI (Gazzetta, 1929, 59, 620—642).—X-Ray examination of the green products obtained by heating mixtures of cobaltous and zinc nitrates in air at 800—1000° shows that they consist of cubic crystals of zinc cobaltite ( $a$  8.06 Å.) mixed with hexagonal crystals which are practically identical with those of zinc oxide ( $a$  3.24 Å.). Products containing more than 30—40% Co, when heated for a long time at 1000°, also show the lines of cobaltous oxide. The products obtained by heating solid solutions of cobaltous and zinc hydroxides or basic carbonates in a vacuum contain all the cobalt in the bivalent state. Those containing less than 30% CoO are green and consist of hexagonal solid solutions of cobaltous oxide in the zinc oxide lattice, whilst above 70% CoO they are pink and consist of cubic solid solutions of zinc oxide in the cobaltous oxide lattice. The colour of Rin-

mann's green is due to the presence of the hexagonal solid solutions. The presence of zinc cobaltite deepens the green colour. Zinc cobaltite dissociates above 900–1000° into oxygen and the oxides of the bivalent metals.

The pink products obtained by calcination of mixtures of cobaltous and magnesium oxides consist of cubic solid solutions of the former oxide in magnesium oxide, and do not contain tervalent cobalt, if surface oxidation during cooling is prevented. The cobaltite of magnesium, which can be obtained only at relatively low temperatures, is less stable than that of zinc and dissociates on heating into the above-mentioned solid solutions of the two bivalent oxides, which are miscible in all proportions in the solid state.

The colour of Thénard's blue is due to cubic cobaltous aluminate having a spinel structure ( $a$  8.06 Å.), which is mixed with alumina. The products containing more than 50 mol.-% CoO are deeper in colour and contain tervalent cobalt as the compound  $\text{CoCo}_2\text{O}_4$ , which is isomorphous with cobaltous aluminate and has practically identical lattice dimensions.

The green products obtained by calcining stannic oxide with cobaltous compounds consist of mixtures of cobaltous orthostannate,  $\text{Co}_2\text{SnO}_4$  (cubic spinel structure,  $a$  8.61 Å.), with stannic oxide.

O. J. WALKER.

**Lattice constants of epydidymite.** B. GOSSNER and F. MUSSGUTH (Festschr. V. Goldschmidt, 1927, 117–126; Chem. Zentr., 1929, ii, 277).—Epydidymite,  $\text{BeSi}_2\text{O}_5 \cdot \text{NaHSiO}_3$ , rhombic pseudo-hexagonal, has  $a$  7.33,  $b$  12.73,  $c$  13.60 Å., the unit cell containing 8 mols.

A. A. ELDRIDGE.

**Crystal structure of tetramethyl-, trimethyl-, and methyltriethyl-ammonium chlorostannates.** R. W. G. WYCKOFF and R. B. COREY (Amer. J. Sci., 1929, [v], 19, 437–445).—The crystal of tetramethylammonium chlorostannate is cubic, containing 4 mols. to the unit cell, the edge of which measures 12.87 Å. The positions of the tin, chlorine, nitrogen, and carbon atoms are  $4b$ ,  $24a$ ,  $8c$ , and  $32a$ , respectively. Trimethylammonium chlorostannate also contains 4 mols. to the unit cell, of edge 12.19 Å. The length of the edge of unit cube of methyltriethylammonium chlorostannate is 13.51 Å. There are 4 mols. to the unit cell.

C. W. GIBBY.

**Shape and size of the cellulose and caoutchouc micelles.** J. HENGSTENBERG and H. MARK (Z. Krist., 1928, 69, 271–284; Chem. Zentr., 1929, i, 3088).—In native cellulose the micellar section perpendicular to the fibre axis is a rhombus of side  $55 \pm 5$  Å.; the micellar length is greater than 600 Å. The micelle of viscose is smaller than that of ramie, and the micelle is shortened in passing from ramie to mercerised cellulose. The section of the caoutchouc crystallite perpendicular to the direction of extension is a rectangle with ratio of sides 1:3. Observations of the width of lines at the temperature of liquid air gave the same results as at the ordinary temperature. On extension by more than 280% the crystals are replaced by the fibre diagram of stretched rubber. Hence the size of the crystallites depends on the choice of conditions.

A. A. ELDRIDGE.

#### X-Ray investigations of cellulose derivatives.

#### IV. Fibre diagrams of copper-alkali-cellulose.

C. TROGUS and K. HESS (Z. physikal. Chem., 1929, B, 6, 1–21; cf. Messmer, A., 1927, 619).—The above system has been studied over the range of concentration in which cellulose is wholly or partly insoluble. Curves are given to show the relation between absorption of copper by ramie fibre and the concentration of copper in a cuprammonium solution. From the space diagram of cellulose-copper tetrammine hydroxide-sodium hydroxide it is inferred that in the insoluble range the fibres consist of a mixture of two compounds,  $[\text{Cu}(\text{C}_6\text{H}_{10}\text{O}_5)_2]_2\text{Na}_2$  and  $[\text{Cu}(\text{C}_6\text{H}_{10}\text{O}_5)_2]_2[\text{Cu}(\text{NH}_3)_4]_2\text{Na}_2$ . This inference is supported by X-ray examination of cellulose which has been treated with cuprammonium hydroxide, the existence of two compounds with periods 10.5 and 15.7 Å. being clearly shown. When copper is removed by means of sodium hydroxide, both compounds give cellulose hydrate. The experiments indicate that alteration of the lattice through substitution or salt formation takes place both along the axis of the fibres and at right angles to it. The change brought about in cellulose by the action of copper and alkali is of a definite chemical nature.

F. L. USHER.

#### Systematic structure theory. II–IV. C.

HERMANN (Z. Krist., 1929, 69, 226–249, 250–270, 533–555; Chem. Zentr., 1929, ii, 254).

**Theory of liquid crystals.** E. ALEXANDER and K. HERRMANN (Z. Krist., 1928, 69, 285–299; Chem. Zentr., 1929, ii, 250).—It is supposed that liquid crystals “crystallise” in a space-group additional to the crystalline space-groups (3 dimensions), the space-groups being two- or uni-dimensional for smectic and nematic substances, respectively.

A. A. ELDRIDGE.

**Asymmetry of corrosion figures produced by an isotropic active liquid.** L. ROYER (Compt. rend., 1929, 189, 932–933; cf. A., 1929, 631, 750).—Calamine (rhombic hemimorphic) when etched with an inactive organic acid gives on (010) and (0 $\bar{1}$ 0) figures with no centre of symmetry, but symmetrical relatively to (100) and for which the zone axis [001] is a binary axis of symmetry. The same faces etched by an active acid, whilst otherwise similar, show no symmetry relative to (100), the crystal thus displaying a tetartohedral form. Crystals of *d*- and *l*-tartaric acid etched by ethyl, *d*-sec.-butyl, isoamyl, and *l*-sec.-amyl alcohols, *z*- (fermentation) and *d*-lactic acids, *d*-menthol, and *d*- and *l*-terpineol show that a *d*-crystal etched by a *d*-liquid gives figures which are enantiomorphous with those formed by a *l*-liquid on a *l*-crystal, but quite different from those formed by a *d*-liquid on a *l*-crystal, or by a *l*-liquid on a *d*-crystal, these two again being enantiomorphous *inter se*.

C. A. SILBERRAD.

**Structure of silver-antimony alloys.** M. G. RAEDER (Z. physikal. Chem., 1929, B, 6, 40–42; cf. A., 1928, 597).—The new structural elements recently found by Westgren, Hägg, and Eriksson (cf. A., 1929, 1139) in silver-antimony alloys had already been indicated by anomalies in the overvoltage-composition curves.

F. L. USHER.

**X-Ray investigations of copper amalgams.** N. KATOH (Z. physikal. Chem., 1929, B, 6, 27—39; cf. Terrey and Wright, A., 1929, 16).—Powder diagrams of copper amalgams containing not more than 27% Cu show the presence of a  $\gamma$ -phase with a 9.401 Å., which is unaltered after the amalgam has been subjected to a pressure of 10,000 kg./cm.<sup>2</sup> Above 29.9% Cu an  $\alpha$ -phase appears, which has been identified as copper, and the lattice constants of the two phases remain unchanged as the proportion of copper is increased. Amalgams with more than 75% Cu are therefore not homogeneous at the ordinary temperature, contrary to the statement of Tammann and Stassfurth (cf. A., 1925, ii, 377). F. L. USHER.

**Magnetic properties of some compounds of manganese.** L. F. BATES (Phil. Mag., 1929, [vii], 8, 714—732; cf. A., 1928, 468; Whitmore, A., 1929, 386).—The magnetic properties of manganese arsenide, MnAs, and manganese phosphide, MnP, have been examined at temperatures above their magnetic critical points, i.e., above 45° and 40°, respectively, by a balance method which is described. At these temperatures the compounds are strongly paramagnetic. The ferromagnetic properties of the specimens employed were first determined. The maximum intensity of magnetisation of the arsenide, when packed in powder form to a density of 3.68 g. per c.c., was 203.2 c.g.s. units with a field strength of 760 gauss, at 0°. This did not represent saturation. Hysteresis curves were also obtained at the ordinary temperature and at the temperature of liquid air. In the latter case, for the same field, the magnetisation was 220.2 units. The magnetic properties of the specimen of phosphide were less pronounced. The hysteresis was small and, for a field of 760 gauss and packing of 2.24 g. per c.c., the maximum intensity of magnetisation was 24.0 c.g.s. units. In the paramagnetic region of temperature the susceptibility of the arsenide is practically constant over a range of temperature from 90° to 130°, after which the Weiss law is obeyed. The Weiss law is obeyed throughout by magnesium phosphide, at any rate up to 265°. The nature of the marked temperature hysteresis shown by the arsenide at the critical point is discussed. M. S. BURR.

**Magnetic properties of isolated ferromagnetic atoms.** F. W. CONSTANT (Physical Rev., 1929, [ii], 34, 1217—1224).—The behaviour of the elementary atomic magnet when surrounded by non-magnetic atoms was investigated with alloys of 90% and 95% platinum with cobalt and nickel, respectively, by measuring the intensity of magnetisation for constant applied magnetic force at different temperatures up to the Curie point, and by constructing hysteresis loops at given temperatures. Only the cobalt alloys were magnetic; the moment per cobalt atom being greater than for pure cobalt, the platinum may contribute to the magnetism. The Curie points fell rapidly with decreasing cobalt content. Results are in agreement with Heisenberg's theory of ferromagnetism. N. M. BLIGH.

**Saturation magnetisation of nickel-cobalt alloys and the atomic moments of nickel and cobalt.** P. WEISS, R. FORRER, and F. BIRCH

(Compt. rend., 1929, 189, 789—791; cf. A., 1929, 1369).—The saturation magnetisation and its variation with temperature down to that of liquid air have been determined for nine nickel-cobalt alloys of composition varying from pure nickel to pure cobalt, and the results (given by a curve) extrapolated to show absolute saturation at absolute zero. The coefficient of magnetic hardness ( $\alpha$ ) varies continuously for the  $\gamma$ -alloys and increases very rapidly (to values of the order of 200) for the H-alloys. The magnetic moment deduced for pure nickel is 3 magnetons (with some indication of 4 for the H-alloys); that for cobalt in  $\gamma$ -alloys is 9 and in H-alloys 8.5. The absence of any breach of continuity between the  $\gamma$ - and H-alloys is attributed to the number of adjoining atoms in the face-centred cubic lattice ( $\gamma$ ) being the same as that in the hexagonal lattice (H). C. A. SILBERRAD.

**Determinations with the aid of liquid helium.** V. Superconductivity of cupric sulphide. W. MEISSNER (Z. Physik, 1929, 58, 570—572).—Between 1.66° and 1.55° Abs. the resistance of a filament of cupric sulphide decreases to an immeasurably small value. A. J. MEE.

**Sulphide colours on metallic copper.** F. H. CONSTABLE (Proc. Roy. Soc., 1929, A, 125, 630—635; cf. A., 1928, 106).—An apparatus is described by means of which spectrophotometric observations of the reflected light from films of increasing thickness, formed by the action of a mixture of hydrogen sulphide and air on metallic copper, may be carried out as the reaction proceeds. The resistance is obtained from a direct-reading millivoltmeter showing the *P.D.* across the copper film when a measured small current is passed through it. It is found that by activating the copper surface at low temperature *in situ* by alternate oxidation and reduction, and leaving the cold activated metal in air for periods varying from 5 min. to 1 hr., the rate at which the sulphide colour sequence is formed is greatly reduced owing to the presence of an invisible oxide film. High-temperature reduction (about 600°) results in a surface which can be exposed to air for hours with impunity, the rate of formation of sulphide colours being only very slightly decreased owing to the slowness of low-temperature oxidation of surfaces so prepared. There is evidence that the interference colours are of a similar nature to those produced during the oxidation of copper (cf. A., 1927, 930).

L. L. BIRCUMSHAW.

**Thermoelastic properties of ferromagnetic metals and the molecular field.** E. BAUER (J. Phys. Radium, 1929, [vi], 10, 345—359).—The theory of the molecular field of Weiss has received extended application, so that it gives not only the expression for the energy of a ferro-magnetic substance, but also the "equation of state" of such substances. It is possible to calculate their entropy and free energy as a function of the temperature and specific volume. From the curves of magnetisation, with the help of this theory, the anomalies in the compressibilities and dilatation may be accounted for fairly satisfactorily in the case of nickel. The results for iron are not so good. F. J. WILKINS.



**Changes in the dimensions of metallic wires produced by torsion. I. Soft-drawn copper.** T. LONSDALE (Phil. Mag., 1929, [vii], 8, 703—713).—Determinations have been made of the changes in length of soft-drawn copper wire when twisted at the ordinary temperature under a constant load which is small in comparison with the load necessary to produce permanent set. The apparatus employed is described. Considerable elongations are produced, even under very small tensions, and under somewhat larger tensions much greater elongations are observed for the same degree of twist. Within the range of tension and rate of twist employed, the elongation is a function merely of the torsion and tension applied to a given wire, and not of the rate of twist or of the length of time after twist. M. S. BURR.

**Influence of mechanical deformation on the transition points of iron and steel.** F. SAUERWALD and T. SPERLING (Z. Physik, 1929, 56, 544—547).—From the cooling and heating curves during deformation it follows that the Ac1 point is 7° lower, Ac3 4° lower, and Ar3 about 4° higher. The Ar1 point is displaced at most 1°. Suggestions for these changes are given.

**Plasticity of crystals.** W. BOAS and E. SCHMID (Z. Physik, 1929, 56, 516—523).—A mathematical discussion of the relation between slip-tension, thrust, elasticity, and tenacity in various crystal lattices. The quadratic expression of von Mises (Z. angew. Math. Mech., 1928, 8, 161) is considered in relation to experimental data.

**Production of large zinc crystals.** M. ICHIHARA (Tech. Rep. Tôhoku, 1929, 8, 1—7).—The strain-annealing method of obtaining single crystals was applied to zinc; the largest crystals were obtained after severe deformation, and not after a small critical strain as in the case of copper and aluminium. One inch diameter chill-cast bars were forged at 300° to 10 mm. square bars, heated for 2 days at 410°, and then just below the m. p. for a few hours. Single crystals 8×80 mm. were thus obtained. These crystals deform by slip on the (0001) planes and failure occurs on the basal plane.

C. J. SMITHELLS.

**Twinning plane in a zinc crystal.** M. ICHIHARA (Tech. Rep. Tôhoku, 1929, 8, 9—19).—The directions of primary twin lamellæ formed on (0001), (10 $\bar{1}$ 0), and (11 $\bar{2}$ 0) surfaces of zinc single crystals were measured. It is shown that the (10 $\bar{1}$ 2) plane is the twinning plane. The directions of secondary twin lamellæ occurring in the primary twins show that the secondary twins result from rotation through 180° about an axis normal to the twinning plane. C. J. SMITHELLS.

**Dynamic allotropic state of selenium. I and II.** G. BRIEGLEB (Z. physikal. Chem., 1929, 144, 321—339, 340—358; see also A., 1929, 250).—A special Soxhlet apparatus is described for extracting with cold carbon disulphide samples of vitreous selenium obtained by quenching fused selenium. This form of selenium has been shown to be amorphous by X-ray examination. As extraction proceeds a diminution in the rate of dissolution is observed. This is not due to change of surface area, but solely to

a change in the composition of the selenium, and may be ascribed to the presence of two forms, Se'' and Se', of which Se'' dissolves more rapidly than Se', although the absolute solubilities are practically the same. The composition of the selenium depends on the temperature to which the mass has been heated before quenching. By comparing amounts extracted after  $\frac{1}{2}$  hr., it was found that samples of selenium, supercooled to 120° and then quenched, give approximately 55% of Se''. The amount diminishes as the initial temperature rises until samples quenched from 650° give only about 14%. The result is independent of the modification of selenium fused. Spectrographic examination of the solution in carbon disulphide indicates a change in the state of the solute with increasing dilution. An X-ray investigation of all the solid phases of selenium by the Debye-Scherrer method has established the identity of Marc's non-conducting metalloid selenium and conducting metallic selenium. The different behaviour is simply due to difference in size of particle. Red monoclinic selenium is identical with the partly blackened monoclinic selenium. All the different modifications of solid selenium are to be attributed to the transformation of a dipole molecular lattice, Se<sub>2</sub>, which is the principal component of monoclinic selenium, into an atomic lattice, Se<sub>1</sub>, the principal component of hexagonal selenium. Se<sub>1</sub> and Se<sub>2</sub> may be identified with Se' and Se'', respectively, rise in temperature resulting in a shifting of the equilibrium Se<sub>2</sub>  $\rightleftharpoons$  2Se<sub>1</sub> towards the right. The equilibrium in the solid and fused states is represented by a pseudo-binary diagram, and in solution by a pseudo-ternary diagram. M. S. BURR.

**Temperature law of ionic conductivity of solid lead halides.** A. SMEKAL (Z. Physik, 1929, 58, 322—332).—It is suggested that the formula given by Seith (A., 1929, 1136) for the change of the dipolar ionic conductivity of solid lead iodide should be revised:  $k = 2.95 \times 10^{-4} \times e^{-1140/T} + 8.0 \times 10^{-4} \times e^{-14720/T}$ . The second term of this equation corresponds with the cation portion of the conducting power. Thus, unlike previously investigated solid ionic conductors, the two-term conductivity formula is directly traceable to the dipolar character of the conductivity process at high temperature. On account of the free ion character of the conductivity term due to the anion as against the lattice ion character of the cation constituent, it is possible that the transport numbers of dipole solid ionic conductors of the type of PbI<sub>2</sub> are not necessarily determined by the chemical nature of the material, but may be modified by the structure of the conductor (e.g., grain size, and previous thermal history). The temperatures of sudden increase of reaction velocity in Hedvall's powder reactions of barium oxide with lead chloride and iodide are in agreement with the diffusion coefficients of lead ions in the two salts.

J. W. SMITH.

**Pierce acoustic interferometer as an instrument for the determination of velocity and absorption.** W. H. PIELEMEIER (Physical Rev., 1929, [ii], 34, 1184—1203).—The Pierce interferometer was used to investigate the absorption of high-



frequency sound ( $3 \times 10^5$ — $14 \times 10^5$  cycles per sec.) in air and in carbon dioxide, and the relations of the results to the velocity of sound at these frequencies. Evidence was found of a variation of wave velocity with intensity. The absorption by air and carbon dioxide increases with the frequency throughout the range.

N. M. BLIGH.

**Fusion curve of helium.** II. F. SIMON, M. RUHEMANN, and W. A. M. EDWARDS (Z. physikal. Chem., 1929, B, 6, 62—77; cf. A., 1929, 497).—The fusion curve for helium from  $12^\circ$  Abs. and 800 kg./cm.<sup>2</sup> to  $42^\circ$  Abs. and 5600 kg./cm.<sup>2</sup> has been drawn. Within the limits of the considerable errors involved in both temperature and pressure measurements the curve is in agreement with a semi-empirical formula previously deduced (cf. A., 1929, 386). A calorimetric method was used for low pressures, and the convenient method of capillary blockage by the solid for high pressures.

F. L. USHER.

**Latent heat of vaporisation and surface tension.** W. HERZ (Z. Elektrochem., 1929, 35, 851—853).—Existing data show that the increase in latent heat of vaporisation,  $L$ , as the temperature of a liquid falls from the critical temperature to the reduced temperature  $8/12$  diminishes with successive decrements of  $1/12$  in the temperature, the value of  $L$  at  $11/12$  being about 50—60% of the value at  $8/12$ . The increase in the surface tension,  $\gamma$ , on the other hand, tends to rise with successive decrements of  $1/12$  in the temperature, and the value of  $\gamma$  at  $11/12$  is only about 20% of the value at  $8/12$ . For a given reduced temperature the quotient of  $L$  by the capillary constant has approximately the same value for all non-associated liquids.

R. CUTHILL.

**Specific heat at lines of equal internal energy and equal heat content.** H. MACHE (Monatsh., 1929, 53 and 54, 1002—1007).—Theoretical and mainly mathematical.

L. S. THEOBALD.

**Specific heats of tantalum, tungsten, and beryllium between  $100^\circ$  and  $900^\circ$ .** A. MAGNUS and H. HOLZMANN (Ann. Physik, 1929, [v], 3, 585—613).—The experiments were carried out in the Magnus copper calorimeter. The construction of a suitable thermo-regulator for use with the calorimeter is described. By the elimination of convection currents it is ensured that the temperature change of the calorimeter during the readings does not exceed  $1/200,000$ — $1/100,000^\circ$  per min. This plays an important part in the accurate determination of the final temperature by extrapolation. To prevent oxidation of the test substance, the heating was carried out in an hermetically sealed vessel. Using this apparatus, the specific heats of tantalum, tungsten, and beryllium were determined between  $100^\circ$  and  $900^\circ$ . The true atomic heat can be expressed exactly for tantalum and tungsten by an interpolation formula involving two constants, and for beryllium by a formula involving one constant. The atomic heat of tantalum at constant volume can be expressed exactly by the formula of Born and Brody,  $C_v = 3R(1 - 3R\sigma T)$ , if  $\sigma$  is given the value  $-0.1972 \times 10^{-4}$ . The  $C_v$  values for tungsten and beryllium exceed somewhat the value  $3R$ . The change with temperature is not linear.

A. J. MEE.

**Method for extrapolating specific heat curves of organic compounds below the temperatures of liquid air.** K. K. KELLEY, G. S. PARKS, and H. M. HUFFMAN (J. Physical Chem., 1929, 33, 1802—1805).—The equation  $C_p$  (per g.-mol.)  $= (A + BT)C_p^0$ , where  $C_p^0$  is the molal specific heat of the standard substance for the two classes into which organic compounds can be divided, is derived.  $A$  and  $B$  are evaluated from the molal heat capacities at  $90^\circ$  and  $120^\circ$  Abs. The method has been satisfactorily used (A., 1929, 990) for the revision of the entropies and free energies of 19 organic compounds.

L. S. THEOBALD.

**Heat capacity of nitric oxide from  $14^\circ$  Abs. to the b. p. and the heat of vaporisation. Vapour pressures of solid and liquid phases. Entropy from spectroscopic data.** H. L. JOHNSTON and W. F. GIAUQUE (J. Amer. Chem. Soc., 1929, 51, 3194—3214).—The specific heats were measured from  $15$ – $57^\circ$  Abs. to the b. p.;  $\beta_v = 119$  in the Debye equation. The m. p. is  $109.49^\circ$  Abs. and the molar heat of fusion at the m. p.  $549.5$  g.-cal./ $1^\circ$ . A transition involving very small energy change may occur at  $52.64^\circ$  Abs. The molar heat of evaporation at the b. p.,  $121.36^\circ$  Abs., is  $3292.6$  g.-cal. The vapour pressure is given by  $\log p(\text{cm.}) = -867/T + 0.00076T + 9.05125$  for the solid and  $\log p(\text{cm.}) = -776/T - 0.002364T + 8.562128$  for the liquid. The triple point pressure is  $16.438$  cm. The molal entropy at the b. p. is  $42.94$  g.-cal./ $1^\circ$ , or, corrected to the state of an ideal gas,  $43.03$  g.-cal./ $1^\circ$ . This value is slightly higher than that calculated from spectroscopic data and the discrepancy is attributed to the presence in the solid state of equimolecular quantities of two polymerised isomerides, e.g.,  $N_2O_2$ .

Elaborate directions are given for preparing nitric oxide which, as calculated by means of Raoult's law from heat capacity measurements just below the m. p., contains less than  $0.001\%$  of impurity. Both liquid and solid nitric oxide are blue, but the sublimed solid is white. Sudden chilling of the liquid yields a solid which, being full of cracks, appears white and opaque.

S. K. TWEEDY.

**Vapour pressure of phosphorus oxychloride.** K. ARII (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 545—551).—The vapour pressure of phosphorus oxychloride has been measured at intervals of  $10^\circ$ , from  $20^\circ$  to its b. p. The latent heat of vaporisation is calculated to be  $8697$  g.-cal. at  $25^\circ$  and  $8210$  g.-cal. at the b. p. From the vapour pressure-temperature curve the b. p. is found to be  $105.3^\circ$ . Phosphorus oxychloride appears to be non-associated in the liquid, since it gives a value of Trouton's constant of  $21.7$ .

F. J. WILKINS.

**Vapour pressure of nitrous acid.** E. ABEL and E. NEUSSER (Monatsh., 1929, 53 and 54, 855—873).—The vapour pressure of aqueous solutions of nitrous acid has been measured at  $25^\circ$ . The vapour consists essentially of nitrous acid and not of nitrous anhydride. At equal ionic concentrations ( $j$ ), the vapour pressure is proportional to the nitrous acid content of the solution and when  $j = 1.4$ ,  $p_{\text{HNO}_2}/[\text{HNO}_2] = k = 0.0336$ . With increasing ionic concentration  $k$  increases according to the expression  $p_{\text{HNO}_2}/[\text{HNO}_2] = k = kf$ ,

where  $f$  is the activity coefficient of nitrous acid and  $k=0.0305$  for  $25^\circ$ .

L. S. THEOBALD.

**Vapour pressure and heat of vaporisation of diphenyl.** J. CHIPMAN and S. B. PELTIER (Ind. Eng. Chem., 1929, 21, 1106—1108).—The vapour pressure of diphenyl has been measured by an isoteniscopic method between  $162.6^\circ$  and  $322.3^\circ$ . The densities of liquid and saturated vapour at the b. p. are 0.85 and  $0.00375 \pm 0.00001$ , respectively. The latent heat of vaporisation at the b. p. is calculated to be  $11470 \pm 50$  g.-cal. per mol., and the entropy of vaporisation at the same temperature is  $21.7$  g.-cal. per degree. The b. p. is  $255.25^\circ$ , in agreement with Jaquerod and Wassner (A., 1904, ii, 538).

C. W. GIBBY.

**Special case of hysteresis phenomenon in physico-chemical systems, and its possible explanation of some biological problems.** N. VON RASCHESKY (Z. Physik, 1929, 58, 523—539; cf. A., 1929, 509).—Systems with several equilibrium states, and therefore showing hysteresis phenomena, are further investigated. A special case is treated. In a given equilibrium state a system can be changed by some external action  $E_1$ , but not by another,  $E_2$ . However, by a sequence of  $E_2$  and  $E_1$ , the system is brought to another equilibrium state in which it can be affected only by a change  $E$ . A possible application of this kind of hysteresis phenomenon to conditioned reflexes is indicated.

A. J. MEE.

**Free energies of formation in fused salts. II. Halides of manganese, cobalt, and iron.** G. DEVORO and A. GUZZI (Gazzetta, 1929, 59, 591—600; cf. A., 1928, 955, 1096).—By the method previously described the free energy of formation in the fused state has been obtained for the following salts at temperatures between  $650^\circ$  and  $950^\circ$ : manganous and cobaltous chlorides, bromides, and iodides, and ferrous chloride. The m. p. and heats of dissolution of some of the salts have also been determined.

O. J. WALKER.

**Equation of state of easily liquefiable hydrocarbons. III. Contraction of density bulbs on evacuation.** M. BECKERS (Bull. Soc. chim. Belg., 1929, 38, 329—341; cf. A., 1928, 116).—The amount of contraction sustained by density bulbs on evacuation has been determined by Travers' method and by a hydrostatic method. The results obtained by the two methods are in satisfactory agreement with one another. They also confirm the empirical equation of Moles and Miravalles (A., 1924, ii, 451) for the calculation of the compressibility of density bulbs. Under pressures between  $2/3$  and  $1/3$  atm. contraction is a linear function of pressure.

M. S. BURR.

**Anomaly of water. II.** W. JAZYNA (JACYNO) (Z. Physik, 1929, 58, 429—435).—It is suggested that the water anomaly between  $0^\circ$  and  $4^\circ$  may be simply explained by assuming that at  $0^\circ$  and  $760$  mm. pressure the melting process is not complete, but proceeds only to the extent of about 98.3%. It is assumed that between  $0^\circ$  and  $30^\circ$  there is a residual melting process or emulsion phenomenon in which the remaining 1.7% of ice crystals, suspended in the liquid, is destroyed.

J. W. SMITH.

**Internal potential energy and coefficient of expansion of water. III.** W. JAZYNA (JACYNO) (Z. Physik, 1929, 58, 436—439).—On the grounds of the theory previously developed (cf. A., 1929, 1225, and preceding abstract) the mean latent heat of vaporisation, the change in the internal potential energy, the internal pressure, and the internal coefficient of expansion have been calculated for water between  $0^\circ$  and the critical temperature.

J. W. SMITH.

**Molecular condition of water.** O. REDLICH (Monatsh., 1929, 53 and 54, 874—887).—Theoretical. The methods utilised by previous investigators in order to elucidate the molecular complexity of water and the results obtained are discussed. Infra-red absorption data agree well with those of magnetic susceptibility in accounting for the variation with temperature of the proportion,  $c$ , of the polymeric, ice-form  $(H_2O)_n$  in water. Similar agreement obtains with specific heat and volume measurements, but the absolute value of  $c$  is uncertain. Thermodynamic formulae relevant to the problem of the molecular condition of water are developed.

L. S. THEOBALD.

**Relation between the gas pressure and the translational energy of the gas molecules.** W. ANDERSON (Z. Physik, 1929, 58, 443—446).—The translational energy of the gas molecules contained in 1 c.c. ( $E_{\text{transl.}}$ ) is shown to be related with  $v$ , their linear velocity (supposed for simplicity to be equal for all molecules), and  $c$ , the limiting velocity, by the equation  $p = (1 + \sqrt{1 - \beta^2})E_{\text{transl.}}/3$ , where  $\beta = v/c$ . With ordinary gases at not too high temperatures  $v$  is much smaller than  $c$ , so  $\beta^2$  may be neglected in comparison with unity, so  $p = 2E_{\text{transl.}}/3$ . With "light quanta gas"  $\beta = 1$ , so  $p = E_{\text{transl.}}/3$ , a result which is not in agreement with the conclusions of other investigators, who give the formula  $p = 2E_{\text{transl.}}/3$ .

J. W. SMITH.

**Viscosity of vapours. I. Influence of molecular association on the viscosity of acetic acid (vapour). II. Relationship between critical constant and gaseous viscosity.** A. G. NASINI (Phil. Mag., 1929, [vii], 8, 596—601, 601—604).—I. To determine the effect of molecular complexity on gaseous viscosity, the viscosity of acetic acid vapour has been determined for a range of temperature from  $90^\circ$  to  $250^\circ$ , at a pressure of about 30 mm. It is assumed that, at  $150$ — $250^\circ$ , only simple molecules are present. The temperature-viscosity curve at lower temperatures has a curvature opposite to that for non-associated compounds. The results are discussed in relation to Sutherland's law.

II. Theoretical. An attempt has been made to determine whether relationships exist between the critical constants and viscosity of gases similar to those deduced by Onnes for liquids. Values for the expressions  $(\eta_c M^{1.6})/(c_c^{2/3} T_c^{1/2}) \times 10^5$  and  $(\eta_c T_c / M^3 p_c^{4/3})^{1.6} \times 10^6$  are tabulated, the symbols having the usual significance. With very few exceptions, constancy is approached for both expressions within the limits of experimental error. Values are also given for the expression  $\eta_c^2 / M$ , where  $M$  is the mol. wt., similar to Rankine's expression  $\eta_c^2 / A$ , where  $A$  is the at. wt.

M. S. BURR.

**Viscosity, heat conductivity, and diffusion in gas mixtures. VI. Viscosity determinations with pure gases by direct measurement and thence those of their mixtures.** M. TRAUTZ and W. LUDEWIGS (Ann. Physik, 1929, [v], 3, 409—428).—The viscosity coefficients of air and hydrogen have been redetermined at 20°, 100°, 200°, and 250°, the results confirming earlier values. The systems hydrogen-carbon monoxide and hydrogen-argon have also been studied at the above temperatures and the cross-sectional ratios  $\eta$  evaluated for these gas pairs. The viscosity coefficients of hydrogen and carbon monoxide mixed with up to 2.75% of iron pentacarbonyl vapour have also been measured and a maximum has been found for the first case. The viscosity coefficient for the carbonyl is calculated to be  $882 \times 10^{-7} \pm 10\%$ . This extrapolation provides a method for ascertaining the viscosity and heat conductivity of vapours of high mol. wt. from data obtained with mixtures containing a small percentage of the vapour. The heat conductivity of the carbonyl vapour, taking into account  $C_p$  measurements, is  $\lambda = k_7 C_p = 3.1 \times 10^{-5}$ . The viscosity of the hydrogen-ethyl ether system has also been studied.

R. A. MORTON.

**Viscosity isotherms of binary mixtures. III. System nitrobenzene-stannic chloride.** F. DE CARLI (Atti R. Accad. Lincei, 1929, [vi], 10, 186—189; cf. A., 1929, 1228).—The m.-p. diagram of the above system reveals the presence of the single compound  $C_6H_5 \cdot NO_2 \cdot SnCl_4$  (m. p. about 11°). The maxima in the viscosity isotherms at 15° and 25° indicate the formation of an additive compound containing 50% of nitrobenzene instead of 31.18% (above compound). It is possible that the viscosity maximum is due to  $2C_6H_5 \cdot NO_2 \cdot SnCl_4$  (48.58% nitrobenzene) and that this is stable only in solution.

O. J. WALKER.

**Vaporisation of binary mixtures. II. Theory of vaporisation of binary mixtures.** M. S. VREVSKI (Z. physikal. Chem., 1929, 144, 359—384; cf. A., 1929, 1374).—By a cyclic process a connexion has been established between the composition of the vapour, the heat of vaporisation, and the differential heat of dilution of binary mixtures. The formula obtained has been applied to the classification of solutions. A connexion has also been established between the form of the vapour-pressure curve and (a) the heat of formation of the solution, and (b) the form of the curve which represents the dependence on concentration of the heat of reaction accompanying vaporisation. A formula has been deduced by which the composition of the vapour can be calculated from thermal quantities. The experimental data for aqueous solutions of methyl alcohol, propyl alcohol, and nitric acid are discussed on the basis of the formulæ put forward. M. S. BURR.

**Vaporisation of binary mixtures. III. Determination of heat of vaporisation of aqueous solutions of hydrogen chloride.** M. S. VREVSKI and G. P. FAERMANN (Z. physikal. Chem., 1929, 144, 385—394).—In an apparatus previously described (cf. A., 1929, 1374), the heat of vaporisation of solutions of hydrogen chloride of different concen-

trations has been determined at 21° and 78°. The results obtained are in good agreement, i.e., to 1%, with the values calculated by means of the formulæ previously obtained (cf. preceding abstract). The observed composition of the vapour is also in good agreement with that calculated from thermal data.

M. S. BURR.

**Appearance and disappearance of azeotropism in binary systems.** W. MUND (Bull. Soc. chim. Belg., 1929, 38, 322—328).—Theoretical. It is shown that, with rising temperature, the condition necessary, but not sufficient, for the appearance of azeotropism of the first kind, i.e., when the pressure isotherm has a maximum, is  $L_1 + H_1 - L_2 > 0$ , and for disappearance,  $L_1 + H_1 - L_2 < 0$ . For azeotropism of the second kind, i.e., when the pressure isotherm has a minimum, the condition for appearance is  $L_2 + H_2 - L_1 < 0$ , and for disappearance,  $L_2 + H_2 - L_1 > 0$ , where  $L_1$  and  $L_2$  are the heats of vaporisation of the less and more volatile constituents, respectively, and  $H_1$  and  $H_2$  the heats of dissolution of 1 g.-mol. of the respective constituents in an infinite quantity of the mixture. The more marked are the inequalities necessary (but not sufficient) for the appearance of azeotropism, the more likely is it that azeotropism will take place. The positive azeotropic deviation,  $P - P_2$ , where  $P$  is the vapour pressure of the mixture and  $P_2$  that of the more volatile constituent in a state of purity, should be a maximum at a temperature such that  $L_2 - L_1 + H_2 - H_1 = H_2/X_1$ , where  $X_1$  is the fraction of the less volatile constituent in the azeotropic mixture. Similarly, in negative azeotropism, i.e., azeotropism of the second kind, the deviation  $P_1 - P$  is a maximum when  $L_1 - L_2 + H_1 - H_2 = H_1/X_2$ . M. S. BURR.

**Permeability of hot metals to hydrogen.** B. C. HENDRICKS and R. R. RALSTON (J. Amer. Chem. Soc., 1929, 51, 3278—3285; cf. Lombard, A., 1928, 1085, 1319).—Zinc is permeable to hydrogen at 300°, and more so at 370°. It increases in crystal size after permeation. Copper is also permeable above 500° and the increase in crystal size probably causes the fissures which appear. Nickel is quite permeable to hydrogen at 470° and above, but there is no accompanying change in crystal size. Richardson's equation for the diffusion coefficient (Phil. Mag., 1904, [vi], 7, 266) is found to hold within experimental error. The calculated average heat of dissociation of hydrogen in nickel is  $20.8 \pm 2$  kg.-cal., a low value which probably becomes lower as the temperature rises. S. K. TWEEDY.

**Solubility of sodium carbonate and a method of determining solubilities at high temperatures.** W. F. SEYER and E. TODD (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 67—70).—The solubility of sodium carbonate has been determined between 16.6° and 173°. A special glass apparatus for use from 50° to 100° and an iron apparatus for use above 100° are described. The solubility of the monohydrate decreases from 35.37° to 149°, at which the anhydrous salt is formed; the solubility of the latter decreases more rapidly with rise of temperature than that of the monohydrate.

N. M. BIGH.

**Solubility of various ferrocyanides in mixtures of [ethyl] alcohol and water.** F. DIAZ DE RADA

and A. G. BERMEJO (Anal. Fis. Quím., 1929, **27**, 701—711).—The solubilities of potassium and sodium ferrocyanides and of the double calcium ammonium, calcium potassium, calcium rubidium, and calcium caesium ferrocyanides in mixtures of ethyl alcohol and water in various proportions have been determined at 20° or 22° by titration with standardised potassium permanganate solution. The two single ferrocyanides are practically insoluble when the solvent contains more than about 80% of alcohol, only a slight coloration being produced on addition of ferric chloride solution. The solubility of the double ferrocyanides decreases as the at. wt. of the alkali metal increases, the solubility of calcium caesium ferrocyanide in water being extremely small.

H. F. GILLBE.

**Solubility of certain anilides in water-acetic acid mixtures.** A. E. BRADFELD and A. F. WILLIAMS (J.C.S., 1929, 2542—2544).—The solubilities of acetanilide, benzanilide, toluenesulphonanilide, *N*-methylacetanilide, and *N*-methyltoluenesulphonanilide in water and acetic acid-water mixtures up to 99% acetic acid have been measured over the temperature range 20—30°.

F. J. WILKINS.

**Distribution of radioactive materials between a solid crystalline and a liquid phase. IV. Distribution of radium between solid crystalline barium nitrate and its saturated aqueous solution at 0° and 25°. V. Distribution of radium between mixed crystals of barium nitrate and lead nitrate and their saturated aqueous solution at 25°.** V. CHLOPIN, A. POLESITSKI, and P. TOLMATSHEV (Z. physikal. Chem., 1929, **145**, 57—78; cf. A., 1928, 830).—IV. The Berthelot-Nernst partition law has been found to hold strictly for the distribution of radium nitrate between crystalline barium nitrate and its saturated aqueous solution. The partition coefficient  $[Ra]_{cryst.}/[Ra]_{soln.}$  decreases rapidly with rise of temperature. When a solution is allowed to deposit crystals at constant temperature with stirring the same equilibrium condition is reached as when the crystals are partly dissolved. It is possible to concentrate radium from a mixture of radium and barium nitrates by fractional crystallisation, but the conditions are less favourable than in the case of the bromides or chlorides.

V. The Berthelot-Nernst rule holds also when the system contains an additional component (lead nitrate) which forms mixed crystals with barium nitrate, provided care is taken to maintain the composition of both solid and liquid phases constant during the distribution. The partition coefficient varies with the composition of both phases, and is always intermediate between the coefficients appertaining to the two principal components.

F. L. USHER.

**Formulae representing adsorption isotherms.** A. BOUTARIC (J. Chim. phys., 1929, **26**, 492—496).—A comparison of the formulae of Freundlich, Perrin, and Schmidt.

C. W. GIBBY.

**Sorption of water vapour by activated charcoals. IV. Isothermals in absence of foreign gases (static method).** A. J. ALLMAND, P. G. T.

HAND, J. E. MANNING, and D. O. SHIELDS (J. Physical Chem., 1929, **33**, 1682—1693; cf. A., 1929, 999).—Data for the sorption of water vapour at 25° by the charcoals previously used are recorded. Hysteresis occurs, but to a smaller extent than when a stream of gas is employed. The effects produced by raising the temperature of outgassing are also less definite than those previously recorded (*loc. cit.*). Experiments carried out at 0° and 15° to determine the influence of temperature indicate that the heat of sorption of water vapour on the particular charcoal used is independent of the amount of water vapour sorbed and is practically equal to the total heat of condensation of vapour to liquid. L. S. THEOBALD.

**Sorption of water vapour by activated charcoals. V. Charcoals extracted by alkali. Resorption, lag or drift, hysteresis.** A. J. ALLMAND, P. G. T. HAND, and J. E. MANNING (J. Physical Chem., 1929, **33**, 1694—1712; cf. preceding abstract).—The influence of previous extraction of charcoals with alkali on the sorption of water vapour has been determined. A single extraction produces a diminution in sorption at the lowest pressures, a higher pressure value at which the isothermal changes direction, and a flatter curve at intermediate pressures. The amount of water retained at zero pressure is less for the extracted charcoal, but the degree of hysteresis is not greatly affected. A second extraction appears to re-activate the charcoal, and this effect is accentuated at pressures greater than 1 atm.

Experiments on resorption show that hysteresis is real and is not due merely to false pressure measurements caused by accumulation in the vapour phase of gases expelled from the charcoal. The results of various sorption and desorption cycles are described. Data concerning the recovery of water by evacuation at high temperatures lead to the conclusion that charcoal after saturation with water can retain appreciable quantities of it even after evacuation at temperatures up to 800°.

L. S. THEOBALD.

**Adsorption of a gaseous admixture from a current of air.** N. A. SCHILOV, L. K. LEPIN, and S. A. VOSNESENSKI (J. Russ. Phys. Chem. Soc., 1929, **61**, 1107—1123, and Kolloid-Z., 1929, **49**, 288—296).—The distribution of chlorine in a layer of adsorbent charcoal through which air containing chlorine had been passed is determined for various rates of flow, types of charcoal, and concentrations of chlorine. A relationship is found between the thickness of a layer of charcoal and the time which elapses before chlorine appears in the issuing air. Two empirical factors are introduced for the characterisation of the purifying action of a layer of adsorbent,  $\theta$ , the time during which unit thickness of the adsorbent layer adsorbs all the chlorine, and  $\tau$ , the time necessary for the formation of a gradient of chlorine concentration within the adsorbent system; the time  $T$  during which any given thickness of layer,  $l$ , will effect complete purification will then be given by  $T = l\theta - \tau$ .

R. TRUSZKOWSKI.

**Adsorption of gases by glass walls. VI. Air and carbon monoxide.** E. MOLES and M. CRESPI (Anal. Fis. Quím., 1929, **27**, 529—534; cf. Crespi, A., 1929, 639).—In continuation of previous work, the

adsorption (g./cm.<sup>2</sup>) on a glass surface between 0.25 and 1 atm. at 20° is given by  $p^{\frac{1}{2}} \times 0.94 \times 10^{-9}$  for air and by  $p^{\frac{1}{2}} \times 1.03 \times 10^{-9}$  for carbon monoxide.

H. F. GILLBE.

**Sorption of water vapour by cellulose and its derivatives.** S. E. SHEPPARD and P. T. NEWSOME (J. Physical Chem., 1929, 33, 1817—1835).—Adsorption and desorption isotherms of cellulose in the form of the natural fibrous material, dried powders, or thin sheets or films have been determined. The amount of water adsorbed per g. increases, at a given temperature, with the vapour pressure to a maximum value for saturation, and the adsorption of water is progressively lowered by any process which degrades the cellulose, but is considerably increased by mercerisation. Cellulose regenerated from cuprammonium solution, or by de-esterification of cellulose acetate, shows a similar effect. This increased adsorption is explained on the basis of the differences in fine structure of native and mercerised cellulose. Sorption in relation to esterification is discussed and evidence for intra-micellar or intra-crystalline absorption of water has been obtained. Sorption hysteresis is shown by all the cellulosic materials examined and a repetition of a sorption cycle reduces the hysteresis. Further investigation of this phase of the subject is necessary.

L. S. THEOBALD.

**Absorption of ammonia, carbon dioxide, and the vapours of organic liquids on titanium, tin, cerium, and thorium dioxide gels.** N. J. NIKITIN and V. I. JURIEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1029—1034; cf. A., 1928, 832).—Carbon dioxide is readily absorbed by stannic oxide and titanium oxide gels, 4 g. of the gels taking up respectively 21.2 and 127.8 c.c. of the gas at 740 mm. and 13°. In general, the absorption by a number of gels of the saturated vapours at about 20° of various organic liquids is in the order  $\text{TiO}_2 > \text{CeO}_2 > \text{SnO}_2 > \text{ThO}_2$ . Thus titania gel takes up 32% of its weight of benzene vapour, ceria gel 11.8%, stannic oxide gel 6.4%, and thoria gel 3.4%.

R. TRUSZKOWSKI.

**Adsorption of oxygen and ozone on silicic acid gel.** A. MAGNUS and K. GRÄHLING (Z. physikal. Chem., 1929, 145, 27—47).—The adsorption of oxygen by silica gel has been measured by a static method over a pressure range 100—760 mm. at 204°, 214.2°, and 224.4°, at which temperatures the isotherms are practically linear. The adsorption of ozone from mixtures with oxygen was measured at partial pressures up to 34 mm. and at the same temperatures by a dynamic method in which changes of concentration near the surface of the adsorbent were minimised by a rapid stream of gas, and from the results of the two series of measurements the adsorption isotherm of ozone was obtained by difference. At the temperatures mentioned the isotherm of ozone is nearly linear at low partial pressures, and the calculated mean heat of adsorption is 5600 g.-cal., with a temperature coefficient of  $-175$  g.-cal./1°, the corresponding values for oxygen being 3200 g.-cal. and  $-30$  g.-cal./1°. By means of a differential manometer the decomposition of the adsorbed ozone was found to follow approximately a unimolecular course, whence it is inferred that the

velocity is determined by the rate of diffusion of the ozone in the adsorbed layer toward "active centres" of the catalyst.

F. L. USHER.

**Adsorption of organic acids on platinum-black.** M. PLATONOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1055—1064).—Measurements of adsorption of fumaric, maleic, succinic, itaconic, mesaconic, and citraconic acids on platinum-black show that the solubility of these acids in a given solvent plays only a secondary part in their adsorption, which is determined primarily by their structure. The adsorption is increased by the presence of an ethylenic linking, except in the cases of fumaric and maleic acids in ethereal solution. In the case of isomeric acids, the more readily reducible *cis*-isomeride is more strongly adsorbed than is the *trans*-isomeride; the *cis*- is to some extent converted into the *trans*-form on adsorption. The shape of the curves expressing velocity of hydrogenation in the presence of platinum-black depends on the relation between the degrees of adsorption of the given substrate and of its reduction products.

R. TRUSZKOWSKI.

**Adsorption from organic solvents by Japanese acid clay.** Y. TANAKA and T. KUWATA (J. Fac. Eng. Tokyo, 1929, 18, 99—107).—The adsorption of indophenol and of *p*-nitroaniline-red from different solvents by Japanese acid clay has been studied. More is adsorbed from benzene and hexane than from other organic solvents, the amounts decreasing in the order: carbon disulphide, various halogen compounds,  $\beta$ -naphthol, phenol, alcohols, amines. Adsorption from solvents of a homologous series increases on ascending the series. The clay behaves similarly to silica gel in organic solvents, but differently in water. The results are interpreted in terms of selective adsorption of polar solvents.

C. W. GIBBY.

**Relation between adsorption and solubility.** N. SATA (Kolloid-Z., 1929, 49, 275—280).—Measurements of the adsorption of *o*-, *m*-, and *p*-hydroxybenzoic acids, citraconic and mesaconic acids, benzoquinone, quinol, and cyclohexane-1:4-dione from aqueous solution by animal charcoal are in accordance with the ordinary adsorption isotherm and indicate that adsorption varies antipathetically with solubility. The relation  $\alpha L^{1/n} = K$  (A., 1920, ii, 358), where  $\alpha$  and  $n$  are the constants of the adsorption isotherm and  $L$  is the solubility, holds only for closely related substances, such as the hydroxybenzoic acids. The adsorption of picric acid from solution in water, ethyl alcohol, acetone, chloroform, benzene, toluene, ethylbenzene, cumene, and nitrobenzene follows the ordinary adsorption isotherm and the above relation holds for the non-associated solvents, such as benzene and toluene, but not for the associated liquids, water and alcohol. The connexion between adsorption and solubility is illustrated by experiments on the adsorption of picric acid from aqueous-alcoholic solutions of varying composition.

E. S. HEDGERS.

**Physical chemistry of colour lake formation.** V. Hydrous oxide-alizarin lakes. H. B. WEISER (J. Physical Chem., 1929, 33, 1713—1723; cf. B., 1928, 131).—From adsorption experiments with alizarin or sodium alizarinate and hydrated aluminium

oxide prepared from amalgamated aluminium or from aluminium chloride, it is concluded that the formation of hydrated oxide-alizarin lakes is usually an exchange adsorption process in which the alizarinate ion displaces an equivalent amount of a less strongly adsorbed anion from the oxide. Depending, however, on the conditions of formation and the age of the oxide, adsorption of alizarinate may be an exchange or a direct adsorption, or both. Lakes are formed by adding sodium alizarinate to hydrated oxide sols stabilised by preferential adsorption of hydrogen ions; if the accompanying anion is the chloride, an amount of sodium chloride equivalent to the alizarinate adsorbed is found in the supernatant liquid. The similarity of the colour of the alumina-alizarin lake and of the alizarinate ion in aqueous solution is due to adsorption of alizarinate radicals of the metallic atoms of the oxide. The ion associated with the alizarinate, *e.g.*, sodium, ammonium, potassium, hydrogen, or calcium, modifies the colour only in so far as the amount of adsorption of the alizarinate ion is affected.

Freshly-formed alumina, free from adsorbed ions, forms a lake from either an aqueous solution of sodium alizarinate or an alcoholic solution of alizarin; since, however, such an oxide ages rapidly, lake formation may be overlooked in such a case. Further, little adsorption takes place unless the size of the primary particles is such that peptisation of the resulting lake as a negative sol can ensue.

L. S. THEOBALD.

**Capillarity. XII. Evaporation factors.** K. SCHULTZE (*Kolloid-Z.*, 1929, 49, 265—270).—The conditions determining the rate of evaporation of salt solutions in capillaries are discussed (concentration, diminution of vapour pressure, motion of liquid, humidity of air, motion of air). Consideration is also given to the conditions determining whether the solid salt will form inside or outside the capillary tube.

E. S. HEDGES.

**Mercury meniscus.** K. C. D. HICKMAN (*J. Opt. Soc. Amer.*, 1929, 19, 190—212).—The relation between the degree of cleanness of mercury and its adhesion to glass is discussed. The absorptive power of glass and mercury may be utilised to coat each with a layer of lubricant, which should have a low boundary friction, but should be so powerfully adsorbed as not to be squeezed out under high pressures, qualifications which suggest an organic molecule with a reactive group at one end for attachment, and an inert group at the other end for slipping. The adhesion of mercury and glass when lubricated by various substances alone and in admixture with butyl phthalate has been studied in glass tubes and by the use of a tilting plate, the meniscus movements in the tubes being photographed. A theory of the movement is proposed and discussed. The lubricating power of water is greatly enhanced by a trace of mercurous nitrate or alkali hydroxide. Heptyl mercaptan in butyl phthalate gives very good lubrication. The best results are obtained in high vacua with benzyl butyl phthalate or benzyl phthalate, with the addition of mercury di-*p*-tolyl for experiments of long duration and of 1% of thioacetanilide for short experiments. In moderate vacua the best results are

given by butyl phthalate and 2% of phenylhydrazine and at atmospheric pressure by water and 1% of mercurous nitrate.

N. M. BLIGH.

**Existence of potassium alum in the surface layer of aqueous solutions.** E. R. WASHBURN (*J. Physical Chem.*, 1929, 33, 1813—1816).—Examination of the physical properties of the crystals which form a crust at the surface of an evaporating solution of potassium alum and spread on the walls of the vessel above the solution (*cf.* A., 1927, 931) shows that these are alum crystals.

L. S. THEOBALD.

**Passivity of metals. III. The quantity and distribution of the superficial oxide.** U. R. EVANS and J. STOCKDALE (*J.C.S.*, 1929, 2651—2660; *cf.* A., 1929, 270).—A method has been devised for the removal of the surface skins of oxidised metals in such a way as to preserve the granules of unoxidised metal enclosed in the oxide. It has been found possible to remove the films formed on copper and iron after exposure to air at the ordinary temperature. The corresponding films on nickel were difficult to remove. A transparent film has also been obtained from stainless steel which had been abraded and exposed to the air. Films formed by heat-tinting on copper, nickel, and iron have also been studied. Square sheets of these metals were heated along one edge in order to produce the usual sequence of interference tints; on removal of the oxide a very thin film was obtained from those portions of the sheet which showed no interference colours. This "invisible" film was, in the case of nickel, remarkably free from metallic inclusions. The oxide removed from copper contained much unchanged metal, the proportion of metallic copper to oxide gradually decreasing as the high-temperature edge is approached. Similar interlocking of metal and oxide was obtained with iron.

Determinations of the colour and weights of oxide per unit area have been made and the results compared with those of Constable (A., 1928, 106). On yellow-tinted iron the film may be removed by undermining at one of two different levels. Undermining at the upper level yields a transparent film consisting of oxide alone in an amount agreeing fairly well with Constable's optical determinations, whilst undermining at a lower level gives a film with a greater amount of oxide and considerable amounts of metal. It is suggested that during the attack of a metal by oxygen four zones are formed: (I) an outer zone consisting wholly of oxide; (II) a zone containing oxide and metal, the proportion of metal gradually increasing towards the interior; (III) a shattered zone fairly free from oxide; and (IV) the unchanged metal.

F. J. WILKINS.

**Movement of liquid streams and drops in an electric field.** E. H. BÜCHNER and A. H. H. VAN ROYEN (*Kolloid-Z.*, 1929, 49, 249—253).—A criticism is made of Humphry's method (A., 1926, 577) of determining cataphoretic migration velocity, in which a thin stream of the sol flows through the dispersion medium between two vertical electrodes and is deflected towards one of the electrodes. The present authors find that for hydrosols of arsenious sulphide and ferric hydroxide the stream broadens out in all



directions, although the sols do not contain both negatively- and positively-charged particles. The rate of motion of the boundary of the stream in the electric field is much greater than could be obtained if the phenomenon were one of cataphoresis. Further, the same phenomenon can readily be observed in coloured molecular aqueous solutions, such as copper sulphate. When the sol is enclosed in a collodion bag containing one electrode, the whole bag moves towards the other electrode, independently of whether the other electrode is positive or negative. When a drop of liquid floating freely in water, to which has been added some substance to make the density equal to that of the drop, is placed between two electrodes, the drop spreads out and may form a bridge between the electrodes. The same phenomena are observed when an alternating current is used. The velocity of spreading decreases with decreasing concentration of solution, is greater for drops of liquid than for streams, and is greater for large drops than for small drops. The phenomena are explained by the difference in electrical conductivity between the sol or solution and the dispersion medium.

E. S. HEDGES.

**New interpretation of the electrocapillary curves of thallium amalgam.** J. EISENBRAND (Z. physikal. Chem., 1929, 144, 463—475).—A formula has been deduced showing the connexion between the applied *P.D.* in electrocapillary measurements and the resulting surface tension, simply on the basis of the additivity of the surface tensions of the two components. The relation between applied *P.D.* and surface tension for a number of thallium amalgams of different concentrations has been determined experimentally and found to be in good agreement with the theoretical values. On plotting, all the curves cut the *P.D.*-surface tension curve for mercury at the same point. It is suggested that, at a certain *P.D.*, either pure thallium or a compound of thallium and mercury has the same surface tension as pure mercury. Hence variations in the proportion of the two constituents present will have no influence on the value of the surface tension for that particular *P.D.* This is not in agreement with the surface adsorption theory of Frumkin and Gorodetskaja (A., 1928, 1193).

M. S. BURR.

**Heat of wetting of carbon by binary liquid mixtures.** F. E. BARTELL and Y. FU (J. Physical Chem., 1929, 33, 1758—1768).—The heats of wetting of carbon by mixtures of alcohol and nitrobenzene, 1-bromonaphthalene and nitrobenzene or carbon disulphide, and acetone and benzene have been determined calorimetrically, and a method for estimating the fraction of the total surface occupied by each component of the binary mixture from the results is suggested. In no case is either of the components exclusively adsorbed; the component with the higher adhesion tension is adsorbed preferentially over a wide range of concentration, whilst that with the lower tension is preferentially adsorbed only at low concentrations, and then only in small amounts over a narrow range of concentration. The general relationship which exists between heat of wetting and adsorption is discussed.

L. S. THEOBALD.

**Intertraction.** (SIR) A. E. WRIGHT (Proc. Roy. Soc., 1929, A, 125, 587—598).—The author's original experiments on vertical and horizontal intertraction between serum and salt solution (A., 1926, 901; 1927, 520) are criticised, and a method is described of conducting the experiments on vertical intertraction in such a manner as to avoid complications introduced by (a) alterations in the specific gravity of the pseudopodial contents, and (b) diffusion from the pseudopodia into the surrounding fluid. It is recommended that in place of the eosin-coloured serum or salt solution, suspensions of red blood-corpuscles in serum and salt solution, or suspensions of Indian ink in serum or salted serum be used. Four methods of demonstrating horizontal intertraction are described, together with experiments showing the conditions which determine, in the case where serum is deposited on the surface of a heavier salt solution, the development of descending apart from horizontal, or horizontal apart from descending, or both forms of intertraction in conjunction.

Photographs are reproduced showing that typical vertical and horizontal pseudopodial intertraction can be obtained between alcohol and water and between salt solution and sugar solution and water. In the case of alcohol, horizontal intertraction is readily demonstrated by superimposing a drop of an alcoholic (50%) suspension of Indian ink upon water of which the surface tension has been lowered by the addition of soap or bile salts. There appears to be a certain optimum difference of surface tension for optimum pseudopodial intertraction; when the difference of surface tension of the attracting fluids is either very great or very small, pseudopodial interpenetration is retarded.

L. L. BIRUMSHAW.

**Rôle of the membranes in electrodialysis.** R. BRADFELD and H. S. BRADFELD (J. Physical Chem., 1929, 33, 1724—1732).—Collodion membranes are rendered more permeable to anions by soaking in protein solutions such as those of hæmoglobin. These covered membranes are positively or negatively charged when used next to the anode or cathode, respectively, except at very low or very high  $p_H$  values. Hæmoglobin-coated membranes are suitable for the salts of strong acids and bases in electrodialysis, whilst proteins with lower isoelectric points are more suitable for salts of weak acids, since they produce less disturbance in the solution which is being purified.

L. S. THEOBALD.

**Augmentation of volume of liquids on the dissolution of solids or gases in them.** A. A. KUROTSCHKIN (J. Russ. Phys. Chem. Soc., 1929, 61, 1219—1251).—The increase in volume,  $dV$ , when hydrated crystalline substances are dissolved in a solvent is equal to that obtained with the anhydrous substance plus the volume of its water of crystallisation. Sodium and potassium hydroxides can be determined from the curves connecting  $dV$  with the concentration;  $dV$  is a linear function of the weight of solute,  $p$ , added. The angle  $\alpha$  made by these curves with the axis of  $p$  is characteristic of the given solute, and the product  $\alpha Md$  is shown to be equal to a constant (2700, or some multiple of 2700 for salts of multivalent metals). The curve  $dV=f(p)$



remains rectilinear up to quite high concentrations of solute. For mixtures,  $dV$  is the algebraic sum of the respective  $dV$  values of the constituent solutes. The relations  $dV = p \cdot \tan \alpha$ ,  $dV = 100/d_1 - 100 + a$ , and  $\mu = d_2 \cdot \tan \alpha$ , are derived, where  $d_1$  and  $d_2$  are respectively the relative densities of the solution and the solute,  $a$  is the percentage concentration of the solute, and  $\mu$  represents the ratio of  $dV$  to the original volume of the solute.

R. TRUSZKOWSKI.

**Ebullioscopic constants.** M. LEVAT-EZERSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1011—1018).—The ratio  $E/M$ , where  $E$  is the ebullioscopic constant of a given solvent and  $M$  its mol. wt., is calculated for 54 organic liquids. In 36 cases the value obtained is very close to 0.3, in 4 cases deviations from this constant are due to association, whilst in 14 cases no explanation can be found for the anomalous values obtained; it is, however, supposed that these are only apparent exceptions, and that re-examination of the vapours of these liquids will reveal association or dissociation.

R. TRUSZKOWSKI.

**Application of the differential ebullioscope to the study of the volatility of dissolved substances.** E. BUREŠ (Rocz. Chem., 1929, 9, 581—589).—Measurements made using Swientoslowski's differential ebullioscope show that the volatility of urethane in 95.4% alcohol solution is fairly great, whilst that of diphenylamine is zero up to concentrations of 6%, and inconsiderable in more concentrated solutions. No perceptible change in the value of  $dp/dt$  could be observed on raising or lowering the pressure of the above systems within narrow limits. Diphenylamine solutions exhibit deviations from Raoult's law which increase as the concentration increases.

R. TRUSZKOWSKI.

**Hydration of sucrose in aqueous solution.** J. W. MCBAIN and S. S. KISTLER (J. Physical Chem., 1929, 33, 1806—1812).—The degree of hydration of sucrose has been determined by means of the ultra-filtration method previously described (J.C.S., 1922, 121, 2325) using methyl alcohol as a reference substance. The results indicate that in dilute solution each molecule of sucrose is hydrated with not less than 4 mols. of water.

L. S. THEOBALD.

**Is Barger's micro-method [for the determination of osmotic pressure] based on the principle of isothermic distillation?** M. JASIŃSKI (Rocz. Chem., 1929, 9, 623—627).—Carminic acid added to a drop of sodium chloride solution is transferred by convection currents to a neighbouring drop of more concentrated solution sealed into the capillary tube. It would hence appear that the variations in the lengths of columns of heterotonic liquids observed in Barger's micro-method are not to any great extent due to isothermal distillation of solvent, but rather to convection currents in the film wetting the walls of the capillary tube between two drops.

R. TRUSZKOWSKI.

**F. p. of aqueous solutions of the halides of cadmium.** F. H. GETMAN (J. Physical Chem., 1929, 33, 1781—1792; cf. A., 1928, 709).—The f. p. of aqueous solutions of cadmium chloride, bromide, and iodide have been determined by means of a platinum resistance thermometer at concentrations

from 0.01 to 0.05M. The activity coefficients, uncorrected for thermal effects, have been calculated. The lack of agreement with the corresponding data obtained from *E.M.F.* measurements is discussed on the basis of complex ion formation.

L. S. THEOBALD.

**Solute molecular volumes in relation to solvation and ionisation.** (SIR) D. O. MASSON (Phil. Mag., 1929, [vii], 8, 218—235).—It is shown that, in a large number of instances, the apparent molecular volume of an electrolyte in aqueous solution is directly proportional to the square root of the volume concentration. In most cases of limited solubility the direct proportionality holds throughout the whole range of the available data. In those cases in which data are available at sufficiently high concentration the direct proportionality ceases at a point corresponding with the composition of a definite hydrate. In this way the monohydrate of sulphuric acid and higher hydrates of nitric acid, hydrochloric acid, ammonium nitrate, and lithium chloride are indicated. It is suggested that the above region of direct proportionality corresponds with the solution of a hydrate in excess of water, whilst beyond that region the solution is not truly aqueous, being either a solution of monohydrate in excess of anhydrous substance or an intermediate mixture of hydrates. It follows that the true solute molecular volume is that of a characteristic hydrate which is determined by the sum of the apparent molecular volume and a quantity which is a function of the degree of hydration. The true molecular volume has a definite value at infinite dilution which increases in direct proportion to the square root of the concentration up to the hydrate point. It is suggested that the true solute molecular volume at infinite dilution is that of the completely ionised hydrate and that the larger measured values at higher concentrations are the averages for mixtures of ionised and non-ionised molecules.

A. E. MITCHELL.

**Stratified settling of fine sediments.** P. G. NUTTING (J. Washington Acad. Sci., 1929, 19, 402—406).—A generalised form of Stokes' law is deduced, of which the ordinary form is a limiting case when the concentration gradient is zero. The settling of particles under gravity is opposed by an upward gradient of kinetic pressure which may cause upward movement of particles of certain sizes. The sharp upper limit of the strata for different sized particles is due to the limited supply. The view that stratified settling is a thermal effect has not been confirmed.

C. W. GIBBY.

**Apparatus for dispersoid analysis and some experiments.** A. H. M. ANDREASEN [with W. JENSEN and J. J. V. LUNDBERG] (Kolloid-Z., 1929, 49, 253—265).—An apparatus of the pipette type for the determination of the degree of dispersity of a suspension is described. The apparatus is a development of an earlier type (B., 1928, 915). Its applicability to different problems is discussed and results are given for some technical products (kaolin and Portland cement).

E. S. HEDGES.

**Influence of the multivalent cations  $\text{Th}^{+++}$  and  $\text{Fe}^{+++}$  on the dispersoidal-chemical properties**

of kaolins. I. I. SHUKOV and M. N. SOKOLOVA (J. Russ. Phys. Chem. Soc., 1929, **61**, 1081—1096).—The adsorption of thorium nitrate on kaolin rises to a maximum value with increasing concentration of salt, after which the curve proceeds horizontally in the case of Gluchov kaolin, and declines slightly in the case of Gluchowietz kaolin. The latter phenomenon is observed with both kaolins for solutions of ferric chloride. This diminution in adsorption is due to smaller hydrolysis in concentrated solutions. Adsorption is in all cases diminished by the addition of nitric or hydrochloric acid to the respective solutions of thorium nitrate or ferric chloride. The reversal of the sign of the charge of suspensions of kaolin to which increasing concentrations of the above salts are added is observed in electro-osmosis at lower concentrations than in cataphoresis experiments; equimolar solutions of thorium nitrate and of ferric chloride have approximately the same effect. Kaolin suspensions are most unstable and can be filtered most rapidly at their isoelectric point; further addition of ferric chloride after this point has been attained increases the stability of such suspensions.

R. TRUSZKOWSKI.

**Theory of emulsions.** H. BECHHOLD and K. SILBEREISEN (Kolloid-Z., 1929, **49**, 301—303).—The liquid pairs glycerol-*isobutyl* alcohol and *isobutyl* alcohol-water have an exceedingly low interfacial tension. The interfacial tension at the boundary of *isobutyl* alcohol and 1% aqueous solutions of sodium lysalbinat and sodium protalbinat has also been measured. From observations on the time taken for the separation into two liquid layers of emulsions of *isobutyl* alcohol in water and of *isobutyl* alcohol in 1% aqueous sodium lysalbinat or protalbinat it is found that emulsions of the latter type are 60—180 times as stable as the pure *isobutyl* alcohol-water emulsions. It is concluded that a low interfacial tension has practically no significance in determining the stability of an emulsion and that viscosity does not play an essential part.

E. S. HEDGES.

**Viscosity and elasticity of sols.** B. RABINOVITSCH (Z. physikal. Chem., 1929, **145**, 1—26).—The rate of flow of a number of liquids, some of which show departures from Poiseuille's law, has been measured in capillary tubes under conditions in which each of the factors pressure, length, and cross-section was varied in turn, the other two remaining constant. The curves showing the relation between flow and one of these variables, in the case of an abnormal liquid, are shown to be resolvable into a linear and a quadratic component the constants of which can be obtained from the experimental figures. An extension of the classical theory of viscosity is proposed, in which the velocity gradient is considered to be a function of the shearing stress ( $s$ ) which, in the case of the substances examined, has the form  $f(s) = 8As_R + 10Bs_R^2$ . This leads to an expression for the distribution of velocity along a radius of the tube, viz.,  $v_r = 2Ap(R^2 - r^2)/l + Bp^2(R^3 - r^3)/12l^2$  (where  $p$  denotes the pressure causing the flow,  $R$  the radius of the tube,  $l$  its length, and  $A$  and  $B$  are experimentally determined constants of the substance), which is valid both for normal liquids

and for those possessing shear elasticity. It is thus possible, from a knowledge of the relation between the rate of flow of a given liquid and one of the variables, to describe its behaviour under any conditions of length, cross-section, and pressure, within the limits of laminar stationary flow. The extended theory also permits all measurements of the rate of flow ( $Q$ ) to be expressed by means of the two-constant formula  $Q/R^3 = As_R + Bs_R^2$ , which completely defines the shear elasticity of the liquid under examination.

F. L. USHER.

**Scattering of light by stannic oxide sols.** B. N. GHOSH (J.C.S., 1929, 2526—2529).—The intensity of the light scattered by stannic oxide sols at different dilutions in which the ratio of  $\text{SnO}_2 : \text{Na}_2\text{O}$  was varied between 7.7 and 1.45 has been measured. As the ratio  $\text{SnO}_2 : \text{Na}_2\text{O}$  is decreased the intensity of the scattered light is first diminished and then increased. Similar measurements made with stannic oxide sols peptised with potassium hydroxide showed that the intensity of the scattered light first remained constant as the ratio  $\text{SnO}_2 : \text{K}_2\text{O}$  was decreased from 7.7 to 1, although further decrease brought about an increase in the intensity. The behaviour of stannic oxide towards alkali is not in accord with the generally accepted view that addition of alkali to the colloidal solution of an acidic oxide causes the particles to become more finely divided. It is suggested that addition of alkali to a stannic oxide sol is accompanied by the separation of the particles into two groups owing to the aggregation of the larger colloidal particles and the further subdivision of the smaller.

F. J. WILKINS.

**Influence of previous history of gelatin on the viscosity of gelatin solutions.** C. E. DAVIS and H. M. SALISBURY (Kolloid-Z., 1929, **49**, 270—275).—The viscosity of gelatin sols has been measured by the Ostwald method. The values are more reproducible at 40° than at 25° and the irregularities at the lower temperature are said to be due to a partial conversion of the sol into the gel state. Viscosity measurements were carried out with specimens of gelatin of different origin and after subjection to various manufacturing processes. The hardest forms of gelatin give the most viscous solutions. The viscosity shows a maximum at  $p_H$  2.5—2.6. The position of the minimum is independent of the source of the gelatin and of the subsequent treatment. Contrary to the criticism of Manning (A., 1925, i, 90), the process of preparing the gelatin solution has no influence on the viscosity.

E. S. HEDGES.

**Stoichiometric relations in hydrochloric acid-gelatin systems from viscosity measurements.** E. K. BACON (J. Physical Chem., 1929, **33**, 1843—1849; cf. A., 1927, 935).—Viscosity measurements at 40° of ash-free gelatin in hydrochloric acid support the view that definite salt formation takes place and that the equivalent weight of the gelatin is approximately 1090 (cf. Hitchcock, A., 1929, 647). Structural changes in gelatin solutions as shown by viscosity changes due to ageing, method of preparation, and temperature are independent of the combining ratio for gelatin and hydrochloric acid.

L. S. THEOBALD.

**Effect of electrolytes and non-electrolytes on the transparency of silicic acid gels.** N. A. YAJNIK and L. N. HAKSAR (*Kolloid-Z.*, 1929, 49, 303—308).—The transparency of silicic acid gels increases with the dilution of the gel. The addition of the sulphates of sodium, potassium, and aluminium to the gel produces a decrease in the transparency, whereas lithium sulphate causes an increase at low concentrations, which, however, becomes smaller at higher concentrations. The chlorides of lithium, sodium, potassium, calcium, strontium, barium, mercury, and aluminium, and the nitrates of lithium, sodium, potassium, calcium, silver, and aluminium, render the gel turbid, the intensity increasing with increasing concentration of the salt. Mineral acids ensure the production of a very clear gel, but hydroxides reduce the transparency. The aliphatic alcohols diminish the transparency to an extent which increases with the mol. wt. of the alcohol. Glycerol and resorcinol, however, increase the transparency. All the other non-electrolytes examined, with the exception of acetaldehyde, reduce the transparency. The transparency of a gel is considered to be greater the slower is the rate of gelatinisation. E. S. HEDGES.

**Gas bubbles in isotropic and deformed gelatin gels.** E. HATSCHER (*Kolloid-Z.*, 1929, 49, 244—249).—Gas bubbles in gelatin gels are lenticular and not spherical. There is reason to believe that this is due to a rupture of the gel when the pressure caused by the growth of the bubble exceeds the tensile strength of the gel. The possible forms of bubbles are considered in this light and are compared with the results of microscopical observations. Experiments are described on the production of bubbles of carbon dioxide in gelatin by diffusing acetic acid into gelatin gels containing sodium carbonate. Microscopical examination reveals furrows on the surface of the bubbles, similar to the structure produced by slow mechanical rupture of the gel. An apparatus is described for studying the rupture produced in a gel by the presence of a growing drop of liquid. The lenticular or spherical shape of gas bubbles affords a criterion of whether the sol-gel transformation is complete, and observations are described which indicate that the transformation is discontinuous. The influence of deformation of the gel by compression or stretching on the shape of the bubbles has also been examined. E. S. HEDGES.

**Electrolyte coagulation of colloids. VII. Coagulation process of tungstic acid sols.** V. KARGIN (*Kolloid-Z.*, 1929, 49, 281—288).—The coagulation of sols of tungstic acid has been followed by both conductometric and potentiometric titration methods. Addition of electrolyte solutions renders the sol acid and this is due to the adsorption of cations which displace an equivalent amount of hydrogen ions from the micelle. Measurements of the minimal amount of various electrolytes required for coagulation show that the greater is the at. wt. of the cation the smaller is the coagulation value and the greater is the amount of hydrogen ions displaced. The anion of the added electrolyte has a stabilising influence which increases with the formula weight of the anion. With increasing concentration of the

electrolyte the amount of anion adsorbed increases and eventually exceeds the adsorption of the cation, but at still higher concentrations the cation is adsorbed strongly again and the displaced hydrogen ions are also re-adsorbed; this is the cause of the minimum observed in the potentiometric titration curve.

E. S. HEDGES.

**Desorption of electrolytes in the coagulation of suspended particles.** S. VOSNESSENSKI, V. LASAREV, and T. PEREVERSEVA (*Kolloid-Z.*, 1929, 49, 297—301).—An electroconductometric examination of the coagulation of kaolin suspensions by electrolytes has shown that when coagulation occurs there is a sudden increase in concentration of electrolyte in the dispersion medium, which is caused by desorption on coagulation. Hydrochloric acid and calcium chloride are desorbed on coagulation more strongly than aluminium chloride and sulphate; in the latter cases the aluminium remains largely adsorbed as hydroxide. The phenomenon is considered in relation to some technical processes, such as the analysis of effluents; an apparent increase in concentration of some constituent is often observed when two effluents are mixed. E. S. HEDGES.

**Morphology of chemical reactions in colloidal media. II.** F. M. SCHEMJAKIN (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 1203—1217; cf. Dunin and Schemjakin, A., 1929, 1008).—A classification of chemical reactions in gels is given. Stellar figures are produced when a drop of silver nitrate is placed on gelatin containing 0.04—0.06*M*-potassium ferrocyanide. Such figures are not obtained on the addition of solutions of the latter substance to agar-agar or gelatin gels containing silver nitrate; in the latter case dendritic figures appear in the field of diffusion, whilst clearly demarcated layers are to be found beneath the drop of ferrocyanide. The addition of a drop of saturated potassium phosphate solution to agar-agar or gelatin gels containing various concentrations of calcium nitrate leads to the formation of a stellar rosette beneath the drop, and of transparent periodic layers of calcium phosphate, whilst wrinkles appear in the external field of diffusion, similar to those formed by mechanical stress. Similar periodic figures are formed by a large number of reactions in gels, such as between lead nitrate and potassium iodide, silver nitrate and potassium dichromate, and others. It is suggested that the phenomenon of periodic precipitation is due to vibrations in the medium, analogous to those taking place when a drop falls into a vessel containing a liquid. R. TRUSZKOWSKI.

**Hydrophile properties of collagen.** L. MEUNIER and K. LE VIET (*Compt. rend.*, 1929, 189, 911—913; cf. Meunier and Seyewetz, A., 1908, i, 586; Meunier and Guyot, B., 1929, 241).—The swelling power of collagen at its isoelectric point (defined as  $G = [P - p]100/p$ , where  $P$  is the weight of collagen swollen in an acetic acid solution of  $p_H$  2.6, centrifuged to remove adherent liquid, and  $p$  that of dry collagen) decreases as the lyophile (particularly the amino-) groups in the molecule are irreversibly transformed into other groups possessing less marked polarity relative to water. Thus 1% (referred to the

weight of dry collagen) of benzoquinone diminishes  $G$  from 443.9 to 261.1, of gallotannic acid from 725.9 to 557.8, and of formaldehyde from 499.3 to 274.8. Quinol and gallic acid act similarly under conditions favourable to oxidation, in the absence of which the combinations formed are reversible and destroyed on washing with water. Thus any substance capable of irreversibly lowering the swelling capacity of collagen is a tanning agent, its power as such being in proportion to the lowering produced.

C. A. SILBERRAD.

**Cell structures and their formation.** M. COPISAROW (Kolloid-Z., 1929, 49, 309—314).—When a 40% solution of formaldehyde is allowed to diffuse into a 5% gelatin gel a periodic structure is obtained, consisting of layers of membranes which are not visible, but become recognisable by the fracture and hardness of the specimen. By varying the concentration of the aldehyde and the duration of the diffusion it is possible to obtain cellular structures. Silver nitrate, tannic acid, and picric acid exert no further structural change on the gelatin-formaldehyde product. Experiments on the crystalline lens of the cow's eye are described; after treatment with 38% formaldehyde, the structure was found to consist of a series of transparent hard layers. An artificial lens was made by placing a lens of gelatin in a saturated aqueous solution of picric acid for a week. When a section was cut through the lens, it was found to consist of alternate concentric layers of yellow, transparent matter and thin, yellowish-brown, turbid membranes. Bands were also formed when the lens was placed in formaldehyde solution, but were recognisable only on drying the lens.

E. S. HEDGES.

**Solid-phase rule.** I. WO. OSTWALD and W. RÖDIGER (Kolloid-Z., 1929, 49, 314—321; cf. A., 1929, 1380).—Previous work relating to the ratio of the amount of colloid peptised to the amount originally present is reviewed and four types of peptisation are distinguished: (1) adsorption peptisation (*e.g.*, carbon and picric acid), (2) dissolution peptisation (ferric hydroxide and hydrochloric acid), (3) peptisation through swelling (gelatin in water), (4) spontaneous colloidal dissolution (cellulose acetate in chloroform). In adsorption- and dissolution-peptisation an optimum of peptisation is observed for medium amounts of the solid phase, and in spontaneous colloidal dissolution and peptisation through swelling the solubility curve rises steadily as a rule. Experiments are described on the solubility of humic acid in sodium hydroxide, sodium citrate, and calcium hydroxide at different concentrations and using varying amounts of humic acid. The solubility varies with the amount of humic acid present in accordance with the solid-phase rule.

E. S. HEDGES.

**Transformations of hydrated oxides.** R. FRICKE (Kolloid-Z., 1929, 49, 229—243).—The literature on hydrated oxides is reviewed with particular reference to the phenomena of ageing. The variation of vapour pressure in the hydration and dehydration of precipitated beryllium hydroxide has been measured; concentrated sulphuric acid cannot dehydrate below the stage  $\text{BeO} \cdot \text{H}_2\text{O}$ . The process

is reversible and the vapour pressure-composition curve resembles a typical swelling curve. Experiments with aged preparations also showed that dehydration below the stage  $\text{BeO} \cdot \text{H}_2\text{O}$  was not possible with concentrated sulphuric acid. The state in which the water is bound in these hydrates is discussed. Aluminium hydroxide would seem to be a much stronger acid than is generally supposed; as a monobasic acid it is as strong as boric acid and its low solubility is responsible for its apparent weakness.

E. S. HEDGES.

**Syneresis.** S. LIEPATOV (Kolloid-Z., 1929, 49, 321—322).—Polemical (cf. Jacoby, A., 1929, 881).

E. S. HEDGES.

**Kinetic theory of diffusion of gases.** K. SHIBA (Bull. Inst. Phys. Chem. Res. Tokyo, 1920, 8, 917—920).—In the diffusion of a gaseous mixture the component gases must, in general, have different diffusion coefficients, on account of the change in position of the centre of mass of the whole system. An expression is deduced for the diffusion coefficient of one component,  $D_1 = c_1 l_1 / 3$ , where  $c_1$  is the mean velocity and  $l_1$  the mean free path.

C. W. GIBBY.

**Equilibrium in the system  $\text{Co}-\text{H}_2\text{O}-\text{CoO}-\text{H}_2$ .** Free energy changes for the reaction (i)  $\text{CoO} + \text{H}_2 = \text{Co} + \text{H}_2\text{O}$  and the reaction (ii)  $\text{Co} + \frac{1}{2}\text{O}_2 = \text{CoO}$ . P. H. EMMETT and J. F. SHULTZ (J. Amer. Chem. Soc., 1929, 51, 3249—3262).—The equilibrium (i) was investigated by a flow method, the constants ( $[\text{H}_2\text{O}]/[\text{H}_2]$ ) being 85 (approx.), 67, 57, and 50.5, respectively, at 335°, 450°, 515°, and 570°. The results do not indicate the formation of solid solutions (*e.g.*, of tricobaltic tetroxide) in the solid phase, and this conclusion is confirmed by X-ray data, which show that only cobaltous oxide and cobalt are present in this phase, and also that the transition between face-centred cubic cobalt and close-packed hexagonal cobalt lies between 340° and 360°. Thermal and free-energy data are calculated for reactions (i) and (ii); the calculated partial pressure of oxygen over cobaltous oxide at 1100° is  $0.5 \times 10^{-7}$  mm.

S. K. TWEEDY.

**Changes in concentration in dilute alkali and alkaline-earth metal amalgams.** F. SKAUPY (Z. Elektrochem., 1929, 35, 862—863).—Comments on Le Blanc and Jäckh's paper (A., 1929, 1016).

R. CUTHILL.

**Determination of dissociation constants of fluorescing substances by quantitative fluorescence measurements.** J. EISENBRAND (Z. physikal. Chem., 1929, 144, 441—462).—The contradictory results obtained for the relation between concentration and intensity of fluorescence of solutions of fluorescing substances is to be attributed to neglect of the influence of light absorption. An apparatus is described by which fluorescence intensity can be measured under conditions which eliminate the disturbing influence of absorption. In dilute solutions, when absorption becomes very small, there is simple proportionality between fluorescence intensity and concentration, as previously recognised, but at higher concentrations the logarithm of the intensity is proportional to the concentration. Since intensity

is proportional to the concentration of fluorescing ion in dilute solution, the dissociation constants of quinine, "metoxyquinoline," and  $\beta$ -naphthol have been determined by fluorescence intensity measurements and are found to be in sufficiently good agreement with those determined by other methods, or to be expected from theoretical considerations. The mean values of  $p_K$  are: quinine, 9.4 ( $K$  is the second dissociation constant), "metoxyquinoline," 8.4, and  $\beta$ -naphthol, 9.6.

M. S. BURR.

**Hydrazine. Hydrolysis of dimethylketazine and the equilibrium between hydrazine and acetone.** E. C. GILBERT (J. Amer. Chem. Soc., 1929, 51, 3394—3409).—The equilibrium between acetone, hydrazine, and acetonehydrazone at 15° has been determined from the solubility of hydrazine picrate in aqueous solutions containing acetone, sodium chloride, and hydrochloric acid, and also by the distribution of acetone between benzene and aqueous hydrazine hydrochloride solutions. The hydrolysis of dimethylketazine has been studied at 15° and 20°, using the method of Brönsted, Kilpatrick, and Kilpatrick (A., 1929, 516). The reaction is reversible and leads to a state of equilibrium in which hydrogen ions, dimethylketazine, acetone, hydrazine, and acetonehydrazone are involved. The kinetics of the reaction have also been studied.

H. BURTON.

**Activity coefficients of the components of a binary mixture.** V. HOLTZSCHMIDT (J. Russ. Phys. Chem. Soc., 1929, 61, 1097—1106).—A mathematical exposition of Lewis' conception of activity coefficients for concentrated solutions (Lewis and Randall, Z. physikal. Chem., 1901, 38, 205).

R. TRUSZKOWSKI.

**Electrolytes in mixed solvents. I. Free energies and heat contents of hydrogen chloride in water-ethyl alcohol solutions.** J. A. V. BUTLER and C. M. ROBERTSON (Proc. Roy. Soc., 1929, A, 125, 694—712).—Measurements have been made of the free energies and heat contents of hydrogen chloride in aqueous alcoholic solutions, obtained by determining the *E.M.F.* of the cell  $H_2[HC][AgCl|Ag]$  at 15°, 25°, and 35°, using a series of solvents containing 25, 50, 75, 95, and 100 mol.-% of alcohol, and in each solvent a series of hydrogen chloride concentrations from 0.01 to 1.0*M*. The free energy of transfer of hydrogen chloride from a solution (1) to a solution (2) is given by  $\Delta F_{(1) \rightarrow (2)} = -(E_2 - E_1)F$ , where  $E$  is the *E.M.F.* and  $F$  the electrochemical equivalent. The free energies of transfer of hydrogen chloride ( $a$ ) in a given solvent from one concentration to another, ( $b$ ) at a given concentration from one solvent to another, can thus be obtained, and knowing the temperature coefficient of  $E$ , the corresponding changes in heat content can be calculated from the Gibbs-Helmholtz equation  $\Delta H = -EF + FT(dE/dT)$ . The apparatus, consisting of hydrogen saturator and experimental cell, is specially designed to prevent the diffusion of hydrogen into the vicinity of the silver chloride electrodes. The values of the *E.M.F.* obtained are in good agreement with those found by Harned and Fleysher in aqueous alcohol solutions, but differ considerably from their measure-

ments in absolute alcohol (cf. A., 1925, ii, 538), whilst Woolcock and Hartley's data for absolute alcohol solutions (A., 1928, 709) are confirmed for the concentrations 0.01 and 1.0*M*, but between these limits their values are about 3 millivolts lower. The free energies indicate that in solutions containing only a small proportion of water, the latter is largely associated with the electrolyte. The heat effects have maximum values in the region 90—95% alcohol. In explanation of this behaviour it is assumed that hydrogen chloride is not completely dissociated in alcoholic solution and that the addition of water increases the degree of dissociation. The marked effect of the addition of traces of water on all the properties of hydrogen chloride in pure alcohol is emphasised. The curves for the temperature coefficients of the *E.M.F.* show the same effect, and are of interest, since  $dE/dT$  is proportional to the entropy change in the reaction.

L. L. BIRCHMANS.

**Mercurous ion.** A. E. BRODSKY (Z. Elektrochem., 1929, 35, 833—837).—The activity coefficient,  $f$ , of the mercurous ion in solutions of mercurous nitrate at various temperatures, calculated from the *E.M.F.* data previously obtained (A., 1926, 247, 688), is related to the concentration,  $c$ , by an equation of the form  $\log f = kc^2$ , but the value of  $k$  at each temperature is only about  $1/\sqrt{2}$  of the value required by Debye's theory. The normal electrode potential,  $E_{H_2}$ , of the mercury electrode in respect of mercurous ions is given as +0.803 volt at 18°. A recalculation of the solubility products of mercurous chloride, bromide, and iodide has also been made.

R. CUTHILL.

**Rôle of hydrogen-ion concentration in the precipitation of calcium and magnesium carbonates.** H. P. CADY, G. KEMMERER, and (Miss) M. E. WEEKS (J. Physical Chem., 1929, 33, 1768—1780).—The  $p_H$  values of solutions of calcium hydrogen carbonate at 25° and 33° and of solutions of magnesium hydrogen carbonate at 33° have been determined, using a potentiometric method. The  $p_H$  at which precipitation of the carbonate takes place is a linear function of the concentration of the oxide concerned. For calcium hydrogen carbonate a rise in temperature of 8° raises the  $p_H$  precipitation value by 0.045 unit. Magnesium hydrogen carbonate solutions lose carbon dioxide before the precipitation value of  $p_H$  is reached, but this is not the case with the calcium salt. Empirical equations giving the  $p_H$  value at which precipitation of the carbonates will occur are recorded.

L. S. THEOBALD.

**Formation of precipitates.** J. WULFF (Z. physikal. Chem., 1929, B, 6, 43—61).—In an evacuated tube containing iodine vapour the form of the deposited crystals depends on the temperature of the cold surface with which the vapour is in contact. Temperature influences both the orientation of the growing crystal and the formation of nuclei. The heaviest precipitation takes place on surfaces of greatest curvature, and on scratches and etched parts. In experiments with molecular beams it is found that 90% of the molecules incident on an iodine surface at -130° condense. On other surfaces, nuclei are formed primarily on scratches and other strained

parts, and the crystals of most frequent occurrence are those in which the principal direction of growth is opposed to the direction of the beam. With silver rods and tubes the reaction velocity increases with decreasing diameter, and in glass capillaries the adsorption increases with curvature. When the rays are incident on a number of different surfaces maintained above the "critical" temperature, the amount of iodine precipitated is proportional to the rate of nucleus formation. On glass surfaces precipitation is heaviest on the parts with greatest curvature, whether convex or concave. F. L. USHER.

**System sodium sulphide-ferrous sulphide.** L. V. STÉCK, M. SLAVIN, and O. C. RALSTON (J. Amer. Chem. Soc., 1929, **51**, 3241—3249).—Between 53 and 73% of ferrous sulphide there is a region in which two liquid phases can form, one being a double compound (assumed to be  $\text{Na}_2\text{S} \cdot \text{FeS}$ ) saturated with ferrous sulphide and the other ferrous sulphide saturated with double compound. A eutectic occurs at  $585^\circ$ , corresponding with 46% of ferrous sulphide. Photomicrographs of polished surfaces for melts of various composition are reproduced. The preparation of pure sodium sulphide and ferrous sulphide is discussed; the former probably melts slightly above  $970^\circ$ . S. K. TWEEDY.

**System  $\text{PbO}_2$ - $\text{Pb}_3\text{O}_4$ - $\text{PbO}$ .** E. MOLES and A. P. VITORIA (Anal. Fis. Quim., 1929, **27**, 520—528).—The equilibrium  $p$ - $T$  curves for the system lead oxide-oxygen have been determined between  $200^\circ$  and  $500^\circ$ . Lead peroxide, heated in a vacuum at  $400^\circ$ , changes completely to red lead, which is stable at this temperature under an oxygen pressure of 0.2 atm.; at  $450$ – $500^\circ$  red lead is converted completely into lead monoxide. The latter is reconverted into red lead when heated at  $400^\circ$  under an oxygen pressure of 190–200 mm. H. F. GILLBE.

**Sulphide-sulphate reaction.** M. TRAUTZ (J. pr. Chem., 1929, [ii], **123**, 346).—Additional references relevant to a previous paper (A., 1929, 884) are given. J. W. BAKER.

**Fusion relations of acmite.** N. L. BOWEN and J. F. SCHAIRER (Amer. J. Sci., 1929, [v], **18**, 365—374).—In the system  $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ - $\text{Fe}_2\text{O}_3$  a eutectic of acmite and quartz is formed at  $850^\circ$ . Pure crystalline acmite melts incongruently at  $990^\circ$ , giving solid hematite, which does not disappear below  $1275^\circ$ , and a liquid containing 28.5% of  $\text{Fe}_2\text{O}_3$ . C. W. GIBBY.

**Reciprocal salt pair  $\text{MgSO}_4$ - $\text{NaNO}_3$ - $\text{H}_2\text{O}$ .** A. BENRATH [with H. PITZLER, N. LLIEFF, W. BEU, A. SCHLOEMER, J. CLERMONT, and S. KOJITSCH] (Caliche, 1929, **11**, 99—126).—At  $15^\circ$  the only double salt present in the solid phase is darapskite, the other solids being  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{NaNO}_3$ . At  $25^\circ$  astrakhanite appears, whilst at  $50^\circ$  the astrakhanite field is considerably extended and darapskite has vanished, the salts  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  being replaced by thenardite and  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ . At  $97^\circ$  astrakhanite is replaced by löwite and vanthoffite, the magnesium sulphate field and those of its double salt derivatives is considerably extended, whilst the magnesium

nitrate field is very small and actually vanishes at a slightly higher temperature. H. F. GILLBE.

**System sodium iodate-sodium nitrate-water.** H. W. FOOTE and J. E. VANCE (Amer. J. Sci., 1929, [v], **18**, 375—382).—The system has been investigated between  $-17.48^\circ$  and  $35^\circ$ . Isotherms were determined at  $0^\circ$ ,  $8^\circ$ ,  $25^\circ$ , and  $35^\circ$ . In the last two isotherms the only solid phases are  $\text{NaNO}_3$  and  $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ . In the  $8^\circ$  isotherm  $\text{NaIO}_3 \cdot 5\text{H}_2\text{O}$  and the double salt  $2\text{NaIO}_3 \cdot 3\text{NaNO}_3 \cdot 15\text{H}_2\text{O}$  appear in addition. At  $0^\circ$  the solid phases are the double salt,  $\text{NaNO}_3$ , and  $\text{NaIO}_3 \cdot 5\text{H}_2\text{O}$ . The transition points are as follows:  $\text{NaNO}_3$ ,  $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ , double salt,  $9.8^\circ$ ;  $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{NaIO}_3 \cdot 5\text{H}_2\text{O}$ , double salt,  $6.6^\circ$ . The eutectic temperatures are: ice, double salt,  $\text{NaNO}_3$  — $17.48^\circ$ ; ice, double salt,  $\text{NaIO}_3 \cdot 5\text{H}_2\text{O}$  — $11.49^\circ$ . C. W. GIBBY.

**Ternary system strontium oxide-sucrose-water.** I, II. W. REINDERS and A. KLINKENBERG (Rec. trav. chim., 1929, **48**, 1227—1245, 1246—1264).—The isotherms of the system strontium oxide-sucrose-water have been determined at  $25^\circ$ ,  $35^\circ$ ,  $45^\circ$ ,  $55^\circ$ ,  $70^\circ$ , and  $90^\circ$ . The stable solid phases are: below  $28^\circ$ ,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ;  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{SrO} \cdot 6\text{H}_2\text{O}$  and  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ;  $28^\circ$  to between  $55^\circ$  and  $70^\circ$ ,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ;  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$ ;  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{SrO} \cdot 6\text{H}_2\text{O}$  and  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ; from  $70^\circ$  to  $85^\circ$ ,  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ;  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$ ;  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{SrO}$  and  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . There are quadruple points at  $28^\circ$ , at which  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$ , and  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{SrO} \cdot 6\text{H}_2\text{O}$  are in equilibrium with a solution containing 1.55%  $\text{SrO}$  and 3.7%  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ; and at  $85^\circ$ , at which  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Sr}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , and  $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$  are in equilibrium with a solution containing 12.1%  $\text{SrO}$  and 0.01%  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ . At temperatures below  $40^\circ$  sugar-rich solutions can set to a gel having a rigid framework of crystal needles which probably have the formula  $2\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 3\text{SrO} \cdot x\text{H}_2\text{O}$ . This is always metastable with respect to the other solid phases. The disaccharate ( $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot 2\text{SrO}$ ) first separates, especially at the higher temperatures, in an unstable form of higher solubility, which changes slowly in contact with the solution to the stable form. The application of the results to the technical separation of sugar from molasses is discussed. J. A. V. BUTLER.

**Four-fluid equilibria.** J. F. CARRIÈRE (Chém. Weekblad, 1929, **26**, 570—571).—Examples of systems characterised by the co-existence of three or four fluid phases are quoted. S. I. LEVY.

**Isomorphism and heat of dissolution.** S. G. MOKRUSCHIN and E. I. KRILOV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1177—1179).—The molar differential heats of dissolution of isomorphous substances are approximately equal to each other, as are also the integral heats of dissolution, whence it follows that a similar condition applies also to heats of dilution. R. TRUSZKOWSKI.

**Large mobility of hydrogen and hydroxyl ions in aqueous solutions.** H. ZAHN (Z. Physik, 1929, **58**, 470—477).—If the oxonium ions in acid solutions are constantly changing protons with water molecules, the transport of positive electricity depends on two kinds of carriers. According to the



calculations of Hückel, the number of protons concerned should decrease in high-frequency fields. In order to test this, the high-frequency conductivity of a hydrochloric acid solution has been compared with that of a solution of potassium chloride, the solutions being such that they conduct equally well at lower frequencies. Under these conditions the high-frequency conductivities of the acid solution should be noticeably smaller than that of the potassium chloride solution. Conversely, the existence of the effect should be demonstrable by preparing two solutions which conduct equally well at high frequency and comparing their conductivities at low frequency. If the theory is correct, there should be an increase in the conductivity of the acid, but very little effect with the potassium chloride except for a small calculable increase due to the Debye-Falkenhagen dispersion effect. For the determination, oscillations of wave-length 4 cm. were used. The results of a large number of comparisons show that the decrease in the high-frequency conductivity of the acid is in no case greater than 2%. Experiments with sodium hydroxide and potassium chloride gave a similar result. The results indicate that the theory of proton exchange between the water molecules in an acid solution is incorrect. Probably a proton is given up at the arrival of the oxonium ion at the cathode during its life period. It is apparent that for both the oxonium and hydroxyl ions the application of Stokes' law to the determination of frictional resistance is quite inadmissible. For the oxonium ion,  $H_3O^+$ , the configuration suggested by Hund, viz., the tetrahedral form with three equal protons lying in a plane, is probably correct.

A. J. MEE.

**Hydrocarbons. II. Determinations of the conductivity of binary salts in dichloroethylene and tetrachloroethane.** P. WALDEN and H. GLOY (Z. physikal. Chem., 1929, **144**, 395—440; cf. Walden and Busch, A., 1929, 401).—The electrical conductivity and dissociation of electrolytes in solvents of low dielectric constant have been investigated at 25°. The solvents selected were tetrachloroethane ( $\epsilon$  8.2) and a mixture of *cis*- and *trans*-dichloroethylene ( $\epsilon$  6.7). The salts were tetra*iso*amylammonium iodide, perchlorate, thiocyanate, and picrate, tri*iso*amylammonium picrate and iodide, di*iso*amylammonium picrate, and tetrapropylammonium picrate. The di- and tri-alkylammonium salts proved to be weak electrolytes, whilst the high conductivity of the tetra-alkylammonium salts indicates that they are strong electrolytes, the difference being more marked than in solvents of high dielectric constant. In solutions of the tetra-alkylammonium salts conductivity determinations have been made up to a dilution of  $v=500,000$ — $1,000,000$  litres and the limiting conductivity,  $\lambda_\infty$ , has been extrapolated. The results show that Kohlrausch's square-root law is valid even in solvents of low ionising power at dilutions greater than 40,000 or 50,000 litres in tetrachloroethane. The cube-root law can also be applied over a similar range, and the  $c^{0.45}$  formula is valid over a somewhat larger range of concentration than the other two. The range of validity is, in all cases, smaller for dichloroethylene, because of its lower dielectric constant. If the lower

limiting dilution at which the square-root law begins to be valid is  $v$ , and  $\epsilon$  the dielectric constant,  $\epsilon^{\frac{1}{3}}/v$  is constant for both these solvents as it is for those of higher dielectric constant. The fluidity,  $1/\eta$ , and limiting conductivity,  $\lambda_\infty$ , have the same temperature coefficient for tetrapropyl- and tetra-amyl-ammonium picrates, i.e.,  $\lambda_\infty \cdot \eta$  is a constant independent of temperature. From this product ionic mobilities have been determined. The classical degree of dissociation,  $\alpha=\lambda_v/\lambda_\infty$ , has been calculated for the different salts, and hence the Ostwald constant,  $K=\alpha^2/(1-\alpha)v$ . The mass action law is thus shown to be fulfilled at high dilutions. The Onsager equation is also discussed in relation to the results obtained, and it is shown that deviations are the greater the smaller is the dielectric constant. The various formulæ for the interpretation of the behaviour of electrolytes, based as they are on physical properties only, neglect to take into account the specific chemical properties of the solvent and solute.

M. S. BURR.

**Absolute measurements of the surface conductivity near the boundary of optically polished glass and solutions of potassium chloride.** J. W. MCBAIN, C. R. PEAKER, and (MISS) A. M. KING (J. Amer. Chem. Soc., 1929, **51**, 3294—3312).—The "surface" conductivity of potassium chloride at 25° was measured directly in slits of capillary width in optically polished glass, quartz, and fused silica. The "surface" conductivity is practically independent of the material of the slit; it increases with the concentration of the solution, but remains of the same order of magnitude as the surface conductivity of an insoluble fatty acid film on water. For 0.001*N*-potassium chloride the specific "surface" conductivity is  $4.3 \times 10^{-8}$  ohm<sup>-1</sup>. The phenomenon is ascribed to mobile ions which are attached to the solid interface and are mainly of opposite sign to the latter. The probable proportion of these ions present is discussed; the mobile ions may be only sufficiently numerous to form about one eighth of a unimolecular layer.

S. K. TWEEDY.

**Phase boundaries "ideal" electrode|electrolyte solution and electrolyte solution|dielectric.** B. KAMIENSKI (Z. physikal. Chem., 1929, **145**, 48—56; cf. A., 1929, 144).—Measurements of the electrode potential of different commercial specimens of carborundum crystals in electrolyte solutions show that its constancy depends on the purity of the material, the potential of very pure crystals being almost independent of the concentration of the solution. On theoretical grounds carborundum is regarded as an ideal "physical" electrode, the potential of which is determined by the nature of the solvent and the size of the ions contained in it. This view is supported by observations of the potential of carborundum in alkaline and acid solutions, where the relative size of the positive and negative ions is reversed. Platinum is a less ideal electrode than carborundum by reason of its slight oxidisability. The interface electrolyte solution|saturated air is considered to be an ideal physical phase boundary at which there is complete conservation of electrical energy. The electric polarisation existing at this interface is satisfactorily accounted for by the change in the free surface energy

produced in consequence of the thermal movement of ions and dipoles.

F. L. USHER.

**Influence of nature of electrolyte on the inversion potential of the photovoltaic effect.** R. AUDUBERT (*Compt. rend.*, 1929, 189, 800—802).—Inversion potentials for gold and platinum electrodes in 19 different electrolytes show that these potentials are independent of the concentration of the electrolytes. Irregularities in the results with oxidising agents and salts of gold and platinum are attributed to slight superficial oxidation in the case of the first-named, and to the small solution pressures of the cations of salts of gold and platinum. Inversion potential depends entirely on electrode potential, the difference between inversion and electrode potentials for gold and platinum being in all electrolytes 45 millivolts. The difference between the inversion potentials of platinum and gold averages 203 millivolts, and is likewise independent of the nature of the electrolyte.

C. A. SILBERRAD.

**Reaction velocities. III.** W. F. BRANDSMA (*Rec. trav. chim.*, 1929, 48, 1205—1218).—Theoretical. The methods of the previous paper (A., 1928, 247) have been applied to bimolecular reactions. Scheffer's formula:  $\log k = (\epsilon_i - \epsilon_t)/RT - (\eta_{ic-1} - \eta_i)/R + C$ , where  $k$  is the velocity coefficient of the reaction,  $\epsilon_i$  and  $\eta_{ic-1}$  the energy and concentration-free entropies on the reacting system, and  $\epsilon_t$ ,  $\eta_i$  the energy and entropy of the intermediate or activated state, is tested by (1) a direct calculation of  $k$  on the basis of the classical theory of collisions, assuming that reaction between two molecules occurs if the reactive parts of the surface hit each other and if a certain minimum energy is exceeded and (2) statistical calculations of  $\epsilon_t$  and  $\eta_i$ . The entropy as well as the energy of activation must be taken into account, the former containing the steric influences. The effect of substitution on the velocity of certain reactions is discussed and it is stated that in some cases the energy, in others the entropy, term is predominant.

J. A. V. BUTLER.

**Inflammation of gaseous mixtures.** P. LAFITTE and M. PRETTE (*Bull. Soc. chim.*, 1929, [iv], 45, 785—798).—The mixed gases (dried unless the contrary is stated) of known composition were passed into a vessel of Pyrex glass or of silica of about 100 c.c. capacity, evacuated to  $10^{-4}$  mm., and placed in an electric furnace, the temperature being measured with a platinum-platinum-rhodium couple. The temperature of the vessel was gradually raised until the gaseous mixture always inflamed, and then starting from a higher temperature gradually diminished until inflammation just failed to occur. The mean of these two temperatures, differing by about  $4^\circ$ , was taken as that of inflammation. The results are shown by curves connecting percentage of hydrogen and temperature of inflammation. These consist practically of two linear portions connected at an elbow. (The temperatures of inflammation for minimum and maximum percentages of hydrogen and of the "elbow" will be given in this order.) Hydrogen and air: 10.1%  $456^\circ$ , 90.45%  $540^\circ$ , 58.8%  $482^\circ$ . These figures are some  $100^\circ$  below those obtained by previous investigators, which is shown to be due to their having exhausted

the explosion vessel with merely a water pump, thus leaving pressures of 12—35 mm. of air or burnt gases. Experiment shows that 20 mm. of burnt gases raises the temperature of inflammation by some  $60^\circ$ , of ordinary air by  $10^\circ$ , and of dried air by less. Hydrogen with a mixture of equal volumes of oxygen and nitrogen gives for 9.7%  $445^\circ$ , 91.35%  $537^\circ$ , and 62.4%  $476^\circ$ . With oxygen and nitrogen in the ratio 7 : 3 it was impossible to prevent the flame striking back to the reservoir of mixed gases. For hydrogen with a mixture of argon (commercial, containing 5% of nitrogen) and oxygen in the ratio 79 : 21 the figures are 12.55%  $460^\circ$ , 89.1%  $545^\circ$ , and ("elbow") 67.0%  $506^\circ$ ; for carbon dioxide in place of argon 6.8%  $509^\circ$ , 89.2%  $552^\circ$ , and 61.5%  $511^\circ$ . Residual burnt gases raise the temperature with argon much as with air, but with carbon dioxide only about half as much. Replacing the 100-c.c. explosion vessel by one of 25 c.c. capacity had no effect. The curve for mixtures of carbon monoxide and air shows no elbow; typical figures are 5.65%  $659^\circ$ , 13.9%  $654^\circ$ , 42.45%  $657^\circ$ , 75.1%  $687^\circ$ , and 92.9%  $727^\circ$ . Residual burnt gases here have no effect, but addition of water vapour causes marked lowering in temperature of inflammation (up to  $30^\circ$ ), and that of hydrogen still greater (up to  $80^\circ$  for 0.05% of hydrogen).

C. A. SILBERRAD.

**Combustion of acetylene.** W. A. BONE (*Nature*, 1929, 124, 839—840).—Polemical (cf. Kistiakowsky and Lenher, A., 1929, 1395).

A. A. ELDRIDGE.

**Kinetics of hydration of meta- and pyrophosphoric acids.** N. FUCHS (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 1035—1044).—A constant,  $K = k/(1-\alpha)$ , where  $k$  is an experimentally determined constant and  $\alpha$  is the degree of dissociation, is obtained for the velocity of hydrolysis of metaphosphoric acid at different concentrations and at different acid  $p_H$  values; it follows from this that only undissociated molecules take part in the reaction. In acid solution the following reactions take place:  $2\text{HPO}_3 + \text{H}_2\text{O} = \text{H}_4\text{P}_2\text{O}_7$ ,  $\text{H}_4\text{P}_2\text{O}_7 + \text{H}_2\text{O} = 2\text{H}_3\text{PO}_4$ ,  $\text{HPO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4$ . Of these, the first is a bimolecular and the third a unimolecular reaction, so that at higher concentrations of metaphosphoric acid the velocity of the first reaction would increase to a much greater extent than that of the third. For this reason, the proportion of pyrophosphoric acid found in the solution after a given time will be much greater for concentrated than for dilute solutions. R. TRUSZKOWSKI.

**Kinetics of the reaction of formaldehyde with hydrogen sulphite and sulphite.** C. WAGNER (*Ber.*, 1929, 62, [B], 2873—2877).—If an excess of formaldehyde is mixed with an aqueous solution of sodium hydrogen sulphite and sulphite the initial reaction occurs according to the scheme  $\text{CH}_2\text{O} + \text{HSO}_3' = \text{CH}_2(\text{OH})\cdot\text{SO}_3'$ , and, after consumption of the hydrogen sulphite, change proceeds to equilibrium in accordance with the equation  $\text{CH}_2\text{O} + \text{SO}_3'' + \text{H}_2\text{O} = \text{CH}_2(\text{OH})\cdot\text{SO}_3' + \text{OH}'$ . In the region between the two processes, a slow increase in hydroxyl-ion concentration, indicated by the change in colour of thymolphthalein, occurs. The time required for complete union with the hydrogen sulphite in a given mixture is therefore readily determined. The first reaction is shown to be bimolecular and its rate increases

with, but not in proportion to, increasing concentration of sulphite. Partial replacement of water in the mixture by methyl or ethyl alcohol does not cause marked change in the rate of reaction, thus giving no indication as to whether formaldehyde hydrate is intermediately produced. H. WREN.

**Hydrolysis of hydrogen cyanide by acids.** V. K. KRIEBLE and J. G. McNALLY (J. Amer. Chem. Soc., 1929, 51, 3368—3375).—Hydrolysis of amygdalin proceeds ten times as rapidly with 5*N*-hydrochloric acid as with 5*N*-sulphuric acid at 25° (cf. Walker and Kriebel, J.C.S., 1909, 95, 1369). The rate of hydrolysis of hydrogen cyanide by hydrochloric acid is much greater than by either hydrobromic or sulphuric acid, and is not dependent on the hydrogen-ion concentration. With 7.84*N*-hydrochloric acid at 30° the rate is about 1000 times that with 1.95*N*-hydrochloric acid. The increased rate of hydrolysis corresponds with the increase in activity of undissociated hydrogen chloride molecules. The following mechanism for the hydrolysis of hydrogen cyanide to formamide is suggested:  $\text{HCN} + \text{HCl} \rightarrow \text{CHCl} \cdot \text{NH} \xrightarrow{\text{H}_2\text{O}} \text{HO} \cdot \text{CHCl} \cdot \text{NH}_2 \rightarrow \text{H} \cdot \text{CO} \cdot \text{NH}_2 + \text{HCl}$ , the rate being controlled by the first addition. The hydrolysis of formamide occurs to the same extent with either 2*N*-hydrochloric or 2*N*-hydrobromic acid. Addition of a second molecule of water to formamide takes place 14,000 times as rapidly as the primary addition of water to hydrogen cyanide. H. BURTON.

**Decomposition of potassium hydrogen oxalate hemihydrate.** J. HUME and J. COLVIN (Proc. Roy. Soc., 1929, A, 125, 635—646).—Crystals of potassium hydrogen oxalate, prepared by mixing solutions containing 18.4 g. of potassium oxalate monohydrate in 100 c.c. of water and 12.6 g. of oxalic acid dihydrate in 320 c.c. of water, cooled to 3°, have been examined microscopically. Above the transition temperature (6.4°), the decomposition  $(\text{KHC}_2\text{O}_4)_2 \cdot \text{H}_2\text{O} \rightarrow 2\text{KHC}_2\text{O}_4 + \text{H}_2\text{O}$  proceeds and is first evidenced by the appearance of black dots at the edges of the crystal. As these increase in size they are seen to be bounded in general by edges parallel to those of the crystal. The rates of advance of the different edges of the interface have been measured by means of a travelling microscope, and are found to be constant for any given edge and to be unaffected by the presence of water vapour. The reaction possesses a high temperature coefficient. It is noted that the nuclei almost invariably form at the edges of the crystal, preferentially at the corners. The fact that different rates of advance of the interfacial edges are found with different batches of crystals is ascribed to slight variations in the conditions during crystallisation, and to the adsorption and subsequent occlusion of one or other of the reactants, potassium oxalate and oxalic acid, by the crystals during growth.

The mass rate of decomposition has been determined under various conditions at  $19.97 \pm 0.01^\circ$  by means of the spiral-spring quartz-fibre balance described by Topley and Whytlaw-Gray (cf. A., 1928, 117). In every case the curve is of the sigmoid type associated with many solid reactions. If a mixture of anhydrous copper sulphate and copper sulphate mono-

hydrate is used to maintain a small, constant pressure of water vapour in the balance case, the maximum slope of the curve is lower and is attained after a much longer induction period than if phosphorus pentoxide is used to absorb water vapour in the case, and it is therefore concluded that the rate of nucleus formation is decreased by the presence of water vapour. This is supported by the values for the linear rates, obtained by solving the decomposition curves on the assumption that the final stage of the decomposition is a contracting circle. The agreement between observed and calculated values is satisfactory, and justifies the analogous procedure with calcium carbonate hexahydrate (cf. Topley and Hume, A., 1928, 1100). The energy of activation of the reaction is of the order of 40,000 g.-cal., close to that found for the decomposition of calcium carbonate hexahydrate. L. L. BIRCHUMSHAW.

**Decomposition of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  to anhydrous  $\text{CaCO}_3$ .** H. G. ROEBERSEN (Rec. trav. chim., 1929, 48, 1219—1226).—The decomposition of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  in contact with solutions containing lime and sugar has been investigated by means of dilatometric and conductimetric measurements. The presence of calcium hydroxide gives rise to an induction period before the decomposition begins, which is not due to calcium or hydroxyl ions alone. Sugar reduces the velocity of the reaction, but does not inhibit it. At 0° the hydrate is more soluble in water than the anhydrous substance. J. A. V. BUTLER.

**Chemical kinetics of the system  $\text{Ag}_2\text{CO}_3 \rightleftharpoons \text{Ag}_2\text{O} + \text{CO}_2$ .** W. D. SPENCER and B. TOPLEY (J.C.S., 1929, 2633—2650).—The decomposition of silver carbonate is a reaction which takes place mainly at the interface between the two solid phases. The decomposition-time curves may be divided roughly into two classes, "normal" and "abnormal." The former can be described quantitatively by the kinetic equation for a reaction which begins at many points simultaneously on the surface of each particle; in the latter the reaction rate falls much more rapidly than corresponds with this equation. Whether the decomposition is "normal" or "abnormal" depends on the pressure of water vapour in the system, for the retardation associated with the abnormal decomposition can be diminished or eliminated by the presence of a sufficient concentration of water vapour. It is suggested that the water vapour is effective in promoting the diffusion of carbon dioxide away from the oxide-carbonate interface.

The decomposition is inhibited by carbon dioxide according to the equation  $R/R_0 = (p_e - p)/(p_e - kp)$ , where  $R$  and  $R_0$  are the rates of decomposition in the presence of carbon dioxide at pressure  $p$  and in a vacuum, respectively;  $p_e$  is the equilibrium pressure. This equation has been developed on the assumption that the vibration of ions from the carbonate lattice on to a part of the oxide lattice which is not covered by adsorbed carbon dioxide may bring about the reaction  $\text{Ag}_2\text{CO}_3 \rightleftharpoons \text{Ag}_2\text{O}(\text{CO}_2)_{\text{adsorbed}} \rightarrow \text{Ag}_2\text{O} + \text{CO}_2$ . The reverse reaction occurs when the ions of the oxide vibrating on to the carbonate happen to have in their immediate neighbourhood an adsorbed molecule of carbon dioxide.

The temperature coefficient is given by  $d \log_e R_0 / d 1/T = 23,000/1.98$ . If it is assumed that a fraction  $\beta$  of the ions at the interface equal to  $e^{-A/RT}$  is activated when the ions possess energy in excess of  $A$ , the value of  $\beta$  obtained from the temperature coefficient is  $6 \times 10^{-13}$ , whilst the theoretical value is  $4 \times 10^{-13}$ .

F. J. WILKINS.

**Reactions in solids.** J. HUME and J. COLVIN (Phil. Mag., 1929, [vii], 8, 589—596).—When one solid changes into another, *e.g.*, monoclinic into rhombic sulphur, or into a solid+gas or liquid, as in the decomposition of calcium carbonate hexahydrate, the reaction consists essentially of the transformation of a metastable crystal lattice into one of greater stability. The formation of nuclei of the new lattice takes place at the surface of the solid, especially where deformation has occurred, and decomposition spreads from these nuclei. According to Langmuir, reaction in a solid takes place only at the interface between two solid phases. Three factors, therefore, should govern the course of reaction: (1) rate of nucleus formation; (2) linear rate of propagation of the interface between the two solid phases; (3) size of reactant particles. It is found that the formation of nuclei is preceded by a more or less prolonged period of induction, the duration of which depends on the previous history of the reactant, whilst the subsequent reaction, after the formation of nuclei, is independent of it. An example of this is the behaviour of manganese oxalate trihydrate at 25°, when kept under its saturated solution in a dilatometer and when thoroughly washed with ice-cold water before being placed in the dilatometer. In the first case the transition to the dihydrate is complete in about 3 hrs. In the second there is a period of induction of 3 days, after which the reaction proceeds at the same rate as before. In reactions with a large rate of nucleus formation the induction period is negligible. The fraction decomposed in a given time  $t$  should be represented by expressions which differ in form according to the relative importance of the different factors considered. If the rate of nucleus formation is very great compared with the linear rate of propagation, the fraction  $\alpha$  decomposed in time  $t$  is  $3(ut/a) - 3(ut/a)^2 + (ut/a)^3$ , where  $u$  is the linear rate of propagation in cm. per sec. and  $a$  the radius of the particle in cm. If the rate of nucleus formation is such that the particle develops only a small number of nuclei before decomposition is complete, that is, before the interface travels completely across the particle,  $\alpha = (ut/a)^3/2 - 3(ut/a)^4/16$  (Topley and Hume, A., 1928, 1100). If the linear rate of propagation is so great that a particle may be regarded as completely decomposed as soon as it develops a nucleus, the rate of decomposition is  $k_0 N_t$ , where  $k_0$  is the number of nuclei forming per sec. and  $N_t$  the number of undecomposed particles present at the time  $t$ , provided there is no infection of undecomposed particles by those already decomposed. This represents a pseudo-unimolecular reaction and should be best fulfilled by small particles. All reactions should approach to this form by reducing the particle size. These views have been tested for the reaction  $S_{\text{monoclinic}} \rightarrow S_{\text{rhombic}}$ . Experiments on the rate of transformation, observed dilatometrically, were carried out with sulphur in a

solid block, *i.e.*, one large particle, in separate small portions, and in a fine powder. The curves obtained by plotting fraction transformed against time were in accordance with the three expressions given above, respectively. The observations of Centnerszwer and Bružs (A., 1926, 581) on the dissociation of cadmium carbonate are also interpreted on the basis of the theory put forward.

M. S. BURR.

**Action of nitric acid on iron.** Z. C. MUTAFTSCHIEV (Z. Elektrochem., 1929, 35, 861—862; cf. A., 1929, 1016).—The action of nitric acid on finely-powdered iron has been investigated. With acid of  $d$  1.39 or 1.42 a slow action continues for many hours, the rate not being affected by application of a magnetic field, whereas with acid not sufficiently concentrated to effect passivation the rate is much increased. Prolonged exposure of the metal to air appears to reduce its reactivity.

R. CUTHILL.

**Effect of oxidising conditions on accelerated electrolytic corrosion tests.** H. S. RAWSON and W. A. TUCKER.—See B., 1929, 1018.

**Corrosion of aluminium alloys in superheated steam.** L. GUILLET and BALLAY.—See B., 1929, 983.

**Solution potentials of aluminium alloys in relation to corrosion.** J. D. EDWARDS and C. S. TAYLOR.—See B., 1929, 983.

**Effect of temperature on the rate of reduction of furfuraldehyde with the catalyst from  $\text{PtO}_2 \cdot \text{H}_2\text{O}$ .** J. S. PIERCE and C. PARKS (J. Amer. Chem. Soc., 1929, 51, 3384—3387).—The rate of reduction of furfuraldehyde (0.1 mol.) in presence of 95% alcohol (75 c.c.), 1 c.c. of 0.1M-ferrous sulphate, and the platinum-black from 0.122 g. of  $\text{PtO}_2 \cdot \text{H}_2\text{O}$  is higher at 40° than at 0°, 20°, or 60° (catalyst rendered inactive more rapidly than at 40°). With double the amount of catalyst the initial reduction rate is greater at 60° than at 40°. In no case is more than 1 mol. of hydrogen added until the catalyst is activated by shaking with oxygen.

H. BURTON.

**Competitive hydrogenations.** H. ADKINS, F. F. DIWOKY, and A. E. BRODERICK (J. Amer. Chem. Soc., 1929, 51, 3418—3423).—Equimolecular mixtures of  $d$ - $\alpha$ -pinene and various unsaturated substances are treated with 1 mol. of hydrogen in presence of different solvents and various catalysts, and the distribution of hydrogen is calculated from the change in rotatory power of the mixture (cf. Vavon and Husson, A., 1923, i, 464). The rate of reduction (platinum oxide catalyst) is almost the same for methyl or ethyl alcohol and acetic acid, but is lower for ethyl acetate and for propyl and butyl alcohols. The distribution of the hydrogen is modified by the solvent. The rate of reduction is reduced considerably by addition of small amounts of zinc and nickel acetates, but the hydrogen distribution is unaffected. The time of reduction of the mixture has no relation to the time necessary for the reduction of the components. With a platinum oxide catalyst and acetic acid as solvent, the percentage addition of hydrogen to the pinene (when mixed with the substance quoted) is: cinnamic acid, 35;  $\alpha$ -methylcinnamic acid, 93; methyl and ethyl  $\beta$ -methylcinnamates, 87 and 91, respectively; "octene," 24; cyclohexene, 15, and allyl alcohol, 8.

With a nickel-kieselguhr catalyst alone at 450°, the corresponding figures for cinnamic acid and "octene" are 20 and 53, respectively. The products obtained during the reduction of furfurylideneacetone vary considerably with the solvent used;  $\beta$ -furylethyl methyl ketone is best prepared in presence of light petroleum.

H. BURTON.

**Thermodynamic theory of catalysis.** R. DUBRISAY (J. Chim. phys., 1929, 26, 497—499; cf. A., 1928, 1334).—A reply to Berthoud (A., 1929, 519).

C. W. GIBBY.

**Significance of exchange or displacement reactions in catalytic processes.** O. BAUDISCH (Ber., 1929, 62, [B], 2699—2705).—Oxygen and nitric oxide exhibit similarities in electronic structure and magnetic properties, and it therefore appears probable that molecular oxygen, like nitric oxide, is primarily co-ordinatively united to ferrous iron with the production of ferrous-oxygen (iron peroxo-) compounds which pass secondarily into ferric salts. This view is supported by observations of the different behaviour of solutions of sodium pentacyanoaquoferroate which have undergone short auto-oxidation and of the ferric solution derived from it towards 5-aminouracil or  $\psi$ -cumidine and by the isolation of the product,  $[(CN)_5Fe(OH) \cdot NH \cdot C_6H_4 \cdot O \cdot SO_2 \cdot C_6H_4 \cdot Me]Na_3$ , from *m*-aminophenyl *p*-toluenesulphonate. The absence of complex ferric ions in auto-oxidised ferrousaquo-solutions is shown by the negative behaviour towards reduced phenolphthalein, which in 0.01% solution gives a red colour with the ferricyanide complex. Attempts to use azides in the study of the catalytic transference of oxygen by iron salts show that these compounds have a weak affinity for bi- and ter-valent iron.

H. WREN.

**Induced reactions and the higher oxides of iron.** D. R. HALE (J. Physical Chem., 1929, 33, 1633—1664; cf. Vannoy, A., 1929, 1396).—From a study of the reactions which take place between (i) hydrogen peroxide, ferrous sulphate, and potassium iodide, and (ii) potassium permanganate, sodium arsenite, and ferrous sulphate in the presence of sodium hydrogen carbonate, it is concluded that the intermediate compound has the formula  $FeO_3$ , whilst that concerned in the action of oxygen on ferrous iron in alkaline solution has the formula  $Fe_2O_4$ . In an induced reaction in which ferrous iron is the inductor, the acceptor is decomposed because the intermediate higher oxide is a more powerful oxidising agent than the actor, and the difference between the action of hydrogen peroxide and permanganate and that of oxygen is ascribed to the greater electrochemical potentials of the first two. These induced reactions belong to the third group of Bancroft's classification (A., 1929, 1019).

L. S. THEOBALD.

**Oxidation of ammonium sulphite to ammonium sulphate with air in the presence of mineral salts.** D. VORLÄNDER and A. LAINAU (J. pr. Chem., 1929, [ii], 123, 351—376).—A systematic investigation of the effect of conditions and added salts on the velocity of atmospheric oxidation of dilute solutions of ammonium sulphite (ammonia into sulphurous acid), using a carefully standardised technique, is described. Under constant conditions of alkalinity,

namely, a 0.1*N*-solution of stoichiometrically neutral ammonium sulphite, almost no catalytic effect is observed on addition of sodium, potassium, ammonium, silver, beryllium, magnesium, zinc, cadmium, titanium, thallium, and uranyl sulphates, ammonium selenite, selenate, tellurate, and molybdate, potassium chromate, sodium tungstate, thiosulphate, and chloroaurate, chloroplatinic and boric acids, arsenious oxide, and disodium hydrogen arsenate. The oxidation velocity is increased by addition of cobalt, ferrous, nickel, copper, cerium, and manganese sulphates, and ammonium vanadate (the magnitude of the effect decreasing in the order given) (cf. Milbauer and Pazourek, A., 1921, ii, 635), whilst the velocity is decreased by excess of hydrogen ions, large excesses of hydroxyl ions, large concentrations of mineral salts, and alkali sulphides. The optimal conditions for catalysis by cobalt sulphate ( $6.6 \times 10^{-5}$  mol. per litre; the effect increasing with increasing concentration) in a 0.1*N*-ammonium sulphite solution are investigated. The velocity of oxidation, which is very small with strongly acid values of  $p_H$ , begins to increase rapidly at about  $p_H$  6, has a sharp maximum at  $p_H$  8.4—8.6, and then decreases rapidly until at  $p_H$  11 it is approximately the same as that in free sulphurous acid. The point of maximum velocity coincides with the maximum intensity of the brown colour of the sulphite-cobalt-ammonia complex salt, and on addition of equivalent amounts of complex cobalt salts in place of cobalt sulphate only those which decompose and give brown solutions (oxypentamminocobalt sulphate) act as catalysts, whilst those which retain their colour (roseocobaltic sulphate) have no catalytic effect. Catalysis is thus due, not to cobalt ions, but to the sulphite-cobalt-ammonia complex salt. Under otherwise constant conditions ( $CoSO_4$ ,  $6.6 \times 10^{-5}$  mol. per litre;  $p_H$  8—9), increasing the sulphite concentration from 0.0005 to 2.0*N* causes an initial rapid increase in the oxidation velocity (approximately proportional to the concentration) up to 0.1*N*, followed by a slower increase to a flattened maximum at 0.5*N*, and finally a gradual decrease. The initial rapid increase is due to the predominant mass action effect, but in more concentrated solutions this is outweighed by the decreasing concentration of oxygen in the solution consequent on its diminished solubility in concentrated salt solutions. That the velocity of oxidation depends, not only on the velocity of dissolution of oxygen in the solution, but also on its concentration follows from the following observations. The curves plotted between the volume of oxygen absorbed from 100 c.c. of air by 0.5, 0.2, and 0.1*N*-ammonium sulphite (without catalyst) and time are not straight lines, but are asymptotic. Similarly, the volume of oxygen absorbed by a 0.1*N*-ammonium sulphite solution ( $CoSO_4$ ,  $6.6 \times 10^{-5}$  mol. per litre) in definite intervals of time from oxygen-nitrogen mixtures in varying proportions is directly proportional to the partial pressure of the oxygen (except for very high oxygen partial pressures when the sulphite concentration becomes considerably altered). In three parallel experiments, (1) without catalyst, (2) with cobalt sulphate, (3) with the same concentration of ferrous sulphate, the ratio of the amount of oxygen absorbed in unit time at 0.21 and

0.97 atm. partial pressure is constant. Moreover, the velocity of oxygen absorption (0.97 atm.) is increased 45% by increasing the concentration of cobalt sulphate from  $6.6 \times 10^{-5}$  to  $6.6 \times 10^{-3}$  mol. per litre, although the dissolution velocity of the oxygen must remain constant. The temperature coefficient of the reaction between 16° and 27° is abnormally low (1.2) owing to the diminished solubility of oxygen at higher temperatures. Simultaneous addition of non-catalytic metallic salts in small concentration has little effect on the activity of cobalt sulphate as a catalyst. Addition of ferrous sulphate causes a slight increase in the activity of cobalt sulphate, but addition of increasing concentrations of copper sulphate causes a marked (increasing) diminution in its activity, an effect also observed with potassium chromate and not altered by increasing the concentration of ammonia in the solution. The decrease in the oxidation velocity caused by large concentrations of neutral salts is due to the diminished solubility of oxygen in such solutions. The oxidation velocity is unaltered by replacement of the ammonia by ammonium carbonate or hydrogen carbonate, or by addition of small amounts of glycerol. A critical summary of the earlier literature is given and the theory of the oxidation is discussed. It is concluded that it is not the sulphito ion, but free sulphurous acid or sulphur dioxide formed by hydrolysis, which is oxidised.

J. W. BAKER.

**Acid and salt effects in catalysed reactions.** XXII. Influence of inert salts on secondary dissociation of dibasic acids. H. M. DAWSON and J. E. SMITH (J.C.S., 1929, 2530—2539).—The velocity coefficients of the reaction between acetone and iodine have been determined at 25° in 0.04*N*-potassium hydrogen oxalate solution containing varying amounts of potassium chloride. The concentrations of the ions  $H^+$ ,  $HC_2O_4^-$ ,  $C_2O_4^{2-}$  have been calculated. The variation of the second stage dissociation constant of oxalic acid is given by the equation  $\log K_x = \log K_0 + a\sqrt{x} - bx$ , where  $x$  is the concentration of potassium chloride and  $a$  and  $b$  are constants. This is of the same form as the equation previously found for the first stage dissociation (A., 1929, 839). The value of  $a$  is twice that of the first stage dissociation, but is only 40% of the theoretical, according to the Debye-Hückel theory.

J. A. V. BUTLER.

**Active solutions of dextrose.** R. WURNER and J. GELOSO (J. Chim. phys., 1929, 26, 447—474).—An alkaline solution of dextrose, after being kept for some time in the dark, decolorises methylene-blue rapidly in the cold. The decolorising power increases with the time of keeping, up to a maximum value which depends on the  $p_H$  of the solution. The same maximum is reached more rapidly the higher is the temperature and the more alkaline the solution. The form of the curve representing the rate of decolorisation varies with the alkalinity. The same substances are produced in the solution at  $p_H$  12 as at  $p_H$  8, but the action on methylene-blue diminishes sharply at  $p_H$  8. The effect of changes of  $p_H$  is reversible. The solution behaves as though it contains a substance  $G'$ , capable of reducing 6 mols. of methylene-blue per 1000 mols. of dextrose initially present, and another,

$G$ , which reduces the remainder more slowly, up to 300 mols. per 1000. The reaction postulated is  $\text{dextrose} \rightarrow G + G' \rightleftharpoons A + H_2$ . Electrometric titration, with potassium ferrocyanide, of dextrose which has reached its maximum reducing power shows that there is a reversible oxidation-reduction equilibrium.  $G'$  produced from laevulose has the same properties as that formed from dextrose; it can be dehydrogenated reversibly by oxygen.

C. W. GIBBY.

**Basic catalysis in the decomposition of diacetone alcohol.** C. C. FRENCH (J. Amer. Chem. Soc., 1929, 51, 3215—3225).—The velocity of decomposition of diacetone alcohol at 25° in solutions of sodium or potassium hydroxide is proportional to the alkali concentration between 0.1 and 0.01*M*, and not to the alkali activity. The velocity in 0.05*M*-alkali solution is progressively diminished by the addition of sodium or potassium halides. The velocity coefficient varies linearly with the total equivalent salt concentration up to a total concentration of 0.25*M*. The linear equations obtained depend only on the anion of the salt present when the cations of the base and salt present are the same. Compared with hydroxyl ion, the phenoxyl ion has a very small effect on the decomposition rate; if the reaction with phenoxyl ion involves a spontaneous water reaction the half-time of the latter exceeds 800 days. The classical dissociation constant of phenol in 0.2*M*-salt solutions is  $1.93 \times 10^{-10}$  at 25°.

S. K. TWEEDY.

**Oxidation-reduction systems of biological importance.** VI. Catalytic effect of iron on oxidation of cysteine. L. MICHAELIS (J. Biol. Chem., 1929, 84, 777—787).—Theoretical consideration of results previously obtained confirms the conclusion (A., 1929, 1011) that the reaction of iron salts with cysteine is analogous to that of cobalt salts, but that the ferro-cysteine-cystine complex has only a transient existence, combining with 2 mols. of cysteine to give ferro-tricysteine and cystine, whilst the corresponding cobalto-cysteine-cystine complex is stable.

C. R. HARRINGTON.

**Autoxidation of abietic acid. Action of catalysts.** G. DUPONT and J. LÉVY (Compt. rend., 1929, 189, 920—922).—An extension of previous work (this vol., 86). The catalytic influence on the autoxidation of a number of phenols, metals, and solvents has been studied by the determination of the values of the constant  $b = 100/p(p_0 - p) \cdot dp/dt$ .

A. A. GOLDBERG.

**Possible relationship between heat of activation and activity in contact catalysis.** E. CREMER and G. M. SCHWAB (Z. physikal. Chem., 1929, 144, 243).—An attempt is made to give a theoretical interpretation of the equation connecting heat of activation and activity previously found experimentally (see this vol., 44).

F. L. USHER.

**Combination of hydrogen and oxygen on the surface of nickel.** R. P. DONNELLY (J.C.S., 1929, 2438—2444).—The rate of combination is proportional to the partial pressure of hydrogen and independent of that of oxygen down to 50 mm. The logarithm of the rate of reaction is proportional to the reciprocal of the absolute temperature. The hypothesis that the combination takes place by molecules of hydrogen



striking adsorbed molecules of oxygen is thus confirmed. No evidence has been obtained that the heterogeneous reaction on the surface of the nickel initiates a homogeneous reaction, spreading into the gas by a chain process, as is the case with platinum (A., 1929, 1150). J. A. V. BUTLER.

**Promoter action in the catalytic oxidation of methane by steam.** B. KUBOTA and T. YAMANAKA (Bull. Chem. Soc. Japan, 1929, 4, 211—220).—The catalytic oxidation of methane to hydrogen and carbon monoxide or dioxide in the presence of nickel can be promoted by various metallic oxides, alumina giving the best yield in the latter case and magnesia in the former. A possible mechanism is discussed.

C. W. GIBBY.

**Formation of liquid hydrocarbons from acetylene. II. Catalytic hydrogenation and condensation of acetylene.** F. FISCHER, K. PETERS, and H. KOCH.—See B., 1929, 966.

**Catalytic formation of hydrogen cyanide from ammonia and carbon monoxide.** P. V. ZIMAKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 997—1009).—The activity of catalysts used in the above reaction declines soon after the commencement of reaction, and the degree of inactivation is proportional to the initial activity; thus uranium dioxide, which has initially more than twice the catalytic power of zirconia, loses 77.3% of its activity 20 min. after the beginning of the reaction, whilst zirconia loses only 14.7% during the same period of time. Previous special purification of the reaction gases in no way affected the above phenomenon, which is not, therefore, due to anti-catalytic impurities introduced. The catalyst can be reactivated by heating in a current of air. Percentage inactivation is much smaller where thin layers of catalyst are used instead of thick ones, showing that the anti-catalyst in question is a reaction product. The reaction of formation of hydrogen cyanide is one of zero degree, expressed by the equation  $d[\text{CN}]/dt = k/f(t)$ . The following side reactions take place:  $2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$ ,  $2\text{CO} = \text{C} + \text{CO}_2$ ,  $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$ . The first of these side reactions is due, not to the catalyst used, but to porous carriers used for these catalysts, viz., pumice, sand, and asbestos. The second reaction is catalysed by uranium dioxide and by ceria, but not by thorium, zirconia, or vanadium oxide. The uranium dioxide becomes coated with a layer of soot, as a result of which it loses its catalytic power on the reaction of hydrogen cyanide formation; activation cannot in this case be effected by heating in a current of air. The amount of carbon dioxide produced by the third side reaction is proportional to the water content of the initial reaction mixture, and to the velocity of the main reaction, in which water is produced; carbon dioxide inactivates by preferential adsorption on the active centres of the catalyst, and can be eluted by heating in a current of air. The velocity equation  $d[\text{CN}]/dt = K/[\text{CO}_2]^{1/2}$  is deduced for systems in equilibrium with respect to adsorption of carbon dioxide; before equilibrium is attained, the velocity curves will be similar to inverted adsorption curves, i.e., the activity of the catalyst will diminish proportionately to the rate of adsorption of carbon dioxide on the active centres.

The velocity of reaction after equilibrium is attained is proportional to the free active surface of the catalyst, and not to the concentration of substrates.

R. TRUSZKOWSKI.

**Catalytic oxidation of hydrogen cyanide.** B. NEUMANN and G. MANKE (Z. Elektrochem., 1929, 35, 751—765).—Mixtures of air and hydrogen cyanide containing approximately 6% of the latter were passed at different speeds over platinum gauze at temperatures between 450° and 900°. At the lower temperatures much hydrogen cyanide remained undecomposed, whilst at the highest temperatures decomposition was complete, but the resulting products were chiefly nitrogen together with some nitrogen tetroxide and very little nitrous anhydride. At 700° the amount of nitrogen produced was at a minimum, that of nitrous anhydride at a maximum, and the percentage of nitrogen tetroxide remained almost unchanged. In another set of experiments, the velocity of the reacting gases was maintained constant and the ratios of the reactants in the mixtures and the temperatures were varied. Complete decomposition of the hydrogen cyanide occurred above 500°, but the proportion of nitrogen increased with rise in temperature and also with increasing hydrogen cyanide content of the reacting mixture. The most satisfactory oxidations were obtained from 6% hydrogen cyanide mixtures at 700°, the nitrogen produced then being lowest. The effect of using several catalysts (one, two, or four platinum gauzes being employed), higher velocities, and pure oxygen, instead of air, was investigated. By using several contact agents it was possible to pass the reactants at greatly increased rates. Higher temperatures were necessary to effect complete decomposition, but the nitrogen produced increased in amount. Other catalysts were studied, viz., ferric oxide alone or containing 5% of bismuth sesquioxide or 10% of potassium oxide, and a mixture of cupric and nickelous oxides. In all cases the catalysts were effective in promoting the decomposition of hydrogen cyanide, but there was a pronounced tendency for large amounts of nitrogen to be produced. The effect of adding bismuth oxide to the ferric oxide was to reduce the amount of resulting nitrogen, especially at the lower temperatures, whilst the potassium oxide caused the nitrogen content to be increased and more so at the lower temperatures.

H. T. S. BRITTON.

**Equilibria in reduction, oxidation, and carbonisation processes in iron. IX.** R. SCHENCK, H. FRANZ, and H. WILLEKE (Z. anorg. Chem., 1929, 184, 1—38; cf. A., 1927, 1030).—The influence of a number of metal oxides on the carbon dioxide/carbon monoxide ratio in the gases in equilibrium with the oxide ("wüstite") and metal ("oxo-austenite") phases in the reduction of ferric oxide by carbon monoxide has been studied at temperatures between 700° and 1050° by the method previously described. This ratio is lowered by the addition of an oxide which can form mixed crystals with ferric or ferrous oxide, e.g., by aluminium oxide (isomorphous with ferric oxide) and by magnesium or manganous oxide (isomorphous with ferrous oxide), and the difficulty of reducing the mixed crystals increases with the

proportion of foreign oxide. The ratio is similarly modified if compounds are formed between the added oxide and either of the iron oxides, as happens with aluminium, magnesium, manganous, and zinc oxides, the first-named forming a spinel with ferrous oxide and the others with ferric oxide. The behaviour of the system containing zinc is further complicated by the presence of zinc vapour in the gas phase. Calcium oxide gives rise to several compounds, among which  $\text{CaO}, \text{Fe}_2\text{O}_3$ ,  $2\text{CaO}, \text{Fe}_2\text{O}_3$ , and  $\text{CaO}, \text{Fe}_3\text{O}_4$  have been recognised, and to a ternary solution phase which is especially difficult to reduce. Oxides which form neither compounds nor mixed crystals, *e.g.*, beryllium oxide, exercise no influence on the course of the reduction.

F. L. USHER.

**Activation of metals by addition of extraneous materials.** R. SCHENCK and H. WESSELKOCK (Z. anorg. Chem., 1929, 184, 39—57).—The displacement of the carbon monoxide-carbon dioxide equilibrium observed when certain non-reducible metal oxides are added to ferric oxide during its reduction leads to the conclusion that the finely-dispersed metal is under these conditions activated with respect to oxygen. The reactivity of cobalt and of nickel toward carbon dioxide has been investigated in order to determine the properties of the added oxide which produce this effect. Pure cobalt forms 5% and nickel less than 1% of carbon monoxide at 900°, whilst neither forms a detectable quantity at 600°. Addition of 10 mols. of magnesium oxide or manganous oxide gives rise to marked reactivity at 600°, up to 40% of carbon monoxide being formed in the case of the latter substance. Calcium oxide has no appreciable influence on cobalt, but slightly activates nickel. Although all three oxides possess the same crystal structure as those of cobalt and nickel and can form mixed crystals, the magnitude of the effect is not in the order of the similarity of the lattice constants as determined at the ordinary temperature. The irregularity of the course of the reaction with carbon dioxide is considered to be due to the physical inhomogeneity of the dispersion of metal in the selected oxide. Cobalt always behaves as the less noble metal. Addition of aluminium oxide, which can form a spinel with the oxides of cobalt or nickel, produces a similar activation of the metal, whilst beryllium oxide, which forms neither a solid solution nor a compound, is without influence. The reactivity of iron towards methane is not affected by any of the oxides mentioned above, and the action is therefore regarded as specific with respect to oxygen. The general conclusion reached from these experiments is that a metal is activated with respect to an element if the former is suitably distributed in a compound capable of forming either mixed crystals or a molecular compound with a compound of the metal with the element in question. This view provides a simple explanation of the absorption of nitrogen by iron in the presence of lithium nitride (cf. Frankenburger, A., 1928, 1341), and of the production of sulphide phosphors.

F. L. USHER.

**Catalytic behaviour of rare-earth oxides.** E. CREMER (Z. physikal. Chem., 1929, 144, 231—242).—A connexion between the atomic structure of an

element and the catalytic properties of its compounds has been sought by studying the decomposition of ethyl alcohol when catalysed by oxides of the rare earths and of other elements of group 3. The heats of activation increase in the order shown in the series aluminium, indium, scandium, yttrium, lanthanum, whilst those of cerium, praseodymium, neodymium, samarium, gadolinium, and dysprosium do not differ appreciably from one another or from that of a mixture of yttrium earths. An experimental relationship,  $c = Ae^{g/a}$ , between the heat of activation ( $g$ ) and the activity of the catalyst ( $c$ ) has been established.

F. L. USHER.

**Decomposition of acetone in contact with platinum.** H. A. TAYLOR (J. Physical Chem., 1929, 33, 1793—1801).—The decomposition of acetone vapour by a hot platinum filament in a vessel at 50° has been investigated at various pressures and at filament temperatures of 844°, 890°, and 916°. The results are identical in form with those of the homogeneous reaction (cf. Hinshelwood and Hutchison, A., 1926, 691). The primary decomposition is unimolecular, having the value 68,400 g.-cal. for the heat of activation compared with 68,500 g.-cal. for the homogeneous reaction, indicating that the hot filament has no catalytic effect. The primary decomposition appears to take place in the gaseous phase in a zone around the filament.

L. S. THEOBALD.

**Electrolytic preparation of hydroxylamine.** II. Combination of [anodic] oxidation with [cathodic] reduction. J. STSCHERBAKOV and D. LIBINA (Z. Elektrochem., 1929, 35, 826—830; cf. A., 1929, 274).—The cathodic reduction of nitric acid to hydroxylamine may be combined with the anodic oxidation of sulphate to persulphate by electrolysis of ammonium sulphate solution in a cell with a mercury cathode consisting of a layer of mercury supported on the porous bottom of a vessel containing a solution of sulphuric and nitric acids. In order to prevent the evolution of hydrogen or oxides of nitrogen at the cathode and so to obtain the best yield of hydroxylamine, the voltage, temperature, and concentration of nitric acid must be maintained within certain fairly narrow limits. Accumulation of salt in the acid solution hinders the reduction.

R. CUTHILL.

**Formation of hydrazine in the electrical degradation of ammonia.** A. KOENIG and O. H. WAGNER (Z. physikal. Chem., 1929, 144, 213—230; cf. A., 1928, 854).—The formation of hydrazine by the decomposition of ammonia, usually very slight, may be greatly increased by a suitable choice of experimental conditions. The yield of hydrazine in a discharge tube, calculated for the same quantity of decomposed ammonia, increases with the velocity of the gas stream. The chemical efficiency of the discharge in ammonia runs counter to the optical effect, *i.e.*, the stronger the discharge glow the smaller is the amount of reaction product for the same electrical expenditure. In favourable examples 80% of the ammonia decomposed in a Siemens tube discharge may be detected as hydrazine. The carbon arc, although yielding approximately the same amount of decomposed ammonia per energy unit, produces much less hydrazine. Spectroscopic investigations show

that the yield of hydrazine is especially good when the Schuster yellowish-green bands are prominent in the spectrum of the discharge light, and is at a minimum when, by reason of a high arc temperature, these are overlapped by a multi-line spectrum. The spectrum of streaming hydrazine vapour does not show the Schuster bands even in the presence of the decomposition products  $\text{NH}_2$  and  $\text{NH}$ , and they are therefore ascribed to the ammonia molecule.

F. L. USHER.

**Oxidation of alkali plumbite to plumbate by sinusoidal alternating current.** III. F. JIRSA (Z. Elektrochem., 1929, 35, 830—833).—The formation of plumbate by electrolysis of alkali plumbite solutions with alternating current (A., 1927, 738) is probably a result of cathodic passivation, inhibiting the reducing action of normal cathodic polarisation, and of the formation of complex ions,  $\text{Pb}^{4+} + 5\text{OH}' \rightleftharpoons 2\text{H}_2\text{O} + \text{HPbO}_3'$ ,  $\text{Pb}^{4+} + 6\text{OH}' \rightleftharpoons 3\text{H}_2\text{O} + \text{PbO}_3''$ ,  $\text{Pb}^{4+} + 8\text{OH}' \rightleftharpoons \text{PbO}_4''' + 4\text{H}_2\text{O}$ , the reduction of the  $\text{Pb}^{4+}$  ion consequently being retarded. If the cathodic passivation is incomplete, as with palladium, the current yield will increase with increase in the current density, since this increases the passivation, and will also depend on the alkali concentration, since the alkali plays a part in the complex ion formation. Nickel, on the other hand, is rendered completely passive, and the alkali concentration influences the yield mainly in so far as it affects the concentration of  $\text{Pb}^{2+}$  ions.

R. CUTHILL.

**Electrolysis of metallic oxides dissolved in fused boric acid and in fused borates (tungsten, molybdenum, zinc).** L. ANDRIEUX (Diss., Paris, 1929).—In the electrolysis of alkali borates the alkali metal is the primary, and amorphous boron the secondary, product. Alkaline-earth borates afford borides and amorphous boron, cerium and manganese borates yield borides, whilst magnesium borate gives very pure boron. The electrolysis of magnesium borate is effected in a graphite crucible, the charge consisting of boric anhydride, magnesium oxide, and magnesium fluoride; the electrolyte is fluid at  $1000^\circ$ , but crystalline pyroborate accumulates at the cathode. The following borides were thus prepared:  $\text{CaB}_6$ ,  $\text{SrB}_6$ ,  $\text{BaB}_6$ ,  $\text{ThB}_6$ ,  $\text{Zr}_3\text{B}_4$ ,  $\text{Cr}_3\text{B}_2$ ,  $\text{MnB}$ . The following borides were also obtained:  $\text{CeB}_6$ ,  $\text{LaB}_6$ ,  $\text{NdB}_6$ ,  $\text{GdB}_6$ ,  $\text{YB}_6$ ,  $\text{ErB}_6$ ,  $\text{YbB}_6$ ,  $\text{TiB}_2$ ,  $\text{VB}_2$ ,  $\text{UB}_3$ . Zinc, tungsten, and molybdenum were obtained electrolytically from borates.

CHEMICAL ABSTRACTS.

**Electrochemical production of hydrogen peroxide.** L. LOWENSTEIN.—See B., 1929, 1013.

**Electrodeposition of silver from argentocyanide solutions.** S. GLASSTONE and E. B. SANIGAR.—See B., 1929, 1018.

**Electrolytic oxidation of ether in presence of perchloric acid.** M. C. MARIE and G. LEJEUNE (Anal. Fis. Quím., 1929, 27, 447—449).—By electrolytic oxidation of ether in presence of perchloric acid with platinum electrodes and a current of 3 amp. a 30% yield of acetaldehyde is obtained; traces only of alcohol and acetic acid are produced, and part of the aldehyde polymerises with the formation of resins.

H. F. GILLBE.

**Electrolytic reduction of an aromatic arsinic acid.** K. NAKADA (Coll. Lect. Inst. Chem. Res., Japan, 1929, 1, 94—98).—3-Nitro-4-hydroxyphenyl-arsinic acid is best reduced to the amino-acid by electrolysis in 2*N*-hydrochloric acid by 2.6 amp. in 1.3 hrs. at  $25^\circ$ ; variations in current density affect the yield but not the product. Some decomposition occurs above  $60^\circ$ . When the acid concentration is above 5*N* salvarsan is formed, and arsanilic acid forms arsenoaniline. At high acid concentration phenolarsinic acid is converted into arsenophenol. Arsinic acids are reduced by cathodes of mercury, lead, and lead amalgam, whilst platinum, nickel, and copper cathodes reduce only the nitro-group.

CHEMICAL ABSTRACTS.

**Electrochemical oxidation of toluene.** R. W. MITCHELL.—See B., 1929, 972.

**Disappearance of hydrogen in discharge tubes.** R. DELAPLACE (Compt. rend., 1929, 189, 849—850).—The disappearance of hydrogen in discharge tubes is attributed to the effect of atomic hydrogen, which can be formed only if water vapour is present. The recombination of atomic hydrogen takes place on the surface of the glass, which becomes heated and gives up carbon monoxide and carbon dioxide. These gases react with hydrogen. If water vapour is excluded from the tube no disappearance of hydrogen is observed.

C. J. SMITHELLS.

**Formation and spectrum of mercury hydride.** M. DZIEDICKI (Spraw. Prace Polsk. Towarz. Fizycz., 1928, 3, 207—239; Chem. Zentr., 1929, i, 3068).—Chemical reaction takes place in the mercury-hydrogen arc, since the pressure falls rapidly and a band spectrum appears. The compound is solid and insoluble in mercury. The reaction ceases below 9 volts; it is most rapid in the cathode dark space. The rate of decomposition of the compound falls with increase of pressure. At a suitable pressure of hydrogen the mercury hydride bands are more readily and energetically emitted than those of hydrogen. The emission of the former is favoured by increase of pressure of the hydrogen.

A. A. ELDRIDGE.

**Reactions of dissociated water vapour.** H. C. UREY and G. I. LAVIN (J. Amer. Chem. Soc., 1929, 51, 3290—3293).—Steam was subjected to an electric discharge as in Wood's method of preparing atomic hydrogen, and an extremely reactive gas containing hydrogen atoms and another constituent, probably hydroxyl molecules, was obtained. Iron and nickel chlorides are immediately reduced to the metal by the gas; a copper sulphate crystal immediately turned black and was apparently reduced to fused metal. Indigotin is reduced to indigo-white, fragments of the solid being torn off and rendered incandescent. Platinum becomes white hot. Acetaldehyde is polymerised with the accompaniment of a luminous glow, and mercury emits a visible violet light consisting of mercury hydride,  $\text{HgH}$ , lines and the 2536 Å. line of mercury. Ethylene is attacked with the formation of some acetaldehyde. Unsaturated oils (cottonseed and linseed oil) are converted into white insoluble solids.

S. K. TWEEDY.

**Energetic efficiency of photosynthesis.** R. WURMSER (*Nature*, 1929, **124**, 912—913).—Polemical against Briggs (*A.*, 1929, 960). A. A. ELDRIDGE.

**Mean life of the catalyst in the photochemical union of chlorine and hydrogen.** D. L. CHAPMAN and P. P. GRIGG (*J.C.S.*, 1929, 2426—2432).—By comparing the rate of the photochemical union of chlorine and hydrogen in a capillary tube with that in a wider tube, the mean life of the catalyst formed by the action of light has been estimated. The life so estimated is approximately proportional to the sensitivity of the mixture over a wide range. A theoretical explanation of this relation is given.

J. A. V. BUTLER.

**Photochemical dissociation. Decomposition of hydrogen chloride in total and in monochromatic ultra-violet light.** I. C. T. SCHULTZ (*J. Chim. phys.*, 1929, **26**, 475—491).—A critical discussion of the principles which should be applied in the experimental investigation of photochemical reactions, with special reference to the combination of hydrogen and chlorine.

C. W. GIBBY.

**Photographic action of slow electrons.** B. ROSSI and G. BERNARDINI (*Atti R. Accad. Lincei*, 1929, [vi], **10**, 182—185).—By using a heavy, fluorescent mineral oil as sensitiser it has been found possible to obtain a photographic action on plates with low-speed electrons of a velocity corresponding with 17.5 volts (cf. Cole, *A.*, 1926, 1189). O. J. WALKER.

**Reactions of ethylene, hydrogen, and the saturated hydrocarbons under the influence of excited mercury.** H. S. TAYLOR and D. G. HILL (*J. Amer. Chem. Soc.*, 1929, **51**, 2922—2936).—The interaction of hydrogen with ethylene and of other saturated hydrocarbons under the influence of excited mercury atoms was investigated under varying conditions. The pressure falls steeply on illumination to a pressure approximately equal to that of the hydrogen originally present. When no hydrogen is present acetylene is usually formed together with hydrogen; otherwise a saturated hydrocarbon, usually methane, is produced the quantitative formation of which is favoured by higher hydrogen concentration. A viscous, nearly colourless oil of terpene-like odour,  $(CH_2)_x$ , of mol. wt. about 230, is deposited. The higher hydrocarbons in absence of hydrogen decompose more readily than the lower; hydrogen in large quantities seems to exert an inhibiting effect.

Experiments with ethylene showed that the primary reaction with hydrogen is the formation of saturated hydrocarbons, but not usually ethane; the composition of the saturated product depends on the concentration of the original mixture, but is independent of the pressure and also practically independent of temperature. The liquid polymeride all passes through saturated hydrocarbon, the latter decomposing and leaving only methane and hydrogen in the gas phase. Methane is uninfluenced either by excited mercury or by atomic hydrogen. The rate of the ethylene reaction depends on both the temperature and composition of the gas. A mechanism is suggested for the reaction which is in accord with the experimental results and with the results of previous experimenters.

S. K. TWEEDY.

**Kinetics, temperature coefficients, and quantum efficiency of photochemical reactions between bromine and propyl, isopropyl, or butyl alcohol in radiation of different wave-lengths.** J. K. VERMA and N. R. DHAR (*Z. anorg. Chem.*, 1929, **184**, 58—62; cf. *A.*, 1929, 516).—All the above reactions are unimolecular with respect to bromine and nearly semimolecular with respect to the alcohols, both in the dark and in the light. The quantum efficiency is abnormally high and increases with rising temperature and with the frequency of the incident radiation. The temperature coefficients of the reactions vary with the wave-length of the light, but in all cases they lie between 1 and 3, the latter being the temperature coefficient of the dark reaction.

F. L. USHER.

**Relation between intensity of light and velocity of photochemical reactions between bromine and propyl, isopropyl, or butyl alcohols.** J. K. VERMA and N. R. DHAR (*Z. anorg. Chem.*, 1929, **184**, 90—96; cf. preceding abstract).—The relation between intensity of light and the velocity of a photochemical reaction depends on the relative predominance of the light and dark reactions. In the reactions investigated the dark reaction is diminished by the addition of potassium bromide, in the presence of which they are greatly accelerated by light, and the relation between intensity and velocity is about 1/4. In the absence of potassium bromide the dark reaction proceeds rapidly, and an increase in the intensity of the light does not exercise so pronounced an effect on the velocity, the ratio being then about 1.

F. L. USHER.

**Action of light of different wave-lengths on cellulose nitrate.** H. B. DEVORE, A. H. PFUND, and V. COFMAN (*J. Physical Chem.*, 1929, **33**, 1836—1842).—The action of light on cellulose nitrate has been investigated spectrographically. Thin films of thickness of the order of 0.001 mm. are gradually decomposed, the mercury arc spectrum from 1900 to 2600 Å. being the most effective. Thicker films containing suitable indicators show that acidity is increased by wave-lengths from 2300 to 6000 Å. with a maximum near 3130 Å. The imbibing power is also increased by exposure to the same spectral region. Brittleness is produced by wave-lengths near 2540 Å. more rapidly than by longer wave-lengths.

L. S. THEOBALD.

**Sterol of cod-liver oil and the photochemical action of some sterols.** L. HUGOUNENQ and E. COUTURE (*Bull. Soc. Chim. biol.*, 1929, **11**, 956—964).—See *A.*, 1929, 895.

**Reactions of atomic hydrogen [with organic compounds].** H. C. UREY and G. I. LAVIN (*J. Amer. Chem. Soc.*, 1929, **51**, 3286—3290).—Atomic hydrogen, prepared by Wood's method, was allowed to react with organic compounds. Azoxybenzene is reduced to aniline through the intermediate stages of azobenzene and hydrazobenzene. Dyes are immediately decolorised, but they partly regain their colour on exposure to air; indigotin is reduced to indigo-white. Benzoic acid and acetamide catalyse the recombination of atomic hydrogen, but are not attacked themselves; formic acid also promotes this recombination,

but is itself slightly reduced to formaldehyde in the process. Acetaldehyde is polymerised to paraldehyde accompanied by a glow consisting of three bands in the region 4000, 4250, and 4260 Å. Certain glowing "active spots" which developed in the apparatus were "poisoned" by acetaldehyde, but recovered their activity when the supply of aldehyde was stopped.

S. K. TWEDDY.

**Constitution of schönite.** M. T. SALAZAR and E. MOLES (Anal. Fis. Quím., 1929, 27, 561—568).—The manner of dehydration of double sulphates of the schönite class has been studied by desiccation at gradually rising temperature and determination of the number of molecules of water lost. The potassium zinc compound loses water continuously up to 75°, when it becomes anhydrous, whilst manganous ammonium sulphate becomes anhydrous at 65°. Werner's formulation of these substances, *i.e.*,  $M'_2(SO_4)_2[M''(H_2O)_6]$ , is therefore regarded as correct. Treatment of either the anhydrous or the monohydrated potassium zinc sulphate with gaseous ammonia produces finally a pentammino-compound, although with the anhydrous salt it is more difficult to pass the triammine stage and the pentammine produced is less stable than the aquopentammine obtained from the monohydrate. Precipitation of the sulphate ion in potassium zinc, manganous ammonium, and ferrous ammonium sulphate solutions (0.002N) at 0° and at 25° yields identical results, indicating absence of hydrolysis. H. F. GILLBE.

**Ammines. III. Derivatives of cupric nitrite.** H. J. S. KING (J.C.S., 1929, 2593—2597).—Normal cupric nitrite is not obtained by the method of Péligot. The green solution prepared from potassium nitrite and cupric sulphate contains the complex anion  $[Cu(NO_2)_5]^{3-}$ . When this solution is filtered into solutions of organic bases complex cupric nitrites are obtained. Evidence is given for the view that in the cupric diammines the co-ordination number of copper is two. The following compounds are described: *dipyridinocupric nitrite*, *picrate*, and *benzoate*, *pentapyridinocupric picrate*, *dianilino*-, *di-p-toluidino*-, and *di-β-naphthylamino-cupric nitrite*.

J. A. V. BUTLER.

**Tetramminocupric nitrate.** R. PORTILLO (Anal. Fis. Quím., 1929, 27, 544—554).—By treatment of a boiling solution of cupric nitrate with ammonia solution until the precipitate first formed redissolves, and cooling, deep blue crystals of the compound  $[Cu(NH_3)_4](NO_3)_2 \cdot d_1^2 \cdot 1.896$ , are obtained; by heating at 150° 2 mols. of ammonia are lost and the bright blue diammine,  $d_2^2 \cdot 2.040$ , is produced. The mol. vol. of ammonia, calculated from the densities of the two ammines, is 14.8 or 16.5, compared with Biltz's value of 18—24. The heat of dissociation  $Q$  of the tetrammine in 300 mols. of water is -17.4 kg.-cal., and in 1000 mols. -19.4 kg.-cal., the increase of  $Q$  with dilution indicating the absence of hydrolysis, which is usually characteristic of the cuprammines; with increase of concentration of ammonia in the solution  $Q$  diminishes to a limiting value of -16.4 kg.-cal. when the ammonia concentration is about 5M, probably on account of an exothermic association of the cuprammine with ammonia. The heat of form-

ation of tetramminecupric nitrate (solid) is +196.5 kg.-cal.

H. F. GILLBE.

**Action of high temperatures on metal sulphides.** PICON (Bull. Soc. chim., 1929, [iv], 45, 907—913; cf. A., 1929, 1012).—Magnesium sulphide heated in a graphite boat in a vacuum volatilises slowly at 1200° and rapidly at 1300° with slight dissociation. Aluminium sulphide behaves similarly, but is rather less volatile. Under similar conditions, molybdenum sulphide ( $Mo_2S_3$ ) is largely dissociated at 1100° and volatilises at 1200°; tungsten disulphide dissociates at 1200° and is not volatile at 2000°, and uranous sulphide dissociates above 1300° and melts and distils at 1600°. In no case does the dissociation appear to be accelerated by the presence of graphite, although molybdenum produced by dissociation of the sulphide forms a carbide not volatile at 2100°.

F. L. USHER.

**Action of mercury salts on iron pentacarbonyl.** III. H. HOCK and H. STUHLMANN (Ber., 1929, 62, [B], 2690—2693; cf. A., 1928, 1344; 1929, 412).—Addition of iron pentacarbonyl to a solution of mercuric acetate in methyl alcohol causes almost quantitative precipitation of the compound  $2Fe(CO)_5 \cdot Hg(OMe)_2$ , decomposed by mercuric chloride in aqueous acetone to the substance  $Fe(CO)_4 \cdot Hg_2Cl_2$ , methyl alcohol, carbon dioxide, and hydrogen chloride, and by hydrochloric acid to iron pentacarbonyl. The compound is also obtained from mercuric methoxide (from sodium methoxide and mercuric chloride) or mercuric oxide in methyl alcohol and iron pentacarbonyl. The compounds  $2Fe(CO)_5 \cdot Hg(OEt)_2$  and  $2Fe(CO)_5 \cdot Hg(OPr^i)_2$  are prepared similarly.

H. WREN.

**Germanium. VI. Improved method of extracting germanium from germanite.** W. PUGH (J.C.S., 1929, 2540—2542; cf. A., 1924, ii, 415).—The roasted ore is treated with concentrated nitric acid, which dissolves arsenic as arsenic acid and removes the greater part of the copper as copper nitrate. The insoluble residue is distilled with concentrated hydrochloric acid and 85% of the germanium is obtained in the first portion of the distillate practically free from arsenic. J. A. V. BUTLER.

**Phosphates and arsenates.** F. EPHRAIM and C. ROSSETTI (Helv. Chim. Acta, 1929, 12, 1025—1033).—Details are given for the preparation of the following phosphates:  $4CuO \cdot P_2O_5 \cdot 1.5H_2O$ ;  $2.5CuO \cdot P_2O_5 \cdot 3H_2O$ ;  $8CuO \cdot 3P_2O_5 \cdot 8H_2O$ ;  $3NiO \cdot P_2O_5 \cdot 8H_2O$ ;  $6BeO \cdot P_2O_5 \cdot 9H_2O$ , and  $4.5BeO \cdot P_2O_5 \cdot 6.5H_2O$ . The following arsenates are also described:  $5NiO \cdot As_2O_5 \cdot 18H_2O$ ;  $4NiO \cdot As_2O_5 \cdot 14H_2O$ ;  $3NiO \cdot As_2O_5 \cdot 11H_2O$ ;  $2.5NiO \cdot As_2O_5 \cdot 8H_2O$ ;  $5CoO \cdot 2As_2O_5 \cdot 15H_2O$ ;  $5CoO \cdot 2As_2O_5 \cdot 28H_2O$ ;  $2.5MnO \cdot As_2O_5 \cdot 3H_2O$ ;  $4.5BeO \cdot As_2O_5 \cdot 9H_2O$ , and  $4BeO \cdot As_2O_5 \cdot 10H_2O$ .

H. BURTON.

**Vanadium ammonium alum.** E. MOLES and P. G. DE PAREDES (Anal. Fis. Quím., 1929, 27, 624—630).—Thermal decomposition of vanadium ammonium alum indicates the existence of three hydrates, containing, respectively, 12, 6, and 3 mols. of water, analogous to chrome alum. On exposure to the air the yellowish-brown solution absorbs

oxygen and becomes blue, owing to the formation of vanadyl ammonium sulphate,  $\text{VOSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 3 \cdot 5\text{H}_2\text{O}$ . The trihydrate rapidly absorbs dry ammonia with the formation of the compound  $(\text{NH}_4)_2[\text{V}(\text{SO}_4)_2] \cdot 3\text{H}_2\text{O} \cdot 5\text{NH}_3$ .

H. F. GILLBE.

**Thioarsenites. I. Potassium compounds. II. Sodium and ammonium compounds. III. Alkaline-earth compounds. H. WÜNSCHENDORFF** (Bull. Soc. chim., 1929, [iv], 45, 889—906; cf. Nilson, A., 1876, ii, 480).—I. The products obtained by the interaction of carefully purified arsenious sulphide and potassium monosulphide have been examined and the following have been prepared:  $\text{KAsS}_2$ , red, rhombic;  $\text{K}_2\text{As}_2\text{S}_7 \cdot 2\text{H}_2\text{O}$ , red needles;  $\text{KAs}_3\text{S}_5 \cdot 1 \cdot 5\text{H}_2\text{O}$ , red, granular, insoluble. The ortho- and pyro-thioarsenite could not be obtained in the solid condition, their solutions decomposing when concentrated into arsenic and potassium orthothioarsenate.

II. Five sodium salts have been prepared, viz.,  $\text{NaAsS}_2$ , dirty brown, prismatic;  $\text{Na}_2\text{As}_2\text{S}_7 \cdot 2\text{H}_2\text{O}$ , brown prisms;  $\text{NaAs}_3\text{S}_5 \cdot 3\text{H}_2\text{O}$ , brown spherites;  $\text{Na}_4\text{As}_2\text{S}_5 \cdot \text{H}_2\text{O}$ , dark orange prisms;  $\text{Na}_3\text{AsS}_3$ . The last two are very unstable, and decompose rapidly with production of arsenic and sodium orthothioarsenate. Only two ammonium salts could be obtained, viz.,  $\text{NH}_4\text{AsS}_2$ , yellow needles, unstable; and  $(\text{NH}_4)_2\text{As}_2\text{S}_7$ , red needles, stable.

III. The following alkaline-earth salts were obtained:  $\text{Ca}(\text{AsS}_2)_2 \cdot 8\text{H}_2\text{O}$ , yellow prisms;  $\text{Ca}_2\text{As}_2\text{S}_5 \cdot 9\text{H}_2\text{O}$ , yellow, triclinic, unstable;  $\text{Sr}(\text{AsS}_2)_2 \cdot 2\text{H}_2\text{O}$ , yellow, amorphous;  $\text{Sr}_2\text{As}_2\text{S}_5 \cdot 7\text{H}_2\text{O}$ , orange, triclinic;  $\text{Sr}_3(\text{AsS}_2)_2 \cdot 6\text{H}_2\text{O}$ , yellowish-white scales;  $\text{Ba}_3\text{As}_2\text{S}_5 \cdot 6\text{H}_2\text{O}$ , brownish-yellow;  $\text{Ba}_2\text{As}_2\text{S}_5 \cdot 5\text{H}_2\text{O}$ , yellow;  $\text{Ba}_3(\text{AsS}_2)_2 \cdot 8\text{H}_2\text{O}$ , yellow prisms;  $\text{Ba}(\text{AsS}_2)_2 \cdot 0 \cdot 5\text{H}_2\text{O}$ , insoluble brown precipitate.

F. L. USHER.

**Arsenic trichloride and sulphur chloride. J. R. PARTINGTON** (J.C.S., 1929, 2577—2578).—The compound  $2\text{AsCl}_3 \cdot 3\text{SCl}_2$ , described by Rose, probably does not exist. An improved method for the preparation of arsenic trichloride is given.

J. A. V. BUTLER.

**Action of sulphur monochloride on antimony pentachloride. J. R. PARTINGTON** (J.C.S., 1929, 2573—2577).—By the action of sulphur monochloride on antimony pentachloride, the compound  $\text{SbCl}_5 \cdot \text{SCl}_2$  has been obtained as amber-coloured crystals, m. p.  $157^\circ$ — $163^\circ$  (decomp.). It is soluble in sulphuryl chloride, but only slightly increases the electrical conductivity of the solvent. It is concluded that it is a non-polar substance, having the formula  $[\text{SbCl}_5 \cdot \text{SCl}_2]$ .

J. A. V. BUTLER.

**Precipitated selenium dioxide. G. F. HOFFMANN and V. LENHER** (J. Amer. Chem. Soc., 1929, 51, 3177—3184).—The interaction of ozone and a solution of selenium in selenium oxychloride yields a precipitate of selenium dioxide. The pure solvent alone is not attacked by ozone unless the latter is bubbled through in a highly subdivided state, when selenium dioxide is again precipitated. No selenium trioxide is formed (cf. Meyer and Pawletta, A., 1927,

532). The precipitated dioxide rapidly absorbs atmospheric moisture and forms selenious acid. Both the sublimed and the precipitated dioxide have a thrice normal mol. wt. in selenium oxychloride solution, and the former oxide has an appreciably higher density than the latter owing to its different physical condition. The precipitated dioxide absorbs dry hydrogen chloride to form the compound  $\text{SeO}_2 \cdot 2\text{HCl}$  and not chloroselenic acid (cf. Worsley and Baker, J.C.S., 1923, 123, 2870).

S. K. TWEEDY.

**Oxidation of selenium dioxide and of tellurium dioxide with lead dioxide. F. C. MATHERS and F. V. GRAHAM** (J. Amer. Chem. Soc., 1929, 51, 3225—3228).—Selenium dioxide and lead dioxide react at  $100^\circ$ , both dry and wet, to form lead selenate, from which ammonium selenate is readily prepared by precipitation with "ammonium carbonate." Metal selenates are obtained by crystallising together solutions of ammonium selenate and metal nitrate. Tellurium dioxide and lead dioxide react similarly, but a 10% excess of the lead oxide is desirable at a temperature of  $170^\circ$ .

S. K. TWEEDY.

**Oxidation of calcium tellurite by heating and the preparation of telluric acid from the calcium tellurate. F. C. MATHERS and G. M. BRADBURY** (J. Amer. Chem. Soc., 1929, 51, 3229—3232).—Calcium tellurate is prepared by heating tellurium dioxide with five equivalents of calcium hydroxide at  $975$ — $1075^\circ$ . The percentage oxidation of the dioxide diminishes at lower temperatures and with smaller proportions of calcium hydroxide. Telluric acid may be obtained from the calcium tellurate by treatment with excess of concentrated nitric acid.

S. K. TWEEDY.

**Complex bromides of quinquivalent molybdenum. F. G. ANGELL, R. G. JAMES, and W. WARDLAW** (J.C.S., 1929, 2578—2589).—Salts of the type  $\text{R}_5[\text{MoOBr}_5]$ , where  $\text{R} = \text{NH}_4$ ,  $\text{K}$ ,  $\text{Rb}$ ,  $\text{C}_5\text{H}_5\text{N}$ , or  $\text{C}_9\text{H}_5\text{N}$ , have been obtained by electrolytic reduction of a solution of molybdenum trioxide in hydrobromic acid at a platinised platinum cathode, followed by addition of the bromide of the corresponding base. F.p. and conductivity determinations showed that these substances are largely hydrolysed in aqueous solutions according to the equation  $\text{R}_5[\text{MoOX}_5] + 5\text{H}_2\text{O} = \text{MoO}_2(\text{OH}) \cdot 3\text{H}_2\text{O} + 2\text{RX} + 3\text{HX}$ . The b. p. in alcoholic solution indicated dissociation into three ions, in accordance with the co-ordination formula given. The existence of the compounds  $\text{Li}[\text{MoOBr}_4 \cdot \text{H}_2\text{O}] \cdot 3\text{H}_2\text{O}$  and  $\text{C}_5\text{H}_5\text{N}[\text{MoOBr}_4]$  has been confirmed and the compound  $\text{C}_9\text{H}_5\text{N}[\text{MoOBr}_4]$  has been prepared. In certain cases intermediate salts of the type  $\text{R}[\text{MoO}_2\text{Br}_2 \cdot 2\text{H}_2\text{O}]$  have been isolated.

J. A. V. BUTLER.

**Chlorine hexoxide. H. J. SCHUMACHER and G. STIEGER** (Z. anorg. Chem., 1929, 184, 272—278; cf. Schumacher and Wagner, A., 1929, 1404; Bodenstein, Padelt, and Schumacher, *ibid.*, 1394; Bodenstein and Schumacher, *ibid.*, 1403).—Although chlorine hexoxide is an intermediate product of the action of light on chlorine dioxide or a mixture of chlorine and ozone, neither process furnishes a convenient method for its preparation. By the inter-



action of chlorine dioxide and ozone at the ordinary temperature it can be prepared easily in large quantities. Both gases should be diluted to avoid explosions. The hexoxide is condensed in the reaction vessel cooled with ice. Attempts to measure the vapour pressure of the purified product showed that it decomposed, slowly at the ordinary temperature, rapidly above 40°, into chlorine, oxygen, and chlorine dioxide. The vapour pressure is approximately 1 mm. at 20° and 5–10 mm. at 40°.

F. L. USHER.

**Action of a series of oxidising substances on manganous salts.** S. T. ORLOVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1185–1197).—The oxidising action of a number of substances on manganous sulphate is in the following order:  $\text{Br}_2 > \text{Na}_2\text{O}_2 > \text{H}_2\text{O}_2 > \text{K}_3\text{Fe}(\text{CN})_6 > \text{I}_2$  (prolonged action)  $> \text{AgNO}_3 > \text{Hg}(\text{NO}_3)_2 > \text{I}_2$  (short action)  $> \text{CuSO}_4 \cdot 5\text{H}_2\text{O} > \text{O}_2$  (atmospheric). In no case does the reaction of oxidation proceed to completion. Atmospheric oxygen, cupric salts, and iodine (short action) tend to give rise to tervalent manganese, whilst bromine, sodium peroxide and air, potassium ferrocyanide, iodine (prolonged action), and silver and mercuric nitrates tend rather to produce quadrivalent manganese dioxide hydrates.

R. TRUSZKOWSKI.

**Hydrated oxides. XVI. Active properties of hydrated oxides.** G. F. HÜTTIG and A. ZÖRNER (Z. anorg. Chem., 1929, 184, 180–192; cf. A., 1929, 510).—Previous work on this subject is summarised and discussed.

F. L. USHER.

**Complex antipyrine metal salts.** E. WILKE-DÖRFURT and H. G. MURECK (Z. anorg. Chem., 1929, 184, 121–134; cf. A., 1928, 494; 1929, 1250).—The preparation and properties of the following complex hexa-antipyrine metal salts are described; the solubilities are recorded: *ferric fluoborate*, m. p. 217–219°,  $d$  (all  $d^{20}$ ) 1.325; *aluminium fluoborate*, m. p. 116–120°,  $d$  1.303; *magnesium fluoborate*, m. p. 165–168°,  $d$  1.289; *calcium fluoborate*, m. p. 210°,  $d$  1.313; *strontium fluoborate*, m. p. 110–111°; *zinc fluoborate*, m. p. 70°,  $d$  1.352; *cadmium fluoborate*, m. p. 170–172°,  $d$  1.359; *manganese fluoborate*, m. p. 180–181°,  $d$  1.359; *ferrous fluoborate* decomp. 90°; *cobaltous fluoborate*, m. p. 170°,  $d$  1.335; *nickelous fluoborate*, m. p. 221–222°,  $d$  1.298; *lead fluoborate*, m. p. 112°,  $d$  1.475; *silver fluoborate*, m. p. 133–134°; *calcium permanganate*; *aluminium permanganate*; *calcium fluosulphonate*; *strontium fluosulphonate*, m. p. 178°; *cadmium fluosulphonate*,  $d$  1.387; *cobalt fluosulphonate*, m. p. 157° (decomp.),  $d$  1.433; *ferric fluosulphonate*,  $d$  1.367; *calcium thiocyanate*, decomp. 107°; *zinc thiocyanate*, m. p. 66°; *aluminium thiocyanate*, m. p. 103–105°; *ferric dichromate*, m. p. 197–198°; *chromic fluoborate*, m. p. 248–250°,  $d$  1.330; *chromic permanganate*; *chromic fluosulphonate*, m. p. 186–187°; *chromic thiocyanate*; *chromic dichromate*; *chromic chlorate*, explodes at 145°; *chromic thiosulphate*; *chromic ferrocyanide*; *chromic ferricyanide*; *chromic picrate*. The extent to which the properties of the salts are respectively due to the anion and to the central atom combined with the antipyrine in the cation is examined. The perchlorate anion confers the greatest stability. The greatest

variety of compounds is produced when tervalent chromium is the central atom in the cation. The antipyrine fluoborates with bivalent central atoms are isomorphous, as are also the complex chromium salts. *Penta-antipyrinecuprous fluoborate*, m. p. 70–75°,  $d$  1.365, also belongs to this series. All the salts described have similar crystalline forms and otherwise resemble one another.

F. L. USHER.

**Products obtained by the thermal decomposition of the hydrates of ferric chloride and nitrate.** N. PARRAVANO and G. MALQUORI (Anal. Fis. Quim., 1929, 27, 454–459).—Previous work is reviewed. The variations of the apparent density  $d$  of compressed cylinders of ferric oxide obtained by treating the hydrated nitrate at 300° have been determined as a function of temperature and of the duration of heating. At temperatures up to 700°  $d$  becomes approximately constant after about 2 hrs., but at higher temperatures there is a slow increase of  $d$  even after 40 hrs.' heating, although the curves indicate an approach to the limiting value of the true density of the oxide. The results indicate that aggregation of the particles takes place at much lower temperatures than those previously assumed. X-Ray examination confirms the view that the difference between the aggregated and non-aggregated oxide is solely one of particle size.

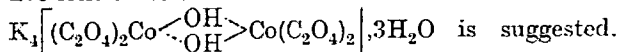
H. F. GILLBE.

**Composition of potassium sodium cobaltinitrite.** L. BONNEAU (Bull. Soc. chim., 1929, [iv], 45, 798–808).—The cobaltinitrite was prepared (i) by adding 10 c.c. of a 0.25*N*-solution of potassium chloride to a boiling mixture of 10 c.c. of a solution containing 292 g. of cobalt nitrate and 187.5 c.c. of acetic acid per litre with 10 c.c. of a 10.92*N*-solution of sodium nitrite to which varying amounts of a solution of sodium chloride containing 280 g. per litre were added; (ii) with larger amounts of potassium chloride and no sodium chloride; and (iii) by adding the potassium chloride solution to one of pure sodium cobaltinitrite. The precipitate was washed successively in 30% sodium acetate solution, water, and alcohol, and dried with ether. (It is appreciably soluble in water, and 10% acetic acid is recommended with a prescribed method of washing.) Cobalt was weighed as sulphate, potassium as perchlorate, and sodium as uranyl zinc sodium acetate. (The factor for the last-named is more accurately 0.01466.) The precipitate obtained when the ratio Na : K exceeds 22 : 1 (best between 25 : 1 and 100 : 1) has a constant composition,  $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ , agreeing with the results of Adie and Wood (J.C.S., 1900, 77, 1076), but differing from those of Vürtheim (A., 1921, ii, 710), whose product was probably partly decomposed in washing. With smaller ratios of Na : K the content of sodium in the precipitate steadily decreases, tending towards  $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot n\text{H}_2\text{O}$ . The product obtained by method (iii) is of less regular composition. Heating increases the proportion of potassium.

C. A. SILBERRAD.

**Polynuclear cobalt complexes containing cobalt in the anion.** E. G. V. PERCIVAL and W. WARDLAW (J.C.S., 1929, 2628–2633).—Potassium cobalt oxyoxalate,  $\text{K}_4[\text{Co}_2\text{O}(\text{C}_2\text{O}_4)_4] \cdot 4\text{H}_2\text{O}$  (cf. Durrant, *ibid.*, 1905, 87, 1781), has been prepared by the

action of hydrogen peroxide on a solution containing cobalt oxalate and potassium oxalate. *Barium, calcium, strontium, lead, and silver* salts were obtained by double decomposition. Cryoscopic and conductivity measurements indicate that the salt yields five ions on solution and the structure



*Potassium cobalt oxymalonate,*

$K_2[Co_2O(C_3H_2O_4)_4] \cdot 6H_2O$ , obtained in the same way, has similar properties. Its solution is readily decomposed on warming. J. A. V. BUTLER.

**Action of potassium oxalate on potassium rhodochloride.** M. DELÉPINE (Anal. Fis. Quím., 1929, 27, 485—493).—The *cis*-form of the salt

$K_3[RhCl_2(C_2O_4)_2]$ , prepared by recrystallisation of the product obtained by heating for 0.5 hr. potassium oxalate with a solution of potassium aquopentachlororuthenate, is dark brown and crystallises with 1 mol. of water, which is not lost at 100°. The *trans*-modification, produced by boiling the *cis*-form with a dilute solution of potassium chloride, resembles the corresponding iridium compound, and forms yellow needles containing 4 mols. of water of crystallisation which are readily lost at 100°. The trioxalate  $K_3[Rh(C_2O_4)_3] \cdot 4.5H_2O$ , obtained by boiling a solution of 3 mols. of potassium oxalate with 1 mol. of potassium aquopentachlororuthenate or hexachlororuthenate, does not become anhydrous below 190°, and readily forms the double salt

$2K_3[Rh(C_2O_4)_3] \cdot KCl \cdot 8H_2O$ . By treatment of the trioxalate solution with silver nitrate solution the salt  $KAg_3[Rh(C_2O_4)_2] \cdot 6H_2O$  separates as orange needles analogous to the iridium and cobalt compounds.

H. F. GILLBE.

**Simplified comparison electrode for potentiometric titrations.** W. ACKERMANN (Z. anal. Chem., 1929, 79, 8—10).—A narrow tube carrying a platinum wire electrode is fused on to the delivery tube of the titration burette, and serves as comparison electrode, the titration liquid itself forming the comparison solution. H. F. HARWOOD.

**Analytical applications of oxidation and reduction potentials.** A. RÍUS Y MIRÓ (Anal. Fis. Quím., 1929, 27, 605—623).—Acid-alkali potentiometric titrations may be conducted with great accuracy by employing an inert metal as indicator electrode and adding to the liquid an oxidising or reducing substance such as potassium dichromate or oxalic acid. H. F. GILLBE.

**Use of antimony electrodes in the differential titration of aqueous and alcoholic solutions.** I. I. SHUKOV and V. M. GORTIKOV (Z. Elektrochem., 1929, 35, 853—860).—In the differential electrometric titration of acid and alkali, the antimony electrode (A., 1929, 899) has the advantages of not requiring the presence of such substances as quinhydrone and of giving accurate results in alkaline solutions. Small amounts of carbonate in hydroxide solutions are clearly indicated on the titration curve, and the antimony electrode is particularly suited for the titration of carbonic acid in water. Titration of acid and alkali can also be carried out satisfactorily in alcoholic solution. R. CUTHILL.

**$p_H$  measurement with the glass electrode and oscillating-valve potentiometer.** L. W. ELDER, jun. (J. Amer. Chem. Soc., 1929, 51, 3266—3272).—The oscillating-valve potentiometer previously described has been simplified and rendered more sensitive (Elder and Wright, A., 1929, 284). Comparative measurements of the potentials of high-resistance glass cells by means of the improved potentiometer and the Lindemann electrode show that the electrode readings were lower than the others by an amount which is constant between  $p_H$  1 and 10 ("free grid potential effect"). This difference between the two measurements is proportional to the resistance of the glass cell as a whole. The observed difference for any one glass electrode being constant, therefore, no error is introduced by measuring  $p_H$  values with the oscillating-valve potentiometer provided the electrode is checked against at least one standard buffer. The asymmetry potentials of electrodes of the bulb type (Hughes, A., 1928, 370) in *N*-hydrochloric acid are constant for a given sample of glass. The effect of 20 hrs.' anodic polarisation at 110 volts disappears after 3 days; the effects of cathodic polarisation are detectable for 9 days. The effect of annealing on the mechanical strains in the glass is overshadowed by some other effect, for annealing causes a decrease in potential which disappears only very slowly. The asymmetry potentials of electrodes prepared by MacInnes and Dole's method are uniformly low, irrespective of the species of glass. The asymmetric potential of a glass electrode is specific and independent of age and resistance for a given species of glass and the measurement of  $p_H$  by means of such electrodes is therefore suggested. S. K. TWEEDY.

**$p_H$  of the colour change of some vegetable indicators.** A. DEL CAMPO, A. RANCAÑO, and G. SUBERO (Anal. Fis. Quím., 1929, 27, 587—594).—The following values of the  $p_H$  at which a marked colour change occurs on addition of alkali to acidified solutions of various vegetable indicators have been determined: *Iris germanica* 7.92, *Geum urbanum* 7.22, *Papaver somniferum* (red flowers) 8.37, and for a mixture of the latter two 8.15. The colour change in each case is from red to green except for the fourth, which is from colourless to green. H. F. GILLBE.

**Determination of chlorine ion in organic liquids.** R. CALATRONI and E. TSCHOPP (Anal. Assoc. Quim. Argentina, 1929, 17, 65—70).—See A., 1929, 962.

**Dichlorofluorescein as an adsorption indicator for the argentometric titration of chlorides.** I. M. KOLTHOFF, W. M. LAUER, and C. J. SUNDE (J. Amer. Chem. Soc., 1929, 51, 3273—3277; A., 1927, 434).—Experiments which show that dichlorofluorescein is a suitable indicator for the argentometric titration of chlorides in very dilute and in weakly acidic solutions are recorded.

S. K. TWEEDY.

**Argentometric studies. II. Determination of halides in presence of sulphites.** O. TOMÍČEK and A. JÁNSKÝ (Coll. Czech. Chem. Comm., 1929, 1, 582—584).—Accurate results are obtained in the potentiometric titration of all halides in the presence of sulphites only in acidified solutions, preferably

about 0.1*N*-sulphurous acid. In solutions of hydrogen sulphites of  $p_H$  about 6.0 only the bromide and the iodide can be determined, whilst with solutions of normal sulphites ( $p_H$  about 8.0) only iodides can be accurately determined.

A. I. VOGEL.

**Determination of iodides and bromides in chlorides.** O. TOMČEK and A. JÁNSKÝ (Coll. Czech. Chem. Comm., 1929, 1, 585–605).—A review of the methods for the determination of iodides in the presence of bromides and chlorides and of bromides in the presence of chlorides is given and the accuracy of some of these has been confirmed. Traces of iodides can be determined directly by potentiometric (argentometric) titration in the presence of excess of chloride, a trace of bromide being necessary. Winkler's apparatus (A., 1916, ii, 109) for the determination of bromides in the presence of excess of chlorides has been improved.

A. I. VOGEL.

**[Detection of] fluorine in mineral waters.** J. C. GIL (Anal. Fis. Quím. [tecn.], 1929, 27, 141–143).—Traces of fluorine in water are detected by evaporation of 500 c.c. to small volume, treatment with barium chloride and acetic acid, and evaporation to dryness. After extraction with water the residue is treated with silica and concentrated sulphuric acid in a vessel above which a drop of water is suspended; after the silicon fluoride evolved has reacted with the water, one drop of barium chloride solution is added, and the mixture evaporated to dryness. On treatment with hydrochloric acid, characteristic crystals of barium fluosilicate may be observed microscopically.

H. F. GILLBE.

**Detection of fluorine in minerals and rocks.** H. LEITMEIER and F. FEIGL (Tsch. Min. Petr. Mitt., 1929, 40, 6–19).—(1) Alizarin method.—The reddish-violet colour given by a soluble zirconium salt with alizarinsulphonic acid is destroyed by fluorides, and in their presence the solution changes to yellow, that of the alizarinsulphonic acid (de Boer, A., 1926, 40). (2) Fluosilicate method.—The mineral mixed with quartz is treated with sulphuric acid and the silicon fluoride evolved collected in a drop of water; silica is then tested for by the benzidine method (this vol., 52).

L. J. SPENCER.

**Determination of fluorine and silica in glasses and enamels containing fluorine.** J. J. HOFFMAN and G. E. F. LUNDELL.—See B., 1929, 1015.

**Test for sulphide-sulphur.** F. FEIGL and H. LEITMEIER (Tsch. Min. Petr. Mitt., 1929, 40, 20–44).—A mixed solution of sodium azide and iodine in potassium iodide gives a vigorous evolution of nitrogen when in contact with sulphide or sulpharsenide minerals (A., 1928, 1106). A large number of minerals have been tested by this method, the liquid being applied to the powder, a fragment or crystal face, streak on a streak-plate, or in micro-sections.

L. J. SPENCER.

**Conductivity titration with visual observation: conductometric determination of sulphate in boiling aqueous solution.** G. JANDER (Z. angew. Chem., 1929, 42, 1037–1038).—Potentiometric and conductometric methods of titration are compared and contrasted, and a method is described whereby the use of a telephone in conductivity determinations

may be avoided. The usual bridge arrangement is used, but the current is rectified by a vacuum thermo-junction and is measured by a galvanometer. By plotting the galvanometer reading against the volume of titrating liquid, it is shown that the difficulty of determining the exact neutral point is obviated by extrapolation, so that the method is very rapid and simple. The method is illustrated by reference to determination of sulphate in conductivity water and in boiling ammonium sulphate solution by titration with barium acetate. It is essential that the reagents should be neutral, as slight acidity gives low values. The method is applicable to the determination of sulphate in potable water.

H. J. DOWDEN.

**Processes occurring in thiosulphate solutions on keeping.** F. L. HAHN and H. CLOS (Z. anal. Chem., 1929, 79, 11–26).—The turbidity of a freshly-prepared thiosulphate solution is not due to the decomposition of thiosulphate into sulphite and sulphur by the action of carbon dioxide, as has been generally supposed, but is caused by the invariable presence in the solid thiosulphate of small amounts of pentathionate. This latter salt rapidly decomposes in solution in the presence of thiosulphate, forming tetrathionate and sulphur. The alteration in titre of a thiosulphate solution on being kept is due to some or all of the following reactions taking place in it, depending on the conditions prevalent: (1)  $5S_2O_3^{2-} + 6H^+ \rightarrow 2S_3O_6^{2-} + 3H_2O$  and  $S_3O_6^{2-} \rightarrow S_4O_6^{2-} + S$ ; (2)  $4S_2O_3^{2-} + 4H^+ + O_2 = 2S_4O_6^{2-} + 2H_2O$ ; (3)  $S_2O_3^{2-} \rightarrow SO_3^{2-} + S$ , and  $SO_3^{2-} + S_4O_6^{2-} \rightarrow S_2O_3^{2-} + S_3O_6^{2-}$ ; (4)  $S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + 2H^+ + SO_4^{2-}$ . Reaction 2 is accelerated catalytically by traces of copper or iron salts, whilst 3 may occur spontaneously or as a result of bacterial action. The increase in titre often observed in an old thiosulphate solution is due to the re-formation of thiosulphate from tetra- and pentathionate, and not to any decomposition product of the thiosulphate itself. Reactions 1, 2, and 3 may be prevented by the addition to the thiosulphate solution of sufficient sodium hydroxide or carbonate to make the solution 0.01*N* in respect of this constituent; such a solution undergoes no change in titre during 3 months.

H. F. HARWOOD.

**Determination of nitric acid and nitrates by reduction with ferrous salts.** J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1929, 67, 8–12; Chem. Zentr., 1929, ii, 73).—With the apparatus employed carbon dioxide is generated in the reaction flask.

A. A. ELDRIDGE.

**Potentiometric determinations with ferricyanide in alkaline solution. II. Arsenic, antimony, tin, and thallium.** C. DEL FRESNO and L. VALDÉS (Anal. Fis. Quím., 1929, 27, 595–604).—Arsenious, antimonous, and stannous compounds in alkaline solution are oxidised quantitatively by ferricyanide, and the latter may be employed for their potentiometric determination. With tin the operation must be conducted in an atmosphere of nitrogen, whilst the titration of antimony and arsenic should be carried out at about 70°. The method when applied to thallium yields results which are about 1% too low.

H. F. GILLBE.

**Test for silicic acid.** F. FEIGL and H. LEITMEIER (Tsch. Min. Petr. Mitt., 1929, 40, 1—5).—The blowpipe test of a silica skeleton in a borax or microcosmic-salt bead is untrustworthy. A soluble silicate forms with ammonium molybdate a complex silicomolybdate, and this with a solution of benzidine in acetic acid and sodium acetate gives a blue coloration. The similar reaction given by molybdic acid is readily distinguished by the addition of oxalic acid, which decomposes the phosphomolybdate.

L. J. SPENCER.

**Analysis of chromiferous silicates.** E. DITTLER (Tsch. Min. Petr. Mitt., 1929, 40, 189—190).—The silicate is fused with sodium peroxide in a silver crucible and the acidified solution of the fused mass, after boiling and filtering, is treated with hydrogen peroxide in order completely to reduce the chromate to chromic ions. After separation of the silica, the sesquioxides are precipitated twice with ammonia and the precipitate is ignited in a current of hydrogen and again fused with sodium peroxide. The iron remains insoluble and the manganese is precipitated with hydrogen peroxide. Chromium is then determined volumetrically, and the aluminium by difference.

L. J. SPENCER.

**Titration of cyanides.** O. RÖER (Tids. Kjemi Berg., 1929, 9, 127—129).—A number of volumetric methods for the determination of cyanides with standardised silver or nickel solutions, together with Schulek's iodometric process (A., 1923, ii, 591), are discussed, and the advantages and disadvantages of each are noted.

H. F. HARWOOD.

**Determination of composition of argon-nitrogen mixtures.** H. FILIPPO (Chem. Weekblad, 1929, 26, 567—568).—An improved differential vapour-pressure method and apparatus are described.

S. I. LEVY.

**Determination of inert gas in mixtures by means of calcium as absorbent.** M. LEATHERMAN and E. P. BARTLETT.—See B., 1929, 999.

**Volumetric determination of potassium with sodium lead cobaltinitrite.** V. I. TOVARNITZKI and P. S. SERGEENKO (Zhur. Sakharoi Prom., 1928, 2, 228—236).—The sodium lead cobaltinitrite reagent is prepared by dissolving sodium nitrite (22 g.), cobalt nitrate (3 g.), and lead nitrate (5 g.) in a little hot water, diluting to 80 c.c., adding 5 c.c. of acetic acid, filtering when precipitation is complete, and protecting the filtrate from light. The solution under examination (50 c.c.), containing 10—20 mg. of potassium, is treated with 2—4 c.c. of the reagent; after stirring for 20 min. an aqueous suspension of barium sulphate is added until the precipitate is light yellow. The precipitate is collected, washed with 200—250 c.c. of water, returned to the beaker, treated with 0.1N-permanganate (50 c.c.) and sulphuric acid (1 : 3, 20 c.c.), diluted to 300—400 c.c., and heated at 100° for 30 min. Excess of 0.1N-sodium oxalate is added, and the solution titrated with permanganate. The factor is 0.0006521. The maximum error is 1—2%. Ammonium ions must be removed.

CHEMICAL ABSTRACTS.

**Zirconium.** V. Detection of traces of potassium in presence of zirconium. R. D. REED and

J. R. WITHROW (J. Amer. Chem. Soc., 1929, 51, 3238—3241).—Unless excess of acetic acid is present, a phosphoric acid solution neutralised by sodium hydroxide yields with sodium cobaltinitrite solution a flaky brown precipitate. Phosphates, therefore, are not suitable for removing zirconium prior to testing for potassium with sodium cobaltinitrite. Ammonia solution is suitable for this purpose, but it is preferable to remove the zirconium as a complex ion by adding tartaric acid, the acidity of the solution being controlled by means of sodium hydroxide and acetic acid.

S. K. TWEEDY.

**Electrochemical determination of cations in salt solutions.** A. BELÁK and Z. VON ALFÖLDY (Biochem. Z., 1929, 214, 110—118).—A method and the apparatus required for the determination of sodium, potassium, and calcium in solutions are described. The metals on electrolysis migrate to a mercury electrode and form amalgams, which are kept in contact with water, and the corresponding hydroxides are titrated. Sodium and potassium are determined with an error less than 1%. With calcium greater difficulty was experienced in that the metal did not form an amalgam so readily and tended to give a film of nitride on the surface of the mercury. By excluding air from the electrode calcium was also determined with an error of 0.6%.

P. W. CLUTTERBUCK.

**Gravimetric determination of sodium by the uranyl zinc acetate method.** II. Application in the presence of rubidium, caesium, potassium, lithium, phosphate, or arsenate. H. H. BARBER and I. M. KOLTHOFF (J. Amer. Chem. Soc., 1929, 51, 3233—3237; cf. A., 1928, 859).—The method previously described may be used in presence of rubidium and caesium. Potassium, if present, must be removed to a large extent, e.g., by precipitation with a solution of ammonium perchlorate in 72% alcohol; as little as 0.005% of sodium can then be detected in presence of potassium. Lithium must be quantitatively removed, e.g., by precipitation in presence of alcohol with ammoniacal ammonium fluoride solution, the excess of fluoride added being removed before precipitation of the sodium. Phosphate and arsenate ions must be removed if present; precipitation by means of magnesia mixture is recommended.

S. K. TWEEDY.

**Determination of calcium.** G. F. J. M. BÄR (Endokrinol., 1928, 1, 90—99; Chem. Zentr., 1929, ii, 198).—Certain modifications in Clark's and de Waard's methods are proposed. The revised procedures give practically identical values, the error being up to 3%.

A. A. ELDRIDGE.

**Determination of calcium oxide in quicklime.** H. A. J. PIETERS and J. H. VAN DER HEIJDEN.—See B., 1929, 977.

**Separation of calcium and magnesium by the oxalate method.** Z. HERRMANN (Z. anorg. Chem., 1929, 184, 289—292; cf. A., 1929, 1159).—X-Ray photographs of calcium oxalate precipitated in the presence of varying proportions of magnesium show the presence of one or both of the salts, but give no indication of the formation either of a compound or of mixed crystals. The co-precipitation of mag-

nesium oxalate with calcium oxalate is, therefore attributed to adsorption. The period of induction occasionally observed in the precipitation of calcium oxalate increases with the degree of supersaturation of the magnesium oxalate. The results are discussed theoretically.

F. L. USHER.

**Sodium tungstate as microchemical reagent for barium.** G. DENIGÈS (Bull. Soc. Pharm. Bordeaux, 1929, 67, 4—7; Chem. Zentr., 1929, ii, 74).—With sodium tungstate barium ions (0.5 g. per litre, or 0.005 mg.) give characteristic octahedra. Calcium and strontium are precipitated in spherocrystals from solutions at greater concentration. Barium sulphate is first reduced on a platinum wire in the blue cone of a Bunsen flame.

A. A. ELDRIDGE.

**Volumetric determination of barium and sulphates.** R. STREBINGER and L. VON ZOMBORY (Z. anal. Chem., 1929, 79, 1—8).—Barium chloride can be accurately titrated with 0.25*N*-sulphuric acid or alkali sulphate in either neutral or acid solutions, using 5—8 drops of a freshly-made 0.2% solution of sodium rhodizonate as indicator; the colour changes at the end-point from red to yellow in neutral solutions, and from red to colourless in acid ones. Direct titration of a sulphate with barium chloride in presence of the above indicator is not possible, but the determination can be carried out by addition of a known volume of standard barium chloride to the sulphate solution, and titration of the excess barium as above.

H. F. HARWOOD.

**Studies on chemical reactions by potentiometric methods. I. Reactions between potassium ferrocyanide and zinc sulphate which have to be taken into consideration in volumetric analysis.** S. SAITÔ (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 921—951).—Observations have been made of the potential change during the titration of potassium ferrocyanide and zinc sulphate in solutions of various acids at various concentrations, both in the usual and the reverse directions. Two complex salts are formed,  $\text{Zn}_2\text{Fe}(\text{CN})_6$  and  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ . The formation of the former proceeds more quickly than that of the latter, which is irreversible and depends largely on the nature of the acid present. When the readings of potential are taken a definite short time after the addition of the solution, in 1—2*N*-acetic acid only the end-point of the formation of  $\text{Zn}_2\text{Fe}(\text{CN})_6$  is observed. If the solution is about 0.003*N* in hydrochloric or sulphuric acid, the end-points of the formation of both complex salts are seen, the latter being the more distinct, and if the acid is 0.1—2*N* only the end-point of the formation of the double complex salt is found, as is also the case if zinc sulphate is titrated into the potassium ferrocyanide solution.

C. W. GIBBY.

**Electrolytic separation of lead and bismuth with controlled potential.** E. M. COLLIN (Analyst, 1929, 54, 654—655).—Three c.c. of nitric acid and 4 or 5 drops of a 50% solution of hydrazine hydrate are added to the solution of lead and bismuth nitrates in a volume of about 60 c.c. Bismuth is then electrolytically deposited at 80—85° according to Sand's method (J.C.S., 1907, 91, 373), but with a 0.01*N*-nitric

acid—quinhydrone auxiliary electrode with an initial current of 1.3 amp. at a cathode potential of —0.45 volt (referred to the quinhydrone electrode), which at the end of the electrolysis is practically zero at a potential of —0.6 volt. About 50% sodium hydroxide solution is then added to the hot electrolyte until the precipitated lead hydroxide is just redissolved. Sodium peroxide is added in small quantities and the solution heated until all brown fumes and precipitate have cleared. After acidification with concentrated nitric acid (20 c.c. in excess) the solution is electrolysed with a current of 6—6.5 amp. The apparatus used is that of Sand (A., 1929, 672). The factors for calculation of  $\text{PbO}_2$  to Pb were determined experimentally as follows: up to 0.1 g., 0.8660; from 0.1 to 0.4 g., 0.8635; from 0.4 to 0.5 g. of lead, 0.8605.

D. G. HEWER.

**Colorimetric determination of minute amounts of copper.** T. CALLAN and J. A. R. HENDERSON (Analyst, 1929, 54, 650—653).—Sodium diethyldithiocarbamate,  $\text{NET}_2\text{CSNa}$ , gives a brown precipitate of the normal copper salt of diethyldithiocarbamic acid with solutions containing copper. It is a more sensitive reagent than potassium ferrocyanide or sodium ethyl xanthate and gives a good gradation in depth of colour with increasing amounts of copper. Iron, which gives a brown colour, and lead, which gives a white turbidity, must be removed from the solution. Zinc gives a white turbidity, but if not more than 0.1 g. per 100 c.c. is present the addition of 2—5 c.c. of ammonia per 100 c.c. prevents interference. Not more than 0.00001 g. of copper per 100 c.c. should be present in the solution to be tested. A suitable aliquot portion of copper solution, freed if necessary from other metals, is diluted in a Nessler cylinder, and made slightly ammoniacal; 10 c.c. of a 0.1% solution of reagent are added, and the whole is diluted to 100 c.c. and mixed. Standard comparison solutions are made with suitable volumes of copper solution containing 0.00001 g. of copper per c.c. The brown colour is stable for 1 hr. and the reagent has been successfully used for determining copper in dyes and rubber-proofed fabrics.

D. G. HEWER.

**Nissenson and Neumann's method for the determination of copper [by boiling with a thio-sulphate].** J. MAJDEL (Z. anal. Chem., 1929, 79, 38—44; cf. A., 1896, ii, 450).—The above method has been critically examined, and the necessary working conditions have been determined. The solution, containing from 25 to 40 c.c. of concentrated sulphuric acid and not more than 0.4—0.5 g. of copper oxide, is diluted to 150 c.c. and heated to boiling. A boiling solution of 5 g. of sodium thiosulphate in 50 c.c. of water is added, and the precipitate collected, washed, dried, and ignited with the filter over the blast. After cooling, the lumps are crushed with a glass rod and the precipitate is reignited for a further 15 min., and finally weighed as oxide; the results agree to 0.05% with those obtained by the electrolytic method. Bismuth, lead, and silver must be absent, and only small amounts of antimony and tin may be present in the solution, but the method affords a separation from all other metals. Free nitric and hydrochloric acids interfere, and must be removed. H. F. HARWOOD.

**Adaptation of the diphenylcarbazine test for mercury to the scheme of qualitative analysis.** A. W. SCOTT (J. Amer. Chem. Soc., 1929, 51, 3351—3352).—To the concentrated acidic solution of the mercury precipitate a few drops of fairly fresh saturated alcoholic solution of diphenylcarbazine and a large excess of solid sodium carbonate (not hydrogen carbonate or acetate) are added. A blue to pink tinge is produced. If the mercury precipitate is dissolved in aqua regia the solution must not be kept very long before the test is carried out.

S. K. TWEEDY.

**Determination of mercurous, bromine, or chlorine ions by Fajans' method.** L. VON ZOMBORY (Z. anorg. Chem., 1929, 184, 237—240; cf. A., 1928, 265).—When potassium bromide or potassium chloride, to which bromophenol-blue has been added as indicator, is titrated with mercurous nitrate solution, the point of equivalence is shown by the colour change from yellow to lilac. Bromocresol-purple acts similarly. In each case the end-point is sharper with bromide than with chloride.

F. L. USHER.

**Determination of manganese in steel and iron by the persulphate-arsenite method.** A. A. BRIGHT and C. P. LABRABEE.—See B., 1929, 1017.

**Iodometric determination of ferric iron and copper.** F. L. HAHN and H. CLOS (Z. anal. Chem., 1929, 79, 26—37).—The above determinations have been studied, and the following procedure is recommended: 10 c.c. of the concentrated iron or copper solution are acidified with 0.5—1 c.c. of 2*N*-acetic acid, potassium iodide and 20 c.c. of benzene are added, and the liquid is at once titrated in a stoppered flask with thiosulphate, with vigorous shaking. If iron is being determined, a little cuprous iodide should be added to the solution as a catalyst. Under these conditions a titration can be carried out in 7—8 min., and no after-blueing results. The presence of mineral acids at a concentration greater than 0.04*N* renders the end-point uncertain. Iron and copper when present together in a solution may be simultaneously determined by the above method, and in a second portion of the solution the copper alone can be determined by repeating the titration after the addition of phosphoric acid and sodium phosphate.

H. F. HARWOOD.

**Determination of titanium and iron in rocks.** H. HUEBER (Tsch. Min. Petr. Mitt., 1929, 40, 192—195).—In the sulphuric acid solution of the sesquioxides the titanium is determined colorimetrically with hydrogen peroxide. The solution is then boiled until the orange-yellow colour disappears and the iron is precipitated with ammonia; the iron is dissolved in dilute hydrochloric acid and determined volumetrically.

L. J. SPENCER.

**Determination of thorium in mud from the cold springs of La Toja, Pontevedra.** F. DIAZ DE RADA (Anal. Fis. Quím., 1929, 27, 631—636).—The co-existence of thorium and radium in the mud from La Toja is indicated by the form of the decay curves; practically all the thorium is present in the fraction soluble in hydrochloric acid. By passing a current of gas at a uniform rate through the solution and

comparison of the rate of discharge of an electro-scope with the rate when a solution of known thorium content is employed, the mud is found to contain thorium and its products prior to the emanation stage in quantity corresponding with about 0.25% of thorium oxide.

H. F. GILLBE.

**Drop method of detection of vanadium and tungsten.** N. A. TANANAEV and G. A. PANTCHENKO (J. Russ. Phys. Chem. Soc., 1929, 61, 1051—1054).—The solution under examination is oxidised by concentrated nitric acid, and a drop is placed on a filter-paper previously wetted with aniline hydrochloride, when a greenish-blue ring forms in the presence of vanadium. This reaction indicates the presence of vanadium at limiting concentrations of not less than 0.3 mg. per c.c. Cations do not interfere with this test, which cannot, however, be made in the presence of chromate, chlorate, hypochlorite, and permanganate ions; should these be present, the solution should first be boiled with concentrated hydrochloric acid. The following method can be used for the detection of tungsten. A drop of solution is placed on a filter-paper wetted with concentrated hydrochloric acid, when a yellow stain due to tungstic acid appears. This stain assumes an intense blue colour on the addition of ammonium thiocyanate and stannous chloride, and this coloration is intensified by the addition of concentrated hydrochloric acid. Molybdenum under the above conditions gives an intense purple stain, which is, however, discharged on further addition of hydrochloric acid. The above reaction is sensitive to not less than 0.004 mg. of tungsten in 0.01 c.c. of solution. Other substances do not interfere.

R. TRUSZKOWSKI.

**Separation of elements of the platinum group and their allies.** I. WADA and S. SAITO (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 749—794).—Metals precipitated by hydrogen sulphide from acid solutions may be divided into two groups, of which the first includes antimony, bismuth, cadmium, copper, gold, lead, mercury, palladium, and tellurium, which may be precipitated from cold slightly acid solutions, and the second, iridium, rhodium, and ruthenium, which may be precipitated from hot and more strongly acid solutions; molybdenum and platinum share the properties of both classes. Conditions of precipitation of the two groups are described together with the method of separation of the individual metals.

H. F. GILLBE.

**[Apparatus for] gas analysis.** E. OTT.—See B., 1929, 999.

**Instrument for colorimetric analysis.** F. ANSELM (Chem. Fabr., 1929, 504—505).—An improved form of Dubosecq colorimeter, in which the alteration in depth of the liquid column is read on a scale engraved on the circumference of the wheel operating the sliding support, is described. A difference of 0.1 mm. in the level of the liquid can thus be easily noted.

H. F. HARWOOD.

**Thermo-regulator.** S. C. COLLINS (J. Physical Chem., 1929, 33, 1850).—An improvement of the model previously described (A., 1927, 849).

L. S. THEOBALD.



**Shape of porcelain evaporating basins, casseroles, and crucibles.** W. VOLKMANN (Chem. Fabr., 1929, 408—409).—Suggestions are made for standardising the shape and relative sizes of a series of porcelain dishes, casseroles, or crucibles. For ordinary evaporating dishes the ratios of the diameters of a series are obtained by drawing lines parallel to the diameter ( $D$ ) of a semicircle at distances apart equal to one tenth the radius; the height ( $H$ ) of the dish is then  $0.4D$  when  $D$  is less than, and  $0.3D$  when  $D$  is greater than, 120 mm. For flat-bottomed dishes  $H=0.25D$  and the ratio of the upper diameter to the lower is  $1:0.866$ , for casseroles  $H=9D/16$  and for crucibles  $H=5D/4$  or  $3D/4$ . A table is given showing the dimensions and capacity of series of dishes and crucibles made in accordance with this scheme.

A. R. POWELL.

**Trap for carrying out reactions in an inert atmosphere.** H. GILMAN and A. P. HEWLETT (Rec. trav. chim., 1929, 48, 1124—1128).—A simple trap, consisting essentially of two bottles connected with a wide syphon tube and containing neutral petroleum of high b. p., for carrying out reactions such as the preparation of Grignard reagents in an inert atmosphere is fully described. Changes in pressure in the reaction vessel due to temperature changes cause siphoning of the hydrocarbon from one bottle into the other so that the reaction mixture is always in contact with the inert gas (nitrogen) with which the apparatus is originally filled.

J. W. BAKER.

**Apparatus for testing Dühring's law for corresponding b. p.** E. F. LINHORST (J. Amer. Chem. Soc., 1929, 51, 3262—3265).—The liquid and reference substance (water) are respectively boiled in vessels fitted with thermometers and provided with reflux condensers which are in communication with each other at the top and with a pump. The temperatures of the vapours of the liquids are measured for varying pressures produced by the pump. By means of this apparatus the law was found to hold very well for alcohol, but not so well for benzene.

S. K. TWEEDY.

**Laboratory vacuum regulator.** W. E. KUENTZEL (J. Amer. Chem. Soc., 1929, 51, 3347—3349).—An improvement of a method previously described (Miller and McKinney, A., 1928, 729) for maintaining a constant pressure in the vapour baths of thermostats heated by boiling liquids. An electric relay, controlled by a mercury column, is used to actuate a stop-cock in the atmospheric lead connected to the vapour bath.

S. K. TWEEDY.

**Automatic cut-off device for a gas-heated laboratory mercury still.** W. E. KUENTZEL (J. Amer. Chem. Soc., 1929, 51, 3349—3351).—The gas supply to the ring burner of a Dennis mercury still is controlled by the height of the mercury column in the still.

S. K. TWEEDY.

**Calorimeter suitable for determining heats of dissolution, with an application to worked and annealed metals.** C. J. SMITH (Proc. Roy. Soc., 1929, A, 125, 619—629).—During the process of cold-working a large part of the work done is converted into heat, but the change in properties of the metal indicates that its potential energy has been increased.

This increase in the potential energy has been measured by determining the difference in the heats of dissolution of the cold-worked and fully annealed metals dissolved in a suitable solvent. The method has the disadvantage that the heat of dissolution is large compared with the differences of energy to be measured, so that the calorimetric method employed must be a delicate one, but this is compensated by its freedom from large thermal losses. Full details are given of a calorimeter suitable for such measurements, based on the continuous-flow principle originally due to Callendar. The most suitable solvent is a concentrated solution of bromine in potassium bromide, and the methods used to overcome the difficulties involved in manipulating such a dissolution are described. The results of measurements with annealed and hard-drawn copper, brass, and zinc indicate that the potential energy stored in cold-working amounts, for the metals examined, only to about 1% of the heat of dissolution. The experimental error is considered to be about 0.3%.

L. L. BIRCUMSHAW.

**Robust microbalance of high sensitivity, suitable for weighing sorbed fibres.** J. W. MCBAIN and H. G. TANNER (Proc. Roy. Soc., 1929, A, 125, 579—586).—Details are given of the construction of a robust and compact fused quartz microbalance of the beam type, sensitive to  $4 \times 10^{-9}$  g. and capable of weighing at least 0.3 g. The balance rests on two carborundum crystal points attached to the fused quartz beam by means of a pyrex joint. The magnetic zero-point adjustment, differing essentially from that proposed by Stock and Ritter (A., 1926, 669), consists of a piece of soft iron wire sealed into a fused quartz tube attached vertically to the centre of the beam, and a horizontal coil placed above and a little to one side of this vertical pin. The inclination of the iron pin towards the centre of the coil, caused by passing an alternating current (60 cycles) through the coil, is proportional to the current. The balance is enclosed in a horizontal glass tube so that it may be used over a wide range of temperature and pressure, including the conditions necessary for freeing from sorbed material the surfaces to be weighed. The use of the balance is illustrated by an account of preliminary measurements of the adsorption of toluene on platinum foil. The results obtained are several times higher than that corresponding with a unimolecular layer on a true plane surface, but this is partly explained by the fact that the platinum employed appeared pitted and scratched when viewed under the microscope. A conception is advanced which would explain higher values of adsorption without reference to the classical assumption of a thick compressed film, and providing an alternative to the hypothesis of multimolecular layers built up by superposition of unimolecular layers.

L. L. BIRCUMSHAW.

**Meniscus corrections involved in the calibration of graduated tubes.** A. MORE (Analyst, 1929, 54, 630—633).—The calibration of graduated tubes involving the double meniscus correction involves difficulties owing to the material differences in published figures. Mercury is not regarded as a suitable calibrating liquid owing to the surface tension

being liable to serious alteration by traces of impurities, the variation in the angle of incidence of the mercury surface and walls of the tube, and the possibility of small air pockets between the mercury and glass at the angular corners at the bottom of sediment tubes. The values of the meniscus corrections for water at 20° in clean glass tubes of circular cross-section for various diameters, interpolated from data in the International Critical Tables, Vol. I, 73, which are derived from theoretical considerations by Bashforth and Adams ("Capillary Action"), are tabulated, together with Treadwell and Hall's, Sutton's, and Winkler's figures, but the most trustworthy values are those of Bashforth and Adams.

D. G. HEWER.

**Liquid air cryostat for temperatures below the triple point of oxygen.** Y. SUGA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 896—899).—Hydrogen is adsorbed by coconut charcoal previously cooled by liquid air boiling under reduced pressure. By drawing the hydrogen out the temperature can be reduced to  $-230^{\circ}$ , and by controlling the rate of withdrawal it can be maintained constant to less than  $0.1^{\circ}$ . The heat of adsorption of hydrogen by coconut charcoal has been measured at  $183^{\circ}$ . The cooling effect of the charcoal at about  $-200^{\circ}$  is 9 g.-cal. per g.

C. W. GIBBY.

**Two hot-wire viscosimeters.** E. G. RICHARDSON (J. Sci. Instr., 1929, 6, 337—343).—The distribution of velocity across a liquid flowing in a cylindrical tube or between two concentric cylinders, one of which is rotating, can be investigated by means of the cooling of an electrically heated wire. A correction for the proximity of solid surfaces, which cause the apparent velocity to be greater than the actual, is based on similar measurements in air.

C. W. GIBBY.

**Universal X-ray photogoniometer. IV.** J. D. BERNAL (J. Sci. Instr., 1929, 6, 343—353).—Experimental details for the adjustment of the instrument and the mounting of crystals are given.

C. W. GIBBY.

**Electrolytic preparation of photo-cells and their application.** L. MÁRTON and E. ROSTÁS (Z.

tech. Phys., 1929, 10, 52—57; Chem. Zentr., 1929, ii, 81).—The preparation of sodium cells having a sensitivity of  $10^{-10}$  amp. per metre-candle is described. The sodium content of the glass renders the method unsuitable for the technical production of potassium cells.

A. A. ELDRIDGE.

**Ring methods for surface tension measurements.** N. E. DORSEY (Science, 1929, 69, 187—188).—The two methods of using the Du Noüy tensiometer for the determination of surface tension are discussed.

L. S. THEOBALD.

**Ebullioscopic apparatus for the study of mixtures of liquids.** W. SWIENTOSLAWSKI (Anal. Fís. Quím., 1929, 27, 439—446).—An apparatus for determination of the b. p. of mixtures of liquids, especially of those containing a large proportion of the more volatile constituent, is described; errors due to partial distillation of the latter while running back from the condenser are largely eliminated.

H. F. GILLBE.

**Simple apparatus for micro-sublimation under reduced pressure.** M. WAGENAAR (Z. anal. Chem., 1929, 79, 44—46).—The apparatus previously described (A., 1927, 128) has now been modified so as to permit of the measurement of temperature and pressure during a sublimation.

H. F. HARWOOD.

**Preparation of litmus paper.** G. KOGAN (Pharm. Zentr., 1929, 70, 725—727).—The precautions necessary in the preparation of a sensitive extract are described.

S. I. LEVY.

**Nomogram for converting observed volumes of gas to normal temperature and pressure.** J. H. COSTE (Analyst, 1929, 54, 656—657).—Four graduated lines,  $P$ ,  $t$ ,  $V_{pt}$  (observed volume), and  $V_{NTP}$  (on which the corrected volume is read), represent the logarithms of the natural numbers inscribed on them, and are placed at appropriate distances apart. The line joining the points on  $P$  and  $t$  is subtended to cut a vertical line  $P/t$  at a point which is then joined to the observed volume point on  $V_{pt}$ , thereby crossing  $V_{NTP}$  to give the corrected volume. Provision is made for correction if the gas is wet.

D. G. HEWER.

## Geochemistry.

**Effect of concentration of sodium chloride on certain biochemical processes in limans.** A. SASLAVSKY and S. CHAIT (Zentr. Bakt. Par., 1929, II, 77, 18—21; Chem. Zentr., 1929, i, 3110).—The reduction observed with sulphur bacteria in dried liman slime depends on the concentration of sodium chloride in the brine.

A. A. ELDRIDGE.

**Siliceous sands of Monte Soratte.** A. MAFFEI (Annali Chim. Appl., 1929, 19, 421—432).—The constitution and geological genesis of the pliocene basin to the north-west of San Oreste, on the slopes of Monte Soratte, have been studied. Sands from this basin contain up to 98% of silica and should be of great value in the glass and ceramic industries.

T. H. POPE.

**Heat of radiation of some radioactive minerals.** A. DORABIALSKA (Rocz. Chem., 1929, 9, 615—622).—The heats of radiation in g.-cal./g. hr. of the following minerals have been measured using Swientoslawski and Dorabialska's adiabatic microcalorimeter (A., 1927, 1163): uraninite  $5.7 \times 10^{-5}$ , johannite  $3.3 \times 10^{-5}$ , thorianite  $7.5 \times 10^{-5}$ , Arendal orangite  $7.2 \times 10^{-4}$ , Langesund orangite  $3.6 \times 10^{-3}$ , thorite  $1.8 \times 10^{-3}$ , and monazite  $3.6 \times 10^{-4}$ . The values obtained for orangite, thorite, and monazite are much higher than those calculated on the basis of the chemical composition of these minerals.

R. TRUSZKOWSKI.

**Analyses of Egyptian metamorphic rocks (schists).** W. F. HUME, H. F. HARWOOD, and H. L. RILEY (Geol. Mag., 1929, 66, 540—547).—Analyses

are recorded and discussed. In the Lawrence Smith method for alkali determinations the ratio rock : ammonium chloride : calcium carbonate should be changed to 1 : 1.5 : 12 and the time of heating should be extended to 2 hrs. when the material is of a soft, flaky character.

L. S. THEOBALD.

**Chemistry of the feldspars.** D. BELANKIN (Bull. Acad. Sci. U.S.S.R., 1929, 571—584).—Although of secondary importance, iron deserves a place in the petrography and classification of the feldspars. In a few cases, such as albite from Kirjabinsk and oligoclase from Murmansk (Mount Medvedka), iron is not present in a form detectable by ordinary analytical methods, but most feldspars contain it in amounts up to 2—3%. Although usually left out of account, barium is commonly present in potasso-sodium feldspars, although mostly absent from plagioclases. Rocks of similar petrographic character, and not only belonging to the same region but apparently derived from one and the same magma, sometimes contain feldspars of widely different baryta content; thus laurvikite from S. Norway contains 0.35% BaO, whereas anorthose of the same origin is free from barium. Similarly, miaskites from the Ilmen mountains normally contain barium, which is not found in syenites from these mountains. Strontium is usually present in feldspars in minimum proportion. The chemical formulæ of the feldspars are discussed, as well as the distribution in the space lattice of the excess oxides. Results are given of a number of analyses of potasso-sodium feldspars and plagioclases of various origins. The analytical data in certain cases seem inexplicable except by assuming the existence of chemical anomalies.

T. H. POPE.

**Beryl from southern Tirol.** E. DITTLER (Tsch. Min. Petr. Mitt., 1929, 40, 188—189).—Massive white beryl has been found in considerable quantity apparently in pegmatite in crystalline schists in the Masull ravine near Merano. Analysis by F. SCHWARZ gave: SiO<sub>2</sub> 66.55, Al<sub>2</sub>O<sub>3</sub> 18.82, BeO 13.47, FeO and CaO traces, Na<sub>2</sub>O 1.04, K<sub>2</sub>O 0.14, H<sub>2</sub>O+ 0.11, total 100.13%; *d* 2.703, *n<sub>w</sub>* 1.571.

L. J. SPENCER.

**Chromiferous smaragdite from Serbia.** E. HARBICH (Tsch. Min. Petr. Mitt., 1929, 40, 191—192).—Finely fibrous emerald-green actinolite occurring in serpentine with chromite and magnesite near Veles contained: SiO<sub>2</sub> 49.74, TiO<sub>2</sub> 0.40, Al<sub>2</sub>O<sub>3</sub> 8.70, Cr<sub>2</sub>O<sub>3</sub> 2.30, Fe<sub>2</sub>O<sub>3</sub> 3.07, MnO 0.04, MgO 20.44, CaO 13.32, Na<sub>2</sub>O 1.20, H<sub>2</sub>O+ 1.52, total 100.73%; *d* 3.022.

L. J. SPENCER.

**Chemical structure of boghead coal.** G. STADNIKOV and L. KASCHTANOV (Brennstoff-Chem., 1929, 10, 417—419).—An examination of the products of the hydrogenation ("berginisation") of Siberian boghead coals, together with previous results of the action of alcoholic potassium hydroxide on these coals (B., 1929, 158), leads to the conclusion that they consist of saturated and unsaturated monocarboxylic acids of the aliphatic series, of cyclic and polycyclic acids, and of neutral oxygenated compounds of cyclic structure. On hydrogenation the cyclic acids eliminate carbon dioxide and are transformed into cyclic hydrocarbons. The products of hydrogenation contain no phenols.

A. B. MANNING.

**Theory of the origin of fusain.** E. HOFFMANN (Brennstoff-Chem., 1929, 10, 419—422).—The mode of occurrence of some specimens of fusain is discussed and it is shown that they cannot have originated in the manner suggested by Lieske (A., 1929, 1036).

A. B. MANNING.

**Theory of the origin of fusain.** R. LIESKE (Brennstoff-Chem., 1929, 10, 422—424).—A reply to Hoffmann (cf. preceding abstract).

A. B. MANNING.

**Fossil resin.** J. CORTELEZZI (Rev. fac. cienc. quim. La Plata, 1929, 5, [2], 25—63).—The amber-like substance had *d* 1.0527, *n<sub>D</sub>* 1.529, *b. p.* 335°, acid value 42.15, saponif. value 109.6, and contained C 76.550, H 10.202, O 13.188, S 0.059, ash (K, Fe, Ca, Mg, SiO<sub>2</sub>, SO<sub>3</sub>) 0.08, H<sub>2</sub>O (100°) 2.30%; essential oils 5.30, bitter substances 7.22, free acids 1.34%.

CHEMICAL ABSTRACTS.

**Sandia mountains meteorite.** H. H. NININGER (Amer. J. Sci., 1929, [v], 18, 412—415).—An analysis is given of the Sandia mountains meteorite. It has an unusually high platinum content.

C. W. GIBBY.

## Organic Chemistry.

**Temperature of fusion of organic compounds.**

**XII. Alternation phenomena.** J. TIMMERMANS (Bull. Soc. chim. Belg., 1929, 38, 295—300).—Theoretical. The difficulties which arise in the methods of enumeration of the carbon atoms in homologous series suggested by Verkade (A., 1926, 686, 1210) and by Nekrassov (A., 1928, 613) are discussed. The interpretations of the different alternation phenomena in carbon chains, put forward by the author on the basis of Hinrichs' theory, have been extended by taking into account Nekrassov's views (*loc. cit.*) on the structure of hydrocarbon chains.

M. S. BURR.

**Wieland's theory and the phenomenon of oxidation of petroleum hydrocarbons.** L. BERMEJO (Anal. Fís. Quim., 1929, 27, 695—700).—

The results obtained in the oxidation of petroleum hydrocarbons by air or oxygen are concordant with the mechanism of oxidation (dehydrogenation) proposed by Wieland. Saturated hydrocarbons may thus yield unsaturated hydrocarbons, and the next stage is the addition of water to the double linking produced, followed by polymerisation, by elimination of water or generation of hydrogen peroxide, or the formation of peroxides.

R. K. CALLOW.

**Direct oxidation of hydrocarbons by air.** P. DUMANOIS and P. MONDAIN-MONVAL (Compt. rend., 1929, 189, 761—763).—When a mixture of pentane and air is slowly heated under pressure at constant volume there is a sudden rapid rise in pressure, accompanied by the formation of carbon dioxide and

aldehyde, immediately prior to the spontaneous explosion of the mixture at 230°. After the explosion aldehyde is, and carbon dioxide is not, present in appreciable quantity. Analogous results were obtained with hexane, heptane, octane, and technical mixtures.

A. A. GOLDBERG.

**Pyrolysis of hydrocarbons. *n*- and *iso*-Butanes.** C. D. HURD and L. U. SPENCE (J. Amer. Chem. Soc., 1929, 51, 3353—3362).—The gases are passed through Pyrex glass tubes at 600° and 700° at about 6 c.c. per sec. At 600°, butane undergoes 22% decomposition into (a) a mixture of methane and propylene, (b) a mixture of ethane and ethylene; little dehydrogenation takes place and the ratio  $a:b=55:40$ . At 700°, 75% fission occurs, and an excess of ethylene is produced by secondary reactions. The general course of the pyrolysis is the same as at 600°. *iso*Butane decomposes at 600°, yielding mixtures of hydrogen and *isobutene* (major decomposition) and methane and propylene; more methane is produced than the change  $\text{CHMe}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{CHMe}$  requires, probably because of further interaction of (active?) hydrogen with *isobutene* or propylene. At 700°, *isobutane* yields more propylene than *isobutene* and a small amount of tar is formed. Decomposition of *n*-butane appears to occur largely through the fission of C-C linkings, whilst *isobutane* undergoes both C-C and C-H linking fission, the latter predominating.

The best analytical procedure is to determine the ethylene derivatives (after removal of any acetylenes formed with alkaline potassium iodomercurate solution) by absorption in varying concentrations of sulphuric acid. *iso*Butene and propylene are best absorbed in 62.4 and 82.5% acid, respectively; ethylene requires fuming sulphuric acid (8%  $\text{SO}_3$ ).

H. BURTON.

**Preparation of isoprene with a theoretical hydrogen value.** H. I. WATERMAN and H. A. VAN WESTEN (Rec. trav. chim., 1929, 48, 1084—1086).—Isoprene, b. p. 34.5—35.0°/762 mm.,  $d_4^{20}$  0.6806,  $n_D^{20}$  1.4194, bromine value (McIlhiney) 234.7 (theoretical 469.5), containing at most very small amounts of dimethylallene or other isomerides is prepared as follows. Crude  $\alpha$ -methyl- $\Delta^2$ -butene obtained by dehydration of amyl alcohol with aluminium oxide at 500° is treated with bromine at  $-15^\circ$ , the vapour of the bromides, b. p. 56—61°/13 mm., passed successively over barium chloride and potassium hydroxide in asbestos vessels, and the product condensed in liquid air and fractionated. The sample so obtained absorbs the theoretical quantity of hydrogen (mean 99.6%; cf. A., 1929, 907), giving  $\beta$ -methylbutane, b. p. 28.7—29.0°/764 mm.,  $n_D^{20}$  1.3542.

J. W. BAKER.

**Preparation of decene with a theoretical hydrogen value.** H. I. WATERMAN, P. VAN'T SPIJKER, and H. A. VAN WESTEN (Rec. trav. chim., 1929, 48, 1097—1102).—A specimen of decene, b. p. 171—173°,  $d_4^{20}$  0.7447,  $n_D^{20}$  1.4259, which may contain isomerides but is free from other hydrocarbons, is prepared by Grosjean's method (A., 1892, 691), repeated fractionation of the product, conversion of the fraction b. p. 170—173°/763 mm. into bromides, b. p. 136—139°/12 mm., with bromine in chloroform at  $-15^\circ$ , regener-

ation of the hydrocarbon by the action of a zinc-copper couple, and final fractionation over sodium. The specimen has a bromine value (McIlhiney) 114.8 (theoretical 114.0) and a theoretical hydrogen value (101.4%), the decane so formed having b. p. 172—173°,  $d_4^{20}$  0.7312,  $n_D^{20}$  1.4124 (cf. Krafft, A., 1882, 1271). Decene preparations described in the literature are untrustworthy.

J. W. BAKER.

**Preparation of hexadecene with a theoretical hydrogen value.** H. I. WATERMAN, P. VAN'T SPIJKER, and H. A. VAN WESTEN (Rec. trav. chim., 1929, 48, 1103—1111; cf. preceding abstract).—Pure hexadecene (possibly containing isomerides), b. p. 157.5°/15.5 mm., m. p. 2.2°,  $d_4^{20}$  0.7825,  $n_D^{20}$  1.4419, bromine value (McIlhiney) 71.2 (theoretical 71.3), is prepared by Krafft's method (A., 1884, 571) and subsequent purification of the product by conversion into the bromides, removal of saturated hydrocarbons by fractionation in a vacuum, regeneration of hexadecene from the bromides by the action of a zinc-copper couple, and final fractionation with a column. The specimen has a theoretical hydrogen value, being reduced to hexadecane, m. p. 16.6°,  $d_4^{20}$  0.7751,  $n_D^{20}$  1.4352. Absorption of hydrogen and bromine by hexadecene occurs more slowly than with the lower homologues, 10 min. being necessary to obtain a theoretical bromine value.

J. W. BAKER.

**Kinetics of the polymerisation of acetylene.** R. N. PEASE (J. Amer. Chem. Soc., 1929, 51, 3470—3475).—The polymerisation of acetylene has been studied, using the flow method. Reaction is detectable at 400° and at 600° regular flashing begins with high flow rates; with low flow rates the experiment can be carried out at 650°. Polymerisation is the only reaction of importance up to 600°. This is a homogeneous, bimolecular reaction; with a glass packing, the rate decreases. The products formed are benzene and other hydrocarbons, which are readily polymerised or carbonised by sulphuric acid.

H. BURTON.

**Regularities in the m. p. of crystalline derivatives of various aliphatic alcohols.** G. B. MALONE and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 3424—3427).—The m. p. (corr.) of the 3:5-dinitrobenzoates of the following alcohols are: methyl, 107.8°; ethyl, 92.7°; *n*-propyl, 73.0°; *n*-butyl, 62.5°; *n*-amyl, 46.4°; *n*-hexyl, 58.4°; *n*-heptyl, 46.9°; *n*-octyl, 60.8°; *n*-nonyl, 52.2°; *isobutyl*, 86.5°; *isoheptyl*, 69.8°; *isoheptyl*, 54.5°; *isooctyl*, 58.3°; *isopropyl*, 122.1°; *sec.-butyl*, 75.6°; *sec.-amyl*, 62.1°; *sec.-hexyl*, 38.6°; *sec.-heptyl*, 49.4°; *sec.-octyl*, 32.2°; *sec.-nonyl*, 42.8°. In the *n*- and *iso*-series, the esters from the even-numbered (carbon atoms) alcohols show a higher m. p. than those from the odd-numbered alcohols; the effect is not pronounced with the lower members of the *n*-series. For the esters from the *sec.*-alcohols the above relationship is reversed.

H. BURTON.

**Behaviour of monohydric alcohols towards ferrous sulphate and hydrogen peroxide.** L. ROSENTHALER (Arch. Pharm., 1929, 8, 599—601).—Fenton's reagent reacts with aqueous methyl, ethyl, and *n*-propyl alcohols, affording the corresponding aldehydes and acids; *isopropyl* alcohol yields acetone and, secondarily, formic acid. *n*-Butyl, *isobutyl*, and

isoamyl alcohols give the corresponding aldehydes and acids and secondary products arising from the further oxidation of the acids. C. C. N. VASS.

**Metal alkoxides and ortho-acid esters. I. Alkoxo-acids and their salts.** H. MEERWEIN and T. BERSIN (Annalen, 1929, 476, 113—150).—The following alkoxides are described: *potassium lithium isopropoxide*,  $[\text{Li}(\text{OPr}^\beta)_2]\text{K}$ ; *potassium beryllium ethoxide*,  $[\text{Be}(\text{OEt})_4]_2\text{K}$ ; *sodium magnesium n-propoxide*; *potassium calcium benzyloxyde*; *potassium zinc methoxide*,  $[\text{Zn}(\text{OMe})_3]\text{K}$ , and *ethoxide*; *sodium zinc isopropoxide*; *aluminium zinc isopropoxide*,  $[\text{Zn}(\text{OPr}^\beta)_3]_3\text{Al}$ ; *zinc boron methoxide*,  $[\text{B}(\text{OMe})_4]_2\text{Zn}$ ; *sodium boron isoamyloxyde*; *potassium boron benzyloxyde*; *sodium boron phenoxide*; *aluminium hydroxoxethoxide*,  $\text{Al}(\text{OH})(\text{OEt})_2$ ; *aluminium cyclohexoxide*; *aluminium dihydroxocyclohexoxide*; *potassium aluminium methoxide*,  $[\text{Al}(\text{OMe})_4]\text{K}$ ; *lithium aluminium methoxide*; *potassium aluminium ethoxide*; *sodium aluminium ethoxide*; *thallium aluminium ethoxide*; *calcium aluminium ethoxide*; *magnesium aluminium ethoxides*,  $[\text{Al}(\text{OEt})_4]_2\text{Mg}$ , b. p. 220—228°/4 mm., m. p. 129°, and  $[\text{Al}(\text{OEt})_6]_2\text{Mg}_3$ , m. p. 240°; *potassium aluminium n-propoxide*, m. p. 157—158°; *potassium aluminium isopropoxide*; *calcium aluminium isopropoxide*, b. p. 230—240°/3 mm., m. p. 124°; *magnesium aluminium isopropoxide*, b. p. 130—142°/2 mm., m. p. 20·2°; *potassium aluminium n-butoxide*, m. p. 164—165°; *lithium aluminium isoamyloxyde*; *potassium aluminium cyclohexoxide*; *potassium aluminium benzyloxyde*, m. p. 128—129°; *sodium aluminium benzyloxyde*, m. p. 226—228°; *copper aluminium ethoxide*; *nickel aluminium ethoxide*; *cobalt aluminium ethoxide*; *sodium antimony methoxide*,  $[\text{Sb}(\text{OMe})_4]\text{Na}$ , and corresponding *ethoxide*; the compounds  $[\text{Sn}(\text{OEt})_6]_2\text{H}_2$ ,  $[\text{Sn}(\text{OEt})_6]\text{HNa}$  and  $[\text{Sn}(\text{OEt})_6]\text{HNa}$ ; *normal potassium tin ethoxide*,  $[\text{Sn}(\text{OEt})_6]\text{K}_2$ ; a *potassium titanium butoxide*,  $[\text{Ti}(\text{OBu})_6]_2\text{H}_2$ ,  $[\text{Ti}(\text{OBu})_6]\text{HK}$ ; a *sodium zirconium ethoxide*,  $[\text{Zr}(\text{OEt})_6]\text{HNa}$  (and corresponding *methoxide*); *sodium tellurium ethoxide*,  $[\text{Te}(\text{OEt})_6]\text{HNa}$ ; *sodium selenium ethoxide*,  $[\text{Se}(\text{OEt})_6]\text{HNa}$ ; and *sodium antimony ethoxide*,  $[\text{Sb}(\text{OEt})_6]\text{Na}$ .

The following substances were prepared incidentally: *methyl antimoniate*,  $\text{Sb}(\text{OMe})_3$ , m. p. 123—124° (corresponding *ethyl*, *isopropyl*, and *n-butyl* esters, b. p. 103°/18 mm., b. p. 103·5°/21 mm., and b. p. 150—151°/16 mm., respectively); *ferric ethoxide*; *stannic ethoxide*; *titanium n-butoxide*, b. p. 177°/6·7 mm.; *zirconium ethoxide*; *methyl orthotellurate*,  $\text{Te}(\text{OMe})_4$ , b. p. 123—124°/17 mm. (corresponding *ethyl* ester, b. p. 107—107·5°/5·5 mm. m. p. 20°); *selenium tetraethoxide*; *antimony pentaethoxide*, b. p. 153°/3·5 mm., m. p. 38°; *antimony chloroethoxide*,  $[\text{SbCl}(\text{OEt})_5]\text{Na}$ ; and *benzyl borate*, b. p. 238—239°/12 mm. R. J. W. LE FÈVRE.

**Reaction of magnesium ethyl bromide with epichlorohydrin.** C. F. KOELSCH and S. M. McELVAIN (J. Amer. Chem. Soc., 1929, 51, 3390—3394).—Magnesium ethyl bromide reacts with epichlorohydrin, yielding a mixture of  $\alpha$ -chloro- $\gamma$ -bromopropan- $\beta$ -ol (main product) and  $\alpha$ -chloropentan- $\beta$ -ol (I), b. p. 157—160°/735 mm.,  $d_{20}^{25}$  1·0143,  $n_D^{25}$  1·4404 (16—19% yield; *acetate*, b. p. 186—188°/740 mm.,

$d_{20}^{25}$  1·0825,  $n_D^{25}$  1·4328; 3:5-dinitrobenzoate, m. p. 83—84°) (cf. Fournau and Tiffeneau, A., 1908, i, 163). Treatment of I with thionyl chloride and diethylaniline gives  $\alpha\beta$ -dichloropentane, b. p. 145·8—146·2°/739 mm.,  $d_{20}^{25}$  1·0767,  $n_D^{25}$  1·4448, also obtained by the addition of chlorine to  $\Delta^2$ -pentene in carbon tetrachloride solution.  $\alpha\beta$ -Dichloropentane reacts slowly with sodium iodide in acetone solution, liberating free iodine (cf. van Duin, A., 1924, i, 702). H. BURTON.

**isoAmyl compounds.** J. TIMMERMANS and (MME.) HENNAUT-ROLAND (Anal. Fis. Quím., 1929, 27, 460—472).—isoAmyl alcohol, prepared by the method of Locquin (A., 1904, i, 546; cf. A., 1902, i, 198), has b. p. 132·0°,  $d_4^{20}$  0·82390,  $n_D^{25}$  1·40853. It yields a glassy mass in liquid air. isoAmyl bromide (cf. Fournier, A., 1906, i, 787) is freed from the alcohol, with which it forms an azeotropic mixture, by treatment with phosphoric oxide. It has m. p. —112·0°, b. p. 120·65°/760 mm.,  $d_4^{20}$  1·22912,  $n_D^{25}$  1·44332. Diisoamyl, prepared from isoamyl bromide and sodium, has m. p. —49·2°, b. p. 160·0°/760 mm.,  $d_4^{20}$  0·73785,  $n_D^{25}$  1·41049. The variation of b. p. with pressure,  $d_4^{25}$  and  $d_4^{20}$ ,  $n_D^{25}$  for H and He lines, dispersion, molecular refractivities, viscosities, and surface tensions and the variation of these properties with temperature have also been determined. The values given in the literature are compared and criticised.

R. K. CALLOW.

**Determination of the constitution of citronellol and rhodinol by the quantitative ozonisation method.** V. GRIGNARD and J. DÈUVRE (Bull. Soc. chim., 1929, [iv], 45, 809—827).—A reply to Verley (A., 1928, 1138, 1139). In part a recapitulation of arguments already advanced (A., 1929, 542). Citronellol when treated with benzoyl chloride and hydrogen chloride, is found by the quantitative ozonisation method to contain 50% of  $\alpha$ - and 50% of  $\beta$ -form, a result inconsistent with Verley's theory of transformation of  $\alpha$ - into  $\beta$ -ozonide (A., 1924, i, 865; 1925, i, 406; 1928, 1138). Successive oxidation with dilute permanganate and chromic acid yields results generally in agreement with those obtained by ozonisation. Verley's theory fails to account for the presence in limonene of 80% of  $\alpha$ - and 20% of  $\beta$ -isomeride (Escourrou, A., 1928, 1357), or Grignard and Savard's results on pulegone and isopulegone (A., 1926, 72, 408; 1928, 765). Ozonisation of isopulegol obtained by heating citronellol with acetic anhydride at 160—180° for 20 hrs. and hydrolysis with alcoholic potassium hydroxide indicated 92% of  $\alpha$ - and only 3% of  $\beta$ -isomeride, the latter being probably due to traces of unchanged citronellol. Similarly, geraniolene, b. p. 141·5—142·5°/758 mm.,  $d_{20}^{25}$  0·757,  $n_D^{25}$  1·4400, obtained from citral, b. p. 107—109°/12 mm. (90%  $\beta$ -isomeride), by oxidation with silver nitrate (cf. Delépine and Bonnet, A., 1909, i, 632) and distillation of the geranic acid (affording 93% of acetone on ozonisation) in hydrogen, yields on ozonisation 48% of formaldehyde, 57% of formic acid, and 84% of acetone, indicating the presence of 90% of  $\beta\alpha'$ -isomeride,  $\text{CMe}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{CMe}\cdot\text{CH}_2$ , and 10% of  $\alpha\alpha'$ -form,  $\text{CH}_2\cdot\text{CMe}\cdot[\text{CH}_2]_3\cdot\text{CMe}\cdot\text{CH}_2$ . No appreciable migration of the double linking has thus occurred, although on Verley's hypothesis considerable isomerisation of  $\alpha'$ -

into  $\beta$ -ozonide should take place. Acetol is not formed when citronellal dimethylacetal is ozonised in acetic acid media (cf. Harries and Comberg, A., 1915, i, 966). Verley's high constants for "pure" citronellal and rhodinal (cf. Waterman and Elsbach, A., 1929, 542) are attributed to the presence of isopulegol. Verley's rhodinal,  $d_4^{20}$  0.8751,  $d_4^{20}$  0.8694, shows an abnormal temperature/density coefficient and neither the refractivity curve nor the rotatory dispersion curve affords any criteria of purity. The semicarbazones similarly afford no definite evidence, being crystalline mixtures of varying proportions of the  $\alpha$ - and  $\beta$ -isomerides both in the active and the racemic state. Thus, citronellal, b. p. 95–96°/19 mm.,  $d_4^{17.5}$  0.86,  $n_D^{17.5}$  1.4507,  $[\alpha]_D^{17.5}$  +9.68°, containing (ozonisation in pyridine) 75% of  $\beta$ - and 19% of  $\alpha$ -isomeride, gives a semicarbazone, m. p. 83.5°, the mother-liquors containing a semicarbazone, m. p. 80.5–81°; a mixture has m. p. 82–83°. Ozonisation of the semicarbazone, m. p. 83.5°, indicates 88% of the  $\beta$ -isomeride. Similarly, citronellal, b. p. 102–103°/24 mm.,  $d_4^{17.5}$  0.8533,  $n_D^{17.5}$  1.4483,  $[\alpha]_D^{17.5}$  +10.3° (86%  $\beta$ -, 14%  $\alpha$ -form), purified by sodium hydrogen sulphite, gives a semicarbazone, m. p. 83.5° (88%  $\beta$ -form, by ozonisation). Comparison with literature data indicates that Verley's pulegone (semicarbazone, m. p. 172°) is essentially  $\alpha$ -isopulegone. *d*-Citronellal, b. p. 90–91°/12 mm.,  $d_4^{16}$  0.855,  $n_D^{16}$  1.4494,  $[\alpha]_D^{16}$  +10.36° (26% of  $\alpha$ - and 70% of  $\beta$ -form), obtained by dehydration of hydroxycitronellol with 10% phosphoric acid, affords two semicarbazones, m. p. 77.5° and 81.5°, the original *d*-citronellol, b. p. 109°/9 mm., yielding with benzoyl chloride at 140–160° for 6 hrs. a *d*-rhodinol, b. p. 109°/9 mm.,  $d_4^{16.8}$  0.8575,  $n_D^{16.8}$  1.4566,  $[\alpha]_D^{16.8}$  +3.23°, containing 36% of  $\alpha$ - and 64% of  $\beta$ -form. Catalytic dehydrogenation in presence of copper yields a rhodinol, b. p. 82–83°/8 mm.,  $d_4^{16.2}$  0.856,  $n_D^{16.2}$  1.4481,  $[\alpha]_D^{16.2}$  +10.23°, containing 34% of  $\alpha$ - and 62% of  $\beta$ -form, and yielding two semicarbazones, m. p. 78–78.5° and 76–76.5°, the former containing (ozonisation) 67% of  $\beta$ -form. Commercial "rhodinol" (Givaudan), b. p. 109–110°/9 mm., giving on ozonisation 86% of acetone, corresponding with the  $\beta$ -form, with benzoyl chloride affords 56% of Barbier and Bouveault's "rhodinol," b. p. 110°/10 mm.,  $d_4^{19}$  0.857,  $n_D^{19}$  1.4562,  $[\alpha]_D^{19}$  –1.3°, containing 42% of  $\alpha$ - and 53% of  $\beta$ -isomeride (cf. A., 1929, 907), which on dehydrogenation yields an *l*-rhodinol, b. p. 89–90°/12 mm.,  $d_4^{17}$  0.856,  $n_D^{17}$  1.4481,  $[\alpha]_D^{17}$  –4.8°, containing 38% of  $\alpha$ - and 62% of  $\beta$ -isomeride, and giving two semicarbazones, m. p. 75°,  $[\alpha]_D^{17}$  –0.4° (64% of  $\beta$ -form by ozonisation), and 64–65°,  $[\alpha]_D^{17}$  –0.05° (62% of  $\beta$ -form). The original Givaudan rhodinol similarly affords, in addition to citral, an *l*-citronellal, b. p. 85–87°/10 mm.,  $d_4^{18}$  0.856,  $n_D^{18}$  1.4499,  $[\alpha]_D^{18}$  –4.41°, containing 20% of  $\alpha$ - and 80% of  $\beta$ -form and giving one semicarbazone, m. p. 80° (91% of  $\beta$ -form by ozonisation). *d*-Citronellal, b. p. 110°/10 mm.,  $d_4^{15}$  0.858,  $[\alpha]_D^{15}$  +2.76°, containing 28% of  $\alpha$ - and 70% of  $\beta$ -isomeride, obtained by dehydration of hydroxycitronellol from Java citronellol, when converted into acetate, saturated with hydrogen chloride at 0°, and treated with basic lead nitrate (cf. Tiemann and Schmidt, A., 1897, i, 198) gives on hydrolysis of the citronellyl acetate a *d*-citronellol, b. p. 113–114°/13 mm.,  $d_4^{18}$  0.856,  $n_D^{18}$  1.4554 (allo-

phanate, m. p. 104.5°), containing (ozonisation) 38% of  $\alpha$ - and 60% of  $\beta$ -form, together with *hydroxycitronellyl acetate*, b. p. 143–146°/13 mm. Dehydration of the hydroxycitronellol, b. p. 140–147°/13 mm., obtained on hydrolysis yields *d*-citronellol, b. p. 110–112°/11 mm.,  $d_4^{19}$  0.854,  $n_D^{19.5}$  1.4533,  $[\alpha]_D^{19.5}$  +3.63° (*allophanate*, m. p. 105°), containing (by ozonisation) 17% of  $\alpha$ - and 80% of  $\beta$ -form, transformation of the  $\beta$ - into the  $\alpha$ -form thus occurring only under the influence of acids. It is accordingly suggested that the semicarbazones of the  $\alpha$ - and  $\beta$ -forms tend to approximate towards eutectic mixtures of about 50% of each form, fractionation affording only racemic and active mixtures. Savard's results (A., 1929, 978) are not necessarily inconsistent with the ozonisation results, since Henri's law is based on observations made with functional groups occupying the  $\alpha\gamma$ -positions. When the distance between the functional groups is greater it is possible that the two groups will exert their normal individual influence and that the group nearest the extremity of the chain will give an absorption band nearest the red.

R. BRIGHTMAN.

Electronic conception in organic chemistry. III. Dissociation and semihydrobenzoin rearrangement of  $\beta$ -acetyl- $\alpha\alpha$ -dimethylglycol. M. MIGHTA (Bull. Chem. Soc. Japan, 1929, 4, 225–234).— $\beta$ -Acetyl- $\alpha\alpha$ -dimethylethylene glycol, b. p. 114°/22 mm., best prepared by the oxidation of mesityl oxide with potassium permanganate during 6 hrs. at 7–8° (cf. Harries and Pappos, A., 1901, i, 673), is converted by excess of boiling dilute sulphuric acid (1:5) during 3 hrs. into acetone, methyl isopropyl ketone, and acetol (identified by conversion into 3-hydroxy-2-methylquinoline), whilst interaction with excess of concentrated sulphuric acid at 0° for 2 hrs. afforded only acetone and methyl isopropyl ketone. Under both conditions dissociation and semihydrobenzoin rearrangement proceed simultaneously. An electronic interpretation of the results is given.

A. I. VOGEL.

Reactions of propargyl acetal. J. GRARD (Compt. rend., 1929, 189, 925–927; cf. A., 1929, 1276).—Treatment of  $\gamma\gamma$ -diethoxy- $\Delta^4$ -propinene in alcoholic solution with ammoniacal cuprous chloride and silver nitrate gives a *mono-cuprous* and a *mono-silver* derivative, respectively; the latter reacts with iodine to form  $\alpha$ -iodo- $\gamma\gamma$ -diethoxy- $\Delta^4$ -propinene and  $\alpha\beta\beta$ -tri-iodoacetaldehyde. Oxidation of the copper compound with potassium ferricyanide yields  $\alpha\alpha\zeta\zeta$ -tetraethoxy- $\Delta^{6\beta}$ -hexadi-inene, m. p. –8°, b. p. 140–141°/3 mm.,  $d_4^{20}$  0.9730,  $n_D^{20}$  1.4638. Treatment of the acetal with urethane gives a *compound*,  $\text{CH}_2\text{C}(\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et}))_2$ , m. p. 180–180.5°; with carbamide, a complex *tri-ureine* is formed. Interaction of  $\gamma\gamma$ -diethoxy- $\Delta^4$ -propinene with magnesium ethyl bromide gives the *substance*  $\text{OEt}\cdot\text{CHEt}\cdot\text{C}(\text{C}\cdot\text{MgBr})_2$ , which with water yields  $\gamma$ -ethoxy- $\Delta^4$ -pentinene, b. p. 108°,  $d_4^{22}$  0.8096,  $n_D^{22}$  1.4072, and with a saturated solution of mercuric chloride yields methyl  $\alpha$ -ethoxypropyl ketone, b. p. 76°/67 mm.,  $d_4^{17}$  0.8849,  $n_D^{14}$  1.4075 (semicarbazone, m. p. 93–95°). Interaction with magnesium phenyl bromide gives  $\gamma$ -ethoxy- $\gamma$ -phenyl- $\Delta^4$ -propinene, b. p. 100–105°/15 mm.,  $d_4^{17}$  1.023,  $n_D^{15}$  1.5365.

A. A. GOLDBERG.



**$\gamma\eta$ -Oxido- $\gamma\eta$ -dimethyl- $\Delta^a$ -octinene.** H. RUPE and G. LANG (Helv. Chim. Acta, 1929, 12, 1133—1141).—Dehydrolinalool (Ruzicka and Fornasir, A., 1919, i, 193; modified method of preparation given) is converted by warming with 85% formic acid into a small amount of an unidentified substance and 57% of  $\gamma\eta$ -oxido- $\gamma\eta$ -dimethyl- $\Delta^a$ -octinene (I), b. p. 165°/750 mm., 50—51°/12 mm.,  $d_4^{20}$  0.8916,  $n_D^{20}$  1.44938 silver derivative; hydroferrocyanic acid compound). Oxidation of I with alkaline potassium permanganate solution affords cinenic acid (Rupe, A., 1900, i, 371), whilst reduction with hydrogen in presence of aqueous alcohol and a nickel catalyst gives  $\gamma\eta$ -oxido- $\gamma\eta$ -dimethyloctane, b. p. 163—164°, 93—95°/80 mm. The last-named compound is converted by treatment with an acetic acid solution of hydrogen bromide into  $\gamma\eta$ -dibromo- $\gamma\eta$ -dimethyloctane, b. p. 119°/12 mm., reduced by zinc dust and acetic acid to  $\gamma\eta$ -dimethyloctane. Partial reduction of I by Straus' method (A., 1906, i, 77) affords  $\gamma\eta$ -oxido- $\gamma\eta$ -dimethyl- $\Delta^a$ -octene, b. p. 162°, 50°/12 mm. The above dibromide condenses with ethyl sodiomalonate, yielding a small amount of ethyl 2:2:6-trimethyl-6-ethylcyclohexane-1:1-dicarboxylate, b. p. 167—170°/11 mm.

H. BURTON.

**Reactions of  $d$ - $\beta$ -octyl chloroformate of interest from the viewpoint of the Walden inversion.** A. J. H. HOUSSA and H. PHILLIPS (J.C.S., 1929, 2510—2515).—By the interaction of optically active  $\beta$ -octyl chloroformate with potassium acetate or potassium benzoate the corresponding ester is produced, together with the alcohol, in an optically pure state. Under the same conditions sodium  $p$ -toluenesulphinate yielded a product which on hydrolysis gave a slightly racemised octanol. When the above reactions were conducted in alcoholic solution the product was an optically pure octanol.

In none of these reactions does a Walden inversion occur, and this is explained as meaning that the carbon-oxygen linking of the asymmetric atom is not ruptured. On the other hand,  $l$ - $\beta$ -octyl chloroformate with pyridine produces  $d$ - $\beta$ -octyl chloride. Here a Walden inversion, without pronounced racemisation, has occurred.

T. H. MORTON.

**Properties of mixed organomagnesium carbonates.** D. IVANOV (Compt. rend., 1929, 189, 930—931).—The organomagnesium carbonates react with magnesium alkyl and aryl halides thus:  $R\cdot O\cdot CO_2\cdot Mg\cdot X + R'\cdot Mg\cdot X' = R\cdot O\cdot Mg\cdot X' + R'\cdot CO_2\cdot Mg\cdot X$ . The excess of  $R'\cdot Mg\cdot X'$  reacts with the  $R'\cdot CO_2\cdot Mg\cdot X$  to give the compound  $R'_3C\cdot O\cdot Mg\cdot X$ . Mineral acids decompose  $R'\cdot CO_2\cdot Mg\cdot X$  and  $R'_3C\cdot O\cdot Mg\cdot X$  to give a carboxylic acid and a tertiary alcohol, respectively. These reactions have been studied for the cases where  $R = Et$ ,  $Bu$ , and *iso*amyl and  $R' = Ph$  and  $CH_2Ph$ ; the carboxylic acid was titrated and the tertiary alcohol weighed. Pyrogenic decomposition of the organomagnesium carbonates takes place in two stages, e.g., (1)  $Et\cdot O\cdot CO_2\cdot MgBr = CO_2 + Et\cdot O\cdot MgBr$ . (2)  $2Et\cdot O\cdot MgBr = 2C_2H_4 + MgBr_2 + MgO + H_2O$ . Reaction 1 begins at 110° and reaction 2 takes place at 200—300°. The pyrogenic decompositions of bromomagnesium, ethyl, *isopropyl*, and benzyl carbonates are shown graphically.

A. A. GOLDBERG.

**Constitution of glycerophosphates.** D. W. HILL and F. L. PYMAN (J.C.S., 1929, 2236—2238; cf. *ibid.*, 1914, 105, 1238).—Calcium  $\alpha$ -glycerophosphate, prepared by the action of calcium chloride on the sodium salt obtained by the interaction of trisodium phosphate and glycerol  $\alpha$ -monochlorohydrin, differs from the so-called calcium  $\alpha$ -glycerophosphate prepared by Bailly (A., 1915, i, 492). Bailly (A., 1917, i, 2) shows that the method used by King and Pyman may yield either the  $\alpha$ - or  $\beta$ -glycerophosphate. In the present work the  $\alpha$ -glycerophosphate has been prepared by a new method which leaves no doubt as to its constitution (Fischer and Pfähler, A., 1920, i, 807), and found to correspond with the salt prepared by the method described above. The quinine salt prepared from Bailly's so-called  $\alpha$ -glycerophosphate has an indefinite m. p. and it is concluded that Bailly's salt is impure.

J. W. PORTER.

**Action of alkaline potassium mercuric iodide on  $\alpha$ - and  $\beta$ -glycerophosphates.** P. FLEURY and J. MARQUE (J. Pharm. Chim., 1929, [viii], 10, 401—404).—Sodium  $\beta$ -glycerophosphate, unlike the  $\alpha$ -isomeride, is not very reactive towards alkaline potassium mercuric iodide. This is in accordance with the fact that primary alcohols are more stable than secondary alcohols towards this reagent. The reaction is a means of differentiating between  $\alpha$ - and  $\beta$ -glycerophosphates.

A. A. GOLDBERG.

**Acetonyl sulphide.** G. T. MATTHAIPOULOS and J. N. ZAGANARIS (J. pr. Chem., 1929, [ii], 123, 333—335).—Dropwise addition of an alcoholic solution of sodium sulphide ( $Na_2S\cdot 9H_2O$ ) to an alcoholic solution of chloroacetone gives acetonyl sulphide, b. p. 130—135°/10 mm. This is oxidised by potassium permanganate and 5% sulphuric acid to the corresponding sulphone (unaltered up to 550°), which gives a barium salt of the *aci*-form and a dioxime, m. p. 75°.

J. W. BAKER.

**Tetramethylethylene sulphide.** M. A. YOUTZ and P. P. PERKINS (J. Amer. Chem. Soc., 1929, 51, 3508—3511).—Tetramethylethylene dibromide reacts with potassium thiocyanate in methyl-alcoholic solution, forming tetramethylethylene dithiocyanate, m. p. 61°, which on treatment with aqueous methyl-alcoholic sodium sulphide yields tetramethylethylene sulphide, b. p. 127° (corr.), m. p. 76.1—76.6°. The sulphide is polymerised readily by treatment with sulphuric acid.

H. BURTON.

**Influence of the sulphur atom on the reactivity of adjacent atoms or groups. III.  $\delta$ - and  $\epsilon$ -Chloro-sulphides.** G. M. BENNETT, F. HEATHCOAT, and A. N. MOSSES (J.C.S., 1929, 2567—2572).—The kinetics of ring closure of some  $\delta$ - and  $\epsilon$ -chlorosulphides to the corresponding sulphonium chlorides has been studied by following the development of ionic chlorine in a 50% aqueous acetone solution. The reaction is unimolecular and the following values of  $k \times 10^{-4}$  (time in min.) at 80° are given: phenyl  $\delta$ -chlorobutyl, 640; phenyl  $\epsilon$ -chloroamyl, 8.4; methyl  $\epsilon$ -chloroamyl sulphide 160. The temperature coefficient of  $k$  per 10° is 2.5—2.6. These values are interpreted as measures of the relative frequency that the sulphur and chlorine atoms come into reacting positions. With ethyl  $\delta$ -chlorobutyl sulphide, b. p. 97—104°/20 mm. (decomp.),

ring closure occurs very rapidly, the oil depositing crystals of *tetramethylene-ethylsulphonium chloride*, m. p. 130—135° (*chloroplatinate*), at the ordinary temperature.

The chloro-compounds were prepared from the corresponding hydroxy-compounds (Bennett and Heathcoat, A., 1929, 421) by the action of thionyl chloride and dimethylaniline in chloroform solution. The following sulphides are described: *phenyl δ-chlorobutyl sulphide*, b. p. 159°/14 mm.,  $d_4^{25}$  (vac.) 1.1269,  $n_D^{25}$  1.56828; *phenyl ε-chloroamyl sulphide*, b. p. 140°/1 mm.,  $d_4^{25}$  (vac.) 1.1065,  $n_D^{25}$  1.56040; *phenyl β-chloroethyl sulphide*, b. p. 117°/12 mm.,  $d_4^{25}$  (vac.) 1.1799,  $n_D^{25}$  1.58369; *phenyl γ-chloropropyl sulphide*, b. p. 142°/15 mm.,  $d_4^{25}$  (vac.) 1.1529,  $n_D^{25}$  1.578483; *methyl ε-chloroamyl sulphide*, b. p. 94°/15 mm.,  $d_4^{25}$  (vac.) 1.0300,  $n_D^{25}$  1.48597; *γ-chlorodipropyl sulphide*, b. p. 87°/16 mm.,  $d_4^{25}$  (vac.) 1.0267,  $n_D^{25}$  1.47779. This last compound when heated in aqueous acetone solution at 150° is slowly hydrolysed. *Phenyltetramethylenesulphonium* and *phenylpentamethylenesulphonium chloroplatinates* and *chloroaurates* are described and also *pentamethylenemethylsulphonium chloroplatinate*.

T. H. MORTON.

**Salts of methanedisulphonic acid.** H. J. BACKER and P. TERPSTRA (Rec. trav. chim., 1929, 48, 1175—1190).—A systematic investigation of the solubility, hydration, and crystalline form of a large number of normal salts of methanedisulphonic acid is described, full crystallographic data being given. The following are described, the figures in parentheses being the solubility of the anhydrous salt in water at 25°: *lithium* (72.71), *sodium* + 2.5H<sub>2</sub>O (38.22), *potassium* (4.46), *rubidium* (4.93), *cæsium* (21.33), *silver* (trimorphous) + 2H<sub>2</sub>O, + 0.5H<sub>2</sub>O, and anhydrous (45.05), *thallium* (6.42), *calcium* + 3H<sub>2</sub>O (32.57), *strontium* + 2H<sub>2</sub>O (2.14), *barium* + 2H<sub>2</sub>O (dimorphous, 0.368 and 0.308), *copper* + 5H<sub>2</sub>O and + 7H<sub>2</sub>O (76.8), *lead* + 2H<sub>2</sub>O (8.40), *ferrous* + 5H<sub>2</sub>O, *cobalt* + 5H<sub>2</sub>O (120.3), *nickel* + 5H<sub>2</sub>O, *lanthanum* + 6H<sub>2</sub>O, and *ammonium* (32.01). In agreement with Fajans and Ephraim's rule (Naturwiss., 1921, 9, 729) minimum solubility occurs with the rubidium salt in which the two ions have nearly equal masses (85.4 and 87).

J. W. BAKER.

**Detection and determination of the carboxyl group by distillation with zinc dust in a current of hydrogen.** A. W. VAN DER HAAR (Rec. trav. chim., 1929, 48, 1170—1174).—By distillation of a large number of acids and their derivatives, lactones, phenols, ketones, aldehydes, alcohols, monoses, bioses, quinones, purine derivatives, and pyrones with zinc dust in a current of hydrogen it is shown that only those substances which have two oxygen atoms united to the same carbon atom give carbon dioxide under these conditions. This method therefore serves as a means of distinguishing between acids (including lactones and anhydrides) and phenols. Since the amount of carbon dioxide evolved is much less than the theoretical, the method cannot be applied quantitatively. A similar rule holds for the evolution of sulphur dioxide from sulphur compounds.

J. W. BAKER.

**Tenacity of hydrocarbon residues to oxygen in acetic esters.** B. V. TRONOV and N. C. SIBGATULLIN

(Ber., 1929, 62, [B], 2850—2856; cf. A., 1929, 1039; this vol., 83).—The rate of hydrolysis of twenty acetic esters by hydrogen bromide has been measured in glacial acetic acid at 18—21°; experiments are performed in sealed tubes and the unused hydrogen bromide is determined by precipitation as silver bromide after a definite interval. The tenacity of the *n*-alkyl residue to oxygen (Me, Et Pr<sup>a</sup>, Bu<sup>a</sup>, *n*-hexyl) increases with length of the hydrocarbon chain; possible indication of periodicity is given by the slightly diminished tenacity of the *n*-hexyl group. Branching in the hydrocarbon chain causes increased tenacity. Esters of primary alcohols are most stable, followed in sequence by those of secondary and tertiary alcohols. Comparison of propyl and allyl acetates shows the tenacity to be weakened by the double linking. In the series phenyl, benzyl, and β-phenylethyl acetates, a periodic influence of the phenyl group is observed. Examination of ethyl acetate, ethylene diacetate, propyl acetate, propylene diacetate, trimethylene diacetate, and triacetin proves that esters of dihydric alcohols are more readily hydrolysed than those of monohydric alcohols and the tenacity is lower when the acid residues are in the vicinal position than when they are further separated from one another. The results are considered to give strong support to the carbonyl scheme of esterification and hydrolysis.

H. WREN.

**Compounds of acetates with inorganic salts.** J. V. DUBSKY and E. TESARIK (Coll. Czech. Chem. Comm., 1929, 1, 571—581).—Interaction of calcium chloride and cupric acetate in aqueous solution at 50—70° yielded *calcium acetatochloride*, [Ca{(OAc)<sub>2</sub>Ca}Cl<sub>2</sub>].10H<sub>2</sub>O. *Calcium acetatobromide*, [Ca{(OAc)<sub>2</sub>Ca}Br<sub>2</sub>].10H<sub>2</sub>O, was prepared from copper acetate (3 mols.), cupric bromide (1 mol.), calcium bromide (3 mols.), and calcium carbonate (3 mols.) at 50—70°.

The following substances were similarly prepared:

[Ca{(OAc)<sub>2</sub>Ca}I<sub>2</sub>].10H<sub>2</sub>O;  
[Ca{(OAc)<sub>2</sub>Ca}](NO<sub>3</sub>)<sub>2</sub>(OAc)<sub>2</sub>Ca.5H<sub>2</sub>O;  
[Ca{(OAc)<sub>2</sub>Ca}](NO<sub>3</sub>)<sub>2</sub>.3.5H<sub>2</sub>O;  
[Sr{(OAc)<sub>2</sub>Sr}].2Cl<sub>2</sub>(OAc)<sub>2</sub>.11H<sub>2</sub>O;  
[Ba{(OAc)<sub>2</sub>Ba}].Cl<sub>2</sub>.6H<sub>2</sub>O. The constitutions assigned to these complex salts are similar to those described by Weinland and others (cf. A., 1923, i, 291; 1924, i, 1160; ii, 45).

A. I. VOGEL.

**Blue colour of "basic lanthanum acetate" with iodine.** Very sensitive reaction for the acetate ion. D. KRÜGER and E. TSCHIRCH (Ber., 1929, 62, [B], 2776—2783).—The basic lanthanum salt obtained by the addition of ammonia or sodium hydroxide to solutions of lanthanum chloride or nitrate yields coloured iodo-compounds only in the presence of acetate or propionate ions. Reaction does not occur in the presence of sodium monochloro- or monoiodo-acetate, phenylacetate, *n*- or *iso*-butyrate, valerate, aminoacetate, tartrate, citrate, malate, salicylate, benzoate, succinate, or formate. Praseodymium exhibits a similar but less rapid action, whereas samarium and yttrium are inactive. The order of addition of the reagents is immaterial, and variation of the iodine concentration within wide limits has no qualitative effect. The sensitiveness of

the "iodine-lanthanum" reaction is of the same order of magnitude as that of "starch iodide." The formation of the blue iodo-compound appears to depend on a peculiar atomic arrangement proper to the basic acetate and propionate, and not on a definite colloidal-chemical condition of the basic salts. Formation of the blue compound does not constitute a very sensitive test for lanthanum, since the reaction is shown by praseodymium and also influenced by earths of which the basic acetates do not adsorb iodine. For acetate the test is more sensitive than any hitherto described and is applicable in presence of a large excess of inorganic ions; if necessary, the latter can be removed to some extent by taking advantage of the relatively considerable solubility of sodium acetate in absolute alcohol. Conditions are less favourable when the acetate ion is present with a large excess of other organic ions. H. WREN.

**Preparation of dichloroacetic acid.** M. DELÉPINE (Bull. Soc. chim., 1929, [iv], 45, 827—833).—By using 2 mols. of sodium cyanide and 1 mol. of chloral hydrate in boiling aqueous solution and extraction with ether after acidifying, dichloroacetic acid is obtained in 90% yield (cf. Pucher, A., 1921, i, 6). If the cyanide and chloral hydrate are mixed cold and left over-night, 90% of the hydrogen cyanide can be recovered by distillation prior to the ether extraction. Similar yields of dichloroacetic acid are obtained if the sodium cyanide is replaced partly by sodium hydroxide or carbonate, or, best, by calcium carbonate. With 0.125 mol. of sodium cyanide, 1 mol. of chloral hydrate, and 1 mol. of precipitated calcium carbonate by heating first at 75°, then to 80—85° during 2 hrs., and finally at 98—100°, acidification, and extraction with ether, dichloroacetic acid, b. p. 91—92°/12 mm., is obtained in yield above 90%.

R. BRIGHTMAN.

**Action of iodine on silver trifluoroacetate in presence of benzene and of chloroform.** F. SWARTS (Anal. Fis. Quím., 1929, 27, 683—691).—In benzene, the reaction appears to be essentially  $\text{CF}_3\cdot\text{CO}_2\text{Ag} + \text{I}_2 + \text{C}_6\text{H}_6 = \text{CF}_3\cdot\text{CO}_2\text{H} + \text{AgI} + \text{C}_6\text{H}_5\text{I}$ . If any peroxide is formed (cf. Gomberg, A., 1923, ii, 235) it is at once decomposed in bringing about iodine substitution. A small quantity of iodine is found as silver iodate and iodoxybenzene. In chloroform, the principal reaction is  $3\text{CF}_3\cdot\text{CO}_2\text{Ag} + \text{I}_2 + \text{CHCl}_3 = \text{CF}_3\cdot\text{CO}_2\text{H} + (\text{CF}_3\cdot\text{CO})_2\text{O} + 2\text{AgI} + \text{AgCl} + \text{COCl}_2$ , the resultant of  $2\text{CF}_3\cdot\text{CO}_2\text{Ag} + \text{I}_2 = (\text{CF}_3\cdot\text{CO})_2\text{O}_2 + 2\text{AgI}$ , followed either by  $(\text{CF}_3\cdot\text{CO})_2\text{O}_2 + \text{CHCl}_3 = (\text{CF}_3\cdot\text{CO})_2\text{O} + \text{COCl}_2 + \text{HCl}$  and  $\text{HCl} + \text{CF}_3\cdot\text{CO}_2\text{Ag} = \text{CF}_3\cdot\text{CO}_2\text{H} + \text{AgCl}$  or by  $(\text{CF}_3\cdot\text{CO})_2\text{O}_2 + \text{CHCl}_3 = \text{CF}_3\cdot\text{CO}_2\text{CCl}_3 + \text{H}_2\text{O} + \text{CF}_3\cdot\text{CO}_2\text{H}$ ,  $2\text{CF}_3\cdot\text{CO}_2\text{CCl}_3 + \text{H}_2\text{O} = \text{CF}_3\cdot\text{CO}_2\text{H} + \text{COCl}_2 + \text{HCl}$ , and  $\text{HCl} + \text{CF}_3\cdot\text{CO}_2\text{Ag} = \text{AgCl} + \text{CF}_3\cdot\text{CO}_2\text{H}$ . A certain amount of dichloromethyl trifluoroacetate also appears to be formed, and a small quantity of silver iodate is recognisable.

R. K. CALLOW.

**Walden inversion. XIII. Influence of substituent groups on optical rotation in  $\alpha$ -substituted aliphatic acids.** P. A. LEVENE and L. A. MIKESKA (J. Biol. Chem., 1929, 84, 571—599).—Among derivatives obtained from optically active  $\alpha$ -substituted aliphatic acids by transformations involving the carboxyl group, it is observed that the

halides and the carbinols rotate in opposite directions, the thiols and the sulphonic acids in the same direction, but the quantitative difference in the rotations is in the same sense as the difference between those of the corresponding carbinol and halide. The previous conclusion (cf. A., 1928, 170) that, in the aliphatic series, the carbinol is configuratively related to the halide which rotates in the opposite direction is therefore confirmed. In the present series of compounds the substituent groups fall into the following (descending) order as regards their effect on optical activity:  $\text{CN}$ ,  $\text{CO}_2\text{Et}$ ,  $\cdot\text{CO}_2\text{H}$ ,  $\cdot\text{CO}\cdot\text{NH}_2$ ,  $\cdot\text{COCl}$ ,  $\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ ,  $\cdot\text{CH}_2\text{hal}$ ,  $\cdot\text{CH}_2\cdot\text{SH}$ ,  $\cdot\text{CH}_2\cdot\text{OH}$ ,  $\cdot\text{CH}_2\cdot\text{NH}_2$ ; thus, in such a series, starting with a dextrorotatory nitrile, the magnitude of the dextrorotation decreases to the thiol, and the rotation is reversed in the carbinol and amine. The carbinols in this series (except  $\beta$ -methyl-*n*-butanol) were racemised by all halogenating agents, probably owing to intermediate formation of an unsaturated compound.

$\alpha$ -Methyl-*n*-valeric acid was resolved through the quinine salt to give the *l*-acid, b. p. 83—84°/4 mm.,  $[\alpha]_D^{25} - 8.13^\circ$  in ether (sodium salt,  $[\alpha]_D^{25} - 3.68^\circ$  in water), and the *d*-acid,  $[\alpha]_D^{25} + 5.58^\circ$  in ether, which was converted successively into *d*- $\alpha$ -methyl-*n*-valeryl chloride, b. p. 45—48°/15 mm.,  $d_4^{25}$  0.963,  $[\alpha]_D^{25} + 4.13^\circ$  in ether, and *d*- $\alpha$ -methyl-*n*-valeramide, m. p. 78°;  $[\alpha]_D^{25} + 5.79^\circ$  in 75% alcohol; the *l*-amide,  $[\alpha]_D^{25} - 5.79^\circ$ , gave *l*- $\alpha$ -methyl-*n*-valeronitrile, b. p. 30—32°/2 mm.,  $d_4^{25}$  0.791,  $[\alpha]_D^{25} - 15.12^\circ$  in ether, which yielded *d*-amino- $\beta$ -methyl-*n*-pentane, b. p. 28—30°/4 mm.,  $d_4^{25}$  0.763,  $[\alpha]_D^{25} + 4.12^\circ$  in ether (hydrochloride,  $[\alpha]_D^{25} + 1.51^\circ$  in 50% alcohol). Ethyl *l*- $\alpha$ -methyl-*n*-valerate had b. p. 78—80°/4 mm.,  $[\alpha]_D^{25} - 7.93^\circ$  in ether; the *d*-ester,  $[\alpha]_D^{25} + 5.67^\circ$ , was reduced to *l*- $\beta$ -methyl-*n*-pentanol, b. p. 147—147.5°,  $[\alpha]_D^{25} - 0.8^\circ$  in ether, which, with phosphorus pentachloride, gave *dl*- $\alpha$ -chloro- $\beta$ -methyl-*n*-pentane, b. p. 110—120°. *d*- $\alpha$ -Amino- $\beta$ -methyl-*n*-pentane, with nitrosyl bromide, yielded *l*- $\alpha$ -bromo- $\beta$ -methyl-*n*-pentane, b. p. 55—65°/10 mm.,  $[\alpha]_D^{25} - 0.94^\circ$  in ether; *d*- $\alpha$ -methyl-*n*-valeryl chloride gave, with potassium hydrogen sulphide, *d*- $\alpha$ -methylthiol-*n*-valeric acid, b. p. 71—72°/23 mm.,  $[\alpha]_D^{25} + 7.49^\circ$  in ether.  $\alpha$ -Methyl-*n*-hexoic acid was resolved by means of cinchonidine, the *l*-acid having b. p. 121—122°/20 mm.,  $d_4^{25}$  0.909,  $[\alpha]_D^{25} - 15.25^\circ$  in ether (sodium salt,  $[\alpha]_D^{25} - 4.25^\circ$  in water); the *d*-acid,  $[\alpha]_D^{25} + 5.42^\circ$ , yielded successively the *d*-acid chloride, b. p. 45—48°/9 mm.,  $d_4^{25}$  0.952,  $[\alpha]_D^{25} + 4.49^\circ$  in ether, the *d*-amide, m. p. 66°,  $[\alpha]_D^{25} + 3.86^\circ$  in 75% alcohol, the *d*-nitrile, b. p. 43—50°/9 mm.,  $d_4^{25}$  0.797,  $[\alpha]_D^{25} + 9.16^\circ$  in ether, and the *l*-amine, b. p. 49—54°/15 mm.,  $[\alpha]_D^{25} - 3.52^\circ$  in ether (hydrochloride,  $[\alpha]_D^{25} - 2.41^\circ$  in water); ethyl *l*- $\alpha$ -methyl-*n*-hexoate,  $[\alpha]_D^{25} - 13.75^\circ$  in ether (*d*-ester, b. p. 58—62°/9 mm.,  $d_4^{25}$  0.860), gave *d*- $\beta$ -methyl-*n*-hexanol, b. p. 71—72°/15 mm.,  $[\alpha]_D^{25} + 2.47^\circ$  in ether. *d*- $\alpha$ -Methyl-*n*-nonoic acid, b. p. 145—147°/4 mm.,  $d_4^{25}$  0.893,  $[\alpha]_D^{25} + 9.16^\circ$  in ether (sodium salt,  $[\alpha]_D^{25} + 0.84^\circ$  in water), obtained by resolution of the racemic acid with cinchonidine (*l*-acid,  $[\alpha]_D^{25} - 13.15^\circ$  in ether), yielded successively the *d*-acid chloride, b. p. 73—74°/1 mm.,  $d_4^{25}$  0.894,  $[\alpha]_D^{25} + 5.02^\circ$  in ether, the *d*-amide, m. p. 78°,  $[\alpha]_D^{25} + 7.07^\circ$  in 95% alcohol, the *d*-nitrile, b. p. 85—94°/7 mm.,  $d_4^{25}$  0.809,  $[\alpha]_D^{25} + 14.74^\circ$  in ether, and the *l*-amine, b. p. 103—105°/25 mm.,  $d_4^{25}$  0.789,

$[\alpha]_D^{25}$   $-3.43^\circ$  in ether (*hydrobromide*,  $[\alpha]_D^{25}$   $-4.61^\circ$  in 75% alcohol); the *l*-nitrile,  $[\alpha]_D^{25}$   $-15.10^\circ$ , gave the *d*-amine,  $[\alpha]_D^{25}$   $+6.05^\circ$  in ether (*hydrobromide*,  $[\alpha]_D^{25}$   $+5.91^\circ$ ); the *l*-amine yielded, with hydrobromic acid and sodium nitrite, *d*- $\alpha$ -bromo- $\beta$ -methyl-*n*-nonane, b. p.  $80-85^\circ/4$  mm.,  $d_4^{25}$  1.082,  $[\alpha]_D^{25}$   $+2.18^\circ$  in ether; *ethyl 1- $\alpha$ -methyl-*n*-nonoate*, b. p.  $122-124^\circ/17$  mm.,  $d_4^{25}$  0.856,  $[\alpha]_D^{25}$   $-8.99^\circ$  in ether, gave *d*- $\beta$ -methyl-*n*-nonanol, b. p.  $80-82^\circ/4$  mm.,  $[\alpha]_D^{25}$   $+4.27^\circ$  in ether.  $\alpha$ -Methyl-*n*-dodecoic acid was resolved with cinchonidine, giving a *d*-acid, b. p.  $153^\circ/1$  mm.,  $d_4^{25}$  0.884,  $[\alpha]_D^{25}$   $+9.12^\circ$  in ether (sodium salt,  $[\alpha]_D^{25}$   $0^\circ$ ), and an *l*-acid,  $[\alpha]_D^{25}$   $-6.38^\circ$  in ether, which yielded the *l*-acid chloride, b. p.  $118-125^\circ/0.5$  mm.,  $d_4^{25}$  0.908,  $[\alpha]_D^{25}$   $-3.35^\circ$  in ether, the *l*-amide, m. p.  $77^\circ$ ,  $[\alpha]_D^{25}$   $-3.01^\circ$  in 95% alcohol, the *l*-nitrile, b. p.  $108-110^\circ/0.5$  mm.,  $[\alpha]_D^{25}$   $-10.87^\circ$  in ether, and the *d*-amine,  $d_4^{25}$  0.806,  $[\alpha]_D^{25}$   $+5.23^\circ$  in ether (*hydrochloride*, m. p.  $118^\circ$ ,  $[\alpha]_D^{25}$   $+3.17^\circ$  in water); the latter amine, with nitrosyl bromide, gave *l*- $\alpha$ -bromo- $\beta$ -methyl-*n*-dodecane, b. p.  $87-90^\circ/0.02$  mm.,  $d_4^{25}$  1.168,  $[\alpha]_D^{25}$   $-0.19^\circ$  in ether. *Ethyl 1- $\alpha$ -methyl-*n*-dodecoate*, b. p.  $141^\circ/1$  mm.,  $d_4^{25}$  0.845,  $[\alpha]_D^{25}$   $-5.89^\circ$  in ether, gave *d*- $\beta$ -methyl-*n*-dodecanol, b. p.  $105^\circ/1.4$  mm.,  $d_4^{25}$  0.844,  $[\alpha]_D^{25}$   $+2.52^\circ$  in ether (*hydrogen phthalate*,  $[\alpha]_D^{25}$   $-0.39^\circ$  in ether). *d*- $\beta$ -Methyl-*n*-butanol,  $[\alpha]_D^{25}$   $-4.73^\circ$  in ether, yielded *d*- $\alpha$ -iodo- $\beta$ -methyl-*n*-butane, b. p.  $47-50^\circ/22$  mm.,  $[\alpha]_D^{25}$   $+5.27^\circ$  in ether, which, with potassium hydrogen sulphide, gave *d*- $\alpha$ -thiol- $\beta$ -methyl-*n*-butane, b. p.  $116-117^\circ$ ,  $[\alpha]_D^{25}$   $+6.92^\circ$  in ether; the latter, when oxidised with permanganate, afforded *d*- $\beta$ -methyl-*n*-butane-sulphonic acid,  $[\alpha]_D^{25}$   $+8.46^\circ$ , barium salt,  $[\alpha]_D^{25}$   $+5.09^\circ$ , both in water). C. R. HARINGTON.

**Highly polymerised compounds. XXXI.** Polyacrylic acid and polyacrylic esters. H. STAUDINGER and E. URECH (Helv. Chim. Acta, 1929, 12, 1107-1133).—Polymerisation of acrylic acid by light at the ordinary temperature, or by heating at  $100^\circ$ ,  $150^\circ$ , and  $200^\circ$ , gives products of varying physical properties (solubility and behaviour in different liquids). The viscosity of solutions of the alkali salts of the polyacrylic acids is greater than for the corresponding acids; the alkali salts dissolve in water after much swelling. The polymerised acids are saturated to bromine and potassium permanganate, and are not oxidised by nitric acid. Methyl acrylate is polymerised readily at  $100^\circ$ , but if the heating is carried out in absence of oxygen, the ester is unchanged after 3 days. At  $150-200^\circ$  polymerisation occurs with explosive violence. The polyacrylic esters cannot be prepared by direct esterification of the acids, but the esters are hydrolysed to the acids by hydriodic, hydrochloric, and nitric acids and 30% potassium hydroxide solution.

Treatment of polymerised methyl acrylate with magnesium methyl iodide in anisole solution at  $100^\circ$  gives the corresponding impure *tert*-alcoholic derivative. This is reduced by a 30% solution of hydrogen iodide in acetic acid at  $120^\circ$  to a solid hydrocarbon, *M* 1250, probably a polymerised cyclohexane derivative. During the polymerisation of the amide and anilide of acrylic acid some imide formation occurs.

[With S. WEHRLLI].—Treatment of polystyrene with ozone in carbon tetrachloride solution, decomposition

of the resulting ozonide with water, and subsequent oxidation of the product formed with nitric acid affords a polyacrylic acid (water-soluble) similar to that obtained from polymerised methyl acrylate by hydrolysis with nitric acid.

H. BURTON.

**Highly polymerised compounds. XXXII.** Structure of organic compounds of high mol. wt. in relation to Kekulé's doctrine of structure. H. STAUDINGER (Helv. Chim. Acta, 1929, 12, 1183-1197).—A lecture.

H. BURTON.

**Chemistry of the three-carbon system. XXIII.** Influence of substituent groups on the tautomeric change. R. P. LINSTADT (J.C.S., 1929, 2498-2510).—The general interpretation of the influence of substituents on the mobility and equilibrium of three-carbon systems, outlined by Ingold, is reviewed in the light of recent quantitative data. It is necessary to recognise the operation of non-polar factors in determining equilibrium and in this connexion attention is directed to the influence of conjugation, steric effects, and strain.

The equilibration of *isohexenoic* esters in alcoholic sodium ethoxide has been investigated and it is found that, although there is a marked tendency towards the  $\beta\gamma$ -ester, the system is complicated by the relatively more rapid formation of *ethyl  $\beta$ -ethoxyisohexoate*, b. p.  $79^\circ/8$  mm.,  $d_4^{27}$  0.9166,  $n_D^{27}$  1.4197, which could be isolated from the higher fractions of the reaction mixture. The two esters, *ethyl  $\Delta^2$ -isohexenoate*, b. p.  $60^\circ/13$  mm.,  $d_4^{27}$  0.8978,  $n_D^{27}$  1.4341, and *ethyl pyroterebate* ( $\Delta^2$ -isohexenoate), b. p.  $58^\circ/11$  mm.,  $d_4^{27}$  0.9134,  $n_D^{27}$  1.4329, were obtained by direct esterification of the acids. The proportions of the three products in the reaction mixture were obtained from the iodine addition, conditioned by the  $\beta\gamma$ -ester, and from a determination of the physical constants. The velocity of the change is greater than with any ester yet investigated and the equilibrium lies approximately at the ratio  $\beta\gamma$  :  $\alpha\beta$ -ester = 90 : 10. The action of thionyl chloride on pyroterebic acid gave a fraction consisting of  $\gamma$ -chloroisohexoyl chloride, from which the corresponding anilide, m. p.  $143.2^\circ$ , and *ethyl ester*, b. p.  $89-92^\circ/13$  mm., were obtained.

T. H. MORTON.

**Modes of addition to conjugated unsaturated systems. II. Reduction of conjugated unsaturated acids by metals dissolving in aqueous media.** H. BURTON and C. K. INGOLD (J.C.S., 1929, 2022-2037; addendum to A., 1929, 1270).—The percentages of 1 : 2-dihydro-isomeride formed in aqueous sodium hydrogen carbonate medium using sodium amalgam were : from vinylacrylic acid 0, from sorbic acid 40, from  $\beta$ -methylsorbic acid 28, from  $\beta\delta$ -dimethylsorbic acid 38%; in aqueous acetic acid vinylacrylic acid yielded 18% and sorbic acid 55% of 1 : 2-dihydro-compound. These results are in accord with the theory put forward. The following substances are described. *Ethyl bromoacetate*, *ethylideneacetone*, and zinc yield *ethyl  $\beta$ -hydroxy- $\beta$ -methyl- $\Delta^2$ -hexenoate*, b. p.  $89-93^\circ/12$  mm., converted by distillation under atmospheric pressure into  *$\beta$ -methylsorbic acid*, m. p.  $120^\circ$  (corresponding *amide*, m. p.  $147-148^\circ$ , and *anilide*, m. p.  $134-135^\circ$ ), and an isomeric  *$\beta$ -methylsorbic acid*, m. p.  $74-76^\circ$ . *Ethyl*

$\beta$ -bromobutyrate and ethyl sodioacetoacetate afford ethyl  $\alpha$ -acetyl- $\beta$ -methylglutarate, b. p. 148—150°/10 mm., from which  $\beta$ -methyl- $\Delta^7$ -hexenoic acid, b. p. 103—105°/9 mm., is derived. A compound,  $C_{14}H_{22}O_4$ , m. p. 198—199°, is isolated from the products of the reduction of  $\beta$ -methylsorbic acid by sodium amalgam in presence of sodium hydrogen carbonate.

H. WREN.

**Derivatives of undecenoic acid.** [MLLE.] J. LEVY and F. WELLISCH (Bull. Soc. chim., 1929, [iv], 45, 930—940).—When treated with perbenzoic acid in chloroform, methyl undecenoate is converted into methyl  $\alpha$ -oxidoundecate, b. p. 148—153°/15 mm.,  $d_4^{20}$  0.959,  $n_D^{20}$  1.447; methyl  $\alpha$ -dihydroxyundecate has m. p. 56—57°. Similarly, ethyl undecenoate yields an ethylene oxide, b. p. 164—168°/16 mm.,  $d_4^{22}$  0.810,  $n_D^{20}$  1.445, which when distilled in presence of zinc chloride isomerises to ethyl  $\alpha$ -ketodecote, b. p. 180—190°/17 mm.,  $d_4^{20}$  0.899,  $n_D^{20}$  1.441 (semicarbazone, m. p. 108—109°); ethyl  $\alpha$ -dihydroxyundecate has m. p. 43—44°.  $\gamma$ -Ethyl- $\Delta^7$ -tridecen- $\gamma$ -ol, b. p. 162—164°/17 mm.,  $d_4^{20}$  0.846,  $n_D^{20}$  1.456, obtained by the action of magnesium ethyl bromide on ethyl undecenoate, with perbenzoic acid similarly affords an ethylene oxide, b. p. 187—192°/17 mm.,  $d_4^{20}$  0.940,  $n_D^{20}$  1.462, hydrolysed to  $\gamma$ -ethyltridecane- $\gamma,\mu,\nu$ -triol, b. p. 210°/19 mm.,  $d_4^{17}$  0.937,  $n_D^{20}$  1.468.  $\delta$ -Propyl- $\Delta^7$ -tetradecen- $\delta$ -ol, b. p. 204—208°/13 mm.,  $d_4^{17}$  0.824,  $n_D^{20}$  1.458 (ethylene oxide derivative, b. p. 175—185°/17 mm.,  $d_4^{17}$  0.855,  $n_D^{20}$  1.451),  $\delta$ -propyltetradecane- $\delta,\nu,\xi$ -triol, m. p. 79°, and  $\alpha,\alpha$ -diphenyl- $\Delta^7$ -undecen- $\alpha$ -ol, b. p. 230°/15 mm.,  $d_4^{17}$  0.949,  $n_D^{20}$  1.556 (ethylene oxide derivative, b. p. 270—280°/17 mm.,  $d_4^{17}$  0.989,  $n_D^{20}$  1.542), are similarly obtained.  $\Delta^7$ -Tridecen- $\gamma$ -one, b. p. 138—142°/17 mm.,  $d_4^{17}$  0.844,  $n_D^{20}$  1.446 [semicarbazone, m. p. 77—78°; oxime, b. p. 168—171°/15 mm., reduced with sodium and alcohol to ethylundecenylamine (hydrochloride, m. p. 85—86°)], from magnesium ethyl bromide and undecenoamide (yield 55%), similarly yields an ethylene oxide, b. p. 172—180°/21 mm., m. p. 37—38° [oxime, b. p. 165—175°/17 mm.,  $d_4^{18}$  0.952,  $n_D^{20}$  1.478, reduced to ethyloxidoundecylamine (hydrochloride, m. p. 82—83°)], which in presence of zinc chloride is isomerised to a product, b. p. 185—195°/21 mm., m. p. 58—59° (semicarbazone, m. p. 84°); tridecan- $\gamma$ -one- $\mu,\nu$ -diol has m. p. 65—66°.  $\Delta^7$ -Tetradecen- $\delta$ -one, b. p. 144—145°/14 mm.,  $d_4^{18}$  0.854,  $n_D^{20}$  1.541 [semicarbazone; oxime, m. p. 182—184°/17 mm.,  $d_4^{18}$  0.862,  $n_D^{20}$  1.471, reduced to propylundecenylamine (hydrochloride, m. p. 68—69°)], similarly obtained, yields an ethylene oxide, m. p. 37—38°, b. p. 180°/15 mm. (oxime, an oil), and  $\alpha$ -phenyl- $\Delta^7$ -undecen- $\alpha$ -one, m. p. 27—28°, b. p. 195°/13 mm. [semicarbazone, m. p. 107°; oxime, m. p. 44—45°, reduced to phenylundecenylamine (hydrochloride, m. p. 116—117°)], an ethylene oxide, m. p. 37—38°, b. p. 225°/14 mm. [oxime, m. p. 50°, yielding with sodium and alcohol phenyloxidoundecenylamine (hydrochloride, m. p. 103—104°)]. Tetradecan- $\delta$ -one- $\nu,\xi$ -diol has m. p. 54°; undecan- $\alpha$ -one- $\alpha$ -diol, m. p. 57—58°.

R. BRIGHTMAN.

**Acid sodium laurates.** P. EKWALL and W. MYLIUS (Ber., 1929, 62, [B], 2687—2690; cf. A., 1929, 676).—By crystallisation of suitable mixtures of the components from aqueous ethyl alcohol the

following acid sodium laurates have been isolated:

$C_{12}H_{23}O_2Na, 2C_{12}H_{23}O_2$ , m. p. 67—68°;  
 $C_{12}H_{23}O_2Na, C_{12}H_{24}O_2$ , m. p. 118—119°;  
 $2C_{12}H_{23}O_2Na, C_{12}H_{24}O_2$ , m. p. 136—138°. The individuality of the substances is confirmed by microscopical examination; determination of mol. wt. in camphor is impossible except in the case of the salt  $2C_{12}H_{23}O_2Na, C_{12}H_{24}O_2$ , on account of the rapid decomposition induced by the high temperature.

H. WREN.

**Transformation of oleic into elaidic acid by means of sulphur.** G. RANKOFF (Ber., 1929, 62, [B], 2712—2717).—When heated with water and 1% of flowers of sulphur at 180° for 3 hrs., oleic acid is converted to the extent of about 50% into elaidic acid, m. p. 44.4°,  $n_D$  1.4308. If the amount of sulphur is increased, the elaidic acid becomes mixed with compounds of higher m. p. which appear to be due to the hydrogen sulphide generated from sulphur and oleic acid. Homogeneous elaidic acid is obtained from oleic acid and saturated sodium hydrogen sulphite solution only if the temperature is not allowed to exceed 150°; the transformation does not begin until sulphur, produced by the reaction  $3NaHSO_3 = Na_2SO_4 + NaHSO_4 + S + H_2O$ , has separated.

H. WREN.

**$\omega$ -Hydroxy-aliphatic acids. II. Conversion of  $\alpha$ -hydroxydecoic acid into chain poly-inter-molecular esters and into a dimeric cyclic ester.** W. H. LYCAN and R. ADAMS (J. Amer. Chem. Soc., 1929, 51, 3450—3464).—When  $\alpha$ -hydroxydecoic acid is heated alone or with various inert solvents (in absence or presence of a catalyst such as *p*-toluene-sulphonic acid) mixtures of esters of the type  $HO[CH_2]_xCO_2 \cdot ([CH_2]_xCO_2)_n \cdot [CH_2]_xCO_2H$  are obtained. These melt at 74—77°, contain free hydroxyl (acetylation) and carboxyl groups, and determination of the mol. wt. by titration gives values of 2000—9000, according to the reaction temperature. Fractional crystallisation of mixtures causes some separation into products with mol. wt. of 1000—9000. These polymerides are hydrolysed by an excess of potassium hydroxide solution to the original acid.

When potassium  $\alpha$ -hydroxydecoate is heated with acetic anhydride and the dry reaction product then distilled in a vacuum (5 mm.), about 5% of the dimeric lactone, m. p. 95—95.5°, of  $\alpha$ -hydroxydecoic acid is obtained. This is hydrolysed by alcoholic potassium hydroxide solution to the original hydroxy-acid.  $\alpha$ -Acetoxydecoic acid, b. p. 168—170°/1 mm., m. p. 35—36° (corr.), can be distilled unchanged.

H. BURTON.

**Preparation of mono-esters of dicarboxylic acids. II.** E. FOURNEAU and S. SABETAY (Bull. Soc. chim., 1929, [iv], 45, 834—842).—The method of preparing mono-esters of dicarboxylic acids previously described (A., 1928, 1115) has now been extended to acids containing an uneven number of carbon atoms. The failure of the method with malonic acid is accordingly exceptional and is not due to the uneven number of carbon atoms. The yields obtained (25—33%), whilst higher than those obtained by Contzen-Crowet (A., 1926, 938) or by Skrabal and Mrazek, are low on account of decomposition of the mono-esters into di-esters and di-acids if the reaction temperature is too

high. Molecular proportions of the di-acid and di-ester are used. Methyl, b. p. 150—151°/10 mm.,  $d^{15}_4$  1.164,  $n^{20}_D$  1.4392, and ethyl hydrogen glutarate, b. p. 143—145°/7 mm.; ethyl hydrogen pimelate, b. p. 162°/6 mm.,  $n^{20}_D$  1.4415; ethyl hydrogen azelate, b. p. 178—179°/5.5 mm., m. p. 28—29°, and methyl hydrogen succinate, m. p. 56°, b. p. 121—123°/4 mm., are described. For the preparation of ethyl hydrogen oxalate a reaction temperature of 120—130° is recommended. Sulphuric acid may be used as catalyst and the hydrogen oxalate is distilled at 5 mm.

R. BRIGHTMAN.

**Preparation of dimethylated polymethylene-dicarboxylic acids and their derivatives.** P. CHUIT, F. BOELSING, and G. MALET (Helv. Chim. Acta, 1929, 12, 1096—1106).—Condensation of  $\alpha$ -dibromononane with ethyl sodiomethylmalonate in alcoholic benzene, hydrolysis of the ester formed, and subsequent thermal decomposition of the intermediate tetracarboxylic acid, m. p. 162°, yields trans- $\alpha\lambda$ -dimethylundecane- $\alpha\lambda$ -dicarboxylic acid, m. p. 67—68° [methyl ester (I), b. p. 167—168°/1.5 mm.,  $d^{15}_4$  0.9525]; the cis-form has not been obtained pure. Reduction of I with sodium and alcohol affords  $\beta\mu$ -dimethyltridecane- $\alpha\lambda$ -diol, b. p. 181°/2 mm., m. p. 11° [corresponding impure dibromide (II), b. p. 184°/4 mm.,  $d^{15}_4$  1.221]. Condensation of  $\alpha\kappa$ -dibromodecane with ethyl sodiomethylmalonate, or methylation of ethyl disiododecane- $\alpha\alpha\mu\mu$ -tetracarboxylate with methyl bromide, and subsequent treatment of the product as above affords cis-, m. p. 66—67.5°, and trans- $\alpha\mu$ -dimethyldodecane- $\alpha\mu$ -dicarboxylic acid, m. p. 111—111.4° (methyl ester, b. p. 179—180°/3.4 mm.,  $d^{15}_4$  0.947; ethyl ester, b. p. 190—191°/3.5 mm.,  $d^{15}_4$  0.932).  $\beta\nu$ -Dimethyltetradecane- $\alpha\xi$ -diol [corresponding impure dibromide (III), b. p. 215°/7 mm.,  $d^{15}_4$  1.166] has b. p. 207—210°/8 mm., m. p. 57.5—58°. Treatment of II with aqueous-alcoholic potassium cyanide and subsequent hydrolysis of the intermediate dinitrile, b. p. 185—186°/0.25 mm.,  $d^{15}_4$  0.887, gives a mixture of cis-, m. p. 50°, and trans- $\beta\mu$ -dimethyltridecane- $\alpha\nu$ -dicarboxylic acid, m. p. 63—64°. Similarly, the dinitrile, b. p. 197°/3 mm., from III furnishes a mixture of cis-, m. p. 66.5—67° (methyl ester, b. p. 178—183°/1.5 mm., m. p. about 13°), and trans- $\beta\nu$ -dimethyltetradecane- $\alpha\xi$ -dicarboxylic acid, m. p. 81—81.5°. cis- and trans- $\alpha\xi$ -Dimethyltetradecane- $\alpha\xi$ -dicarboxylic acids, m. p. 83—84° and 110—110.2°, respectively; cis- and trans- $\alpha\sigma$ -dimethylpentadecane- $\alpha\sigma$ -dicarboxylic acids, m. p. 65—67° and 80—81°, respectively; cis- and trans- $\gamma\nu$ -dimethylpentadecane- $\alpha\sigma$ -dicarboxylic acids, m. p. about 48—51° and about 59—60°, respectively, and trans- $\gamma\xi$ -dimethylhexadecane- $\alpha\nu$ -dicarboxylic acid, m. p. 104—105° (methyl ester, b. p. 205—207°/1.7 mm.,  $d^{15}_4$  0.9518), are prepared from ethyl sodiomethylmalonate and  $\alpha\mu$ -dibromodecane,  $\alpha\nu$ -dibromotridecane, II, and III, respectively. H. BURTON.

**Mechanism of the degradation of fatty acids by mould fungi.** IV. V. SUBRAMANIAM, H. B. STENT, and T. K. WALKER (J.C.S., 1929, 2485—2492; cf. A., 1929, 1271).—The first product of the action of *Aspergillus niger* in calcium succinate media is malic acid, followed after a period of 24—72 hrs. by the formation of pyruvic and malonic acids. It is

supposed that a transitory formation of oxaloacetic acid precedes that of pyruvic acid. From the products of oxidation of succinic acid by hydrogen peroxide, in the presence of a relatively large amount of ferrous salt, malonic acid was isolated and malic acid detected by oxidation to oxaloacetic acid. Oxidation of succinic acid with ammoniacal hydrogen peroxide gave larger yields of malonic acid. Since tartaric acid could not be isolated, fumaric acid cannot be among the intermediate products.

From the similarity of the two degradations the activity of the mould must, in this case, be assigned to a peroxidase action alone. T. H. MORTON.

**$\delta$ -Ketorhammonic acid; derivatives suitable for identification.** E. VOTOČEK and S. MALACHTA (Anal. Fís. Quím., 1929, 27, 494—499).— $\delta$ -Ketorhamnonolactone is formed as a by-product in the preparation of rhamnonolactone by the oxidation of rhamnose with bromine water, and may be prepared by the oxidation of rhamnonolactone with bromine water. In these reactions it is advantageous to add copper-bronze and cuprous oxide in succession to the reaction mixture to remove excess of bromine and hydrobromic acid.  $\delta$ -Ketorhamnonolactone forms an oxime, m. p. 191—192°; phenylhydrazone, m. p. 165°; o-nitrophenylhydrazone, m. p. 192—193°; m-nitrophenylhydrazone, m. p. 190°, and p-bromophenylhydrazone, m. p. 175°.

R. K. CALLOW.

**Preparation of allomucic acid.** S. POSTERNAK and T. POSTERNAK (Helv. Chim. Acta, 1929, 12, 1181—1183).—Experimental details are given for the preparation of allomucic acid (cf. A., 1929, 807) [calcium salt (+4H<sub>2</sub>O); phenylhydrazide, m. p. 218° (decomp.)]. H. BURTON.

**Crystalline aldobionic acid from gum arabic.** M. HEIDELBERGER and F. E. KENDALL (J. Biol. Chem., 1929, 84, 639—653).—The calcium aldobionate previously obtained (A., 1929, 1201) by hydrolysis of gum arabic was converted into the cinchonidine salt,  $[\alpha]_D$  —64.9°, m. p. 172° (decomp.) when anhydrous, converted through the barium salt into the crystalline aldobionic acid, C<sub>12</sub>H<sub>20</sub>O<sub>12</sub>·2H<sub>2</sub>O, m. p. 116°, effervescing at 128°. The compound was obtained more directly by hydrolysis of gum arabic with N-sulphuric acid, followed by removal of the latter, concentration of the solution, and purification of the acid through the barium salt. The yield was 17.5% of the gum employed; the acid had  $[\alpha]_D$  +10.5° to —7.75° (air-dried) and +11.6° to —8.56° (anhydrous) in water; no evidence of lactone formation was obtained. After complete hydrolysis with N-sulphuric acid, glycuronic acid and galactose were obtained. When oxidised with hypiodite the aldobionic acid gave a dicarboxybionic acid,  $[\alpha]_D$  —28.4° to 45.1° in water (calcium salt,  $[\alpha]_D$  —22.83° in water), which, on hydrolysis, yielded galactonic and glycuronic acids. When oxidised with nitric acid, the aldobionic acid afforded saccharic acid; with methyl-alcoholic hydrogene chloride at 100° it gave the methyl aldobionate- $\alpha$ -methylglucoside,  $[\alpha]_D$  +22.8° (the free acid had  $[\alpha]_D$  +5.72° and the sodium salt  $[\alpha]_D$  +5.34°); at 25° the methyl aldobionate- $\beta$ -glucoside,  $[\alpha]_D$  —66.4°, was formed. Both glucosides were hydrolysed at the same (slow) rate and therefore possessed the amylen oxide



structure; the aldobionic acid is therefore regarded as  $\alpha$ (or  $\beta$ )-glycurono-3(or 6)- $\alpha$ -galactose. The mother-liquors from the isolation of the above acid yielded the alcohol-insoluble barium salt of a dicarboxyaldotetric acid,  $C_{21}H_{35}O_{18}(CHO)(CO_2H)_2$ ,  $[\alpha]_D -8.8^\circ$ .

C. R. HARRINGTON.

**cis-trans-Isomeric  $\beta$ -mercaptocrotonic esters, desmotropic thioacetoacetic ester, and their derivatives.** I. H. SCHEIBLER, H. T. TOPOUZADA, and H. A. SCHULZE (J. pr. Chem., 1929, [ii], 124, 1—28).

—The action of ethyl  $\beta$ -chloroisocrotonate on sodium hydrogen sulphide in alcohol gave ethyl  $\beta$ -thiolcrotonate, b. p.  $77^\circ/18$  mm.,  $d_4^{25}$  1.0747,  $n_D$  1.53749 (iron, copper, and lead salts), after repeated fractional distillation. A separation of isomerides formed during the action was effected by treating an ethereal solution successively with cold concentrated potassium hydrogen carbonate, cold concentrated sodium carbonate solution, and distillation of the residue. Ethyl sodio- $\beta$ -thiolcrotonate reacted (1) with benzyl chloride in the presence of sodium ethoxide and ethyl alcohol, producing ethyl  $\beta$ -benzylthiolisocrotonate, b. p.  $193^\circ/12$  mm., accompanied by some ethyl  $\beta$ -benzylthiol- $n$ -crotonate, m. p.  $64^\circ$ ; (2) with benzoyl chloride and ether, giving ethyl  $\beta$ -benzoylthiolcrotonate, b. p.  $195$ — $198^\circ/12$  mm., which with phenylhydrazine afforded benzoylphenylhydrazine; (3) with ethyl chloroformate in ethereal solution to form ethyl  $\beta$ -carbethoxythiolcrotonate, b. p.  $148$ — $150^\circ/11$  mm.; (4) with ethereal acetyl chloride, producing ethyl  $\beta$ -acetylthiolcrotonate, b. p.  $132$ — $133^\circ/12$  mm.; (5) with alcoholic ethyl chloroacetate, with formation of ethyl  $\beta$ -carbethoxymethylthiolcrotonate, b. p.  $168$ — $178^\circ/10$  mm., m. p.  $45^\circ$ .

Treatment of methyl  $\beta$ -chloroisocrotonate, b. p.  $141^\circ/760$  mm., with sodium hydrosulphide led to methyl  $\beta$ -thiolcrotonate, b. p.  $68$ — $69^\circ/12$  mm.,  $d_4^{25}$  1.1124,  $n_D$  1.52217 (lead and copper salts). The sodio-derivative of this ester gave (1) with methyl iodide or diazomethane in ether, methyl  $\beta$ -methylthiolcrotonate, m. p.  $58^\circ$ , b. p.  $117^\circ/12$  mm.; (2) with ethereal benzyl chloride, methyl  $\beta$ -benzylthiol- $n$ -crotonate, b. p.  $185^\circ/12$  mm., m. p.  $73^\circ$ ; (3) with methyl-alcoholic methyl chloroacetate, methyl  $\beta$ -carbethoxymethylthiolcrotonate, b. p.  $172$ — $175^\circ/13$  mm. (corresponding acid, dimorphous, m. p.  $199$ — $203^\circ$  and  $160$ — $161^\circ$ ; also obtained by hydrolysis of the foregoing corresponding ethyl ester).

Ethyl  $\alpha$ -benzylacetoacetate, benzene, and phosphorus pentachloride reacted to form a product which, by treatment with concentrated hydrochloric acid, yielded one of the isomeric  $\beta$ -chloro- $\alpha$ -benzylcrotonic acids, m. p.  $103^\circ$ ; direct esterification of the mixture of acids afforded methyl  $\beta$ -chloro- $\alpha$ -benzylcrotonates, b. p.  $120$ — $140^\circ/12$  mm. and  $140$ — $155^\circ/12$  mm. A mixture of these isomerides was treated with methyl-alcoholic sodium hydrogen sulphide and an oily mixture of methyl  $\beta$ -thiolcrotonates (lead salts) obtained; these reacted with ethereal diazomethane, giving methyl  $\beta$ -methylthiol- $\alpha$ -benzylcrotonates, b. p.  $145$ — $153^\circ/12$  mm.  $\beta$ -Chloroisocrotonyl chloride has b. p.  $135$ — $136^\circ$  (lit.  $122$ — $140^\circ$ ). R. J. W. LE FÈVRE.

**Oxidising action of "sugi" wood.** T. HIGASHI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 831—

838).—The production of acetaldehyde from ethyl alcohol in contact with sugi wood is due to the oxidising action of terpene. H. F. GILLBE.

**Oxidation of acetaldehyde by oxygen.** E. J. BOWEN and E. L. TIETZ (Nature, 1929, 124, 914).—When acetaldehyde is shaken with oxygen at the ordinary temperature a peroxide is formed. The velocity of reaction between the gaseous substances in ultra-violet light is high; it is approximately proportional to the square root of the intensity of the light, proportional to the aldehyde concentration, and independent of the oxygen concentration. A long chain mechanism of the following type is postulated:  $A + h\nu \rightarrow A^+$ ;  $A^+ + O_2 \rightarrow AO_2^+$ ;  $AO_2^+ + A \rightarrow A^+ + AO_2$ ;  $2AO_2^+ \rightarrow ?$  A. A. ELDRIDGE.

**Condensation reactions.** M. GIUA (Atti R. Accad. Sci. Torino, 1929, 64, 89—93; Chem. Zentr., 1929, ii, 159).—When a mixture of *i*-amyl alcohol, isobutyl alcohol, and acetaldehyde is subjected to catalytic dehydration by a mixture of alumina and chromic oxide the following reactions occur:  $C_5H_{11}OH + CH_3CHO = C_6H_{10} + 2H_2O$ ;  $C_5H_{11}OH + CH_3CHO = C_7H_{12} + 2H_2O$ . Acetone, treated with sodium and then acetylene, then saturated with carbon dioxide and fractionated, affords a compound  $C_5H_8O$ , a liquid, b. p.  $102$ — $104^\circ$ , having a penetrating odour,  $\gamma$ -methylbutinenol, and condensation products of acetone. A. A. ELDRIDGE.

**Citronellal. III. Determination of citronellal.** H. I. WATERMAN and E. B. ELSBACH (Rec. trav. chim., 1929, 48, 1087—1091).—Determination of citronellal by Holtappel's method (B., 1928, 587) is rendered untrustworthy by the interaction of the citronellal with the hydrochloric acid liberated from the hydroxylamine hydrochloride, low values being obtained (e.g., 0.1*N*-alcoholic hydrogen chloride reduces the citronellal content by 50% in 1 hr.). Acetic acid, however, is almost without effect, so that more trustworthy results are obtained by using hydroxylamine acetate or, better, an alcoholic solution of free hydroxylamine prepared by neutralisation of the hydrochloride solution and filtration from the precipitated potassium chloride. Peroxides formed by atmospheric oxidation of citronellal oxidise the hydroxylamine and give high apparent values, depending on the time of reaction. On distillation the peroxides are concentrated in the residue, so that the determination must be carried out with freshly-distilled samples from which air has been excluded. J. W. BAKER.

**Enolisation of ketones.** V. GRIGNARD and H. BLANCHON (Rocz. Chem., 1929, 9, 547—580).—The degree of enolisation of a number of ketones on the addition of various organo-magnesium halides, measured by Zerevitinov's method (cf. A., 1911, i, 101), seems to bear no relation to the structure of the given ketone, but, on the whole, increases with the at. wt. of the halide present in the Grignard reagent, and is greater where tertiary organic radicals are present than primary or secondary. Enolisation using magnesium *tert*-butyl chloride amounts for di-*n*-butyl ketone 24%, for acetone 30%, for acetophenone 31%, for cyclopentanone 32.5%, for thujone

41%, for *p*-methylcyclohexanone 50.5%, for menthone 51%, and for mesityl oxide 60%. Of the above ketones, cyclohexanone contains originally 8.2% of enol, *p*-methylcyclohexanone 6.3%, and mesityl oxide 6.3%, whilst the remainder are normally exclusively in the keto-form. No connexion appears thus to exist between the tendency towards allelotropism of a given substance and its degree of enolisation under the influence of Grignard's reagent. The hydrolysis of enolic esters is best accomplished by the use of 10% oxalic acid solution, which stabilises the free enol. The following enols are prepared: *thujonenol*, b. p. 84–86°/12 mm.,  $d_{20}^{25}$  0.9010,  $n_D^{25}$  1.45001, *carvonol*, b. p. 114–115°/12 mm.,  $d_{20}^{25}$  0.957,  $n_D^{25}$  1.51510, and *mesityl oxide enol* (contaminated with ketone), b. p. 134°/12 mm. A second method for the preparation of enols consisted in converting chlorohydrins into acetates by the action of fused sodium acetate, and then hydrolysing the ester so obtained with oxalic acid solution. The degree of enolisation rises with temperature, the optimum temperature using the first method being 40°. The enols are unstable, tautomerising spontaneously to the keto-form in 10–15 hrs.; this reaction is catalysed by traces of acids or alkali, and to a certain extent retarded by benzoquinone, phthalic anhydride, and oxalic acid.

R. TRUSZKOWSKI.

**Odour and constitution.** I. J. VON BRAUN and H. KRÖPER (Ber., 1929, 62, [B], 2880–2885).—A gradual change in odour is observed as the ketonic group in undecanone is shifted from the  $\beta$  to the  $\zeta$  position.

Ethyl heptylmalonate is converted by *n*-propyl bromide into *ethyl n-propyl-n-heptylmalonate*, b. p. 165°/10 mm. (corresponding acid, m. p. 110–111°), which passes into  $\alpha$ -*n-propyl-nonyl* acid, b. p. 160–162°/10 mm. *Ethyl  $\alpha$ -n-propyl-nonyl* acid, b. p. 135°/15 mm., is reduced to  $\beta$ -*n-propyl-n-nonyl alcohol*, b. p. 132–133°/14 mm., which yields successively  $\beta$ -*n-propyl-n-nonyl bromide*, b. p. 127–129°/11 mm., and *trimethyl- $\beta$ -n-propyl-n-nonylammonium bromide*. The corresponding hydroxide is converted by distillation with potassium hydroxide into *dimethyl- $\beta$ -n-propyl-nonylamine*, b. p. 114–116°/13 mm., which, after conversion into the *methiodide*, m. p. 175°, is converted by the Hofmann degradation into  $\beta$ -*propyl- $\Delta^8$ -nonene*, b. p. 88–90°/13.5 mm.,  $d_4^{25}$  0.7630,  $n_D^{25}$  1.4311. Ozonisation of the hydrocarbon affords *n-propyl n-heptyl ketone*, b. p. 106–107°/13 mm., m. p. 4–5°,  $d_4^{25}$  0.8274,  $n_D^{25}$  1.4248 (*oxime*, b. p. 141°/13 mm.; *semicarbazone*, m. p. 54–56°).

*n*-Butyl *n*-hexyl ketone, b. p. 105–106°/12 mm., m. p. 2°,  $d_4^{25}$  0.8278,  $n_D^{25}$  1.4275 (*semicarbazone*, m. p. 75°; *oxime*, b. p. 143°/14 mm.), is prepared by a similar series of changes involving the following compounds: *ethyl n-butyl-n-hexylmalonate*, b. p. 172–175°/15 mm.; *n-butyl-n-hexylmalonic acid*, m. p. 134°;  $\alpha$ -*n-butyl-n-octioic acid*, b. p. 168–170°/13 mm.; *ethyl  $\alpha$ -n-butyl-n-octioate*, b. p. 134–136°/12 mm.;  $\beta$ -*n-butyl-octyl alcohol*, b. p. 131–133°/12 mm.;  $\beta$ -*n-butyl-octyl bromide*, b. p. 132°/12 mm.; *trimethyl- $\beta$ -n-butyl-octylammonium bromide*; *dimethyl- $\beta$ -n-butyl-octylamine*, b. p. 125°/15 mm., and the *methiodide*, m. p. 145°;  $\beta$ -*n-butyl- $\Delta^8$ -octene*, b. p. 88–89°/14 mm.,  $d_4^{25}$  0.7642,  $n_D^{25}$  1.4317.

Distillation of barium *n*-hexoate yields crude di-*n*-amyl ketone, which, after purification through the oxime, b. p. 141–143°/12 mm., has b. p. 104–106°/13 mm., m. p. –4° to –3°,  $d_4^{25}$  0.8330. H. WREN.

**Formation of *l*-threose.** V. DEULOFEU (J.C.S., 1929, 2458–2460).—The diacetamide compound (annexed formula) of *l*-threose has been prepared by degradation of *l*-xylose by Wohl's method, and the sugar obtained in solution. *l*-Xylose is converted into the syrupy oxime, which yields *tetra-acetyl-l-xyloxynitrile*, m. p. 82°, when heated with acetic anhydride and sodium acetate. Treatment of the nitrile with silver oxide in ammonia solution yields the *diacetamide*, m. p. 165–166°, which gives on hydrolysis a solution of *l*-threose,  $[\alpha]_D^{25}$  –24.6°, from which an osazone, m. p. 165–166°, is obtained. The sugar solution reduces Fehling's solution and reacts with  $\alpha$ -naphthol and naphtharesorcinol, but not with resorcinol.

R. K. CALLOW.

**Structure of normal monosaccharides. VI. 2:3:4-Trimethyl- $\delta$ -rhamnonolactone.** J. AVERY and E. L. HIRST (J.C.S., 1929, 2466–2469).—Oxidation of 2:3:4-trimethylrhamnose with bromine water yields 1:2:3:4-trimethyl- $\delta$ -rhamnonolactone, m. p. 40–41°, b. p. 96°/0.15 mm.,  $[\alpha]_D^{25}$  –130° to –78° in water. Treatment with phenylhydrazine yields the *phenylhydrazone*, m. p. 177°. Oxidation with nitric acid and esterification of the product gives methyl arabotrimethoxyglutarate, the identity of which is confirmed by conversion into the corresponding amide and methylamide (Hirst and Smith, A., 1929, 173). The rates of hydrolysis of 2:3:4-trimethyl- $\delta$ -rhamnonolactone to the acid ( $[\alpha]_D^{25}$  +14.5°) and of conversion of the acid into the lactone have been studied polarimetrically, equilibrium at 64% of lactone being attained after 60–80 hrs. in 1.14% aqueous solution. This behaviour is like that of other  $\delta$ -lactones, and the  $\delta$ -structure of the lactone and pyranose constitution of 2:3:4-trimethylrhamnose are thereby confirmed.

R. K. CALLOW.

**Development of a novel form of stereoisomerism in the sugar series. I. Third variety of triacetylmethylrhamnoside.** W. N. HAWORTH, E. L. HIRST, and E. J. MILLER (J.C.S., 1929, 2469–2479).—Of the three varieties of triacetylmethylrhamnoside, the  $\alpha$ -variety (Hirst and Macbeth, A., 1926, 273) and, almost certainly, the  $\beta$ -variety possess the pyranose structure, and to the  $\gamma$ -variety, which differs essentially in the resistance of one acetyl group to hydrolysis by aqueous alkali, a different ring system has hitherto been assigned (Fischer, Bergmann, and Rabe, A., 1921, i, 94). It is now shown, however, that the  $\gamma$ -variety has the same pyranose structure as the other two varieties. Position 2 has been assigned to the resistant acetyl group, and, since only two varieties ( $\alpha$  and  $\beta$ ), can be accounted for by difference in the configuration of the glucosidic methyl group, the hypothesis of obstruction of the free rotation of the 2-acetyl residue by adjacent groups, analogous to the obstacle theory in the diphenyl series, is put forward. The  $\gamma$ -variety is then assigned a con-

figuration with the 2-acetyl group stabilised and interlocked with the groups in positions 1 and 3, on the same side of the ring.

" $\gamma$ "-Triacetyl-methylrhamnoside, m. p.  $83^\circ$ ,  $[\alpha]_D^{25} +35^\circ$  in alcohol or chloroform, and " $\gamma$ "-monoacetyl-methylrhamnoside,  $[\alpha]_D^{25} +10^\circ$  in alcohol, are prepared by a modification of the method of Fischer, Bergmann, and Rabe (*loc. cit.*) with improved yields in the intermediate stages. 2:3:4-Trimethyl- $\beta$ -methylrhamnoside, m. p.  $53-54^\circ$ ,  $[\alpha]_D^{25} +106^\circ$  in water, may be prepared directly from the monoacetyl derivative by the action of methyl iodide and silver oxide containing 10% of sodium hydroxide. Alternatively, by methylation, using silver oxide prepared with barium hydroxide, 2-monoacetyl-3:4-dimethylmethylrhamnoside, m. p.  $67^\circ$ , b. p. about  $90^\circ/0.1$  mm.,  $n_D^{25} 1.4510$ ,  $[\alpha]_D^{25} +36^\circ$  in water, is obtained, and is hydrolysed by dilute hydrochloric acid to 3:4-dimethylrhamnose, m. p.  $91-92^\circ$ , showing rapid mutarotation,  $[\alpha]_D^{25} -10^\circ$  to  $+18.6^\circ$  in water, which yields when methylated 2:3:4-trimethyl- $\beta$ -methylrhamnoside. 2:3:4-Trimethylrhamnose,  $n_D^{25} 1.4570$ ,  $[\alpha]_D^{25} +27^\circ$  in water, is obtained by hydrolysis, and its identity with the product from  $\alpha$ -methylrhamnoside (Hirst and Macbeth, *loc. cit.*) is shown by its conversion into 2:3:4-trimethyl- $\delta$ -rhamnonolactone by the action of bromine water (Avery and Hirst, preceding abstract). 3:4-Dimethyl- $\delta$ -rhamnonolactone, m. p.  $66-68^\circ$ ,  $[\alpha]_D^{25} -153^\circ$  to  $-119^\circ$  in water, is prepared by the oxidation of 3:4-dimethylrhamnose with bromine water. The rates of hydrolysis of the lactone to the acid ( $[\alpha]_D^{25} -15.9^\circ$ ) and of conversion of the acid into the lactone have been studied polarimetrically, equilibrium at 75% of lactone being attained after 100 hrs. in 1.05% solution, behaviour which confirms the  $\delta$ -lactonic structure.

3:4-Dimethylrhamnonamide, m. p.  $152-155^\circ$ , is prepared from the lactone by the action of methyl-alcoholic ammonia, and the presence of an  $\alpha$ -hydroxy-group in this amide is proved by applying Weerman's reaction (A., 1917, i, 546).

R. K. CALLOW.

**Composition of cholla gum. I. Isolation of *l*-arabinose, *d*-galactose, and *l*-rhamnose.** L. SANDS and R. KLAAS (J. Amer. Chem. Soc., 1929, 51, 3441-3446).—The fat-free gum is hydrolysed with 2% sulphuric acid at  $80^\circ$ , whereby 10% of residue is obtained. The extract is neutralised with calcium carbonate, concentrated, and then treated with alcohol, whereby a calcium salt (A) is precipitated; *l*-arabinose is isolated from the mother-liquors. Hydrolysis of the acid from A with 1% sulphuric acid at  $100^\circ$ , and subsequent treatment as above, give *d*-galactose and a calcium salt (B). The acid from B is hydrolysed by 2% sulphuric acid at  $120^\circ$  to *l*-rhamnose and galacturonic acid. The composition of the dry gum is ash (8.4%), uronic acid (11.5%), arabinose (53.2%), rhamnose (5.5%), galactose (8.4%).

H. BURTON.

**Structure of methylated sugars. I.** C. H. WHITNAH (J. Amer. Chem. Soc., 1929, 51, 3490-3493).—Methylation of dextrose with methyl sulphate and sodium hydroxide solution at  $30^\circ$ , so that the mixture is alkaline to bromothymol-blue and acid to phenolphthalein, gives a product which appears to be

an active or  $\gamma$ -sugar (permanganate oxidation and acid hydrolysis).

H. BURTON.

**Reaction of borate and sugars. II. Optical activity of sugars in borax solution and configuration of mutarotatory isomerides.** M. LEVY and E. A. DOISY. III. F. p. lowering of sugars in borax solutions. M. LEVY (J. Biol. Chem., 1929, 84, 749-762, 763-769).—II. A 0.5M-solution of  $\alpha$ - or  $\beta$ -glucose in 0.05M-borax mutarotates to  $[\alpha]_D +48^\circ$ ; when hydrochloric acid (1.1 equivalents) is added the rotation rises to  $[\alpha]_D +58^\circ$  and then falls to  $+52.3^\circ$ ; this is explained by the liberation of a predominance of  $\alpha$ -glucose from the glucose-borate complex. The rotation of  $\alpha$ -methylglucoside is slightly diminished by the presence of borax, but returns immediately to the normal value on addition of acid. The optical rotation of 2:3:4:6-tetramethylglucose and the rate of oxidation of this compound by hypoiodite are not significantly affected by borax. The glucosidic hydroxyl group and the hydroxyl group attached to the 2-carbon atom are therefore regarded as essential for the reaction with borate, and since the  $\alpha$ -glucose borate predominates  $\alpha$ -glucose must contain these groups in the *cis*-position. In the case of other aldoses similar conclusions are reached.

III. F.-p. determinations in borax solutions of sugars confirm the conclusion that combination takes place between a free sugar and borate, but not between a glucoside or a methylated sugar and borate. The compound formed is thought to consist of 1 mol. of sugar and 1 mol. of sodium metaborate.

C. R. HARRINGTON.

**1-Acyl derivatives of glucose. Synthesis of  $\alpha$ -benzylglucoside.** B. HELFERICH and R. GOOTZ (Ber., 1929, 62, [B], 2788-2792).—Acetobromoglucose is converted by sodium formate in boiling aqueous acetone into  $\beta$ -1-formyltetra-acetyl-*d*-glucose, m. p.  $121^\circ$  (corr.),  $[\alpha]_D^{25} +6.4^\circ$  in chloroform; the  $\beta$ -configuration is established by its non-identity with the  $\alpha$ -derivative obtained under non-reproducible conditions (cf. Gootz, Diss., Greifswald, 1929). Acetobromoglucose and silver methyl phthalate in benzene afford  $\beta$ -1-*o*-carboxymethylbenzoyltetra-acetyl-*d*-glucose, m. p.  $116.5^\circ$  (corr.),  $[\alpha]_D^{25} -7.4^\circ$  in chloroform, whereas silver *p*-toluenesulphonate in boiling ether yields 1-*p*-toluenesulphonyltetra-acetyl-*d*-glucose, highest observed m. p.  $95^\circ$ ,  $[\alpha]_D^{25} +135.6^\circ$  in chloroform, rapidly changing.  $\beta$ -1-Trichloroacetyltetra-acetyl-*d*-glucose, m. p.  $132^\circ$  (corr.),  $[\alpha]_D^{25} -4.2^\circ$  in chloroform, is converted by phenol at  $170^\circ$  into  $\beta$ -tetra-acetylphenylglucoside, m. p.  $127^\circ$ ,  $[\alpha]_D^{25} -29.6^\circ$  in benzene, but the method is not applicable with other phenols.  $\alpha$ -Acetoiodoglucose, conveniently prepared from acetobromoglucose and sodium iodide in acetone at the ordinary temperature, is converted by benzyl alcohol in boiling benzene into tetra-acetyl- $\alpha$ -benzyl-*d*-glucoside, m. p.  $111^\circ$  (corr.),  $[\alpha]_D^{25} +143.3^\circ$  in chloroform,  $[\alpha]_D^{25} +134.3^\circ$  in alcohol, hydrolysed by sodium methoxide in chloroform to  $\alpha$ -benzylglucoside, m. p.  $122^\circ$ ,  $[\alpha]_D^{25} +131^\circ$  in water, which is stable towards emulsin but readily hydrolysed by  $\alpha$ -glucosidase from yeast.

H. WREN.

**Acetone [isopropylidene] compounds of the sugars and their derivatives. XVI. Mixed acyl**

**derivatives of isopropylideneglucose.** H. OHLE, E. EULER, and R. LICHTENSTEIN (Ber., 1929, 62, [B], 2885—2893; cf. A., 1924, i, 497; 1926, 151).—3-Acetylglucose isopropylidene ether, m. p. 122—123°,  $[\alpha]_D^{25}$   $-26.29^\circ$  in alcohol, is converted by a trace of potassium hydroxide in alcohol into 6-acetylglucose isopropylidene ether, m. p. 145°. isopropylidene-glucose and acetic anhydride in pyridine afford 6-acetylglucose isopropylidene ether, m. p. 148°. 3-Acetyl-isopropylideneglucose and benzoyl chloride in pyridine yield 3-acetyl-5 : 6-dibenzoylglucose isopropylidene ether, m. p. 90°,  $[\alpha]_D^{25}$   $-26.64^\circ$  in chloroform. 3-Acetyl-5 : 6-di-*p*-sulphonylglucose isopropylidene ether, m. p. 92°,  $[\alpha]_D^{25}$   $-28.76^\circ$  in chloroform, is prepared with certainty by the short treatment of 5 : 6-di-*p*-toluenesulphonylglucose isopropylidene ether with boiling acetic anhydride, whereas the sulphonation of 3-acetylglucose isopropylidene ether in pyridine gives irregular results. 6-Acetylglucose isopropylidene ether and *p*-toluenesulphonyl chloride in pyridine yield a mixture of 5-*p*-toluenesulphonyl-6-acetylglucose isopropylidene ether, m. p. 133°,  $[\alpha]_D^{25}$   $+16.72^\circ$  in chloroform, and the disulphonyl compound. 3 : 5-Diacetyl-6-benzoylglucose isopropylidene ether, m. p. 108°,  $[\alpha]_D^{25}$   $+7.08^\circ$  in chloroform, is derived from 6-benzoylisopropylideneglucose and boiling acetic anhydride or acetic anhydride and pyridine. 6-*p*-Toluenesulphonyl-1 : 2-isopropylideneglucose and boiling acetic anhydride give 6-*p*-toluenesulphonyl-3 : 5-diacetylglucose isopropylidene ether, m. p. 94°,  $[\alpha]_D^{25}$   $+4.69^\circ$ , which could not be obtained crystalline by the pyridine method. 6-*p*-Toluenesulphonyl-3 : 5-dibenzoylglucose isopropylidene ether, m. p. 97—100°,  $[\alpha]_D^{25}$   $-66.42^\circ$  in chloroform, is prepared by the pyridine method. 5-*p*-Toluenesulphonyl-6-benzoyl-3-acetylglucose isopropylidene ether, m. p. 151°,  $[\alpha]_D^{25}$   $+0.98^\circ$  in chloroform, is obtained by means of acetic anhydride alone or in presence of pyridine. 5-*p*-Toluenesulphonyl-3 : 6-dibenzoylglucose isopropylidene ether, m. p. 143.5—144.5°,  $[\alpha]_D^{25}$   $-24.07^\circ$ , is described. 3- $\alpha$ -Naphthalenesulphonylglucose diisopropylidene ether, m. p. 110—111°,  $[\alpha]_D^{25}$   $-149.2^\circ$  in chloroform,  $[\alpha]_D^{25}$   $-147.5^\circ$  in alcohol, and 3- $\beta$ -naphthalenesulphonylglucose diisopropylidene ether, m. p. 106°,  $[\alpha]_D^{25}$   $-71.47^\circ$  in alcohol, have been prepared.

Josephson's formulation of glucose derivatives (A., 1929, 1278) is criticised. H. WREN.

**Model experiments based on the theory of alcoholic fermentation. II. Oxidation of 1 : 2-isopropylidene-3 : 6-anhydroglucofuranose.** H. OHLE and H. ERLBACH (Ber., 1929, 62, [B], 2758—2760; cf. A., 1929, 913).—Oxidation of isopropylidene-3 : 6-anhydroglucofuranose by aqueous permanganate causes removal of the 6-carbon atom with production of potassium isopropylidene-1-xyluronate, gradual decomp. above 260°,  $[\alpha]_D^{25}$   $-51.1^\circ$  in water. The corresponding calcium salt, decomp. above 260°, and the phenylhydrazide of 1-xyluronic acid phenyllosazone, m. p. 165—170°,  $[\alpha]_D^{25}$  about  $+3.34^\circ$  in pyridine, are described. H. WREN.

**Two isomeric crystalline compounds of *d*-mannose with calcium chloride.** J. K. DALE

(Bur. Stand. J. Res., 1929, 3, 459—468).—On cooling a concentrated solution of  $\beta$ -*d*-mannose in concentrated calcium chloride the compound  $C_6H_{12}O_6 \cdot CaCl_2 \cdot 4H_2O$  m. p. 101—102° (corr.),  $[\alpha]_D^{25}$   $+6.72^\circ$ , separates. The compound showed an extremely rapid initial rate of mutarotation from about  $[\alpha]_D^{25}$   $-30^\circ$  to a positive maximum, varying with the solvent and the temperature, followed by a slow decrease to a constant value; hence it appears that the sugar in the compound is a new form of mannose. Application of Hudson's rule indicates that it is the  $\beta$ -form corresponding in ring structure with  $\alpha$ -mannose,  $[\alpha]_D^{25}$   $+30^\circ$ , and having an initial  $[\alpha]_D^{25}$  of  $-60^\circ$  in aqueous solution. When this compound is dissolved in hot absolute alcohol and the solution set aside to cool, hard triangular prisms of the compound  $C_6H_{12}O_6 \cdot CaCl_2 \cdot 2H_2O$ , m. p. 159—160° (corr.),  $[\alpha]_D^{25}$   $+6.73^\circ$ , separate. This substance is derived from the previously known  $\beta$ -mannose and, unlike the first, is readily converted into a penta-acetate. A. R. POWELL.

**Acetone [isopropylidene] compounds of mercaptals of certain monosaccharides. II. Derivatives of *d*-mannose.** E. PACSU and C. VON KARY (Ber., 1929, 62, [B], 2811—2817; cf. A., 1924, i, 712).—*d*-Mannose diethylmercaptal is converted by acetone in the presence of anhydrous copper sulphate into 2 : 3-isopropylidenemannose diethylmercaptal,  $C_{12}H_{26}O_5S_2$ , m. p. 94°,  $[\alpha]_D^{25}$   $-11.30^\circ$  in *s*-tetrachloroethane, and the non-crystalline 2 : 5 : 5 : 6-diisopropylidenemannose diethylmercaptal. Treatment of the isopropylidene compound with metallic sodium in ether yields the sodium derivative, which, with methyl iodide, affords a non-crystalline (?) methyl-2 : 3-isopropylidenemannose diethylmercaptal, leading to a syrupy methyl-*d*-mannose diethylmercaptal. The (?) 4 : 5 : 6-trimethyl-2 : 3-isopropylidene-*d*-mannose diethylmercaptal obtained by means of methyl sulphate and the product obtained by removing the isopropylidene group from it are non-crystalline.

*d*-Mannose, benzyl mercaptan, and hydrogen chloride afford *d*-mannose dibenzylmercaptal,  $C_{20}H_{26}O_5S_2$ , m. p. 126°,  $[\alpha]_D^{25}$   $-32.92^\circ$  in pyridine, converted by acetone and concentrated sulphuric acid into 2 : 3 : 5 : 6-diisopropylidene-*d*-mannose dibenzylmercaptal,  $[\alpha]_D^{25}$  about  $+66.26^\circ$  in *s*-tetrachloroethane. It is converted by treatment with sodium hydroxide and methyl sulphate followed by hydrolysis of the product with aqueous-alcoholic hydrochloric acid into 4-methyl-*d*-mannose dibenzylmercaptal, m. p. 188°,  $[\alpha]_D^{25}$   $-106.62^\circ$  in pyridine. The intermediate diisopropylidene compound is converted by mercuric chloride in boiling ethyl alcohol into the ethylglucoside of 4-methylmannose, hydrolysed to the non-crystalline 4-methyl-*d*-mannose,  $[\alpha]_D^{25}$   $-7.38^\circ$  (non-mutarotatory). The methylmannose yields a phenylhydrazone, m. p. 179°, and a phenyllosazone, decomp. 198°,  $[\alpha]_D^{25}$   $-35.12^\circ$  (final value in pyridine-alcohol), identical with that derived from 4-methyl-*d*-glucose, thus establishing the position of the alkyl group in the mannose molecule. H. WREN.

**Unsaturated reduction products of the sugars. XIII. Gentibial and the ring structure of glucal.** M. BERGMANN and W. FREUDENBERG (Ber., 1929, 62, [B], 2783—2788).—Hepta-acetylmygdalin

in glacial acetic acid is converted by hydrogen in presence of spongy palladium into *hepta-acetyl-gentiobiose*, m. p. 178° (corr.),  $[\alpha]_D^{20} +35.31^\circ$  to  $+30.4^\circ$  in anhydrous pyridine. It is converted successively into octa-acetylgentiobiose, m. p. 192—193.5° (corr.), and acetobromogentiobiose, which is transformed by zinc dust and acetic acid into *hexa-acetylgentiobial*, m. p. 126° (corr.),  $[\alpha]_D^{20} -15.1^\circ$  in pyridine. Hydrolysis of the last-named compound by methyl-alcoholic ammonia affords *gentiobial*,  $C_{12}H_{20}O_9$ , m. p. 194° (corr.),  $[\alpha]_D^{20} -5.8^\circ$  in water. Hydrogenation of hexa-acetylgentiobial affords *hexa-acetylhydrogentiobial*, m. p. 132—133° (corr.),  $[\alpha]_D^{20} +11.1^\circ$  in pyridine, whence *hydrogentiobial* (*monohydrate* and *hemihydrate*,  $[\alpha]_D^{20} -9.9^\circ$  in water). Fission of hydrogentiobial with emulsin yields hydroglucal, m. p. 86°,  $[\alpha]_D^{20} +16.3^\circ$  in water, and dextrose. It follows, therefore, that gentiobial is a 6-glucosidoglucal and that glucal contains the pyran ring. Cellobial is a 4-glucosidoglucal and lactal a 6-galactosidoglucal. H. WREN.

**Third sugar constituent of scammonin.** E. VOTOČEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1929, 1, 606—609).—When scammonin in 96% alcohol is treated with aqueous barium hydroxide until the alkaline reaction persists (about 5 days) scammonic acid is obtained, purified by precipitation from its alcoholic solution by ether. The acid was hydrolysed by warm 10% sulphuric acid and the syrup produced was fermented to remove dextrose, and then repeatedly extracted with small quantities of ether. Crystals of rhamnose,  $[\alpha]_D^{20} +8.4^\circ$  in water [*p*-bromophenylhydrazone, m. p. 167°; *p*-bromophenyllosazone, m. p. 222° (decomp.)], separated from the residual syrup and the mother-liquor was shown to contain rhodose and rhamnose by treatment with phenylmethylhydrazine in a carbon dioxide atmosphere. A. I. VOGEL.

**Relation between chemical constitution and action on micro-organisms.** VIII. Glucosides of simple and chlorinated *p*-hydroxybenzoic acids and their esters. T. SABALITSCHKA and F. L. SCHWEITZER (Arch. Pharm., 1929, 267, 675—685).—The sodium salt of methyl *p*-hydroxyphenylbenzoate, prepared from the phenol and sodium methoxide, condenses with  $\beta$ -tetra-acetylbromoglucose in aqueous acetone solution to give methyl *p*- $\beta$ -tetra-acetyl-*d*-glucosidoxybenzoate, m. p. 162.5°,  $[\alpha]_D^{20} -24.0^\circ$  in chloroform, in 25% yield, hydrolysed by aqueous barium hydroxide to *p*- $\beta$ -glucosidoxybenzoic acid, m. p. 213°,  $[\alpha]_D^{20} -79.2^\circ$  in water (methyl ester, m. p. 169°,  $[\alpha]_D^{20} -78.1^\circ$  in water; treatment with emulsin confirmed the  $\beta$ -configuration). The sodium salt of methyl 3-chloro-4-hydroxybenzoate and  $\beta$ -tetra-acetylbromoglucose in aqueous acetone solution similarly afforded methyl 3-chloro-4-tetra-acetyl-*d*-glucosidoxybenzoate, m. p. 137.5°,  $[\alpha]_D^{20} -44.9^\circ$  in chloroform, in 30% yield, converted by heating for 30 hrs. with saturated aqueous barium hydroxide into 3-chloro-4- $\beta$ -*d*-glucosidoxybenzoic acid, m. p. 183° (decomp.),  $[\alpha]_D^{20} -70.7^\circ$  in water (methyl ester, m. p. 214.5°,  $[\alpha]_D^{20} -50.3^\circ$  in methyl alcohol). Methyl 3:5-dichloro-4- $\beta$ -tetra-acetyl-*d*-glucosidoxybenzoate, m. p. 112°,  $[\alpha]_D^{20} -8.2^\circ$  in chloroform, similarly prepared from methyl 3:5-dichloro-4-hydroxybenzoate in 10% yield, gives 3:5-dichloro-

4- $\beta$ -*d*-glucosidoxybenzamide (decomp. about 150°, depending on rate of heating) when treated in methyl-alcoholic solution with ammonia. The bactericidal activities to *Staphylococcus pyogenes aureus* were (phenol=1): *p*-hydroxybenzoic acid 3.6, glucoside of latter, 3.0; methyl *p*-hydroxybenzoate, 2.6, glucoside of latter, 2.7; 3-chloro-4-hydroxybenzoic acid, 37.0, glucoside of latter, 4.3. These results are not in accord with the work of Glaser and others (cf. A., 1924, i, 797), which requires the complete loss of bactericidal activity of an active substance on conversion into its glucoside. A. I. VOGEL.

**Compounds of hydroxyanthraquinones with acetylated sugars.** A. MÜLLER (Ber., 1929, 62, [B], 2793—2811).—The possible existence of dihydroxyanthraquinone diglucosides, including such as contain the sugar residues attached to the same benzene nucleus, is established, and hence also the possibility of the preparation of an alizarin diglucoside,  $\alpha$ -Hydroxyl groups, when protected by  $\beta$ -hydroxyl groups, cannot be caused to react with halogeno-sugars by use of an excess of the latter, prolongation of the reaction, or raising the temperature. It appears therefore possible that ruberythric acid is a monobioside (cf. Zemplén and Müller, A., 1929, 1281).

2-Hydroxyanthraquinone is converted by acetobromoglucose in presence of dry silver oxide and quinoline into 2-hydroxyanthraquinone-tetra-acetylglucoside,  $C_{14}H_8O_2 \cdot O \cdot C_6H_7O_5Ac_4 \cdot 0.5EtOH$ , colourless needles, m. p. 164°, or pale yellow needles or rosettes, m. p. 132°. The variety of higher m. p. passes into that of lower m. p. when its solution in alcohol and ether is exposed to sunlight; the reverse change occurs in the dark. 2:6-Dihydroxyanthraquinone-ditetra-acetylglucoside, m. p. 252° after softening at 241°,  $[\alpha]_D^{20} -5.49^\circ$  in *s*-tetrachloroethane, and 2:6-dihydroxyanthraquinone-dihepta-acetylcellobioside, m. p. 287°,  $[\alpha]_D^{20} -5.26^\circ$  in *s*-tetrachloroethane, 2:7-dihydroxyanthraquinone-ditetra-acetylglucoside, m. p. 244° after softening at 240°, and 2:7-dihydroxyanthraquinone-dihepta-acetylcellobioside, m. p. 246°, are analogously prepared. 1-Hydroxyanthraquinone-2-tetra-acetylglucoside has m. p. 205°,  $[\alpha]_D^{20} -7.32^\circ$  in *s*-tetrachloroethane. Anthragallol affords 1:2:3-trihydroxyanthraquinone-tritetra-acetylglucoside, m. p. 134—135°,  $[\alpha]_D^{20} -5.68^\circ$  in *s*-tetrachloroethane, whereas purpurin gives 1:4-dihydroxyanthraquinone-2-tetra-acetylglucoside, m. p. 204°,  $[\alpha]_D^{20} -6.04^\circ$  in *s*-tetrachloroethane, and 1:4-dihydroxyanthraquinone-2-hepta-acetylcellobioside, m. p. 267°,  $[\alpha]_D^{20} -7.65^\circ$  in *s*-tetrachloroethane. 1:5-Dihydroxyanthraquinone-2-tetra-acetylglucoside, m. p. 235°,  $[\alpha]_D^{20} -7.33^\circ$  in *s*-tetrachloroethane; 1-hydroxyanthraquinone-2:6-ditetra-acetylglucoside, m. p. 258°,  $[\alpha]_D^{20} -6.43^\circ$  in *s*-tetrachloroethane; 1-hydroxyanthraquinone-2:7-ditetra-acetylglucoside, m. p. 260°,  $[\alpha]_D^{20} -7.30^\circ$  in *s*-tetrachloroethane; 1:5-dihydroxyanthraquinone-2:6-ditetra-acetylglucoside, m. p. 275°,  $[\alpha]_D^{20} -8.97^\circ$  in *s*-tetrachloroethane; 1:8-dihydroxyanthraquinone-2:7-ditetra-acetylglucoside, m. p. 297°, and 1:5:8-trihydroxyanthraquinone-2-tetra-acetylglucoside, m. p. 236°,  $[\alpha]_D^{20} -9.89^\circ$  in *s*-tetrachloroethane, are described.

1-Hydroxyanthraquinone somewhat unexpectedly yields anthraquinone-1-tetra-acetylglucoside, m. p. 200°,

$[\alpha]_D^{25}$   $-8.44^\circ$  in *s*-tetrachloroethane; 1-hydroxyanthracene behaves similarly, but the glucoside could not be isolated. *Anthraquinone-1:4-ditetra-acetylglucoside*, m. p.  $254^\circ$ ,  $[\alpha]_D^{25}$   $-9.75^\circ$  in *s*-tetrachloroethane, *anthraquinone-1:5-ditetra-acetylglucoside*, m. p.  $167^\circ$ ,  $[\alpha]_D^{25}$   $-10.91^\circ$  in *s*-tetrachloroethane, and 1-hydroxyanthraquinone-8-tetra-acetylglucoside, m. p.  $212^\circ$ ,  $[\alpha]_D^{25}$   $-8.89^\circ$  in *s*-tetrachloroethane, have been prepared. H. WREN.

**Characterisation of starches and their amyloses.** T. C. TAYLOR and R. P. WALTON (J. Amer. Chem. Soc., 1929, 51, 3431—3440).—Using a slight modification of the method described by Taylor and Iddles (B., 1926, 717), the  $\alpha$ - and  $\beta$ -amylose ratio has been determined for wheat (24:76) and tapioca (17:83) starches. The wheat starch has the highest  $\alpha$ -amylose content so far observed. Tapioca starch has unusually low phosphorus and fatty acid contents, whilst wheat starch is similar to other cereal starches (*loc. cit.*). Nitration of tapioca, maize, and potato starches and their  $\alpha$ - and  $\beta$ -amyloses with nitric acid (*d* 1.52) at  $2-6^\circ$ , subsequent precipitation of the nitro-compounds with sulphuric acid, and stabilisation of the product by boiling with water for 24 hrs., affords products which are similar in nitrogen content, solubility in acetone, and rotatory power.

H. BURTON.

**Polysaccharides. XLII. Physical structure of starch.** P. KARRER and E. VON KRAUSS (Helv. Chim. Acta, 1929, 12, 1144—1152).—When potato or tapioca starch is boiled with water and the resulting paste centrifuged, two phases are obtained: (a) clear and mobile, (b) viscous and opalescent. The viscous phase is washed with water, affording a further phase (c). The viscosity of *b* is 1.5—1.8 times that of *a* or *c*. The values for *a* and *c* show no alteration with diminished pressure, but the values for *b* decrease with increased pressure, as do the values for the original starch solutions. There is no relationship between the viscosity and the phosphorus content of the various fractions. Acetylation of the dry starches (obtained by concentrating the extracts in a vacuum and subsequent precipitation with alcohol) with acetic anhydride and pyridine gives (a) a mobile solution, (b) a more viscous solution, and (c) a gel. Precipitation of the starch acetates with water furnishes products which are only partly soluble in organic solvents; differences, similar to those of the original fractions, are shown.

H. BURTON.

**Nature of coloured products formed by the action of iodine on starch and its derivatives.** A. PICTET and H. VOGEL (Anal. Fís. Quím., 1929, 27, 450—453).—The fact that isotrihexosan and dextrin-*osan* (A., 1929, 914) both give colorations with iodine is evidence in favour of the chemical theory of the starch-iodine reaction. The iodine compound of isotrihexosan has the empirical composition  $(C_6H_{10}O_5)_3I$ , but is probably a mixture. The reaction is regarded as probably involving  $I_3'$  ions and the oxygen of the anhydride linking. R. K. CALLOW.

**Polysaccharides. V. Glycogen.** W. N. HAWORTH, E. L. HIRST, and J. I. WEBB (J.C.S., 1929, 2479—2485).—Glycogen is purified by electrodialysis, whereby the ash content is reduced to 0.37%, but

traces of phosphorus are not removed. After preliminary treatment by precipitation from aqueous solution by alcohol, it is possible to obtain glycogen triacetate, decomp.  $177^\circ$ ,  $[\alpha]_D^{25}$   $+163^\circ$  in chloroform, which strongly resembles starch triacetate, in almost quantitative yield by the action of acetic anhydride in acetic acid in presence of sulphur dioxide and chlorine at  $55^\circ$ , or of acetic anhydride in pyridine at  $80^\circ$ . Glycogen regenerated by the action of cold alcoholic potassium hydroxide is indistinguishable from the original material. The triacetate is converted quantitatively by methyl-alcoholic hydrogen chloride into methylglucoside. By six to seven treatments with methyl sulphate and sodium hydroxide in acetone, the triacetate is converted into trimethylglycogen, m. p.  $147^\circ$  after softening at  $135^\circ$ ,  $[\alpha]_D^{25}$   $+208^\circ$  in chloroform, which is indistinguishable from trimethylstarch, and yields 2:3:6-trimethylglucose when hydrolysed. The close similarity of the derivatives obtained from glycogen and starch (A., 1928, 1360) supports the view that the latter are similarly constituted, and such differences as exist may be attributed to a difference in the size of their respective micelles. R. K. CALLOW.

**Interaction of hydrogen fluoride with cellulose.** B. HELFERICH and S. BÖTTGER (Annalen, 1929, 476, 150—170).—Dried cellulose dissolved with cooling and exclusion of atmospheric moisture in 4—5 parts by weight of hydrogen fluoride followed by removal of the solvent by a stream of dry air at  $30^\circ$  gave a syrup, which was dissolved in ice-cold water and the residual hydrogen fluoride neutralised by calcium carbonate; the clear filtrate by evaporation under reduced pressure gave *cellan*,  $[\alpha]_D^{25}$   $+143.4^\circ$  in water. Precipitation of a similar hydrogen fluoride solution of cellulose with ether gave a preparation having  $[\alpha]_D^{25}$   $+32.1^\circ$ . Protracted boiling of cellan with pyridine-acetic anhydride mixture afforded *acetylcellan*, m. p.  $170-175^\circ$ ,  $[\alpha]_D^{25}$   $+127.7^\circ$  in chloroform, hydrolysed to cellan by boiling with methyl-alcoholic sodium methoxide and to methylglucoside by heating for 70 hrs. at  $125^\circ$  with dilute methyl-alcoholic hydrogen chloride. Identical treatment of anhydrous dextrose with hydrogen fluoride gave a *polyglucosan* (acetyl derivative,  $[\alpha]_D^{25}$   $+126.5^\circ$  in chloroform). Anhydrous cellobiose formed similarly *polycellobiosan*,  $[\alpha]_D^{25}$   $+144.1^\circ$  in water (acetyl derivative,  $[\alpha]_D^{25}$   $+126.5^\circ$  in chloroform). Results of mol.-wt. determinations of the above substances in camphor, water, or bromoform solutions and also experimental details relating to measurements of optical rotation in liquid hydrogen fluoride are given. R. J. W. LE FEVRE.

**Cellulose benzyl ethers.** T. NAKASHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 12, 121—125).—See A., 1929, 684.

**Cellulose ethers.** H. NIETHAMMER and W. KÖNIG (Cellulosechem., 1929, 10, 201—205).—By the action of *p*-chlorobenzyl chloride and 2:4-dinitrochlorobenzene on alkali-cellulose the lower cellulose *p*-chlorobenzyl and cellulose 2:4-dinitrophenyl ethers have been obtained. It is possible to produce the latter still retaining the fibrous cellulose structure with a low nitrogen content. Reduction, diazotisation, and coupling results in a fibre in which the colour is



an integral part of the structure. Under suitable conditions etherification with *p*-chlorobenzyl chloride may proceed to two thirds of the theoretical.

T. H. MORTON.

**Celluloseamine and celluloseaniline.** I. SAKURADA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 12, 113—130).—See A., 1929, 684.

**Formation of tertiary amines in the reduction of nitriles and carbonyl compounds in basic solution.** A. SKITA and F. KEIL.—See A., 1929, 1436.

**Influence of poles and polar linkings on the course pursued by elimination reactions. VI. 1 : 1-Elimination in the degradation of quaternary ammonium hydroxides.** C. K. INGOLD and J. A. JESSOP (J.C.S., 1929, 2357—2361).—The theory of the decomposition of the above hydroxides is discussed, and it is shown that the decomposition should always give olefines and never paraffins. The decomposition of fluoryl-9-trimethylammonium and -triethylammonium hydroxides has been investigated and found to be in accordance with theory. In the case of the former substance the products of decomposition were dimethyl-9-fluorylamine, trimethylamine, 9-fluoryl ether, and bis-*oo'*-diphenylene-ethylene (difluorylidene). The formation of the last-named substance is the main point of interest, since it was shown to be a primary product of the decomposition, and therefore the first record of 1 : 1-elimination from a quaternary ammonium hydroxide. Corresponding products appear in the decomposition of fluoryl-9-triethylammonium hydroxide. An explanation of the 1 : 1-elimination, based on the structure of fluorene, is offered.

*Fluoryl-9-trimethylammonium bromide*, m. p. 189—190° (decomp.), and *picrate*, m. p. 175°, and *fluoryl-9-triethylammonium picrate*, m. p. 166°, were prepared by the general method. *Dimethyl-9-fluorylamine* and its *picrate*, m. p. 203—204°, are also described.

J. W. PORTER.

**Cerebrosides. X. Sphingosine.** E. KLENK (Z. physiol. Chem., 1929, 185, 169—182).—Evidence is brought forward that sphingosine, like the fatty acids of brain lipins, is a multiple of C<sub>6</sub> (cf. A., 1928, 868). New and published analyses of various sphingosine derivatives support the formula C<sub>18</sub>H<sub>37</sub>O<sub>2</sub>N, rather than the previously accepted formula C<sub>17</sub>H<sub>35</sub>O<sub>2</sub>N (cf. Levene and West, A., 1914, i, 308, 1141). Treatment of triacetyl-sphingosine, m. p. 102—102.5° (improved method of preparation given), with ozonised oxygen in acetic acid solution, and subsequent reductive fission of the ozonide with hydrogen and palladised barium sulphate (cf. Fischer, A., 1928, 989) affords tetradecoic acid and aldehyde, and not tridecoic acid as reported by Levene and West (*loc. cit.*). Oxidation of sphingosine sulphate by Levene and West's method also gives tetradecoic acid; other acidic oxidation products are also formed. Dihydro-sphingosine is oxidised similarly to palmitic and not pentadecoic acid (Levene and West). Sphingosine is, therefore, probably Me·[CH<sub>2</sub>]<sub>12</sub>·CH·CH·[CH(OH)]<sub>2</sub>·CH<sub>2</sub>·NH<sub>2</sub> (the positions of the hydroxyl and amino-groups are assumed arbitrarily).

[With R. HÄRLE].—Dihydrosphingosine picrate

sinters at 88—89° and melts at 157° (cf. Levene and West, A., 1916, i, 219); the *hydrobromide*, C<sub>18</sub>H<sub>39</sub>O<sub>2</sub>N·HBr, has m. p. 270° (decomp.) after sintering at 95°.

H. BURTON.

**Preparation of monoamino-acids from picrates.** G. J. COX and H. KING (J. Biol. Chem., 1929, 84, 533—534).—The picrate is suspended in water and the suspension is shaken with two successive portions of aniline, which removes the whole of the picric acid; the aqueous layer is freed from aniline by extraction with ether and evaporated. Proline and glycine can thus be regenerated from their picrates in a yield of 90%.

C. R. HARRINGTON.

**Synthesis of glycine.** W. K. ANSLOW and H. KING (J.C.S., 1929, 2463—2466).—In the method of Ling and Nanji (A., 1922, i, 1124) for the preparation of glycine by hydrolysis of methyleneaminoacetonitrile the yield obtained does not exceed 57%; after the first stage of hydrolysis with barium hydroxide no barium methyleneglycine can be isolated, but glycine may be isolated in yields of up to 71%.

Aminoacetonitrile hydrogen sulphate is obtained in 87% yield by hydrolysis of methyleneaminoacetonitrile by a modification of Klages' process (A., 1903, i, 469), and is then hydrolysed by boiling barium hydroxide solution. After removal of barium as sulphate, crude glycine is obtained by evaporation, and pure glycine is obtained by recrystallisation from water in an overall yield of 84%.

R. K. CALLOW.

**Resolution of chloroacetyl-*dl*-leucine into its optical components by means of  $\alpha$ -phenylethylamine.** E. ABDERHALDEN and A. SCHMITZ (Biochem. Z., 1929, 214, 158—160).—When  $\alpha$ -phenylethylamine carbonate is added to an aqueous solution of chloroacetyl-*dl*-leucine, the *phenylethylamine* salt of chloroacetyl-*l*-leucine, m. p. 178°, is precipitated, and on treatment with hydrochloric acid gives chloroacetyl-*l*-leucine, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -13.4° in alcohol. The *d*-isomeride, m. p. 169—170°, is obtained from the mother-liquors by conversion into the *l*-*phenylethylamine* salt, m. p. 169—170°, which, with similar treatment, gives chloroacetyl-*d*-leucine, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12.7° in alcohol.

P. W. CLUTTERBUCK.

**Fission of selenocynoacetic acid.** O. BEHAGHEL and M. ROLLMANN (Ber., 1929, 62, [B], 2696—2699; cf. Frerichs, A., 1903, i, 609).—The action of hydrochloric acid on selenocynoacetic acid yields primarily *diselenodiacetic acid*, (Se·CH<sub>2</sub>·CO<sub>2</sub>H)<sub>2</sub>, m. p. 101°, and cyanogen (whence cyanic and hydrocyanic acids); ammonia, carbon dioxide, hydrocyanic acid, and small amounts of oxalic acid are also present among the final products. The initial products of the action of alkali hydroxide are cyanic, hydrocyanic, and diselenodiacetic acids, from which selenolactic and selenodiacetic acids and hydrogen selenide are produced. 2 : 4-*Dinitrophenylselenoacetic acid*, m. p. 168°, and 2 : 4 : 2' : 4'-*tetranitrodiphenylselenide*, m. p. 195—196°, are incidentally described.

H. WREN.

**Decarboxylated peptides and their derivatives. II.** J. VON BRAUN, A. BAHN, and W. MÜNCH (Ber., 1929, 62, [B], 2766—2776; cf. A., 1927, 344).—In contrast to the decarboxylated dipeptides, the corresponding tri- and tetra-peptides are pharma-

cologically inactive even after replacement of the basic hydrogen atom by methyl, ethyl, propyl, or more complex alkyl groups. Introduction of a more complex peptide component in the dipeptide is either without influence on the abrupt change in activity caused by passage from the ethyl to the higher homologue (*loc. cit.*) or completely destroys such activity.

$\beta$ -Hydroxyethylamine and  $\alpha$ -bromoisohexoyl bromide in ethereal solution afford the non-crystalline  $\alpha$ -bromoisohexo- $\beta$ -hydroxyethylamide,  $C_4H_9\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot OH$ , converted by ethylamine in benzene at  $100^\circ$  into *N*-ethyl-leucinedecarboxyserine [ $\alpha$ -ethylaminoisohexo- $\beta$ -hydroxyethylamide], m. p.  $114^\circ$ , b. p. about  $180^\circ/10$  mm. (slight decomp.) (hygroscopic *hydrochloride*, m. p.  $137^\circ$ ; *picrate*, m. p.  $183$ — $185^\circ$ ); *N*-isoamyl-leucinedecarboxyserine, m. p.  $95^\circ$ , b. p.  $200$ — $210^\circ/10$  mm. (very hygroscopic *hydrochloride*; *picrate*, m. p.  $131^\circ$ ), is produced similarly.  $\beta$ -*p*-Hydroxyphenylethylamine and  $\alpha$ -bromopropionyl bromide afford  $\alpha$ -bromopropion- $\beta$ -*p*-hydroxyphenylethylamide, m. p.  $122^\circ$  (cf. Guggenheim, A., 1913, i, 773), with small amounts of its *o*-bromopropionyl derivative, m. p.  $137^\circ$ . Treatment of the monobromopropionyl compound with the appropriate amine yields the non-crystalline *N*-ethylalanyldecarboxytyrosine [ $\alpha$ -ethylaminopropion- $\beta'$ -*p*-hydroxyphenylethylamide] (*hydrochloride*, m. p.  $60^\circ$ ) and *N*-isoamylalanyldecarboxytyrosine (*hydrochloride*, m. p.  $68^\circ$ ). Anisaldehyde is readily converted by hydrogen in presence of nickel into anisyl alcohol, transformed by the usual methods into *p*-anisylacetoneitrile, which is reduced to  $\beta$ -*p*-anisylethylamine, b. p.  $132$ — $134^\circ/14$  mm. (accompanied by the corresponding secondary and possibly tertiary base). The monoamines are converted successively into  $\alpha$ -bromopropion- $\beta'$ -*p*-anisylethylamide, m. p.  $122^\circ$ , and *N*-ethylalanyl-*O*-methyldecarboxytyrosine [ $\alpha$ -ethylaminopropion- $\beta'$ -*p*-anisylethylamide], b. p.  $190$ — $192^\circ/0.2$  mm. (*hydrochloride*, m. p.  $135$ — $138^\circ$ ), or *N*-isoamylalanyl-*O*-methyldecarboxytyrosine, b. p.  $203$ — $206^\circ/0.8$  mm. (*hydrochloride*, m. p.  $157^\circ$ ).

Addition of ethereal chloroacetyl chloride to aqueous di- $\beta\beta'$ -aminodiethyl disulphide in presence of potassium carbonate affords di- $\beta\beta'$ -chloroacetamidodiethyl disulphide, m. p.  $116^\circ$ , converted by a large excess of the requisite base into di-(*N*-ethylglycyl)decarboxycystine [di- $\beta\beta'$ -ethylaminoacetamidodiethyl disulphide],  $(NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot S)_2$ , m. p.  $64^\circ$ , or di-(*N*-isoamylglycyl)decarboxycystine (*hydrochloride*, m. p.  $215^\circ$ ).

3- $\beta$ -Aminoethylindole (cf. Majima and Hoshino, A., 1925, i, 1450) is transformed by chloroacetyl chloride into 3- $\beta$ -chloroacetamidoethylindole, m. p.  $93^\circ$ , and thence into *N*-ethylglycyldecarboxytryptophan [3- $\beta$ -ethylaminoacetamidoethylindole] (*hydrochloride*, m. p.  $148^\circ$ ) and *N*-isoamylglycyldecarboxytryptophan, m. p.  $74$ — $75^\circ$  (*hydrochloride*, m. p.  $156^\circ$ ).

$\alpha$ -Aminoisohexomethylamide (*loc. cit.*) and  $\alpha$ -bromopropionyl bromide give  $\alpha\alpha'$ -bromopropionamidoisohexomethylamide, m. p.  $150^\circ$ , whence *N*-ethylalanyl-leucyldecarboxyglycine [ $\alpha\alpha'$ -ethylaminopropionamidoisohexomethylamide], b. p.  $179$ — $183^\circ/4$  mm. (very hygroscopic *hydrochloride*; *picrate*, m. p.  $180$ — $182^\circ$ ), *N*-*n*-propylalanyl-leucyldecarboxyglycine, b. p.  $180$ —

$184^\circ/3$  mm. (*picrate*, m. p.  $163^\circ$ ; very hygroscopic *hydrochloride*), and *N*-isohexylalanyl-leucyldecarboxyglycine, b. p.  $202$ — $206^\circ/3$  mm. (*hydrochloride*, m. p.  $174^\circ$ ; *picrate*, m. p.  $199^\circ$ ).

$\alpha$ -Aminopropionisoamylamide is converted by chloroacetyl chloride into  $\alpha$ -chloroacetamidopropionisoamylamide, m. p.  $130^\circ$ , whence *N*-ethylglycylalanyl-decarboxyleucine [ $\alpha$ -ethylaminoacetamidopropionylisoamylamide], b. p. about  $190^\circ/3.5$  mm., and *N*-*n*-propylglycylalanyldecarboxyleucine, b. p.  $195$ — $199^\circ/(?)3.5$  mm.; the corresponding non-crystalline *picrates* and very hygroscopic *hydrochlorides* are described.

$\alpha$ -Chloroacetamidoisohexoethylamide, m. p.  $133^\circ$ , yields *N*-methylglycyl-leucyldecarboxyalanine [ $\alpha$ -methylaminoacetamidoisohexoethylamide], b. p.  $198$ — $200^\circ/12$  mm., m. p.  $71$ — $73^\circ$  (*picrate*, m. p.  $180^\circ$ ; hygroscopic *hydrochloride*, m. p.  $206$ — $208^\circ$ ), *N*-ethylglycyl-leucyldecarboxyalanine, b. p.  $171$ — $174^\circ/3.5$  mm. (*hydrochloride*, m. p.  $169^\circ$ ; *picrate*, m. p.  $205^\circ$ ), *N*-propylglycyl-leucyldecarboxyalanine, b. p.  $178$ — $182^\circ/3.5$  mm. (*hydrochloride*, m. p.  $168^\circ$ ; *picrate*, m. p.  $190^\circ$ ), and *N*-isoamylglycyl-leucyldecarboxyalanine, b. p.  $191$ — $194^\circ/?$  mm. (*picrate*, m. p.  $138^\circ$ ; very hygroscopic *hydrochloride*). Glycyl-leucyldecarboxyalanine could not be obtained homogeneous.

$\alpha\alpha'$ -Bromopropionamidoisohexoethylamide, m. p.  $151^\circ$ , is converted by ammonia into a mixture of the secondary base,  $NH[CHMe\cdot CO\cdot NH\cdot CH(C_4H_9)\cdot CO\cdot NH_2]_2$ , m. p.  $230$ — $233^\circ$  (*hydrochloride*, m. p.  $246^\circ$ ), and  $\alpha\alpha'$ -aminopropionamidoisohexoethylamide (*hydrochloride*, m. p.  $75$ — $77^\circ$ ). The primary base is transformed by chloroacetyl chloride into chloroacetylalanyl-leucyldecarboxyalanine, m. p.  $225^\circ$ , whence *N*-ethylglycylalanyl-leucyldecarboxyalanine, m. p.  $163^\circ$  (*hydrochloride*, m. p.  $225^\circ$ ; *picrate*, m. p.  $172$ — $177^\circ$ ), and *N*-isoamylglycylalanyl-leucyldecarboxyalanine, m. p.  $150^\circ$  [*hydrochloride*, m. p.  $238^\circ$ ; *picrate*, m. p. (indef.)  $80$ — $100^\circ$ ].

H. WREN.

**Salts of fulminic acid.** III. L. WÖHLER and A. WEBER. IV. L. WÖHLER and A. BERTHMANN (Ber., 1929, 62, [B], 2742—2748, 2748—2758; cf. A., 1917, i, 383).—III. The following salts are prepared by shaking a solution of mercury fulminate in anhydrous methyl or ethyl alcohol with the requisite amalgam (if necessary at a low temperature to avoid polymerisation) until mercury is no longer present in solution: *potassium fulminate*, *d* 1.80; *calcium*, *strontium*, and *barium fulminates* (all + 1MeOH). Silver fulminate has *d* 4.09. Silver fulminate and aniline give the compound  $AgCNO\cdot 2PhNH_2$ . Ammonium iodide and silver fulminate in methyl alcohol yield the complex salt,  $NH_4[Ag(CNO)_2]$ ; the *magnesium* compound,  $Mg[Ag(CNO)_2]_2$ , is prepared analogously from magnesium chloride. Magnesium and ammonium fulminates could not be isolated. Independently of the valency of their metal, the fulminates add pyridine to form well-crystallised, feebly explosive compounds which readily lose part of their pyridine when warmed. The following salts are obtained from mercury fulminate and the requisite amalgam in pyridine:

$Zn(CNO)_2\cdot 2C_5H_5N$ ;  $Cu(CNO)_2\cdot 2C_5H_5N$ ;  
 $AgCNO\cdot C_5H_5N$ ;  $Cd(CNO)_2\cdot 2C_5H_5N$ ;  
 $Hg(CNO)_2\cdot 2C_5H_5N$ ; (?)  $Pb(CNO)_2\cdot 2C_5H_5N$ . The alkali and alkaline-earth fulminates do not add

pyridine. Analysis of the fulminates is effected by dissolving in an excess of thiosulphate and titration of the residual thiosulphate with iodine. The process is accurate and independent of the concentration with mercury fulminate if rapidly performed; with silver and cuprous fulminates preliminary conversion into the alcohol-soluble zinc fulminate is necessary.

IV. The double salt,  $2\text{Hg}(\text{CNO})_2 \cdot \text{Na}_2\text{S}_2\text{O}_3$ , separates when a filtered solution of mercury fulminate in aqueous sodium thiosulphate is preserved. Treatment of saturated solutions of sodium chloride and potassium bromide with mercury fulminate affords the compounds  $\text{Hg}(\text{CNO})_2 \cdot \text{NaCl}$  and  $\text{Hg}(\text{CNO})_2 \cdot \text{KBr}$ . Double salts with magnesium or calcium chloride are described. Mercury fulminate and zinc amalgam in 25% ammonia yield the compound  $\text{Zn}(\text{CNO})_2 \cdot 2\text{NH}_3$ ; the analogous manganese salt,  $\text{Mn}(\text{CNO})_2 \cdot 2\text{NH}_3$ , is obtained by use of methyl-alcoholic ammonia. In contrast to the simple fulminates, the following complex fulminates are crystalline. Sodium nickel fulminate,  $\text{Na}_2[\text{Ni}(\text{CNO})_4]$  (pentahydrate and anhydrous), obtained by adding nickel sulphate to a solution of sodium fulminate until the precipitated nickel hydroxide is not further dissolved; the cobalt salt,  $\text{K}_5[\text{Co}_2(\text{CNO})_{11}] \cdot 22\text{H}_2\text{O}$  and anhydrous, prepared analogously; the platinum compound,  $\text{Na}_2[\text{Pt}(\text{CNO})_4]$  (pentahydrate and anhydrous), from sodium fulminate and platinum chloride, converted by double decomposition into the compounds  $\text{Ca}[\text{Pt}(\text{CNO})_4]$  (pentahydrate and anhydrous),  $\text{Sr}[\text{Pt}(\text{CNO})_4]$ , and  $\text{Ba}[\text{Pt}(\text{CNO})_4]$  (trihydrate and anhydrous); the salts  $\text{Na}_2[\text{Pd}(\text{CNO})_4] \cdot 5\text{H}_2\text{O}$  and  $\text{Na}[\text{Au}(\text{CNO})_2]$ . Cuprous chloride and sodium or strontium fulminate afford the compounds  $\text{Na}[\text{Cu}(\text{CNO})_2]$  and  $\text{Sr}[\text{Cu}_2(\text{CNO})_4] \cdot 2\text{H}_2\text{O}$ , respectively. The cuprous fulminate is converted by concentrated cupric nitrate solution into the salt  $\text{Cu}[\text{Cu}_2(\text{CNO})_4] \cdot 2\text{H}_2\text{O}$ . Under different conditions the sodium salt,  $\text{Na}_2[\text{Cu}(\text{CNO})_3] \cdot 3\text{H}_2\text{O}$ , is prepared. With excess of cuprous chloride, the alkaline-earth fulminates yield the compounds  $\text{Ca}[\text{Cu}(\text{CNO})_3] \cdot 3\text{H}_2\text{O}$ ,  $\text{Sr}[\text{Cu}(\text{CNO})_3] \cdot 6\text{H}_2\text{O}$ , and  $\text{Ba}[\text{Cu}(\text{CNO})_3] \cdot 4\text{H}_2\text{O}$ . The close analogy between the new fulminates and the corresponding cyanides is emphasised. H. WREN.

#### Methylenedithiocarbamic acid and derivatives.

T. G. LEVI and L. GIMIGNANI (Gazzetta, 1929, 59, 681—686).—Carbon disulphide, formaldehyde (trioxymethylene), and alcoholic ammonia condense in the cold to give a quantitative yield of ammonium methylenedithiocarbamate,  $(\text{CH}_2 \cdot \text{N} \cdot \text{CS}_2 \cdot \text{NH}_4)_3$  (I), m. p. 154° (decomp.), which is converted into its components by prolonged treatment with boiling water. Methylenedithiocarbamic acid (silver, zinc, mercury, nickel, and cobalt salts) could not be obtained in a state of purity. Potassium ferricyanide converts I into the disulphide,  $[(\text{CH}_2 \cdot \text{N} \cdot \text{CS} \cdot \text{S})_2]_3$ , whilst cyanogen bromide affords the monosulphide,  $[(\text{CH}_2 \cdot \text{N} \cdot \text{CS} \cdot \text{S})_2]_3$ . Methylation of I in alcoholic suspension with methyl iodide furnishes trimeric methyl methylenedithiocarbamate, m. p. 182°, which by heating with saturated alcoholic ammonia in a sealed tube at 90° yields 75% of trimeric *as*-methylenedithiocarbamide, m. p. 181° (cf. Emmelmayer, Monatsh., 1891, 12, 90; Dixon and Taylor, J.C.S., 1916, 109, 1244).

C. W. SHOPPEE.

**Unsaturated aliphatic nitriles.** A. VERMEULEN and L. ADRIAENS (Bull. Soc. chim. Belg., 1929, 38, 301—309).—Dehydration of methyl *n*-propyl ketone cyanohydrin with phosphoric oxide in a little chloroform and fractionation of the product gives two fractions, (1) b. p. 135—140°/760 mm. and (2) b. p. 157—158°/760 mm. By treatment with hydrogen chloride fraction 2 gives only  $\beta$ -chloro- $\alpha$ -methylvaleronitrile (I), b. p. 76—76.5°/12 mm.,  $d_4^{20}$  1.00952,  $n_D^{20}$  1.44243, whilst fraction 1 gives a mixture of I (55%) and  $\alpha$ -chloromethylvaleronitrile (II), b. p. 87—88°/10 mm.,  $d_4^{20}$  1.01034,  $n_D^{20}$  1.44274 (45%). By regeneration of the unsaturated nitriles from these chloro-compounds with quinoline at 100°, II yields only  $\alpha$ -methylenevaleronitrile (III), b. p. 135.7—135.9°/757 mm.,  $d_4^{20}$  0.81574,  $n_D^{20}$  1.42283, whilst I gives a mixture of the two geometrical isomerides, b. p. 138.7—139.1°/761 mm.,  $d_4^{20}$  0.81767,  $n_D^{20}$  1.42865 (25%), and b. p. 158.4—158.6°/772 mm.,  $d_4^{20}$  0.82802,  $n_D^{20}$  1.43336, of  $\alpha$ -methyl- $\Delta^2$ -pentenonitrile (IV). In the original dehydration, therefore, fraction 1 is a constant-b. p. mixture of III (37%) and the low-b. p. geometrical isomeride of IV (44.8%), whilst fraction 2 consists only of the high-b. p. geometrical isomeride of IV (18.2%), the proportions in parentheses being those of the total products formed. Contrary to the observation of Macq (A., 1927, 652) (who did not separate the fraction of low b. p.), interconversion of the two geometrical isomerides by sodium phenoxide could not be effected, this reagent being without action on all three products of the reaction. J. W. BAKER.

**Action of light on potassium ferrocyanide solution.** II. O. BAUDISCH (Ber., 1929, 62, [B], 2706—2712; cf. A., 1922, i, 993).—Examination of the behaviour of aqueous potassium ferrocyanide towards light under conditions which ensure the complete absence of oxygen, as well as in the presence of air, leads to the following conclusions. Ordinary ferrous ions in addition to pentacyanoaquoferroate ions are produced when solutions of potassium ferrocyanide, neutral or feebly acid with carbonic acid, are exposed to the carbon arc light or sunlight in the absence of air. In the presence of air and light, the yellow ferroate ions are instantaneously oxidised to the dark violet pentacyanoaquoferriate ions, which react with the first-named ions, giving more complicated products with only a pale yellow colour. Formation of these products is inhibited by the addition of sodium azide, and, under these conditions, the yellow potassium ferrocyanide solution is directly oxidised to the dark violet potassium pentacyanoaquoferriate. In an air-free system, the iron atom of potassium ferrocyanide is activated by light as a consequence of the mobilisation of its subsidiary valencies; in the dark, the original, inactive compound is rapidly re-formed. In the presence of air and light, peroxo-compounds possessing unusual oxidative powers (cf. this vol., 41) are produced in addition to the usual ferric and ferrous complex ions. H. WREN.

**Beryllium dimethyl.** H. GILMAN and F. SCHULZE (Rec. trav. chim., 1929, 48, 1129—1132).—An ethereal solution of beryllium dimethyl (Gilman and Schulze, A., 1928, 50) at the ordinary temperature has no action on *as*-diphenylethylene or di-

phenyl sulphone. Measurements of the volume of gas evolved when the reaction mixture is decomposed with moist ether show that reaction occurs with azobenzene, 1 mol. of beryllium dimethyl reacting with 2 mols. of azobenzene probably in accordance with one or both of the schemes  $\text{NPh.NPh} + 2\text{BeMe}_2 \rightarrow$  (a)  $[\text{NPh}(\text{BeMe})]_2 + \text{C}_2\text{H}_6$  or (b)  $\text{Be}(\text{NPhMe.NPh})_2$ .

J. W. BAKER.

**Method of coupling organic radicals by the Grignard reagent.** J. H. GARDNER and P. BORGSTROM (J. Amer. Chem. Soc., 1929, 51, 3375—3377).—When a Grignard reagent is added to a suspension of silver bromide in ether and the intermediate silver aryl decomposed by boiling the solution (with or without added benzene; silver alkyls decompose without heating), diaryls and dialkyls are obtained in 25—72% yield. Diphenyl, di-*p*-tolyl, di-*p*-anisyl, dibenzyl, dicyclohexyl, and *n*-octane were prepared. Individual substances were not isolated from magnesium *iso*- and *sec*-butyl bromides.

H. BURTON.

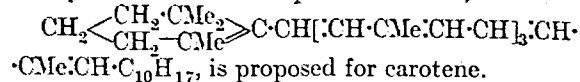
**Distillation of magnesium dimethyl from magnesium methyl chloride.** H. GILMAN and R. E. BROWN (Rec. trav. chim., 1929, 48, 1133—1135).—Distillation of magnesium methyl chloride at 190°/0.2 mm. gives magnesium dimethyl as a white crystalline substance probably obtained by a process of ether sublimation. This observation is in agreement with earlier views (Gilman and Schulze, A., 1928, 50) on the existence of the equilibrium  $2\text{RMgX} \rightleftharpoons \text{MgR}_2 + \text{MgX}_2$ .

J. W. BAKER.

**Constitution of dimagnesium acetylenyl bromide.** K. KLEINFELLER (Ber., 1929, 62, [B], 2736—2738).—Dimagnesium acetylenyl bromide affords an instance of the transition of a liquid substance with atomic linking into a substance of identical composition with ionic linking. When preserved for 3—4 weeks, the liquid compound becomes solid and crystalline without any other sign of alteration. Its original activity towards organic and inorganic compounds is lost, but acetylene is vigorously evolved when water is added. As usually formulated, the action consists in a disproportionation into magnesium carbide and bromide. Establishment of the equilibrium is catalytically accelerated by bromobenzene, ethylene bromide, allyl bromide, and *s*-tetrachloroethane. The bearing of the observations on the work of Schlenk and Schlenk (A., 1929, 687) is discussed.

H. WREN.

**Plant colouring matters. XVI. Carotene. I.** P. KARRER and A. HELFENSTEIN (Helv. Chim. Acta, 1929, 12, 1142—1144).—Oxidation of a benzene solution of carotene with aqueous potassium permanganate at the ordinary temperature affords a substance similar to, and probably identical with, ionone. Like ionone, it is oxidised further to *as*-dimethylsuccinic acid. A partial formula,



is proposed for carotene.

H. BURTON.

**Stereochemistry of dicyclic ring-systems. V.  $\Delta^9$ : $^{10}$ -Octahydronaphthalene.** W. HÜCKEL, R. DANNEEL, A. SCHWARTZ, and A. GERCKE (Annalen, 1929, 474, 121—144).—The authors doubt the

homogeneity of the  $\Delta^9$ : $^{10}$ -octahydronaphthalene described by Nametkin and Glagolev (A., 1929, 921); the pure substance has now been obtained by two methods: from *trans*-2-cyclopentylcyclopentan-1-ol by treatment with zinc chloride at 140° (to be described in a future memoir), and in the following way.

The mixture of octahydronaphthalenes, obtained from  $\beta$ -decalol (containing all four isomerides) by dehydration with zinc chloride, by treatment with ethyl nitrite and hydrochloric acid yields a mixture of nitrosochlorides (I), (II), and (III). 9-Nitroso-10-chlorodecahydronaphthalene (I), blue, m. p. 91°, gradually decomposes on keeping, but by treatment with sodium methoxide affords  $\Delta^9$ : $^{10}$ -octahydronaphthalene, b. p. 194°/750 mm., 79°/14 mm., m. p. -34°,  $d_4^{20}$  0.9170,  $n_D^{20}$  1.49963 (the purity and homogeneity of this preparation are shown by the form of the setting-point and m.-p. curves), together with traces of an oxime, m. p. 150° (benzoyl derivative, m. p. 136°), of an unsaturated ketone,  $\text{C}_{10}\text{H}_{14}\text{O}$  (IV), and a chloro-compound, m. p. 144°, also obtained from I by treatment with piperidine in alcoholic solution. The yield of I is better from  $\beta$ -decalol mixtures rich in *cis*- $\beta$ -decalol than from those rich in *trans*- $\beta$ -decalol.  $\Delta^9$ : $^{10}$ -Octahydronaphthalene yields a dibromide, m. p. 163—164°, and by treatment with chlorine in chloroform solution at -20° a liquid dichloride, followed by a tetrachloride, m. p. 167°. The hydrocarbon gives a negative Baeyer test, but can be oxidised with potassium permanganate to  $\delta$ -ketosebacic acid. Ozonisation in light petroleum at 0° affords an extremely stable ozonide,  $\text{C}_{10}\text{H}_{16}\text{O}_3$ , m. p. 168°, which can be distilled in a vacuum, and is unaffected by boiling water, zinc dust in ether, or aluminium amalgam. Ozonisation in glacial acetic acid furnishes cyclodecane-1 : 6-dione (V), m. p. 100°, unaccompanied by aldehydic products, together with  $\delta$ -ketosebacic acid, m. p. 116°, and a substance, which by treatment with 20% sodium hydroxide yields an unsaturated ketone,  $\text{C}_{10}\text{H}_{14}\text{O}$  (VI), b. p. 125—128°/18 mm., dimorphic,  $\alpha$ -form, m. p. 37°,  $\beta$ -form, m. p. 52° [oxime (VII), m. p. 137°; benzoyloximino-compound, m. p. 118°; semicarbazone, m. p. 192—195°]. The mother-liquors from the ozonisation in petroleum yield a residue by evaporation, which by treatment with sodium hydroxide gives the ketone VI. Ozonisation of the crude mixture of octahydronaphthalenes in acetic acid affords a small yield of the diketone V, accompanied by aldehydic products, a ketone  $\text{C}_{10}\text{H}_{14}\text{O}$  (? VI) (oxime, m. p. 137°; semicarbazone, m. p. 192—199°),  $\delta$ -ketosebacic acid, *trans*-cyclohexanediadicetic acid, and two liquid acid fractions, b. p. 145—180°/13 mm., and 180—210°/13 mm.; the formation of *trans*-cyclohexanediadicetic acid shows that *trans*- $\Delta^2$ -octahydronaphthalene is a constituent of the mixture (Leroux, Ann. Chim., 1910, [viii], 21, 458). The diketone V is extremely sensitive towards reagents, and is slowly converted by heating with water, and more rapidly by acids or alkalis, into VI; by oximation under special conditions V yields the diroxime, m. p. 231° (together with a little of VII), which is unaffected by catalytic reduction in acetic acid with platinum-black, but is converted by treatment with sodium and alcohol into 1 : 6-diaminocyclodecane, m. p. 50°, b. p. 135—140°/5 mm. [red monopicrate, m. p. 210° (decomp.)],

together with a liquid I : 6-diaminocyclodecane, b. p. 122—128°/5 mm. [yellow picrate, m. p. 249° (decomp.)]. By catalytic reduction with platinum-black in glacial acetic acid V furnishes cyclodecane-1 : 6-diol, m. p. 148°.

From the alcohol washings of the blue nitrosochloride I is obtained a white nitrosochloride,  $C_{10}H_{16}ONCl$ , II, m. p. 135° (nitrolpiperidide, m. p. 181°). The blue, liquid nitrosochloride III by treatment with zinc and acetic acid yields a mixture of octahydronaphthalenes, b. p. 74—77°/16 mm., from which nitrosyl chloride furnishes a small quantity of I, and three ketonic fractions, b. p. 90—110°/15 mm., 110—140°/15 mm., and 200°/15 mm., accompanied by traces of an amine. The ketonic fraction, b. p. 110—140°/15 mm., yields a mixture of semicarbazones, m. p. 233°, from which methyl alcohol extracts *trans*- $\alpha$ -decalonesemicarbazone, m. p. 230°; from the residue chloroform extracts a semicarbazone, m. p. 240°, converted by hydrolysis with oxalic acid into IV, b. p. 122—128°/14 mm. [oxime (VIII), m. p. 150°; benzoyloximino-compound (IX), m. p. 136°]. The residual semicarbazone, m. p. above 275°, by hydrolysis yields an unsaturated ketone,  $C_{10}H_{14}O$ , b. p. 90—110°/17 mm. [oxime (X), m. p. 157°; benzoyloximino-compound (XI), m. p. 134·5°]. The oximes, VIII and X, differ in their crystal form, but melt at 149° when mixed; their benzoyl derivatives, IX and XI, give a mixed m. p. 132—133°.

$\Delta^9$ : $^{10}$ -Octahydronaphthalene and the *trans*- $\Delta^2$ -isomeride are compared with regard to reduction and oxidation (for heats of combustion and X-ray diagrams see Katz, A., 1928, 464, 1312). *trans*- $\Delta^2$ -Octahydronaphthalene is hydrogenated by platinum-black in glacial acetic acid or in ether approximately three times as rapidly as the  $\Delta^9$ : $^{10}$ -isomeride, the reduction in both cases proceeding in acetic acid at 1·5 times the velocity in ether, and gives homogeneous *trans*-decahydronaphthalene [ $n_D^{20}$  1·47015 (acetic acid), 1·4699 (ether)], which solidifies completely in solid carbon dioxide.  $\Delta^9$ : $^{10}$ -Octahydronaphthalene, by hydrogenation with platinum-black in acetic acid, affords a mixture of *cis*- and *trans*-decahydronaphthalenes in the ratio 2 : 1 ( $n_D^{20}$  1·4767), a similar mixture in the ratio 1 : 1 ( $n_D^{20}$  1·4750) being obtained in ethereal solution; neither preparation solidifies in solid carbon dioxide.

Potassium permanganate oxidises  $\Delta^2$ -octahydronaphthalene much more quickly than the  $\Delta^9$ : $^{10}$ -isomeride; on the other hand, the latter is converted with extreme rapidity by perbenzoic acid into  $\Delta^9$ : $^{10}$ -octahydronaphthalene oxide, b. p. 82—83°/12 mm.,  $d_4^{20}$  0·9970,  $n_D^{20}$  1·48338, which gives an X-ray diagram in which the outer ring present in that of  $\Delta^9$ : $^{10}$ -octahydronaphthalene is completely absent. By hydration with 0·02*N*-perchloric acid the oxide yields octahydronaphthalene-9 : 10-diol, which appears to contain a variable amount (up to 1 mol.) of water of crystallisation; the lowest fraction has m. p. 79—89°, and the highest m. p. 84·5—92° (cf. Nametkin and Glagolev, *loc. cit.*); the glycol gives a diacetate, m. p. 169°, and by treatment with concentrated sulphuric acid at -10° to 0° undergoes the pinacol-pinacoloin change to yield cyclohexanone-2-spirocyclopentane (oxime, m. p. 64°; semicarbazone, m. p. 192°), previously obtained by Meiser (A., 1899, i, 741).

*cis*- $\alpha$ -Decalol *p*-toluenesulphonate, m. p. 93°, by hydrolysis with methyl-alcoholic potassium hydroxide yields a mixture of octahydronaphthalenes, m. p. -60° to -40°, from which a blue nitrosochloride, m. p. 91°, and a white nitrosochloride, m. p. 127°, are obtainable, and affording by oxidation with potassium permanganate a glycol, m. p. 68—69°, and succinic acid.

The dibromide, m. p. 61°, derived from the mixture of *cis*- $\Delta^1$ - and *cis*- $\Delta^2$ -octahydronaphthalene obtained from *cis*- $\beta$ -decalol by dehydration with potassium hydrogen sulphate (A., 1925, i, 1254), has the formula  $C_{10}H_{16}Br_2$ . C. W. SHOPPEE.

**Osmium as hydrogenating catalyst.** N. D. ZELINSKI and M. B. TUROVA-POLLAK (Ber., 1929, 62, [B], 2865—2869).—The catalyst is prepared by soaking asbestos in aqueous osmic acid and formaldehyde, adding potassium hydroxide, and completing the reduction at 60°. The product is washed with water, acidified with acetic acid, again washed, and dried at 120°. It is finally heated with hydrogen at 150°. Its activity has been examined towards benzene, cyclohexadiene, *o*- and *p*-xylene, mesitylene, indene, naphthalene, thujene, acetone, methyl ethyl ketone, cyclopentanone, and methylcyclopentanone. It is a very active reducing catalyst which operates at lower temperatures than platinum or palladium. When used with compounds of high b. p. it requires periodical reactivation by washing with benzene or cyclohexane in an atmosphere of hydrogen, which removes the adsorbed products of the catalysis; if necessary, the temperature must be raised to 250—300°. It can be used continuously for several months without loss of activity. Prolonged contact with substances undergoing catalysis at temperatures above 150° causes incipient decomposition. The dehydrogenating activity of osmium is less pronounced than that of palladium or platinum, and therefore it is used advantageously as a hydrogenating catalyst.

H. WREN.

**Highly polymerised compounds.** XXVI. **Organic colloids.** H. STAUDINGER (Ber., 1929, 62, [B], 2893—2908).—Investigation of synthetic polymerides shows that in solution the macromolecules are to be regarded as primary colloidal particles, and the analogous behaviour of natural products shows that the colloidal molecules are not homogeneous, but mixtures of polymeric homologues. For substances in which colloidal properties are dependent on the size of the molecule the expression "molecular colloids" is introduced. Their study necessitates a knowledge of their constitution in the sense of Kekulé's theories. Very complex polymerides are characterised by instability in solution towards chemical agents and rise in temperature. Stability increases with decreasing length of the molecule. Molecular colloids may be homopolar (polystyrenes; caoutchouc), heteropolar (polyacrylates), or possess dipolar character (polyacrylic acid; polyvinyl alcohol). They have cyclic structure, but the two parts of the ring are arranged parallel to one another, forming "double thread molecules." The proof that molecules of the dimension of a colloidal particle can pass into solution is afforded by the poly-

styrenes, in which the dissolution process is the same for all members of the series and the molecules become dissolved. The amorphous or crystalline nature of solid molecular colloids does not depend on homogeneity, but on the structure of the molecule. Symmetrical compounds are crystalline (polyethylene oxides, polyoxymethylenes, paraffins), whereas polyindenes, polystyrenes, etc. are amorphous, probably because the irregularly oriented side-chains hamper the lattice arrangement. The amorphous is not principally differentiated from the crystalline condition, since there is a certain arrangement of the molecules and only the lattice arrangement of the atoms is missing. The process of dissolution does not differ essentially with amorphous and crystalline substances, since the molecular lattice forces are little greater than the intermolecular forces of long, amorphous molecules; it is influenced enormously by the length of the molecule. The differences between association colloids and molecular colloids are discussed in detail, as are also the relationships of the latter to suspensoids and emulsoids. Among inorganic colloids the molecular colloids play an unimportant part, although the polymeric silicic acids belong to this group.

H. WREN.

**Highly polymerised compounds. XXVII.**

**Viscosity of polystyrene solutions (I). XXVIII.**

**Degradation of macromolecular polystyrenes.**

**XXIX. Viscosity of polystyrene solutions (II).**

**XXX. Association and solvation of polystyrenes.** H. STAUDINGER (Ber., 1929, 62, [B], 2909—2912, 2912—2920, 2921—2932, 2933—2943).—**XXVII.** [With K. FREY.]—The anomalous viscosity phenomena exhibited by eucolloidal polystyrene prepared at a low temperature is not due to change of structure within a disperse system, and the solution behaves quite differently from that of an association colloid or a heteropolar and co-ordinative molecular colloid. The viscosity of a solution of polystyrene in benzene is not affected by prolonged intensive agitation. Cooling of solutions in benzene, carbon tetrachloride, or carbon disulphide to 0°, -80°, or -180° does not affect the relative viscosity, measured at 20°. No change is effected by dilution followed by concentration and then dilution. Separation of a solution in benzene into more and less viscous fractions cannot be effected by centrifuging.

**XXVIII.** [With K. FREY, P. GARBSCH, and S. WEHRLI.]—The observation that the relative viscosity of dilute solutions of eucolloidal polystyrene is not diminished by rise in temperature has caused the abandonment of the view that the material is an equilibrated mixture of short and very long molecules (cf. A., 1929, 305) in favour of the hypothesis that it consists of multi-membered rings which may be compared with double threads. In consequence of their size, these molecules are labile, are very readily cracked, and ultimately pass into hemicolloids, from which they differ in magnitude of the rings. The action of a small quantity of bromine causes a very marked decrease in the viscosity of eucolloidal polystyrene; subsequent addition of bases does not restore the original viscosity. The change is due to a diminution in the size of the molecules, since it is effected by substances which are able to rupture carbon chains

(chlorine, oxidising agents such as nitrogen oxides, perbenzoic acid, and, particularly, ozone), but not by iodine, acids, or bases. The viscosity of hemicolloidal polystyrenes is not affected by bromine. Eucolloidal polystyrene suffers cracking in boiling tetrahydronaphthalene and to a smaller extent in boiling xylene or benzene. The degraded product has hemicolloidal properties, but the viscosity of its solutions is much higher than that of hemicolloidal polystyrene, mean mol. wt. 12,000, prepared by means of tin tetrachloride. Cracking of polystyrene in benzene containing glacial acetic acid at 200° gives a degraded product which does not appear to contain acetyl groups. The material obtained by polymerisation of styrene in tetrahydronaphthalene at 200° has a much smaller mean mol. wt. than that obtained by depolymerisation of macromolecular polystyrene under the same conditions.

**XXIX.** [With H. MACHEMER.]—Recognition of the effect of oxygen in depolymerising complex molecules (see above) has caused a repetition of previous work (A., 1929, 305) under more stringent conditions, whereby a product, polymerised at 260°, is found to have about the same relative viscosity as that prepared previously at 130°. The new products are transparent, completely colourless glasses. The relatively simple polymerides obtained above 200° are brittle and friable, whereas the more complex material is extraordinarily tenacious. Partial polymerisation at 65° or 100° affords an unusually elastic mass, showing that this condition is proper to mixtures of very complex and less complex polymerides. With hemicolloids, an increase in the viscosity of solutions accompanies an increase in mean mol. wt., but an exact relationship cannot be established. With eucolloids still greater difficulty is experienced, since the solutions do not conform to the Hagen-Poiseuille law. This non-obedience is not conditioned by the high viscosity of the solutions, since it is not exhibited by very concentrated hemicolloids, by olive or castor oil, or resin solutions, which contain relatively small molecules. It is attributed to the parallel orientation of the long molecules in the flowing liquid (as opposed to their irregular arrangement in the resting phase), whereby the resistance to flow is diminished. The phenomenon is designated "macromolecular viscosity" and affords a mode of distinguishing between eucolloidal and hemicolloidal solutions. The polymeric homologous polystyrenes are degraded in benzene at 150°, 210°, and 260° in complete absence of oxygen. In absence of solvent, the homogeneous polystyrenes suffer depolymerisation at 260°, but not at 150° or 210°, whereas the technical product, owing to the presence of peroxides, is greatly changed above 130°. The alteration appears to depend on the liquefaction of the mass. Macromolecular polystyrenes, prepared by different methods, are converted by sufficiently protracted action of bromine into portions of the same order of magnitude.

**XXX.** [With W. HEUER.]—Hemicolloids are characterised by conformity with the Hagen-Poiseuille law at different temperatures. In very concentrated solution the relative viscosity changes with alteration of temperature, since association occurs as with compounds of lower mol. wt. This association must not be regarded as micelle formation, since it differs



fundamentally from an electrically-charged soap micelle. Observations of the relative viscosity of very dilute solutions of macromolecular polystyrene in tetrahydronaphthalene at 20°, 40°, and 60° give no evidence of association. With increasing concentration, slight association appears to occur. Observations on the viscosity of eucolloidal solutions as measured in instruments with varied length and diameter of capillary confirm the author's theory (see above) with regard to non-conformity with the Hagen-Poiseuille law.

Measurements are recorded of the relative viscosity of highly-polymerised polystyrene in carbon tetrachloride, pyridine, and ethyl acetate at 20°, 40°, and 60° and  $\eta = 10, 30$ , and 60 cm. H. WREN.

**Selective action of a catalyst of hydrogenation.** M. BOURGUEL and (MLLE.) V. GREDY (Compt. rend., 1929, 189, 757—759).—If in the process previously described (A., 1928, 28) when hydrogenation by the palladium catalyst has been carried to the point where all acetylenic linkings have been reduced to ethylenic and the latter are being attacked, a further quantity of acetylenic compound is added, the velocity of catalysis immediately reverts to its original value, returning again to the velocity for attack of the ethylenic linking when the additional acetylenic linkings have been reduced thus far. This is experimentally demonstrated with phenylacetylene and ethyl heptinene-carboxylate. These results are held to disprove any hypothesis of the reversibility of the catalytic action of palladium. C. A. SILBERRAD.

**s-Triphenylbenzene; amorphous resins and lacs.** D. VÖRLÄNDER, E. FISCHER, and H. WILLE (Ber., 1929, 62, [B], 2836—2844; cf. Vorländer and others, A., 1925, i, 1255).—Under all conditions, s-triphenylbenzene solidifies to a solid, crystalline mass without marked under-cooling from the amorphous, molten condition. If the hydrocarbon is brominated, nitrated, aminated, etc., the crystalline substituted products, in consequence of the dissymmetry of the molecule, form transparent, colourless, amorphous lacs permanent at 15—20° when the amorphous, molten products are rapidly cooled. The lacs become crystalline solids when warmed.

1:3:5-Triphenylbenzene, m. p. 169°, from acetophenone and aniline hydrochloride at 170—175°, is converted by the gradual addition of nitric acid ( $d 1.52$ ) to its solution in boiling glacial acetic acid into 1:3-diphenyl-5-p-nitrophenylbenzene, m. p. 142—143° (corr.) (yield 70%), and more highly nitrated compounds. It is oxidised by chromic acid in glacial acetic acid to benzoic and p-nitrobenzoic acids, 5-p-nitrophenylbenzene-1:3-dicarboxylic acid, m. p. 300° (corr. decomp.) after softening at 294° [methyl ester, m. p. 246° (corr., decomp.) after softening at 241°; ethyl ester, m. p. 172—174°], and 3-phenyl-5-p-nitrophenylbenzoic acid, m. p. 215.5° (corr.) [methyl ester, m. p. 155—156° (corr.); ethyl ester, m. p. 121° (corr.); n-propyl ester, m. p. 133—136° (corr.); sodium salt; p-ethoxybenzeneazophenyl ester, m. p. 104—106° after softening; 3-phenyl-5-p-nitrophenylbenzoyl chloride, m. p. 90.5°; 3-phenyl-5-p-nitrophenylbenzamide, m. p. 175—176° (corr.)]. Further oxidation of 3-phenyl-5-p-nitrophenylbenzoic acid with chromic acid affords

p-nitrophenylbenzenedicarboxylic acid. Treatment of 1:3:5-triphenylbenzene with boiling nitric acid affords  $\alpha$ -tetranitrotriphenylbenzene, m. p. above 260°, and p-nitrobenzoic acid.

1:3-Diphenyl-5-p-nitrophenylbenzene is reduced by stannous chloride and acetic acid saturated with hydrogen chloride to 1:3-diphenyl-5-p-aminophenylbenzene, m. p. 138.5° (corr.) [hydrochloride, m. p. about 204—206°; monoacetyl derivative, m. p. 244° (corr.)], converted by alcoholic potassium hydroxide into aminotriphenylbenzene and by molten sodium hydroxide and air into a dark violet dye; diacetyl derivative, m. p. 146° (corr.)]. The following derivatives of 1:3-diphenyl-5-p-aminophenylbenzene are described: benzylidene, m. p. 151°; cinnamylidene, m. p. 179° (corr.); p-nitrobenzylidene, m. p. 228° (corr.); anisylidene, m. p. 196—198° (corr.); ethoxybenzylidene, m. p. 177° (corr.); terephthalylidene,  $C_6H_4(CH:NC_2H_5)_{17}2$ , m. p. 272° (corr.); p-azoxybenzylidene,  $N_2O(C_6H_4 \cdot CH:NC_2H_5)_{17}2$ , m. p. 238° (corr.).

H. WREN.

**Electrolytic chlorination of benzene in methyl alcohol.** P. JAYLES.—See A., 1929, 1403.

**Decomposition of phenyl iodide dichloride.** E. V. ZAPPI and V. DEULOFEU (Bull. Soc. chim., 1929, [iv], 45, 848—854).—Phenyl iodide dichloride is rapidly decomposed by allyl alcohol at the ordinary temperature, yielding about 37% of its chlorine as hydrogen chloride, about 37% as p-chloroiodobenzene, and the remaining 26% as free chlorine which rapidly combines with the allyl alcohol, the decomposition being thus represented:  $4PhICl_2 = Cl_2 + 3HCl + 3C_6H_4ICl + PhI$ . Dilution with methyl, ethyl, propyl, isopropyl, butyl, sec.-amyl, octyl, or benzyl alcohol, or with benzene, toluene, xylene, acetaldehyde, or light petroleum, does not appreciably affect the course of the decomposition, but in presence of water the formation of hydrogen chloride is increased, about 52% of the chlorine being eliminated in this form, probably in consequence of the reaction:  $PhICl_2 + H_2O = 2HCl + PhIO$ . Dilution with chlorinated solvents such as chloroform or carbon tetrachloride considerably increases the liberation of molecular chlorine and nearly 50% is eliminated as such, the decomposition being represented approximately:  $2PhICl_2 = Cl_2 + HCl + C_6H_4ICl + PhI$ . Allyl acetate or butyrate does not produce the same result and the decomposition is accordingly not due simply to the presence of a double linking. R. BRIGHTMAN.

**Dinitration of m-dichlorobenzene.** A. T. DANN (J.C.S., 1929, 2460—2462).—Nitration of m-dichlorobenzene under regulated conditions in concentrated sulphuric acid, the mixture being heated at 99° for 1 hr., yields a mixture of 85% of 1:3-dichloro-4:6-dinitrobenzene (I), m. p. 101.0°, and 15% of 1:3-dichloro-2:4-dinitrobenzene (II), m. p. 68.0°, with a negligible amount of other isomerides (cf. Davies and Hickox, J.C.S., 1922, 124, 2649). I is obtained pure by recrystallisation from alcohol, and II by recrystallisation of the residue from concentrated sulphuric acid, or by nitration of 1:3-dichloro-2-nitrobenzene. The eutectic in the m.-p. curve of mixtures of I and II is at 48.1°, 62% of II. R. K. CALLOW.

**Syntheses with metal carbonyls.** G. GALLAS and A. ALONSO (Anal. Fis. Quim., 1929, 27, 663—667).—By the action of xylene solutions of nickel carbonyl on organic compounds containing a labile halogen atom (*p*-dichloro-, *o*-dibromo-, chloronitro-, and chlorodinitro-benzenes) substances of high m. p. but of so far unknown composition are produced. The nickel of the carbonyl molecule is probably substituted by an organic group. H. F. GILLBE.

**Sulphonic acids of *m*- and *p*-xylenes and mesitylene and their derivatives.** A. F. HOLLEMANN (Anal. Fis. Quim., 1929, 27, 473—484).—[With H. J. CHOUFOER.]—Mainly an account of work already abstracted (Holleman and Choufoer, A., 1924, i, 1071; Choufoer, A., 1925, i, 896). Nitration of *p*-xylenesulphonic acid in fuming sulphuric acid yields a mixture of isomerides. Conversion of this into the acid chlorides and extraction with ether yields the least soluble 2-nitro-*p*-xylene-3-sulphonyl chloride, m. p. 109.5°. This is hydrolysed and reduced by iron powder to yield the 2-amino-compound, which is diazotised, converted into the disulphide, and then oxidised by permanganate to *p*-xylene-2 : 3-disulphonic acid. The acid is converted by phosphorus pentachloride into an anhydride, m. p. 139—190°.

[With N. J. G. ALOZERY.]—Treatment of mesitylene with sulphuryl chloride and chlorosulphonic acid yields mesitylenedisulphonyl chloride, m. p. 125° (corr.) (amide, m. p. 244°), which yields on nitration nitromesitylenedisulphonyl chloride, m. p. 193—199.5° (corr.). R. K. CALLOW.

**Formation of aromatic hydrocarbons by dehydrogenating catalysis.** N. D. ZELINSKI and I. N. TITZ (Ber., 1929, 62, [B], 2369—2373; cf. A., 1927, 47).—*xy*-Diphenylpropane is unchanged by passage over platinised charcoal at 300—310° in an atmosphere of carbon dioxide. Stilbene at 300° affords phenanthrene quantitatively. Hydrindane gives a mixture of unchanged material and hydrindene (cf. Zelinski and Borissov, A., 1925, i, 122).  $\alpha\beta$ -Dicyclohexylethane is dehydrogenated successively to dibenzyl, 9 : 10-dihydrophenanthrene, and phenanthrene. H. WREN.

**Preparation of magnesium triphenylmethyl chloride.** H. GILMAN and E. A. ZOELLNER (J. Amer. Chem. Soc., 1929, 51, 3493—3496).—A mixture of magnesium (0.021 atom), iodine (0.025 atom), and ether (0.39 mol.) is stirred until all the iodine has reacted, and triphenylmethyl chloride (0.01 mol.) is then added all at once. After the initial reaction (produced by heating) is over the mixture is refluxed gently for 3 hrs. The yield of Grignard reagent, determined by an acid titration method (cf. A., 1929, 800), is 96%. H. BURTON.

**Reaction between alkali-metal alkyls and quaternary phosphonium halides.** D. D. COFFMAN and C. S. MARVEL (J. Amer. Chem. Soc., 1929, 51, 3496—3501).—Sodium triphenylmethyl (I) reacts with tetraethylphosphonium iodide in ethereal solution at the ordinary temperature, forming triphenylmethane, triethylphosphine, and sodium iodide. Triphenyldiphenylmethylphosphonium bromide and I or lithium *n*-butyl (II) afford triphenylphosphinedi-

phenylmethane (Staudinger and Meyer, A., 1920, i, 106) in good yield. Triphenylisopropylphosphonium bromide and I give a coloured solution, which when exposed to moist air becomes colourless, and furnishes diphenylisopropylphosphine oxide, m. p. 142—143°. This is probably formed thus:  $\text{CHMe}_2\cdot\text{PPh}_3\text{Br} \xrightarrow{\text{Na-CPh}_3} \text{CMe}_2\cdot\text{PPh}_3 \xrightarrow{\text{H}_2\text{O}} \text{CHMe}_2\cdot\text{PPh}_3\cdot\text{OH} \rightarrow \text{CHMe}_2\cdot\text{PPh}_2\cdot\text{O} + \text{C}_6\text{H}_6$ . Similarly, triphenylmethylphosphonium iodide and I yield diphenylmethylphosphine oxide (basic carbonate, m. p. 109—111° with evolution of gas), whilst triphenylethylphosphonium iodide and II afford diphenylethylphosphine oxide.

H. BURTON.

**Rearrangement reactions of magnesium  $\alpha$ -naphthylmethyl chloride.** H. GILMAN and J. E. KIRBY (J. Amer. Chem. Soc., 1929, 51, 3475—3478).— $\alpha$ -Naphthylmethyl chloride (from the carbinol and thionyl chloride) reacts readily with magnesium forming the Grignard reagent (cf. Mayer and Sieglitz, A., 1922, i, 740; Conant, Small, and Sloan, A., 1926, 842), which behaves normally with carbon dioxide, methyl sulphate, and phenylcarbimide, but abnormally with ethyl chloroformate (yielding 1-methyl- $\beta$ -naphthoic acid; cf. Weitzenböck and Lieb, A., 1912, i, 547) and formaldehyde [forming di- $\alpha$ -naphthylethane, an unidentified fraction, b. p. 100—130°/6 mm., and probably 1-methyl- $\beta$ -naphthylcarbinol, b. p. 167—170°/6 mm., m. p. 121° (phenylcarbimide derivative, m. p. 125°)].

Magnesium  $\beta$ -naphthylmethyl bromide and carbon dioxide give  $\beta$ -naphthylacetic acid. H. BURTON.

**Synthesis of anthracene homologues. II. 2 : 3 : 6-Trimethylanthracene.** G. T. MORGAN and E. A. COULSON (J.C.S., 1929, 2551—2559).—From the heavy neutral oils of low-temperature tar from the carbonisation of bituminous coal a hydrocarbon has been isolated which is identical with 2 : 3 : 6-trimethylanthracene obtained by synthesis.

Details are given for the preparation of 5-iodo- $\psi$ -cumene from  $\psi$ -cumidine. The Grignard compound of the former substance gives with *p*-toluonitrile 2 : 4 : 5 : 4'-tetramethylbenzophenone, b. p. 220°/22 mm. (oxime, m. p. 151°), also produced by the condensation of  $\psi$ -cumene (for which details of preparation from  $\psi$ -cumidine are given) with *p*-toluoyl chloride in the presence of aluminium chloride. The ketone gives on boiling for 8 hrs. a small quantity of 2 : 3 : 6-trimethyl-9-anthrone, m. p. 196° (corr.). If the refluxing process is continued for 6 days 2 : 3 : 6-trimethylanthracene, m. p. 255° (corr.), can be isolated. 4-Methylphthalic acid was prepared from 3-nitro-*p*-toluidine and gave on condensation with *o*-xylene in the presence of aluminium chloride (?) 3 : 4 : 3'-trimethylbenzophenone-6'-carboxylic acid, m. p. 162° (corr.), and this latter compound yielded, on heating in sulphuric acid to 120—130°, 2 : 3 : 6-trimethylanthraquinone, m. p. 240° (corr.), identical with that formed by the oxidation of the hydrocarbon with chromic anhydride. When 4-methylphthalic acid is condensed with toluene there is formed (?) 3 : 4'-dimethylbenzophenone-6-carboxylic acid, m. p. 164° (corr.), which by a process similar to the above yielded 2 : 6-dimethylanthraquinone (A., 1929, 1436). Reduction of the trimethylanthraquinone with zinc

and aqueous ammonia gives the corresponding anthracene homologue, whilst reduction with tin and hydrochloric acid in boiling acetic acid yields 2 : 3 : 6-trimethyl-9-anthrone (see above). The yield of the isomeric 10-anthrone is small. *o*-Cumene was oxidised to trimellitic acid, which was found to melt at 238°.

T. H. MORTON.

**Organic compounds with reversible oxidisability.** C. MOURET and C. DUFRAISSE (Anal. Fis. Quim., 1929, 27, 516–519).—A summary of the authors' views of the analogy of the oxidation of rubrene and hæmoglobin (cf. A., 1929, 922).

R. K. CALLOW.

**Arylsulphonalkylamides.** L. DÉMENY (Rec. trav. chim., 1929, 48, 1145–1154).—By the action of the appropriate amine on *o*-, *m*-, and *p*-nitrobenzenesulphonyl chlorides the following new sulphonylalkylamides are prepared: *p*-nitrobenzenesulphon-methylamide, m. p. 110°; -ethylamide, m. p. 103°; -*n*-propylamide, m. p. 84°; -*n*-butylamide, m. p. 84°; -*n*-amylamide, m. p. 63°; -*n*-hexylamide, m. p. 71°; -*n*-heptylamide, m. p. 83°; *m*-nitrobenzenesulphon-*n*-propylamide, m. p. 61°; -*n*-amylamide, m. p. 59°; -*n*-hexylamide, m. p. 67°; -*n*-heptylamide, m. p. 71°; *o*-nitrobenzenesulphon-methylamide, m. p. 113°; -ethylamide, m. p. 103°; -*n*-propylamide, m. p. 70°; -*n*-butylamide, m. p. 61°; -*n*-amylamide, m. p. 48°; -*n*-hexylamide, m. p. 62°; -*n*-heptylamide, m. p. 65°. With the exception of the amides (*o*- has highest m. p.) and methylamides (*m*- has highest m. p.) the *p*-derivatives all have the highest m. p. Various other chemical and physical properties of the *o*-, *m*-, and *p*-isomerides are compared.

J. W. BAKER.

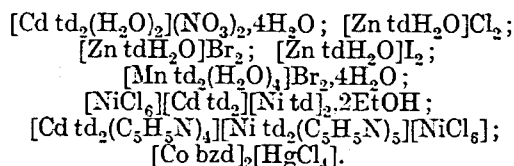
**Influence of solvents in the preparation of cyclic thiocarbamides.** E. MARAGONI and M. J. LAMORT (Rev. Farm., Buenos Aires, 1929, [2], 2, 332–339; cf. A., 1929, 1057).—Toluene gives good results with xanthate, tetralin is active, whilst with sulphur a red, soluble compound, but no thiocarbamide, is obtained. Acetophenone and benzophenone give no results; acetone and methyl ethyl ketone are satisfactory. Diethyl ether gives a poor yield; diamyl ether and isoamyl acetate give a moderate yield.

CHEMICAL ABSTRACTS.

**9-Aminofluorene.** A. ECKERT and J. GRANZMÜLLER (J. pr. Chem., 1929, [ii], 123, 330–332).—Bromination of 9-acetamidofluorene in acetic acid at 100° gives 2 : 7-dibromo-9-acetamidofluorene, m. p. 268° (decomp., in sealed tube), oxidised by sodium dichromate in acetic acid with a few drops of sulphuric acid to 2 : 7-dibromofluorenone. The corresponding chloro-compound could not be obtained.

J. W. BAKER.

**Stereochemistry of diphenyl and its derivatives.** III. G. SPACU (Bul. Soc. Stiinte Cluj, 1928, 4, 210–224; Chem. Zentr., 1929, ii, 165).—It was sought to prepare complex salts from metallic salts and tolidine analogous to those obtainable from benzidine. Not more than two molecules of the base, usually only one, could be combined with the metallic atom owing to the diminished mobility of the molecule. The following compounds (td = tolidine) are described:  $[\text{Co td}(\text{H}_2\text{O})\text{Cl}_2]$ ;  $[\text{Co td}(\text{H}_2\text{O})\text{Br}_2]$ ;  $[\text{Ni td}(\text{H}_2\text{O})\text{Cl}_2 \cdot \text{H}_2\text{O}]$ ;  $[\text{Ni td}(\text{H}_2\text{O})_4]\text{Br}_2$ ;  $[\text{Cd td}]\text{Cl}_2$ ;  $[\text{Cd td}]\text{Br}_2$ ;



A. A. ELDRIDGE.

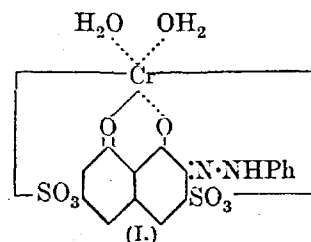
**Derivatives of *p*-phenylenediamine.** H. MEYER.—See B., 1929, 973.

**Cleavage of azo-dyes by sulphites.** Cleavage of 4-hydroxyazobenzene-5-carboxylic acid and 4-hydroxy-3-methylazobenzene-5-carboxylic acid. K. H. ENGEL (J. Amer. Chem. Soc., 1929, 51, 3483–3489).—Reduction of 4-hydroxyazobenzene-5-carboxylic acid, m. p. 220.5° (corr.) (1 mol.), with ammonium sulphite solution under the conditions previously described (A., 1929, 1439) gives aniline (0.65 mol.), ammonium phenylsulphamate (0.35 mol.), ammonium 5-disulphoaminosalicylate (0.584 mol.) (tribarium salt + 2H<sub>2</sub>O), and ammonium 5-amino-*N*-sulphosalicylate (0.416 mol.). Rearrangement of the above disulphonic acid with dilute mineral acid affords 5-amino-3-sulphosalicylic acid (also obtained by direct sulphonation of 5-aminosalicylic acid), whilst the corresponding *N*-sulphonic acid furnishes a soluble acid, probably an *O*-sulphonic acid.

4-Hydroxy-3-methylazobenzene-5-carboxylic acid, m. p. 202° (corr.), is similarly reduced to aniline (0.66 mol.) and its *N*-sulphonic acid (0.34 mol.), and the *N*-mono- (0.48 mol.) and -di-sulphonic acids (0.48 mol.) of 5-amino-2-hydroxy-*m*-toluic acid. Rearrangement of the mixed sulphonic acids gives a mixture of 5-amino-2-hydroxy-*m*-toluic acid and its *O*-sulphonic acid. The amount of sulphate formed during this reduction increases with rise of reduction temperature; the yield of the *N*-disulphonic acid is thereby diminished.

H. BURTON.

**Chrome dyes; chromotrope 2R.** I. E. ROSENHAUER, W. WIRTH, and R. KÖNIGER (Ber., 1929, 62, [B], 2717–2724).—Under definite conditions chromotrope 2R is converted by potassium dichromate and sulphuric acid in the



presence of water into the homogeneous lake, to which the constitution is assigned for the following reasons. It behaves as an internally complex salt, very sparingly soluble in hot water and very stable, particularly towards mineral acids. It

is converted by reductive fission with stannous chloride and hydrochloric acid into aniline and 3-amino-4 : 5-dihydroxynaphthalene-2 : 7-disulphonic acid, converted by fuming nitric acid into the corresponding hydroxynaphthaquinonedisulphonic acid. Since the same compounds are obtained by the reduction of chromotrope 2R, its molecule must be present also in the lake. The last-named compound can also be obtained by the use of chrome alum or chromic chloride and can be converted into the dye in

80% yield by boiling glacial acetic acid containing an excess of crystalline sodium acetate. Similar observations with 3- $\alpha$ -naphthaleneazo-4:5-dihydroxynaphthalene-2:7-disulphonic acid are recorded. For the production of a chrome lake the presence of two hydroxyl groups appears necessary, since a compound of this type is not produced from Mars-red G [carmoisin] (from 4-hydroxynaphthalenesulphonic acid and diazotised naphthionic acid) and chromic salts. Both sulphonic acid groups appear to participate in the salt formation and, since 3-*p*-sulphobenzeneazo-4:5-dihydroxynaphthalenesulphonic acid yields a stable lake, the position of the sulphonic groups seems immaterial. There is no acid residue, derived from the chromium salt employed, attached to the chromium atom in the lakes. If chromates are used, a blue lake can be obtained from Mars-red G which appears identical with that derived from the 4-sulphonic acid of eriochrome blue-black B (4-hydroxynaphthalenesulphonic acid and diazotised 4-amino-3-hydroxynaphthalenesulphonic acid). H. WREN.

**Anomalous diazo-coupling with unsaturated phenols.** A. QUILICO and M. FREMI (Gazzetta, 1929, 59, 600—611).—Diazotised *p*-nitroaniline couples normally with *o*- and *p*-propenylphenol (improved preparation described) in aqueous alkaline solution to give 4-*p*-nitrobenzeneazo-2-propenylphenol, softens at 70°, and 2-*p*-nitrobenzeneazo-4-propenylphenol, softens 100—110° and decomposes 135—140°, respectively. On the contrary, *p*-nitrobenzenediazonium sulphate, purified by successive dissolution in glacial acetic acid and precipitation with ether, suspended in alcohol, and treated with an ice-cold alcoholic solution of *p*-propenylphenol, affords 60% of *p*-hydroxybenzaldehyde-*p*-nitrophenylhydrazone (I), m. p. 275° (decomp.), together with a nitrogenous substance, m. p. 223°, soluble in cold alkali with production of an intense blue colour, and separated by its insolubility in alcohol (cf. A., 1928, 997). By methylation with methyl sulphate, I gives anisaldehyde-*p*-nitrophenylhydrazone, m. p. 161°, and by acetylation with acetic anhydride *p*-acetoxybenzaldehyde-*N*-acetyl-*p*-nitrophenylhydrazone (II), m. p. 166°. *p*-Hydroxybenzaldehyde condenses with *p*-nitrophenylhydrazine to give a *p*-nitrophenylhydrazone, which may be a stereoisomeride of I, since it differs slightly from it, but melts alone or mixed with I at 275° (decomp.); by treatment with acetic anhydride it gives II. *p*-Nitrobenzenediazonium sulphate and *o*-propenylphenol similarly yield 25% of *o*-hydroxybenzaldehyde-*p*-nitrophenylhydrazone (III), m. p. 225°, together with a substance, m. p. 223°, insoluble in alcohol and giving a blue colour with alkalis. The product obtained from salicylaldehyde and *p*-nitrophenylhydrazine is identical with III, which by acetylation with acetic anhydride gives *o*-acetoxybenzaldehyde-*N*-acetyl-*p*-nitrophenylhydrazone, m. p. 166°.

C. W. SHOPPEE.

**Direction of carbon valencies in methane derivatives.** D. VORLÄNDER [with O. RITTER] (Ber., 1929, 62, [B], 2824—2831).—Observations of the presence or absence of liquid-crystalline properties in derivatives of carbamide and thiocarbamide and of carbodi-imide lead to the conclusion that the linear

constitution  $E=C=E$  is preferable to the angular formula  $E \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} E$ .

The following compounds are described: *p*-ethoxy-diazoaminobenzene, m. p. 110—112° (slight decomp.), and thence *p*-ethoxy-*p'*-aminoazobenzene, m. p. 127—129° [hydrochloride, m. p. about 225° (decomp.)], and its *N*-acyl derivatives, formyl, m. p. I 176°, m. p. II 168°, acetyl, m. p. 212—213°, propionyl, m. p. 200—202°, *n*-butyryl, m. p. 198° after slight softening, *n*-hexoyl, m. p. 164—165°, *n*-heptoyl, m. p. 158°, *n*-octoyl, m. p. 156° after softening, palmityl, m. p. 152—153°, benzoyl, m. p. 230—232°. *p*-Ethoxy-*p'*-aminoazobenzene is converted by carbon disulphide and sulphur in alcohol or by phenylthiocarbamide into *s*-di-*p*-ethoxybenzeneazophenylthiocarbamide,  $S:C(NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OEt)_2$ , m. p. 207°, transformed by mercuric oxide in dry benzene into di-*p*-ethoxybenzeneazophenylcarbodi-imide,  $C:(N \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OEt)_2$ , m. p. I 166°, m. p. II 157°, which is re-transformed by hydrogen sulphide in naphthalene at 80—90° into the non-liquid-crystalline carbamide. *s*-Di-*p*-ethoxybenzeneazophenylcarbamide, m. p. about 306° (decomp.), is prepared from the thiocarbamide and mercuric oxide in alcohol, from the di-imide and acetic acid, or from the carbimide,  $CO:N \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot OEt$ , m. p. I 141°, m. p. II 117° (from carbonyl chloride and aminoethoxyazobenzene). The carbimide is transformed by the requisite alcohol into the corresponding methyl-, m. p. I 166°, m. p. II 160°, ethyl-, m. p. 165°, and isopropyl-, m. p. 161°, urethanes.

*p*-Amino-*p'*-ethoxyazobenzene reacts readily with aromatic aldehydes giving *p*-benzylideneamino-*p'*-ethoxyazobenzene, m. p. 135—137° and 201—203°, *p*-cinnamylideneamino-*p'*-ethoxyazobenzene, m. p. 159° and 244°, and *p*-anisylideneamino-*p'*-ethoxyazobenzene, m. p. 155—156° after softening at 154°.

*p*-Acetamido-*p'*-ethoxyazobenzene is converted by hydrogen peroxide in glacial acetic acid into (?) *p*-acetamido-*p'*-ethoxyazoxybenzene, m. p. 199—201°, whence *p*-amino-*p'*-ethoxyazoxybenzene, m. p. 142—145°. The following compounds are incidentally described: *p*-methoxydiazoaminobenzene, m. p. 88—90°; *p*-amino-*p'*-methoxyazobenzene, m. p. 151—153°; *s*-di-*p*-methoxybenzeneazophenylthiocarbamide, m. p. about 215° after darkening; di-*p*-methoxybenzeneazophenylcarbodi-imide, m. p. 165°; *p*-formamido-*p'*-methoxyazobenzene, m. p. 178°; *p*-acetamido-*p'*-methoxyazobenzene, m. p. 183°.

H. WREN.

**Direction of the carbon valencies in benzene derivatives.** D. VORLÄNDER [with E. SCHROEDTER and W. ZEH] (Ber., 1929, 62, [B], 2831—2835).—Examination of the esters of the three isomeric phthalic acids with complex groups shows that the liquid crystalline condition is not observed with *ortho*-derivatives even when the side-chain is greatly extended. The chains do not become more parallel to one another but remain divergent, following an angle of 60°. With the *meta*-compounds, slight liquid-crystalline properties are observed if the side-chain is sufficiently prolonged, corresponding thus with the obtuse angle of 120°, but the presence of a substituent in the *para*-position in the phenolic portion

of the ester is requisite. With the *p*-acid, the linear form of the molecule has an extremely pronounced effect on the crystalline properties of the compounds.

The following compounds are described: *p*-methoxybenzeneazophenyl phthalate, m. p. 200° after softening and darkening at about 196°, isophthalate, m. p. II 255—257°, m. p. I 263—266° after softening at 252°, and terephthalate (supracrystalline), m. p. II 252—255°, decomp. above 330°; *p*-ethoxybenzeneazophenyl phthalate, m. p. 214—215° after softening and darkening at about 211°, isophthalate, m. p. II 247—249°, and m. p. I 253—255°, and terephthalate, m. p. II 240—242° after darkening at 237°, decomp. 340—348°; benzeneazobenzeneazophenyl phthalate,  $C_6H_4(CO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_5)_2$ , m. p. 257° after softening at 255°, isophthalate, m. p. II 286°, m. p. I above 292°, and terephthalate, decomp. above 390°; *p*-ethoxybenzeneazophenyl trimesate, m. p. 242—244° after darkening and softening, and *p*-methoxybenzeneazophenyl trimesate, m. p. 245—246° after darkening.

H. WREN.

**Reactions of the diazohydrates.** D. BIGIANI (Atti R. Accad. Lincei, 1929, [vi], 9, 1118—1121).—The structure for diazohydrates suggested by Angeli and Cambi readily explains the conversion of *iso*- into normal diazo hydrate, which is analogous to the Beckmann transformation, consisting in the migration of the oxygen atom from one nitrogen atom to another. When taking place in presence of hydrochloric acid, the change is probably accompanied by intermediate formation of diazonium chloride:  $NPh \cdot N \cdot OH \rightarrow NPhCl \cdot N \rightarrow OH \cdot NPh \cdot N \rightarrow O \cdot NPh \cdot NH$ . The fact that the sodium salt of an *isodiazohydrate* does not react with  $\beta$ -naphthol, arsenite, etc., whilst the free *isodiazohydrate* readily reacts, is analogous to the different behaviour of sodium nitrite and free nitrous acid towards phenols, etc., and that of benzaldoxime and its sodium derivative towards potassium cyanide.

T. H. POPE.

**Tenacity of organic radicals to oxygen in ethers.** B. V. TRONOV and L. V. LADIGINA (Ber., 1929, 62, [B], 2844—2850; cf. A., 1928, 44).—The rate of fission of a series of phenyl alkyl ethers in glacial acetic acid by hydrogen bromide has been measured at 18—20°; the phenyl group remains attached to the oxygen atom. Secondary radicals are separated from oxygen about ten times as rapidly as primary, and tertiary radicals yet more easily. Lengthening of the chain of normal primary aliphatic radicals causes increase in the tenacity towards oxygen, whereas, as far as ascertained, branching in the hydrocarbon chain retards fission in a degree which increases as the substituent approaches the oxygen atom. The benzene nucleus, separated from the oxygen atom, facilitates fission more powerfully than a double linking. Ring formation appears to exert no decided influence. Comparison of diethyl, dipropyl, diisopropyl, and methyl isopropyl ether gives no direct information with respect to dependence of tenacity on the nature of the radicals; the apparent discrepancy between this observation and those with phenyl alkyl ethers is probably explained by the intermediate production of oxonium compounds in the present case. The phenyl ethers,  $PhO \cdot [CH_2]_n \cdot OPh$  ( $n=1, 2$ , or  $3$ ), are hydrolysed with increasing difficulty as the phenyl groups draw

nearer to one another. With the acetals  $CH_2(OMe)_2$  and  $CHMe(OEt)_2$  the rates of reaction are in about the same ratio as with ethers containing the same radicals; ethyl orthoformate is more rapidly decomposed.

The following ethers are described in detail: *phenyl sec.-butyl ether*, b. p. 195—196°/763 mm.,  $d_4^{20}$  0.9415, from phenol, *sec.-butyl bromide*, and sodium in ethyl alcohol; *phenyl *n*-hexyl ether*, b. p. 243—243.5°/739 mm.,  $d_4^{20}$  0.9189; *phenyl cyclohexyl ether*, b. p. 252—254°/744 mm.,  $d_4^{20}$  0.9795.

H. WREN.

**Direct introduction of sulphur into aromatic hydrocarbons.** H. B. GLASS and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 3428—3430).—When benzene is heated with sulphur at 350° for 24 hrs., thiophenol, diphenyl sulphide and disulphide, diphenylene disulphide (thioanthrene), and hydrogen sulphide are formed. The first product formed is probably thiophenol. With ethylbenzene a good yield of 2:4-diphenylthiophen is obtained as the sole product.

H. BURTON.

**Effect of structure of organic halides on their rate of reaction with inorganic halides. III. Effect of the phenylthiol,  $\alpha$ - and  $\beta$ -naphthoxy-groups.** W. R. KIRNER and G. H. RICHTER (J. Amer. Chem. Soc., 1929, 51, 3409—3418; cf. A., 1924, i, 273; 1926, 1224; 1928, 1214).—The reactivities of substituted alkyl halides of the type  $R \cdot [CH_2]_n \cdot Cl$ , where  $n=2$  and  $3$ , and  $R=SPh$  and  $O \cdot C_{10}H_7$  ( $\alpha$ - and  $\beta$ -), have been determined by studying the velocity of reaction with potassium iodide in acetone solution. Comparison of the results obtained with those previously described (*loc. cit.*), where  $R=SMe$ ,  $OPh$ , and  $Ph$ , shows that in every case the chlorine atom is more reactive in the  $\gamma$ - than in the  $\beta$ -position to the same group; the ratios at 50° vary between 1.53:1 ( $Ph$ ) and 6.14:1 ( $O \cdot C_{10}H_7 \cdot \alpha$ ). The temperature coefficient is always higher for the substituted ethyl chlorides. The phenylthiol group in either the  $\beta$ - or  $\gamma$ -position activates the chlorine atom about twice as strongly as a phenoxy-group in the same position.  $\beta$ -Phenylethyl chloride has a higher reactivity than either  $\beta$ -phenylthiol- or  $\beta$ -phenoxy-ethyl chlorides, but  $\gamma$ -phenylpropyl chloride is less reactive than the  $\gamma$ -phenylthiol- or  $\gamma$ -phenoxy-propyl chlorides.  $\alpha$ - and  $\beta$ -Naphthoxy-groups are equally active and are similar to the phenoxy-group.  $\beta$ -Phenylthioethyl chloride is less reactive than the  $\beta$ -methylthiol derivative, but for the  $\gamma$ -derivatives the reverse is true. All the above  $\beta$ -substituted ethyl chlorides are less reactive than ethyl chloride, whilst all the  $\gamma$ -substituted propyl chlorides are more reactive than *n*-propyl chloride.

*Phenyl  $\beta$ -hydroxyethyl sulphide*, b. p. 115—116°/2 mm.,  $d_4^{20}$  1.1431,  $n_D^{20}$  1.5917, and *phenyl  $\gamma$ -hydroxypropyl sulphide*, b. p. 134—135°/2 mm.,  $d_4^{20}$  1.1178,  $n_D^{20}$  1.5813, are prepared from sodium thiophenoxide and the requisite chlorohydrin (cf. Bennett and Berry, A., 1927, 871). The corresponding chloro-sulphides have b. p. 100—101°/4 mm.,  $d_4^{20}$  1.1808,  $n_D^{20}$  1.5838, and b. p. 116—117°/4 mm.,  $d_4^{20}$  1.1536,  $n_D^{20}$  1.5752, respectively.  $\alpha$ -Naphthyl  $\beta$ -hydroxyethyl ether, b. p. 167°/2 mm., m. p. 22—24° (lit. 42°), and  $\alpha$ -naphthyl  $\gamma$ -hydroxypropyl ether, m. p. 65.5—66.5°, are converted by Darzens' reaction into  $\alpha$ -naphthyl  $\beta$ -chloroethyl ether, b. p.

145—147°/1.5 mm.,  $d_4^{20}$  1.1972,  $n_D^{20}$  1.6139, and  $\alpha$ -naphthyl  $\gamma$ -chloropropyl ether, b. p. 167—168°/1 mm.,  $d_4^{20}$  1.1665,  $n_D^{20}$  1.6025, respectively.  $\beta$ -Naphthyl  $\gamma$ -chloropropyl ether has m. p. 47—47.5°. H. BURTON.

**cycloHexanediols. II. Esters of cis- and trans-quinitol.** L. PALFRAY and B. ROTHSTEIN (Bull. Soc. chim., 1929, [iv], 45, 855—862).—With 2 or more mols. of acetyl chloride or acetic anhydride in presence of pyridine, *cis*-quinitol affords a mixture of *cis*- and *trans*-diacetates, isomerisation being promoted by increase of temperature or period of reaction and the presence of halogen. Acetic acid produces isomerisation more slowly. With 1 mol. of acetyl chloride, no monoacetate was obtained, but a mixture of unchanged quinitol, diacetate (mainly *trans*-), and a viscous residue, b. p. 132—133°/16 mm.,  $d_4^{20}$  1.099,  $n_D^{20}$  1.465. With *trans*-quinitol neither acetyl chloride nor acetic anhydride produced isomerisation. With cinnamic acid *cis*-quinitol affords a mixture of *cis*-, m. p. 122°, and *trans*-cinnamates, m. p. 189°, the latter being sparingly soluble in alcohol, but benzoyl chloride in chloroform gives *cis*-dibenzoate, m. p. 116—117°, no isomerisation taking place. The *trans*-dibenzoate has m. p. 151°. With 1 mol. of benzoyl chloride the dibenzoate formed is accompanied by a liquid, b. p. 171°/1 mm., possibly the monobenzoate, which, however, slowly deposits crystals of dibenzoate. Partial hydrolysis of the dibenzoate yielded a substance, m. p. 58° (monobenzoate?). Propionyl chloride converts industrial quinitol quantitatively into a mixture of *cis*-, m. p. 39.5—40°, and *trans*-propionates, m. p. 75.5—76°; isovaleryl chloride similarly yields a liquid isovalerate, b. p. 181—184°/17 mm.,  $d_4^{20}$  0.9867,  $n_D^{20}$  1.4478; *trans*-quinitol forms the same product. Silver isovalerate and *cis*-1:4-dibromocyclohexane yield  $\Delta^3$ -cyclohexenol and *cis*-dibromocyclohexane. Attempts to obtain the phthalate from phthalic acid, alone or in presence of solvent, failed. (Cf. A., 1928, 632.) R. BRIGHTMAN.

**New compounds of pyrocatechol with trivalent iron.** E. SELLÉS (Anal. Fis. Quím., 1929, 27, 569—586).—The compound  $[\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3]\text{H}_3(\text{C}_5\text{H}_{11}\text{N})_3 \cdot 2\text{EtOH}$ , dark violet, giving red solutions, is prepared by interaction of basic ferric acetate (Weinland and Gussmann, A., 1910, i, 457) with pyrocatechol and piperidine in alcoholic solution in the proportions Fe : pyrocatechol : piperidine 1 : 3 : 3. It is also obtained from ferric nitrate in presence of sodium acetate or from the chloride in presence of excess of piperidine. It decomposes at 100° to give a black compound. The analogous guanidine salt,  $[\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3]\text{H}_3(\text{CH}_5\text{N}_3)_3 \cdot 0.5\text{H}_2\text{O}$ , is obtained similarly from ferric acetate in aqueous solution, whilst if the reagents are used in the proportion Fe : pyrocatechol : guanidine 1 : 2 : 1, the compound  $\{[\text{C}_6\text{H}_4\text{O}_2 \cdot \text{Fe} \cdot \text{OC}_6\text{H}_4\text{O}]_2\text{CH}_5\text{N}_3\}_2 \cdot \text{H}_2\text{O}$ , black, giving violet solutions, is formed. With pyridine only the compound  $[\text{C}_6\text{H}_4\text{O}_2 \cdot \text{Fe} \cdot \text{OC}_6\text{H}_4\text{O}]\text{H}_5\text{C}_5\text{H}_5\text{N}$  is obtained, and not the tripyrocatechyl compound. With pyrocatechol and piperidine in the proportions Fe : pyrocatechol : piperidine 1 : 1 : 1 or 2 : 3 : 2, basic ferric acetate forms the compounds  $[\text{Fe}_2(\text{C}_5\text{H}_{11}\text{N})_2(\text{C}_6\text{H}_4\text{O}_2)_3(\text{EtOH})_4]$  and

$[\text{Fe}_2(\text{C}_5\text{H}_{11}\text{N})_2(\text{C}_6\text{H}_4\text{O}_2)_3(\text{MeOH})_6]$ , giving violet solutions, which are un-ionised. R. K. CALLOW.

**Alkoxy-derivatives of diphenyl ether.** C. A. DORAN (J. Amer. Chem. Soc., 1929, 51, 3447—3450).—*m*-Bromoanisole reacts with potassium *m*-methoxyphenoxide at 300—320° in presence of freshly-reduced, finely-divided copper powder, yielding 26% of 3 : 3'-dimethoxydiphenyl ether, b. p. 332—334°. 3 : 3'-Diethoxy-, b. p. 341—344°; 3-methoxy-3'-ethoxy-, b. p. 338—341°; 3 : 4'-dimethoxy-, b. p. 336—338° (from *p*-bromoanisole), and 2 : 3'-dimethoxy-diphenyl ether, b. p. 326—329°, m. p. 33—34° (from *o*-bromoanisole), are obtained similarly. When a diazonium salt is decomposed under a layer of benzene, the yield of phenol is much improved and the formation of tarry by-products is eliminated. H. BURTON.

**Isomerisation of ergosterol.** C. E. BILLS and W. M. COX, jun. (J. Biol. Chem., 1929, 84, 455—462).—Attempts to prepare the *isoergosterol* of Reindel, Walter, and Rauch (A., 1927, 241) led to a product with m. p. 138°,  $[\alpha]_D^{25}$  -40°. When a solution of ergosterol in chloroform is shaken with concentrated hydrochloric acid an *isomeride*,  $[\alpha]_{546}^{25}$  -53.5°, is obtained. Isomerisation is complete in 4 hrs. Similar treatment with hydrobromic acid affords a different *isomeride*,  $[\alpha]_{546}^{25}$  -48.5°, the change being complete in 1 hr., whilst fusion of ergosterol with cinnamoyl chloride, followed by hydrolysis of the product with alcoholic potassium hydroxide, gives a third *isomeride*,  $[\alpha]_{546}^{25}$  -39.2°. All three isomerides had m. p. 140° and were interconvertible on treatment with the appropriate acid. The question of the natural occurrence of isomeric forms of ergosterol is discussed.

C. R. HARRINGTON.

**Neoergosterol.** K. BONSTEDT (Z. physiol. Chem., 1929, 185, 165—168).—Ergopinacol (Windaus and Borgeaud, A., 1928, 425) contains six double linkings (perbenzoic acid), whilst neoergosterol,  $\text{C}_{27}\text{H}_{42}$  (or  $\text{C}_{27}\text{H}_{40}\text{O}$ ), m. p. 154° (corr.),  $[\alpha]_D^{25}$  -11° in chloroform (cf. *loc. cit.*) [dibromide, m. p. 212° (decomp.); acetate, m. p. 118° (corr.; dibromide, m. p. 183°)], contains only one. The Salkowski and Liebermann-Burchard colour reactions are given by ergopinacol, but not by neoergosterol. Reduction of neoergosteryl acetate with hydrogen in presence of platinum and acetic acid affords a hydrocarbon,  $\text{C}_{27}\text{H}_{44}$ , m. p. 69°,  $[\alpha]_D^{25}$  +26.9° in chloroform; neoergosterol is unaffected by sodium and alcohol. The production of neoergosterol from ergopinacol probably involves the formation of an aromatic ring system. H. BURTON.

**Zymosterol, a dextrorotatory sterol of yeast.** H. PENAU and G. TANRET (Bull. Soc. Chim. biol., 1929, 11, 929—936).—See A., 1929, 809.

**cycloHexylethyl alcohol and some of its homologues.** G. DARZENS (Compt. rend., 1929, 189, 852—854).—Reduction of ethyl phenylacetate with sodium and alcohol gives, besides the main yield of phenylethyl alcohol, a small quantity of cyclohexylethyl alcohol. This is identical with that obtained by the reduction of ethyl cyclohexylacetate with sodium and amyl alcohol (m. p. of pyruvate semicarbazide, 170—171°). The *o*-, *m*-, and *p*-



*methylcyclohexyl alcohols*, b. p. 115—117°/22 mm., 116—117°/23 mm., and 106—107°/12 mm., respectively, are described, the *pyruvate semicarbazides* of which melt at 139—140°, 157—158°, and 160—161°.

A. A. GOLDBERG.

**Dehydration of a hydroxyethyl side-chain with potassium hydroxide. II. Aminostyrenes.** S. SABETAY and T. MINTSOV (Bull. Soc. chim., 1929, [iv], 45, 842—848).—*p*-Aminostyrene, m. p. 23·5°, b. p. 98—100°/4 mm.,  $d_{20}^{25}$  1·012,  $n_D^{25}$  1·6250 (*hydrochloride*), and *o*-aminostyrene, b. p. 97—98°/8 mm.,  $d_{20}^{25}$  1·015,  $n_D^{25}$  1·613 (*hydrochloride*), have been obtained by heating the corresponding amino- $\beta$ -phenylethyl alcohol with potassium hydroxide in a partial vacuum.  $\beta$ -*o*-Amino-phenylethyl alcohol, b. p. 152—153°/6 mm., with a faint indolic odour, is obtained by reduction of  $\beta$ -*o*-nitro-phenylethyl alcohol with zinc powder and calcium chloride. Styrene is obtained in 33% yield by similar dehydration of  $\beta$ -phenylethyl alcohol residues, b. p. 84—100°/5 mm.  $\beta$ -cyclohexyl ethyl alcohol, b. p. 97—99°/15 mm.,  $d_{20}^{25}$  0·9148,  $n_D^{25}$  1·467, from ethylene oxide and magnesium cyclohexyl chloride, is unchanged when distilled with potassium hydroxide.

R. BRIGHTMAN.

**Three homologues of ephedrine.** E. FOURNEAU and C. E. BARRELET (Anal. Fis. Quím., 1929, 27, 500—507).—Independently of Hyde, Browning, and Adams (A., 1928, 1143),  $\beta$ -methylamino- $\alpha$ -phenyl-*n*-butyl alcohol (*picrate*, m. p. 168°) has been prepared by the same method. When it is heated with hydrochloric acid at 100° for 12 hrs., it is partly converted into its *stereoisomeride* (*p*-form), m. p. 81° (*hydrochloride*, m. p. 145°; *picrate*, m. p. 149°), also found as a by-product in the above method of preparation. The mixture is separated by recrystallisation of the *picrates*.  $\beta$ -Methylamino- $\alpha$ -phenyl-*n*-butyl alcohol could not be resolved into its optical isomerides by means of the tartrates, but this was accomplished by means of its salts with *D*- and *L*-N-phenylalanine-amide-4-arsinic acids. The following are described: salt of *D*-base and *L*-acid,  $[\alpha]_D^{25}$  -1·72°; *L*-base, m. p. 43° (*hydrochloride*, m. p. 236°,  $[\alpha]_D^{25}$  -37·23°); *D*-base (*hydrochloride*, m. p. 236°,  $[\alpha]_D^{25}$  -36·50°). The *D*-base, whilst much less active than ephedrine, exerts a larger hypertension than the *L*-base.

*iso*Valeryl chloride and benzene in presence of aluminium chloride give *isovalerophenone*, b. p. 225—235°, which yields  $\alpha$ -bromoisovalerophenone, m. p. 52°, b. p. 145—155°, from which is obtained  $\alpha$ -methylaminoisovalerophenone (*hydrochloride*, m. p. 211°; *picrate*, m. p. 144°), which is reduced to  $\alpha$ -phenyl- $\beta$ -methylaminoisovalerophenone (*hydrochloride*, m. p. 252°; *picrate*, m. p. 133°). By a similar series of reactions, starting from  $\alpha$ -bromo- $\beta$ -phenylethyl methyl ketone, b. p. 158°/30 mm., the following are prepared:  $\alpha$ -dimethylamino- $\beta$ -phenylethyl methyl ketone, b. p. 160°/20 mm. (*hydrochloride*, m. p. 173°; *picrate*, m. p. 142°);  $\alpha$ -dimethylamino- $\beta$ -phenylethylmethylcarbinol (*hydrochloride*, m. p. 177°; *hydrochloride* of benzoate, m. p. 182°; *methiodide*, m. p. 191°; *picrate*, m. p. 120°);  $\alpha$ -methylamino- $\beta$ -phenylethyl methyl ketone, b. p. 150°/20 mm. (*hydrochloride*, m. p. 146°; *picrate*, m. p. 162°) (obtained in poor yield);  $\alpha$ -methylamino- $\beta$ -phenylethylmethylcarbinol (*hydrochloride*, m. p. 147°; *picrate*, m. p. 145°).

R. K. CALLOW.

**A homologue of ephedrine.** J. SÁENZ DE BURUAGA (Anal. Fis. Quím., 1929, 27, 712—716).—*p*-Tolyl ethyl ketone, b. p. 234—235°, is prepared from toluene and propionyl chloride and yields *p*-tolyl  $\alpha$ -bromoethyl ketone, m. p. 80°, which condenses with methylamine to give *p*-tolyl  $\alpha$ -methylaminoethyl ketone (*methiodide*, m. p. 199—200°; *picrate*, m. p. 170°), isolated as the *hydrochloride*, m. p. 232°, which is catalytically reduced to *p*-tolyl- $\alpha$ -methylaminoethylcarbinol [ $\beta$ -*p*-tolyl- $\alpha$ -methylamino-*n*-propyl alcohol] (*hydrochloride*, m. p. 222°; *methiodide*, m. p. 175°; *picrate*, m. p. 179°).

[With LÉVY and TIFFENEAU].—This homologue of ephedrine is more toxic than ephedrine, the lethal dose being 0·045 g./kg. (rabbit), and the hypertensive action is weaker and very brief. R. K. CALLOW.

**Reducing action of aliphatic Grignard reagents.** F. F. BLICKE and L. D. POWERS (J. Amer. Chem. Soc., 1929, 51, 3378—3383).—The diphenylpropylcarbinol, m. p. 65°, of Klages and Heilmann (A., 1904, i, 487) is benzhydrol; reduction of benzophenone occurs during the treatment with magnesium propyl bromide. Diphenylpropylcarbinol, m. p. 33—34°, is prepared by the action of magnesium phenyl bromide on ethyl butyrate or phenyl propyl ketone (cf. Skraup and Freundlich, A., 1922, i, 539). Benzhydrol is also formed in 22—74% yield during the treatment of benzophenone with magnesium *iso*-propyl and *iso*amyl bromides, and magnesium *n*- and *iso*-butyl iodides. The corresponding diphenylcarbinol is also obtained (9—65%) from magnesium *n*-propyl bromide and *p*-bromobenzophenone, phenyl  $\alpha$ -naphthyl, phenyl diphenyl, and phenyl benzyl ketones. The first stage of interaction of the Grignard reagent and ketone is formulated:  $R_2CO + R'MgX \rightarrow R_2C\cdot\dot{C}OMgX + R'$ . These free radicals may combine to give the tertiary alcohol; or the former can undergo reduction to  $CHR_2\cdot OMgX$ , whilst the radical  $R'$  is oxidised (dehydrogenated) to form an unsaturated hydrocarbon. H. BURTON.

**Condensation of fluorene with acetone. I. Action of magnesium 9-fluorenyl bromide on (a) acetone, (b) diacetone alcohol.** The question of two forms of 9-isopropylidene-fluorene. P. MAITLAND and S. H. TUCKER (J.C.S., 1929, 2559—2567).—The above reactions have been investigated in connexion with the constitution of the product,  $C_{19}H_{20}O$ , m. p. 76—78°, obtained from fluorene and acetone in presence of potassium hydroxide. Neither reaction is simple, and several products are obtained in small yield from each. Magnesium 9-fluorenyl bromide is prepared by a modification of Courtot's method (A., 1916, i, 475). After separation of fluorene from the product obtained with diacetone alcohol by heating in xylene at 137°, the solvent is distilled off, the residue heated to eliminate water by decomposition, and then distilled under reduced pressure. The fractions obtained yield, besides fluorene, 9-fluorenyldimethylcarbinol, m. p. 99—101° (Courtot, *loc. cit.*, 103°), 9:9'-difluorenyl, and a phototropic substance,  $C_{19}H_{18}$ , m. p. 80—82° (I). On one occasion a compound,  $C_{19}H_{18}$  (II), m. p. 58—61°, was isolated, and on another,  $\alpha$ -9-fluorenyl- $\alpha$ - $\gamma$ -

*trimethyltrimethylene glycol* (III), m. p. 110—112°. Large amounts of uncrystallisable oil are obtained. The isomeric compounds I and II are probably  $\alpha$ -diphenylene- $\beta\beta$ -dimethyl- $\Delta^{\alpha\gamma}$ - and - $\Delta^{\alpha\delta}$ -pentadiene, respectively. Reduction of I with hydriodic acid yields  $\beta$ -9-fluorenyl- $\delta$ -methylpentane, m. p. 101—103°, accompanied by a substance,  $C_{19}H_{20}$ , m. p. 51—55°.

The product obtained from acetone under similar conditions at 125° is distilled under reduced pressure after removal of xylene and yields chiefly 9-fluorenyl-dimethylcarbinol (50—60% yield, calculated on unrecovered fluorene), accompanied by 9:9'-difluorenyl and uncrystallisable oil. When the reaction is carried out at 135°, 9-isopropylidene fluorene, m. p. 113—117°, and a small amount of II are isolated. The substance, m. p. 89°, described by Courtot (*loc. cit.*) as 9-isopropylidene fluorene could not be isolated, and the assumption of the existence of stereoisomeric forms by Schlenk and Bergmann (A., 1928, 1038), who also obtained only the compound of higher m. p., is untenable. 9-isoPropylidene fluorene is also obtained by interaction of magnesium isopropyl bromide with fluorenone. It yields 9-bromofluorenyldimethylcarbinyl bromide, m. p. 126—127°, with bromine, and is reduced by hydriodic acid to 9-isopropylfluorene, m. p. 53—55°, also obtained from the potassium derivative of 9-carbethoxyfluorene and isopropyl iodide, followed by hydrolysis and elimination of carbon dioxide.

9-Fluorenyldimethylcarbinyl bromide, m. p. 98—103°, is obtained by the action of hydrogen bromide on 9-fluorenyldimethylcarbinol. The iodide could not be obtained from this by the action of sodium iodide in acetone.

R. K. CALLOW.

**Heteropolar compounds of carbon. X. Association and colour in methoxytriphenylcarbenium salts.** W. DILTHEY, W. ALFUSS, and L. NEUHAUS (Ber., 1929, 62, [B], 2738—2741; for nomenclature see Dilthey and Dinklage, A., 1929, 1067).—Contrary to the observations of Lifschitz and Girbes (A., 1928, 1001), there appears to be no connexion between association and colour in the case of methoxytriphenylmethyl salts. Determination of the mol. wt. of trianisylmethyl perchlorate in freezing nitrobenzene gives values somewhat lower than those recorded by Lifschitz, whereas in the boiling solvent high and very variable values are observed. Heating is effected internally by an electrically heated platinum spiral which appears to cause decomposition of the salt, since when a Landsberger-Beckmann method is employed the values in the boiling and freezing solution are nearly identical. With internal heating, similar results are obtained in freezing and boiling phenol, in which rise of temperature does not increase the intensity of the colour. The latter phenomenon is not accompanied by marked displacement of the absorption spectrum and is tentatively attributed to displacement of the equilibrium between the colourless carbonium and coloured carbenium salt with change of temperature in nitrobenzene solution.

H. WREN.

**Relative stability of isomerides according to absorption spectra. II. Isomerisation of ethylene oxides and dehydration of glycols.**

(MME.) P. RAMART-LUCAS and E. SALMON-LEGAGNEUR (Bull. Soc. chim., 1929, [iv], 45, 718—734).—A more detailed account of work already published (A., 1929, 815). The action of magnesium methyl iodide on benzil (cf. Tiffeneau and Lévy, A., 1927, 1184) or methylbenzoin gives a  $\beta\gamma$ -diphenylbutane- $\beta\gamma$ -diol, m. p. 116—117°, stereoisomeric with the pinacol, m. p. 122°, obtained by reduction of acetophenone with magnesium amalgam. Similarly, dehydration of  $\beta\gamma$ -diphenylbutan- $\gamma$ -ol, m. p. 65—66°, in presence of sulphuric acid and pumice, yields two stereoisomeric forms of  $\beta\gamma$ -diphenyl- $\Delta^{\delta}$ -butene, m. p. 65—66° and 104°. Contrary to the usual rule, the  $\alpha$ - or stable form is the isomeride of lower m. p., the isomeride, m. p. 104°, being converted into the isomeride, m. p. 65—66°, when heated in presence of sulphuric acid and pumice. With perbenzoic acid (Lévy and Lagrave, A., 1925, i, 679) the  $\alpha$ -isomeride is converted into the  $\alpha$ -form of  $\alpha\beta$ -diphenyl- $\alpha\beta$ -dimethylethylene oxide, m. p. 52—53°, the  $\beta$ -isomeride similarly yielding the  $\beta$ -stereoisomeric oxide, m. p. 107°.  $\alpha\alpha$ -Diphenyl- $\beta$ -methyl- $\Delta^{\alpha}$ -propene has m. p. 52—53° (cf. Sabatier and Murat, A., 1916, i, 205), b. p. 150—152°/15 mm., dehydration of the *tert*-alcohol being complete only when heated under atmospheric pressure in presence of acid and pumice.  $\alpha\alpha$ -Diphenyl- $\beta\beta$ -dimethylethylene oxide has m. p. 61—62°, b. p. 162—163°/15 mm. Phenyl  $\alpha$ -phenylisopropyl ketone, m. p. 46—47°, b. p. 185—186°/16 mm. (*oxime*, m. p. 192—193°), is obtained [(Mme.) BRUZEAU] from magnesium phenyl bromide and phenyldimethylacetone nitrile by hydrolysis of the ketimine salt (cf. A., 1928, 522). When heated at 500—600° in presence of kieselguhr the pinacols, oxides, and ketones are converted into a fluorescent hydrocarbon,  $C_{16}H_{14}$ , m. p. 74—75° (*picrate*, m. p. 108—109°), which from its mode of formation might be expected to be 9:10-dimethylantracene, but is not identical with the hydrocarbon to which Barnett and Matthews (A., 1926, 1030) assign that structure.

R. BRIGHTMAN.

**Auto-oxidation of abietic acid.** G. DUPONT and J. LÉVY (Compt. rend., 1929, 189, 763—765).—From measurements of the rate of oxidation of abietic acid by oxygen at constant volume and at constant pressure a theory of the mechanism of the reaction has been developed. Denoting the molecule of abietic acid by "A" and the final product of oxidation by "AO<sub>2</sub>," there is an intermediate stage, "AO," which acts as catalyst to the reaction. A. A. GOLDBERG.

**Chlorination of *p*-nitrophenylacetonitrile.** V. V. NEKRASOV and A. V. SOKOLOV (J. Russ. Phys. Chem. Soc., 1929, 61, 899—902).—Direct chlorination of *p*-nitrophenylacetonitrile at 120° in bright daylight for 11 hrs. affords *p*-nitrophenyldichloroacetonitrile, b. p. 149—149.5°/0.6 mm.,  $d^{20}_4$  1.4465,  $n^{20}_D$  1.5710, which with hydrochloric acid in ethereal solution gives the corresponding acid, m. p. 171—172°. Oxidation of the nitrile with potassium permanganate yields *p*-nitrobenzoic acid only. With alkali hydroxides the nitrile gives an intense purple colour, due probably to the formation of a quinonoid structure,  $\text{NO}_2\text{Na}:\text{C}_6\text{H}_4:\text{CH}:\text{CN}$ .

M. ZNEGINTZOV.

**Erlenmeyer's triclinic cinnamic acid and the double compounds of *cis*- and *trans*-cinnamic**

acids. A. W. K. DE JONG (Rec. trav. chim., 1929, 48, 1042).—Crystallographic measurements (by ESCHER and F. W. JONG) of the double compound of *cis*- and *trans*-cinnamic acids show that this is identical with the triclinic (*iso*)cinnamic acid of Erlenmeyer jun. and others (A., 1907, i, 318), all the measurements showing close agreement with those of Fock (*loc. cit.*) for the latter acid. J. W. BAKER.

**Action of nitric acid on ethylene derivatives.**  
**III. Properties of the nitration products of some esters of nitrocinnamic acids.** J. VAN DER LEE (Rec. trav. chim., 1929, 48, 1136—1144).—Nitration of methyl *p*- and *m*-nitrocinnamates gives products similar to those obtained from the ethylesters (A., 1926, 1245) and thus are obtained methyl  $\alpha$ -nitro- $\beta$ -nitrate- $\beta$ -*p*-nitrophenylpropionate, m. p. 108°, and methyl  $\alpha$ -nitro- $\beta$ -nitrate- $\beta$ -*m*-nitrophenylpropionate, m. p. 105—106°, which are converted (with loss of nitric acid) by moist ether into substances, m. p. 105—106° and 100°, respectively. Ethyl  $\alpha$ -nitro- $\beta$ -nitrate- $\beta$ -*p*-nitrophenylpropionate (I) (crystallographic data by P. TERPSTRA;  $a:b:c=0.9878:1:0.5790$ ;  $\beta=86^\circ 7'$ ) reacts with methylamine in benzene to give a substance, m. p. 87°, which is probably ethyl  $\alpha$ -nitro- $\beta$ -methylamino- $\beta$ -*p*-nitrophenylpropionate, the same compound being obtained by the action of methylamine in benzene on ethyl  $\alpha$ -*p*-dinitrocinnamate (II). Aniline reacts similarly with the nitrate-group, since the theoretical quantity of aniline nitrate is precipitated, but the other product could not be obtained crystalline. *p*-Toluidine, however, reacts with I to give *p*-nitrobenzylidene-*p*-toluidine, identical with specimens obtained either by condensation of *p*-nitrobenzaldehyde with *p*-toluidine, or by the action of the latter on II. The mechanism of these reactions is formulated thus:  $\text{CHR}(\text{O}\cdot\text{NO}_2)\cdot\text{CH}(\text{NO}_2)\cdot\text{CO}_2\text{Et} + 2\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2 \rightarrow \text{CHR}:\text{C}(\text{NO}_2)\cdot\text{CO}_2\text{Et}$  (III) +  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2\cdot\text{HNO}_3$ ;  $\text{II} + \text{C}_6\text{H}_4\text{Me}\cdot\text{NH}_2 \rightarrow \text{III}$ ;  $\text{III} \rightarrow \text{CHR}:\text{N}\cdot\text{C}_6\text{H}_4\text{Me} + \text{CH}_2(\text{NO}_2)\cdot\text{CO}_2\text{Et}$  ( $\text{R}=\text{p}\text{-NO}_2\cdot\text{C}_6\text{H}_4$ ). Conversion of the isomeride m. p. 74—74.5° of ethyl  $\alpha$ -*m*-dinitrocinnamate (*loc. cit.*) into the form of m. p. 105—106° is effected by the action of bright sunlight in benzene solution. J. W. BAKER.

**Homologous salols.** C. K. KRAUZ and J. REMENEC (Coll. Czech. Chem. Comm., 1929, 1, 610—616).—The following salicylates were prepared by heating together equimolecular proportions of the phenol and of salicylic acid in the presence of 0.5 mol. of phosphorus oxychloride at 120—130°: *o*-, *m*-, and *p*-, m. p. 36.5°, -ethylphenyl salicylates; *o*-, *m*-, and *p*-, m. p. 57°, -propylphenyl salicylates; *o*-, *m*-, and *p*-, m. p. 47—47.5°, -isopropylphenyl salicylates. *p*- $\alpha$ -Ethyl-*n*-propylphenyl salicylate has m. p. 44.5—45°. *p*-Ethyl- and *p*-propyl-phenol are obtained by the Clemmensen reduction of *p*-hydroxyacetophenone and *p*-hydroxypropiofenone, respectively. *n*-Propylbenzene- $\alpha$ -sulphonic acid, considered by Claus and Welzel (A., 1890, 503) to be an *o*-compound, is shown to be the *p*-derivative, since it gives *p*-propylphenol by alkaline fusion. *o*-Ethylphenol, from *o*-aminoethylbenzene, has b. p. 210—212°. A. I. VOGEL.

**Electrolytic reduction of some aromatic acids.**  
 F. SOMLO (Z. Elektrochem., 1929, 35, 769—780).—

The cathodic reduction at a specially prepared lead cathode in a diaphragm cell of salicylic, phthalic, gallic, pyrogallolcarboxylic, phloroglucinolcarboxylic, and quinolcarboxylic acids in aqueous and aqueous-alcoholic solutions have been investigated. Salicylic acid is reduced to salicyl alcohol. Phthalic acid is converted into  $\Delta^{3:5}$ -dihydrophthalic acid, whilst from alcoholic solutions the ester of this acid may be obtained. The four polyhydroxycarboxylic acids lose their carboxyl groups with the evolution of carbon monoxide. H. T. S. BRITTON.

**Relation between chemical constitution and action on micro-organisms.** VIII. Glucosides of simple and chlorinated *p*-hydroxybenzoic acids and their esters. T. SABALITSCHKA and F. L. SCHWEITZER.—See this vol., 71.

**Two apparent cases of liquid crystal formation.**  
 A. E. BRADFIELD and B. JONES (J.C.S., 1929, 2660—2661).—*p*-*n*-Propoxybenzoic acid melts at 145.6° to a milky liquid, clear at 156°. *p*-*n*-Butoxybenzoic acid (prepared by refluxing the hydroxy-acid with butyl iodide and potassium hydroxide solution) melts at 146.7° to a milky liquid, clear at 160.2°.

R. K. CALLOW.

[Hoesch syntheses with thiocyanobenzene.]  
 W. BORSCHKE and J. NIEMANN (Ber., 1929, 62, [B], 2943; cf. A., 1929, 1064).—2:4-Dihydroxybenziminothiophenyl ether hydrochloride has been described by Adams (A., 1923, i, 931). H. WREN.

**Preparation of 2:3-dimethoxyphenylacetone-nitrile.** F. MONTEQUI (Anal. Fís. Quím., 1929, 27, 692—694).—In connexion with a proposed synthesis of corydaline, 2:3-dimethoxyphenylacetone-nitrile has been prepared by the following series of reactions. Guaiacol is converted by treatment with chloroform and aqueous-alcoholic sodium hydroxide into 2-hydroxy-3-methoxybenzaldehyde. Methylation and a Cannizzaro reaction yield 2:3-dimethoxybenzyl alcohol, which is converted into the chloride; this, when heated with alcoholic potassium cyanide and a little potassium iodide yields 2:3-dimethoxyphenylacetone-nitrile as an oil which solidifies in a freezing mixture. The acid, m. p. 82°, is obtained by hydrolysis. R. K. CALLOW.

**Studies in "strainless" rings.** I.  $\beta$ -Substituted stereoisomeric decalins. K. A. N. RAO (J.C.S., 1929, 1954—1969).—In the abstract of the above paper (A., 1929, 1297) the following compounds should have been indicated as new:  $\omega$ -imide of trans-decahydronaphthalene-2:2-dicyanoacetic acid, m. p. 280° (decomp.);  $\omega$ -imides of  $\alpha\alpha'$ -dicarbamyl-*cis*- and -*trans*-decahydronaphthalene-2:2-diacetic acid, m. p. 260—261° (decomp.) and 234—235°, respectively; ethyl *cis*-decalin-2:2-diacetate, b. p. 213°/21 mm. The following data should be substituted for those given (*loc. cit.*): methyl *trans*-decalin-2:2-diacetate, b. p. 190°/12 mm. (not 192°/12 mm.); the *trans*-anilic acid B (stable form) has m. p. 165—166° (not 159—161°) and A (unstable form) m. p. 204° (not 165—166°); ethyl 2-carboxy-*trans*-decalin-2-acetate (not the dicyano-ester) has b. p. 200°/18 mm. etc. Ethyl *trans*-decahydro- $\beta$ -naphthylidenecyanoacetate has b. p. 208°/14 mm.,  $d_4^{25}$  1.06067,

$n_D^{25}$  1.51299. Also, in line 10 from the end of the abstract, for "hydrolysis of" read "removal of the carbethoxy-group from."

**Spectroscopic study of N-aminonaphthalimide and some derivatives.** A. OSTROGOVICH and E. TANASESCU (Bul. Soc. Stiinte Cluj, 1929, 4, 368—398; Chem. Zentr., 1929, ii, 304—305).—The following compounds are described: *N*-phenylmethyl-, m. p. 214—215°; *N*-phenylethyl-, m. p. 151—152°; *N*-phenylpropyl-, m. p. 154—155°; *N*-phenylhexyl-, m. p. 108—109°; *N*-phenylcetyl-, m. p. 97—98°; *N*-*o*-tolyl-, m. p. 248—249°; *N*-*m*-tolyl-, m. p. 209—210°; *N*-*p*-tolyl-, m. p. 207—208°; *N*- $\alpha$ -naphthyl-, m. p. 277—278° (decomp.); *N*- $\beta$ -naphthyl-, m. p. 268°; *N*-*o*-nitrophenyl-, m. p. 281—282°; and *N*-*p*-nitrophenylaminonaphthalimide, m. p. above 300°; *as*-phenylpropyl-, m. p. 130—131°; *as*-phenylhexyl-, m. p. 77—78°; and *as*-phenylcetylhydrazine hydrochloride, m. p. 62°, were prepared. *N*-Aminonaphthalimide and its derivatives give a continuous spectrum with one relatively sharp line in the visible portion and another in the ultra-violet. The introduction of a phenyl group produces in small concentrations a slight bathochromic, and in higher concentrations a slight hypsochromic effect. With the further introduction of an alkyl group there is an increasing bathochromic effect for ethyl and propyl, less marked for hexyl, and hypsochromic for cetyl. The tolyl radical is less,  $\alpha$ - and  $\beta$ -naphthyl more, bathochromic than phenyl. A. A. ELDRIDGE.

**Diphenyl; 5:5'-substituted diphenic acids.** F. PUFER (Ber., 1929, 62, [B], 2817—2824).—Confirmation of the theory of Mills (Chem. and Ind., 1926, 45, 884, 905) and Meisenheimer (A., 1927, 766) with regard to the optical activity of diphenyl derivatives is found in the non-resolvability of 5:5'-disubstituted diphenic acids.

4-Nitro-2-aminobenzoic acid is converted successively into 2-iodo-4-nitrobenzoic acid, m. p. 146—147°, and methyl 2-iodo-4-nitrobenzoate, m. p. 94°, which, with copper powder at 200°, affords methyl 5:5'-dinitrodiphenate, m. p. 161°, whence 5:5'-dinitrodiphenic acid, m. p. 285—287° (decomp.) [ $+2\text{MeOH}$ ], and 5:5'-dinitrodiphenic anhydride, m. p. 265°; the *brucine* salt, m. p. 190—200°, of the acid is described. 2-Amino-4-acetamidobenzoic acid, m. p. 215° (decomp.), is converted by diazotisation and subsequent treatment with ammoniacal cuprous oxide through the crude diacetyl derivative into 5:5'-diaminodiphenic acid, m. p. 265° (decomp.) (methyl ester, m. p. 220—222°), also obtained by reducing the dinitro acid with sodium sulphide; 5:5'-diacetamidodiphenic acid, gradually darkening above 300°, but not molten below 430°, is described. 5:5'-Dibenzamidodiphenic acid, m. p. 340—341° (decomp.) (normal *brucine* salt, m. p. 198—200°), is converted by short treatment with acetic (or propionic) anhydride into 5:5'-dibenzamidodiphenic anhydride, m. p. 288—289° (decomp.), whereas more prolonged treatment appears to involve replacement of the benzoyl by the acetyl group. Ethyl hydrogen 5:5'-dibenzamidodiphenate, m. p. 174°, and 5:5'-dibenzamidodiphenanilic acid, m. p. 291—292° (decomp.), are described. 5:5'-Di-

*p*-nitrobenzamidodiphenic acid, m. p. 350—352°, and 5:5'-di-*m*-nitrobenzamidodiphenic acid, m. p. 274° (anhydride, m. p. 296—297°), have been prepared.

H. WREN.

**Knoevenagel condensation of aromatic aldehydes with malonic acid, and Rodionov's  $\beta$ -amino- $\beta$ -arylethane- $\alpha\alpha$ -dicarboxylic acids.** T. BOEHM (Arch. Pharm., 1929, 267, 702—714).—Contrary to the experience of Knoevenagel (A., 1899, i, 144) it is found that arylidenemalonic acids can be readily obtained by the condensation of aromatic aldehydes with malonic acid in the presence of aniline and alcohol. No substituted acrylic acids are formed under the experimental conditions employed and the final products are the same independently of the order in which the reagents are mixed. The best yields are obtained by initial condensation of the aldehydes with aniline to the Schiff's bases, followed by the addition of malonic acid in alcoholic solution. *o*-Nitrobenzaldehyde thus yields aniline *o*-nitrobenzylidenemalonate, m. p. 130—131°, in 80% yield, converted by 2 mols. of potassium hydroxide followed by acidification with hydrochloric acid into the corresponding malonic acid, m. p. 161—162° (decomp.) (potassium hydrogen salt), and by repeated evaporation in an open vessel during 1—2 hrs. with alcohol into *o*-nitrophenylacrylic acid, m. p. 240—241°, in about 50% yield (no acrylic acid is formed by heating under reflux). *p*-Nitrobenzaldehyde similarly gives aniline *p*-nitrobenzylidenemalonate, m. p. 146—147° (decomp.), the free acid (sinters 210°, partly decomp. 227°, m. p. 285—286°, as *p*-nitrocinnamic acid; Stuart, J.C.S., 1883, 43, 408; 1885, 47, 155, gave m. p. 227°), and *p*-nitrophenylacrylic acid, the last-named in 50% yield. *m*-Nitrobenzylidenemalonic acid has m. p. 209—210° (lit. 202—204°; 205°). Piperonylideneaniline and malonic acid in aqueous or alcoholic solution give 3:4-methylene-dioxybenzylidenemalonic acid, m. p. 193—194° (decomp.), in 40% yield (sodium hydrogen salt), whilst *p*-methoxybenzylidenemalonic acid, m. p. 195—196° (decomp.), is similarly produced in 50% yield from anisaldehydeanil.

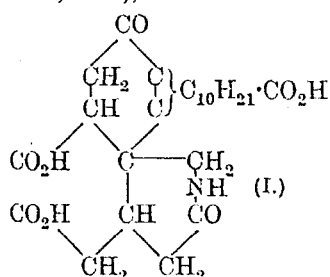
The compounds described by Rodionov and others (A., 1929, 557) as  $\beta$ -amino- $\beta$ -arylethane- $\alpha\alpha$ -dicarboxylic acids are shown to be salts of the base with the unsaturated acid. Thus benzaldehyde, malonic acid, and piperidine react in alcoholic solution to form piperidine benzylidenemalonate (I), m. p. 157° (also produced by mixing benzylidenemalonic acid and piperidine in alcoholic solution). Similarly, piperidine, malonic acid, and piperonal give piperidine piperonylidene-malonate, m. p. 151—152° (decomp.) (II), whilst benzaldehyde, malonic acid, and alcoholic ammonia furnish benzylidenemalonamide, m. p. 161—163° (decomp.). Observations supporting the salt-formation view are: (1) reduction with palladised barium sulphate and hydrogen of I to benzylmalonic acid, m. p. 120—121°, and of II to piperonylmalonic acid, m. p. 154—156°; (2) Rodionov's "amino-acids" can be prepared by interaction of the unsaturated acid with the base; (3) treatment of the "amino-acids" with alkali does not give the salts previously prepared by Goldstein (A., 1895, i, 470; 1896, i, 435), but results in the elimination of the base. The  $\beta$ -piperidyl- $\beta$ -phenyl-,  $\beta$ -piperidyl- $\beta$ -piperonyl-, and  $\beta$ -amino-

$\beta$ -phenylethane- $\alpha\alpha$ -dicarboxylic acids of Rodionov and others (*loc. cit.*) are therefore non-existent.

Salicylideneaniline reacts with malonic acid in alcohol to give *aniline coumarincarboxylate*, m. p. 159–160°, decomposed by excess of 10% hydrochloric acid to coumarincarboxylic acid, m. p. 187–189°, and converted into coumarincarboxyanilide, m. p. 248–250°, by heating at 250°.

A. I. VOGEL.

**Bile acids. XXV.** M. SCHENCK and H. KIRCHHOFF (*Z. physiol. Chem.*, 1929, **185**, 183–192).—Hydrolysis of bilianic acid oximelactam (*diisooxime*) (cf. A., 1928, 1134) with 20% hydrochloric acid, affords the ketolactamtricarboxylic acid (I) (two forms; cf. A., 1928, 1007), both of which on reduction with amalgam-



ated zinc and hydrochloric acid afford a *lactamtricarboxylic acid* (II),  $C_{24}H_{35}O_7N$ , decomp. 274°,  $[\alpha]_D^{25} +16.96^\circ$  in 1.5% sodium hydroxide solution, and an *acid*,  $C_{24}H_{35}O_7N$ , not melted at 300°, probably a lactonic lactamdicarboxylic acid. Hydrolysis

of II with 40% hydrochloric acid gives the aminotetracarboxylic acid,  $C_{24}H_{35}O_8N$ , previously described (A., 1927, 665).

Hydrolysis of *isobilianic acid diisooxime* (A., 1928, 639) with 20% hydrochloric acid yields a *ketolactamtricarboxylic acid*,  $C_{24}H_{35}O_8N$ , decomp. 248–250° after previous sintering, hydrolysed further to the corresponding amino-acid.

H. BURTON.

**Ursodeoxycholic acid. III.** K. KAZIRO (*Z. physiol. Chem.*, 1929, **185**, 151–164; cf. Shoda, A., 1928, 666).—Details are given for the extraction of ursodeoxycholic acid (I),  $C_{24}H_{40}O_4$ , m. p. 198° (*diacetyl* derivative, m. p. 98–102°), from bear bile. Ursodehydroxycholic acid (II), m. p. 161° (Schoda, *loc. cit.*) (*mono-* and *di-semicarbazones*, m. p. 205° and above 290°, respectively), yields a *furfurylidene* derivative ( $+2H_2O$ ), m. p. 216–217° (cf. A., 1928, 644); *furfurylidenehydroxycholic acid* has m. p. 237–239°. Oxidation of I with sodium hypobromite gives mainly a hydroxytricarboxylic acid (III),  $C_{24}H_{38}O_7$ , m. p. 234–235° (cf. Schoda, *loc. cit.*) [ethyl ester, m. p. 128–129°; *acetyl* derivative ( $+H_2O$ ), sinters at 141°, melts to a turbid liquid at 145–150°, and becomes clear at 225°]; a small amount of a gelatinous acid, probably isomeric with III, is also formed. Oxidation of II with alkaline potassium permanganate yields mainly *ursodeoxybilianic acid* (IV),  $C_{24}H_{36}O_7 \cdot H_2O$ , m. p. 230–232° (*methyl ester*, m. p. 152°) (also produced by oxidising III with chromic oxide in acetic acid solution); a small amount of the isomeric *isoursodeoxybilianic acid* ( $+2H_2O$ ), m. p. 239–241° after sintering at 235°, is obtained also. Oxidation of II or IV with nitric acid (*d* 1.4) affords the same *pentacarboxylic acid*,  $C_{24}H_{36}O_{10}$ , m. p. 231°, purified only with difficulty. Reduction of IV with amalgamated zinc and hydrochloric and acetic acids furnishes lithobilianic acid, m. p. 276–278° (Borsche and Hallwass, A., 1922, i, 1159). The

orientation of the two hydroxyl groups in ursodeoxycholic acid is discussed briefly.

H. BURTON.

**Triple spiran system.** P. PFEIFFER, R. SEYDEL, and A. HANSEN (*J. pr. Chem.*, 1929, [ii], **123**, 347–350).—Condensation of pentaerythritol with *cyclohexanone-4-carboxylic acid* in the presence of sulphuric acid yields the triple spiran *acid*, m. p. 255–257° (*methyl ester*, m. p. 139°; *ammonium salt*), which forms an ethyl ester identical with that obtained by Pfeiffer and Backes (A., 1928, 413) by similar condensation with ethyl *cyclohexanone-4-carboxylate*. Resolution of the spiran acid has not yet been effected owing to the non-crystalline nature of its alkaloid salts.

J. W. BAKER.

**Nuclear syntheses of ketimines and ketones by condensation of nitriles with aromatic and heterocyclic compounds. I.** Ketimines and ketones from benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, naphthalene, and thiophen. J. HOUBEN and W. FISCHER (*J. pr. Chem.*, 1929, [ii], **123**, 313–329; cf. A., 1929, 1302).—Condensation of trichloroacetonitrile with various aromatic hydrocarbons in the presence of aluminium chloride and anhydrous hydrogen chloride at 0° gives good yields of ketones (or the corresponding ketimino-compounds) of the type  $ArCO \cdot CCl_3$ , direct substitution of the aromatic nucleus taking place. Thus benzene, toluene, *o*-, *m*-, and *p*-xylenes with trichloroacetonitrile give, respectively,  $\omega$ -trichloroacetophenone (70% yield); *p*-tolyl trichloromethyl ketone, b. p. 137°/10 mm. (93%) (decomposed by heating with sodium hydroxide into chloroform and *p*-toluic acid); 4-*o*-, b. p. 167–168°/16 mm. (60%), and 4-*m*-, b. p. 150–152°/14 mm. (94%), *-xylyl trichloromethyl ketone* (the *ketimine hydrochloride* also being isolated in the latter case), and 3:6-dimethylphenyl trichloromethyl ketone, b. p. 148–150°/17 mm. (44%), together with a 39% yield of the *ketimine hydrochloride*, m. p. 125–129° (decomp.) (by carrying out the reaction in chlorobenzene at 50–60°). Similarly, condensation of mesitylene gives the more stable *trichloroacetimidomesitylene*, b. p. 160–170°/15 mm., 135–139°/0.5 mm. (68%), a further 5% being isolated as the *hydrochloride*, m. p. 128–130° (decomp.). By heating with 10% sodium hydroxide either the *ketimine* or its *hydrochloride* undergoes quantitative fission into *s*-trimethylbenzonitrile and chloroform, the alkali acting merely as a catalyst. This decomposition constitutes a new method for the preparation of aromatic nitriles. Polynuclear and heterocyclic aromatic compounds condense similarly with trichloroacetonitrile and thus from naphthalene and thiophen are obtained, respectively, *naphthyl* ( $\alpha$  or  $\beta$ ) *trichloromethyl ketone*, m. p., indefinite, 120–150° (29%), and  $\alpha$ -*thiophenyl trichloromethyl ketone*, b. p. 140–145°/12 mm. (35%), converted by dilute sodium hydroxide into thiophen- $\alpha$ -carboxylic acid.

J. W. BAKER.

**Benzophenone derivatives. I.** Chlorohydroxybenzophenones. **II.** Chlorohydroxymethylbenzophenones. **III.** Action of phosphorus pentachloride on anisole. M. HAYASHI (*J. pr. Chem.*, 1929, [ii], **123**, 289–312).—I. Condensation of benzoyl chloride and *o*-chloroanisole with aluminium

chloride in *s*-tetrachloroethane at 120–130° gives 3-chloro-4-hydroxybenzophenone (I), m. p. 180–181° (probably identical with the product, m. p. 176°, obtained by Nencki and Stöber) (48.3%), 3-chloro-4-methoxybenzophenone, m. p. 99–99.5° [identical with the product obtained by Blakey, Jones, and Scarborough (A., 1928, 66), and by methylation of I, and converted into I by the action of aluminium chloride] (42.4%), and the *benzoyl* derivative (II), m. p. 84–84.5°, of I (1.2%). Similar condensation of *o*-chlorophenol gives I (44%), 3-chloro-2-hydroxybenzophenone (III), m. p. 92.5–93° (17%) (*methyl ether*, b. p. 173–174°/5 mm.), and *o*-chlorophenyl benzoate (30%), whilst *p*-chloroanisole gives 5-chloro-2-hydroxybenzophenone (IV), m. p. 95–95.5° (60.5%) (*methyl ether*, m. p. 100.5–101°), and *p*-chlorophenyl benzoate (22%). *p*-Chlorophenol gives the same products as *p*-chloroanisole, but in the proportions 8.5 and 76.5%, respectively.

II. Condensation of *o*-toluoyl chloride as above with *o*-chloroanisole gives 3-chloro-4-hydroxyphenyl *o*-tolyl ketone (V), m. p. 128–129° (25%), and its *methyl ether*, m. p. 106–106.5° (58%) (also by methylation of V), oxidised by alkaline potassium permanganate to *o*-(3'-chloro-4'-methoxybenzoyl)benzoic acid. With *p*-chloroanisole the sole product is 5-chloro-2-hydroxyphenyl *o*-tolyl ketone (VI), m. p. 67.5–68° (49.7%) (*methyl ether*, m. p. 101.5–102°), whilst *p*-chlorophenol gives VI (19.7%) and *p*-chlorophenyl *o*-toluate, m. p. 46.5–47° (78.7%). With *m*-toluoyl chloride, *o*-chloroanisole gives 3-chloro-4-hydroxyphenyl *m*-tolyl ketone (VII), m. p. 145–146° (14.7%), and its *methyl ether*, m. p. 105–105.5° (81%) (also by methylation of VII), whilst with *p*-chloroanisole the sole product is 5-chloro-2-hydroxyphenyl *m*-tolyl ketone, m. p. 106–106.5° (63%) (*methyl ether*, m. p. 70.5–71°).

III. By condensation of a specimen of chloroanisole obtained by the action of phosphorus pentachloride on anisole (Autenrieth, A., 1895, i, 511) with benzoyl, *o*- and *m*-toluoyl chlorides small yields (for details original must be consulted) of the products obtained from pure *o*-chloroanisole can be isolated, together with the expected products derived from the *p*-compound. Also by condensation with phthalic anhydride and aluminium chloride in *s*-tetrachloroethane at 70–75° a 4.6% yield of *o*-(3'-chloro-4'-hydroxybenzoyl)benzoic acid is obtained, together with 15.5% of *o*-(5'-chloro-2'-hydroxybenzoyl)benzoic acid. Hence the specimen of *p*-chloroanisole obtained by Autenrieth's method must contain at least 10% of the *o*-compound which cannot be separated by fractional distillation but may be detected and determined by the condensations described above. J. W. BAKER.

Condensation of  $\beta\beta$ -dimethylacrylyl chloride with benzene. Synthesis of phenyl  $\beta\beta$ -dimethylvinyl ketone. G. DARZENS (Compt. rend., 1929, 189, 766–768).—Condensation of  $\beta\beta$ -dimethylacrylyl chloride with benzene, by means of aluminium chloride, affords phenyl  $\beta\beta$ -dimethylvinyl [ $\beta$ -methylpropenyl] ketone, b. p. 134–136°/12 mm., in 40% yield. This substance is stable and all attempts to obtain a dimethylhydrindone by ring-closure failed. It forms a *dibromide* but gives no oxime, phenylhydrazone, or sodium hydrogen sulphite compound. Oxidation with alkaline permanganate yields benzoic

acid. The non-formation of a hydrindone is attributed to induced positive polarity of the  $\beta$ -carbon atom of the propenyl radical. A. A. GOLDBERG.

3:3-Diphenyl-1-hydrindone and its derivatives. Synthesis of 1:1-diphenyl-indene and -hydrindene. P. GAGNON (Ann. Chim., 1929, [x], 12, 296–343).—Triphenylpropionic acid (obtained by heating together malonic acid, acetic anhydride, and triphenylcarbinol) by warming with concentrated sulphuric acid at 40–45° passes into  $\gamma\gamma$ -diphenyl- $\alpha$ -hydrindone, m. p. 131–132° (A., 1929, 318) [*phenylhydrazone*, m. p. 184–185° (M.b.); *semicarbazone*, m. p. 250–251° (M.b.); *hydrazone*, m. p. 107–108° (decomp.) (M.b.); *azine*, m. p. 261–262° (M.b.); *oxime*, m. p. 163–164° (lit. 155–156°); *oxime hydrochloride*, m. p. 175° (M.b.)]. This substance resists oxidation by nitric acid (*d* 1.2) and reduction by sodium and alcohol or by catalytic hydrogenation; it gives with benzaldehyde in the presence of potassium hydroxide two (stereoisomeric?) 2-benzylidene-3:3-diphenyl-1-hydrindones, m. p. 171–172° and 191–192° (M.b.).

$\gamma\gamma$ -Diphenyl- $\alpha$ -hydrindoneoxime by reduction with sodium and alcohol gives 3:3-diphenyl-1-hydrindylamine, m. p. 89–93° [*hydrochloride*, m. p. 175–185° (sulphuric acid bath), 191–193° (M.b.); *oxalate*, m. p. 238–240° (M.b.); *acetyl* derivative, m. p. 192–193° (M.b.); *benzoyl* derivative, m. p. 192–193° (M.b.); *benzylidene* derivative, m. p. 180–181°]. The amine, when boiled with paraldehyde, forms a crystalline substance, m. p. 138–139°.

Treatment of 3:3-diphenyl-1-hydrindylamine with excess of methyl iodide gives 3:3-diphenyl-1-hydrindyltrimethylammonium iodide, m. p. 174–175° (M.b.), thermal decomposition of which gives high yields (in contrast to similar decompositions of 3:3-diphenyl-1-hydrindylamine hydrochloride) of 1:1-diphenylindene, m. p. 91–92°. This compound is transformed by bromine in ether into its *dibromide*, m. p. 132–133°, which by treatment with alcoholic sodium methoxide gives 2(or 3)-bromo-1:1-diphenylindene, m. p. 103–104°, and with acetic acid and iron regenerates the parent hydrocarbon. 1:1-Diphenylhydrindene, m. p. 67–68°, is obtained by catalytic or sodium-alcohol reduction of 1:1-diphenylindene and also by the action of alcoholic sodium ethoxide under pressure on 3:3-diphenyl-1-hydrindone-hydrazone or -semicarbazone.

(M.b. indicates m. p. taken on Maquenne block.)

R. J. W. LE FÈVRE.

Preparation of dibenzoylmethane. J. PASCUAL (Anal. Fis. Quím., 1929, 27, 668–670).—Dibenzoylmethane is obtained in 73% yield by the following method. Sodamide (2 mols.) is added to acetophenone (1 mol.) and ethyl benzoate (1.5 mols.) in ether solution. After addition of water and acetic acid the copper salt is precipitated, separated, and decomposed with hydrochloric acid in suspension in ether. R. K. CALLOW.

Anisil. I, II. J. VAN ALPHEN (Rec. trav. chim., 1929, 48, 1121–1123, 1199–1204).—Nitration of anisil (I) (4:4-dimethoxybenzil), best prepared by oxidation of anisoin (II) (Böster, A., 1881, 421) with boiling 5% potassium permanganate in 10% sodium hydroxide



solution or by Staudinger's method (A., 1912, i, 567), follows two courses according to the conditions, through 3:5:3':5'-tetranitroanisil to dinitroanisic acid, or through 2:4-dinitroanisole to 2:4:6-trinitroanisole. 3:3':5'5'-*Tetranitro-4:4'-dimethoxybenzil* (III), m. p. 233°, is the main product of the action of 100% nitric acid at 0° on anisil (together with 2:4:6-trinitroanisole) or on anisoin (together with 2:4-dinitroanisole). Boiling absolute nitric acid converts anisoin into 2:4:6-trinitroanisole, 3:5-dinitroanisic acid, and a little III. Mixed nitric and sulphuric acids at 0° convert anisil solely into 2:4:6-trinitroanisole, whilst the action of a boiling mixture of nitric acid and acetic anhydride on either I or II gives 2:4-dinitroanisole and a trace of III. The last-mentioned reaction is not preceded by oxidation of anisil to anisic acid, since the latter under the conditions of the experiment gives only mononitroanisic acid. In agreement with these results, boiling nitric acid converts III into 3:5-dinitroanisic acid, whilst with boiling mixed acids it gives 2:4:6-trinitroanisole. Bromine in glacial acetic acid converts I or II into 3:3'-*dibromoanisil*, m. p. 233°, which is nitrated with 100% nitric acid at the ordinary temperature to 3:3'-*dibromo-5:5'-dinitroanisil*, m. p. 220°, converted by concentrated sulphuric acid into 2-bromo-4:6-dinitroanisole. When III is heated with an alcoholic solution of the appropriate amine at 100° in a sealed tube the methoxy-group is replaced and thus are obtained 4:4'-*diamino*-, m. p. 271°; 4:4'-*dimethylamino*-, m. p. 223°; 4:4'-*diethylamino*-, m. p. 201°; 4:4'-*di-n-propylamino*-, m. p. 150°; 4:4'-*di-n-butylamino*-, m. p. 138°; 4:4'-*di-n-amylamino*-, m. p. 126°; 4:4'-*di-n-hexylamino*-, m. p. 133°; and 4:4'-*di-n-heptylamino*-, m. p. 122°, -3:3':5:5'-*tetranitrobenzil*. The m. p. of these derivatives agree with Timmermans' rule (Bull. Soc. chim. Belg., 1919, 28, 392), since they converge, with lengthening hydrocarbon chains, to a limit round about 117°, but superimposed on this is a second effect due to the symmetry of the molecule, causing an oscillation effect, the m. p. being alternately higher and lower than would be expected from the rule (cf. Franchimont, A., 1897, ii, 542). The 4:4'-*dianilino*-derivative, m. p. 285°, is prepared by heating III with aniline at 100° and precipitating the product with alcohol.

Nitration of I or II with absolute nitric acid and acetic anhydride at 0° yields 3:3'-*dinitroanisil*, m. p. 212° (further nitrated to III). By boiling with an equivalent quantity of hydrazine hydrate or heating the reactants in a sealed tube at 100°, anisil is converted into its *monohydrazone*, m. p. 143° (decomp.), but with prolonged heating the dihydrazone, m. p. 122° (Schlenk and Bergmann, A., 1928, 1031, give 118°) (*di-p-chlorobenzylidene* derivative, m. p. 184°), is obtained. *Anisilazine*, m. p. 165°, is obtained by heating anisil with an aqueous-alcoholic solution of hydrazine sulphate, or by partial hydrolysis of the monohydrazone with aqueous-alcoholic sulphuric acid. The general application of the former method is indicated by the similar preparation of benzilazine, m. p. 206° (lit. 202°).

J. W. BAKER.

**Derivatives of methylnaphthalenes.** A. MADI-NAVEITIA and J. SÁENZ DE BURUAGA (Anal. Fís.

Quím., 1929, 27, 647—658).—Oxidation of 2-methylnaphthalene with chromic acid in acetic acid yields 2-methyl- $\alpha$ -naphthaquinone, m. p. 106° (additive compounds with quinol, m. p. 108.5°, and  $\alpha$ -naphthol, m. p. 61°), which yields phthalic acid on oxidation with nitric acid. It is reduced by hydrogen in presence of platinum oxide-platinum-black or by zinc dust and acetic acid to 1:4-dihydroxy-2-methylnaphthalene, isolated as the *acetyl* derivative, m. p. 112°. Nitration of 2-methylnaphthalene in nitric acid yields the mononitro-derivative, m. p. 80°, accompanied by small amounts of the *dinitro*-compound, m. p. 206°. The latter is obtained in good yield by nitration in sulphuric acid, and the *trinitro*-compound, m. p. 182°, is obtained with fuming nitric acid. 1(?)*-Amino-2-methylnaphthalene*, isolated as the *sulphate*, m. p. 210°, is obtained by reduction of the mononitro-derivative with tin and hydrochloric acid, and yields a small amount of phthalic acid when oxidised with nitric acid.

In connexion with the determination of the constitution of plumbagin (A., 1928, 1376), parallel experiments have been carried out with  $\alpha$ -naphthaquinone and with plumbagin. The additive compounds of plumbagin with quinol, m. p. 115°, and with  $\alpha$ -naphthol, m. p. 78°, resemble those of 2-methyl- $\alpha$ -naphthaquinone rather than  $\alpha$ -naphthaquinone, and it is concluded that plumbagin is probably 5-hydroxy-3-methyl- $\alpha$ -naphthaquinone. Whilst naphthaquinone oxidises hydriodic acid quantitatively, 2-methyl- $\alpha$ -naphthaquinone reacts incompletely. Again, 2-methyl- $\alpha$ -naphthaquinone does not react with nitrogen trioxide or hypochlorous acid under the same conditions as  $\alpha$ -naphthaquinone. R. K. CALLOW.

**2(3):10-Dichloro-1-hydroxy-4:9-anthraquinone.** H. RAUDNITZ [with J. MATTAUSCH] (Ber., 1929, 62, [B], 2761—2765; cf. Green, A., 1926, 839).—The action of thionyl chloride on quinzarin at 120° affords 10-chloro-1-hydroxy-4:9-anthraquinone (*loc. cit.*); at 130°, the dichloro- and trichloro-compounds are produced, whereas at 160° or 180°, tetrachloro- and sulphurated substances are formed. 2(3):10-*Dichloro-1-hydroxy-4:9-anthraquinone*, m. p. 241°, most conveniently prepared at 135—140°, is converted by sulphuric acid at 150° into 2-chloroquinizarin, m. p. 239—240°, the structure of which is established by comparison with the product derived from phthalic anhydride and 2-chloroquinol. 2-*Chloro-1:4-diacetoxy-9:10-anthraquinone* has m. p. 209—210°. The dichloro-compound is converted by acetic anhydride containing a trace of concentrated sulphuric acid into 2(3):10-*dichloro-1-acetoxy-4:9-anthraquinone*, m. p. 174°, and by boiling aniline, alone or in presence of boric acid, into 2(3)-*chloro-10-anilino-1-hydroxy-4:9-anthraquinone*.

H. WREN.

**Quebrachitol from the serum of *Hevea* latex.** T. G. LEVI (Gazzetta, 1929, 59, 550—552).—An improved method of extraction of quebrachitol from the serum of rubber latex is described (cf. Contardi, A., 1925, i, 277). The serum, preferably of slab rubber, after removal of proteins if necessary with tannic acid, is evaporated to dryness. Crystallisation of the residue from acetic acid yields quebrachitol (12.5 g. per kg. of serum). The following esters were

prepared by heating with the appropriate acid chloride: *isovalerate*, m. p.  $151^{\circ}$  (lit.  $137^{\circ}$ ); *laurate*, m. p.  $32^{\circ}$ ; *palmitate*, m. p.  $83^{\circ}$  or  $58^{\circ}$  (?) (lit.  $75^{\circ}$ ).

R. K. CALLOW.

#### Saponins and related substances. XXII.

A. W. VAN DER HAAR (Rec. trav. chim., 1929, 48, 1155—1165).—By extraction of the fat-freed seed kernels of *Mimusops Elengi*, L., with methyl alcohol and purification by processes of dialysation and ether precipitation (Boersma, Meded. Lands Plantentuin Buitenzorg, 1902, 2, 96) the saponin (water 10%; ash 1.8%) is obtained together with sucrose and *d*-quercitol. Hydrolysis of the saponin with aqueous-alcoholic sulphuric and hydrochloric acids gives the crystalline *sapogenin*,  $C_{25}H_{40}(OH)_3 \cdot CO_2H$ , m. p.  $325-326^{\circ}$ ,  $[\alpha]_D^{25} +78.4^{\circ}$  [methyl ester, m. p.  $220^{\circ}$  (triacetyl derivative, m. p.  $148^{\circ}$ )] (35.2%), *l*-arabinose (26.7%), *l*-rhamnose (27%), and dextrose (12.4%) calculated on water and ash-free material. These products agree well with the equation  $C_{57}H_{94}O_{28} + 3H_2O = C_{25}H_{40}O_5 + 2C_6H_{12}O_5 + 2C_3H_8O_3 + C_6H_{12}O_6$ , the formula thus assigned to the saponin being in good agreement with the analytical data of Boersma (*loc. cit.*). Distillation of the sapogenin with zinc dust in a current of hydrogen gives a terpene hydrocarbon (or mixture) probably in accordance with the equation  $C_{25}H_{40}(OH)_3 \cdot CO_2H + H_2 \rightarrow 2C_{14}H_{20} + CO_2 + 3H_2O$ . J. W. BAKER.

#### Saponins and related substances. XXIII.

Saponin from the seed kernels of *Achras Sapota*, L., and its hydrolysis. A. W. VAN DER HAAR (Rec. trav. chim., 1929, 48, 1166—1169).—Hydrolysis of the saponin isolated from the seed kernels is represented by the same equation as that previously given (preceding abstract) for the hydrolysis of the saponin from *Mimusops Elengi*, L., and yields the same sapogenin. Identity of the two saponins is thus rendered very probable. J. W. BAKER.

Bixin. VI. I. J. RINKES (Rec. trav. chim., 1929, 48, 1093—1096).—The methyl hydrogen  $\beta$ -methylmuconate, m. p.  $123^{\circ}$  (obtained by oxidation of the degradation product  $C_8H_{10}O_3$  of methylbixin with silver oxide; A., 1929, 931), does not depress the m. p. of the methyl hydrogen ester,  $CO_2H \cdot CH : CMe \cdot CH : CH \cdot CO_2Me$  (I), m. p.  $126^{\circ}$ , obtained by half esterification of *trans*- $\beta$ -methylmuconic acid, m. p.  $231^{\circ}$  (*loc. cit.*  $229^{\circ}$ ), with 0.3% methyl-alcoholic hydrogen chloride (crystalline forms also identical), but depresses that of the methyl hydrogen ester,  $CO_2Me \cdot CH : CMe \cdot CH : CH \cdot CO_2H$  (II), m. p.  $120-121^{\circ}$ , obtained by partial hydrolysis of the dimethyl ester, m. p.  $58-59^{\circ}$  (obtained by the action of methyl sulphate and potassium hydroxide on the *trans*-acid), with cold methyl-alcoholic potassium hydroxide. The structure of I is confirmed by ozonolysis (1 mol.  $O_3$ ), the products being methyl  $\beta$ -acetylacrylate and  $\beta$ -formyl- $\beta$ -methylacrylic acid [*p*-nitrophenylhydrazone, m. p.  $232^{\circ}$  (decomp.); semicarbazone, m. p.  $257^{\circ}$  (decomp.)], not identical with  $\beta$ -acetylacrylic acid [*p*-nitrophenylhydrazone, m. p.  $216^{\circ}$ ; semicarbazone, m. p.  $218^{\circ}$  (decomp.)], which results from the ozonolysis of II. These results agree with Kuhn and Winterstein's formula for bixin (A., 1928, 644).

J. W. BAKER.

An isomeride of cineole (1:4-cineole). G. AUSTERWEIL (Bull. Soc. chim., 1929, [iv], 45, 862—869).—Rectification of the fraction of b. p.  $170-179^{\circ}$  obtained from terpineol residues affords, after fractionation (at 11 mm.) and elimination of the terpenic alcohols by the boric ester method, 12—15% of 1:4-cineole, b. p.  $173-174^{\circ}$ ,  $d_4^{20}$  0.8997,  $n_D^{20}$  1.4501, which possibly contains traces of 1:8-cineole, but yields no additive products with phosphoric acid, resorcinol, tetraiodopyrrole, or hydrochloric acid. With hydrobromic acid it yields terpinene hydrobromide, m. p.  $58^{\circ}$ , and with hydrogen chloride in acetic acid, terpinene hydrochloride, m. p.  $51^{\circ}$ . Oxidation with boiling potassium permanganate gives a dibasic acid, m. p.  $156^{\circ}$ . Since 1:4-cineole is found in the distillation residues of terpineol made from crystalline terpin (1:8-terpin), the 1:4-cineole obtained from industrial terpineol is probably formed by successive hydration and dehydration of  $\gamma$ -terpineol, or of 4-terpineol formed from  $\alpha$ -pinene or nopinene by a similar series of reactions (cf. Simonsen, Rao, and Shintre, B., 1928, 316). R. BRIGHTMAN.

Apparent racemisation of pinene. J. B. CONANT and G. H. CARLSON (J. Amer. Chem. Soc., 1929, 51, 3464—3469).—When *d*-pinene is heated at  $200^{\circ}$  in the liquid or gaseous phase rearrangement into dipentene occurs and not racemisation as concluded by Smith (A., 1927, 212). The amount of dipentene formed is determined by catalytic reduction (platinum oxide) in presence of acetic acid. Dipentene absorbs 2 mols. of hydrogen, pinene only 1 mol. Some polymerisation occurs during the heating (cf. Wallach, A., 1907, i, 228). *d*-Pinane rearranges slowly at  $200^{\circ}$ ; at  $285^{\circ}$  the rate is comparable with that for *d*-pinene. Unsaturated compounds and polymerised material are again produced. H. BURTON.

Preparation of pinene with a theoretical hydrogen value. H. I. WATERMAN, P. VAN'T SPIJKER, and H. A. VAN WESTEN (Rec. trav. chim., 1929, 48, 1191—1198).—A pure specimen of  $\alpha$ -pinene, b. p.  $156.2^{\circ}/767$  mm.,  $d_4^{20}$  0.8582,  $n_D^{20}$  1.4658, is prepared by careful fractionation of turpentine, purification of the fractions of b. p.  $156-158^{\circ}$  through the nitrosochloride, and further fractionation over sodium. With special precautions to avoid rise of temperature both during catalytic reduction and isolation of the product this specimen has a theoretical hydrogen value (99.9%), the reduction product, pinane, having  $d_4^{20}$  0.8561,  $n_D^{20}$  1.4616. Without such precautions catalytic isomerisation of a portion of the  $\alpha$ -pinene first to limonene and then to *p*-cymene and *p*-menthane causes a low hydrogen value to be obtained. Owing to the complex action of bromine on pinene, determination of the bromine value gives no indication as to the nature of the sample. J. W. BAKER.

Camphorophorone. II. The nitrosohydroxylamine. G. SANNA (Gazzetta, 1929, 59, 611—619; cf. A., 1929, 931).—The hydroxylamino-derivative of camphorophorone obtained by Harries (A., 1899, i, 583, 629) is converted by nitrous acid into an isonitroamine (nitrosohydroxylamine) (I), melting at  $35^{\circ}$  to give a blue liquid; the semicarbazone of I, m. p.  $205^{\circ}$  (decomp.), is remarkably stable as compared with I. When treated with 1 mol. of hydroxylamine in alcohol,

I gives camphorophoroneoxime, m. p. 115°. I is very unstable: evaporation of its ethereal solution in a vacuum at the ordinary temperature produces nitrosodihydrocamphorophorone (II), melting at 80—82° to give a blue liquid, identical with the substance obtained by Harries and Maftus (*loc. cit.*), and camphorophorone. With 1 mol. of nitrous acid, I gives II, camphorophorone, and a substance, m. p. about 65°. These results are discussed with regard to the tautomeric forms,  $\cdot\text{N}(\text{NO})\cdot\text{OH}$ ,  $\cdot\text{N}(\text{N}\cdot\text{OH})\cdot\text{O}$ , of the nitrosohydroxylamino-group. C. W. SHOPPEE.

**Interaction of diphenylbenzylpyronone and hydroxylamine.** II. I. SCHETTLE, N. LAPKIN, and N. PERSTNEV (J. Russ. Phys. Chem. Soc., 1929, 61, 903—908; cf. A., 1929, 327).—Wedekind's researches on the preparation, properties, and structure of the reaction product of diphenylbenzylpyronone and hydroxylamine are critically examined.

By the action of hydroxylamine on pyronone in alcoholic solution a crystalline compound, m. p. 157° (decomp.), is obtained, which on recrystallisation from hot alcohol decomposes to the original pyronone, m. p. 171°. When the acetyl derivative of diphenylbenzylpyronone reacts with hydroxylamine, the same result is obtained. It is suggested that the hydroxylamine compound is not an oxime, but a quaternary ammonium salt. M. ZVEGINTZOV.

**Syntheses of polyhydroxychalkones, polyhydroxyhydrochalkones, and polyhydroxyflavanones.** VI. Synthesis of butein, butin, and phloretin. J. SHINODA, S. SATO, and M. KAWAGOE (J. Pharm. Soc. Japan, 1929, 49, No. 571, 123—125).—Attempts to repeat Göschke and Tambor's synthesis (A., 1912, i, 30) of butin by condensing protocatechualdehyde with phloracetophenone in alcoholic alkaline solution were unsuccessful. The condensation of the acid chloride of dicarbethoxycaffeic acid (prepared by using thionyl chloride) with resorcinol in dry nitrobenzene-ether solution in the presence of aluminium chloride at 100° gave a yellow product; this was heated with 10% potassium hydroxide (hydrogen atmosphere) and the solution acidified, when butein, m. p. 210—215° (decomp.), was obtained in 60% yield. The latter was converted by boiling alcoholic hydrochloric acid into butin, m. p. 224—226°. By heating butein for 4 hrs. with sodium acetate (or sulphuric acid) and acetic anhydride diacetylcaffeic acid, m. p. 198°, but no acetylbutein was obtained. If the reaction proceeds for 30 min. only tetra-acetylbutein is formed (cf. Perkin and Hummel, J.C.S., 1904, 85, 1459). Treatment of butein with methyl sulphate and 10% potassium hydroxide gave dimethylcaffeic acid, m. p. 178—179°. Phloretin, m. p. 261°, was similarly synthesised by the condensation of phloroglucinol with carbethoxy-*p*-hydrocumaryl chloride.

*p*-Carbethoxyoxyhydrocinnamic acid, m. p. 106°, was obtained by reducing *p*-carbethoxyoxycinnamic acid (cf. A., 1929, 189) in the presence of platinum.

A. I. VOGEL.

**Cyclamin and cyclamyretin.** F. BUREŠ and J. BERGAUER (Rocz. Chem., 1929, 9, 581—589; cf. A., 1929, 1306).—A method for the preparation of cyclamin,  $\text{C}_{60}\text{H}_{90}\text{O}_{30}$ , m. p. 254° (decomp.),  $[\alpha]_D^{25}$  —33.65°

in methyl alcohol, —23.35° in pyridine, is given. Cyclamin gives a 36.5% yield of cyclamyretin, m. p. 237—239° (decomp.),  $[\alpha]_D^{25}$  +27.92°, probable formula  $\text{C}_{35}\text{H}_{60}\text{O}_5$ , on exhaustive hydrolysis with 2% aqueous and alcoholic mineral acids. The following derivatives of cyclamyretin were prepared: *dimethyl*, m. p. 126—129°; *dibenzoyl*, m. p. 216°; *monoxime*, m. p. 208° (decomp.); *semicarbazone*, m. p. 275°; *dicarboxylic acid*, m. p. 182° (decomp.), by oxidation with bromine; an acid product, m. p. 160°, by oxidation with chlorine, and probably a *dinitro*-ester of cyclamyretincarboxylic acid, m. p. 187°, by the action of nitric acid. Cyclamyretin has no hæmolytic action either *in vivo* or *in vitro*. R. TRUSZKOWSKI.

**Trimethyl- and trimethylethyl-thiophen.** M. A. YOUTZ and P. P. PERKINS (J. Amer. Chem. Soc., 1929, 51, 3511—3516).—Hydrolysis of ethyl  $\alpha\beta$ -diacetobutyrate with 20% potassium carbonate gives  $\gamma$ -methylacetonylaceton, b. p. 71°/10 mm. (all b. p. and m. p. except this are corr.),  $d_4^{25}$  0.9527,  $n_D^{25}$  1.4260 [*disemicarbazone*, m. p. 219—220°; *p*-nitrophenylhydrazon (or possibly the pyrrole derivative), m. p. 112—113°], which on treatment with phosphorus pentasulphide yields 2:3:5-trimethylthiophen, b. p. 163—165°/746 mm.,  $d_4^{25}$  0.9753,  $n_D^{25}$  1.5131. This is converted by the usual Friedel-Crafts method into the 4-acetyl derivative, b. p. 248—249°/748 mm.,  $d_4^{25}$  1.0891,  $n_D^{25}$  1.5454 (*semicarbazone*, m. p. 157°; *p*-nitrophenylhydrazon, m. p. 162.5—163°; *phenylhydrazon*), which is reduced by Clemmensen's method to 2:3:5-trimethyl-4-ethylthiophen, b. p. 204—206°/748 mm.,  $d_4^{25}$  0.9609,  $n_D^{25}$  1.5132.

Hydrolysis of ethyl diacetodiethylsuccinate with aqueous potassium carbonate affords no  $\gamma\delta$ -diethylacetonylaceton.  $\gamma\delta$ -Dimethylacetonylaceton is not obtained by the action of sodium on methyl  $\alpha$ -chloroethyl ketone (Vladesco, A., 1892, 810) or its diethylacetal, b. p. 80—84°/36 mm.,  $d_4^{25}$  0.9773. Methyl  $\alpha$ -chloroethyl ketone condenses with the sodium derivative of methyl  $\alpha$ -cyanoethyl ketone (which may be 4:5-dimethylisooxazole) yielding a substance, probably  $\beta$ -aceto- $\alpha$ -methylbutyronitrile, b. p. 171°/760 mm., 75°/25 mm.,  $d_4^{25}$  0.957.

H. BURTON.

**Derivatives of dihydropentindole.** II. S. G. P. PLANT (J.C.S., 1929, 2493—2498).—When cyclopentanone-*p*-nitrophenylhydrazon, m. p. 154°, is heated with 30% sulphuric acid and cyclopentanone, it gives 5-nitrodihydropentindole, m. p. 165°, whilst 7-nitrodihydropentindole, m. p. 123°, is similarly obtained from the corresponding *o*-nitrophenylhydrazon. cyclopentanone-*m*-nitrophenylhydrazon, m. p. 120°, gives a mixture of 6(or 4)-, m. p. 199° (75%), and 4(or 6)-, m. p. 153° (25%), nitrodihydropentindoles, separated by fractional crystallisation from alcohol and identical, respectively, with the products of hydrolysis of the corresponding two nitro-8-acetyldihydropentindoles, m. p. 154° and 195° (Perkin and Plant, J.C.S., 1923, 123, 3242). By the action of 66% potassium hydroxide and benzoyl chloride or ethyl chloroformate on dihydropentindole are obtained, respectively, 8-benzoyldihydropentindole, m. p. 99°, and ethyl dihydropentindole-8-carboxylate, m. p. 84°, converted by glacial acetic and nitric (*d* 1.4)

acids at 55° or 65° into 10-nitro-9-hydroxy-8-benzoyl-tetrahydropentindole (I), m. p. 187° [together with 4(or 6)-nitro-8-benzoyldihydropentindole, m. p. 160°], and ethyl 10-nitro-9-hydroxytetrahydropentindole-8-carboxylate (II), m. p. 128°. These and the corresponding 8-acetyl compound (III) (*loc. cit.*) differ considerably in their reactions with alkalis. Thus I (which is insoluble in 20% aqueous potassium hydroxide) is converted by boiling aqueous-alcoholic potassium hydroxide into  $\gamma$ -o-benzamidobenzoylbutyric acid, m. p. 170—171°, which is further converted by 15% aqueous potassium hydroxide at 100° into  $\beta$ -2-phenyl-4-quinolone-3-propionic acid, m. p. 218—220°. Aqueous potassium hydroxide (7%) at the ordinary temperature slowly converts II into  $\gamma$ -o-carbethoxyaminobenzoylbutyric acid, m. p. 152°, which is further converted into  $\gamma$ -o-aminobenzoylbutyric acid, m. p. 125—126°, whilst III is readily soluble in 20% aqueous potassium hydroxide at the ordinary temperature, giving 10-nitro-9-hydroxytetrahydropentindole, m. p. 160° (decomp.). In contrast to the corresponding derivatives of 9-acetyltetrahydrocarbazole, I, II, and III are all stable to alcohol. J. W. BAKER.

**Synthesis of 2(4)-quinolyl mercaptans.** E. ROSENHAUER, H. HOFFMANN, and W. PEUSER (Ber., 1929, 62, [B], 2730—2736).—Addition of 2-chloro-4-methylquinoline to a cold, saturated solution of thiocarbamide in alcohol causes, after some hours, the separation of the *thiuronium chloride*,  $\text{Me}\cdot\text{C}_9\text{H}_5\text{N}\cdot\text{S}(\text{NH}_2)_2\cdot\text{NH}_2\text{Cl}$ , decomp. 180°; if the solution is heated or the cold mixture is treated with ammonia or sodium carbonate, 2-thiol-4-methylquinoline, m. p. 266°, and cyanamide (polymerised to dicyanodiamide) are produced. 4:4'-Dimethyl-2:2'-diquinolyl disulphide, m. p. 167°, is described. Analogously, 2-chloroquinoline affords the *thiuronium chloride*,  $\text{C}_{10}\text{H}_9\text{N}_3\text{S}\cdot\text{Cl}$ , decomp. 174°, and 2-thiolquinoline, m. p. 174°. 2-Chloro-4-methylquinoline methiodide and thiocarbamide yield 1:4-dimethyl-2-thioquinolone, m. p. 138°; 1-methyl-2-thioquinolone, m. p. 118°, is obtained analogously.

4-Chloro-2-methylquinoline and thiocarbamide in cold alcohol afford the *thiuronium chloride*,  $\text{C}_{11}\text{H}_{12}\text{N}_3\text{S}\cdot\text{Cl}$ , which when gently warmed under the influence of alkali yields a labile base which becomes decomposed mainly into cyanamide and 4-thiol-2-methylquinoline, m. p. 194°; as subsidiary reaction the mercaptan and thiuronium chloride yield 2:2'-dimethyl-4:4'-diquinolyl sulphide, m. p. 154°; if, however, the alkali acts on the thiuronium chloride in boiling solution, the products are the sulphide, thiocarbamide, and dicyanodiamide with only traces of the mercaptan. 4-Chloro-2-methylquinoline methiodide and thiocarbamide in boiling alcohol afford the dimethiodide of 2:2'-dimethyl-4:4'-diquinolyl sulphide, decomp. 263°. H. WREN.

**Condensation of pyruvic acid with aromatic amines and aldehydes.** III. S. WEIL, R. JAKOBSONÓWNA, and B. DAWIDOWICZ (Rocz. Chem., 1929, 9, 661—666; cf. A., 1928, 527).—The following products have been obtained by condensation of o-anisidine with pyruvic acid and various aromatic aldehydes in boiling alcoholic solution: with piperonal, 8-methoxy-2-(3':4'-methylenedioxyphenyl)quin-

oline-4-carboxylic acid (+2.5H<sub>2</sub>O), m. p. 192—194°; with vanillin, 8-methoxy-2-(p-hydroxy-m-methoxyphenyl)quinoline-4-carboxylic acid (+2H<sub>2</sub>O), m. p. 210°; with m-nitrobenzaldehyde, 8-methoxy-2-(m-nitrophenyl)quinoline-4-carboxylic acid, m. p. 252—253° (decomp.); with salicylaldehyde, 8-methoxy-2-(o-hydroxyphenyl)quinoline-4-carboxylic acid (+0.5H<sub>2</sub>O), m. p. 192—194°, and with cinnamaldehyde, 8-methoxy-2-styrylquinoline-4-carboxylic acid, m. p. 243—244°. The last-named product yields a dibromo-derivative, m. p. 175—178°, and, on reduction, a dihydro-derivative, m. p. 168—170°. In cold ethereal solution, the products of condensation are not quinolines, but diketopyrrolidines; thus o-anisidine, pyruvic acid, and p-dimethylaminobenzaldehyde condense to form 2:3-diketo-5-(p-dimethylaminophenyl)-1-(o-anisyl)-pyrrolidine, m. p. 161°. R. TRUSZKOWSKI.

**Alteration of pyrazolines in contact with free oxygen.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 869—872; cf. A., 1925, i, 1185; 1928, 186).—The liberation of nitrogen from pyrazolines in contact with air or oxidising agents is due to fixation of oxygen prior to the decomposition; in the absence of oxygen, pyrazolines are unchanged in contact with porous substances (cf. Maire, A., 1908, i, 290) or by heat, ultra-violet light, etc., which act as catalysts when oxygen is present, and the variable amounts of nitrogen evolved are determined by variations in the rate or extent of this previous decomposition. Low results in the determination of nitrogen in pyrazolines are due to such decomposition preceding combustion. R. BRIGHTMAN.

**Nature of ketones formed in the regulated oxidation of pyrazolines.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 873—877; cf. A., 1928, 186).—Atmospheric oxidation of 3-methyl-5-isopropylpyrazoline gives methyl isoamyl ketone (semicarbazone, m. p. 142—143°) and isobutyrideneacetone, the latter in slight excess. When this mixture is steam-distilled, treated with hydrazine hydrate, and distilled in nitrogen, isobutyrideneacetone is converted into the pyrazoline and methyl isoamyl ketone into the ketazine,  $(\text{CHMe}\cdot[\text{CH}_2]_2\cdot\text{CMe}\cdot\text{N})_2$ , b. p. 134°/15 mm.,  $d_4^{20}$  0.8432,  $n_D^{20}$  1.4614. With 3-methyl-5-isobutylpyrazoline,  $\beta$ -methylheptan- $\zeta$ -one (semicarbazone, m. p. 152—153°; ketazine, b. p. 153—154°/15 mm.,  $d_4^{20}$  0.8999,  $n_D^{20}$  1.4633) is the main product. Since the purified pyrazoline gives the same result, the presence of the saturated ketone is not due to the reducing action of hydrazine on isoamylideneacetone in the preparation of the pyrazoline. R. BRIGHTMAN.

**Basic compounds formed in the regulated oxidation of pyrazolines.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 877—884).—The basic residue obtained in the oxidation of pyrazolines after steam-distillation of the ketones (cf. preceding abstract) contains the pyrazole corresponding with the original pyrazoline, a mixture of ketazines of the unsaturated ketone from which the pyrazoline is obtained, and of the corresponding saturated ketones and pyrazolines of the same mol. wt. as the ketazines, formed by isomeric change (cf. Curtius and Zinkeisen, A., 1899, i, 165). Thus with 20% excess

of potassium ferricyanide below 20°, 3-methyl-5-isopropylpyrazoline yields 3-methyl-5-isopropylpyrazole, b. p. 124—126°/14 mm., m. p. 58—59°, a mixture, b. p. 130—160°/14 mm.,  $n_D^{25}$  1.4952,  $d_4^{25}$  0.9491, of the azines of isobutylidenacetone and methyl isoamyl ketone, with traces of an oxadiazine, and a fraction, b. p. 170—200°/14 mm., containing 5-methyl-3:5-diisobutylidenemethylpyrazoline and 5-methyl-3:5-diisoamylpyrazoline, and probably small amounts of their oxidation products. Similarly, 3-methyl-5-isobutylpyrazoline gives 3-methyl-5-isobutylpyrazole, b. p. 131—132°/10 mm., a fraction, b. p. 145—165°/14 mm.,  $d_4^{25}$  0.8702,  $n_D^{25}$  1.4683, containing the azines of isoamylidenacetone and  $\beta$ -methylheptan-5-one, and a fraction, b. p. 165—200°/14 mm., probably a mixture of 5-methyl-3:5-diisoamylidenepyrzoline and 5-methyl-3:5-di- $\epsilon$ -methylamylpyrazoline. Similar mixtures of ketones, azines, and pyrazolines, formed by spontaneous oxidation, are obtained in the preparation of pyrazolines (A., 1929, 1183).

R. BRIGHTMAN.

**Mechanism of the regulated oxidation of pyrazolines.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 884—888).—The authors suggest that an unstable peroxide,  $\text{CHR}\cdot\text{CH}_2\cdot\text{CMe}_2\text{O}-\text{O}-\text{N:NH}$ , is first formed by addition of 1 mol. of oxygen to 1 mol. of pyrazoline, and this decomposes into the unsaturated ketazine, nitrogen, and hydrogen peroxide. "Nascent" water from the hydrogen peroxide.

forms a second additive compound,  $\text{CHR}\cdot\text{CH}_2\cdot\text{CMe}_2\text{OH}-\text{NH}-\text{N}$ , with a second mol. of pyrazoline, which similarly decomposes into nitrogen, water, and saturated ketazine. Part of the peroxide also decomposes into the dihydro-oxdiazine  $\text{CHR}\cdot\text{CH}_2\cdot\text{CMe}_2\text{O}-\text{NH}-\text{N}$  or oxdiazine

$\text{CR}\cdot\text{CH}\cdot\text{CMe}_2\text{O}-\text{NH}-\text{N}$ , found in the azine fractions. Since the saturated ketone is formed in increasing amounts as the mol. wt. of the pyrazolines increases, addition of 1 mol. of oxygen to 2 mols. of pyrazoline is excluded, because such additive compounds would yield the unsaturated and saturated ketones in equal amounts. Support for the mechanism suggested is found in the oxidation of benzylhydrazine to benzylideneazine and hydrazine (Wohl and Oesterlin, A. 1900, i, 698).

R. BRIGHTMAN.

**Formation and stability of the 2-o-thiophenyl-4:5-dihydroglyoxalines.** E. W. McCLELLAND and L. A. WARREN (J.C.S., 1929, 2621—2628).—2:3-Dithiosulphindene reacts with ethylenediamine in boiling alcohol to give 2-o-thiophenyl-2:4-dihydroglyoxaline (I), m. p. 244° (decomp.; softens 210°) [picrate, m. p. 242° (decomp.); silver salt], together with traces of III (below). Methylation of I with methyl iodide converts it into 2-o-methylthiol-4:5-dihydroglyoxaline (II), m. p. 100° (isolated as its hydriodide, m. p. 208°; picrate, m. p. 207°; oily nitroso-compound), identical with the product obtained by the following syntheses. 2-Methylthiolbenzoic acid is converted by thionyl chloride into its chloride, m. p. 75—76°, and thence by aqueous ammonia in ethereal solution into the amide, m. p. 149—150°, dehydrated by phosphoric oxide in xylene to the nitrile, m. p. 36°. This is converted

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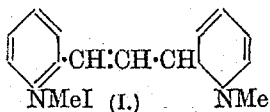
by Kindler's method (A., 1923, i, 568) into the thioamide, m. p. 128—131°, which when heated with an excess of ethylenediamine and a little water yields II, isolated as the hydriodide. Alternatively, an alcoholic solution of the nitrile and ethylenediamine saturated with hydrogen sulphide at -15° is heated under pressure at 110°, or dry hydrogen chloride is passed at 260—270° into molten di-2-methylthiolbenzoyl-ethylenediamine, m. p. 191—192°, obtained by direct condensation of 2-methylthiolbenzoyl chloride with ethylenediamine in ethereal solution. Bromine in glacial acetic acid converts I into the dihydrobromide, m. p. 283°, of 2:2'-oo'-dithiophenyl-4:5-dihydroglyoxaline (III), m. p. 198° [picrate, m. p. 247—248° (decomp.)], the free base being liberated on treatment with alkali. When a suspension of III in carbon tetrachloride is triturated with a solution of bromine in the same solvent and the product boiled with glacial acetic acid, or III is brominated in hot chloroform solution it gives the tricyclic hydrobromide (IV), m. p. 259° [picrate, m. p. 241—242° (decomp.)], which liberates iodine from potassium iodide, and is reduced by hydrogen sulphide to I. Treatment with alkali, however, does not give the corresponding tricyclic base, but converts it into III. When I, III, or IV is boiled with excess of bromine in glacial acetic acid the tricyclic perbromide,  $\text{C}_9\text{H}_8\text{N}_2\text{SHBr}_2\cdot\text{Br}_2$ , m. p. 139—140°, is obtained, converted into IV by boiling with water. An analogous series of perhalides is obtained from II, which by similar treatment with excess of bromine gives a substance,  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{S}_2\text{HBr}_2\cdot\text{Br}_2$ , m. p. 128—134°, whilst the action of iodine in hot alcohol converts the hydriodide of II into a substance,  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{SHI}_2$ , m. p. 114°. The failure to isolate the tricyclic base indicates that the S:N linking is unstable and is analogous to that in the 2-keto-1:2-dihydrobenzthiazoles, the relative stability of its salts being attributed to the increased positive character of sulphur resulting from their polar nature.

J. W. BAKER.

**6(or 8)-Nitro-1-phenylphthalazine: a correction.** J. N. RÂY (J.C.S., 1929, 2661).—The substance, m. p. 165—167°, described by Aggarwal, Darbari, and Rây (A., 1929, 1314) as 6(or 8)-nitro-1-phenylphthalazine is probably unchanged *m*-nitrobenzaldehydedibenzylhydrazone rendered impure by some substance of higher nitrogen content.

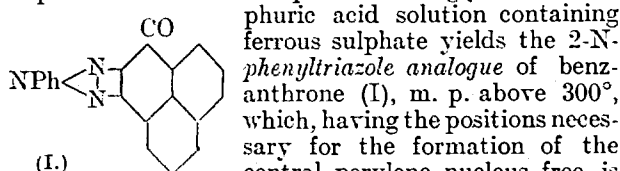
J. W. BAKER.

**Synthesis of carbopyridinecyanines.** E. ROSENHAUER and F. BARLET (Ber., 1929, 62, [B], 2724—2729).—The action of chloroform on a solution of 2-methylpyridine methiodide in boiling alcohol in presence of a large excess of potassium hydroxide affords 1:1'-dimethyl-2:2'-carbopyridinecyanine iodide (I), decomp. 244° (corresponding picrate, decomp. 227°, and bromide, decomp. 248.5—249.5°). 1:1'-Diethyl-2:2'-carbopyridinecyanine iodide, decomp. 265°, is analogously prepared. 6-Phenyl-2-methylpyridine is transformed into its methiodide, m. p. 188°, which affords 6:6'-diphenyl-



1:1'-dimethyl-2:2'-carbopyridinecyanine iodide, decomp. 232° (corresponding picrate, decomp. 223°). 1:1'-Dimethyl-4:4'-carbopyridinecyanine iodide, decomp. 226.5° (corresponding picrate, decomp. 203°), is described. H. WREN.

**Polycondensed heteronuclear systems.** G. CHARRIER (Atti R. Accad. Lincei, 1929, [vi], 10, 101—105).—Condensation of 2-N-phenyl-1:2-naphtho-1:2:3-triazolequinone with glycerol in sulphuric acid solution containing ferrous sulphate yields the 2-N-phenyltriazole analogue of benzanthrone (I), m. p. above 300°, which, having the positions necessary for the formation of the central perylene nucleus free, is able to undergo condensation to the 2-N-phenyltriazole analogues of violanthrone and isoviolanthrone.



T. H. POPE.

**Formation of hæmin derivatives by pyrogenic reactions.** IV. Degradation of hæmin to ætiomesoporphyrin and optoporphin; preparation of optoporphin from pyratin chloride. Spectrochemical reaction of ætioporphyrins with sulphuric acid. O. SCHUMM (Z. physiol. Chem., 1929, 185, 81—98).—When hæmin is heated with liquid paraffin at 350° for 140 min. and the product freed from iron by the phenol-oxalic acid method (A., 1929, 581), 4% of ætiomesoporphyrin is obtained. When decarboxylation is carried out at 390—400° for 5—6 hrs., subsequent removal of iron affords optoporphin (I), C<sub>26</sub>H<sub>26</sub>N<sub>4</sub> (chloroform-sulphuric acid value 15); I is probably either a hexamethyl- or a dimethyldiethyl-porphin. During this high-temperature reaction decarboxylated hæmateric acid (protoporphyrin) is also formed. Similar treatment of pyratin chloride (A., 1928, 1263) also gives I, indicating that the degradation hæmin → I occurs through the intermediate iron salt of ætiomesoporphyrin and pyroporphyrin.

Ætiomeso- and ætiopyro-porphyrins may be distinguished by the difference between the absorption spectra of solutions in 98% sulphuric acid. The positions of the principal absorption bands of these and various other porphyrins, in ethereal and sulphuric acid solutions, have been determined.

H. BURTON.

**Nitration of 3-hydroxy-1:4-benzisooxazine and its 7- and 8-acetamido-derivatives.** I. E. BALABAN (J.C.S., 1929, 2607—2610).—Nitration of 3-hydroxy-1:4-benzisooxazine (I) with nitric (*d* 1.42) and sulphuric acids at 0° affords a mixture of the 6-nitro-derivative, m. p. 235° (62%; Newbery and Phillips, A., 1929, 78), and a substance, m. p. 155—157° (38%), not identical with any of the nitrobenzisooxazines described by Newbery and Phillips (*loc. cit.*), which is probably 2-nitro-3-hydroxy-1:4-benzisooxazine, reduced by stannous chloride and hydrochloric acid to I (87% yield) and by iron and very dilute acetic acid to a base (acetyl derivative, m. p. 233°). Nitration of the 7-acetamido-derivative of I gives only the 6-nitro-derivative, m. p. 276°, hydrolysed by 16% hydrochloric acid to 6-nitro-7-amino-3-hydroxy-1:4-benzisooxazine, decomp. 317°, which is

deaminated and reduced to 6-amino-3-hydroxy-1:4-benzisooxazine (II). Nitration of the 8-acetamido-derivative of I gives a mixture, separated by fractional crystallisation from 50% acetic acid, of the 6-nitro-, m. p. 295—297° (decomp.) (77%), and 7-nitro-+2H<sub>2</sub>O and anhydrous, m. p. 254° (23%), derivatives. The 6-nitro-compound is deacetylated to 6-nitro-8-amino-3-hydroxy-1:4-benzisooxazine, decomp. about 300° (hydrochloride, decomp. 302°), which is deaminated and reduced to II. The 7-nitro-compound is similarly converted successively into 7-nitro-8-amino-3-hydroxy-1:4-benzisooxazine, m. p. 302° (decomp.), and 7-nitro-3-hydroxy-1:4-benzisooxazine. J. W. BAKER.

**Cyanine dyes from quaternary salts of methyl- $\alpha$ - and - $\beta$ -naphthathiazoles.** F. M. HAMER (J.C.S., 1929, 2598—2607).—1-Methyl- $\alpha$ -naphthathiazole (I) (anhydrous, m. p. 57—58°) forms a methiodide, m. p. 262° (decomp.) (Smith, J.C.S., 1923, 123, 2288, gives m. p. 245°), and an ethiodide, m. p. 233° (decomp.), much more readily than does 2-methyl- $\beta$ -naphthathiazole (II), the ethiodide, +H<sub>2</sub>O and anhydrous, m. p. 209° (decomp.), of the latter being prepared by the action of ethyl *p*-toluenesulphonate at 180—190°. By condensation of these four quaternary salts with 2-iodoquinoline methiodide or ethiodide the following thio- $\psi$ -cyanines are obtained, all of which are photographic sensitisers for the bluish-green, the sensitising maximum and the head of the chief absorption band showing a shift of 150—200 Å. towards the red relative to the corresponding benzthiazole derivatives: 1':2-dimethyl-, m. p. 248° (decomp.); 2-methyl-1'-ethyl-, m. p. 243° (decomp.); 1'-methyl-2-ethyl-, m. p. 270° (decomp.); 1:2-diethyl-, m. p. 263° (decomp.), -3:4-benzthio- $\psi$ -cyanine iodides; 1':2-dimethyl-, m. p. 293° (decomp.); 2-methyl-1'-ethyl-, m. p. 296° (decomp.); 1'-methyl-2-ethyl-, m. p. ca. 293° (decomp.); and 1':2-diethyl-, m. p. 296° (decomp.), -5:6-benzthio- $\psi$ -cyanine iodides. Similarly, by condensation of the methiodides and ethiodides of I and II with ethyl orthoformate are obtained 2:2'-dimethyl-, m. p. ca. 240° (decomp.), and 2:2'-diethyl-, m. p. 263° (decomp.), -3:4:3':4'-dibenzthiocarbocyanine iodides; 2:2'-dimethyl-, m. p. 300° (decomp.), and 2:2'-diethyl-, m. p. 294° (decomp.), -5:6:5':6'-dibenzthiocarbocyanine iodides [corresponding bromide of last-named, m. p. 274° (decomp.)]. The chief absorption band of these carbocyanine dyes is still further displaced towards the red, and the two ethiodides are powerful sensitisers, whilst the sensitising action of the methiodides is very feeble. The methiodide and ethiodide of I condense with ethyl orthoacetate in pyridine to give thiocarbocyanines containing the chain :CH·CMe·CH· (cf. Hamer, A., 1929, 197), and thus are obtained 2:2':8-trimethyl-, m. p. ca. 298° (decomp.), and 8-methyl-2:2'-diethyl-, m. p. ca. 298° (decomp.), -5:6:5':6'-dibenzthiocarbocyanine iodides, the absorption maximum being shifted 350 Å. towards the red compared with the parent thiocarbocyanines containing two benzthiazole nuclei. The alkiodides of II will not condense with ethyl orthoacetate. The ethiodides of I and II condense with *p*-dimethylaminobenzaldehyde in boiling alcohol containing piperidine to yield, respectively, 1-*p*-dimethylaminostyryl- $\alpha$ -naphthathiazole ethiodide, m. p. 256° (decomp.), and 2-*p*-dimethyl-



aminostyryl- $\beta$ -naphthathiazole ethiodide, m. p. 213° (decomp.) (both being sensitisers), and with *p*-nitrosodimethylaniline to give, respectively, the *p*-dimethylaminoanils of  $\alpha$ -naphthathiazole-1-aldehyde ethiodide, m. p. 222° (decomp.), and  $\beta$ -naphthathiazole-2-aldehyde ethiodide, m. p. ca. 214° (decomp.), both these anils being desensitisers.

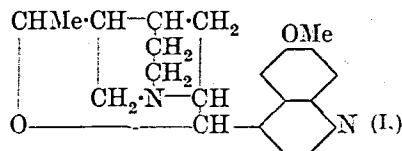
J. W. BAKER.

**isoQuinidine.** A. KONOPNICKI and J. SZUSZKO (Bull. Acad. Polonaise, 1929, A, 340—360).—isoQuinidine is best prepared by dissolving anhydrous quinidine in sulphuric acid (*d* 1.80), warming at 70—80° for 1.75 hrs., pouring on to ice when cold, neutralising the excess of acid, and extracting with ether. The first crop from the ethereal solution consists of pure isoquinidine; the remaining crops are mixed with quinidine and may be separated therefrom by fractional crystallisation of the hydriodides (quinidine hydriodide has m. p. 264°, whilst isoquinidine hydriodide has m. p. 232°). The total yield is about 50%. isoQuinidine has m. p. 72° (anhydrous) or 139—140° (+3H<sub>2</sub>O),  $[\alpha]_D^{25}$  -9.7° in 96% alcohol, and is unimolecular in boiling benzene. The base exhibits a blue fluorescence in oxyacid solutions, is unchanged by treatment with acid chlorides (in presence or absence of alkali), with acetic anhydride, with the Grignard reagent, and with phenylhydrazine or semicarbazide. Only salt formation occurs with dilute mineral acids, but prolonged treatment with concentrated sulphuric acid apparently causes sulphonation. isoQuinidine forms a methiodide, m. p. 242—244° (decomp.),  $[\alpha]_D^{25}$  -39.3° in 96% alcohol, when treated with methyl-alcoholic methyl iodide (1 mol.) at the ordinary temperature, and a dimethiodide, m. p. 232—234° (decomp.), when heated with an excess of methyl-alcoholic methyl iodide at 110—120°. With hydrogen peroxide it gives a 90% yield of isoquinidine oxide, m. p. 110° (3H<sub>2</sub>O; 0.25COMe<sub>2</sub>) [picrate, m. p. 190° (decomp.); dihydriodide]. With bromine in chloroform and glacial acetic acid, respectively, isoquinidine forms perbromides, C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>·HBr·Br<sub>2</sub>, m. p. 210° (decomp.), and C<sub>20</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>·HBr·Br<sub>3</sub>, m. p. 219—221° (decomp.), respectively: both perbromides yield isoquinidine with dilute alkalis, an important fact in deciding the constitution of the base. By heating isoquinidine with 49% hydrobromic acid at 140° the dihydrobromide, m. p. 288° (decomp.),  $[\alpha]_D^{25}$  +181.8° in water, of hydrobromoapoquinidine is formed, which with a slight excess of ammonia affords hydrobromoapoquinidine, m. p. 202° (decomp.),  $[\alpha]_D^{25}$  +202.1° in water, identical with the substance,  $[\alpha]_D^{25}$  +201.7° in water, obtained by subjecting quinidine to similar treatment.

When isoquinidine sulphate (from 1 mol. of alkaloid and 1 mol. of sulphuric acid in alcohol in the presence of ether) is heated at 135—140°, or when the free base is heated with 25% acetic acid in a sealed tube at 100°, there is formed isoquinicine (I) (hydriodide, with 1.5H<sub>2</sub>O, m. p. 189°,  $[\alpha]_D^{25}$  -30.7° in 96% alcohol), which does not react with phenylhydrazine, nitrophenylhydrazine, hydroxylamine, or semicarbazide, but yields a cherry-red colour with diazobenzene-sulphonic acid (also given after a long time by isoquinidine, but not by quinidine). *N*-Acetyliso-

quinicine, m. p. 97° (hydriodide), is formed on warming I with acetic anhydride and anhydrous sodium acetate, whilst nitrous acid converts I into *N*-nitrosoisoquinicine [hydriodide, m. p. 98° (decomp.)]. When isoquinicine is treated with methyl iodide in ether (better in presence of alkali) there results *N*-methylisoquinicine, m. p. 108—110°,  $[\alpha]_D^{25}$  +16.8° in 96% alcohol, also produced by boiling isoquinidine methiodide with 10% aqueous sodium hydroxide [hydriodide, +1H<sub>2</sub>O, m. p. 248—250° (decomp.)]; picrate, m. p. 226° (decomp.); methiodide, m. p. 235—236° (decomp.)]. Equimolecular proportions of bromine in 10% acetic acid and isoquinicine in glacial acetic acid give bromoisoquinicine, m. p. 140—141° (decomp.); *N*-methylisoquinicine under similar conditions, or in chloroform solution, affords bromo-*N*-methylisoquinicine, m. p. 155° (decomp.).

*N*-Methylisoquinicine is unaffected by heating with 20% phosphoric acid at 140°, but when heated with 15% hydrobromic acid at 140° apo-*N*-methylisoquinicine, m. p. 238°,  $[\alpha]_D^{25}$  +16° in 96% alcohol [picrate, m. p. 235° (decomp.)]; methiodide, m. p. 267° (decomp.)], is produced. Diazomethane in ether converts the last-named base into *N*-methylisoquinicine, m. p. 108—110°. Determination of the active hydrogen atoms in the bases by Zerevitinov's method (magnesium methyl iodide in anisole) showed that quinidine and apo-*N*-methylisoquinidine contain one hydroxyl group, whilst *N*-methylisoquinicine and isoquinidine contain no hydroxyl group.



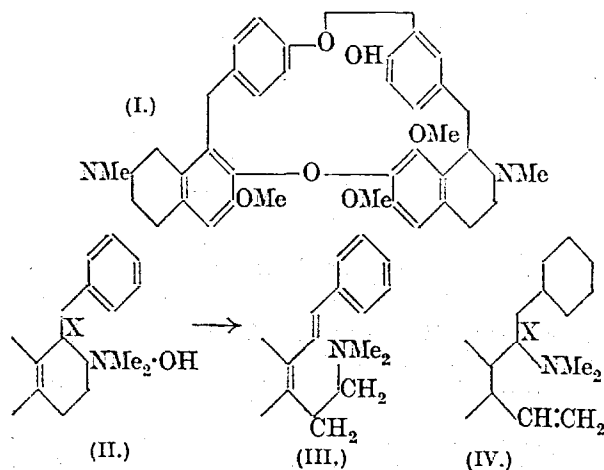
The above reactions are interpreted using I as the formula for isoquinidine.

A. I. VOGEL.

**Papaverine-like bases.** C. MANNICH and M. FALBER (Arch. Pharm., 1929, 267, 601—609; cf. A., 1927, 579).—A base containing six ethoxyl groups in the benzylisoquinoline skeleton is described. Apiole-aldehyde was treated with nitromethane and methyl-alcoholic potassium hydroxide at -5° to -10°. Addition of 6% hydrochloric acid at -10° gave  $\omega$ -nitro-2:5-dimethoxy-3:4-methylenedioxy-styrene, m. p. 164°, which sodium methoxide converts at 0° into  $\beta$ -nitro- $\alpha$ -2:5-trimethoxy-3:4-methylenedioxy-ethylbenzene, m. p. 99°. This substance is reduced by either hydrogen and platinum-black under pressure or by sodium amalgam to  $\beta$ -methoxy- $\beta$ -(2:5-dimethoxy-3:4-methylenedioxyphenyl)ethylamine, b. p. 167°/12 mm. (hydrochloride, decomp. 178°; *N*-benzoyl derivative, m. p. 132°). The phenylacetyl derivative, m. p. 140°, of this base when treated with phosphorus oxychloride affords 5:8-dimethoxy-6:7-methylenedioxy-1-benzylisoquinoline, m. p. 53—55° (hydrochloride, decomp. 199°; picrate, m. p. 209°); the homopiperonyl derivative, m. p. 138°, is similarly converted into 5:8-dimethoxy-6:7-methylenedioxy-(3':4'-methylenedioxybenzyl)isoquinoline, m. p. 82° (hydrochloride, decomp. 190°); the non-crystalline homoveratroyl compound (details of the preparation of homoveratroyl chloride from homoveratric acid

and thionyl chloride are given) yields 5 : 8-dimethoxy-6 : 7-methylenedioxy-1-(3' : 4'-methylenedioxybenzyl)isoquinoline, m. p. 58—61° [hydrochloride, m. p. 246°; picrolonate, m. p. 233° (decomp.)]. Resorcyaldehyde dimethyl ether was similarly converted into  $\omega$ -nitro-2 : 4-dimethoxystyrene, m. p. 106.5°, which with sodium methoxide gives 2 : 4-dimethoxy- $\beta$ -nitro- $\alpha$ -methoxyethylbenzene, m. p. 72°. This is reduced by sodium amalgam, in acetic acid solution to  $\beta$ -methoxy- $\beta$ -(2 : 4-dimethoxyphenyl)ethylamine, m. p. 32.5—33.5°, b. p. 163—164°/10 mm. (chloroaurate, m. p. 162°; phenylacetyl derivative, m. p. 95.5°; homopiperonyl derivative, m. p. 133.5°; homoveratroyl derivative, m. p. 85—86°). C. C. N. VASS.

**Constitution of oxyacanthine.** F. VON BRUCHHAUSEN and H. SCHOLTZE (Arch. Pharm., 1929, 8, 617—628).—The authors have independently arrived at the structure I for oxyacanthine, which has the same empirical composition as that put forward by Späth and Pikel (A., 1929, 1319) but differs in regard to the orientation of the groups attached to the isoquinoline skeleton. The production of an optically inactive base as well as an optically active mixture of metho-bases when the *O*-methyl ether of I undergoes Hofmann degradation, is represented structurally as the formation of III and IV from II. The mother-



liquor from *Berberis vulgaris*, after removal of oxyacanthine, berberine, and phenolic substances, gives on concentration a base,  $C_{19}H_{22}ON_2$  (hydrochloride, m. p. 250°), containing no methoxyl or methylimino-groups.

Treatment of oxyacanthine in alcoholic solution with an equivalent of hydrochloric acid and precipitation with ammonia yields a base,  $C_{36}H_{38}O_6N_2$ , m. p. 260°,  $[\alpha]_D^{25} -94.9^\circ$ , containing three methoxyl and two methylimino-groups. Nitrosodiethylurethane and alcoholic alkali convert oxyacanthine into its ethyl ether,  $C_{38}H_{42}O_2(OMe)(OEt)_3$ , and Hofmann degradation of I affords an optically inactive methine base,  $C_{40}H_{46}O_6N_2$ , m. p. 152°; methyl sulphate, followed by boiling alkali, converts this base into a nitrogen-free substance, m. p. 243°. Hofmann degradation of oxyacanthine ethyl ether yields an inactive methine base,  $C_{41}H_{48}O_6N_2$ , m. p. 126°. Oxidation of oxyacanthine methyl ether with alkaline 5% potassium permanganate gives oxalic acid and an acid (V),  $C_{14}H_5O_5 \cdot OMe$ , m. p. 303°, purified through its methyl

ester, m. p. 96°, b. p. 220—230°/12 mm., and separated from a more soluble acid (17.63%OMe) by acetic acid, in which it is insoluble. Fusion of V with solid potassium hydroxide at 250° gives an equimolecular compound, m. p. 195—196°, of *p*-hydroxybenzoic acid and protocatechuic acid.

Condensation of methyl vanillate and methyl *p*-bromobenzoate by the method of Faltis and Troller (A., 1928, 433) affords the methyl ester, m. p. 72—73°, b. p. 235—250°/12 mm., of 2-methoxydiphenyl ether 4 : 4'-dicarboxylic acid, m. p. 254°.

Oxidation of the above base (m. p. 126°) yields an acid (ethoxy-acid corresponding with acid of m. p. 303°), m. p. 270—274° (methyl ester, m. p. 61°), and other acids (?). When the product of hydrolysis of the urethane of oxyacanthine is oxidised with permanganate acids containing nitrogen are formed.

C. C. N. VASS.

**Microchemical reactions for strychnine.** M. WAGENAAR (Pharm. Weekblad, 1929, 66, 1073—1078).—The most sensitive reagents are gold and platinum chlorides, picric acid, and mercuric iodide in presence of potassium iodide, with each of which 0.1 mg. can be detected, at dilutions of 1 in 1000—5000.

S. I. LEVY.

**Sinomenine and disinomenine.** IX. **Acutumine and sinactine.** K. GOTO and H. SUDZUKI (Bull. Chem. Soc. Japan, 1929, 4, 220—224).—In addition to sinomenine, diversine, and disinomenine, the root of *Sinomenium acutum*, Rehd. et Wills, contains acutumine and sinactine. *Acutumine*, m. p. 240°, was isolated from the chloroform extract of diversine; the root content is about 1% of that of sinomenine. Its molecular formula is either  $C_{29}H_{27}O_8N$  or  $C_{21}H_{27}O_8N$ , and it forms a gold double salt, m. p. 199—200°, and a hydrochloride,  $[\alpha]_D^{25} +60.20^\circ$ . *Acutumine* contains no phenolic hydroxyl group; it contains three methoxyl groups, one NMe grouping, one ketone group (semicarbazone, m. p. above 290°), and probably one carboxyl group. Its absorption spectrum resembles that of narceine.

*Sinactine*, m. p. 174°,  $[\alpha]_D^{25} -312^\circ$  in chloroform (gold double salt; platinum double salt, m. p. 245—247°), isolated as sparingly soluble hydrochloride, m. p. 272° (decomp.), from the chloroform extract of the alkaloids, has the molecular formula  $C_{19}H_{21}O_4N$ , and contains no phenol group or NMe group, but one methylenedioxy-group and two methoxyl groups are present. Its absorption spectrum almost coincides with that of laudanoline, and hence it belongs to the tetrahydropapaverine group of alkaloids.

A. I. VOGEL.

**Reinecke's salt as a microchemical test for alkaloids.** L. ROSENTHALER (Amer. J. Pharm., 1929, 101, 724—725).—The approximate crystalline appearance of the precipitates formed from Reinecke's salt and 17 alkaloids is described (cf. Christensen, A., 1892, 1000).

E. H. SHARPLES.

**Nitration of benzyl derivatives of certain phosphorus, arsenic, and antimony compounds.** F. CHALLENGER and A. T. PETERS (J.C.S., 1929, 2610—2621).—Nitration of tribenzylphosphine oxide with nitric acid (*d* 1.5) at 0° gives tri-*p*-nitrotribenzylphosphine oxide, m. p. 273° (Collie, J.C.S., 1889, 55,

223), together with a small amount of a *substance*, m. p. 158°. Oxidation of either the purified or crude nitration product with potassium permanganate gives 95% of *p*- and 3% of *o*-nitrobenzoic acids, but no *m*-acid could be detected. The unnitrated oxide is much more resistant to permanganate oxidation. Similarly, nitration of dibenzylphosphinic acid gives *di-p*-nitrodibenzylphosphinic acid, m. p. 225—226°, only *p*-nitrobenzoic acid being obtained on oxidation. Arsenic trichloride reacts with magnesium benzyl chloride to give tribenzylarsine (which fumes in air, giving benzaldehyde and I), dibenzylarsinic acid (I), and tribenzylarsine oxide (II) (the two last-named being formed by oxidation of the arsine), whilst when arsenic tribromide is used tetrabenzylarsonium bromide, m. p. 175—177° (*picrate*, m. p. 173°), is also obtained. Tribenzylarsine reacts with bromine in chloroform at 0° to give a crude unstable *dibromide*, m. p. 110—115°, converted by water into the hydroxybromide and by aqueous sodium hydroxide into the oxide. Nitration of I gives only *di-p*-nitrodibenzylarsinic acid, m. p. 210—211°, whilst II similarly yields *tri-p*-nitrotribenzylarsine oxide, m. p. 230°, accompanied by some of the corresponding *hydroxynitrate*, m. p. 189° (decomp.). Oxidation of the crude nitration mixture in both cases gives *p*-nitrobenzoic acid and a trace of *o*-nitrobenzoic acid, but no *meta*. Antimony trichloride reacts with magnesium benzyl chloride to give *tribenzylstibine dihydroxide* (III), m. p. 161° (then again solidifying and remaining unchanged to 250°), which gradually decomposes into benzaldehyde and dibenzyl, and is converted into the corresponding *dichloride*, m. p. 108°, by the action of concentrated hydrochloric acid on its chloroform solution. Nitration of III gives a substance, m. p. 115°, probably trinitrotribenzylstibine hydroxynitrate, which on oxidation gives mainly *p*- with a trace of *o*-nitrobenzoic acids. The results are somewhat analogous to those obtained by Ingold, Shaw, and Wilson (A., 1928, 782) on the nitration of phosphorus, arsenic, and antimony compounds of the type  $[MCH_2PhMe_3]X$ , but no evidence of *meta*-nitration could be detected. The stability of the *p*-nitrobenzyl derivatives towards alkali decreases in the order  $P > As > Sb$ .

J. W. BAKER.

**Action of aromatic Grignard reagents on arylarsine oxides.** F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1929, 51, 3479—3483).—Mercury diphenyl, di-*p*-tolyl, di-*p*-anisyl, and di- $\alpha$ -naphthyl are prepared in 62—90% yield from mercuric chloride and the requisite Grignard reagents. When these are heated with arsenious chloride at 130—140°, the corresponding dichloroarylsines are obtained. These are hydrolysed to the arylarsine oxides by warm 10% sodium hydroxide solution. Where the above method is not practicable, the oxides are obtained by the usual method from the arylarsinic acids. Treatment of the arylarsine oxides with magnesium aryl halides furnishes tetra-arylsine oxides,  $(R_2As)_2O$ . The mixed oxides,  $(RR'As)_2O$ , are usually obtained as oils, and are purified by way of the corresponding tetrachlorides, diarylsinic acids, chlorodiarylsines, and subsequent hydrolysis. The following are described: phenyl-, m. p. 144—146° (lit. 119—120° and 129—

130°), *p*-tolyl-, m. p. 188—189° (lit. 156°), *p*-anisyl-, m. p. 114—116°, and  $\alpha$ -naphthyl-arsine oxides, m. p. 245°; phenyl-*p*-anisyl-, m. p. 167—169°, phenyl- $\alpha$ -naphthyl-, m. p. 175—176°, phenyldiphenyl-, m. p. 218—220°, and *p*-anisyldiphenyl-arsinic acids, m. p. 228—231°; chlorophenyl-*p*-anisyl-, chlorophenyl- $\alpha$ -naphthyl-, chlorophenyldiphenyl-, m. p. 83—85°, and chloro-*p*-anisyldiphenyl-arsines; diphenyldi-*p*-tolyl-, m. p. 75—77°, diphenyldi-*p*-anisyl-, diphenyldi- $\alpha$ -naphthyl-, diphenyldidiphenyl-, tetra-*p*-tolyl-, m. p. 108°, tetra-*p*-anisyl-, m. p. 128—129°, and tetra- $\alpha$ -naphthyl-arsine oxides, m. p. 250—251°.

H. BURTON.

**Manufacture of *o*-hydroxybenzylaminearsinic acids and their aroyl derivatives.** I. G. FARBER-IND. A.-G.—See B., 1929, 997.

**Preparation of mercury diphenyl by the Grignard reagent.** P. BORSTROM and M. M. DEWAR (J. Amer. Chem. Soc., 1929, 51, 3387—3389).—Optimum yields of mercury diphenyl are obtained from magnesium phenyl bromide and mercuric chloride or bromide with 85 mols.-% of the mercuric halide, an excess of the Grignard reagent, and absence of metallic magnesium. The mercury diphenyl must not remain in contact with the mercuric halide unless the Grignard reagent is present.

H. BURTON.

**Mercuration of hemimellitic acid.** F. C. WHITMORE and R. P. PERKINS (J. Amer. Chem. Soc., 1929, 51, 3352—3353).—Sodium hemimellitate and mercuric acetate react in boiling aqueous solution forming anhydro-2-hydroxymercuriisophthalic acid. This is converted by iodine in potassium iodide solution into 2-iodoisophthalic acid, m. p. 243—244° (lit. 236—238°), and by hydrochloric acid into isophthalic acid.

H. BURTON.

**Mercuration of naphthoic acids. I.  $\alpha$ -Naphthoic acid.** F. C. WHITMORE and A. L. FOX (J. Amer. Chem. Soc., 1929, 51, 3363—3367).—Sodium  $\alpha$ -naphthoate and mercuric acetate react in boiling aqueous solution, yielding a mixture of 5- (mainly) and 8-hydroxymercuri-derivatives, and an alkali-insoluble dimercurated derivative. The above mixture could not be separated by fractionation, but after conversion into the chloromercuri-derivatives and subsequent treatment with an acetic acid solution of chlorine, 5- and 8-chloro- $\alpha$ -naphthoic acids are obtained. 8-Chloro- $\alpha$ -naphthoic acid (not esterified by prolonged treatment with methyl-alcoholic hydrogen chloride) is obtained similarly from the mercuration product of naphthalic acid (A., 1929, 946).

$\alpha$ -Naphthoic acid is conveniently prepared from magnesium  $\alpha$ -naphthyl bromide and carbon dioxide or by the hydrolysis of  $\alpha$ -naphthonitrile (prepared by fusion of a mixture of sodium naphthalene-1-sulphonate and cyanide) with a mixture of acetic acid sulphuric acids.

H. BURTON.

**Mercury compounds of thiophen and selenophen.** H. V. A. BRISCOE, J. B. PEEL, and G. W. YOUNG (J.C.S., 1929, 2589—2593).—Thiophen is converted by shaking with a concentrated solution of mercuric acetate into *diacetoxymercurithiophen* (I), transformed by warm concentrated aqueous sodium chloride into dichloromercurithiophen (Volhard, A.,

1892, 828), and decomposed with excess of bromine water to give tetrabromothiophen. Similarly, with basic mercuric sulphate (Denigès' solution) thiophen gives *dihydroxymercurithiophen mercurisulphate* (II),  $C_4H_2S(HgOH)_2.HgSO_4$  (cf. Spielmann and Schotz, A., 1919, ii, 433), which reacts with 5 mols. of iodine, giving, mainly, tetraiodothiophen. Boiling aqueous potassium hydroxide converts I and II into the same dihydroxy-derivative. By similar reactions selenophen is converted into *diacetoxymercuriselenophen* (III), converted by bromine water into tetrabromo-selenophen, by potassium iodide into *di-iodoselenophen*, m. p.  $45^\circ$ , and by boiling sodium chloride solution into *dichloromercuriselenophen*, whilst with mercuric sulphate selenophen gives *dihydroxymercuriselenophen mercurisulphate* (IV). Boiling aqueous potassium hydroxide converts III and IV into *dihydroxymercuriselenophen*. All these mercury derivatives are insoluble powders, decomposing (in some cases explosively) when heated, and are only partly decomposed by boiling with concentrated hydrochloric acid. In sulphuric acid they give the indophenin reaction. J. W. BAKER.

**Arylselenoglycollic acids.** O. BEHAGHEL and M. ROLLMANN (J. pr. Chem., 1929, [ii], 123, 336—345).—Decomposition of aryl selenocyanates by aqueous-alcoholic sodium hydroxide probably occurs thus:  $2ArSeCN + 2NaOH \rightarrow Ar_2Se_2 + NaCN + NaOCN + H_2O$ , the diselenides being further attacked by alkali to give aryl selenomercaptans and seleninic or selenonic acids, since addition of sodium chloroacetate to the reaction mixture gives the corresponding aryl-selenoglycollic acid,  $ArSe.CH_2.CO_2H$ . Several substituted phenyl selenocyanates are prepared by Bauer's method (A., 1913, i, 263), the following being new: *o*-tolyl, b. p.  $135^\circ/20$  mm.; *o*-anisyl, b. p.  $185$ — $190^\circ/20$  mm.; *p*-anisyl, m. p.  $65^\circ$ , *selenocyanates*. From the appropriate selenocyanate are obtained: *o*-nitrophenyl-, m. p.  $165^\circ$ ; *p*-nitrophenyl-, m. p.  $119$ — $120^\circ$ ; *p*-tolyl-, m. p.  $97$ — $98^\circ$ ; *o*-anisyl-, m. p.  $86$ — $87^\circ$ ; *p*-anisyl-, m. p.  $69$ — $70^\circ$ ; *o*-chlorophenyl-, m. p.  $98$ — $99^\circ$ , and *p*-chlorophenyl-, m. p.  $113$ — $114^\circ$ , *-selenoglycollic acids*. Reduction of the *o*-nitrophenyl compound with iron and 20% acetic acid at  $100^\circ$  gives the *anhydride*,  $C_6H_4 \begin{smallmatrix} \text{Se}-CH_2 \\ \diagup \quad \diagdown \\ NH-CO \end{smallmatrix}$ , m. p.  $182^\circ$ , of the *o*-amino-acid, whilst the *p*-compound gives *p*-aminophenylselenoglycollic acid, m. p.  $156^\circ$ . By the action of potassium ethyl xanthate on the diazonium salt obtained from the last-named and hydrolysis with potassium hydroxide, an alcoholic solution of the potassium salt of the *p*-thiol derivative is obtained. This reacts with sodium chloroacetate to give *p*-carboxymethylthiophenylselenoacetic acid,  $CO_2H.CH_2.S.C_6H_4.Se.CH_2.CO_2H$ , m. p.  $204$ — $205^\circ$ , and with methyl sulphate to give *methyl p*-methylthiophenylselenoglycollate, from which is obtained the corresponding acid, m. p.  $75$ — $76^\circ$ . *m*-Nitrophenylselenoglycollic acid, m. p.  $90$ — $91^\circ$ , is obtained by the action of selenoglycollic acid on *m*-nitrobenzene-diazonium chloride. The following *selenides* are obtained as by-products in the above reactions: *pp'*-ditolyl, m. p.  $286^\circ$ , and *pp'*-dianisyl (not pure). These are not obtained by simple distillation of the

pure selenocyanates, since *o*-tolyl selenocyanate is unaltered by heating at  $150^\circ$  and subsequent distillation in a vacuum. J. W. BAKER.

**Organic derivatives of silicon. XLI. Octa-*p*-tolylsilicotetran, octa-*p*-tolylcyclosilicotetran, and other products from di-*p*-tolylsilicon dichloride.** A. R. STEELE and F. S. KIPPING (J.C.S., 1929, 2545—2550).—Pure di-*p*-tolylsilicon dichloride, b. p.  $237$ — $239^\circ/50$  mm. (obtained by systematic fractionation of the product prepared by Kipping and Murray's method, A., 1928, 79), reacts slowly with sodium in boiling toluene. The crystalline products of the reaction are *octa-p*-tolylsilicotetran (I), m. p.  $290$ — $293^\circ$ , and *octa-p*-tolylcyclosilicotetran (II), m. p.  $310^\circ$ , these corresponding with products A and B obtained similarly from the diphenylsilicon dichloride (Kipping and Sands, J.C.S., 1921, 119, 830). Iodine in dry benzene solution converts I into its *di-iodide*, m. p. ca.  $300^\circ$  (decomp.), which is quantitatively hydrolysed by warm aqueous acetone to *octa-p*-tolylsilicotetran oxide, m. p.  $228$ — $229^\circ$ . Aqueous alkali and piperidine readily react with I, giving hydrogen and trianhydrotrisdi-*p*-tolylsilicanediol, but II is only slowly attacked by this reagent even at  $100^\circ$ , giving, finally, di-*p*-tolylsilicanediol or its condensation products. The acetone extract of the original reaction product gives only amorphous substances (main product), separated by fractional precipitation with alcohol into a graded series of amorphous powders, m. p.  $120^\circ$  downwards, and of approximate composition  $Si_4(C_7H_7)_8O$ , but probably not chemically identical with this oxide. From the mineral residue of the reaction with sodium is isolated an amorphous substance, charring without melting at high temperatures, insoluble in all the organic solvents investigated, and of composition  $[Si(C_7H_7)_2]_n$ . This does not give hydrogen with aqueous alkali and piperidine and does not react with iodine in benzene. When the original reaction with sodium is carried out in boiling xylene no crystalline products can be isolated and analysis of the amorphous fractions suggests the presence of compounds containing the group  $Si(C_7H_7)_3$ . The reaction products and their properties are compared with those in the corresponding diphenyl series (*loc. cit.* and J.C.S., 1921, 119, 840). J. W. BAKER.

**Hydrolysis of wheat gliadin by pepsin and trypsin in relation to the formation of diketopiperazines.** A. BLANCHETIÈRE (Compt. rend., 1929, 189, 784—786).—The formation of diketopiperazine by the hydrolysis of gliadin by pepsin and trypsin is analogous to that by the hydrolysis of ovalbumin by these ferments. There is a relation between the amount of diketopiperazine formed and the amino-acids which constitute gliadin and ovalbumin. A. A. GOLDBERG.

**Anhydride complex from edestin containing hexone bases.** N. J. GAVRILOV and M. M. BOTVINIK (Biochem. Z., 1929, 214, 119—133).—The phosphotungstic acid precipitate of the product of autoclave hydrolysis of edestin contains considerable amounts of hexone bases. The precipitate possesses an anhydride character and gives a negative ninhydrin and positive picric acid reaction. After complete hydrolysis, the presence of histidine and arginine was detected.

Only small amounts of the anhydride are removed by exhaustive extraction of the mono- and di-amino-acid fractions with organic solvents, *e.g.*, ethyl acetate. Histidine forms complexes with mono-amino-acids which are not precipitated with phosphotungstic acid. In the phosphotungstic acid fraction a compound of mono-amino-acid with hexonic acid is isolated by way of the silver salt.

P. W. CLUTTERBUCK.

**Denaturation of proteins. II. Effect of heat and of ultra-violet light on the rotatory dispersive powers of pseudoglobulin solutions.** M. SPIEGEL-ADOLF (Biochem. Z., 1929, 213, 475—488).—The effects of heat, of addition of acid and alkali, and of irradiation with ultra-violet light on the rotatory dispersive powers of unextracted sterile pseudoglobulin solutions have been studied. The dispersion quotients for the normal and heated solutions to which acid or alkali has been added lie between 1.88 and 2.00; those for irradiated solutions between 2.2 and 2.9, and those for solutions both heated and irradiated between the values found for normal saturated substances and those found for ketones. When the values of  $[\alpha]$  for different wave-lengths of the various solutions are plotted (Lowry and Dickson, J.C.S., 1913, 103, 1067) curves indicating normal rotatory dispersion are obtained. The characteristic wave-length  $\lambda_0$  remains unchanged in the case of acidified or heated solutions or of solutions made alkaline, but it is considerably increased in the case of solutions irradiated in the presence of acid or alkali.

W. MCCARTNEY.

**Thermo-stabilisation of protein solutions with sucrose and with glycerol.** A. BELLINSSON (Biochem. Z., 1929, 213, 399—405).—The physico-chemical properties of rabbit serum and of egg-albumin are not much affected when the substances are heated with glycerol or with sucrose. The anti-coagulating effect of glycerol is less than that of sucrose and varies with the temperature of heating and with the concentration used. The thermo-stability of the serum-protein increases with the concentration of sucrose and can be made complete at 62°; that of albumin can be made complete at 75°.

W. MCCARTNEY.

**Determination of halogens in organic substances.** G. ILLARI (Annali Chim. Appl., 1929, 19, 443—453).—A modification of Gasparini's method (A., 1907, ii, 650; B., 1908, 430), which permits the accurate determination of chlorine, bromine, or iodine in organic compounds, is described. The tube joining the first with the second electrolytic cell, which is also provided with a tap-funnel, enters this second cell laterally at a point 10 mm. from the bottom. The oxidising agent used is nitric acid (*d* 1.4) for bromo- and iodo-derivatives, and 15 c.c. of nitric acid (*d* 1.4) mixed with 1 c.c. of 70% mercuric nitrate solution for chloro-compounds (cf. Heller, A., 1929, 528, 1158).

T. H. POPE.

**Modified Van Slyke amino-nitrogen apparatus.** F. C. KOCH (J. Biol. Chem., 1929, 84, 601—603).—A technical modification of the apparatus of Van Slyke (A., 1916, ii, 61 etc.) is described.

C. R. HARRINGTON.

## Biochemistry.

**Chemical constitution of respiratory enzymes.** O. WARBURG (Z. Elektrochem., 1929, 35, 549—551; cf. A., 1928, 795).—The reversible reaction between carbon monoxide and hæmoglobin is influenced by an oxidation catalyst, present in mammals to the extent of 1 g. per 100,000 kg. of cell substance. Absorption spectra of the carbon monoxide compounds of each of the following: the respiratory enzyme, hæmin, chlorocruorin, and hæmoglobin, were measured by either (1) stopping the respiration of cells by carbon monoxide in the dark, illuminating the same layer successively with different coloured light, but having equal intensities, and measuring for each wave-length the various increases in respiration thus produced, or (2) estimating the intensities of the different radiations which caused the same increase in respiration.

H. T. S. BRITTON.

**Water emitted by evaporation and its bearing on respiratory exchanges in homeotherms. The ratio water: oxygen.** A. MAYER and G. NICHITA (Compt. rend., 1929, 189, 869—870).—The ratio of water secreted to the oxygen consumed by a rabbit has been determined, and its bearing on the regulation of the body temperature is examined.

A. A. GOLDBERG.

**Evaluation of 5% and 7% carbon dioxide mixtures as respiratory stimulants.** E. HELLER,

W. KILLICHES, and C. K. DRINKER (J. Ind. Hygiene, 1929, 11, 293—300).—The response of normal individuals to the breathing of 5 and 7% carbon dioxide-air mixtures is very variable from person to person and is not constant even with the same person at different times. The maximum increase in breathing obtainable is effected with the 7% carbon dioxide-air mixture, and as this mixture only rarely gives rise to slight untoward symptoms it is apparently to be preferred in resuscitation work.

W. O. KERMACK.

**Use of 7% carbon dioxide and 93% oxygen in the treatment of carbon monoxide poisoning.** C. K. DRINKER and J. SHAUGHNESSY (J. Ind. Hygiene, 1929, 11, 301—314).—The treatment of persons suffering from acute carbon monoxide poisoning is best carried out by the inhalation during the first 5—20 min. of mixtures containing 7% of carbon dioxide and 93% of oxygen, followed by the usual mixture containing 5% of carbon dioxide and 95% of oxygen.

W. O. KERMACK.

**Tissue tension and carbon monoxide poisoning.** J. A. CAMPBELL (J. Physiol., 1929, 68, 81—96).—Carbon monoxide poisoning reduces the oxygen and carbon dioxide tensions of the blood to a greater extent than that produced by a similar loss of function of hæmoglobin. Animals can be acclimatised to 0.25% of carbon monoxide in air, and the effects of

carbon monoxide poisoning are similar to those due to exposure to low oxygen pressure. The carbon monoxide tension of the tissues is only one third that of the inspired air. E. BOYLAND.

**Effect of breathing high concentrations of carbon dioxide on urinary excretion of water.** G. E. SIMPSON (J. Biol. Chem., 1929, 84, 413—418).—The volume of urine was diminished by breathing high concentrations of carbon dioxide. No change was observed in the composition of the blood-serum, but the water and chloride contents of the red corpuscles were increased. C. R. HARRINGTON.

**Source of expired carbon dioxide in decapitated eviscerated cats.** J. K. W. FERGUSON, L. IRVING, and F. B. PLEWES (J. Physiol., 1929, 68, 265—276).—Evisceration raises the respiratory quotient to a figure occasionally above unity. The extra carbon dioxide is not due to a change in metabolism, but rather to a change in the acid-base equilibrium, carbon dioxide being given off from blood, muscles, and bone. E. BOYLAND.

**Partial pressures of oxygen and carbon dioxide in arterial blood and alveolar air.** A. V. BOCK, D. B. DILL, H. T. EDWARDS, L. J. HENDERSON, and J. H. TALBOT (J. Physiol., 1929, 68, 277—291).—The difference between the oxygen pressures of arterial blood and alveolar air is much greater than the difference between the carbon dioxide pressures. The difference in oxygen pressures of blood and air increases with the partial pressure of oxygen. E. BOYLAND.

**Equilibria between carbon dioxide and phosphate solutions. Theory of the carbon dioxide fixation curve.** F. MAINZER and T. C. SHEN (Biochem. Z., 1929, 215, 137—151).—The equilibria between phosphate solutions and carbon dioxide were studied in solutions of the same phosphate concentration and varying  $p_{\text{H}}$  and in solutions of varying phosphate concentration maintaining the same ratio between primary and secondary phosphate. The curve is determined by  $p_{\text{H}}$ ; changes of concentration have more effect in alkaline solutions. The action of strong and weak acids is considered. In acidosis a flat carbon dioxide curve does not necessarily indicate hydræmia. J. H. BIRKINSHAW.

**Protein coagulation and its reversal. Preparation of completely coagulated hæmoglobin.** M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1929, 13, 121—132).—The preparation of hæmoglobin coagulated by heat, acid, and by treatment with urea has been studied, and it is shown that in the first two cases denaturation, as indicated by the amount of nitrogen remaining in solution, is complete. The denaturation of hæmoglobin takes place under conditions exactly similar to that of ovalbumin. K. V. THIMANN.

**Protein coagulation and its reversal. Reversal of the coagulation of hæmoglobin.** A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1929, 13, 133—143).—If horse or ox hæmoglobin is coagulated by heat and at once treated with feebly alkaline solutions, it slowly redissolves. From the solution crystals have been obtained which closely resemble those of the

original native hæmoglobin. The properties of a solution of this "reversed" hæmoglobin resemble those of the native protein in colour, solubility, absorption spectrum, heat coagulation, and equilibrium constant for combination with carbon monoxide and oxygen. Similar results have been observed for coagulation by acid and by urea. It is concluded that the coagulation of hæmoglobin, and therefore probably of other proteins, is reversible. K. V. THIMANN.

**Rate of settling of blood-corpuscles and surface tension.** F. V. VON HAHN (Biochem. Z., 1929, 215, 215).—The discovery by Pines and Joffe (A., 1929, 1325) that no relationship exists between rate of settling of blood-corpuscles and surface tension was made previously by the author (A., 1927, 70).

**Intensity of action of the catalase of blood.** A. I. ALEXEEV, K. I. RÚSSINOVA, and A. N. JAROSLAVZEV (Biochem. Z., 1929, 214, 310—319).—The catalase content of the blood of 202 healthy men and women has been determined by a modification (in which the amount of hydrogen peroxide used was increased to 5 c.c.) of the method of Bach and Zubkova (Sbornik Arb. rein u. angew. Chem., 1923, 1, 69). The men's blood had a higher catalase content than that of the women, whilst there is more catalase in the blood of those who live at a high altitude than in that of those who do not. W. MCCARTNEY.

**Proteolytic enzymes in serum. X. XII. Significance of the complement in blood coagulation. II.** H. J. FUCHS and E. HARTMANN. IV. H. J. FUCHS (Z. Immunitäts., 1929, 58, 1—13, 14—22; Chem. Zentr., 1929, i, 3115).—By treatment with calcium phosphate and centrifuging the proserozyme was separated from the plasma, which no longer coagulates spontaneously and has lost its complement action. The substance which causes coagulation and complement activity is not specific and is thermolabile. The prothrombin content of blood appears to be closely associated with complement function. Proserozyme separated by means of colloidal magnesium hydroxide and liberated by means of carbon dioxide and dialysis also exhibits coagulation and complementary activity. A. A. ELDRIDGE.

**Potentiometric and colorimetric determination of  $p_{\text{H}}$  in serum.** H. SCHREUS and K. SCHULZE (Z. ges. exp. Med., 1929, 64, 540—552; Chem. Zentr., 1929, ii, 333).—The methods of Hollo and Weiss and of Bálint are modified in detail for clinical purposes. A. A. ELDRIDGE.

**Electrokinetic phenomena. I. Adsorption of serum-proteins by quartz and paraffin oil.** H. A. ABRAMSON (J. Gen. Physiol., 1929, 13, 169—177).—The presence of serum in concentrations of  $10^{-7}$  upwards modifies the cataphoresis of fine quartz particles and paraffin oil droplets, a constant mobility being reached at concentration  $10^{-4}$ . In a 1:50 serum dilution, the particles show an isoelectric point between 4.7 and 4.8, thus apparently possessing the properties of the serum-albumin adsorbed. K. V. THIMANN.

**Modification *in vitro* of blood-cholesterol.** A. H. ROFFO and H. DEGIORGI (Bull. Soc. Chim. biol., 1929, 11, 1062—1066).—The cholesterol content of a



0.02% chloroform solution, as determined by Liebermann's method, is reduced to non-weighable traces after exposure for 18 min. to X-ray irradiation. The cholesterol content of 14 specimens of blood-serum, before and after irradiation, is tabulated. The destruction of the cholesterol is proportional to the time of irradiation, and is the greater the smaller is the initial concentration of the cholesterol. The decomposition products cause a marked lowering of the surface tension of the blood-serum.

C. C. N. VASS.

**Determination of blood-fat.** J. L. STODDARD and P. E. DRURY (J. Biol. Chem., 1929, 84, 741—748).—Blood is added to a mixture of alcohol and ether and the solution is boiled and filtered. An aliquot portion of the filtrate is concentrated and hydrolysed with sodium hydroxide; the solution is evaporated after partial neutralisation, the soaps are extracted with water, and the fatty acids are precipitated with hydrochloric acid, collected in a Gooch crucible, dissolved in alcohol, and titrated. Cholesterol may be determined colorimetrically in the chloroform extract of the residue obtained by evaporation of the solution after titration of the fatty acids.

C. R. HARRINGTON.

**Influence of formaldehyde on the precipitation of nitrogenous substances of serum by trichloroacetic acid.** M. MASCRÉ and M. HERBAIN (Compt. rend., 1929, 189, 876—878).—In the presence of formaldehyde, trichloroacetic acid precipitates not only the proteins of serum, but also some of the simpler nitrogenous constituents.

A. A. GOLDBERG.

**Determination of glutathione with special reference to human blood.** W. C. HESS (J. Wash. Acad. Sci., 1929, 19, 419—425).—The determination of total and reduced glutathione in human blood is described, use being made both of the iodometric method of Okuda (cf. A., 1926, 190; 1929, 1191), and of the colorimetric method of Sullivan (cf. A., 1926, 1266). No free cystine or cysteine is found in human blood. Ergothioneine does not interfere with the determination. About 95% of the total glutathione in normal human blood (approximately 62 mg. per 100 c.c.) is in the reduced form.

W. O. KERMACK.

**Solubility of uric acid in the blood.** O. S. GIBBS (Science, 1929, 70, 241—242).—Direct evidence that uric acid occurring in the blood of a fowl is in a soluble form is cited.

L. S. THEOBALD.

**Micro-determination of sugar and its application to the study of blood-sugar.** E. J. BIGWOOD (Bull. Soc. chim. Belg., 1929, 38, 317—321).—A summary of the methods available for the micro-determination of blood-sugar. In the method of Hagedorn and Jensen (A., 1923, ii, 265, 440) deproteinisation with cold tungstic acid gives the same results as with warm zinc hydroxide in the case of blood-serum, but 20% higher results with blood itself. The determination is not affected by the traces of nitrogenous substances (uric acid and creatinine), and only 80% of the reducing material is fermentable with yeast, the proportion of non-fermentable substances being greater in blood itself than in the serum.

J. W. BAKER.

**Effect of substances which inhibit coagulation on the reducing colloids of plasma.** S. DONHOFFER and M. DONHOFFER-MITTAG (Biochem. Z., 1929, 214, 389—394).—Determinations by the methods of Hagedorn and of Bang of the reducing powers of plasma and of serum to which sodium citrate, fluoride, or oxalate or hirudin has been added show that whilst the Hagedorn method gives concordant results for both serum and plasma the Bang method gives results higher for plasma than for serum when the salts are used, and higher for serum than for plasma when hirudin is used. The difference is due to the effect of the anti-coagulants on the capability for precipitation of certain reducing colloids.

W. MCCARTNEY.

**The liver as a source of fibrinogen.** D. R. DRURY and P. D. MCMASTER (J. Exp. Med., 1929, 50, 569—581).—Excision of the liver causes a decrease in blood-fibrinogen of rabbits.

E. BOYLAND.

**Purification of hæmolytic amboceptor.** H. VON EULER and E. BRUNIUS (Svensk Kem. Tidskr., 1929, 41, 258—263).—The hæmolytic amboceptor in the serum of rabbits immunised with goat's red blood-corpuscles has been purified by adsorbing it in faintly acid solution on the stromata of the homologous goat corpuscles and then eluting it from the centrifuged stromata by means of dilute ammonia containing 0.85% of sodium chloride. The adsorption on the stromata reaches about 60% of the amboceptor present at  $p_H$  4.64—5.89, but is only 25% at  $p_H$  8.54. About 75% of the adsorbed amboceptor is removed by dilute ammonia, less than 30% is eluted by dilute acetic acid, whilst very little is removed by disodium hydrogen phosphate solution.

W. O. KERMACK.

**Effect of electrolytes in physiological salt solution on the titre of hæmolytic amboceptors.** H. SCHMIDT and H. GROSS (Biochem. Z., 1929, 215, 61—68).—Small amounts of acid and alkali considerably lower the titre of hæmolytic amboceptors. The acid effect is the stronger. Potassium and calcium salts to a concentration of 0.01% inhibit, and magnesium salts at 0.25—0.005% favour immune hæmolysis. This is a cation action, probably on the red blood-cells. In hæmolysis and complement-fixation experiments the chemical purity of the sodium chloride solutions is of great importance.

J. H. BIRKINSHAW.

**Fractionation and concentration of hæmolytic immune-sera.** H. SCHULTZE and H. GROSS (Biochem. Z., 1929, 215, 115—125).—Hæmolysin of serum is distributed between stable and labile protein. The euglobulin fractions are separated in amounts which vary, depending on the conditions, and differ in hæmolysin content. Fresh, unheated serum behaves differently from old, heated serum. By combining ammonium sulphate precipitation with electrodialysis, stable enriched hæmolysin solutions can be obtained if the hæmolysin is not attached chiefly to labile protein.

J. H. BIRKINSHAW.

**Chemo-immunological studies on conjugated carbohydrate-proteins.** I. Synthesis of *p*-aminophenol- $\beta$ -glucoside, *p*-aminophenol- $\beta$ -galactoside, and their coupling with serum-

globulin. II. Immunological specificity of synthetic sugar-protein antigens. W. E. GOEBEL and O. T. AVERY (J. Exp. Med., 1929, 50, 521—533, 534—550).—I. By the interaction of tetra-acetylglucose in xylene solution with silver *p*-nitrophenoxide at the ordinary temperature *p*-nitrophenyltetra-acetyl- $\beta$ -glucoside, m. p. 172—173°,  $[\alpha]_D^{25}$  —40.8° in chloroform, is formed, which, on hydrolysis at 4° with barium hydroxide solution, yields *p*-nitrophenyl- $\beta$ -glucoside, m. p. 165°,  $[\alpha]_D^{25}$  —79.6° in methyl alcohol. *p*-Aminophenyl- $\beta$ -glucoside, m. p. 160—161°,  $[\alpha]_D^{25}$  —64.1° in methyl alcohol, is formed on reduction of the latter compound with hydrogen in presence of a platinum oxide catalyst. By an analogous series of reactions the following derivatives of galactose have been obtained: *p*-nitrophenyltetra-acetyl- $\beta$ -galactoside, m. p. 144—145°,  $[\alpha]_D^{25}$  —8.3° in chloroform, *p*-nitrophenyl- $\beta$ -galactoside, m. p. 181—182°, *p*-aminophenyl- $\beta$ -galactoside, m. p. 158—159°,  $[\alpha]_D^{25}$  —40.5° in methyl alcohol. Glucoazoprotein and galactozoprotein were prepared by diazotising the corresponding *p*-aminophenyl-hexoside and coupling with a native protein.

II. Solutions of these azoproteins reacted specifically with their homologous antisera and cross reactions were faint or absent. The formation of a precipitate between the azoprotein and its antiserum was inhibited by the homologous *p*-aminophenyl-hexoside, but not by the isomeric compound. The hexose itself did not bring about inhibition.

W. O. KERMACK.

Serological differentiation of steric isomerides (antigens containing tartaric acid). II. K. LANDSTEINER and J. VAN DER SCHEER (J. Exp. Med., 1929, 50, 407—418).—*d*-*p*-Nitrotartranilic acid, m. p. 212—213°,  $[\alpha]_D^{25}$  +130°, obtained by heating *d*-tartaric acid and *p*-nitroaniline at 155—170°, is reduced by zinc dust and hydrochloric acid to the *p*-aminotartranilic acid, decomp. 285°,  $[\alpha]_D^{25}$  +99.2°. By analogous methods the following compounds have also been prepared: *l*-nitrotartranilic acid, m. p. 211—212°,  $[\alpha]_D^{25}$  —120°, *p*-nitromesotartranilic acid, m. p. 193—194°, *l*-*p*-aminotartranilic acid, decomp. 285°,  $[\alpha]_D^{25}$  —98.6°, *meso*-*p*-aminotartranilic acid, decomp. 285°. The three aminotartranilic acids were diazotised and coupled with native proteins to yield *l*-, *d*- and *meso*-azoproteins. Antiserum prepared by the use of the *d*-azoprotein precipitated specifically with a solution of the *d*-azoprotein, but very little if at all with the *l*- or *meso*-azoprotein. Similar specificity was shown by the antisera of the *l*- and *meso*-azoproteins. Specific inhibition of precipitation between an azoprotein and its homologous antiserum was brought about by the presence in the solution of the corresponding amino- or nitro-tartranilic acid and to some extent but less completely or specifically by the corresponding tartaric acid. W. O. KERMACK.

Fate of acetylcholine in the blood. VI. F. PLATTNER and O. GALEHR (Pflüger's Archiv, 1928, 220, 606—611; Chem. Zentr., 1929, ii, 65).—The fission of acetylcholine at blood corpuscles or animal charcoal or in serum is reversibly inhibited by narcotics in a measure dependent on the concentration of the latter.

A. A. ELDRIDGE.

Histamine and acetylcholine in the spleen of the ox and the horse. H. H. DALE and H. W. DUDLEY (J. Physiol., 1929, 68, 97—123).—Histamine and acetylcholine from the spleen were identified both chemically and physiologically.

E. BOYLAND.

Depressor substances in certain tissue extracts. R. H. MAJOR and C. J. WEBER (J. Pharm. Exp. Ther., 1929, 37, 367—378).—Brain extracts contain a substance which is neither histamine nor choline, but lowers the blood-pressure of the dog and atropinised rabbit. Extracts of liver in some cases raise, and in others lower, the blood-pressure of atropinised rabbits, thus appearing to contain both this substance and histamine. Lung extracts exhibit the effects of histamine alone.

K. V. THIMANN.

Sex differences in the cholesterol content of tissues. E. N. CHAMBERLAIN (J. Physiol., 1929, 68, 259—264).—Suprarenal glands of non-pregnant doe rabbits contained more cholesterol than those of male animals. The ovaries were also rich in cholesterol.

E. BOYLAND.

Fine structure, tensile strength, and contractility of animal tissues. K. H. MEYER (Biochem. Z., 1929, 214, 253—281).—From a study of the relationships between the arrangement of the molecules in materials such as rubber and cellulose (stretched and unstretched) and their physical properties the probable structure of the protein molecule and hence of animal tissues is deduced. The functions of the tissues are also taken into consideration.

W. MCCARTNEY.

Physico-chemical properties of the vitreous body. W. S. DUKE-ELDER (J. Physiol., 1929, 68, 155—165).—The vitreous body is a simple gel.

E. BOYLAND.

Nuclein metabolism. XVIII. Nucleotidase content of individual organs of different animals. W. DEUTSCH and K. RÖSLER (Z. physiol. Chem., 1929, 185, 146—150).—The nucleotidase values (number of units in 1 g. of dry preparation; A., 1928, 550) of the pancreas, liver, kidney, spleen, thymus gland, blood-serum, pus- and blood-leucocytes, mucous membrane of the small intestine, and bone-marrow of the ox, dog, pig, and man (liver and blood-serum only) have been determined. No nucleotidase is found in the pancreas and bone-marrow; values of 0.15—2.54 (limits) are found for other organs and preparations.

H. BURTON.

Mummification of the ancient Egyptians: chemical analysis of a Vatican Museum mummy. A. TULLI (Atti R. Accad. Lincei, 1929, [vi], 9, 1111—1114; cf. A., 1929, 715).—The tissues near the vertebrae of the neck of another mummy in the Egyptian Museum of the Vatican contain no soda, heavy metals, or arsenic. Gum-resins appear to be the mummifying agents used.

T. H. POPE.

Production of acid by the stomach. R. KELLER (Biochem. Z., 1929, 214, 395—400).—Electrolytic processes accompany the production of acid in the wall of the stomach. The delomorphous cells of the gastric glands where the production takes

place are distinguished from neighbouring cells by their high alkalinity.

W. MCCARTNEY.

**Variations of gastric acidity during secretion.** D. R. WEBSTER (Amer. J. Physiol., 1929, 90, 718—726).—Stimulation of the gastric glands produces a secretion of an acid juice, followed by juice less acid but rich in mucin.

E. BOYLAND.

**Enzymes of the gastric juice of the river crayfish.** P. KRÜGER and E. GRAETZ (Zool. Jahrb., 1928, 45, 463—514; Chem. Zentr., 1929, ii, 53).—The following enzymes were detected: peptidase, esterase, amylase, maltase, invertase, lichenase,  $\beta$ -glucosidase, and a protease similar to yeast-trypsin. The composition of the gastric juice is recorded.

A. A. ELDRIDGE.

**Effect of the vegetative nerves on the choline content of saliva.** K. UCHIDA (Z. ges. exp. Med., 1928, 62, 671—677; Chem. Zentr., 1929, i, 3111—3112).—Alcoholic extracts of animal saliva contain a substance which, after acetylation, behaves towards the frog's heart like acetylcholine. After sympathetic stimulation the content of this substance is ten times as great as after stimulation of the vagus, the dry matter being four times as great in the first case.

A. A. ELDRIDGE.

**Lipase activity of saliva.** A. PELUFFO (Compt. rend. Soc. Biol., 1929, 100, 115—116; Chem. Zentr., 1929, i, 3109).—Lipase was detected stalagmometrically in human and dog's saliva. Sodium fluoride or thymol, but not mercuric chloride, inhibits the action of the enzyme, which is destroyed at 65°. Unlike pancreas lipase, it is quinine-resistant. It is active only between  $p_H$  6 and 9.

A. A. ELDRIDGE.

**Calcium studies. IV. Calcium content of cerebrospinal fluid. V. Relationship between the calcium content of cerebrospinal fluid and blood-serum.** A. CANTAROW (Arch. Int. Med., 1929, 44, 667—669, 670—675).—IV. The calcium contents of 68 normal cerebrospinal fluids vary from 4.52 to 5.5 mg. per 100 c.c. In fluids from diseased persons a larger variation is found, those from cases of atopic disorders, pulmonary tuberculosis, syphilis, and inflammatory diseases of meninges and brain frequently having a concentration well above the normal.

V. The calcium contents of the blood-serum and of the cerebrospinal fluid have been determined in 199 cases, including 68 normals. In the latter group the calcium content of the fluid is approximately 50% of that of the serum.

W. O. KERMACK.

**Electrolysis of urine.** H. HUMMEL (Z. ges. exp. Med., 1929, 64, 516—521; Chem. Zentr., 1929, ii, 319).—A precipitate, soluble in hydrochloric acid, is formed at the anode, where considerable frothing occurs; at the anode the urine was darker, but clear. When filtered urine, after precipitation with alkali, is employed, neither the cathodic precipitation nor the anodic colour is observed.

A. A. ELDRIDGE.

**Changes in urine brought about by sleep and other factors.** G. E. SIMPSON (J. Biol. Chem., 1929, 84, 393—411).—When normal subjects were kept in bed without food, 200 c.c. of water being given hourly during the day, the excretion of phos-

phate was less during sleep than during waking hours. The reverse condition was observed when two meals were given, the subjects remaining at rest, and when food was withheld but normal activity was permitted during the day. The effect of posture was pronounced, the phosphate (and water) excretion being much reduced during a period of standing between two periods of rest in bed.

C. R. HAREINGTON.

**Test of kidney function with urea.** E. MÖLLER (Acta med. Scand., 1928, Suppl. 26, 259—269; Chem. Zentr., 1929, i, 3127).—The excretion of urea by man is dependent on the quantity of urine and on the blood-urea level. Above (normally) 2 c.c. per min. of urine excreted the quantity of urea depends only on the blood-urea.

A. A. ELDRIDGE.

**Colloid chemistry of urine. VII. Surface activity of urine in relation to bodily effort and mental excitement.** F. V. VON HAHN (Biochem. Z., 1929, 215, 106—114; cf. A., 1927, 70).—The surface activity of urine is not affected by bodily effort, but is considerably increased by mental excitement.

J. H. BIRKINSHAW.

**Determination of allantoin in human urine.** A. ESTABLIER Y COSTA (Bull. Soc. Chim. biol., 1929, 11, 965—974).—The urine, after successive precipitations by phosphotungstic acid, lead acetate, and silver acetate and removal of the heavy metals by hydrogen sulphide, is made alkaline with magnesia and filtered (cf. Wiechowski, A., 1910, ii, 634). Treatment of the filtrate with a 0.2% solution of mercuric acetate in sodium acetate solution precipitates the whole of the allantoin in 1½ hrs. together with some urea. The precipitate is suspended in dilute acetic acid solution and decomposed by hydrogen sulphide. One half of the filtrate is hydrolysed by hydrochloric acid under pressure to give ammonia arising from 100% of the urea-nitrogen and 97% of the allantoin nitrogen (cf. Benedict and Gephart, A., 1909, ii, 103). The urea content of the filtrate is determined by the urease method of Plimmer and Skelton (A., 1914, ii, 306). The difference in the amounts of ammonia obtained in these determinations affords the allantoin content of the urine.

C. C. N. VASS.

**Determination of allantoin in human urine.** F. MOCOROA (Bull. Soc. Chim. biol., 1929, 11, 975—979).—The filtrate from the decomposition of the mercuric acetate precipitate (see preceding abstract) is concentrated to 5 c.c. and treated with 5 c.c. of a saturated solution of barium chloride containing 5% of pure crystalline barium hydroxide, 200 c.c. of an alcohol-ether mixture (2:1) are added, and the mixture is kept at 0° for 24 hrs. The precipitate is collected, dried, and hydrolysed by hydrochloric acid under pressure. The amount of ammonia formed corresponds with 97% of the allantoin-nitrogen. The results show a good agreement with those obtained by the method described in the preceding abstract.

C. C. N. VASS.

**Urinary uric acid.** D. GANASSINI (Arch. Ist. Biochim. Ital., 1929, 1, 167—174).—Arthaud and Butte's method of determining uric acid, based on the precipitation of cuprous urate in presence of copper sulphate, sodium thiosulphate, and Rochelle salt

(Compt. rend. Soc. Biol., 1889), renders it easy to follow variations in the excretion of uric acid.

T. H. POPE.

**Hepatogenic hypoglycæmia associated with primary liver-cell carcinoma.** W. H. NADLER and J. A. WOLFER (Arch. Int. Med., 1929, 44, 700—710).—A case of hypoglycæmia apparently of hepatic origin is described, associated with a cancerous growth in the liver.

W. O. KERMACK.

**Relation between cancer and lipid metabolism.** I. F. BURGHEIM (Klin. Woch., 1929, 8, 828—830; Chem. Zentr., 1929, ii, 67).—In cancer, but not otherwise, X-irradiation causes a transient increase in the blood-cholesterol: the value falls on removal of the tumour. The histochemical picture shows large amounts of cholesterol in malignant, but not in benign, tumours.

A. A. ELDRIDGE.

**Blood-cholesterol in cholelithiasis.** R. H. O. B. ROBINSON (Lancet, 1929, ii, 540—543).—Blood-cholesterol is high in cholelithiasis and obstructive jaundice, and is low in anæmia and ether anæsthesia.

E. BOYLAND.

**Effects of repeated subcutaneous injections of sucrose on diabetics. Pathogenesis of hyperglycæmia and glycosuria.** D. LO MONACO and A. LEONE (Arch. Farm. sperim., 1929, 47, 219—240, 267—272).—Tests on ten patients show that the repeated daily injection of large doses of sucrose in concentrated solution gradually diminishes the hyperglycæmia down to or below the normal level, causes the partial or complete disappearance of the glycosuria, diminishes the daily output of urine, causes the complete disappearance of acetone from the urine, and improves the general health. The mechanism of these effects is discussed.

T. H. POPE.

**Transformation of fats into sugars *in vivo*. Application to the treatment of diabetes.** F. MIGNON (Bull. Soc. Chim. biol., 1929, 11, 943—955).—The feeding of fat or oil to starving dogs does not increase the glycogen reserve in the liver or muscle. Substitution of fat for the sugar without increasing the proteins in the diet of severe diabetics causes glycosuria, hyperglycæmia, and ketosuria to disappear, with arrest of emaciation and of nitrogenous deficiency (cf. Newburgh and Marsh, Arch. Int. Med., 1923, 31, 455).

C. C. N. VASS.

**Change of the isoelectric point of serum in acute infectious diseases.** P. H. ROSSIER (Arch. Phys. biol., 1927, 6, 129—138; Chem. Zentr., 1929, i, 3114).—The isoelectric point of the serum is displaced towards the acid side during fever.

A. A. ELDRIDGE.

**Metabolism of the child in parenteral administration of protein.** I—III. O. BECK (Jahrb. Kinderheilk., 1927, 117, 140—171; 1928, 119, 300—323; 1928, 122, 168; Chem. Zentr., 1929, i, 3116).—Changes in nitrogen metabolism in infectious fever are not comparable with those after protein therapy. After the first administration of protein the  $p_H$  of the urine falls and acidosis is established; further injections cause acidosis or alkalosis. The effect of injection of various substances was studied.

A. A. ELDRIDGE.

**Presence of iodine in rocks, soils, and water and its relation to goitre.** H. CAUER (J. Landw., 1929, 77, 251—274).—Numerous analytical data are recorded and the relation between the natural occurrence of iodine and the incidence of endemic goitre is discussed.

A. G. POLLARD.

**Rickets in rats. X. Fasting tetany and phosphate tetany.** A. T. SHOHL and H. B. BROWN (J. Biol. Chem., 1929, 84, 501—509).—Rachitic rats were subjected to fasting or to administration of a diet containing excess of phosphate. In both cases a condition resulted which was shown to be true tetany by the type of electrical reactions exhibited by the animals, and is regarded as being due to excessively high blood-phosphorus.

C. R. HARRINGTON.

**Blood changes in experimental cholesteryl ester sclerosis.** I. REMESOV (Pflüger's Archiv, 1929, 221, 534—548; Chem. Zentr., 1929, ii, 317—318).—Ingestion by rabbits of cholesterol dissolved in sunflower oil, or injection of colloidal cholesterol, causes an increase in blood-cholesteryl ester, and the activity of the serum-lipase is markedly reduced, apparently owing to an adsorptive reversible union of certain groups of the lipase by the cholesterol. The activity is restored by addition of phosphates. Changes in the arterial walls are related to lipæmia and to the deposition of fat in the tissue.

A. A. ELDRIDGE.

**Metabolism of aluminium.** I. Determination of small amounts of aluminium in biological material. II. Absorption and deposition of aluminium in the dog. III. Absorption and excretion of aluminium in normal man. F. P. UNDERHILL and F. I. PETERMAN. IV. Fate of intravenously injected aluminium. F. P. UNDERHILL, F. I. PETERMAN, and S. L. STEEL. V. Relation of age to the amount of aluminium in tissues of dogs. F. P. UNDERHILL and F. I. PETERMAN. VI. Occurrence of aluminium in human liver and kidney. VII. Aluminium content of some fresh foods. F. P. UNDERHILL, F. I. PETERMAN, E. G. GROSS, and A. C. KRAUSE. VIII. Toxic effects produced by subcutaneous injection of aluminium salts. F. P. UNDERHILL, F. I. PETERMAN, and A. SPERANDEO (Amer. J. Physiol., 1929, 90, 1—14, 15—39, 40—51, 52—61, 62—66, 67—71, 72—75, 76—82).—I. Aluminium is determined colorimetrically as the red alizarin lake.

II. Aluminium occurs to 0.0003—0.0004% in the blood of normal dogs, and to a greater extent in the liver, kidney, brain, and spleen, but not in the muscles or genital organs. Aluminium is absorbed from the diet and is stored in various tissues and excreted in bile.

III. The blood of normal men contains less than 0.0002% of aluminium.

IV. After intravenous injection of aluminium, it is excreted in the bile and into the alimentary canal. The excretion through the intestine has no relation to phosphate concentration.

V. The aluminium content of tissues of dogs increased with age. Considerable amounts of aluminium were found in the lungs of old dogs.

VI. The liver and kidney tissue of human subjects contained from 0.00013 to 0.00117% of aluminium.

VII. Many fresh foods contain aluminium. Apples, oranges, melons, and eggs are relatively poor in aluminium.

VIII. Doses of 5–8 g. of aluminium chloride or sulphate per kg. body-weight, injected into rats, guinea-pigs, and rabbits, cause death in 2–11 days. The liver, kidney, and sometimes the spleen are affected.

E. BOYLAND.

**Copper metabolism of the rat.** C. W. LINDOW, W. H. PETERSON, and H. STEENBOCK (J. Biol. Chem., 1929, 84, 419–436).—The total copper in the body of a rat on normal diet increased from 0.0108 mg. at birth to 0.4422 mg. in adult life. Administration of copper to a pregnant rat did not increase the copper content of the young at birth, but administration during growth caused an increase of 200–300% in the copper content of the adult animal; the additional copper was found for the most part in the liver. Young rats suffering from nutritional anaemia showed no change in their copper content from the age of 3 weeks to their death at 9–11 weeks. On a normal diet copper is excreted by adult rats in the proportion of two thirds in the faeces and one third in the urine; when additional copper is administered the excretion is almost entirely by way of the faeces. Such administration of copper to adult rats results in storage of some of the metal, which is eliminated in the course of 4–5 weeks when the extra copper is withheld from the diet.

C. R. HARRINGTON.

**Utilisation of calcium carbonate and citrate by laying and non-laying pullets.** W. C. RUSSELL and F. G. McDONALD (J. Biol. Chem., 1929, 84, 463–474).—Pullets at the stage of commencing egg production were kept on a diet low in calcium which was supplemented by the addition of sub-optimal amounts of calcium carbonate or calcium citrate; in both cases the calcium content of the excreta was reduced during the period of egg production, indicating that both calcium salts could be utilised for egg-shell formation. The quality of the eggs produced was similar in both cases. During non-laying periods the percentage retention of phosphorus is very high, whilst during laying periods there is a tendency for the phosphorus balance to become negative.

C. R. HARRINGTON.

**Protein and mineral metabolism in pregnant sows on a normal or high-calcium diet compared with a calcium-deficient diet.** R. E. EVANS (J. Agric. Sci., 1929, 19, 752–798).—Normal sows stored 1439 g. of nitrogen, and sows receiving a calcium-deficient diet stored 1125 g. during the gestation period. Addition of calcium carbonate to the diet of sows increased the mineral retention. Dietetic lime equilibrium was attained by sows receiving a calcium-deficient diet with 2 g. of calcium oxide per day, whilst the average retention of normal sows was 6.4 g. of calcium oxide. The phosphate retention of lime-deficient animals was in three cases higher than that for normal sows, but the total retention during gestation was only 647 g. against 720 g. for the normal animals. In a similar way calcium-deficient animals retained 111 g. of

potassium oxide and 203 g. of sodium oxide against 201 g. and 152 g., respectively, in animals of the other group.

E. HOLMES.

**Influence of addition of calcium carbonate to a ration low in lime on appetite and digestibility of food in swine.** R. E. EVANS (J. Agric. Sci., 1929, 19, 799–801).—Animals on a calcium-deficient diet suffer periodically from loss of appetite although the ration is otherwise satisfactory, but 22 digestion trials failed to show enhanced digestibility of the organic constituents of the food on adding calcium carbonate to such a ration (see preceding abstract).

E. HOLMES.

**Iodine content of organs of pigs in various stages of development and manner of the transition of iodine from mother to foetus and new-born pigling: iodine content of common foodstuffs.** H. COURTH (Landw. Jahrb., 1929, 69, 565–598; Bied. Zentr., 1929, 58, 497–498).—The average iodine content of pig's thyroid in spring and summer is  $4 \times 10^{-3}$ – $7 \times 10^{-6}$  g. Other organs have relatively insignificant amounts. An iodine correlation between thyroid and inner-secretory glands exists only in the case of normal adult testicles. This is not the case with ovaries. The small quantity of iodine found in the foetus towards the end of the period of gestation cannot be explained by an embryonic-hormonal function of the gland. The potential reserve of iodine for the whole organism is supplied mainly by the mother's milk, especially the colostrum, so that the later intake of iodine is merely that requisite for the increasing body-weight. With iodine-free feeding the mother during lactation supplies the necessary quantity of iodine for her young from her potential iodine reserve. During the temporary reduction of the potential iodine reserve, there is always a sufficiency for the maintenance of healthy body condition for the nourishment of the foetus and for milk production even when no iodine is detectable in the daily ration. The iodine reserve is probably replenished later from natural sources.

A. G. POLLARD.

**Effect of iodine on cattle.** S. WEISER and A. ZAITSCHEK (Fortschr. Landw., 1929, 4, 275; Bied. Zentr., 1929, 58, 499).—Administration of iodine to cows stimulated their sexual functions.

A. G. POLLARD.

**Transformation of ionised and biological iodine.** II. G. PFEIFFER (Biochem. Z., 1929, 215, 197–202; cf. A., 1929, 1486).—The iodine metabolism of dogs from which half the thyroid gland had been removed as control was studied. The transport of potassium iodide differs little from that of other iodine compounds when the dose is within physiological limits. The transformation of potassium iodide is negligible, but plant iodine compounds are largely resorbed and stored in the thyroid even when the potential iodine reserve is considerable. The upper limit of iodine storage in the thyroid is 1900–2000  $\gamma$  per g. of fresh organ.

J. H. BIRKINSHAW.

**Value of dried sugar-beet pulp and molasses-sugar-beet pulp in the nutrition of swine. Value of whole sugar-beet in the nutrition of swine.** H. E. WOODMAN, A. N. DUCKHAM, and M. H. FRENCH

(*J. Agric. Sci.*, 1929, **19**, 656—668, 669—676).—Digestion trials with pigs and large-scale feeding trials under farm conditions have shown that pigs can digest dried sugar-beet pulp and molasses-sugar-beet pulp almost as well as ruminants. Although the capacity of pigs for digesting fibre is usually regarded as very limited, in the present case the fibre digestion coefficients were 84.4 and 84.3% for the fibre from these two sources, probably because this fibre is not lignified.

Whole sugar-beet suitably grated may replace barley meal up to 25% of the total ration in the production of bacon pigs. The digestion coefficient of the organic matter of sugar-beet was 91.9, of nitrogen-free extractives and fibre 97.1 and 90.1, and of crude protein only 40.0%. E. HOLMES.

**Food value of the potato for albino rats.** A. GALAMINI (*Atti R. Accad. Lincei*, 1929, [vi], **9**, 1169—1170).—Albino rats are kept alive for a prolonged period by a daily ration of 50 g. of boiled potato and 4 g. of butter, but this is insufficient for normal growth in a growing rat. The addition, after 120 days of the above diet, of 1—2.5 g. daily of fibrin resulted in normal increase in weight. The food value of the potato-butter diet is improved also by addition of alcohol or Osborne's mixture of salts, the adult rat then increasing in weight. If these additions are stopped, the gain in weight is lost. T. H. POPE.

**Carbohydrate content of the chief proteins of foodstuffs and a colorimetric method for the determination of nitrogen-free sugar in protein.** J. TILLMANS and K. PHILIPPI (*Biochem. Z.*, 1929, **215**, 36—60).—A method for the determination of nitrogen-free carbohydrate in protein depends on the colour produced with thymol or orcinol in sulphuric acid. To 9 c.c. of sulphuric acid and 6 c.c. of water are added 0.5 c.c. of 2% orcinol solution in dilute sulphuric acid and 1 c.c. of protein solution containing 0.01—0.04% of dextrose. The colour is compared with a dextrose standard. To obtain reproducible results a standard method of purification of the protein must be adopted.

The caseinogen of cow's and goat's milk, myosin, and certain kinds of meat gave dextrose values of 0.36—0.89%, egg-yolk 6.5%, egg-white 3.5%, legumin at least 5%, glycinin at least 5.1%, glutenin 8%, pea globulin 1.8%, approximately. The carbohydrate of protein is partly firmly bound and partly removable by alkali. J. H. BIRKINSHAW.

**[Nutritive value of] bread.** I. ABELIN (*Biochem. Z.*, 1929, **215**, 162—190).—Rats fed on a bread diet were checked in growth and became ill. There was no difference between white and brown wheaten bread and rye bread in this respect. Even the addition of milk and fresh carrots to the diet did not produce much improvement. The unsuitability of a bread diet is due to various causes, such as insufficient vitamin and the excess of phosphoric acid over calcium. A periodic change in the kind of bread used often proved beneficial.

J. H. BIRKINSHAW.

**Significance of plant sterols for animal organisms. VII. Sterol absorption, measured in the blood of the portal vein.** D. YUASA (*Z. physiol.*

*Chem.*, 1929, **185**, 116—118).—Dogs fed with a 5% solution of cholesterol in olive oil show a 25—50% increase in the cholesterol content of the portal vein blood. With triolein alone, or with sitosterol, a decreased cholesterol content is found. The results support the view that plant sterols are not absorbed by animals (Schönheimer and Yuasa, A., 1929, 212).

H. BURTON.

**Significance of plant sterols for animal organisms. VIII. Sterol balance in the laying hen.** R. SCHÖNHEIMER (*Z. physiol. Chem.*, 1929, **185**, 119—122).—The total cholesterol of the eggs laid during 28—30 days is greater than the total sterol (plant) in the food. Furthermore, about 90% of the food sterol is excreted in the faeces. The animal must, therefore, synthesise cholesterol.

H. BURTON.

**Relation of bile acids to food cholesterol. II.** R. HUMMEL (*Z. physiol. Chem.*, 1929, **185**, 105—115).—When mice are fed with a mixture of cholesterol and glycocholic, cholic, deoxycholic, apocholeic, or dehydrocholic acid, an increased amount of cholesterol is found in the liver. The accumulation is most marked with cholic acid, least with dehydrocholic acid (cf. Loeffler, A., 1928, 1398). Feeding with the acids alone causes only a slight increase in the liver-cholesterol. If after 12 days' feeding with the above mixtures both substances are omitted, the liver-cholesterol becomes normal after 8—10 days; omission of the cholesterol only causes an alternation in the cholesterol content except with dehydrocholic acid (decreases to the normal).

H. BURTON.

**Action-radiation of muscle and growth action of the electro-dynamic field.** W. W. SIEBERT (*Biochem. Z.*, 1929, **215**, 152—161).—When muscle is electrically stimulated there are two phenomena which promote the rate of budding of yeast: the action of an electric field and the "action-radiation" (mitogenetic action) which is connected with the oxidation processes produced by muscular activity.

J. H. BIRKINSHAW.

**Acid-base equilibrium in frog's muscle.** A. D. RITCHIE (*J. Physiol.*, 1929, **68**, 295—304).—On stimulation the amount of base present in muscle decreases by an amount equivalent to the lactic acid formed. Minced tissue on keeping produces more acid than is equivalent to the decrease in the amount of base. This is due to protein hydrolysis liberating both basic and acidic groups. E. BOYLAND.

**Muscle contraction. VII. Rôle of potassium.** E. ERNST and L. SCHEFFER. **VIII. Displacement of water as basis of convulsions.** E. ERNST (*Pflüger's Archiv*, 1928, **220**, 655—671, 672—690; *Chem. Zentr.*, 1929, i, 3117).—On stimulation of muscle part of the potassium passes into the perfusion liquid; the effect is not due to fatigue, formation of lactic acid, or increase of permeability, but is independently connected with the contraction. The theory that the production of ions is the primary process of muscle contraction is supported.

A. A. ELDRIDGE.

**Amount of work and acid production of muscle.** I. O. RIESSER and W. SCHNEIDER (*Pflüger's*



Archiv, 1929, 221, 713—719; Chem. Zentr., 1929, i, 3117).—The influence of load on the fatigue of frog's muscle was studied. The lactic acid increases with the load, but not proportionally.

A. A. ELDRIDGE.

**Amount of work and acid production of muscle. II. III.** T. NAGAYA (Pflüger's Archiv, 1929, 221, 720—732, 733—741; Chem. Zentr., 1929, i, 3117).—II. The production of lactic and phosphoric acids increases with the number of stimulations of working muscle and with the load, falling to a minimum with further increase in the amount of work. It is concluded that the production of lactic and phosphoric acids is a function of the extension.

III. A similar conclusion was reached from experiments with frog's heart muscle. A. A. ELDRIDGE.

**Production of lactic acid and consumption of oxygen during tonic contraction of striated muscle.** S. G. ZONDEK and F. MATAKAS (Biochem. Z., 1929, 214, 320—342; cf. A., 1928, 86).—Nicotine and novocaine have now been added to the substances tested with regard to their effects on production of lactic acid and on sensitivity in muscle. Nicotine produces very little lactic acid and has only a very slight effect on anaërobic glycolysis. It causes increased consumption of oxygen. Novocaine, which causes production of lactic acid and raises the tonus of muscle, also causes disappearance of excitability. The differences in behaviour of the various excitants used and the fact that contraction begins before the appearance of lactic acid show that the acid neither causes nor maintains the process of contraction. Tonic contraction may be related rather to some process in which the muscle is damaged or may run parallel with such a process. W. MCCARTNEY.

**Carbohydrate metabolism of muscle. II.** Lactacidogen, lactic acid, glycogen, total carbohydrate, and dry residue of striated muscle of the foetus of *Bos taurus*. F. USUELLI (Arch. Fisiol., 1928, 26, 15 pp.; Chem. Zentr., 1929, ii, 187).—The striated muscle of the adult ox and of the foetus contains similar amounts of inorganic phosphorus and lactacidogen, but the latter contains the larger percentage of total carbohydrate, glycogen, and lactic acid.

A. A. ELDRIDGE.

**Determination of phosphagen and other phosphorus compounds in muscle-tissue.** G. P. EGGLETON and P. EGGLETON (J. Physiol., 1929, 68, 193—211).—As phosphagen does not diffuse from muscle it may not be creatinephosphoric acid, but a compound of colloid nature. Improvements in the determination of the creatinephosphoric acid of muscle are described. Pyrophosphate is determined by Lohmann's method (A., 1929, 1098). Stimulation of muscle increases the amount of inorganic phosphate and hexosemonophosphate at the expense of the phosphagen; the pyrophosphate is unchanged. That part of the sartorius muscle adjacent to the nerve does not differ from the part remote from the nerve, in respect to its phosphagen content. In anaërobiosis the phosphagen first disappears, followed by the pyrophosphate and insoluble esters, while the free phosphate and the hexosemonophosphate increase in amount. Blood, spleen, and kidney contain no

phosphagen, but smooth muscle and heart-muscle contain small amounts. E. BOYLAND.

**Excretion of acid in urine during work. IV.** Excretion of lactic and phosphoric acids in relation to urinary acidity. M. S. RESNITSCHENKO and N. P. KOSMIN (Biochem. Z., 1929, 215, 26—35; cf. A., 1929, 1193).—Running causes a large increase in the lactic acid excreted in the urine and in its acidity, the amount being governed by the muscular effort exerted. The determination of the urinary acidity thus gives a measure of fatigue. The acid phosphate is only slightly increased by work.

J. H. BIRKINSHAW.

**Is the glycogen content of striated muscle altered in tonic contraction?** E. WERTHEIMER (Pflüger's Archiv, 1928, 221, 139—143; Chem. Zentr., 1929, ii, 188).—In guinea-pig muscles no loss, or a relatively small loss, of glycogen was observed.

A. A. ELDRIDGE.

**Glycogen formation in liver of young white rat after oral administration of glycerol.** L. F. CATRON and H. B. LEWIS (J. Biol. Chem., 1929, 84, 553—559).—The glycogen content of the livers of fasting young white rats was raised from an average basal value of 0.09% to an average maximum of 3.24% by oral administration of glycerol.

C. R. HARRINGTON.

**Lævulose and dextrose in intermediary metabolism.** F. BERTRAM (Z. ges. exp. Med., 1929, 64, 295—302; Chem. Zentr., 1929, ii, 63).—Lævulose, administered orally, causes a smaller rise of blood-sugar than does dextrose. Whilst dextrose or adrenaline hyperglycemia is increased by previous administration of calcium and diminished by that of potassium, lævulose or parasympathetic glycemia is increased by potassium and unaffected by calcium.

A. A. ELDRIDGE.

**Ammonia and sugar metabolism of surviving organs under the influence of poisons inhibiting oxidation.** A. BORNSTEIN and H. F. ROESE (Arch. exp. Path. Pharm., 1929, 145, 277—296).—The liver and limbs of dogs when perfused with dog's blood containing potassium cyanide or carbon monoxide give up ammonia and lactic acid to the perfusing fluid. This effect is also observed when the blood is deficient in oxygen, but not with small or moderate doses of quinine, but only with excessively large concentrations of this drug. Under conditions such that oxidation is inhibited, as in presence of cyanide and carbon monoxide, the rate of disappearance of dextrose from the fluid perfusing the limbs is not decreased and is frequently increased. W. O. KERMACK.

**Metabolism of amines. I. Trimethylamine.** W. D. LANGLEY (J. Biol. Chem., 1929, 84, 561—570).—Trimethylamine in amounts up to 125 mg. per kg. is oxidised by the rabbit to the extent of 80—96%, the greater part of the nitrogen appearing as carbamide in the urine. The excretion of ammonia was not influenced and the urine contained no methylamine and only traces of dimethylamine.

C. R. HARRINGTON.

**Metabolism of amino-acids. II. Rate of absorption of amino-acids from gastro-intestinal tract of white rats.** R. H. WILSON and H. B.

LEWIS (J. Biol. Chem., 1929, **84**, 511—531).—The rates of absorption of the following amino-acids, after oral administration of the free acids (or of their sodium salts) to white rats, were in descending order of magnitude: *D*-alanine, *DL*-alanine, glycine (sodium salt), *D*-glutamic acid (sodium salt), glycine, *DL*-alanine (sodium salt), *L*-leucine (sodium salt). The rate of absorption is independent of the absolute amount and concentration of the amino-acid in the intestine. The results are discussed in relation to the changes in the nitrogenous composition of the blood observed after ingestion of various amino-acids.

C. R. HARRINGTON.

**Oxidation of glutamic acid in the animal body.** M. OESTERLIN (Biochem. Z., 1929, **215**, 203—204).—A criticism of the results of von Beznák (A., 1929, 466).

J. H. BIRKINSHAW.

**Rôle of the liver and of the intestine in the deamination of amino-acids.** A. BORNSTEIN (Biochem. Z., 1929, **214**, 374—381).—In fasting dogs from which the gastro-intestinal canal, pancreas, spleen, kidneys, and liver have been removed, the hepatic artery being ligatured and the inferior *Vena cava* being preserved as far as possible, intravenous injection of glycine or of alanine produces no increase in the amount of ammonia in the blood. If the dogs are treated in the same way except that the liver is not removed, the injections produce an increase in the amount of blood-ammonia. The increase is greater than that which occurs in normal dogs and it persists for a longer period. It follows that in the dog deamination of amino-acids occurs largely in the liver.

W. MCCARTNEY.

**Arginine feeding and creatine-creatinine excretion in man.** E. C. HYDE and W. C. ROSE (J. Biol. Chem., 1929, **84**, 535—541).—Prolonged oral administration of a daily dose of 1.606 g. of arginine monohydrochloride had no effect on the excretion of creatine and creatinine by the male or female human subject.

C. R. HARRINGTON.

**Kinetics of penetration. I. Equations for the entrance of electrolytes.** W. J. V. OSTERHOUT (J. Gen. Physiol., 1929, **13**, 261—294).—Mathematical. The rate of increase of molecules within the vacuole of a cell exposed to a weak acid is calculated for three cases: (1) entrance of molecules alone, (2) entrance of ions alone, (3) entrance of molecules and ions simultaneously. Equations are also given for the penetration of the protoplasm by various combinations of salt and acid, and for the change of velocity of penetration with  $p_{\text{H}}$ .

K. V. THIMANN.

**Distribution of arsenic in the body in a fatal case of poisoning by hydrogen arsenide.** F. J. T. GRIGG (Analyst, 1929, **54**, 659—660).—The liberation of hydrogen arsenide resulted from the treatment of zinc slimes with sulphuric acid during the recovery of gold by the cyanide process, and the plant had been in operation some time before the operator was taken ill and died in 9 days. The organs contained the following amounts of arsenic (mg. per kg.): brain, 1.4, 1.0; lungs, 2.59, 2.3; stomach and contents, 0.1, 0.3; spleen, 0.48, 2.2; kidney, 0.36, 1.3, and liver, 6.9, 4.4.

D. G. HEWER.

**Influence of intravenous injection of calcium chloride on the fat, sugar, calcium, and potassium of the blood.** P. CAPRA (Arch. Farm. speriment., 1929, **47**, 161—176, 273—275).—Study of 17 cases shows that administration of 0.1 g. of calcium chloride after the nocturnal fast results in: increase of the total cholesterol in the blood in 9 cases, diminution in 5, and no change in 3; a distinct parallelism between the total and the free cholesterol, increase of the latter largely determining the total increase; the phosphatides and the cholesteryl esters show irregular variation, with a certain degree of parallelism between the two; no change in the sugar, no change or increase in the calcium, and diminution or a constant low value of potassium.

T. H. POPE.

**Behaviour of colloidal lead in experimental animals.** G. PARONI (Arch. Ist. Biochim. Ital., 1929, **1**, 226—254).—The results of experiments on the tolerance of animals towards Ganassini's colloidal lead (A., 1929, 1336) confirm those obtained by other authors. In relation to its lead content (0.5%), this colloidal solution is less toxic than others and only in doses exceeding 0.05 g. per kg. body-weight causes serious symptoms, especially degenerative lesions of the hæmopoietic organs, and the hepatic and renal tissues. The solution shows marked penetrability and diffuses as a colloidal liquid, but the lead appears later in various tissues as granular lead and as a dissolved amorphous, saline compound.

T. H. POPE.

**Hypoglycæmic action of colloidal sulphur.** G. PENNETTI (Arch. Int. Pharm., 1928, **34**, 214—223; Chem. Zentr., 1929, ii, 59).—In normal, hyperglycæmic, or depancreatized animals colloidal sulphur, administered subcutaneously in doses not exceeding the optimal, produces hypoglycæmia; in larger doses it causes hyperglycæmia and disturbance of the respiratory function.

A. A. ELDRIDGE.

**Rate of elimination of glyceryl trinitrate from the blood after intravenous administration in dogs.** L. A. CRANDALL, C. D. LEAKE, A. S. LOEVENHART, and C. W. MUEHLBERGER (J. Pharm. Exp. Ther., 1929, **37**, 283—296).—Glyceryl trinitrate is very rapidly eliminated from the blood stream of dogs after intravenous injection, an average of 13.9% being detectable after 1 min., and disappearance being complete in 20 min. after administration. The rate of elimination is unaffected by anaesthesia.

K. V. THIMANN.

**Effect of repeated administration of diethylbarbituric acid and cyclohexenylethylbarbituric acid.** N. B. EDDY (J. Pharm. Exp. Ther., 1929, **37**, 261—271).—Repeated administration of 15—25% of the average fatal dose of diethylbarbituric acid did not lead to the development of tolerance in cats. A slight cumulative effect disappeared on continuation of the dosage, and is attributed to a lag in the excretion of the drug (cf. following abstract). *cyclohexenylethylbarbituric acid* gave similar results but no cumulative effect.

K. V. THIMANN.

**Excretion of diethylbarbituric acid during its continued administration.** N. B. EDDY (J. Pharm. Exp. Ther., 1929, **37**, 273—282).—The amount of "barbital" excreted is less than that administered.

but slowly increases to a maximum of about 80% after 2 weeks of daily administration. K. V. THIMANN.

**Chemical constitution and physiological action. Behaviour of the stereoisomeric  $\alpha$ -bromoiso-valeryl-*l*-asparagines.** S. BERLINGOZZI and M. FURLA (Annali Chim. Appl., 1929, 19, 406—415).—As regards the water-oil distribution coefficient which, according to Overton's and Meyer's theories, is of fundamental importance in the mechanism of hypnotic action, the two non-enantiomorphous, stereoisomeric  $\alpha$ -bromoisovaleryl-*l*-asparagines (cf. A., 1926, 819) differ markedly, the values of this coefficient being 0.133 and 0.073, respectively, for the *d*- and *l*-forms. The former is more highly hypnotic towards fish than the latter to approximately the extent indicated by the distribution coefficients.

T. H. POPE.

**Pharmacology of some *p*-hydroxybenzoic acid esters: their fate in the organism and toxicity.** K. SCHÜBEL and J. MANGER (Arch. exp. Path. Pharm., 1929, 146, 208—222).—In cats, dogs, and rabbits, methyl, ethyl, or propyl *p*-hydroxybenzoate administered by mouth is hydrolysed in the intestine. The free acid is partly destroyed in the organism and partly excreted in the urine, partly in the form of its salts and partly coupled with glycine or sulphuric acid. Of the three esters the methyl ester is the most toxic, whilst the propyl ester is the strongest antiseptic.

W. O. KERMACK.

**Toxicology of *p*-chlorobenzoic acid and its sodium salt ("microbin").** K. SCHÜBEL and J. MANGER (Arch. exp. Path. Pharm., 1929, 146, 223—231).—Sodium *p*-chlorobenzoate (microbin) administered by mouth even in small doses to dogs or cats causes vomiting. The acid or its sodium salt when given to rabbits in large doses (1—2 g. per kg.) has a toxic action, particularly on the liver and kidneys, producing glycosuria and albuminuria. About 10—70% of the *p*-chlorobenzoic acid administered is recovered in the urine.

W. O. KERMACK.

**Behaviour of potassium and calcium in dog's blood in histamine shock.** G. KUSCHINSKY (Z. ges. exp. Med., 1929, 64, 563—568; Chem. Zentr., 1929, ii, 318).—The serum- and plasma-potassium contents were markedly, and the calcium contents only slightly, increased. In whole blood the potassium increase was smaller, whilst the calcium was sometimes diminished.

A. A. ELDRIDGE.

**Physiological action of some homologues of betaine and choline esters.** R. R. RENSHAW and R. HUNT (J. Pharm. Exp. Ther., 1929, 37, 309—337).—A large number of these compounds were tested and the fatal dose for mice and the effect on the nervous system of pithed or anaesthetised cats were determined. Lowering of blood-pressure, preventable by atropine, was shown by acetylcholine and its dimethylbenzyl homologue, by tetra- $\beta$ -hydroxyethylammonium chloride and the esters of dimethylbenzylcarboxymethylammonium bromide. Esters of the tributyl and triisoamyl homologues of betaine gave a rise of blood-pressure unaffected by atropine, whilst esters of the triethyl and tripropyl homologues abolished the rise of blood-pressure produced by small doses of

nicotine. The methyl and ethyl esters are, with one exception, more toxic than the free betaines.

K. V. THIMANN.

**Action of ephedrine on the blood-sugar.** E. LEYKO and G. MÉHES (J. Physiol., 1929, 68, 247—258).—Ephedrine hydrochloride increases the blood-sugar, and its antagonistic effect to insulin can be shown in the dog. It has no effect on the denervated pupil of the cat.

E. BOYLAND.

**Effect of parasympathetic poisons on blood-sugar.** H. WULF (Biochem. Z., 1929, 214, 382—388; cf. Lang and Vas, A., 1928, 326).—Administration of pilocarpine to rabbits produces hyperglycaemia even after section of the spinal cord at the level of the atlanto-occipital articulation, but hyperglycaemia due to pilocarpine is inhibited by ergotamine. The blood-sugar level in normal fasting rabbits is not appreciably affected by administration of atropine.

W. MCCARTNEY.

***l*-Cocaine and *d*- $\psi$ -cocaine; toxicity towards and destructibility by the animal organism.** F. MERCIER and J. RÉGNIER (Compt. rend., 1929, 189, 872—874).—*d*- $\psi$ -Cocaine hydrochloride is destroyed by the dog more quickly and is therefore less toxic than *l*-cocaine hydrochloride.

A. A. GOLDBERG.

**Action of polarised light on cocaine.** D. I. MACHT and H. LEACH (Arch. exp. Path. Pharm., 1929, 146, 177—207).—Solutions of cocaine were subjected to the action of polarised light and were then examined by a large number of methods in respect of their pharmacological and physical properties. Evidence is obtained of the decomposition of a larger portion of the cocaine in the solution irradiated with polarised light than in either of the control solutions (irradiated with non-polarised light of the same intensity, and non-irradiated). Differences are claimed to have been found in the action of polarised light on the *d*- and *l*-isomerides. The action of the light on cocaine is considered to effect hydrolysis and to cause partial racemisation.

W. O. KERMACK.

**Action of light on melanin and pyrocatechol substance in the skin-skeleton of beetles.** H. SCHMALFUSS and H. BARTHEMEYER (Biochem. Z., 1929, 215, 79—84).—Light destroys melanin and melanogen, and particularly pyrocatechol substances in the wing-covers of beetles.

J. H. BIRKINSHAW.

**Melanins from adrenaline.** P. SACCARDI (Atti R. Accad. Lincei, 1929, [vi], 9, 1114—1117).—Subcutaneous administration to a rabbit of a slightly alkaline solution of the melanin-like substance obtained by oxidising adrenaline by means of chlorine water (A., 1923, i, 126, 135) causes melanuria, characteristic melanoderma and trichoderma, and browning of the subcutaneous connective tissue. The analogy between pyrrole derivatives, natural melanins, and adrenaline-black is thus evident, and it appears that, under definite physiological and pathological conditions, adrenaline may give rise to melanins.

T. H. POPE.

**Behaviour of amylase towards starch.** G. RADAELI (Pathologica, 1929, 20, 268—279; Chem. Zentr., 1929, ii, 53—54).—In presence of electrolytes

salivary amylase is adsorbed by rice, maize, or potato starch. Adsorption is more complete in acid than in alkaline medium. In presence of sodium chloride amylase is almost quantitatively adsorbed by rice starch.

A. A. ELDRIDGE.

**Effect of potassium, calcium, and thyroxine on acetaldehyde formation in minced muscle.** A. SIMON and A. BLAZSÓ (Biochem. Z., 1929, 215, 91—101).—Calcium ions cause an increase in acetaldehyde formation by minced rabbit muscle after 6 hrs. and a decrease after 18 hrs.; potassium ions cause a decrease in both cases. Thyroxine in small amounts increases and in larger amounts usually decreases aldehyde formation.

J. H. BIRKINSHAW.

**$p_H$  measurements with the quinhydrone electrode in succinodehydrogenase solutions at 37°.** J. LEHMANN (Skand. Arch. Physiol., 1929, 55, 286—306; Chem. Zentr., 1929, i, 3126).—Constant potentials were obtained up to  $p_H$  7.10, the corresponding  $p_H$  values agreeing to 0.01 with those obtained by means of the hydrogen electrode. Up to  $p_H$  7.70 values of similar accuracy can be obtained by taking readings 1—1.5 min. after the addition of quinhydrone to the enzyme solution at 37°.

A. A. ELDRIDGE.

**Methylene-blue method for the study of biological dehydrogenation. I.  $p_H$  measurements with the quinhydrone electrode at 37° in succinodehydrogenase solutions in presence of methylene-blue.** J. LEHMANN (Skand. Arch. Physiol., 1929, 55, 307—315; Chem. Zentr., 1929, i, 3126).—By means of the quinhydrone electrode  $p_H$  measurements can be made in the systems methylene-blue-leuco-methylene-blue and succinic-fumaric acids at 37° with an accuracy of 0.01—0.03 up to  $p_H$  8.

A. A. ELDRIDGE.

**Methylene-blue reduction. I—III.** G. SCHWARZ (Milchwirt. Forsch., 1929, 7, 540—557, 558—571, 572—582; Chem. Zentr., 1929, ii, 362).—The reduction of methylene-blue depends on the presence of ferrous hydroxide; ferrous ions are not sufficient. Lactose fission products of aldehydic nature are largely concerned. The reduction is favoured by decomposition products of milk proteins. The  $p_H$  of milk is favourable to the reduction of methylene-blue. The separation of the Schardinger enzyme is described.

A. A. ELDRIDGE.

**Specificity of animal phosphatases.** C. HOMMERBERG (Z. physiol. Chem., 1929, 185, 123—145).—Kidney phosphatase (Erdtman, A., 1928, 671, 1157) and bone phosphatase (cf. Martland and Robison, A., 1927, 699; 1929, 603) have the same action on glycerophosphate, hexosemonophosphate, and hexosediphosphate. The decomposition of the diphosphate is catalysed in both stages equally well by kidney phosphatase as by bone phosphatase. Sodium borate retards the initial action of both preparations on glycerophosphate; glycerol has a slight inhibitory action (cf. Martland and Robison, *loc. cit.*). The velocity coefficients of the fission reactions increase with increasing amount of enzyme.

Whereas magnesium ions activate kidney phosphatase (Erdtman, *loc. cit.*), they retard or have no action on bone phosphatase preparations. The

different solubilities of the enzyme extracts in alcohol, the different  $p_H$  optima (Akasawa, J. Biochem. Japan, 1928, 10, 157), and the variation in the activation by magnesium are probably due to admixed substances in the enzyme preparations. There are no specific glyce-ro-, hexosemono-, or hexosediphosphatases.

H. BURTON.

**Enzymic decomposition of nicotine.** Y. KUNO (Bul. Sci. Fak. Terkult. Kjusu, 1929, 3, 291).—The author has been unable to confirm the results of Fodor and Reifenberg (A., 1925, i, 1519), who claimed that an enzyme capable of decomposing nicotine exists in tobacco juice and extract.

W. O. KERMACK.

**Rennin-like activity of *Galium* spp.** D. AYE (Pharm. Ztg., 1929, 74, 1125—1126).—Aqueous extracts of three species of bedstraw were evaporated to dryness at a low temperature and the dry extract was mixed with lactose so that the quantities taken for test bore a definite relation to the original weight of the plants extracted. It was thus found that *Galium mollugo* and *G. verum* have pronounced and almost equal curdling potency (6 g. of *G. mollugo* are equivalent to 8—10 g. of *G. verum*, or to 0.0001 g. of rennet powder), whereas *G. palustre* is almost inactive.

W. A. SILVESTER.

**Concentration of pepsin and chemistry of its action.** B. LUSIG (Biochem. Z., 1929, 215, 205—214).—From Merck's "pepsin absolutum" a preparation having about four times the activity was prepared by dialysis for 48 hrs. from  $p_H$  1.8 to 5—5.2 and subsequent precipitation with 50% acetone. Adsorption methods led in some cases to increased activity, but there were larger losses on elution. A solution of this concentrated pepsin after 3—4 min. at 65° was inactive. Determinations of refractive index, optical activity, nitrogen, amino-, carboxyl, methoxyl, and methylimino-groups, and tryptophan were performed on several preparations of pepsin of varying activity. Inactivation by heat produces no change in refractive index, indicating no increase in amino- and carboxyl groups. There was a small but constant increase in hydrogen and decrease in carbon with inactivation. This suggests a hydrolysis of a CO-NH linking. The decrease in polypeptide carboxyl and the increase in total amino- and carboxyl groups indicate a deaggregation of the pepsin molecule.

J. H. BIRKINSHAW.

**Enzymic liberation of halogens from iodine-bromine-protein compounds.** E. MISLOWITZER (Med. Klin., 1929, 25, 472—473; Chem. Zentr., 1929, ii, 63—64).—The proportion of bromine eliminated by water, pepsin, and trypsin from commercial preparations was determined.

A. A. ELDRIDGE.

**Determination of trypsin and enterokinase.** K. LINDERSTRÖM-LANG and E. M. STEENBERG (Compt. rend. Lab. Carlsberg, 1929, 17, No. 16, 1—31).—A modification of the method of Willstätter, Waldschmidt-Leitz, Dunaiturria, and Künstner (cf. A., 1927, 174) for the determination of trypsin and enterokinase is given depending on the measurement of the increase of carboxyl groups at  $p_H$  9.1 and at 30° in the mixture of enzyme, activator, and substrate. For the substrate caseinogen has been found to be the

most suitable protein. To effect maximum activation of trypsin about thirty times as much enterokinase is required when the substrate is caseinogen as when it is gelatin. Details are given for the preparation of a highly purified erepsin-free kinase solution depending on adsorption with alumina followed by dialysis and precipitation of the inactive protein with tannic acid.

W. O. KERMACK.

**Determination and separation of the proteolytic enzymes in green malt.** K. LINDERSTRÖM-LANG and M. SATO (Compt. rend. Lab. Carlsberg, 1929, 17, No. 17, 1—40).—The peptidase of green malt (determined by measuring its action on *DL*-leucylglycine at  $p_H$  8.0) becomes inactivated when the aqueous solution is kept, so that solutions can readily be obtained containing only the proteinase (determined by measuring its action on edestin at  $p_H$  4.1), which is stable under the above conditions. To obtain solutions of the peptidase free from proteinase, the latter may be adsorbed by ferric hydroxide at  $p_H$  8.0 from a solution containing 44% of glycerol, which prevents destruction of the peptidase. In this way practically all the proteinase is removed and up to 50% of the peptidase is left in solution. The adsorbed peptidase is readily eluted by means of phosphate or ammonia solutions, whilst the proteinase is removed with greater difficulty by phosphate and apparently not at all by ammonia. Maximum adsorption takes place in the case of proteinase at  $p_H$  4.7 and 8.0 and in the case of peptidase at  $p_H$  4.7, so that the best separation is effected at  $p_H$  8.0. The proteinase is also adsorbed by alumina or kaolin, but the separation is not sharp, and much of the peptidase activity is lost when the elimination of the proteinase is accomplished by means of these adsorbents. The effect of the hydrogen-ion concentration on the adsorption of the enzymes by alumina and kaolin has also been investigated, and additional work is described on the variations of the activity of the enzymes at different hydrogen-ion concentrations (cf. Mill and Linderström-Lang, A., 1929, 957). The action of the extracts on *DL*-leucylglycylglycine is parallel under all conditions to its action on *DL*-leucylglycine, so that it appears probable that the same peptidase effects the hydrolysis of both the tripeptide and the dipeptide.

W. O. KERMACK.

**Action of fluorine and of iodine on urease.** M. JACOBY (Biochem. Z., 1929, 214, 368—373; cf. A., 1928, 1158).—Fluoride acts on urease in media buffered with various salts and the action is most pronounced when the media are acid. In unbuffered media the ammonia which is formed by decomposition of urea alters the reaction and weakens the effect of the fluoride. Sodium iodide has a powerful inhibiting effect, which increases first rapidly, then slowly, with the amount used, on the activity of urease. The action of the iodide is most pronounced when the medium is faintly alkaline. Even when the amount of iodide used is very large the activity of the enzyme is never completely destroyed. Sodium thiocyanate does not inhibit the action of urease.

W. McCARTNEY.

**Cell-free fermentation.** A. LEBEDEV (Biochem. Z., 1929, 214, 488—496; cf. A., 1928, 673).—The

results of Kostytschev and Schulgina (A., 1929, 724) cannot be confirmed and their views are rejected.

W. McCARTNEY.

**Glutathione. I. Preparation in crystalline form; identification.** E. C. KENDALL, B. F. MCKENZIE, and H. L. MASON (J. Biol. Chem., 1929, 84, 657—674; cf. Hopkins, A., 1929, 1491).—Baker's yeast (45 kg.) is extracted with water (200 litres) and benzene (9600 c.c.), the suspension is further treated with 60 litres of water, and, after 2 hrs., with sulphuric acid and barium hydroxide in equivalent amounts; it is then cleared on the centrifuge and precipitated with lead acetate, the precipitate is decomposed with sulphuric acid, and the filtrate is adjusted to  $p_H$  4.0 by addition of barium hydroxide and again filtered. Barium is removed by treatment with excess of sulphuric acid and the filtrate is precipitated with phosphotungstic acid at 0°, the precipitate is removed, and the solution adjusted to  $p_H$  7.0 with barium hydroxide; after filtration from the barium phosphotungstate the solution is freed from barium with excess of sulphuric acid and treated with mercuric sulphate. The solution obtained on recovery from the mercury precipitate in the usual manner is concentrated to a small volume; on keeping the solution crystallisation sets in. The yield is about 23 g. of crystalline glutathione,  $C_{10}H_{17}O_6N_3S$ , m. p. 190—192°. When hydrolysed with hydrochloric acid the substance yielded glutamic acid hydrochloride. After benzylation of the hydrolysis products hippuric acid was obtained; the mother-liquor from the latter yielded cystine. Glutathione thus appeared to be a tripeptide containing glutamic acid, glycine, and cystine. Glutathione was treated with nitrous acid and the product was hydrolysed; no glutamic acid was obtained, but benzylation of the solution caused the formation of hippuric acid. When glutathione was oxidised with hydrogen peroxide, no ether-soluble organic acids were formed; hydrolysis of the oxidation product afforded succinic acid, but no glycine or glutamic acid. Glutathione is therefore probably glutamic acid in which the carboxyl group adjacent to the amino-group is linked to glycine and the second carboxyl group to cystine. Glutathione is not readily hydrolysed by boiling with 0.1N-hydrochloric acid.

C. R. HARRINGTON.

**Dissimilarity of inner and outer protoplasmic surfaces in *Valonia*.** II. E. B. DAMON (J. Gen. Physiol., 1929, 13, 207—221).—The *P.D.* between the inner and outer surfaces of the protoplasm of *Valonia macrophysa* has been measured, improvements on the author's earlier technique (*ibid.*, 1927, 11, 193) being embodied. The entire surface of the cell was wetted with artificial sap. The *P.D.* varies continuously between 25 and 35 millivolts, the changes being ascribed to penetration of potassium chloride into the protoplasm.

K. V. THIMANN.

**Protoplasmic potentials in *Halicystis*.** L. R. BLINKS (J. Gen. Physiol., 1929, 13, 223—229).—The *P.D.* across the protoplasm of *Halicystis* has been measured (cf. preceding abstract). It is reduced or abolished by contact with certain salt solutions.

K. V. THIMANN.

**Pigment of *Blepharisma*.** R. EMERSON (J. Gen. Physiol., 1929, 13, 159—161).—The alcoholic extract of the red pigment of *Blepharisma* changes colour with  $p_H$ . Its absorption spectrum shows three bands between 450 and 600  $\mu$ . K. V. THIMANN.

**Metabolism of two protozoans.** R. EMERSON (J. Gen. Physiol., 1929, 13, 153—158).—Measurements of the respiration of *Amoeba proteus* and *Blepharisma undulans* have been made. The respiratory quotient in each case was about 1. *Blepharisma* shows distinct anaërobic metabolism. K. V. THIMANN.

**Oxygen consumption of *Colpidium colpoda*.** R. A. PETERS (J. Physiol., 1929, 68, Proc. Physiol. Soc., ii—iii).—Young cultures of *C. colpoda* use 0.2 c.c. of oxygen per week per million organisms, equivalent to 10 litres per kg. per hr. 0.005*M*-Potassium cyanide stops the oxygen consumption and causes cytolysis. E. BOYLAND.

**Evolution of asparaginase in cultures of *Aspergillus niger*.** D. BACH (Bull. Soc. Chim. biol., 1929, 11, 994—1006).—Only in old cultures and then in negligible quantity has asparaginase been observed in the fluid media; it is an endo-enzyme. Mycelia grown on media the nitrogen source of which is ammonium salts, asparagine, peptone, or urea show a comparable enzymic activity which gradually falls to a minimum after 6 days' growth, rising again to a maximum which may be greater than that of the young mycelia and thereafter gradually diminishing. The second maximum is attributed to a true proteolysis. Asparaginase is one of the deamidases employed by the fungus to liberate ammonia from the degradation products of the protein molecule. C. C. N. VASS.

**Evolution of urease in cultures of *Aspergillus niger*.** D. BACH (Bull. Soc. Chim. biol., 1929, 11, 1007—1015).—Urease does not pass into the fluid medium; it is present in the mycelia grown on media containing ammonium salts, asparagine, urea, or peptone, and reaches its highest concentrations when the medium contains urea or peptone. In the last-named medium, the urease activity remains high during the initial stages of growth and then rapidly decreases and is almost absent when proteolysis commences. In media containing asparagine or ammonium salts the lower urease activity is augmented during the first six days of growth and then rapidly decreases. It thus appears that urease and asparaginase are produced in the mycelia of *A. niger* in almost an inverse ratio (cf. preceding abstract). C. C. N. VASS.

**Are the urease and asparaginase of *Aspergillus niger* endo-enzymes?** D. BACH (Bull. Soc. Chim. biol., 1929, 11, 1016—1024).—The filtrate obtained through paper from dry powdered mycelia of *A. niger* in buffer solutions possesses about one fifth of the urease or asparaginase activity of the mycelia. Prolonged extraction, especially in regard to asparaginase, causes destruction of the enzymic activities. The filtrates from extracts of the mycelia, ground with sand, if filtered through paper are opalescent liquids possessing three times the activity of the extracts described above; but if the extracts are filtered through a Chamberland filter they are inactive.

Asparaginase and urease are therefore regarded as endo-cellular enzymes of the fungus. C. C. N. VASS.

**Decomposition of gluconic acid by fungi.** C. WEHMER (Ber., 1929, 62, [B], 2672—2674; cf. A., 1928, 1164).—Calcium gluconate is converted by *A. mutatus* into calcium carbonate; oxalic, citric, or tartaric acid is not immediately formed and the production of fumaric or malic acid is doubtful. Sodium gluconate is, however, transformed into sodium oxalate. The calcium salts of other organic acids (lactic, malic) which are soluble in water give calcium carbonate, whereas the sodium, potassium, or ammonium hydrogen salts afford oxalate, the normal salts being attacked with greater difficulty. H. WREN.

**Production of gluconic and ketogluconic acids by *Bacterium gluconicum*, *B. xylinum*, and *B. xylinoides*.** S. HERMANN (Biochem. Z., 1929, 214, 357—367; cf. A., 1928, 330).—*B. gluconicum* converts dextrose, gluconic acid, sodium and calcium gluconates, and lævulose into 5-ketogluconic acid. Yields of up to 70% of the keto-acid are obtained. *B. xylinum* and *B. xylinoides* convert dextrose and salts of gluconic acid, but not the acid itself, into the keto-acid. Lævulose is not converted into the keto-acid by *B. xylinum*. *B. xylinum* and *B. xylinoides* act much more slowly on dextrose than does *B. gluconicum*, but in the presence of calcium carbonate the difference in the rates of action is not very great. W. MCCARTNEY.

**Acids produced in fermentation of maize by *Clostridium acetobutylicum*.** H. R. STILES, W. K. PETERSON, and E. B. FRED (J. Biol. Chem., 1929, 84, 437—453).—Fermentation of maize with *C. acetobutylicum* yielded, under ordinary conditions, 27% of a mixture of ethyl and butyl alcohols and acetone, and 2.3% of total acids; in presence of excess of calcium carbonate the yield of solvents was 16.4% and of acid 16.3%. In the latter case the volatile acids constituted 15% and consisted of 0.07% of formic, 6.31% of acetic, and 8.62% of butyric acids. The non-volatile fraction contained a mixture of hydroxy-acids. Curves are given showing the changes in the individual volatile acids during the course of the fermentation. Extra formic acid added to the fermentation mixture was destroyed; this supports the hypothesis that formic acid is the precursor of the hydrogen and carbon dioxide which are produced during the fermentation. C. R. HARRINGTON.

**Fermentation of dihydroxyacetone.** A. I. VIRTANEN, H. KARSTRÖM, and O. TURPEINEN (Naturwiss., 1929, 17, 877).—The fermentation of dihydroxyacetone by *B. coli* has been studied. Phosphate addition (optimal effect 1%  $P_2O_5$ ) accelerates the fermentation of dextrose and dihydroxyacetone to the same extent, i.e., at  $p_H$  6.2 the rate is 70—80% greater than in water. Dextrose yields 40% of lactic acid, 20% of succinic acid, 10% of acetic acid, and 10% of alcohol, whilst dihydroxyacetone gives glycerol, acetic, and formic acids, the proportions under the best conditions being 42.6, 30, and 17%, respectively. The fermentation of dihydroxyacetone is regarded primarily as a Cannizzaro reaction, giving glycerol



and glyceric acid. The fact that phosphate addition plays the same part with dextrose as with dihydroxy-acetone indicates a similar mechanism for fermentation in both cases.

R. A. MORTON.

**Fermentation of dextrose, lævulose, and arabinose by organisms from spoiled tomato products.** C. S. PEDERSON (New York State Agric. Exp. Sta. Tech. Bull. No. 151, 1929, 22 pp.).—Yeast extract containing 3% of dextrose, lævulose, or arabinose was inoculated with the organisms obtained from spoiled tomato products (cf. B., 1930, 35), and, after incubation for 1 month at 25°, the fermentation products were examined. The organisms *Lactobacillus lycopersici*, *L. gayoni*, *L. pentoaceticus*, *L. mannitolæum*, and *Leuconostoc pleofructi* produce lactic and acetic acids, ethyl alcohol, and carbon dioxide from dextrose and mannitol, lactic and acetic acids and carbon dioxide from lævulose. *Lactobacillus plantarum* produces lactic acid almost exclusively from both sugars. Identification of the lactic acid by preparing the zinc salt showed that the acid from the *Leuconostoc* culture is the levorotatory form, whereas all the other organisms produce the inactive acid. Lactic and acetic acids are the main products from arabinose, carbon dioxide being formed in small amounts.

H. J. DOWDEN.

**Starch-like radiate crystals produced by *Bacterium marginatum* in starch media.** L. McCULLOCH (J. Agric. Res., 1929, 39, 495—501).—Spherocrystals up to 140  $\mu$  in diameter, formed by *B. marginatum* in culture media containing starch and a sugar or an alcohol, have not yet been identified chemically.

E. HOLMES.

**Action of bacteria on fat. I. Relative merits of various differential plating media for lipase-producing organisms. II. Microscopic study of emulsion of oil in an agar medium.** R. H. TURNER (J. Infect. Dis., 1929, 44, 126—133, 134—141).

CHEMICAL ABSTRACTS.

**Production of histamine, tyramine, bronchospastic and arteriospastic substances in blood broth by pure cultures of micro-organisms.** K. K. KOESSLER, M. T. HANKE, and M. S. SHEPPARD (J. Infect. Dis., 1928, 43, 363—377).

CHEMICAL ABSTRACTS.

**Micro-organisms. V. Biochemistry of *Paraplectrum fætidum*.** W. GRIMMER and S. RAUSCHNING (Milchwirt. Forsch., 1929, 7, 534—539; Chem. Zentr., 1929, ii, 314).—The action of *P. fætidum* (not in symbiosis with *B. mesentericus*) on caseinogen produces tyrosine and leucine; nearly half of the soluble nitrogen was present as ammonia. The chief product is butyric acid; secondary degradation of tyrosine probably gave hydroxyphenylacetic acid.

A. A. ELDRIDGE.

***Bacillus pyocyaneus*.** N. P. SHERWOOD, T. L. JOHNSON, and I. RADOTINCKY (Univ. Kansas Sci. Bull., 1926, 16, 91—99).—Animal charcoal, added to dextrose broth, appears to adsorb the pigments. All strains produced indole and hydrogen cyanide, only one reduced nitrate, whilst eleven strains blackened lead acetate.

CHEMICAL ABSTRACTS.

**Preparation of relatively pure bacteriophage.** A. P. KRUEGER and H. T. TAMADA (J. Gen. Physiol., 1929, 13, 145—151).—The particles of bacteriophage, which are negatively charged, migrate under the influence of an electric current into a 0.5% gel of purified agar. The gel is then extracted with water or saline. The resulting protein-free solution produces complete lysis of susceptible bacteria at an average dilution of  $10^{-10}$ . The method is adaptable to large or small scale and also to determinations of the charge on biological particles.

K. V. THIMANN.

**Influence of bacteriophage on *Bacterium tumefaciens*; potential studies of filtrates.** N. A. BROWN and A. J. QUIRK (J. Agric. Res., 1929, 39, 503—530).—Normal plant juices were always more acid than the fresh juice of tumour tissue occasioned by *B. tumefaciens*, and the total acid was greater in the tumour juice. The oxidation potential was always greater (more negative) in the fresh tumour juice, but as oxidation proceeded the  $p_H$  relations were reversed. The presence of a bacteriophage or inhibiting principle to *B. tumefaciens* growing in beef-bouillon cultures was established. The development of *B. tumefaciens* and its bacteriophage in various media, as affected by  $p_H$  and other factors, is discussed.

E. HOLMES.

**Botulinus toxin. V. Influence of nitro-genous and lipoid compounds on the potency of botulinus toxin.** E. W. SOMMER and H. SOMMER (J. Infect. Dis., 1928, 43, 496—506).

CHEMICAL ABSTRACTS.

**Poison produced by *Bacterium enteritidis* and *B. aertrycke* which is active in mice when given by mouth.** S. E. BRANHAM, L. ROBEY, and L. A. DAY (J. Infect. Dis., 1928, 43, 507—515).

CHEMICAL ABSTRACTS.

**Extracellular production of toxin by *Clostridium botulinum*, type B. Glucose inhibition of extracellular toxin-producing enzymes of *C. botulinum*. Destruction of diphtheria toxin by bacteria.** C. N. STARK, J. M. SHERMAN, and P. STARK (J. Infect. Dis., 1928, 43, 565, 566—568, 569—570).

CHEMICAL ABSTRACTS.

**Hæmolytic substance in pneumococcus culture broth.** G. M. SICKLES and J. M. COFFEY (J. Infect. Dis., 1928, 43, 490—495).—The absorption behaviour of the thermolabile substance is described.

CHEMICAL ABSTRACTS.

**Proteus hæmolysin.** J. F. NORTON, E. VERDER, and C. RIDGWAY (J. Infect. Dis., 1928, 43, 458—460).—The substance, characteristic of the proteus group of bacteria, which is lytic for red blood-cells is heat-labile, formed during the early growth of a culture, and is destroyed by phenol disinfectants.

CHEMICAL ABSTRACTS.

**Action of saponin on antitoxin.** D. A. SCOTT and D. GLAISTER (J. Biol. Chem., 1929, 84, 475—485).—Acidification of a solution of diphtheria antitoxin in presence of saponin causes a precipitation of a saponin-protein complex which reaches a maximum at  $p_H$  4.0. The amount of precipitate is proportional to the concentration of saponin up to 0.75% of the latter, but the composition of the precipitate is constant, the saponin:protein ratio being 1.26. There

was an absolute loss of activity in the precipitate and no purification of the antitoxin was effected. The presence of 1% of sodium chloride prevented the precipitation, and the saponin could be recovered from the precipitate by treatment of the latter with dilute sodium hydroxide or 2% sodium chloride. In the case of insulin (cf. Harington and Scott, A., 1929, 851) the precipitate which forms at  $p_H$  4.0 consists of a saponin-protein complex, whilst that which appears at  $p_H$  5.6 is free from saponin. C. R. HARINGTON.

**Size of bacteria as the cause of the logarithmic order of death.** O. RAHN (J. Gen. Physiol., 1929, 13, 179—205).—Theoretical. If each cell contains one essential molecule, the inactivation of which, by heat or disinfection, causes death, then it is calculated that death takes place according to a logarithmic curve, as is found experimentally. If the cell contains many such essential molecules, the reaction changes to a type similar to that found for complex organisms, i.e., a latent period followed by a short period of rapid death. The death rate  $K$  in recorded experiments is generally either constant, agreeing with the calculations for only one essential molecule, or decreasing with time. The latter effect is explained as due to the superposition of a graded variation in resistance on the logarithmic curve. The reason for the logarithmic effect is the variation in size of the cells.

K. V. THIMANN.

**Chemical and bacterial inhibition of gas formation in bacterial cultures.** M. ISHIKAWA (J. Infect. Dis., 1928, 43, 311—320).—The suppression of formation of gas in bacterial cultures by bismuth nitrate, oxynitrate, carbonate, and gallate, ammonium benzoate and nitrate, sodium benzoate, nitrate, fluoride, iodate, and salicylate, potassium dichromate and chlorate was studied. CHEMICAL ABSTRACTS.

**Germicidal action of hydroxy-soaps.** A. H. EGGERTH (J. Exp. Med., 1929, 50, 299—313).— $\alpha$ -Hydroxy-soaps are germicidal to certain organisms; the germicidal action increases with mol. wt. up to the soap of  $\alpha$ -hydroxystearic acid; soaps with more carbon atoms are less effective. The introduction of a hydroxy-group into saturated soaps increases specificity, but hydroxylated unsaturated soaps are less selective. E. BOYLAND.

**Tetraiodophenolphthalein as an antiseptic and germicide of the biliary tract.** A. C. NICKEL (J. Pharm. Exp. Ther., 1929, 37, 359—366).—Tetraiodophenolphthalein has a germicidal effect, in dilutions up to 1:100,000, on streptococci and staphylococci obtained from gall-bladders. It has no effect on colon bacilli. K. V. THIMANN.

**A new quinoline derivative in the treatment of infection.** G. ARMITAGE and J. GORDON (Lancet, 1929, ii, 968—970).—2-*p*-Dimethylaminoanil-6-methyl-quinoline methochloride is a useful antiseptic of low toxicity. E. BOYLAND.

**Influence of iodide on bacterial decomposition of nitrogenous substances.** M. ISHIKAWA (J. Infect. Dis., 1928, 43, 321—326).—Potassium iodide and iodate inhibit the formation of ammonia by cultures of proteolytic organisms and the production of amino-acids by the proteolytic bacteria-free

enzyme. Potassium iodide decreases the liberation of ammonia from urea by urea-splitting bacteria.

CHEMICAL ABSTRACTS.

**Catalytic decomposition of some iodine compounds.** (Theory of iodine antiseptics.) E. CHARGAFF (Biochem. Z., 1929, 215, 69—78).—The presence of cysteine or thioglycolic acid catalyses the removal of iodine from the antiseptics iodoform, iodol, euophene, aristol, nosophene, vioform in aqueous suspension and diffused light at 37°. Free iodine is not detected. The decomposition of iodoform in carbon disulphide and in ether with and without thioglycolic acid was followed quantitatively.

J. H. BIRKINSHAW.

**Bactericidal action of ultra-violet light. I. Reaction to monochromatic radiations. II. Effect of various environmental factors and conditions.** F. L. GATES (J. Gen. Physiol., 1929, 13, 231—248, 249—260).—I. Cultures of *S. aureus* on agar were exposed to ultra-violet radiation of selected frequencies, covered after exposure with a second layer of agar, and counted after incubation. The energy of the radiation, as measured by thermopiles, was plotted against percentage deaths. Curves of a logarithmic type, but with three modifications, were obtained: (a) an initial period of no deaths, (b) first 20% of bacteria destroyed by less energy than the average for the rest, (c) last 10% of bacteria destroyed by more average energy than the rest. The theoretical significance of the curves is discussed (cf. Rahn, above).

II. The Bunsen-Roscoe reciprocity law does not hold with accuracy for bactericidal action of ultra-violet light. The longer wave-length limit for bactericidal action is about 310  $\mu$ . The temperature coefficient for 10° rise approaches 1, indicating that the reaction is physical or photochemical. Neither polarisation of the incident light nor variation in the  $p_H$  of the substrate between 4.5 and 7.5 has any effect on the reaction. K. V. THIMANN.

**Action of adrenaline. IV. Influence of adrenaline on lactic acid production and blood-sugar utilisation. Effect of adrenaline on arterial and venous blood-sugar in men.** C. F. CORI and G. T. CORI (J. Biol. Chem., 1929, 84, 683—698, 699—701).—Subcutaneous administration of 0.2 mg. of adrenaline per kg. to rabbits raises the blood-lactic acid from 11 mg. to a maximum of 74 mg. per 100 c.c. in 1 hr., the normal value being reached again in 5 hrs.; the hyperglycæmia persists for about the same length of time as the increase in lactic acid. Simultaneous administration of insulin suppresses the hyperglycæmia, but has little effect on the rise in the lactic acid. The latter increase must come from the muscles, since the normal arterio-venous difference of 0.3 mg. of lactic acid per 100 c.c. is increased to more than 10 mg. after adrenaline. The normal arterio-venous difference in blood-sugar is not affected in adrenaline hyperglycæmia, but is trebled in alimentary hyperglycæmia; this failure of utilisation of blood-sugar by the peripheral tissues affords the explanation of the production of hyperglycæmia, under the influence of adrenaline, from the limited amount of sugar available to the liver.

Adrenaline hyperglycæmia in man is not accompanied by any alteration in the arterio-venous difference in blood-sugar concentration.

C. R. HARRINGTON.

Comparison of the glycogenolytic responses to adrenaline administered by the subcutaneous and intravenous routes. G. S. EADIE (*Amer. J. Physiol.*, 1929, 90, 711—717).—The hyperglycæmic response to adrenaline varies with the dose on subcutaneous injection, but the response to intravenous injection is independent of the dose.

E. BOYLAND.

Hormone of the suprarenal cortex. F. DE MIRA and J. FONTES (*Compt. rend. Soc. Biol.*, 1929, 100, 602—604; *Chem. Zentr.*, 1929, ii, 181).—The finely divided cortex was boiled for 5 min. with 0.1N-hydrochloric acid; if the filtrate contained adrenaline, it was made alkaline with sodium hydrogen carbonate, treated with a current of air, and again acidified. Experiments on re-stimulation of muscle are described.

A. A. ELDRIDGE.

Substances in secretin extract influencing blood-sugar. I. H. HELLER (*Arch. exp. Path. Pharm.*, 1929, 145, 343—358).—Extracts have been made of the mucous membrane of the upper part of the small intestine of rabbits and oxen, which when injected subcutaneously into a rabbit lower the blood-sugar. This action is only slight when the blood-sugar is at its fasting level, but after it has been raised either by administration of dextrose or by injection of adrenaline it is much more marked. The presence of choline and histamine in these extracts does not account for their activity. If ergotamine or atropine is administered along with the extract its activity is lessened, but not completely annulled. The active substance could not be obtained from the lower part of the small intestine. It is not destroyed by boiling or when subjected to the action of pepsin or trypsin, and gives no protein reactions. On these and other grounds it is concluded that it is not identical with either insulin or secretin.

W. O. KERMACK.

Substitutes for insulin. V—VIII. E. KAUFMANN (*Z. ges. exp. Med.*, 1928, 62, 147—153, 154—159, 160—164, 739—744; *Chem. Zentr.*, 1929, i, 3112).—Hypoglycæmic agents were extracted from oat, rye, wheat, and rice bran, pea, bean, and lentil shells; tolerance in diabetes depends on the content of hypoglycæmic substance. Substances having the same property are obtainable from yeast and Cortex Syzgi Jambolani.

A. A. ELDRIDGE.

Influence of insulin on the fat content of serum. A. A. CHRISTOMANOS (*Biochem. Z.*, 1929, 214, 482—487).—The free acid content, the iodine value of ether-soluble unsaturated compounds, and the total content of ether-soluble fat of serum from the blood of healthy and diabetic persons before and after administration of insulin have been determined. Serum heated for 3—4 hrs. at 8—12 atm. has also been investigated in the same way. Both in healthy and in diabetic persons administration of insulin caused a decrease in the contents of free acid, of unsaturated compounds, and of ether-soluble fat of the unheated serum. The content of free acid and of fat in the serum was

increased by the heat treatment and the increase was greater after administration of insulin than before.

W. MCCARTNEY.

Effect of insulin on blood-amino-nitrogen of the rabbit. F. BISCHOFF and M. L. LONG (*J. Biol. Chem.*, 1929, 84, 629—638).—The blood-amino-nitrogen of rabbits falls during a fasting period of 48 hrs. Neither insulin nor adrenaline followed by insulin had any effect on the amino-nitrogen of the blood of rabbits.

C. R. HARRINGTON.

Influence of speed of resorption on the action of insulin. W. REDISCH and B. M. BLOCH (*Endokrinol.*, 1928, 1, 241—250; *Chem. Zentr.*, 1929, ii, 182).—Insulin hypoglycæmia is lengthened by simultaneous injection of a protein or gum acacia, owing to diminution of the speed of resorption of the insulin. Insulin dialyses slowly from admixtures with gum acacia, and not at all from admixtures with protein.

A. A. ELDRIDGE.

Effect of insulin and thyroxine on liver autolysis. A. SIMON (*Biochem. Z.*, 1929, 215, 102—105; cf. A., 1929, 725).—Thyroxine influences liver autolysis; the absence of any effect in previous experiments was due to the strong buffering (0.1N-phosphate). Insulin does not affect the autolysis.

J. H. BIRKINSHAW.

Behaviour of thyroxine in the animal organism. E. ABDERHALDEN and E. WERTHEIMER (*Pflüger's Archiv*, 1928, 221, 82—92; *Chem. Zentr.*, 1929, ii, 315).—The absorption of thyroxine from its solutions by various tissues was determined by subsequently feeding the material to tadpoles. Muscle-tissue was most active, and liver-tissue least active. Boiling somewhat increases the activity. The absorbed thyroxine can be regained by boiling only in quite small amount.

A. A. ELDRIDGE.

Action of the thyroid hormone. R. WEIL (*Klin. Woch.*, 1929, 8, 652; *Chem. Zentr.*, 1929, ii, 315—316).—Although thyroxine has no proteolytic properties, and has no effect on enzymic fission of protein, it increases the autolysis of guinea-pig's liver at neutral reaction.

A. A. ELDRIDGE.

Action of the parathyroid hormone. M. REISS (*Endokrinol.*, 1928, 2, 161—169; *Chem. Zentr.*, 1929, ii, 180).—The rise in blood-calcium is caused by mobilisation of tissue-calcium and not by retardation of its removal from the blood. "Parathyroidin" facilitates the resorption of calcium chloride from the gastro-intestinal tract.

A. A. ELDRIDGE.

Antidiuretic effect of the separated principles of the pituitary gland. A. HEMINGWAY and J. M. PETERSON (*J. Physiol.*, 1929, 68, 238—246).—Both "pitressin" and "pitocin" increase the concentration of urinary chlorides. Pitressin is a vaso-constrictor and is twenty times as active as pitocin in inhibiting diuresis in man.

E. BOYLAND.

Is there a heart hormone? G. J. KATZ and E. A. LEIBENSOHN (*Pflüger's Archiv*, 1928, 221, 213—214; *Chem. Zentr.*, 1929, ii, 180).—Positive experiments on the frog's heart with extracts of the heart and endocrine glands of a warm-blooded animal are recorded.

A. A. ELDRIDGE.



**Heart hormone.** L. HABERLANDT (Med. Klin., 1929, 25, 560; Chem. Zentr., 1929, ii, 180).

**So-called heart hormone.** E. T. OPPENHEIMER (Amer. J. Physiol., 1929, 90, 656—667).—Extracts of heart, liver, muscle, or lung contain a substance which augments the heart-beat. The substance resembles histamine and is stable at 100°.

E. BOYLAND.

**Physiological activity of adenine compounds.** A. N. DEURY and A. SZENT-GYÖRGYI (J. Physiol., 1929, 68, 213—237).—Adenylic acid extracted from heart-muscle, spleen, or brain, and adenosine from yeast reduced the rate of beating of the mammalian heart after intravenous injection. E. BOYLAND.

**"Progynon," a crystalline female sexual hormone.** A. BUTENANDT (Naturwiss., 1929, 17, 879).—The crude oil from urine of pregnancy, of activity  $3 \times 10^4$  units (Schering-Kalbaum), was purified by repeated treatment with aqueous alcohol and light petroleum, impurities being extracted by the latter solvent; the hormone remains in the aqueous alcohol, from which it can be extracted by means of ether, benzene, or ethyl acetate. The oil can thus be enriched stage by stage until the activity reaches  $5 \times 10^5$  units per g. Cautious hydrolysis with dilute acid followed by successive treatments with alkali of increasing concentration results in an alkali-soluble fraction of  $1.5-2 \times 10^5$  units per g. activity. Fractional distillation in a high vacuum yields an oil, b. p. 130—150°/0.02—0.03 mm., of activity  $5 \times 10^6$  units per g. Slow sublimation in a vacuum or treatment with solvents gives a crystalline material (*progynon*) of activity  $8 \times 10^6$  units, which crystallises from ethyl acetate or dilute alcohol in colourless plates, m. p. 240° (decomp.) (C 78.31, H 8.13%). The molecular formulae  $C_{31}H_{50}O_2$  or  $C_{29}H_{48}O_2$  are considered (cf. digitaligenin  $C_{29}H_{48}O_2$ , bufotalin  $C_{24}H_{30}O_2$ ). The hormone does not appear to be related either to proteins or to carbohydrates. Two oxygen atoms appear to be connected with a lactone group, the third oxygen atom being possibly in a hydroxyl group. The substance is neutral in aqueous alcohol, and is insoluble in cold aqueous alkali, but dissolves on heating and can be recovered unchanged by extraction of the acidified solution with ether. Progynon undergoes catalytic hydrogenation with loss of activity. It gives no colour tests with acetic anhydride, sulphuric acid, or ferric chloride.

R. A. MORTON.

**Attempted isolation of the female sexual hormone: precipitation with antimony pentachloride.** H. GOLDHAMMER (Biochem. Z., 1929, 215, 1—5).—By precipitation of the unsaponifiable, chloroform-soluble fraction of placental extracts and of the urine of pregnancy with antimony pentachloride, a compound of the sexual hormone is obtained from which the hormone can be isolated in highly active form by the action of sodium hydroxide. The blue colour given by antimony trichloride with placental extracts is not due to the hormone.

J. H. BIRKINSHAW.

**Relation between quantity and action of female sexual hormone.** A. LIPSCHÜTZ (Biochem. Z., 1929, 215, 222—255).—The reaction of the castrated

mouse to the female sexual hormone varies with the degree of purity of the preparation used, the more impure preparations produce the greater reaction per unit. The frequency curve in group experiments was steeper with the purified sample. Pure preparations may be 100 times as effective when distributed over 6 doses in 3 days as when administered as one dose. The difference between slightly and highly purified preparations is attributed to differences in velocity of resorption and excretion. It may, however, be due to a "denaturing" effect on purification. Normal oestrus occurs when a definite hormone concentration is maintained in the blood for a definite time. This is in accord with the "all-or-nothing" law. The reaction to the hormone is dependent on whether previous smears have been made; if no smears have been taken oestrus is delayed for about 24 hrs.

J. H. BIRKINSHAW.

**Testicular hormone.** T. F. GALLAGHER and F. C. KOCH (J. Biol. Chem., 1929, 84, 495—500).—Testicular tissue from bulls was extracted with alcohol, the latter was removed by distillation, and the residue was extracted with benzene; after complete evaporation of the solvent the material was dissolved so far as possible in cold acetone. The acetone-soluble portion was active in producing comb growth in capons in daily doses of 0.03 g. The material was dissolved in hexane, and the solution was shaken with 70% alcohol, the portion recovered by evaporation of the alcohol was dissolved in ether, and the ethereal solution was washed with sodium hydroxide solution and with water; the material which remained in solution in the ether was active in daily doses of 0.28—0.50 mg.

C. R. HARRINGTON.

**Vitamin-A content of green and white leaves of market head lettuce.** M. H. KRAMER, G. BOEHM, and R. E. WILLIAMS (J. Home Econ., 1929, 21, 679—680).—The dark green outer leaves of a Californian head lettuce contained at least thirty times as much vitamin-A as the white inner leaves.

CHEMICAL ABSTRACTS.

**Alleged vitamin-A reaction with antimony trichloride and its appearance in the oxidative change of cholesterol.** I. H. GOLDHAMMER and F. M. KUEN (Biochem. Z., 1929, 215, 6—11).—The blue colour with antimony trichloride (Carr and Price, A., 1926, 870) was obtained with liver-oil, placenta, serum, oxycholesterol, cholesterol melted under oxygen or irradiated, and ergosterol from yeast. The chromogen is produced from cholesterol only in presence of oxygen. The blue colour is concealed by the rose-red reaction of pure cholesterol and by the presence of fats; after removal of fats and sterols the blue colour is permanent except with liver-oil. The chromogen is stable in presence of oxygen at 140—150°.

J. H. BIRKINSHAW.

**Effect of vitamin deficiencies on carbohydrate metabolism.** I. Influence of uncomplicated vitamin-B deficiency on blood of albino rats. B. SURE and M. E. SMITH (J. Biol. Chem., 1929, 84, 727—740).—Vitamin-B deficiency in white rats causes increase in the total blood-sugar which is accounted for by increase in the non-fermentable



reducing substances. In the terminal stages of the deficiency hypoglycemia and acidosis supervene.

C. R. HARRINGTON.

**Differences in the C : N quotient in rat's urine in inanition and lack of vitamin-B.** J. ROCHE (Compt. rend. Soc. Biol., 1929, 99, 671—673; Chem. Zentr., 1929, ii, 186).—Inanition leads in the rat to a fall in the C : N ratio. At the commencement of avitaminosis-B normal C : N values are observed, but this is followed by a sustained rise.

A. A. ELDRIDGE.

**Disappearance of vitamin-B in the germination of cereals.** J. HLAVATY (Compt. rend. Soc. Biol., 1929, 100, 587—589; Chem. Zentr., 1929, ii, 313).—The vitamin-B disappears from germinating beans or vetches more rapidly in soil than in a germination vessel. The minimum content is reached in 27 days.

A. A. ELDRIDGE.

**Vitamin-C concentrates from lemon juice.** D. P. GRETHER and C. G. KING (J. Biol. Chem., 1929, 84, 771—776).—Lemon juice was treated with basic lead carbonate until evolution of carbon dioxide ceased; the filtrate was subjected to exhaustive fermentation with yeast, and, after removal of the latter, was treated with lead acetate, which precipitated inactive material. The active substance was precipitated by adjusting the  $p_H$  of the filtrate to 7.2—7.4; the precipitate was decomposed with hydrochloric acid, the solution was shaken out with butyl alcohol, and the aqueous layer made 90% with respect to alcohol in order to remove lead chloride. The final solution was evaporated and the residue dissolved in water to 20% of the volume of the original juice; the preparation so obtained retained almost the whole of the antiscorbutic activity of the lemon juice. Further purification was effected by addition of acetone to the concentrated aqueous solution, which removed ammonium chloride, and reduced the solids to 0.5—1 mg. per c.c. of original juice. The active substance was soluble in absolute acetone.

C. R. HARRINGTON.

**Green tea as source of vitamin-C.** H. E. MUNSSELL and H. B. KIRBY (J. Home Econ., 1929, 21, 514—518).—A sample of Japanese green tea contained little vitamin-C. CHEMICAL ABSTRACTS.

**Effect of acidity on the formation of vitamin-C.** A. LUETTMERDING (Compt. rend. Soc. Biol., 1929, 100, 589—591; Chem. Zentr., 1929, ii, 313—314).—When wheat, beans, or oats are grown in water acidified with citric acid the formation of vitamin-C is more rapid than when distilled water is used, and the increase is approximately proportional to the acidity.

A. A. ELDRIDGE.

**Effects of overdosage with vitamin-D.** R. F. LIGHT, G. MILLER, and C. N. FREY (J. Biol. Chem., 1929, 84, 487—494).—Administration of amounts of vitamin-D 10,000 times in excess of the curative dose has no pathological effect on white rats. Administration of 100,000 times the curative dose produces emaciation, respiratory distress, and ultimately death; the ash content of the bones, heart, and kidneys, and that of the body as a whole shows a

decrease, the negative balance being more marked in the case of phosphorus than in that of calcium.

C. R. HARRINGTON.

**Physiological evaluation of ergosterol preparations.** J. VAN NIEKERK and J. W. R. EVERSE (Biochem. Z., 1929, 215, 85—90).—A method for the standardisation of ergosterol preparations is based on X-ray control of the healing of rachitic joints of rats.

J. H. BIRKINSHAW.

**Ergosteryl esters and their behaviour on ultra-violet irradiation.** A. WINDAUS and O. RYGH (Nachr. Ges. Wiss. Göttingen, 1928, 202—216; Chem. Zentr., 1929, ii, 322).—A study of ergosteryl acetate, benzoate, palmitate, allophanate, phenylurethane, and naphthylurethane. The irradiated esters, whilst physiologically inactive or nearly so, afforded highly antirachitic products on hydrolysis. It is concluded that the effect on ergosterol and its esters of ultra-violet light is the same, but that the presence of a free secondary alcoholic hydroxyl group is essential for physiological activity. The slight activity of certain esters, e.g., the acetate, is attributed to fission by an esterase.

A. A. ELDRIDGE.

**Influence of wave-lengths on vitamin-[D] formation.** T. REITER (Naturwiss., 1929, 17, 876—877).—The formation of injurious substances in the irradiation of milk and other foods is ascribed to rays between 240 and 280  $\mu$ . It is possible to obtain complete activation without adopting special precautions such as the exclusion of atmospheric oxygen or the use of an atmosphere of nitrogen provided that a filter cutting off sharply at 280  $\mu$  is placed between the light source and the substance irradiated. The material undergoes no change in taste or odour. The absorption spectrum of irradiated ergosterol in oil solution has been studied in relation to the effect of filtered and unfiltered light. Using a filter transmitting no further than 280  $\mu$ , the formation of vitamin-D proceeds smoothly and a product of constant absorption spectrum is obtained. The irradiation can be extended over several hours with no appreciable change in absorption. The product exhibits high antirachitic potency (0.2%) and appears to be free from deleterious substances.

R. A. MORTON.

**Simple methods for measuring respiration rates [in plants].** W. N. JONES (Ann. Bot., 1929, 43, 841—846).—In one method a simple apparatus is described for measuring the volumes of carbon dioxide produced and oxygen absorbed during plant respiration. With this apparatus the mean value for the respiratory quotient of germinating pea seeds was found to be 1.03 (range 0.99—1.05). A second method, based on the change in  $p_H$  which may occur as a result of evolution of carbon dioxide during respiration, is described. Bromocresol-purple is used as indicator and the standard  $p_H$  used for comparison of colour is 6.2. The time taken for a solution mildly alkaline with lime water to change to the standard colour is a measure of the rate of evolution of carbon dioxide.

P. G. MARSHALL.

**Decomposition of hexoses in plants. V. Content and activity of oxidoreductase of plants. Connexion between anoxybiosis and oxybiosis.**

V. ZALESKI and E. SCHATALOVA-ZALESKAJA (Biochem. Z., 1929, 214, 343—356; cf. A., 1929, 105, 1498).—The seeds, buds and, to a smaller extent, subterranean reserve depôts of plants contain oxidoreductase the activity of which is influenced, in a degree which varies among the different organs of the plant, by damaging the structure of cell or tissue. During maturation the power of the seeds to cause alcoholic fermentation decreases as a result of alterations which take place in the medium. It is unnecessary to assume the formation of zymogens to account for the decrease. Alterations in the medium also account completely for the increase which occurs during the early stages of germination in the activity of the oxidoreductase, although atmospheric oxygen here plays an important part. The enzyme which causes fermentation is deposited in the seeds, particularly in those of leguminous plants. By producing or consuming activators of various kinds plants regulate the extent and rate of decomposition of sugars, and in some cases plants which have been damaged produce hydrogen acceptors which accelerate the decomposition. Very rarely alcohol formed by anoxybiosis is used by plants for resynthesis. The spores of mushroom and also *Aspergillus* which has been cultivated in peptone solution are rich in oxidoreductase and can produce alcohol under certain conditions.

W. MCCARTNEY.

**Permeability of plant-cell membranes to sugar.** R. S. IRAMDAR and K. V. VARADPANDE (Nature, 1929, 124, 875—876).—Measurements of respiratory intensity changes on injection of dextrose solutions into leaves of *Artocarpus integrifolia* indicate that the permeability of the cell membranes is affected by the concentration of the dextrose solution.

A. A. ELDRIDGE.

**Absorption of potash and phosphoric acid by cereals in early growth.** T. SCHRADER (Fortschr. Landw., 1929, 4, 230—233; Chem. Zentr., 1929, ii, 342).—Different varieties of rye, wheat, barley, and oats show, even in the earliest stages of growth, differences in content and absorption of nutrient materials. Potassium is absorbed more rapidly than phosphoric acid.

A. A. ELDRIDGE.

**Physiology of apples. XI. Relation between mineral constitution of apples and soil.** (Miss) J. W. BROWN (Ann. Bot., 1929, 43, 817—831).—Two varieties from ten orchards were examined in 1925 and 1926, and determinations of total ash, potash, phosphate, lime, magnesia, and iron are recorded. Seasonal variations are generally small, although the mineral content (as a percentage of fresh weight) tends to be higher in 1926. This is possibly due to the higher rainfall of the earlier months, which would promote bacterial action in the soil. More sandy soils with a lower moisture content produce apples with a lower percentage of total ash. For similar types of soil the phosphate content of apples varies with the "relative solubility" (ratio of phosphate soluble in 1.0% citric acid to total phosphate) of the soil phosphate, and is always higher with soils of a high moisture content. The "relative solubility" of soil phosphates is increased by a high silica content and by a low content of iron, aluminium, and organic

matter. Relations between the "relative solubility" of the potash of soils and its content in apples are even closer than those of phosphate. The magnesia content of the fresh apples tends to be influenced by the total magnesia content of the soil and it is also raised in the case of soils with a high moisture content. The lime content of apples appears to depend on that of the soil, whilst the iron content of the soil seems to have little influence on that of the apples. The distribution of mineral constituents in the soil influences the effect of any one constituent on its content in the apples (e.g., lime on phosphate and potash). Good keeping qualities of the apple are associated with high potash, phosphate, and sugar contents together with low nitrogen content.

P. G. MARSHALL.

**Copper content of Oklahoma wheat and those of other states.** J. E. WEBSTER and F. JANSMA (Science, 1929, 70, 174).—The copper contents of wheat from various parts of the United States varied from 4.2 to 8.7 mg. per kg. of fresh wheat or 239 to 497 mg. per kg. of ash. The values are normal for each state, although the amounts of copper found in the wheat from the northern districts are somewhat lower than the average. No relationship was detected between the copper and ash contents.

L. S. THEOBALD.

**Determination of sulphur and phosphorus in plants.** G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1929, 189, 886—890).—The usual procedure involving calcination gives low results owing to loss of these elements by volatilisation. The proposed method consists in treating the plant with fuming nitric acid, the subsequent procedure being the same as that used in the determination of sulphur in arable earth (B., 1927, 556, 709, 951). The sulphate is precipitated with barium hydroxide and the phosphate titrated with uranium acetate.

A. A. GOLDBERG.

**Determination of manganese in plant ash.** M. GARNIER (Bull. Sci. pharmacol., 1929, 36, 140—146; Chem. Zentr., 1929, ii, 75).—Manganese was detected by Bertrand's method in 45 plants. The fungus *Craterellus cornucopioides* contained an unusually large amount of manganese: 17.13 mg. per 100 g., or 127.64 mg. per 100 g. of ash. The manganese content of plants from calcareous or primary rocks were not sensibly different.

A. A. ELDRIDGE.

**Ash of flowers of *Opuntia vulgaris*, Mill.** H. WUNSCHENDORFF (Bull. Sci. pharmacol., 1929, 36, 133—136; Chem. Zentr., 1929, ii, 68).—The ash of the flowers and the ovaries, respectively, contains:  $\text{SiO}_2$  29.88, 11.12; Ca 14.30, 22.98; chloride 5.67, 11.80;  $\text{Fe}_2\text{O}_3$  1.68, 0.76; MnO 0.45, 0.80%; Ca:Mg 3.02, 6.48; total ash 8.84, 18.75%.

A. A. ELDRIDGE.

**Some sea-weeds containing iodine.** P. DAN-GEARD (Compt. rend., 1929, 189, 862—864).—The iodine content of various sea-weeds is discussed.

A. A. GOLDBERG.

**Metabolism of flours. I. Flour of cotyledons.** L. GENEVOIS (Bull. Soc. Chim. biol., 1929, 11, 980—985).—The flour of the cotyledon of the pea, in contrast to that of wheat, possesses intensities of respir-



ation and fermentation weaker than but similar to those of the whole kernel. C. C. N. VASS.

**Amylase from *Zea mais*.** V. N. PATWARDHAN (J. Indian Inst. Sci., 1929, 12, A, 185—190).—The optimum temperature for both saccharifying and liquefying actions of the amylase of malted *Zea mais* is 55–60°, but there is only a slow decrease in activity up to 70°. The saccharifying power is greatest at  $p_H$  5.0, whilst the maximum liquefying power is at a somewhat more acid reaction. The enzyme passes through parchment but not through collodion membranes. When the dialysis in collodion membranes is continued for 2–3 days the activity is almost completely lost and is not restored by addition of the dialysate to the dialysed material within the sac. This loss of activity is apparently not due to the action of proteolytic enzymes associated with the amylase and is so far unexplained. Maltose is formed as the result of the action of the enzyme on starch.

W. O. KERMACK.

**Enzymes from the seeds of *Caesalpinia bonducella*.** V. N. PATWARDHAN (J. Indian Inst. Sci., 1929, 12, A, 191—192).—The decorticated resting seeds of *Caesalpinia bonducella* (Gajga) contain protease, urease, amylase, peroxidase, catalase, and oxidases (in very small quantity), but no invertase, lipase or other esterase. After germination the lipase is still absent although the original seeds and the cotyledons contain considerable quantities of oil. The enzymes present in the seeds increase in activity during germination.

W. O. KERMACK.

**Relation of picking time to acetaldehyde content and core breakdown of Bartlett pears.** C. P. HARLEY (J. Agric. Res., 1929, 39, 483—493).—Pears contained no acetaldehyde at picking, but developed distinct quantities after 2 days at 22–24°; the accumulation was more rapid in late-picked than in less mature fruits, and reached a maximum at the time of core breakdown. The amount of carbon dioxide developed in the intercellular gas was maximal some time before breakdown. Large amounts of carbon dioxide were sometimes accompanied by large quantities of oxygen, but in general increase in carbon dioxide was accompanied by decrease in oxygen. Respiration in Bartlett pears may be in part intramolecular. The relation of carbon dioxide production and core breakdown appears to be the establishment of optimum conditions for acetaldehyde formation. Dead or injured cells in browned tissue appear incapable of forming or retaining acetaldehyde.

E. HOLMES.

**Variations in the composition of fresh branches of *Amelanchier vulgaris*, Moench.** M. BRIDEL and J. RABATÉ (Compt. rend., 1929, 189, 775—777).—The amounts of ameliaroside and of reducible and hydrolysable sugars in the branches of *A. vulgaris*, Moench, vary considerably from month to month.

A. A. GOLDBERG.

**Formation of essential oil in the coriander plant.** A. TSCHERNUKHIN (Masloboino-Zhir. Delo, 1926, No. 12, 34—36).—Reduction processes are complicated by complex rearrangements in the course of

formation of secondary alcohols from aldehydes, esterification, and dehydration to cyclic hydrocarbons.

CHEMICAL ABSTRACTS.

**Liquorice root and liquorice extract. IV. A new substance in Chinese liquorice root.** P. A. HOUSEMAN and C. K. SWIFT (Amer. J. Pharm., 1929, 101, 679—687; cf. B., 1921, 674).—By aqueous extraction of the alcoholic extract of Chinese liquorice root a compound,  $C_{20}H_{12}O_9$ , m. p. 202—204° (uncorr.),  $\alpha_D + 48.8^\circ$  (acetyl derivative, m. p. 165—170°), has been isolated. Its reactions are described; acid hydrolysis gives three yellow, crystalline substances, m. p. 124—127°, 135—137°, and 189—191°, respectively. These have similar properties to certain lapachol derivatives (Hooker, J.C.S., 1896, 69, 1355, 1381). That of m. p. 189—191°,  $C_{15}H_{14}O_4$  (acetyl derivative, m. p. 175—177°), is identical with, or closely related to, hydroxy- $\alpha$ -lapachone.

E. H. SHARPLES.

**Carbohydrates in the bulb of *Allium scorodoprasum*.** Y. KIHARA (Proc. Imp. Acad. Tokyo, 1929, 5, 349—350).—*Scorodose*, m. p. about 200° (after previous sintering), a carbohydrate of the formula  $(C_6H_{10}O_5)_4$  which is obtained from the dried bulbs of *Allium scorodoprasum* in approximately 46% yield as a white, tasteless, hygroscopic powder, yields only laevulose on hydrolysis. *Scorodose acetate* (44.8% Ac) has m. p. 85—90°, and the *benzoate* m. p. 159°. The bulbs also contain some sucrose and arabinose.

W. O. KERMACK.

**Chemical composition of girasole [Jerusalem artichoke] and chicory grown in Minnesota.** H. P. TRAUB, C. J. THOR, L. ZELENY, and J. J. WILLAMAN (J. Agric. Res., 1929, 39, 551—555).—The best varieties of girasole and chicory grown in Minnesota contained 15% and 17.4% of total sugars, respectively, the latter containing relatively more laevulose. Girasole tubers contain relatively more sugar than the tops.

E. HOLMES.

**Presence of  $\beta$ -ionone in a natural product.** S. SABETAY (Compt. rend., 1929, 189, 808—809, and Bull. Soc. chim., 1929, [iv], 45, 1169—1172).—The fraction of essence of *Boronia megastigma* boiling at 131—135°/10 mm.,  $n_D^{20} 1.4910$ , gave a semicarbazide, m. p. 149°, and a *p*-bromophenylhydrazone, m. p. 120°. It is therefore concluded that this fraction is identical with  $\beta$ -ionone.

A. A. GOLDBERG.

**Theosterols of cacao.** H. LABRÉ, H. DE BALSAC, and R. LERAT (Compt. rend., 1929, 189, 864—866).—A method for the isolation of  $\alpha$ - and  $\beta$ -sterol from the cacao plant, and the sterol content of various cacao butters, are given. The husks are much richer in sterol than either the germs or beans.

A. A. GOLDBERG.

**New basic compound in Jackbean from which urea is split off by a liver enzyme.** M. KITAGAWA and T. TOMITA (Proc. Imp. Acad. Tokyo, 1929, 5, 380—383).—The compound isolated from Jackbean meal from which urea is eliminated by the action of aqueous extracts of pig's liver has the formula  $C_5H_{11}O_3N_4$  [copper salt,  $(C_5H_{10}O_3N_4)_2Cu$ ; copper sulphate double salt,  $C_5H_{11}O_3N_4 \cdot 2CuSO_4$ ; picrate,  $C_5H_{11}O_3N_4 \cdot 2C_6H_3O_7N_3$ , m. p. 155—158°; flavianate,  $C_5H_{11}O_3N_4 \cdot 2C_{10}H_6O_8N_2S$ , m. p. 185°]. The compound is not identical with arginine.

W. O. KERMACK.

**Botanical and chemical study of *Bikukulla eximia*, with a key to the North American species of *Bikukulla*.** W. W. EGGLESTON, O. F. BLACK, and J. W. KELLY (J. Agric. Res., 1929, 39, 477—481).—*Bikukulla eximia* contains, when dried, 2.3% of crude alkaloids of which neither the portion soluble nor that insoluble in hydrochloric acid is very toxic to mice. The latter compound (for which the name *eximine* is proposed), colourless needles, soluble in alcohol and chloroform, but not in water, had m. p. 165° (uncorr.) (picrate, m. p. 175°). E. HOLMES.

**Pigment of red algæ.** R. LEMBERG (Naturwiss., 1929, 17, 878; cf. A., 1929, 962).—The colour components are related to bile-pigments. Energetic reduction with hydrogen iodide and acetic acid yields a mixture of pyrrole bases and carboxylic acids, whilst reduction with sodium amalgam gives a chromogen responding to Ehrlich's reaction and oxidised in air to urobilin. R. A. MORTON.

**Protocatechuic acid in pigmented onion scales; relation to disease resistance.** K. P. LINK, A. D. DICKSON, and J. C. WALKER (J. Biol. Chem., 1929, 84, 719—725).—A better yield of protocatechuic acid than that previously described (A., 1929, 613) is obtained as follows: dried onion scales are extracted with acetone in a continuous extractor, the residue obtained on evaporation of the acetone solution is dissolved in water and precipitated with lead acetate, the lead precipitate is decomposed with dilute sulphuric acid, and the solution is concentrated to a syrup, which is taken up in acetone, and the solution is boiled with charcoal and allowed to evaporate at the ordinary temperature to crystallisation. The yield varies from zero in bleached scales to 0.125% in highly pigmented scales. The maximum yield hitherto obtained accounts for 35—40% of the toxicity of the crude extracts. C. R. HARRINGTON.

**Rust resistance in wheat. I—III.** R. NEWTON, J. V. LEHMANN, and A. E. CLARKE. **IV.** R. NEWTON and J. A. ANDERSON (Canad. J. Res., 1929, 1, 5—35, 86—99).—IV. The resistance may be due to the liberation of phenolic compounds, the determination of which in wheat press juice has been studied. Compounds of the flavone type are the principal phenolic compounds present.

#### CHEMICAL ABSTRACTS.

**Behaviour of living and frozen wood in ultra-violet light.** M. HARTINGER, L. LINSBAUER, and A. EIBL (Biochem. Z., 1929, 215, 191—196).—The inner part of the bark of living twigs shows fluorescent colours in ultra-violet light characteristic for each species. These colours disappear when the twig is frozen and this part of the bark appears brown. Dried twigs show a fluorescence different from that given by living twigs. J. H. BIRKINSHAW.

**Disintegration of animal tissues by nitric acid.** R. VLODESCO (Bull. Soc. Chim. biol., 1929, 11, 986—994).—Determinations of the inorganic phosphorus by the method of Copaux (cf. A., 1927, 787) and of the total phosphorus of various organs of the ox, horse, and dog are tabulated. C. C. N. VASS.

**Hydrogen peroxide-sulphuric acid decomposition for micro-determination of iodine.** G.

PFEIFFER (Biochem. Z., 1929, 215, 126—136; cf. A., 1929, 110).—The hydrogen peroxide-sulphuric acid micro-method for iodine is applicable to all organic materials. Special precautions are necessary when fats are present. J. H. BIRKINSHAW.

**Determination of nitrogenous constituents of blood and serous fluids by fractional precipitation with mercuric chloride.** B. LUSTIG and K. FÜRST (Biochem. Z., 1929, 215, 286—292).—The blood is deproteinised by mixing with an equal volume of a mixture of 5 parts of 10% sodium sulphate solution and 1 part 20% acetic acid and heated in the boiling water-bath, filtered, and the filtrate brought to  $p_H$  5.6 and made up to a known volume. The determination then proceeds as with the authors' method for similar determination in urine (A., 1929, 593). Tables indicate the purine-, ammonia-, creatinine-, creatine-, amino-acid-, and urea-nitrogen in horse serum, normal serum, serum with high residual nitrogen, and ascitic serum. The values agree with those obtained by other trustworthy methods. P. W. CLUTTERBUCK.

**Determination of sulphur in blood-serum and organic products.** A. LESURE and A. DUNEZ (J. Pharm. Chim., 1929, [viii], 10, 433—442; cf. A., 1929, 950).—Full details of the method are described. For the determination of sulphur in organic products and tissues, more satisfactory oxidation is obtained by the addition of perchloric acid to the fuming nitric acid (cf. Lematte, Kehane, and Boinot, B., 1927, 890). E. H. SHARPLES.

**Determination of cysteine, cystine, and their derivatives in tissues and biological fluids.** Y. OKUDA and K. KATAI (J. Dept. Agric. Kyushu, 1929, 2, 133—148).—The method previously described for the determination of cystine and cysteine (cf. Katai, A., 1926, 190; 1929, 1191) has been applied to the tissues of animals and plants. The most convenient protein precipitant is sulphosalicylic acid, which is preferable to trichloroacetic acid. Most animal tissues contain both cystine and cysteine. Certain plants contain no cysteine, but roots and seeds contain both cystine and cysteine.

W. O. KERMACK.

**Antimony-antimony trioxide electrode for determination of dissociation constants of local anaesthetics and of related compounds.** F. FENWICK and E. GILMAN (J. Biol. Chem., 1924, 84, 605—628).—The antimony-antimony trioxide electrode (cf. Roberts and Fenwick, A., 1928, 1098) has been employed to determine the  $p_H$  of solutions of various concentrations of some local anaesthetics, and, from the results, the basic dissociation constants were calculated. In a series of four related naphthalene derivatives, increasing basicity ran parallel with increasing anaesthetic effect, and the relation of structure to basicity was the same as that observed by Vliet and Adams (A., 1926, 1037) for the similar procaine series. Determinations by this method indicated for procaine  $K_b$   $29.9 \times 10^{-6}$ , and for aniline  $K_b$   $2.13 \times 10^{-10}$  at 25°; determinations with these and the other related compounds by means of the hydrogen electrode gave irregular results.

C. R. HARRINGTON.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

FEBRUARY, 1930.

### General, Physical, and Inorganic Chemistry.

**Arc and spark radiation from hydrogen in the extreme ultra-violet.** J. THOMSON (Phil. Mag., 1929, [vii], 8, 977—992; cf. A., 1929, 1123).—Further experiments have been conducted which support the view that the ionising radiations emitted by point discharges in hydrogen emanate from the gas itself. The variation in intensity of the radiations was studied quantitatively as the current flowing in the discharge was varied, and the results are discussed with reference to the view that the intensity of arc radiation from a discharge varies directly as the discharge current, and that the intensity of spark radiation varies as the square of the current. Rough tests were made by measuring the photo-electric current in a cell due to the glow discharge of a neon lamp, and results were in accordance with the theory.

N. M. BLIGH.

**Hydrogen spectra obtained by electronic collision in a mixture of hydrogen and mercury vapour.** S. VENCOV (Compt. rend., 1929, 189, 1073—1075).—The luminous intensity of the discharge produced in the author's apparatus (A., 1929, 968) is greater for mixtures of hydrogen (0.01—1 mm. pressure) and mercury vapour ( $1-2 \times 10^{-3}$  mm. pressure) than for hydrogen alone. At all pressures of hydrogen, and at potentials of 10.4—25 volts, the mercury arc lines  $2p-ms$ ,  $2p-md$ , and  $1s-2p$  were obtained, and are attributed to electronic collision with the normal mercury atom. Balmer lines were not observed below 16.5 volts, and at 20 volts the first three of the series were visible. The intensity of the continuous spectrum appears to depend on the degree of dissociation of the hydrogen, which is greatest around the filament, rather than on the electric field. The HgH bands 3728, 3500, 3275, and 2345 Å. obtained below 50 volts are associated with the bands 3064 and 2811 Å. due to water vapour.

J. GRANT.

**Additional lines in the secondary spectrum of hydrogen.** F. C. CONNELLY (Proc. Physical Soc., 1929, 42, 28—33).—About 280 lines between  $\lambda$  4735 and 4018 Å. not given by Gale, Monk, and Lee (cf. A., 1928, 1166) and 55 lines given by them but not found in this investigation are tabulated (cf. also Finkelburg, A., 1929, 118).

N. M. BLIGH.

**Multiple line spectrum of hydrogen.** P. DAS (Z. Physik, 1930, 59, 243—253).—Theoretical. The frequencies of a number of the lines of the multiple line spectrum of hydrogen are calculated from a formula, and compared with those obtained experimentally by different observers. The formula derived

is only a first approximation, and is not accurate over the whole range of the multiple line spectrum.

A. J. MEE.

**Intensity distribution in the fine structure of hydrogen.** L. GOLDSTEIN (J. Phys. Radium, 1929, [vi], 10, 439—447).—Mathematical. The intensities, proportional to the square of the amplitude of the electric moment, for the fine structure of various series of hydrogen lines are calculated by Dirac's theory (cf. A., 1928, 344). According to theory the violet is stronger than the red component in the Balmer series. In the Balmer and Paschen series the intensity relation of the two groups is greater than that found experimentally.

N. M. BLIGH.

**Gas discharge in hydrogen.** E. LAU and O. RIECHENHEIM (Ann. Physik, 1929, [v], 3, 840—848).—The occurrence of striæ in Wood's hydrogen discharge is conditioned by recombination of  $H_1$  to  $H_2$  and indeed originates from the negative ions arising from the recombination. The direction of the gas stream affects the position of the layers and the phenomenon throws light on the processes involved. The number of layers occurring in the presence of a catalyst is a measure of the catalytic effect.

R. A. MORTON.

**Structure of the line  $H_\alpha$  and the period of rotation of the solar chromosphere.** G. ABETTI and B. NOVAKOVA (Atti R. Accad. Lincei, [vii], 10, 227—230).—Further proof is adduced with regard to the dissymmetry of the line  $H_\alpha$  at the edge of the sun, where the emission component  $H_{\alpha_2}$  is considered as consisting of two emission components  $H_{\alpha_2}$  (violet) and  $H_{\alpha_2'}$  (red). The fact that the total dissymmetry calculated on this basis appears to be double the actual value is explained, and results obtained by Novakova, using a Moll microphotometer on Arcetri spectrograms, confirm the result.

G. E. WENTWORTH.

**Structure of lithium red bands.** K. WURM (Z. Physik, 1929, 59, 35—41).—The fine structure of six bands of lithium at 6554, 6659, 6983, 7176, 7309, and 7497 Å. has been examined. They have the same ground state as the bands of the blue-green system and are arranged with their simple  $P$  and  $R$  branches as a  $^1\Sigma \rightarrow ^1\Sigma$  electron jump. From an analysis of the fine structure the resulting moments of inertia and molecular radii of the different states have been determined. Considerations of the dissociation products show that, in the ground state, the molecule splits into two normal lithium atoms and in the

excited state into one normal and one excited  $2P$  atom. All the bands show a marked intensity change.  
W. R. ANGUS.

**Transition probabilities in lithium. IV. B. TRUMPY** (Z. Physik, 1929, 57, 787—796).—New determinations of the intensities of the lines of the principal series of lithium are described. The results show that Hargreaves' calculated values are not very satisfactory; a more complete agreement with the values calculated is obtained by using Hartree's method.  
R. W. LUNT.

**Band spectrum of lithium hydride. G. NAKAMURA** (Z. Physik, 1930, 59, 218—242; cf. A., 1929, 625).—Lithium vapour heated in an atmosphere of hydrogen shows a new absorption spectrum in the ultra-violet which is in the nature of a multiple line spectrum. The lines measured were between 307 and 436 m $\mu$ . It was possible to classify practically all the lines of the absorption spectrum and almost all the strong emission lines. A number of the absorption lines coincide with the emission lines obtained by Watson, although the absorption spectrum is much simpler. The LiH molecule alone seems to be concerned in the production of the spectrum, and the system definitely belongs to the transition  $^1\Sigma \rightarrow ^1\Sigma$ , which is strongest, as predicted by Hund. The single bands consist of a  $P$  and an  $R$  branch which are faded towards the red. The moment of inertia of the molecule in the normal state is  $3.7 \times 10^{-40}$  g. cm.<sup>2</sup>, whereas for the excited molecule it is  $9.3 \times 10^{-40}$  g. cm.<sup>2</sup> These values correspond with nuclear distances of  $1.6 \times 10^{-8}$  cm. and  $2.5 \times 10^{-8}$  cm., respectively. The dissociation work is 59 kg.-cal. The decomposition of the normal molecule is in the first instance into one lithium and one hydrogen atom, whilst the excited molecule decomposes into an excited ( $2^2P$ ) lithium atom and a normal hydrogen atom, in agreement with theory.  
A. J. MEE.

**Bands of the carbon molecule. G. H. DIEKE and W. LOCHE-HOLTGREVEN** (Nature, 1930, 125, 51—52).—Ten bands (of which seven were investigated for fine structure) were studied; they must be due to a symmetrical molecule and the nuclear spin of the atoms in question is zero. The molecular constants calculated from these bands are very near to those of the Swan bands.  
A. A. ELDRIDGE.

**Bands of the carbon molecule. R. C. JOHNSON** (Nature, 1930, 125, 89—90).—Dieke and Lochte-Holtgreven's work (see above) is supported. The system is well shown in a tube containing carbon electrodes, some hydrogen, and 30—40 mm. pressure of argon, and is also produced under high-temperature conditions of the carbon arc in hydrogen.  
L. S. THEOBALD.

**Visible afterglow of active nitrogen. G. CARO and J. KAPLAN** (Z. Physik, 1929, 58, 769—780).—The spectrum of the visible afterglow was investigated at  $-80^\circ$ , at the ordinary temperature, and at a high temperature. The spectrum contains the first positive group of bands. This is emitted by molecules in the metastable state  $A_0$ , further excited by atoms in metastable states  $2P$  and  $2D$ , to states  $B_{12}$  and  $B_6$ , respectively. The atoms and molecules

may attain their metastable states by absorption of energy of recombination, but the afterglow spectrum is independent of the energy of dissociation. This removes a difficulty of the earlier hypotheses.

A. B. D. CASSIE.  
**Ultra-violet bands of the neutral oxygen molecule. W. LOCHE-HOLTGREVEN and G. H. DIEKE** (Ann. Physik, 1929, [v], 3, 937—977).—All the available material (cf. Runge, Physica, 1921, 1, 254; Fesefeldt, A., 1928, 457) has been collated. An attempt is made to classify all the observed lines and to evaluate rotation constants and extend the work of earlier investigators. The interpretation of the bands and their fine structure is discussed.  
R. A. MORTON.

**Dissociation work of oxygen. R. MECKE** (Naturwiss., 1929, 17, 996).—The value of 7.05 volts obtained for the work necessary to decompose the oxygen molecule into two normal atoms, by finding the convergence limit of the ultra-violet absorption spectrum of oxygen, is incorrect because the atoms are not in the normal ( $3P$ ) state, but in the  $1D$  state. The correction is not yet known, but an accurate determination of the dissociation energy can be made by using the data of Norrish on the photochemical decomposition of nitrogen dioxide (cf. A., 1929, 893, 1022). The value derived is 5.6 volts (128 kg.-cal.), whilst the excitation energy of the  $1D$  term is 1.4 volts.  
A. J. MEE.

**Magnesium triplets in arc and solar spectra. M. E. WARGA** (Pub. Allegheny Obs. Univ. Pittsburgh, 1929, 6, 151—157).—New values for the wave-lengths of the ultra-violet and green triplets of Mg I have been obtained. The differences observed on comparison with the Fraunhofer spectrum are smaller than the relativity shift for the violet, but larger for the green, lines. The wave-lengths of some copper, calcium, iron, and sodium lines are given.

CHEMICAL ABSTRACTS.  
**Resonance series of sulphur vapour. P. SWINGS** (Compt. rend., 1929, 189, 982—983).—By the use of a cylindrical fused quartz vessel, the two portions of which were enclosed in separate electric furnaces, it was possible to follow variations in the resonance spectrum of sulphur with variations in pressure and temperature. Four series of doublets excited by the mercury lines 3655, 3132, 3126, and 2968 were obtained, comprising 6, 24, 23, and 20 terms ( $\Delta\nu$  34, 18, 168, and 16 cm.<sup>-1</sup>), respectively. The line 3132 belongs to a branch  $R$  of the absorption spectrum of  $S_2$ .  
J. GRANT.

**Band spectra of zinc vapour. H. VOLKRINGER** (Compt. rend., 1929, 189, 1264—1265).—A list of lines (2983—3282 Å.) in the band spectrum, obtained by an electrodeless discharge in zinc vapour heated to redness in a fused silica tube, is given. The bands have a fine complex structure and although the large spaces separating the lines indicate a molecule with a very small moment of inertia, it is doubtful if they are due to a zinc hydride.  
J. GRANT.

**Hyperfine structure and nuclear moment. H. SCHÜLER and H. BRÜCK** (Z. Physik, 1929, 58, 735—742).—The hyperfine structure of cadmium and

tellurium is discussed on lines given in earlier papers (A., 1929, 967), and isotopes are suggested for both.

A. B. D. CASSIE.

**Arc spectrum of arsenic.** W. F. MEGGERS and T. L. DE BRUIN (Bur. Stand. J. Res., 1929, 3, 765—781).—The emission spectrum of metallic arsenic vaporised in graphite or copper arcs has been examined and wave-lengths were measured between 1889.85 and 10023.98 Å. The spectrum is simple, but difficult to analyse, as many important lines lie in the far infra-red or ultra-violet. A fairly complete analysis of the As I spectrum has been made. Forty-two levels are identified. The normal state is represented by a  $^4S_2$  term, for which the absolute value is estimated to be 80692.72, giving an ionisation potential of about 10 volts.

C. J. SMITHELLS.

**As III spectrum.** A. S. RAO and A. L. NARAYAN (Z. Physik, 1929, 57, 865—868).—By a careful examination of the spectra of the element under various conditions of excitation many lines are found which appear to belong to As III. Tables are given showing the electronic configurations, the corresponding theoretical terms according to Hund's theory, the quadruplets of As III, and a classification of the wave-lengths of As III.

W. R. ANGUS.

**Spectrum of arsenic in the extreme ultra-violet.** P. QUENEY (J. Phys. Radium, 1929, [vi], 10, 448—452).—Using the apparatus previously described (cf. A., 1929, 1206) the spectrum of arsenic by the electrodeless discharge for the range 2500—700 Å. was investigated. Wave-lengths and intensities of all the known lines are tabulated. The strongest lines of As V and As IV are classified by the scheme already applied to zinc, gallium, and germanium (cf. Lang, A., 1928, 99). The irregular doublet law is illustrated for homologous lines of the series Zn II, Ga III, Ge IV, As V, and Zn I, Ga II, Ge III, As IV, and the doublet and triplet separations are tabulated for the same series.

N. M. BLIGH.

**Zeeman effect and hyperfine structure of the antimony arc spectrum.** H. LÖWENTHAL (Z. Physik, 1929, 57, 822—834).—The Zeeman effect for 18 lines of the antimony arc spectrum in the region 2311—4033 Å. has been measured with a grating spectrometer.

R. W. LUNT.

**First spectrum of xenon.** W. F. MEGGERS, T. L. DE BRUIN, and C. J. HUMPHREYS (Bur. Stand. J. Res., 1929, 3, 731—763).—Discharge tubes were filled with pure xenon and operated so as to emit only the spectrum of neutral xenon atoms. Wave-lengths from 3442.77 to 10107.2 Å. have been determined for 318 lines and relative intensities estimated. Analysis of these data has resulted in the identification of spectral terms, which account for practically all the observed lines.

C. J. SMITHELLS.

**Series in the xenon arc spectrum.** W. GREMMER (Z. Physik, 1930, 59, 154—167).—A concave grating of 4 m. radius of curvature was used for photographing the arc spectrum of xenon. For the calibration, neon lines were used and some xenon lines previously accurately determined by Merrill, Otsuka, and Meggers. It is to be expected that in the violet the principal series will be combinations of the type

$1s - mp_k$ , as has been found for other rare gases. There are some recurring constant frequency differences in the violet which help in the ordering of the spectrum. The accurate limit for at least one series has to be calculated. The best series for this purpose were the  $1s_5 - mp_8$ , and the two hydrogen-like series  $1s_2 - mX$  and  $1s_2 - mY$ . A large number of lines are classified and their intensities noted (cf. preceding abstract).

A. J. MEE.

**New method for the study of voltage-intensity relations and its application to the mercury 2537 Å. line.** F. C. OSTENSEN (Physical Rev., 1929, [ii], 34, 1352—1356).—To eliminate the effect of secondary electrons a beam of electrons was concentrated by a magnetic field to avoid striking any metal surface until it reached a collector to trap all secondaries, thus ensuring a specified velocity for the exciting electrons. The method was applied to a study of the variation with electron velocity of the intensity of the 2537 Å. mercury line. A maximum intensity was found at 6 volts, above which the rate of falling is much greater than was found by other investigators, owing to the elimination of the secondary electrons.

N. M. BLIGH.

**Life and concentration of metastable atoms and the quenching of mercury resonance radiation.** E. GAVIOLA (Physical Rev., 1929, [ii], 34, 1373—1384; cf. A., 1929, 226, 486).—Theoretical. The dependence of life and concentration of optically excited metastable mercury atoms on experimental conditions, foreign gas pressures, and intensity of illumination is examined. A maximum life of  $10^{-2}$  sec. under the experimental conditions and different effects of foreign gases on the accumulation of excited atoms are explained. An improved general formula for the quenching of mercury resonance radiation is deduced (cf. Foote, A., 1927, 999). The efficiencies of collisions of the second kind of metastable mercury atoms with nitrogen, argon, and helium molecules are calculated. The concentration of metastable atoms is shown to increase with the square root of the intensity of the exciting light and not with the exciting light itself as previously supposed.

N. M. BLIGH.

**Behaviour of the mercury line 1849.57 ( $1^1S_0 - 2^1P_1$ ).** A. T. WILLIAMS (Nature, 1929, 124, 985—986).—Under all the conditions examined, the persistence of the lines 2536.52 ( $1^1S^3P$ ) and 1942.0 Å. ( $2^1S^2P$ , Hg<sup>+</sup>) is much greater than that of the line 1849.57 Å., which is a theoretical, but not an experimental, "raie ultime."

A. A. ELDRIDGE.

**Bands of continuous spectrum in mercury.** W. H. CREW and W. N. THORNTON (J. Opt. Soc. Amer., 1929, 19, 358—366; cf. A., 1929, 1; Robertson, MacKinnon, and Zinn, *ibid.*, 237).—The mercury vapour spectrum was excited using variations in the electrical circuit, which produced certain changes in the character of the spectra. Two strong bands of continuous radiation having maxima at about  $\lambda$  4500 and 3300 were obtained, and four weak lines in agreement with the wave-length distribution of intensity calculated from the recombination theory of continuous spectra. It is concluded that those changes which reduce the current density in the arc enhance the continuous bands and reduce the intensity of the

line spectrum, and also diminish the dissociation of molecules in the arc. Low temperature of the vapour also favours the production of bands. The bands of the continuous spectra are attributed to molecular radiations.

N. M. BLIGH.

**Energy increase in elementary processes.** H. BEUTLER and E. RABINOVITSCH (Z. physikal. Chem., 1929, B, 6, 233—239; cf. A., 1929, 238).—Further investigation of the fluorescence spectrum of irradiated mercury vapour to which nitrogen has been added confirms the formation of doubly-activated mercury atoms, corresponding with the process:  $\text{Hg}^* + \text{Hg}^* = \text{Hg}^{**} + \text{Hg}$ . The same effect was obtained with water vapour and with ammonia instead of nitrogen.

O. J. WALKER.

**Quantified rotation of the thallium atom.** R. G. LOYARTE (Physikal. Z., 1929, 30, 923—925).—The emission lines 2288.07 and 2139.4 Å. of thallium which also appear in absorption are hitherto unclassified. It is shown that they belong to a series of lines the wave-numbers of which differ from those of series lines by  $\pm 7571.8 (\Delta\nu)$ . This constant wave-number difference is ascribed to the rotation jump from the level  $n=0$  to  $n=1$ , i.e., to the simultaneous occurrence of level changes for the light-emitting electrons and discontinuous changes in the rotation of the atoms. On the assumption that the discrete value of the rotational energy of the atom corresponds with the free-axial rotator of wave mechanics, the moment of inertia of the atom is  $J=0.73 \times 10^{-42}$  g. cm.<sup>2</sup> This value is of the same order as that derived from magnetic susceptibilities.

R. A. MORTON.

**New types of emission spectra.** L. VEGARD (Nature, 1930, 125, 14).

**Ultimate lines in the spectra of elements in the gaseous state.** B. DE LA ROCHE (Bull. Soc. chim., 1929, [iv], 45, 922—930).—By progressive dilution of an element in the gaseous condition with an indifferent gas it has been observed that certain characteristic lines in its emission spectrum persist after the majority have been suppressed. These "raies ultimes" have been studied with a view to determine the relative sensitiveness of the spectral reactions of various elements. The elements examined were generally introduced in the form of a gaseous compound and diluted with nitrogen in steps of 10 times down to a limit of 1 in  $10^6$ . Hydrogen, nitrogen, carbon, and silicon were easily detected at a dilution of  $10^6$ , boron at  $10^5$ , chlorine, fluorine, and phosphorus at  $10^4$ , bromine and sulphur at  $3 \times 10^2$ . Tables are given showing the wave-lengths of the lines visible at the different dilutions.

F. L. USHER.

**Excitation of spectra for the investigation of hyperfine structure.** H. SCHÜLER (Z. Physik, 1930, 59, 149—153).—A discharge tube suitable for observing the glow emitted by metallic vapours at low temperatures (those of liquid air and liquid hydrogen) is described. The structure of the lines emitted is discussed with reference to the Doppler effect, which is diminished at low temperatures, and it is shown that there is a satisfactory confirmation of the structure on this basis. The same principle can also be used for absorption. It is possible with

the apparatus described to obtain very favourable conditions for fine absorption lines. A variation of the tube is also described.

A. J. MEE.

**Complex spectra.** J. C. SLATER (Physical Rev., 1929, [ii], 34, 1293—1322).—Mainly mathematical. The method of wave mechanics is applied to the theory of atomic multiplets. Hund's scheme for the classification of terms into multiplets is derived directly from theory, and definite formulæ are deduced for the intervals between multiplets in place of the previous empirical rule. Hund's rule, that terms of large  $L$  and  $S$  values lie lowest, is found to have no general significance; the present theory agrees with the rule where obeyed, and with the exceptions.

N. M. BLIGH.

**Spiral forms in gas discharges.** S. P. MCCALLUM and W. T. PERRY (Nature, 1929, 124, 984—985).—The conditions necessary for the appearance of spiral forms of electrodeless discharge in slightly impure argon and neon are described.

A. A. ELDRIDGE.

**Continuous spectra of gases.** W. FINKELNBURG (Physikal. Z., 1930, 31, 1—25).—A summary of experimental and theoretical work.

A. J. MEE.

**Is the continuous spectrum of the under-water spark temperature radiation?** B. WREDE (Ann. Physik, 1929, [v], 3, 823—839).—In the continuous spectrum of the under-water spark an intensity displacement towards shorter wave-lengths occurs when the energy of the discharge is increased, using electrodes of zinc, cadmium, copper, lead, or tin. The displacement is less marked with aluminium and magnesium, both these metals exhibiting a specially intense continuous spectrum. No intensity displacements could be detected for the spark spectra of any of the metals in air. The relative values for the intensity shift in the case of the zinc under-water spark conform to Wien's law showing the presence of temperature radiation. By comparison with the spectrum of the positive crater of the carbon arc, the temperature of the zinc under-water spark is estimated to be of the order 7500° Abs. for smaller discharge energy and 10,000° Abs. for greater energy.

R. A. MORTON.

**Theory of resonance widening of spectral lines.** J. FRENKEL (Z. Physik, 1930, 59, 198—207).—Theoretical. Holtsmark's theory of the widening of spectral lines, based on the "classical" view of atomic resonance, is remodelled on the basis of the quantum theory, the "classical" resonance being replaced by the Heisenberg exchange resonance between identical atoms of a given kind. The case of two atoms is first dealt with, and then the case of a multiple atomic system. In dealing with the latter it is necessary to assume that only one atom is excited, the rest remaining in the normal state. The theory leads to the proposition that there is proportionality between the widening of certain lines and their intensity. Some of the deficiencies of the theory are mentioned.

A. J. MEE.

**New quartz spectrograph.** H. F. KURTZ (J. Opt. Soc. Amer., 1929, 19, 378—383).—A description of the instrument and the methods adopted to meet the qualifications of a clean sharp spectrum



with minimum curvature, easy and constant adjustment no relative vibration of parts, a bilateral slit with non-oxidisable jaws, wholly enclosed, allowing easy addition of accessory illuminating or photometric apparatus.

N. M. BLIGH.

**Spectral terms and chemical valency.** A. T. WILLIAMS (Compt. rend., 1929, 189, 1075—1077).—The validity for the elements of the third column of the periodic table of the author's rule  $V=R\pm 1$  is discussed,  $V$  being the chemical valency and  $R$  the spectral multiplicity. For the elements lanthanum to gadolinium the relations  $V=R-f\pm 1$  apply, where  $f$  is the number of electrons in the  $4f$  orbits. For elements 65—71,  $V=R-(f-2n)\pm 1$ , in which  $n$  increases integrally from 1 for terbium to 7 for lutecium. For the elements silicon, germanium, tin, and lead the valency changes from 4 to 2 as the quantities  ${}^3P_0-{}^3P_1$ ,  ${}^3P_1-{}^3P_2$ , and  $\Sigma\Delta v$  increase, but although the terms of the elements of the sub-group nitrogen to bismuth show the same differences, these elements have the same valencies.

J. GRANT.

**K-Absorption discontinuities of manganous and chromate ions.** D. M. YOST (Phil. Mag., 1929, [vii], 8, 845—847).—The absorption discontinuities of manganous and chromate ions in solution have the same wave-lengths as the corresponding ions in the crystalline state.

C. W. GIBBY.

**Precision measurements of the K-series for titanium and vanadium.** S. VON FRIESEN (Z. Physik, 1929, 58, 781—793).—A tube spectrometer constructed for high-vacuum work by Siegbahn is described. The lines  $\alpha_1$ ,  $\alpha_2$ , and  $\beta_1$  of the K-series for titanium and vanadium were measured accurately with this instrument. The K lines  $\beta'$ ,  $\beta''$ ,  $\beta_2$ , and  $\beta'''$  were determined with a precision vacuum spectrometer.

A. B. D. CASSIE.

**M-Series of the rare earths.** E. LINDBERG (Z. Physik, 1929, 57, 797—803).—The lines  $M_{III}N_V$ ,  $M_{IV}N_{VI}$ ,  $M_VN_{VII}$ , and  $M_VN_{III}$ , together with the satellites of the lines  $M_{IV}N_{VI}$  and  $M_VN_{VII}$ , have been measured to  $\pm 3$  X. for lutecium, ytterbium, erbium, holmium, dysprosium, terbium, gadolinium, europium, samarium, neodymium, praseodymium, and cerium.

R. W. LUNT.

**Intensity measurements on the Compton effect for soft X-rays.** R. H. VARIAN (J. Opt. Soc. Amer., 1929, 19, 351—357).—Using a special X-ray tube having thin aluminium foil windows and large power capacity, spectrograms showing the Compton effect for copper  $K\alpha$  rays scattered from carbon and paraffin were obtained. The ratio of the intensity of the modified component to that of the unmodified was determined as a function of the scattering angle. The  $L$  electrons in carbon make a considerable contribution to the unmodified component. The results do not agree with Jauncey's theory (cf. A., 1925, ii, 747), and Wentzel's intensity predictions (cf. A., 1927, 804) are not easily susceptible to experimental check.

N. M. BLIGH.

**Polarisation of X-radiation.** W. DUANE (Proc. Nat. Acad. Sci., 1929, 15, 805—815; cf. A., 1928, 819).—A detailed description of the method of measuring the quantity of radiation resulting from

impact of electrons on a stream of mercury atoms in the direction of the electron stream ( $n_1$ ) and perpendicular thereto ( $n_2$ ) is given. Defining degree of polarisation as  $p=(n_1-n_2)/(n_1+n_2)$ , the mean value of  $p$  is 0.497. This only partly supports existing theory, which requires total polarisation in the plane containing the direction of motion of the electrons, but it is in agreement with Sommerfeld (J. Opt. Soc. Amer., 1928, 16, 375).

C. A. SILBERRAD.

**Gas ionisation by means of positive ions and the secondary emission from platinum.** T. I. CÂMPAN (Physikal. Z., 1929, 30, 858—865).—The ionisation of hydrogen and nitrogen by means of positive K-ions (velocities up to 140 volts) has been studied by Lenard's opposed field method over the pressure ranges 0.0003—0.1 mm. mercury for hydrogen and 0.0003—0.054 mm. for nitrogen. The maximal ionisation for positive K-ions is of the order 0.01%, hence the opposed field method is not suitable for such determinations, since other and stronger secondary phenomena mask the effect. The impact of positive K-ions on platinum brings about a secondary emission detectable for very small ionic velocities; e.g., with 28 volts it amounts to 0.01% and increases to 1.2% at 128 volts. The secondary emission from platinum is strongly increased if the surface of the metal is covered by an adsorbed layer of nitrogen molecules, but the emission at once falls to its original value if the metal is outgassed.

R. A. MORTON.

**Columnar ionisation in gases at higher pressures.** G. JAFFÉ (Physikal. Z., 1929, 30, 849—856; cf. A., 1929, 621).—The theory of ionisation in columns has been tested experimentally by determining the saturation curves for air, oxygen, carbon dioxide, and hydrogen at higher pressures (up to 4500 mm. and 6000 mm. for the different gases). The theoretical values agree quantitatively with the experimental data over a wide range (0.5—100 for the significant parameter). On account of the use of certain constants, the values of which are somewhat uncertain, the recombination coefficients can be evaluated only indirectly and approximately.

R. A. MORTON.

**Oxide-coated filaments.** J. A. BECKER (Physical Rev., 1929, [ii], 34, 1323—1351).—A proposed theory of the changes in activity in oxide-coated filaments is confirmed experimentally. A comparison of the behaviour of the filaments and those with composite surfaces indicates that the former owe their high activity to adsorbed metallic barium. The changes in emission from a coated filament produced by changes in plate potential and by currents sent into or drawn from it, are ascribed to electrolysis of the oxide. When electrons are sent into the filament, barium is deposited on the surface and the activity increases to a maximum and then decreases. When current is drawn from the oxide, oxygen is deposited on the surface, increasing the activity if beneath the adsorbed barium and decreasing it if above. Both barium and oxygen diffuse readily from the surface into the oxide and *vice versa*. A high precision technique is employed for determination of the relative rates of evaporation of small amounts of electropositive and electronegative materials. It was

found experimentally that metallic barium evaporates from a well-broken-down filament if the temperature is not too high; oxygen evaporates if an emission limited current is drawn; metallic barium deposited by electrolysis or by evaporation on the oxide surface produces activity changes similar to those produced by barium on tungsten; oxygen brought to the surface of the oxide by drawing current from it, in some cases increases and in other cases decreases the activity; most of the current through the oxide is carried by electrons, but a small part is carried by ions. The conductivity of the oxide does not obey Ohm's law; some of the conductivity is due to a diffusion current which may flow against an opposing field. The complex time changes occurring in the filaments are considered.

N. M. Blich.

**Relations between the normal photo-electric effect and electrical surface properties of different metals.** R. SUHRMANN (Physikal. Z., 1929, 30, 939—942).—The effect of strong heating and of electron bombardment on the photo-electric properties of metals has been studied. Really pure platinum gold or silver surfaces have little or no power of emitting electrons under the action of ultra-violet rays in the quartz region. Hydrogen, adsorbed as ions, advances the long-wave limit of excitation and greatly increases the sensitivity. The inner charge of gas in metals which absorb hydrogen is driven out by brief heating of the metal in a high vacuum, but hydrogen ions and possibly hydrogen atoms are retained at the surface. The ions appear to effect the displacement of the long-wave limit.

R. A. MORTON.

**Ionisation of argon by metastable neon atoms.** F. M. PENNING (Z. Physik, 1929, 57, 723—738).—In order to confirm some conclusions of previous experiments on argon-neon mixtures, namely, that the ionisation of argon can take place as the result of collisions between neutral argon atoms and metastable (excited) neon atoms, the dielectric strength of argon-neon mixtures has been investigated. Theory predicts that if the above assumption were correct the dielectric strength should increase when the gas mixture is subjected to intense irradiation. A number of experiments are described which exemplify this effect, which is a maximum for mixtures containing about 0.001% A. The effect diminishes rapidly with increase in argon concentration from 0.01% upwards.

R. W. LUNT.

**Quantum theoretical calculation of the masses of the proton and electron.** R. FÜRTH (Physikal. Z., 1929, 30, 895—898).—A fuller account of work already published (A., 1929, 1123, 1209).

R. A. MORTON.

**Single scattering of single electrons.** O. KLEMPERER (Ann. Physik, 1929, [v], 3, 849—878).—The angular distribution of singly-scattered electrons for 9 and 18 kilovolts, using celluloid, aluminium, and beryllium scattering sheets, has been studied by means of the Geiger point counter. The counter, closed by means of a celluloid window, registers single electrons with an efficiency which varies little over the range 18—5 kilovolts, but falls steeply for lower velocities. The observed velocity distribution is very much

flatter than the Rutherford distribution for scattered  $\alpha$ -particles or canal rays and does not conform exactly with any theory so far advanced. The course of the scattering distribution for large deflexions lends confirmation to wave-mechanical ideas of the spin and relativistic change in mass of the electron as contrasted with the classical relativity treatment of Darwin. By means of an electrical transverse field, the existence among the scattered electrons of two groups of velocities has been established, one corresponding with nucleus scattering without retardation, and the other arising from electron scattering with a loss of velocity determined by the angular deflexion. The X-ray emission from the foil is very weak compared with the electronic scattering. The angular distribution for multiple scattering, recorded by a multiplication counter, has been studied. The yield of scattered electrons for large angles of deflexion corresponds, as regards order of magnitude, with Rutherford's formula.

R. A. MORTON.

**Specular [regular] and total reflexion of electrons.** E. RUPP (Physikal. Z., 1929, 30, 935—939).—With a fine stream of electrons impinging on a silver surface, regular reflexion increases markedly with decreasing angle of incidence, and is very well shown for rapid electrons. The reflexion curves indicate two separate effects, regular reflexion and scattering in all directions. Investigation of the rôle of different metals shows that the reflexion of electrons without loss of velocity always increases with decreasing velocity, and the scattering effect increases with decreasing atomic number. The half-breadth value of the reflexion curve also increases with decreasing atomic number. For elements in the same vertical column of the periodic table the intensity of the reflexion maximum increases with decreasing atomic number. For thin superimposed layers of nickel and copper total reflexion should occur at 80° for 100 volts and it is shown that the principles applicable to optical total reflexion are quantitatively valid for electrons. Possible applications to other problems are discussed.

R. A. MORTON.

**Theory of formation of large ions and droplets.** A. VÉRONNET (Compt. rend., 1929, 189, 1249—1251).—A mathematical interpretation of the formation of large ions (Langevin and Broglie) by the attraction between an atom and an electron expressed in terms of the position of the free electron on its orbit, and the position of the orbit with respect to exterior electrons. The theory is applied to water droplets, to the solar corona, and to other cosmic phenomena. The green line of the aurora borealis is probably produced by the nuclei of large ions which behave as solid particles (cf. Vegard, A., 1927, 91, 285).

J. GRANT.

**Differences in the directions of ejection of X-ray photo-electrons from various atomic levels.** E. C. WATSON and J. A. VAN DEN AKKER (Proc. Roy. Soc., 1929, A, 126, 138—143).—The use of the Wilson expansion-chamber method for determining the directions in which photo-electrons are ejected by X-rays has the disadvantage that the particular energy level in the atom from which the electron is ejected in general cannot be determined.

This difficulty may be avoided by using the magnetic spectrograph previously developed by Watson (Physikal. Rev., 1927, 30, 479) for studying the velocity of the X-ray electrons as a function of the angle of emission. Photographs are reproduced of magnetic spectra of the electrons emerging at various angles from thin films of (1) evaporated tungsten traversed by primary X-rays from a silver target, (2) sputtered silver chloride traversed by primary X-rays from molybdenum, (3) sputtered gold traversed by primary X-rays from molybdenum, and (4) evaporated nickel before and after exposure to gaseous chlorine, traversed by primary X-rays from molybdenum. It is concluded from the experimental results that the distribution in space of the photo-electrons thrown out of the  $L_{II}$  and  $L_{III}$  levels by any given X-radiation is more isotropic than that of the electrons thrown out of the  $K$  or  $L_I$  levels by the same radiation.

L. L. BIRCUMSHAW.

**Capture of electrons by molecules.** V. A. BAILEY (Phil. Mag., 1929, [vii], 8, 1112—1114; cf. A., 1929, 231).—Polemical against Loeb (cf. *ibid.*, 1359).

N. M. BLIGH.

**Visible electron diffraction.** A. DAUVILLIER (Nature, 1930, 125, 50).—A film of microcrystalline particles of zinc oxide is employed.

A. A. ELDRIDGE.

**Scattering of electrons by gold.** N. F. MOTT (Nature, 1929, 124, 986).—Theoretical.

A. A. ELDRIDGE.

**Grating errors and electronic charge.** S. FAGENBERG (Nature, 1930, 125, 13—14).

**Reflexion of protons from calcite.** A. J. DEMPSTER (Nature, 1930, 125, 51).—Hydrogen positive rays give a complex reflexion pattern when allowed to fall on a cleavage face of a calcite crystal at almost grazing incidence. The lines may be due to diffraction of the rays at the two-dimensional gratings formed by rows of atoms in the crystal surface. A line is a velocity spectrum of the protons; no undeflected pattern was observed.

A. A. ELDRIDGE.

**Positive emission of palladium.** M. WOLFKE and J. ROLINSKI (Physikal. Z., 1929, 30, 817—818).—Chemically pure palladium wire or foil shows a strong emission of ions (at. wt. 20—40, probably alkali ions) which ceases only after heating for several hours at 1200°. After eliminating this "fresh" emission the palladium can be reactivated by heating in hydrogen, air, or in the presence of moisture, and especially by applying exceedingly thin films of organic substances. After treatment with nascent hydrogen, the palladium exhibits a very quickly decreasing emission of light ions, probably protons. Palladium tubes and "osmo" tubes no longer show the "fresh" emission after 30 hrs. at 1200°, and after this treatment no positive emission is shown with diffusing hydrogen.

R. A. MORTON.

**Attraction phenomena of mercury in a high vacuum.** W. I. ROMANOFF (Physikal. Z., 1929, 30, 871—876).—The character of the attraction between two surfaces separated by a gaseous layer has been investigated theoretically and the results have been confirmed experimentally. The thickness

of the gas layer determines the strength of the attraction. Other factors enter into the problem only by affecting the thickness of the gas layer.

R. A. MORTON.

**Effective cross-section curves for hydrocarbon chains.** E. BRÜCHE (Physikal. Z., 1929, 30, 815—817).—The effective cross-section curves for methane, ethane, propane, and butane all show a marked maximum at the same velocity of electrons, but the height of the curve (area-velocity) increases with increasing mol. wt. By making simple assumptions on the basis of spherical and of rod-like aggregates the cross-section curves have been calculated, the agreement with experiment being good in either case but rather better for the rod model. The distances between successive carbon nuclei appear to be constant at 2.2—2.3 Å. in agreement with data from other lines of work.

R. A. MORTON.

**Activation of matter.** G. REBOUL (Compt. rend., 1929, 189, 1256—1257).—Bare metals or metals covered with paper or cardboard are activated by contact with or substitution for the grid electrode of a resistance cell passing 1—2 milliamp. at about 10,000 volts. They blacken a photographic plate after an exposure of 4 hrs. to 2 days, and ionise air with an activity which decreases exponentially with time.

J. GRANT.

**Packing effect in atomic nuclei.** H. H. WOLFF (Physikal. Z., 1929, 30, 812—815).—On the basis of Aston's accurate determinations of atomic weights, the respective rôles of protons and electrons in the mass defect due to packing have been investigated. For electrons the mean value is  $-0.0031$  (unit=mass of hydrogen atom), whilst for protons a mean value of  $0.010$  is obtained, this value tending to decrease somewhat as the atomic weight increases. Explanations of the results are put forward.

R. A. MORTON.

**At. wt. of chlorine. Ratio NOCl:Ag.** A. F. SCOTT and C. R. JOHNSON (J. Physical Chem., 1929, 33, 1975—1986).—The value of the ratio NOCl:Ag obtained nephelometrically from three samples of nitrosyl chloride is  $0.606827 \pm 0.0000017$ , giving a calculated value of 35.4565 ( $N=14.008$ ,  $Ag=107.880$ ) for the at. wt. of chlorine. An improved method for the preparation and purification of nitrosyl chloride from the reaction between nitrosylsulphuric acid and hydrogen chloride is described together with evidence that hydrogen chloride, chlorine, nitrogen, oxygen, and the oxides of nitrogen can be completely removed from this compound by fractional distillation. Precautions against photochemical decomposition were taken.

L. S. THEOBALD.

**Determination of the content of radioactive substances mixed with inactive matter by means of  $\alpha$ -rays.** A. B. VERIGO (Bull. Acad. Sci. U.S.S.R., 1929, 519—532).—Measurements have been made of the radioactive power of mixtures of black uranium oxide ( $U_3O_8$ ), uranium ore, active barium chloride, radium chloride, etc., in proportions varying from 1:1 to 1:5000, with chalk, clay, soda, inactive barium chloride, salts of copper, mercury, and calcium, etc. The materials were finely ground and strewn in a layer 1 mm. deep on a disc, the measure-

ments being made with the  $\alpha$ -ray electroscope and the results compared with those similarly obtained with black uranium oxide. With decrease in the concentration of the radioactive substance, the activity of such mixtures decreases in direct proportion to the volume concentration, that is, to the ratio of the volume of active substance present to the total volume of the mixture. The volume concentration  $C_v$  may be expressed by  $1/(1+\rho_1 d_2/\rho_2 d_1)$ , where  $\rho_1$  and  $\rho_2$  are the respective densities of the finely-divided active and inactive substances and  $d_1$  and  $d_2$  their amounts by weight. If  $A_0$  and  $A$  are the activities of the active substance and mixture, respectively,  $A=A_0/(1+\rho_1 d_2/\rho_2 d_1)$ , so that  $d_1/d_2$  is ascertainable and thus also the content of active substance in the mixture. This formula gives concordant results when the densities are determined on the triturated materials, but errors of 5–7% may arise if the values for the densities are taken from reference tables. In the latter case, it is of great importance that the degree of trituration of the active and inactive substances should be the same throughout the mixture, as only then can the ratio of their densities in the triturated state be the same as the ratio of the densities taken from the tables.

T. H. POPE.

**Heat emission of polonium.** (Mlle.) A. DORABIALSKA (Compt. rend., 1929, 189, 988–989).—A mean value of 24.0 g.-cal./hr.  $\pm 1.2\%$  (compared with an amount of polonium in radioactive equilibrium with 1 g. of radium) was found for polonium deposited on silver or nickel, or enclosed in a copper tube. The calculated number of  $\alpha$ -particles is then  $3.35 \times 10^{10}$ /sec., and their velocity  $1.59 \times 10^9$  cm./sec.

J. GRANT.

**Preparation of radium emanation.** O. ERBACHER and H. KÄDING (Naturwiss., 1929, 17, 997).—Peters and Weil (A., 1929, 1124) have claimed to have obtained a new penetrating  $\gamma$ -radiation from the first disintegration product of radium. Part of the work has been repeated, but it was not possible to find any trace of this radiation, which must proceed from a very short-lived substance. A. J. MEE.

**Group formation of radioactive atoms.** O. HAHN and O. WERNER (Naturwiss., 1929, 17, 961–962).—The observation of Chamié and of Herszfeld and Jedrzejowski (A., 1929, 620) that atoms of radioactive elements congregate into groups in solutions, is ascribed to hydrolysis. Whereas thorium-C shows the group formation in solutions in which hydrolysis may be expected, in the presence of substances which prevent hydrolysis no grouping is observed.

J. A. V. BUTLER.

**New interpretation of the regularities in radioactive disintegrations.** M. WOLFFE (Physikal. Z., 1929, 30, 899–901).—Theoretical. The probability of disintegration of a single atom from the instant of its genesis to the expiration of a time  $T$  determined by the initial conditions is zero; it then suddenly rises to unity and the atom disintegrates.

R. A. MORTON.

**Radiation responsible for the final rise in the absorption curves obtained with radium-(D+E).** G. FOURNIER and M. GUILLOT (Compt. rend., 1929,

189, 1079–1081).—The rise appears to be due to a primary  $\gamma$ -radiation emitted by the source, the effect of which is apparent only when the primary  $\beta$ -radiation is sufficiently attenuated. J. GRANT.

**Nature of the absorbable radiation accompanying the  $\alpha$ -rays of polonium.** (MME.) I. CURIE and F. JOLIOT (Compt. rend., 1929, 189, 1270–1272).—Strong sources of polonium produce an  $H$ -radiation with a maximum path of 16 cm. in air, resulting probably from transmutation of nitrogen, and mistaken for  $\gamma$ -radiation by Russell and Chadwick (A., 1914, ii, 87). Sources on nickel or silver give an  $H$ -radiation 0.2 as intense (path 14.5 cm.) due probably to occluded gases, whilst for silver there is also a superposed  $X$ -radiation ( $\lambda$  3.9 Å.) corresponding with the  $L$ -radiation of this element.

J. GRANT.

**Scattering of  $\beta$ -particles by light gases and the magnetic moment of the electron.** M. C. HENDERSON (Phil. Mag., 1929, [vii], 8, 847–857).—The scattering of  $\beta$ -particles by hydrogen, helium, argon, nitrogen, and air has been investigated. The scattering is single up to pressures of about 2 cm. for argon, 6 cm. for nitrogen, 50 cm. for helium, and 70 cm. for hydrogen, above which plural scattering predominates. The scattering power exceeds that calculated from the formula  $1.2N^2 + N$ , where  $N$  is the atomic number, and can be represented within 8% by  $1.2N^2 + 3.3N$ . The electron cannot have a magnetic moment as large as one Bohr magneton. C. W. GIBBY.

**Influence of temperature of the collector on yield by recoil from  $\beta$ -ray disintegration of thorium-B.** K. DONAT and K. PHILIPP (Z. Physik, 1929, 59, 6–13).—An apparatus for the study of recoil of atoms on to a low-temperature collector is described. The percentage of atoms collected compared with the theoretical number obtainable was, at  $20^\circ$  2–6.5, at  $-90^\circ$  8.9–14.4, at  $-180^\circ$  22.7. Further cooling to  $-245^\circ$  did not increase the yield. Factors influencing the yield are discussed.

A. B. D. CASSIE.

**Product of the radioactive disintegration of potassium.** A. V. FROST and O. FROST (Nature, 1930, 125, 48).—The calcium oxide was extracted from a microcline (11% K, 0.042% Ca) from Miask, Urals, and, after purification, used for a determination of the at. wt. of calcium. The value obtained (40.21, 40.24) is in accordance with the calculations of Hevesy and Logstrup (A., 1928, 684) if a loss of part of the calcium is assumed.

A. A. ELDRIDGE.

[Product of the radioactive disintegration of potassium.] A. HOLMES and R. W. LAWSON (Nature, 1920, 125, 48; cf. preceding abstract).—Loss of calcium would predominantly affect the proportion of  $\text{Ca}^{40.07}$ , and would raise the experimental value. The age to be considered is, however,  $2 \times 10^8$ , instead of  $10^9$ , years; the amount of  $\text{Ca}^{41}$  in the microcline calcium would then be only 5%, and the at. wt. of the microcline calcium is calculated to be 40.1.

A. A. ELDRIDGE.

**Counting of  $\alpha$ - and  $H$ -particles with the multiplication counter.** H. FRÄNZ (Physikal. Z., 1929, 30, 810–812).—The Geiger counter (cf. A., 1928,

114, 228, 367) has been adapted to the counting of  $\alpha$ - and  $H$ -particles in the presence of intense  $\beta$ - and  $\gamma$ -radiation, for the purpose of studying atomic disintegration and reflexion of  $\alpha$ -particles using the  $\alpha$ -emission from radium-*C*. The counter is improved by filling with hydrogen and using a special oscillograph instead of a thread electrometer. Examples of the performance of the new apparatus are given. Using  $\alpha$ -particles of 6.3 cm. residual range with a mean angle of  $125^\circ$  the yield in disintegrated aluminium atoms cannot exceed 10 per million. STETTER, in a discussion, described experiments on similar lines.

R. A. MORTON.

**Apparatus useful in the investigation of radioactivity.** O. ERBACHER, K. PHILIPP, and K. DONAT (Physikal. Z., 1929, 30, 913—918).—Principally devoted to experimental devices. Methods are described for opening specimen tubes, for the construction of a glass water-bath, of an air-tight  $\gamma$ -ray electroscope, an  $\alpha$ -particle electroscope, and a vessel for obtaining the active precipitate from dry radium and thorium preparations of high emanating power.

R. A. MORTON.

**Radioactive substances in the service of chemical and physico-chemical research.** O. HAHN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 535—542).—Examples are given of the utility of radioactive elements in following reactions in which the active substance acts as "indicator" in virtue of its adsorption on precipitates. The "emanation" method depends on the fact that substances of spongy texture allow emanations to diffuse outward much more freely than coarsely crystalline substances in which the outer geometrical surface is but little different from the total effective surface. Relative and absolute surface measurements can be made in this way, e.g., on ferric hydroxide and aluminium hydroxide gels, on barium chloride (dehydrated, fused, and crystalline), barium sulphate, and glass. By means of experiments at different temperatures data on softening and other processes involving dislocation of structure can be obtained.

R. A. MORTON.

**Wave mechanics of  $\alpha$ -ray tracks.** N. F. MOTT (Proc. Roy. Soc., 1929, A, 126, 79—84).—Mathematical. It is shown how one of the most typically particle-like properties of matter, i.e., the ray tracks formed by an  $\alpha$ -particle in a Wilson cloud chamber, can be derived from wave mechanics.

L. L. BIRCUMSHAW.

**Activation of metals in high vacuum to sorbents of any kind, including inert gases.** (FRAU) M. A. SCHIRMANN (Physikal. Z., 1929, 30, 876—879).—Thermal molecular streaming or transpiration of gases through narrow passages in porous activated materials depends on the temperature difference between the ends of a "tube" and on the ratio between the "tube" width ( $A$ ) and the mean free path ( $\lambda$ ) of the gas molecules. The equilibrium condition when  $A \ll \lambda$  is given by  $p_1/p_2 = (T_2/T_1)^{1/2}$ . Metals can be activated by treatment designed to fix  $A$  at a suitable mean value, and if they are then heated, a temperature difference is set up between the outside and the inside of the metal. Such out-gassed and activated metals exhibit sorption even of

the inert gases, the process being termed thermal molecular sorption on account of the reversible, purely gas-kinetic nature of the phenomenon. The hypothesis involves a definite relationship between  $A$  and  $\lambda$  for optimal effect, and experimental tests on the sorption of argon, neon, helium, nitrogen, etc., by means of platinum, palladium, and silver, provide confirmation of this and other relationships implicit in the conception of thermal molecular adsorption (cf. A., 1926, 1223).

R. A. MORTON.

**Pseudo-components of hydrogen.** A. SMITS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 951—960).—A discussion of the  $P$ - $X$ ,  $T$ - $X$ , and  $P$ - $T$  diagrams of hydrogen, which is considered as a pseudo-binary system of  $\alpha$ - and  $\beta$ -hydrogen. Ordinary hydrogen, in the solid, liquid, and gaseous states, thus consists of different equilibrium mixtures of the pseudo-components, of which the proportions are dependent on temperature. The b. p. of the  $\alpha$ - and  $\beta$ -forms are given respectively as  $20.26^\circ$  and  $20.43^\circ$  Abs. The natural b. p. of hydrogen,  $20.39^\circ$  Abs., corresponds with a mixture containing 99.7% of  $\alpha$ -hydrogen. Solid hydrogen forms mixed crystals very rich in the  $\alpha$ -form.

F. G. TRYHORN.

**Relativistic treatment of the [electronic] problem of many bodies.** L. GOLDSTEIN (Compt. rend., 1929, 189, 984—986).—For the relativistic treatment of electronic problems the "configuration universe," built up from configuration space and time, should be added to the four-dimensional universe. Breit's equation (Physical Rev., 1929, 34, 533) is employed to this end and is applied to the approximate determination of the electronic levels of helium.

J. GRANT.

**Electronic waves.** (SIR) J. J. THOMSON (Phil. Mag., 1929, [vii], 8, 1073—1092; cf. A., 1929, 231).—Mathematical. The energy in the waves accompanying a moving electron is investigated when the electron changes its velocity under the influence of an electric force. The distribution of electric waves when an electron passes through a crystal is calculated.

N. M. BLYTH.

**Stability relationships of principal and subsidiary [electronic] configurations.** A. F. RICHTER (Z. physikal. Chem., 1929, B, 6, 111—114).—The shapes of the curves showing the relation between atomic number and the work required to detach the first and second electrons from an atom are explained on the basis of the Lessheim-Samuel modification of the Bohr-Stoner scheme for the sub-grouping of electrons, and the ratio of the stabilities of the principal electronic configurations. F. L. USHER.

**Light yield in excitation by electronic impacts.** W. HANLE [with W. SCHAFFERNICHT] (Physikal. Z., 1929, 30, 901—905).—Under simplified experimental conditions the intensity of the light depends only on the electron velocity. The absolute value of the light yield has been determined for two cases: 3 quanta at line Hg 5461 are emitted per thousand gas-kinetic collisions between 60-volt electrons and mercury atoms; 8 quanta of the green helium lines at 5016 are emitted per ten thousand collisions using 50-volt electrons. The optical excitation function,

i.e., the function expressing yields at different electron velocities (in relative terms), has been determined for a considerable number of lines. In every case at least one maximum is recorded, the different lines being characterised by the position, height, and sharpness of the maximum. R. A. MORTON.

**Determination of the course of levels in the periodic system from the values of the eighth group.** V. DOLEJŠEK and K. PESTRECOV (Physikal. Z., 1929, 30, 898—899).—An equation of the type  $\nu/R = a + bN + cN^2 + dN^3 + eN^4$  applies to the rare gases with considerable accuracy and to a smaller extent to other elements, but the differences between the calculated and measured  $\nu/R$  values show periodic variations. The above equation holds for the six inert gases and for three other elements in the eighth group. Sommerfeld's formula for the relativity levels is of the same form, and it is possible to connect the equation with screening constants.

R. A. MORTON.

**Calculation of the electron affinity of hydrogen.** H. BETHE (Z. Physik, 1929, 57, 815—821).—The electron affinity of hydrogen calculated by the method of Hylleras is +17000 g.-cal. The electron distribution in  $H^-$ , He, and  $Li^+$  is discussed.

R. W. LUNT.

**Quantum-mechanical transference of energy between atomic systems.** J. FRENKEL (Z. Physik, 1929, 58, 794—804).—Mathematical.

A. B. D. CASSIE.

**Two theorems on the degeneration of gases.** F. I. G. RAWLINS (Z. Physik, 1929, 58, 830—832).—Mathematical.

A. B. D. CASSIE.

**Atomic transformations and their significance in chemistry and physics.** O. HAHN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 52—60).—A lecture on the history of atomic transformations from Becquerel to Millikan.

W. E. DOWNEY.

**Determination of the range of frequencies within the group of mechanical waves of an electron.** H. T. FLINT (Proc. Roy. Soc., 1929, A, 126, 40—63).—Mathematical.

L. L. BIRCUMSHAW.

**Wave mechanics and the dual aspect of matter and radiation.** A. M. MOSHARRAFA (Proc. Roy. Soc., 1929, A, 126, 35—40).—Mathematical. A principle of "reciprocal duality" between matter and radiation is proposed.

L. L. BIRCUMSHAW.

**Theory of the Faraday effect.** L. ROSENFELD (Z. Physik, 1929, 57, 835—854).—Mathematical.

R. W. LUNT.

**Melde's experiment and Sommerfeld's conditions.** L. DÉCOMBE (Compt. rend., 1929, 189, 1251—1253).—The applicability of Melde's conditions of acoustic resonance (*ibid.*, 684) to the case of an electron having a speed ( $v$ ) too great to justify the assumption that  $\sqrt{1-v/c^2}=1$ , is discussed. Two relations are obtained by considering the radial and azimuthal phenomena, and it is shown that Sommerfeld's conditions then conform with that of Melde.

J. GRANT.

**Magnetic moments of atomic nuclei.** E. FERMI (Nature, 1930, 125, 16).—Using for the

$s$ -terms Dirac's theory of the electron, and for the  $p$ -terms Pauli's method, the separations of the hyperfine structures for caesium and sodium lead to values of  $\mu/\mu_0$  (the ratio of the Bohr magneton to the magnetic moment of the nucleus) for  $k=1/2, 1, 3/2$ , and  $\infty$  as follows: caesium 1950, 1460, 1300, 980; sodium 890, 670, 600, 450.

A. A. ELDRIDGE.

**Heats of dissociation and absorption spectra of some complex molecules.** T. IREDALE and W. N. W. WALLACE (Phil. Mag., 1929, [vii], 8, 1093—1099).—The theory of the relation of thermal energy of decomposition to minimum light energy for photochemical decomposition is discussed. Investigations were made on methyl, ethyl, isoamyl, and isopropyl iodides, iodobenzene, allyl iodide, and *o*-iodotoluene. The long wave-length limits of the absorption bands in the liquid state were measured with a Hilger quartz spectrograph; the heats of binding were calculated from thermochemical data, and the heats of dissociation from the absorption limit. Satisfactory agreement is obtained.

N. M. BLIGH.

**Absorption spectra of water vapour and ammonia.** R. MEOKE (Physikal. Z., 1929, 30, 907—910).—Carbon dioxide, ammonia, and water vapour have been studied in the region 6000—10,000 Å., using sensitised plates. Carbon dioxide shows little absorption, ammonia shows three absorption bands, 8800 ( $3\nu_1 + \nu_2$ ), 7920 ( $4\nu_1$ ), 6470 Å. ( $5\nu_1$ ), the middle band being by far the most intense, whilst water vapour exhibits six bands at 9400 ( $3\nu_1$ ), 9050 ( $3\nu_2$ ), 8230 ( $3\nu_1 + \nu_3$ ), 7220 ( $4\nu_1$ ), 6960 ( $4\nu_2$ ), and 6530 Å. ( $4\nu_1 + \nu_3$ ). The interpretation of the results is discussed briefly.

R. A. MORTON.

**Absorption of copper *d*- and *l*-tartrates and of their mixture.** T. D. GHEORGHIU (Compt. rend., 1929, 189, 1260—1261).—The tartrates were prepared from *d*- or *l*-tartaric acid and copper acetate, and were dissolved in potassium hydroxide solution. Both solutions had the same absorption, but that of the mixture 1:1 was 19% higher.

J. GRANT.

**Absorption spectra of blood and blood constituents.** R. SUHRMANN (Physikal. Z., 1929, 30, 959—965).—The absorption of blood and of blood-corpuscles has been determined in the region 230—600  $\mu$ . A large, well-defined band is shown at 413  $\mu$  (max.) and less prominent maxima occur at 280, 340, 542, and 577  $\mu$ . Plasma shows a band at 280  $\mu$  which is weak in comparison with the bands described above. The curves characteristic of blood constituents for healthy people are fairly constant both as regards wave-length and intensity of absorption. In rats deficiency of vitamin-A or -D induces well-marked changes in absorption spectra which have diagnostic value.

R. A. MORTON.

**Ultra-violet absorption of inorganic salt solutions. I. Absorption of chlorides.** J. VON KOCZKÁS (Z. Physik, 1930, 59, 274—288).—The results of previous workers in this field have been somewhat contradictory, and some of the work here described is repetition. It was found that for aqueous solutions of the chlorides of calcium, strontium, and barium, there was a selective absorption band in the



middle ultra-violet region. The centres of the bands were approximately in the same place, viz., at 2690 Å., for all three chlorides. These results agree with those of Viterbi (A., 1927, 1122), but are at variance with the observations of Getman, who found no selective absorption with aqueous solutions of barium chloride. Getman also found sharp bands for manganous, zinc, and aluminium chloride solutions, but these could not be repeated. The molecular extinction coefficient decreases from barium to calcium. The Lambert-Beer law holds for nickel chloride. For cupric chloride the Lambert law, but not the Beer law, holds. For ferric chloride neither law is accurate. This may be due to hydrolysis, the colloidal particles making the absorption anomalous. A. J. MEE.

**Ultra-violet absorption of hydroxyl ion.** H. LEY and B. ARENDS (Z. physikal. Chem., 1929, B, 6, 240—246).—A preliminary report of ultra-violet absorption spectrum measurements with aqueous solutions of the alkali and alkaline-earth hydroxides. These solutions all give an absorption maximum at 186 mμ, which is characteristic of the hydroxyl ion. No maximum was obtained with pure water.

O. J. WALKER.

**Influence of magnetic fields on the lines of the NO β-bands and the doublet character of the NO δ-bands.** R. SCHMID (Z. Physik, 1929, 59, 42—47).—The apparatus is described in detail. The β-bands are resolved and investigated. The lines split into doublets in the magnetic field, the resolution increasing with diminishing rotational quantum number, the outer components being resolved into normal triplets. The doublet character of the δ-bands has been determined and it is deduced that the ground level is  $^2S$ . The term system of the NO molecule is compared with that of the Al atom.

J. FARQUHARSON.

**Structure of the CH band at 3143 Å. and a new NH band at 2530 Å.** T. HORI (Z. Physik, 1929, 59, 91—101).—The CH band was excited by a condensed spark between carbon and tungsten electrodes (about 1 cm. apart) in an atmosphere of hydrogen at 7—10 cm. In addition to the bands at 3900 and 4300 Å. a strong band with an intensity maximum at 3143 Å. appears. The combination relationships between the bands at 3143, 3900, and 4300 Å. have demonstrated that all have the same end state,  $^2\Pi$ . The band 3143 Å. has been analysed and corresponds with a  $^2\Sigma \rightarrow ^2\Pi$  transition. The moment of inertia in the  $^2\Sigma$  state is  $1.94 \times 10^{-40}$ .

By sparking between tungsten and sodium or lithium electrodes in an atmosphere of hydrogen and nitrogen at 7—10 cm. pressure, a new band at 2530 Å. was found, corresponding with a  $^1\Sigma \rightarrow ^1\Pi$  transition.

W. R. ANGUS.

**Extinction of fluorescence in solutions of dyes.** A. W. BANOW (Z. Physik, 1929, 58, 811—822).—A three hundred-fold increase in viscosity had no effect on the extinction curve. The absorption spectrum, which changes considerably with rapid, and slightly with slow extinction, was investigated with increasing concentration of the dye in solution and adsorbed on colloid particles. The curves for the two are alike. Hence extinction of fluorescence in solution is

probably due to polymerisation, although other factors may have an influence. A. B. D. CASSIE.

**Fluorescence of solutions. Molecular induction, polarisation, and duration of emission; photochemistry.** F. PERRIN (Ann. Physique, 1929, [x], 12, 169—275).—The theoretical implications of the experimental work on fluorescence carried out by the author and his colleagues (cf. A., 1929, 36, 1127; 1928, 346; 1927, 609; etc.), and also by other investigators, are discussed. The essential difference between fluorescence and phosphorescence does not depend on differences in the length of time during which emission persists. Molecules which have been excited to a state of internal instability by the absorption of incident light emit fluorescence spontaneously on returning to their normal state, and the mean life of the excited molecules represents the mean duration of fluorescence. True fluorescence is characterised by the expression  $\tau = \rho \tau_0$ , where  $\tau$  is the mean life of the excited molecules,  $\tau_0$  the reciprocal of the coefficient of probability of emission, and  $\rho$  the light yield in photons. If, on the other hand, the excited molecules, between absorption and emission of light, pass through an intermediate stable or metastable state, and can emit light only after receiving a certain increment of energy from the surrounding medium, the emission is a phosphorescence and is characterised by the increase to an indefinite extent, at low temperatures, of the time of emission. True fluorescence must also be distinguished from the Raman effect, not only by its intensity and selectivity, but because, in fluorescence, the spectrum of the radiation emitted is characteristic of the substance irradiated, whilst in the Raman effect it is the variation of frequency which is determined by the medium. Two definite types of fluorescence may be recognised: (1) Optical resonance observed in monatomic gases (metallic vapours) and resulting in the emission of monochromatic light of a frequency identical with that of the exciting radiation. (2) Fluorescence with a mean frequency less than that of the incident radiation. The first may be explained on the basis of the classical electromagnetic theory, but a satisfactory explanation of the second can be reached only by the application of the quantum theory. The return of the excited molecule to the normal state may take place, not only by emission of light, but also by interaction with another material system and production of kinetic energy. As a result the amount and mean duration of fluorescence are diminished. Deactivation takes place by resonance when an ordinary molecule of the same kind, or more generally a molecule with synchronous vibrations, is present in the neighbourhood of the activated molecule. It may also take place in another way through the presence of anti-oxygens (cf. A., 1927, 609) with loosely-bound electrons. The transference of energy resulting in deactivation in this case might be described as "collision of the third kind." Fluorescence light from solutions is, in general, partly polarised. From consideration of the laws of Brownian movement of rotation, the value of  $p$ , the degree of polarisation of the fluorescence light observed perpendicularly to the electric vector of a

polarised exciting wave, is equal to  $p_0/[1+(1-\frac{1}{3}p_0)RT\tau/V\eta]$ , where  $p_0$  is the value the degree of polarisation would have if the molecules did not rotate,  $V$  is the gram-molecular volume in solution,  $\tau$  the duration of fluorescence, and  $\eta$  the viscosity of the solution. It can be shown that this formula holds if, at a given temperature, when  $V$ ,  $p_0$ , and  $\tau$  have the same values for solvents of different viscosity, the reciprocal of the polarisation of the fluorescent light is a linear function of the reciprocal of the viscosity. This relationship has been tested by an experimental method which is described, and is found to be verified for solutions of fluorescein, resorufin, and quinine hydrogen sulphate in mixtures of water and glycerol in varying proportions, and of chlorophyll in castor oil, cyclohexanol, paraffin, and light petroleum. Values of  $\tau$  have been calculated, and are found, for most colouring matters which have a brilliant fluorescence, to be of the order of  $0.5 \times 10^{-8}$  sec., but anthracene, from experiments in dried Canada balsam and solidified alcohol, has a mean period of excitation of  $25 \times 10^{-8}$  sec. By studying the polarisation in the presence of the two different types of inhibitors mentioned above, the diminution in the mean period of excitation can be followed. The fluorescence of long duration of uranyl salts is also discussed (cf. A., 1929, 1127). Negative catalysis in photochemical reactions is considered. Its relation to induced deactivation of fluorescent molecules by inhibitors is indicated. It is also shown that the behaviour of anti-oxygenic compounds towards fluorescent substances supports the theory that auto-oxidations are chain reactions.

M. S. BURR.

**Fluorescence and temperature radiation.** P. PRINGSHEIM (Z. Physik, 1929, 57, 739—746).—Arguments are developed to show that a continual diminution in temperature in a gas fluorescing at a frequency greater than that of the exciting radiation (anti-Stokes fluorescence) is in accord with the second law. Lecture experiments in illustration are described.

R. W. LUNT.

**Raman effect.** V. Pinene and menthene. G. B. BONINO and L. BRÜLL (Gazzetta, 1929, 59, 729—733).—The Raman spectra of both *l*-pinene and menthene show lines for 3.28, 3.42, and 3.51  $\mu$  corresponding, respectively, with CH linkings of the aromatic nucleus type ( $\beta$ ), and of the saturated aliphatic types ( $\alpha$  and  $\gamma$ ). The mean of these lines, 3.40  $\mu$ , agrees closely with the infra-red band at 3.38  $\mu$  measured by Coblentz for *l*-pinene.

F. G. TRYHORN.

**Effective optical arrangement for observing the Raman effect in liquids and its application to the Raman spectrum of benzene.** R. BÄR (Physikal. Z., 1929, 30, 856—858).—The light from a mercury lamp is focussed by means of two lenses at the near end of a tube 1 metre long. Between this point and the lenses the scattering vessel is fitted with a broad conical end closed by means of a flat plate of glass. A small concave dentists' mirror is placed at the centre of the plate at an angle of  $45^\circ$  so that the scattered light can be reflected on to the slit of the spectrograph. The arrangement is highly efficient.

By means of a Zeiss filter (C, monochromat) it has been possible to make more certain the origin of certain Raman lines of benzene. The line  $\nu=21758$  arises both from the 4047 and 4358 Å. lines ( $\Delta\nu=1180$  and 2947), whilst the line 19990 confirms the Raman frequency 2947. Certain alleged Raman lines appear to be spurious, e.g.,  $\Delta\nu$  1360 has not been confirmed. The frequency 3179 is obtained quite definitely. Doubt is cast on the values  $\Delta\nu=266$  and 2630.

R. A. MORTON.

**Fluorescence sensitised in a liquid medium (transference of activation by molecular induction).** J. PERRIN and (Mlle.) CHOUCROUN (Compt. rend., 1929, 189, 1213—1216).—Perrin's theory (A., 1928, 1338) is extended by the introduction of "transference activation" by means of which a quantum of activation of one normal molecule can be transferred directly by induction to a normal molecule of another species at a distance without change in velocity. This transference has been demonstrated for a liquid medium in the case of phenosafranine, which produced under the experimental conditions a red and a greenish fluorescence. A slight secondary fluorescence due to illumination of the solution by its own fluorescence was also observed.

J. GRANT.

**Smekal-Raman effect in hydrogen-like atoms.** B. PODOLSKY and V. ROJANSKY (Physical Rev., 1929, [ii], 34, 1367—1372).—Mathematical. The method previously applied to dispersion by atomic hydrogen (cf. A., 1928, 577) is developed for the case of a hydrogen-like atom and yields intensity formulæ involving only summations, allowing intensity evaluations to be made more easily than from the extension of Schrödinger's method for treating dispersion. It is applied in detail to the first two levels of hydrogen, and formulæ are derived for the intensities of the Smekal-Raman lines with a shift corresponding with the first absorption line.

N. M. Blich.

**Raman effect of high-melting substances.** A. PETRIKALN and J. HOCHBERG (Z. Physik, 1929, 59, 114—116).—An apparatus for determining the Raman spectra of molten solids has been constructed. The necessary temperature is obtained by circulation of hot concentrated sulphuric acid, and it is possible with this apparatus to investigate substances melting up to  $280^\circ$ . An examination of the Raman spectrum of an eutectic mixture of sodium nitrate and potassium nitrate, m. p.  $217^\circ$ , showed a well-defined line corresponding with 9.6  $\mu$  in agreement with results obtained for the Raman effect of aqueous solutions of nitrates.

W. R. ANGUS.

**Optical anisotropy and theoretical intensities of Raman lines in diatomic gases.** C. MANNEBACK (Nature, 1930, 125, 88—89).—Theoretical. The scattering bound with the vibrational transitions  $|\Delta\nu|=1, 2, \dots$  and  $\Delta\nu=0$  is considered.

L. S. THEOBALD.

**Dipole moments of organic molecules in benzene solution.** O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1929, B, 6, 152—158; cf. *ibid.*, B, 4, 217).—A continuation of previous work. The following dipole moments have been determined: dibenzyl ketone, 2.65; *n*-butaldehyde, 2.46; paraldehyde, 1.9; benzoin, 3.46; benzil, 3.71; quinol

dimethyl ether, 1.74; nitroquinol dimethyl ether,  $4.56 \times 10^{-18}$ . Support is found for the view that the influence of phenyl on the keto-group is general.

F. L. USHER.

#### Electric moments of some non-rigid molecules.

A. WEISSBERGER and R. SÄNGEWALD (Physikal. Z., 1929, 30, 792—801).—The existence of electric moments for disubstituted benzene derivatives with identical substituents containing oxygen is ascribed to a non-symmetrical arrangement of the substituents, the oxygen valencies being inclined at an angle to each other and rotation about single linkings being possible. The electric moment of quinol diethyl ether varies little ( $1.72$ — $1.76 \times 10^{-18}$  e.s.u.) for the following solvents: benzene, carbon tetrachloride, cyclohexane, carbon disulphide. The values for dimethyl, diethyl, and di-*n*-propyl ethers are 1.32, 1.22, and  $0.86 \times 10^{-18}$  e.s.u., respectively. Benzene solutions of dimethyl, diethyl, di-*n*-butyl, and di-*n*-octyl ethers of quinol yield the respective values 1.81, 1.76, 1.79, and  $1.63 \times 10^{-18}$  e.s.u. Using the same solvent the moments for diethylbenzene and *p*-xylylene dichloride were 0.2 and 2.23, the former value being indistinguishable from zero by the method used. In addition, the dimethyl ethers of resorcinol and pyrocatechol gave values of 1.58 and 1.31, whilst the diethyl ethers gave 1.70 and 1.37. With the aid of certain assumptions the moment for the dimethyl ether of quinol is calculated from that of anisole (1.16) to be 1.64, as against the observed value 1.81. Caution should be used in basing stereochemical arguments on dipole moments for substances of this type as the anomalies cannot always be foreseen in any quantitative sense.

R. A. MORTON.

**Dielectric constant and association.** J. MALSCH (Physikal. Z., 1929, 30, 837—839).—The dielectric constant of liquids the molecules of which exhibit dipole structure decreases with increasing field strength for high fields. The dipole moments ( $\mu$ ) of benzyl, *n*-amyl, *n*-butyl, and *n*-propyl alcohols calculated from  $\Delta\epsilon/\epsilon$  agree fairly well with the observed values, these liquids having  $\epsilon$  values of 13.5, 16, 18.5, and 22, respectively. The agreement is bad for methyl and ethyl alcohols, nitrobenzene, and water, the dielectric constants being 26, 33, 36, and 80, respectively. The discrepancies, which are most marked with high  $\epsilon$  values, are ascribed to association.

R. A. MORTON.

**Change in dielectric constant of a very rarefied gas by means of electrons.** S. BENNER (Ann. Physik, 1929, [v], 3, 993—996).—Considerations, mainly theoretical, arising out of the work of Bergmann and Düring (A., 1929, 742).

R. A. MORTON.

**Dielectric polarisation of liquids.** VI. Ethyl iodide, ethyl alcohol, *n*-butyl alcohol, and *n*-octyl alcohol. VII. Isomeric octyl alcohols and molecular orientation. C. P. SMYTH and W. N. STROOPS (J. Amer. Chem. Soc., 1929, 51, 3312—3329, 3330—3341).—VI. The densities and dielectric constants of the above substances in hexane or heptane were measured at temperatures between about  $-100^\circ$  and  $90^\circ$  and at various concentrations. The effect of orientation is less in ethyl iodide than

in ethyl bromide. The polarisations of ethyl iodide in heptane conform to Debye's theory, but in the case of the alcohols molecular orientation exerts a great and complicated effect which prevents the exact application of Debye's theory. The results indicate that the electric moment of the molecule of a primary alcohol is independent of the length of the carbon chain. Anomalous dispersion and absorption for a wave-length of 600 metres appears to take place in the case of the pure alcohols and their solutions.

VII. The dielectric constants of 22 isomeric octyl alcohols have been measured over a wide temperature range (e.g.  $-40^\circ$  to  $70^\circ$ ); a tendency of anomalous dispersion and absorption for a wave-length of 600 m. was indicated. The polarisation of  $\beta$ -methylheptan- $\gamma$ -ol in benzene was determined; the electric moment of the molecule is only slightly lower than that of *n*-octyl alcohol. The dielectric constants of the various isomerides differ largely and attempts are made to explain this on the basis of the two possible simple orientations which two doublets in adjacent molecules could be expected to adopt. The explanations suggested are in harmony with the observed tendencies towards anomalous dispersion and also with certain unpublished X-ray diffraction data which show that, in general, where an abnormally high dielectric constant indicates that alcohol molecules are probably forming aggregates by the negative end of one doublet attracting the positive end of the other (first type of orientation) double molecules probably exist, whilst there are probably single molecules when the low dielectric constant indicates the interaction of single molecules in an orientation of the second type, i.e., when the doublets are parallel and in opposite directions.

S. K. TWEEDY.

**Rotatory dispersion of organic compounds.** XVIII. Potassium borotartrate. XIX. Validity of Drude's equation. T. M. LOWRY (J.C.S., 1929, 2853—2858, 2858—2863).—XVIII. An equimolecular mixture of potassium hydrogen tartrate, tartaric acid, and boric acid deposits *potassium borotartrate*,  $\text{KB}(\text{C}_4\text{H}_4\text{O}_6)_2$ . Potentiometric titrations of solutions of borotartronic acid indicate that it is comparable in strength with hydrochloric acid and is decomposed by excess of alkali. The new borotartrate contains a quadricovalent complex ion analogous to that of the fluoroborates. It has a higher rotatory power,  $(M)_{4358}^{25} + 287^\circ$ , than any recorded hitherto in solutions of tartaric acid or tartrates containing boric acid.

XIX. The squared term which Livens proposes to add to Drude's equation is too small to be detected in measurements of the rotatory dispersion of organic compounds, and is unproved even in the case of quartz. The infra-red term postulated by R. Wood, and more recently by C. E. Wood and Nicholas, in transparent organic compounds which exhibit anomalous dispersion is purely hypothetical, since no case is known in which the infra-red absorption bands of these compounds are optically active. The theoretical deductions of Kuhn endorse the validity of Drude's equation and are in general agreement with empirical observations as to the sign and relative magnitudes of the partial rotations due to centres of fixed and of induced asymmetry. F. G. TRYHORN.

**Influence of solvents and other factors on the rotation of optically active compounds. XXVIII. Rotation dispersion of mannitol and some of its derivatives. Rotation dispersion curves.** T. S. PATTERSON and A. R. TODD (J.C.S., 1929, 2876—2889).—The lines of the characteristic diagrams for hexacetyl-, hexabenzoyl-, hexanitro-, tribenzylidene-, and tri-*m*-nitrobenzylidene-mannitol pass almost exactly through the zero point of the diagram and in consequence the whole behaviour of these substances may be expressed by a simple formula. The rotational behaviour of these compounds is given by  $[\alpha]_D(\lambda^2 - 0.04) = 0.26 \times [\alpha]_{0.5461}$ . The rotation of mannitol in water and in glycerol solutions decreases with fall of temperature and would apparently become zero for all wave-lengths at about  $-3^\circ$ . It is suggested that the four types into which temperature-rotation curves have been divided by Wood and Nicholas (A., 1928, 817) are merely parts of the general curve previously discussed (J.C.S., 1916, 109, 1141).

F. G. TRYHORN.

**Influence of temperature and solvents on the rotatory powers of active substances.** R. LUCAS and (MLLE.) D. BIQUARD (Compt. rend., 1929, 189, 1077—1079).—Determinations of  $[\alpha]$  at 17—257° for solutions of *l*-fenchone in cyclohexane, benzene, acetic, sulphuric, formic, and phosphoric acids, for *d*-cyanocamphor in benzene and methyl and ethyl alcohols, and for *d*-anisylcamphor and methyl malate have been made, using the lines 5780, 5460, and 4358 Å. Temperature and solvent exert parallel effects on  $[\alpha]$ , but the results provide no evidence for the existence of a mixture of two active forms.

J. GRANT.

**Optical heterogeneity of a fused quartz disc.** L. W. TILTON and A. Q. TOOL (Bur. Stand. J. Res., 1929, 3, 619—628).—A 60° quartz prism to be used as a refractive index standard together with nine smaller prisms were cut from one disc, and the indices of refraction measured for five different wave-lengths. The standard was found to be uniform within  $\pm 4 \times 10^{-6}$  in its refractive index.

C. J. SMITHELLS.

**Optical constants of carbon in the infra-red region.** E. LITZENBERGER (Ann. Physik, 1929, [v], 3, 800—802).—Calculated and observed reflecting powers in the region 6—13  $\mu$  are in sufficiently good agreement to indicate a constant influence of the bound electrons on optical properties in the infra-red.

R. A. MORTON.

**Optical superposition among menthylamines and menthols.** J. READ and R. A. STOREY (Nature, 1930, 125, 86—87).—The sum of any two of the values of  $[\alpha]_D$  (in chloroform) for the four menthylamine bases is approximately equal in magnitude and opposite in sign to the sum of the values for the other two. This relationship also holds for 14 derivatives of each base; it is general for menthylamine derivatives of the type  $R \cdot CH_2 \cdot CO \cdot NHR'$ . The asymmetric group Me/H has a constant value of 25.4 units and the magnitude of the optical effect of this group is retained throughout the stereoisomerides, independently of the other two asymmetric groups present. A close parallelism between the optical rotations of the menthylamines and the corresponding menthols

so far as they are known is pointed out and it is predicted that the value of  $[\alpha]_D$  for *d*-neoisomenthol will be  $+2.6^\circ$ .

L. S. THEOBALD.

**Dispersion and absorption of sodium chloride in its residual ray region.** M. CZERNY (Physikal. Z., 1929, 30, 910).—The reflexion of light in the residual ray region from polished rock-salt surfaces and also the transmission of light from 44 to 65  $\mu$  through thin plates can be expressed by means of a normal dispersion formula applicable to data in other spectral regions. There are some discrepancies; e.g., a reflexion maximum at 38  $\mu$  does not fit the formula.

R. A. MORTON.

**Filled-space numbers [calculated] from dielectric constants and from refractive indices of gases.** W. HERZ (Z. anorg. Chem., 1929, 184, 295—297; cf. A., 1927, 498).—Values of the expressions  $(\epsilon - 1)/(\epsilon + 2)$  and  $(n^2 - 1)/(n^2 + 2)$ , denoting filled-space numbers, have been calculated for 25 gases and vapours. The substances chosen fall into two classes; in the first the expressions have approximately the same value, and in the second the dielectric constant quotient is from 2 to 21 times as great as the refractive index quotient. The first group comprises substances which do not form dipoles, and the second those the molecules of which possess considerable electric moment.

F. L. USHER.

**Dipole properties and displacement of absorption bands of homopolar molecules in solutions.** G. SCHEIBE and E. LEDERLE (Z. physikal. Chem., 1929, B, 6, 247—250).—It is shown that there is an empirical relationship between the displacement of absorption bands of homopolar molecules in various solvents and the molar volume of the solvent. The displacement of the maximum of an absorption band can be expressed quantitatively in terms of the dipole moments and radii of the various components by an equation which contains no arbitrary constants.

O. J. WALKER.

**Benzene ring problem.** R. REINICKE (Z. Elektrochem., 1929, 35, 877—880).—The space formula for benzene previously proposed (A., 1929, 1432) has been modified somewhat. The new formula, which has a centre of symmetry and a threefold axis of symmetry, and has its hydrogen atoms at the corners of a regular octahedron, is in satisfactory agreement with the facts of benzene substitution, and will also account for the differences in reactivity between the two rings of the naphthalene molecule.

R. CUTHILL.

**Magnetic and optical properties of the benzene ring in aromatic compounds.** S. BHAGAVANTAM (Proc. Roy. Soc., 1929, A, 126, 143—154).—Since it has been shown by Lonsdale (A., 1929, 750) that hexamethylbenzene crystallises in the triclinic system with one molecule in the unit cell, and that the carbon atoms in the molecule form flat hexagonal rings parallel to a cleavage plane, this compound is suitable for the study of the magnetic and optical properties of the benzene ring in its substitution products. The three principal g.-molecular magnetic susceptibilities, determined by means of a Curie balance, are  $-105$ ,  $-116$ , and  $-190 \times 10^{-6}$ , respectively, whilst the principal refractive indices for 5870 Å. are 1.8012,

1-7475, and 1-5032. The dispersion is very weak, unlike the cases that are usually met with in the organic field. The directions of the largest diamagnetic susceptibility and the least optical polarisability coincide with each other and with the normal to the plane of the benzene ring, phenomena which are believed to be characteristic of aromatic compounds. In the plane of the ring there is a slight magnetic and optical anisotropy, the sequence of magnitude being the same for both the magnetic and optical moments. This behaviour is typical of aliphatic compounds, but has not so far been observed in an aromatic substance. The observations with the crystal agree well with the values for the molecular anisotropy of benzene derivatives in the fluid state, derived from studies on light scattering and magnetic birefringence. A consideration of the cases of toluene, *p*-xylene, *m*-xylene, and hexamethylbenzene shows that the influence of the methyl groups is to diminish the magnetic anisotropy and to enhance the optical anisotropy of the benzene ring. An explanation of the asymmetry in the plane of the ring is suggested on the basis of an anisotropic carbon atom, of which the orbital areas of the valency electrons are not all similar (cf. Lonsdale, *loc. cit.*).

L. L. BIRCHUMSHAW.

**Influence of molecular form and anisotropy on the refractivity and dielectric behaviour of liquids.** K. S. KRISHNAN (Proc. Roy. Soc., 1929, A, 126, 155—164).—The theory recently developed by Raman and Krishnan (cf. A., 1928, 113, 348), based on the assumption that the molecules of a liquid are optically and electrically anisotropic, and that the polarisation field acting on a molecule is a function of its orientation, is discussed in relation to the actual experimental results available for benzene. The constants in the formulæ expressing the deviations from the Lorentz refraction formula are calculated from data on light-scattering by benzene and its variation with temperature. The change in the Lorentz refraction constant on passing from the vapour to the liquid state and the effect of temperature and pressure on the constant are evaluated numerically, and found to be in satisfactory agreement with experiment, as is the application of the theory to the dielectric behaviour of liquid benzene.

L. L. BIRCHUMSHAW.

**Complex salts and electroaffinity.** G. URBAIN (Anal. Fis. Quím., 1929, 27, 508—515).—Theoretical. H. F. GILLBE.

**Relation of the molecular volume at the m. p. to the ionic radii in alkali halides.** W. HERZ (Z. anorg. Chem., 1929, 184, 303—304; cf. A., 1925, ii, 840).—The ratio of the volumes occupied by a molecule of each of the liquid alkali halides at the m. p. to the sum of the (spherical) ionic volumes deduced from X-ray measurements is nearly constant, varying from 1.73 to 2.52. The m. p. is therefore considered to be a significant point on the scale of corresponding states as applied to ionic radii.

F. L. USHER.

**Structural principles of compounds of boron and hydrogen.** W. HELLRIEGEL (Z. anorg. Chem., 1929, 185, 65—95).—Theoretical. The structure of the known hydrides of boron is discussed on the basis

of the tervalency of boron and of a special type of association designated "boron linking," the latter serving to bind together units of the "normal" hydrides  $B_nH_{n+2}$ . A simplified rational nomenclature is proposed. F. L. USHER.

**Discontinuous change of properties in series of chemical compounds.** H. G. GRIMM and H. WOLFF (Prob. mod. Physik, Debye-Sommerfeld Festschr., 1928, 173—182; Chem. Zentr., 1929, ii, 377).—A discussion. A. A. ELDRIDGE.

**Transition from non-polar to polar linking.** R. SAMUEL and L. LORENZ (Z. Physik, 1929, 59, 53—82).—It is shown that the transition from non-polar to polar types of linking depends on two factors, firstly on the ionisation potential of the electro-positive half of the molecule, and secondly on the electron affinities of the atoms of the molecule. The latter is modified by such factors as heat of solvation. On these grounds an explanation is offered for the change in the equilibrium between polar and non-polar molecules with change in external conditions, e.g., changes in state. The phenomena of dissolution and hydrolysis are discussed from the point of view of this theory and the behaviour of acidic, basic, and amphoteric hydroxides is accounted for. Finally, the differences in the characters of acids with the same central atom produced by changing the surrounding atoms are discussed. J. W. SMITH.

**Magnetic moment of the oxygen atom.** O. E. KURT and T. E. PHIPPS (Physical Rev., 1929, [ii], 34, 1357—1366).—The atomic-ray method of Stern and Gerlach was employed; atomic oxygen was formed by an electrodeless ring discharge and the ray was detected by its oxidising action on freshly-sublimed litharge, the effect being intensified by initially saturating the oxygen with water vapour. The deflected rays consisted of an undeviated central line and a broad displaced line on each side. Hydrogen was substituted as a reference substance, and from the separations obtained the calculated magneton values were 0 and  $\pm 1.67$ ; those expected from the spectroscopic oxygen ground term are 0,  $\pm 3/2$ , and  $\pm 3$ , from which the effective magneton numbers, due to overlapping of images, would be 0 and  $\pm 1.71$ .

N. M. BLIGH.

**Kerr effect, scattering of light, and molecular structure.** K. L. WOLF, G. BRIEGLEB, and H. A. STUART (Z. physikal. Chem., 1929, B, 6, 163—209).—Theories of molecular anisotropy and of the depolarisation of scattered light are reviewed and discussed, particularly with regard to their application to the theory of atomic dipoles and the elucidation of molecular structure. The calculation of electrical and optical molecular constants from measurements of the Kerr effect and of depolarisation effects is dealt with and illustrated in the case of several simple inorganic and organic molecules.

O. J. WALKER.

**Rate of molecular collisions in liquid systems.** M. JOWETT (Phil. Mag., 1929, [vii], 8, 1059—1072; cf. Norrish and Smith, A., 1928, 249).—Theoretical. An attempt is made to calculate collision rates in liquids by application of the kinetic theory of diffusion, with the use of the concept of persistence of velocity.

Collision rates are found to be higher than those calculated by gas formulæ, and higher by a multiple which is probably constant for each liquid medium at any one temperature. Approximate formulæ are given for the general calculation of this multiple, which is of the order of 10. The temperature coefficient of collision rates is negative and approximately equal to that of viscosity. This introduces a correction into calculations of energies of activation for bimolecular reactions in liquid systems.

N. M. BLIGH.

#### Efficiency of production of fluorescent X-rays.

A. H. COMPTON (Phil. Mag., 1929, [vii], 8, 961—977).—The quantum theory of the emission of fluorescent X-rays leads to intensities greater than, and to an excitation of  $\beta$ -rays by the X-rays less than, those found experimentally. Homogeneous X-rays were allowed to fall on a radiator the fluorescence yield of which was to be determined, and from a study of the ionisation currents, values for the fluorescence yield, or ratio of the number of fluorescent  $K$  quanta to the number of photo-electrons ejected from the  $K$  shell, were found to be 0.68 for a molybdenum radiator, 0.56 for bromine, 0.54 for selenium, and 0.37 for nickel. The values seem to be independent of the wave-length of the exciting rays, and agree with those computed indirectly by Auger (cf. A., 1926, 1188) on the compound photo-electric effect. An expression is derived for calculating the relative intensities of two X-ray beams of different wave-length, in terms of the ionisation currents obtained and other factors.

N. M. BLIGH.

**X-Ray spectra by means of cinematography, oscillography, and fluorescence.** H. SEEMANN and K. F. SCHOTZKY (Naturwiss., 1929, 17, 960—961).—Improved methods of observing X-ray spectra by means of the cinematograph and oscillograph and by fluorescence are illustrated.

J. A. V. BUTLER.

#### Introduction of gas atoms into crystal lattices.

U. DEHLINGER (Z. physikal. Chem., 1929, B, 6, 127—134; cf. A., 1927, 924).—A discussion of the results of X-ray measurements and the decomposition curve of antimony oxides, in connexion with the mode of combination of oxygen in the antimony tetroxide lattice in stages ending with the formation of the pentoxide. Symmetrical arrangements are shown to occur when the oxygen atoms are not polarised in antimony tetroxide and the oxide  $\text{Sb}_6\text{O}_{13}$ , both of which are colourless. As the oxygen content is raised from  $\text{Sb}_6\text{O}_{13}$  to  $\text{Sb}_2\text{O}_5$  the oxygen atoms are considerably polarised and the solid darkens in colour.

F. L. USHER.

**Analysis of diaphragm system for the X-ray standard ionisation chamber.** L. S. TAYLOR (Bur. Stand. J. Res., 1929, 3, 807—827).—Errors arising from the assumption that the X-ray tube focus is a point source, and from the use of different types and arrangements of diaphragm with a standard ionisation chamber, are discussed.

C. J. SMITHELLS.

**Avoidance of contamination of the anticathode during the working of an analysis X-ray tube.** H. SEEMANN, P. GALLITELLI, and O. KANTOROWICZ (Z. Physik, 1929, 58, 823—829).—Vacua such as are

now attainable eliminate the deposit of impurity on the anticathode. Pure metal is best obtained on the anticathode by electrolytic deposition. This layer can carry the substance to be analysed.

A. B. D. CASSIE.

**X-Ray study of some lead salts.** M. MATHIEU (Bull. Soc. chim., 1929, [iv], 45, 1002—1008).—The crystal structures of a number of salts have been determined and are discussed. It is concluded that there is closer isomorphism between salts in which a substituted element enters a complex group than between those in which it plays the part of an ion.

C. W. GIBBY.

**X-Ray studies on binary systems of iron with nitrogen, phosphorus, arsenic, antimony, and bismuth.** G. HÄGG (Nova Acta Soc. Sci. Upsalensis, 1929, [iv], 7, 1—95; cf. A., 1929, 124).—The crystal structure and composition of intermediary phases were investigated in the binary phases of iron and the other elements of the group. Laue, powder, and rotation spectral photograms were obtained using iron  $K$  radiation, and for the two Fe-As phases, chromium  $K$  radiation. The preparation and analysis of the alloys are described. The  $\gamma'$  iron-nitrogen phase corresponds with  $\text{Fe}_4\text{N}$ , crystallising in a cubic lattice with  $a$  3.789 Å., and the unit cell containing one molecule; two possible structures were found. In the  $\epsilon$  phase with 8—11% of nitrogen, the iron atoms form a hexagonal close-packed lattice, the cell dimensions ranging from  $a$  2.695,  $c$  4.362 to  $a$  2.77,  $c$  4.42 Å. In the  $\zeta$  phase, possibly identical with  $\text{Fe}_2\text{N}$ , and having the maximum nitrogen content, the iron atoms form an orthorhombic lattice with  $a$  2.758,  $b$  4.819,  $c$  4.419 Å. Attempts to form cobalt and nickel nitrides were unsuccessful. Alloys containing up to 28.8% of phosphorus were investigated. The  $\text{Fe}_3\text{P}$  ( $\epsilon$ ) phase forms a tetragonal body-centred cell with  $a$  9.09,  $c$  4.446 Å., the unit cell containing 8 mols., probable space-group  $S_6^2$ . The  $\text{Fe}_2\text{P}$  ( $\zeta$ ) phase forms a hexagonal lattice with  $a$  5.852,  $c$  3.453 Å., the unit cell containing 3 mols., and space-group  $D_{3d}^2$  or  $D_{3d}^3$ . A possible  $\eta$  phase  $\text{FeP}$  was inconclusive. Alloys containing up to 56.9% of arsenic were investigated. The  $\text{Fe}_2\text{As}$  ( $\epsilon$ ) phase forms a tetragonal lattice with  $a$  3.627,  $c$  5.973 Å.; the unit cell contains 2 mols. The  $\text{Fe}_3\text{As}_2$  ( $\zeta$ ) phase is unstable below 795°. The  $\text{FeAs}$  ( $\eta$ ) phase has an orthorhombic structure with  $a$  3.366,  $b$  6.016,  $c$  5.428 Å., the unit cell containing 4 mols., probable space-group  $V_6^2$ . The  $\epsilon$  phase of the system Fe-Sb is a solid solution of iron in  $\text{FeSb}$  of composition 63.5—65.5% Sb. The dimensions of the hexagonal cell decrease from  $a$  4.106,  $c$  5.145 to  $a$  4.066,  $c$  5.127 Å. The unit cell contains 2 iron and 2 antimony atoms; the excess iron atoms are placed in the interstices of the lattice, explaining the decrease in dimensions with increasing antimony content. The  $\text{FeSb}_2$  ( $\zeta$ ) phase is orthorhombic with  $a$  3.189,  $b$  5.819,  $c$  6.520 Å.; the unit cell contains 2 mols., the space-group is  $V_6^2$ . X-Ray analyses confirmed the mutual insolubility of iron and bismuth.

N. M. BLIGH.

**Determination of orientation of crystals in rolled metal from X-ray patterns taken by the monochromatic pin-hole method.** W. P. DAVEY



C. C. NITCHIE, and M. L. FULLER (Amer. Inst. Min. Met. Eng. Tech. Pub., 1929, No. 243, 10 pp.).

#### CHEMICAL ABSTRACTS.

**Dimorphism in the aliphatic dicarboxylic acid series (azelaic acid).** W. A. CASPARI (J.C.S., 1929, 2709—2712).—Crystallisation of azelaic acid from warm saturated solutions gives a  $\beta$ -modification, which, like the  $\alpha$ -form obtained by the slow evaporation of solutions at the ordinary temperature, is monoclinic-prismatic and tabular on (001), but does not show (110). The values  $a$  5.61, 9.72;  $b$  9.48, 4.83;  $c$  27.20, 27.14 Å.,  $\beta$  136° 30', 129° 30' were found respectively for the  $\beta$ - and  $\alpha$ -forms by X-ray examination. The unit cell of each form contains 4 mols. The molecules thus have the same length of chain and are laid along the  $c$  axis in both polymorphs. The two forms cannot be distinguished by m. p., and it is suggested that the difference between them lies in the manner in which the molecules are grouped into aggregates.

F. G. TRYHORN.

**Mosaic crystals.** F. ZWICKY (Proc. Nat. Acad. Sci., 1929, 15, 816—822; cf. Smekal, A., 1929, 871).—The theory that ideal crystals, although dynamically stable, are not so thermodynamically is put forward. The thermodynamically stable forms are not completely characterised by the lattice structure deduced from X-ray analysis. In addition to the primary structure there is a secondary structure, also showing perfect regularity, which in general is to be interpreted as a slight variation in density, the elementary spacing of which is usually between 100 and 10,000 Å. "Structure insensitive" properties are due to the primary (lattice) structure, "structure sensitive" properties, e.g., elastic limit, breaking strength, thermal and electrical conductivity, to the secondary structure. The grounds for these conclusions and in particular for applying them to explain microscopic cracks in crystals are briefly given. Several deductions are drawn and shown to explain observed effects: spacings of 1.2  $\mu$  in bismuth, and of 2  $\mu$  in copper brought out by etching; apparent "Bragg reflexion" in the visible region from a crystal of potassium chlorate; production of a spectrum on illuminating an etched crystal of zinc with white light; the ease with which slipping occurs; and the hysteresis properties of single crystals.

C. A. SILBERRAD.

**Aggregation of atoms to molecules and crystals from the point of view of the atomic forms derived from a consideration of space lattices. II. Oxygen and doubly-linked carbon. III. Nitrogen.** R. REINICKE (Z. Elektrochem., 1929, 35, 880—909).—The theory previously developed in connexion with the structure of the benzene molecule (A., 1929, 1432) has been extended to the elucidation of the spatial configuration of a variety of organic and inorganic compounds. The results are in satisfactory quantitative agreement with experimental data and with the conception of the tetrahedral carbon atom.

R. CUTHILL.

**Energy changes by a variation from the crystallographic group.** H. M. EVJEN (Physical Rev., 1929, [ii], 34, 1385—1390).—Theoretical. The possibility of energy minima by a systematic departure

from the perfectly symmetrical crystal lattice is investigated and established for crystals of the rock-salt type, using the concept of "mosaic" structure (cf. Zwicky, A., 1929, 630).

N. M. BLIGH.

**Determination of the direction of the axis of a fibrous arrangement of micro-crystals.** S. TAKEYAMA (Mem. Coll. Sci. Kyoto, 1929, 12, 257—260).—The "crystallographic globe" of Yoshida (Japan. J. Physics, 1927, 4, 133) is used in examining the Laue photograph of the specimen.

W. E. DOWNEY.

**Arrangement of the micro-crystals in compressed single-crystal plates of aluminium.** Y. FUKAMI (Mem. Coll. Sci. Kyoto, 1929, 12, 261—264).—The orientations of the cubic micro-crystals of aluminium were found to be scattered by compression, to some extent around the (110) axis, which made the smallest inclination against the surface of the aluminium plate. The amount of such scattering increased with the reduction in thickness of the plate by compression, so that the arrangement tended to be fibrous.

W. E. DOWNEY.

**Crystallographic study of the diammines and tetrammines of palladium and platinum dichlorides.** A. M. BOLDYREVA (Ann. Inst. Platine, 1929, 7, 170—178).—The salts  $4\text{PdCl}_2 \cdot 4\text{NH}_3$ ,  $\text{PdCl}_2 \cdot 2\text{NH}_3$ ,  $4\text{PtCl}_2 \cdot 4\text{NH}_3$ ,  $\text{PtCl}_2 \cdot 2\text{NH}_3$ , and  $\text{PtCl}_2 \cdot 4\text{NH}_3 \cdot n\text{H}_2\text{O}$  all belong to the tetragonal system, and are uniaxial.

R. TRUSZKOWSKI.

**$\beta$ -Ammonium chloride and related crystal forms.** A. JOHNSON (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 492—505).—The ordinary or  $\beta$ -form of ammonium chloride has a cubic lattice and is isomorphous with caesium chloride. At 184°,  $\beta$ -ammonium chloride is converted into the  $\alpha$ -form, which has a face-centred cubic structure and is isomorphous with potassium chloride. The isomerism of other ammonium and alkali metal salts is also discussed.

W. E. DOWNEY.

**Crystal structure of calcium sulphate dihydrate (yeso).** J. PALACIOS and J. CABRERA (Anal. Fis. Quím., 1929, 27, 535—543).—The face-centred parallelepiped contains 4 mols. per unit cell, and has  $a$  10.45,  $b$  15.15,  $c$  5.67 Å.,  $\beta$  147° 20'.

H. F. GILLBE.

**Crystal structure of the A-modifications of sesquioxides of the rare earths.** W. ZACHARIASEN (Z. Krist., 1929, 70, 187—189; Chem. Zentr., 1929, ii, 526).—Polemical against Pauling (A., 1929, 1223).

A. A. ELDRIDGE.

**Ternary rhodium salts.** O. E. ZVJAGINSTSEV, E. A. VORONOVA, and S. I. CHORUNZHENKOV (Ann. Inst. Platine, 1929, 7, 113—117).—The optical and crystallographic properties of Wilm's chloronitrate are studied; this salt crystallises in the hexagonal system, and has the following elements of symmetry:  $\bar{C}L_3(\lambda_6)3L_23P$ . Conductivity measurements show that the salt dissociates into five ions in solution. Its formula is  $(\text{NH}_4)_3[\text{RhCl}_5(\text{NH}_4\text{Cl})]\text{NO}_3$ .

R. TRUSZKOWSKI.

**Space-group of potassium sulphate.** W. EHRENBURG and C. HERMANN (Z. Krist., 1929, 70, 163—170; Chem. Zentr., 1929, ii, 526).—The space-

group is  $v_s^s$ . Potassium and caesium sulphate, which have corresponding structures, are compared.

A. A. ELDRIDGE.

**Lattice constant of  $\alpha$ -iron.** G. MAYER (Z. Krist., 1929, 70, 383—384; Chem. Zentr., 1929, ii, 525—526).—Pure  $\alpha$ -iron (from iron pentacarbonyl) has  $a$  2.861<sub>06±3</sub> Å. at 22°. A. A. ELDRIDGE.

**Symmetry of potash feldspars.** T. BARTH (Fortschr. Min. Kryst. Petr., 1929, 13, 31—35; Chem. Zentr., 1929, ii, 408).—Microcline and orthoclase have an identical space lattice. The symmetry is discussed. A. A. ELDRIDGE.

**Comparative X-ray examination of silicates.** B. GOSSNER and F. MUSSGUG (Z. Krist., 1929, 70, 171—184; Chem. Zentr., 1929, ii, 544—545).—Eucrase has a monoclinic unit cell,  $a$  4.63,  $b$  14.30,  $c$  4.71 Å.,  $\beta$  100° 16';  $a:b:c=0.3237:1:0.3332$  (obs.), containing 4 mols. of  $\text{HAlO}_2, \text{BeSiO}_3$ ; space-group  $C_{2h}^2$ . Datolite has  $a$  9.64,  $b$  7.62,  $c$  4.82 Å.,  $\beta$  90° 9';  $a:b:c=0.6329:1:0.6345$  (obs.); the unit cell contains 4 mols. of  $\text{HBO}_2, \text{CaSiO}_3$ ; space-group  $C_{2h}^2$ . Willemite has  $a$  8.41,  $b$  5.14,  $c$  10.73 Å.;  $a:b:c=1.639:1:2.093$  (obs.);  $d$  3.472; the unit cell contains 4 mols. of  $\text{H}_2\text{ZnO}_2, \text{ZnSiO}_3$ ; space-group  $C_{2h}^2$ . A. A. ELDRIDGE.

**Regular intergrowth of staurolite with cyanite and their crystal structure.** E. SCHIEBOLD and G. M. CARDOSO (Fortschr. Min. Kryst. Petr., 1929, 13, 61—62; Chem. Zentr., 1929, ii, 408).—Cyanite has a pseudorhombic unit cell,  $b_0$  7.88,  $c_0$  5.65,  $[411]$  26.87 Å.,  $\alpha$  90° 5'; the rhombic unit cell of staurolite has  $a_0$  7.81,  $b_0$  5.64,  $c_0$  16.59 Å.,  $\alpha$  90° 0'. The unit cell of cyanite contains 2 mols. of  $\text{HFe}_2\text{Al}_9(\text{SiO}_6)_4$ ; that of staurolite contains 16 mols. of  $\text{Al}_2\text{O}_3, \text{SiO}_2$ .

A. A. ELDRIDGE.

**Structure of analcime.** W. HARTWIG (Fortschr. Min. Kryst. Petr., 1929, 13, 38—39; Chem. Zentr., 1929, ii, 544).—Crystals,  $d$  2.267±0.001, having the composition  $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , gave the value 13.68±0.02 for the length of side of the unit cube. The lattice is body-centred, with 16 mols. in the unit cube.

A. A. ELDRIDGE.

**Crystal structure of cryolite.** G. MENZER (Fortschr. Min. Kryst. Petr., 1929, 13, 56—57; Chem. Zentr., 1929, ii, 544).—The simple monoclinic lattice has  $a$  5.392±0.01,  $b$  5.594±0.01,  $c$  7.764±0.02 Å., with 2 mols. of  $\text{Na}_3\text{AlF}_6$  in the unit cell; hence  $a:b:c=0.964±0.003:1:1.388±0.005$ , which is in good accord with experimental values. The space-group is  $C_{2h}^2$  or  $C_{2h}^3$ . A. A. ELDRIDGE.

**Lattice constants of wollastonite.** B. GOSSNER and F. MUSSGUG (Zentr. Min. Geol., 1929, A, 175—185; Chem. Zentr., 1929, ii, 849).—Wollastonite has  $a$  15.31,  $b$  7.35,  $c$  7.08 Å.,  $\beta$  95° 25';  $d$  2.899; whence the unit cell contains 12 mols. of  $\text{CaSiO}_3$ . The space-group is probably  $C_{2h}^2$ . A. A. ELDRIDGE.

**"Trillings."** F. BERNAUER (Fortschr. Min. Kryst. Petr., 1929, 13, 36; Chem. Zentr., 1929, ii, 407).—Experiments on organic and inorganic substances, crystallised from fusion or from solutions in presence of suitable addenda, are described. Supercooling is necessary for the formation of trillings.

A. A. ELDRIDGE.

**Theory of recrystallisation.** G. TAMMANN (Z. anorg. Chem., 1929, 185, 1—34; cf. A., 1929, 1225).—Results obtained during the past 20 years are discussed with reference to (1) the condition of a crystal after plastic deformation, (2) the formation of recrystallisation nuclei, (3) nature of the interstitial material, (4) displacement of grain boundaries, and (5) change in orientation of crystallites. Deformation of single crystals leads to an increase in the thermodynamic potential of atoms lying in the slip planes and in their immediate neighbourhood. In consequence of this the lattice parameter has not the same value everywhere, as shown by a broadening of the X-ray interference lines in cold-worked metals. On heating, the lines resume their normal sharpness at temperatures far below that at which any structural change occurs. The formation of recrystallisation nuclei takes place mainly, in cold-worked metals, at places of increased potential; in stretched tin, for example, heating at 100° develops large numbers of small crystals along the Lüders-Hartmann lines. The interstitial substance can be isolated, in soft metals, by dissolution of the metal in suitable solvents, in the form of a honeycomb-like structure which usually consists of a thin film of oxide or silicate. The formation of these films exerts a dominating influence on the growth of individual crystals as affected by temperature. In a freshly-solidified metal the grains are hindered from growing owing to the film of interstitial substance preventing contact, whilst an adequate rise of temperature promotes dissolution of the film and consequent growth of the crystals until a fresh film is formed. Factors determining the extent and direction of growth are discussed fully. Cold-working leads to formation of larger crystals owing to mechanical rupture of the films. At the commencement of recrystallisation the grain size is uniform, but later assumes a Maxwell distribution about a mean size. F. L. USHER.

**Dependence of the minimum temperature of recrystallisation on the fundamental characteristic values of solids.** A. BOCHVAR (J. Appl. Phys., Moscow, 1927, 4, 47—53).—The hypothesis that in every solid substance the amplitude of the atomic vibrations at the recrystallisation point is a definite fraction of the mean atomic distance is proposed. Hence  $T_{\text{recryst.}}/T_{\text{fusion}}=\text{const.}=0.38$  (approx.).

CHEMICAL ABSTRACTS.

**Mechanism of ionic conduction in solid compounds [of the class of] good conductors.** W. JOST (Z. physikal. Chem., 1929, B, 6, 88—102).—Polemical against Smekal (A., 1929, 1146).

F. L. USHER.

**[Mechanism of ionic conduction in solid compounds of the class of good conductors.]** A. SMEKAL (Z. physikal. Chem., 1929, B, 6, 103—110).—A reply to Jost (preceding abstract). F. L. USHER.

**Electrical resistance of thin metal layers.** W. BRAUNBEK (Z. Physik, 1930, 59, 191—197).—Earlier work of Volmer and Estermann on the vaporisation coefficients of solid and liquid mercury involved the measurement of the resistance of thin layers of mercury. The results then obtained are collected and discussed, the variation of the specific resistance

of the mercury with the thickness of the layer being determined. The curve of specific resistance against thickness shows that for very thin layers the specific resistance is very great, but it falls at first rapidly, then slowly, with increasing thickness, approaching asymptotically the value for thick layers. It is a remarkable fact that the same form of curve is obtained although the experimental conditions may be entirely different. Experiments were carried out over the temperature range of  $0^{\circ}$  to  $-30^{\circ}$ , and the curves had the same form at all temperatures.

A. J. MEE.

**Electrical resistance law at low temperatures.** F. BLOCH (Z. Physik, 1930, 59, 208—214).—Theoretical. The theoretical electrical resistance law at low temperatures is found to be a  $T^5$  law.

A. J. MEE.

**Magnetic properties of nickel-manganese alloys.** S. KAYA and A. KUSSMANN (Naturwiss., 1929, 17, 995—996).—The magnetic properties of nickel-manganese alloys of various compositions were investigated. The Curie point of these alloys starts at that of pure nickel ( $356^{\circ}$ ), but is lowered by the addition of manganese until it reaches ordinary temperatures with 25% of manganese. With increasing manganese content, at ordinary temperatures there is a distinct increase in the saturation value for small manganese contents, an effect which is still present at the temperature of liquid air. Between 5 and 10% Mn, the curve reaches a maximum, which, at ordinary temperatures, lies about 10%, at  $-193^{\circ}$  about 20%, higher than the corresponding value for pure nickel. With alloys containing more than about 10% Mn some transformation occurs in the alloy at a temperature between  $400^{\circ}$  and  $600^{\circ}$ . An alloy which has been slowly cooled through this temperature range and tempered is more highly magnetic than one which has been rapidly cooled through this stage. With increasing manganese content there is a greater difference between the two states, so that rapidly cooled alloys containing 24% Mn have only a fraction of the magnetisability they have if cooled slowly.

A. J. MEE.

**Diamagnetism of solid bismuth.** P. EHRENFEST (Z. Physik, 1929, 58, 719—721).—The high diamagnetic susceptibility of bismuth per g.-atom seems due to electronic orbits encircling more than one atom, the electrons being coupled to give a group of zero magnetic moment. A. B. D. CASSIE.

**Law connecting different properties of ferromagnetic crystals.** N. S. AKULOV (Z. Physik, 1930, 59, 254—264).—Mathematical. A number of formulæ derived for various magnetic properties of single crystals are in good agreement with experiment. The change of electrical resistance of a crystal under the influence of a magnetic field is also calculated. As a result of these formulæ a law connecting the different properties of ferromagnetic crystals is obtained.

A. J. MEE.

**Absolute saturation of ferromagnetic substances and extrapolation formulæ for the same in terms of field and temperature.** P. WEISS and R. FORRER (Ann. Physique, 1929, [x], 12, 279—374).—An examination of the atomic moments of ferro-

magnetic substances to test the Weiss magneton as a common measure of all atomic moments (cf. A., 1929, 5). Various extrapolation formulæ are considered for calculating absolute saturation at  $0^{\circ}$  Abs. The causes of error in previous determinations (chiefly impure materials and neglect of magnetic anisotropy) are discussed. Full details of the apparatus and method used in determining  $\sigma$  for values of  $H$  up to 19,900 gauss ( $H_c=18,550$  gauss), and at temperatures from the ordinary down to that of liquid air, are given. The reduction in saturated magnetisation due to the substance examined being in powder form is discussed, and instances are given where it is as much as 9% (iron) and 4% (nickel). Results for the Weiss magneton are calculated for various metals and compounds at different temperatures.

C. A. SILBERRAD.

**Magnetostriction of single crystals of cobalt.** Z. NISHIYAMA (Sci. Rep. Tôhoku Imp. Univ., 1929, 18, 341—357).—Magnetisation of single crystals of cobalt in the direction (0001) results in a small contraction ( $dl/l=4\times 10^{-6}$ ) in the transverse and longitudinal axes of the specimen. When the crystal is magnetised in the (1010) the longitudinal contraction is relatively great ( $dl/l=20\times 10^{-6}$ ), the contraction in the (1120) direction is twice as great as this, and there is a corresponding increase in length in the (0010) direction. Application of the magnetic field in the plane (1010) causes a contraction in the longitudinal direction and a corresponding contraction in the transverse direction. In polycrystalline aggregates there is a contraction in the longitudinal and an expansion in the transverse direction, the resulting effect being a small contraction in volume.

A. R. POWELL.

**Heat evolution during the magnetisation of steels.** K. HONDA, J. ÔKUBO, and T. HIRONO (Sci. Rep. Tôhoku Imp. Univ., 1929, 18, 409—417).—Experiments on three steels have shown that the heat evolution in ergs during magnetisation is approximately equal to the hysteresis loss magnetically observed and that more than 50% of the energy applied in magnetisation in a strong field is dissipated as heat. These facts are in accordance with the authors' theory of magnetisation (*ibid.*, 1917, 6, 183).

A. R. POWELL.

**Barkhausen effect.** F. PREISACH (Ann. Physik, 1929, [v], 3, 737—799).—The hysteresis loop results from the superposition of continuous and discontinuous processes exhibiting respectively a parallelism with reversible and irreversible processes. No simple general relation between the steepness of the magnetisation curve and the Barkhausen effect can be traced. The effect on the magnetisation curve of pre-treatment and of the elastic condition has been studied for iron, nickel, and alloys. New data concerning the characteristics of the Barkhausen effect have been obtained and it is found that existing theories of ferromagnetism are not only inadequate but in some respects opposed to the data. Some of the results may be harmonised with the basic ideas of the Weiss-Heisenberg theory.

R. A. MORTON.

**Magnetic properties of mesomorphic substances.** G. FOËX (J. Phys. Radium, 1929, [vi], 10,

421—438).—The magnetisation coefficients of a number of diamagnetic organic compounds contained in quartz tubes and carefully purified from ferromagnetic impurities were measured as a function of the temperature by Faraday's method, using an apparatus previously described (cf. A., 1926, 932). The orientation of the nematic and the magnetisation of the ferromagnetic molecules vary with temperature according to similar laws. The curves show a similarity to those of nickel and ferro-cobalt. The passage from the nematic to the liquid state may be regarded either as a change of state or as a passage through a Curie point without change of phase. The magnetic properties of *p*-azoxyanisole are discussed in relation to the theory of diamagnetism.

N. M. BLIGH.

**Magnetic viscosity.** C. LAPP (Ann. Physique, 1929, [x], 12, 276—277).—A reply to Bozorth (Physical Rev., 1928, 32, 124). The criterion employed by the author proves conclusively that the time lag in magnetisation observed by him (cf. B., 1927, 845) is due to magnetic viscosity and not to induced currents as suggested by Bozorth (*loc. cit.*). M. S. BURR.

**Determination of mol. wt. by Horstmann's combination of vapour-pressure measurements.** I. Molecular formula of auric chloride. W. FISCHER (Z. anorg. Chem., 1929, 184, 333—344).—The method of calculation of mol. wts. by combination of directly determined vapour pressures with those obtained by a transport method is described, together with a static method for the measurement of the vapour pressure of a substance which undergoes heterogeneous dissociation. By application of the method the molecular formula of auric chloride vapour between 150° and 260° is found to be  $\text{Au}_2\text{Cl}_6$ .

H. F. GILLBE.

**Thermodynamics and kinetics of thermoelectric phenomena in crystals, especially the Bridgman effect.** II. P. EHRENFEST and A. J. RUTGERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 883—893).—Mathematical.

**Dependence of some electrical and electro-optical constants of nitrobenzene and nitrotoluenes on the degree of purity.** F. HEHLGANS (Physikal. Z., 1929, 30, 942—946).—Nitrobenzene purified in the ordinary way still contains impurities capable of influencing the physical constants. Improved methods of purification result in the following changes: specific resistance in  $\text{ohm/cm.}^3$   $5 \times 10^7$  to  $1 \times 10^{10}$ ; breakdown voltage  $5 \times 10^4$  to  $15 \times 10^4$  (volt/cm.<sup>3</sup>); Kerr constant for 5461 Å.,  $22 \times 10^{-6}$  to  $41 \times 10^{-6}$ ; dielectric constant 36.4—38.4. For *m*-nitrotoluene the Kerr constant is  $1.43 \times 10^{-4}$  and the dielectric constant is 29.3.

R. A. MORTON.

**Measurements with the aid of liquid helium.** IV. W. MEISSNER and H. SCHEFFERS (Physikal. Z., 1929, 30, 827—836).—The resistance of gold (two single crystals and one wire, all of very high purity) has been studied at temperatures between 1.30° and 78.5° Abs. and in magnetic fields up to 13,000 gauss. It is best to compare  $\Delta R/R_0$  and not  $\Delta R/R$  with the field strength  $H$  ( $R_0$  being the resistance at 0° without magnetic field). For the high field strengths so far applied  $dR/dH$  is strikingly independent of  $H$

and of temperature. The magnitude  $V^{-1/3} \cdot d\rho_0/dH$  ( $\rho_0$  being the specific resistance at the characteristic temperature  $\theta$  of the metal and  $V$  its atomic volume) for various metals has been studied in relation to positions in the periodic system. The quantity is approximately constant for each group and does not vary greatly from group to group. Only arsenic, antimony, bismuth, and the ferromagnetic elements show discrepancies (cf. Kapitza, A., 1929, 632).

R. A. MORTON.

**Mechanism of rectification in the cuprous oxide rectifier.** W. SCHOTTKY and W. DEUTSCHMANN (Physikal. Z., 1929, 30, 839—846).—Experiments on the electrical properties of the high-resistance film responsible for the rectifying action are detailed and a preliminary interpretation is given.

R. A. MORTON.

**Disturbance of the super-conductance of the compound  $\text{Bi}_5\text{Tl}_3$  and of the alloys Sn-Bi and Sn-Cd by magnetic fields.** W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 874—882).—The fall of the magnetic threshold value for  $\text{Bi}_5\text{Tl}_3$  with decreasing temperature is much steeper than for pure super-conductors. This compound which becomes super-conductive above 4.2° Abs. requires a field higher than 1250 gauss to disturb its super-conductance. The value 6.5° Abs. is found by extrapolation for the transition point of  $\text{Bi}_5\text{Tl}_3$ . The eutectic mixtures of the systems Sn-Bi and Sn-Cd have been studied to determine whether the behaviour of  $\text{Bi}_5\text{Tl}_3$  is a general one for alloys. From the results it is stated that for the same temperature difference from the transition point higher field intensities are required to restore the resistance in the case of alloys than in that of pure super-conductors. Extrapolation of the results for  $\text{Bi}_5\text{Tl}_3$  indicates that at 1.3° Abs. a field of 9 kilogauss would be necessary to disturb the super-conductance. This would render possible the production of such intense magnetic fields with a solenoid of  $\text{Bi}_5\text{Tl}_3$  wire without production of heat.

F. G. TRYHORN.

**Electric conductivity of fused silica.** F. LAUSTER (Z. Physik, 1929, 59, 83—90).—The specific resistance-temperature curve for fused silica shows first a minimum, then rises to a secondary minimum, and finally falls continuously towards the temperature axis. Silica fused in a vacuum has a much lower specific resistance which varies almost regularly with temperature. Pure silica is most likely an ordinary conductor. The rapid temperature variation of resistance of ordinary fused silica is too uncertain for its use as a sensitive thermometer.

A. B. D. CASSIE.

**Kerr effect in gases and vapours.** I. Method and results for sulphur dioxide, methyl chloride, methyl bromide, ethyl chloride, and dimethyl ether. H. A. STUART (Z. Physik, 1929, 59, 13—34).—A method for accurate measurement of electric double refraction in gases and vapours is described. A source of error in Brace's compensator is discussed. The Kerr constants are as follows: sulphur dioxide  $9.2 \times 10^{-15}$ , methyl chloride  $35.6 \times 10^{-15}$ , methyl bromide  $44.5 \times 10^{-15}$ , dimethyl ether  $4.9 \times 10^{-15}$ , ethyl chloride  $53.3 \times 10^{-15}$ . The axes of the optical deformation

ellipsoid are calculated for methyl chloride, methyl bromide, and dimethyl ether. Models hitherto suggested for ethyl chloride do not fit the results, but assuming a valency angle of  $110^\circ$ , the angle between the electric dipole and the principal axis of the deformation ellipsoid is approximately  $15^\circ$ .

A. B. D. CASSIE.

**Effect of crystalline structure on magnetic susceptibilities of a new magnetic balance based on the principle of interference of light.** S. S. BHATNAGAR and R. N. MATHUR (Phil. Mag., 1929, [vii], 8, 1041—1055).—An apparatus of increased sensitivity is described, depending on the measurement of the displacements of the substance in a magnetic field in terms of the shift of interference fringes, using an adapted Rayleigh interferometer. Changes in susceptibility were expected to throw light on changes of crystalline structure. Investigations were made on rhombic and monoclinic sulphur and on yellow and red mercuric iodide; the values found for the specific diamagnetic susceptibilities  $\times 10^6$  were 0.487, 0.462, 0.272, and 0.272, respectively. No definite results could be obtained for plastic sulphur.

N. M. BLIGH.

**Susceptibility of nitric oxide at different temperatures.** J. AHARONI and P. SCHERRER (Z. Physik, 1929, 58, 749—765).—The mean magnetic moment of the nitric oxide molecule was determined at two temperatures, and the results agree with Van Vleck's theory (cf. A., 1927, 609; 1928, 572).

A. B. D. CASSIE.

**Allotropic modifications of sulphur. I. Cryoscopy of sulphur.** C. R. PLATZMANN (Bull. Chem. Soc. Japan, 1929, 4, 235—243).—The lowering of the m. p. of sulphur ( $114.5^\circ$ ) by various organic substances has been investigated and a value of 213 obtained for the cryoscopic constant of sulphur. From this the latent heat of fusion of sulphur is calculated to be 14.1 kg.-cal./g. Acids like  $\alpha$ -naphthoic acid and thiophen-2-carboxylic acid tend to form double molecules in solution in sulphur. Arsenious sulphide forms single  $As_2S_3$  molecules in dilute sulphur solutions, but polymerises in more concentrated solutions. Selenium tetrachloride gives only half the normal mol. wt., probably due to the formation of selenium and sulphur monochlorides.

O. J. WALKER.

**Thermal conductivity of a single crystal of bismuth in a transverse magnetic field.** G. W. C. KAYE and W. F. HIGGINS (Phil. Mag., 1929, [vii], 8, 1056—1059).—Using an apparatus previously described (cf. A., 1929, 385) the change in thermal conductivity of a bismuth crystal was measured for various orientations of the crystal, the heat-flow being in each case perpendicular to the magnetic field, and results are plotted for fields up to 11,000 gauss. The decrease in thermal conductivity varied from 4.9 to 16%.

N. M. BLIGH.

**B. p. of water as a function of the pressure.** A. ZMACZYNSKI and A. BONHOURE (Compt. rend., 1929, 189, 1069—1070).—Swientoslawski's apparatus (A., 1929, 255) was used, and an accuracy of  $0.002^\circ$  obtained. Measurements between pressures ( $p$ ) of 683—832 mm. of mercury were shown by the

method of least squares to correspond with the function  $\theta = 57.2587 + 0.0793722p - 35.5273 \times 10^{-6}p^2 + 6.6950 \times 10^{-9}p^3$ , where  $\theta$  is the b. p. on the normal hydrogen scale.

J. GRANT.

**Heats of fusion of some paraffin hydrocarbons.** G. S. PARKS and S. S. TODD (Ind. Eng. Chem., 1930, 21, 1235—1237).—The heats of fusion of hexamethylmethane, *n*-eicosane, *n*-pentacosane, and *n*-tritriacontane have been measured by a method of mixtures. No direct regularity exists, but on plotting the molal entropies of fusion against the number of carbon atoms in the chain a regular curve is obtained with an average deviation of only 0.3 g.-cal. By means of the equation for this curve, the fusion data for the entire series of normal hydrocarbons from methane to tritriacontane have been calculated. Branched-chain isomerides showed an apparent progressive decrease of the entropy of fusion with an increase in the amount of branching, but the effect cannot be predicted.

H. S. GARLICK.

**Influence of water vapour on the heat radiation of exploding gaseous mixtures. Specific heat of water vapour at high temperatures.** K. WOHL and G. VON ELBE (Z. physikal. Chem., 1929, B, 6, 78; cf. A., 1929, 1394).—A misquotation in a paper recently published is corrected.

F. L. USHER.

**Extension of Trouton's rule to the critical point.** V. A. KIREEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1369—1376).—Empirical formulæ connecting Trouton's coefficient at the b. p. with the critical constant and with the internal energy of the molecules of substance are derived. Trouton's rule is shown to be applicable to liquids also at their critical point.

R. TRUSZKOWSKI.

**Determination of  $C_p/C_v$ .** R. RINKEL (Physikal. Z., 1929, 30, 805).—A simpler and more accurate development of the work of Rüchardt (cf. A., 1929, 497) is described.

R. A. MORTON.

**Halides of the rare earths. III. Iodides of the elements of the cerite earths and redetermination of the m. p. of the chlorides.** G. JANTSCH, H. GRUBITSCH, F. HOFFMANN, and H. ALBER (Z. anorg. Chem., 1929, 185, 49—64; cf. A., 1927, 530; 1929, 1407).—Redetermination of the m. p. of the chlorides of lanthanum, neodymium, samarium, and europium has given the following values:  $862^\circ$ ,  $760^\circ$ ,  $678^\circ$ , and  $623^\circ$  in the order named, with an error of  $\pm 2^\circ$ . Ceric and praseodymium chlorides melted over the intervals  $795$ — $812^\circ$  and  $769$ — $782^\circ$ , respectively, owing probably to the presence of different modifications. Materials from different sources were used and their purity was checked spectroscopically. Anhydrous iodides have been prepared by the method of Ephraim (A., 1928, 217; 1929, 864) and, in the case of ceric iodide, that of Matignon (A., 1906, ii, 675), but attempts to prepare europium iodide were unsuccessful on account of its reducibility even at low temperatures. The m. p. of the iodides of lanthanum, ceric cerium, praseodymium, and neodymium are:  $761^\circ$ ,  $752^\circ$ ,  $733^\circ$ , and  $775^\circ \pm 2^\circ$ . Samarium iodide melted over the interval  $816$ — $824^\circ$ , with decomposition.

F. L. USHER.

**M. p. of calcium, strontium, and barium.** H. HARTMANN and G. MAY (Z. anorg. Chem., 1929, 185, 167—171).—The m. p. of strontium containing 0.3% Fe and 0.6% N is  $752^{\circ} \pm 2^{\circ}$ , and of barium containing 1.7% Fe and 0.8% N,  $658^{\circ} \pm 1^{\circ}$ . F. L. USHER.

**Thermal expansion of liquids according to van der Waals.** J. E. VERSHAFFELT (Phil. Mag., 1929, [vii], 8, 858—860).—An objection to the conclusions of Thatté (A., 1929, 754). C. W. GIBBY.

**Calorimetric determination of the difference of energy content of the two modifications of hydrogen.** G. VON ELBE and F. SIMON (Z. physikal. Chem., 1929, B, 6, 79—87; cf. Eucken and Hiller, A., 1929, 497).—From data furnished by the band spectrum of hydrogen the energy of rotation at different temperatures can be calculated both for equilibrium mixtures of the para- and ortho-modifications and for a mixture containing a constant proportion. The heat change associated with the transformation of the latter mixture into the former can be thus shown to be 78 g.-cal. at  $77.5^{\circ}$  Abs. and 247 g.-cal. at  $20.4^{\circ}$  Abs. These quantities have been determined experimentally by measuring the heats of adsorption and of desorption of ordinary hydrogen on charcoal at the temperatures mentioned. Since the charcoal brings about a rapid change into the equilibrium mixture, the difference between the two thermal quantities represents the heat of transformation. The mean results obtained are:  $74 \pm 7$  g.-cal. per mol. at  $77.5^{\circ}$  Abs., and  $241 \pm 10$  g.-cal. per mol. at  $20.4^{\circ}$  Abs., in agreement with theory.

F. L. USHER.

**Absolute maximum of the integral Joule-Thomson effect.** L. SCHAMES (Z. Physik, 1929, 57, 808—814).—A maximum in the total Joule-Thomson effect occurs for points that lie before the expansion on the inversion curve of the differential Joule-Thomson effect. The question as to whether an absolute maximum can be determined among these maxima is raised. The characteristic curves (see Ann. Physik, 1918, [iv], 57, 321—346) in a reduced pressure-temperature-enthalpy diagram for a monatomic substance obeying the van der Waals equation are drawn and discussed. The real inversion curve of the differential Joule-Thomson effect is shown to end at its point of intersection *M* with the saturated vapour-pressure curve, but its theoretical prolongation into the unstable region is considered. The value of the isothermal enthalpy change in expansion from points on the above inversion curve are calculated and the corresponding curve is drawn. This enthalpy change is a measure of the integral Joule-Thomson effect and it is shown that it increases as the inversion curve is traversed from the real into the unstable region. Hence the maximum real integral Joule-Thomson effect is obtained when the expansion starts from the end-point *M* of the inversion curve. The theoretical reduced temperature of *M* is determined as 0.778 and this is compared with the values calculated from the empirical data for a series of gases. The temperature of the point *N* of maximum cooling and that of the point *L* of maximum enthalpy of the saturated vapour are determined theoretically as 0.97 and 0.90, respectively, whilst the experimental

data show that the temperatures of the points *L* and *M* are identical for all the gases investigated.

H. A. JAHN.

**Determination of absolute zero of temperature from coefficient of thermal expansion and compressibility of gases at low pressures.** L. SCHAMES (Z. Physik, 1929, 57, 804—807).—Using the values of Holborn and Otto (A., 1925, ii, 851) for the second virial coefficient and those of Henning and Heuse and of Chappuis for the mean coefficient of expansion and compressibility of helium, hydrogen, nitrogen, and air at pressures of about 1 mm. the value  $-273.14^{\circ} \pm 0.01^{\circ}$  is calculated for the absolute zero of temperature. This is compared with Roebuck's value  $-273.15^{\circ}$  from the Joule-Thomson effect for air.

H. A. JAHN.

**Equation of state for a surface.** N. BARULESCU (Physikal. Z., 1930, 31, 48—56).—Theoretical. The existence of a surface tension for gases and saturated vapours is assumed, since the same molecular forces are present as in liquids. Using Laplace's method, the equation for evaluating the surface tension is obtained, and applied to a number of saturated vapours. The variation of the surface tension with temperature is investigated. It reaches a maximum with rising temperature, and then decreases. The maximum lies in the neighbourhood of the critical point, and the temperatures at which the maxima occur for different vapours are corresponding temperatures. It is pointed out that the surface tension of a liquid as usually measured ("relative surface tension") is really the interfacial tension between the liquid and its saturated vapour, and is equal to its true surface tension diminished by that of the saturated vapour. These observations are applied to Kelvin's theorem relating to vapour pressure over curved surfaces, and to Eötvös' law, the contradiction between the theoretical law and the experimental facts being explained. In order to explain the constant *d* in the usual Eötvös equation it is assumed that there are two surface tensions coming into play at the surface of a liquid, an inner and an outer tension. This assumption leads to the derivation of the new equation of state for the surface:  $\alpha_r V^{2/3} = K \tau e^{-\Delta/T}$ , where  $\alpha_r$  is the relative surface tension of the liquid, *V* is the molecular volume,  $\tau = (T_c - T)$ , *T<sub>c</sub>* being the critical temperature, and  $\Delta$  is a constant or, in the case of abnormal substances, depends on the temperature. The accuracy of this equation is tested and it is found to be more satisfactory than the usual Eötvös equation. A. J. MEE.

**Vapour pressures and vapour-pressure constant of carbon monoxide.** K. CLUSIUS and W. TESKE (Z. physikal. Chem., 1929, B, 6, 135—151).—The vapour pressure of carbon monoxide has been measured by a comparison of vapour-pressure thermometers containing oxygen, nitrogen, and carbon monoxide. From the results the heat of vaporisation at the absolute zero is found to be  $1904.6$  g.-cal., and the vapour-pressure constant  $-0.066 \pm 0.05$ . The latter does not agree with the value calculated from the extended Sackur-Tetrode equation. Possible explanations of the discrepancy are discussed.

F. L. USHER.



**Chemical constants and vapour-pressure constants.** A. EUCKEN (Physikal. Z., 1929, 30, 818—826).—Recent work in band spectra enables moments of inertia and chemical constants to be calculated. The integration constants  $J_K$  of the reaction isochores for various homogeneous gas equilibria show satisfactory agreement between the empirical values and those calculated;  $j_p$  and  $j_K$  are compared and  $J_K$  obtained empirically for a number of heterogeneous reactions agrees well with  $\Sigma j_K$ .

R. A. MORTON.

**Vapour-pressure curve of liquid helium.** W. H. KEESOM, S. WEBER, and G. NØRGAARD (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 864—873).—Measurements, corrected for the difference in thermomolecular pressure between the bulb and the hot-wire manometer of the helium thermometers employed, have been made of the vapour-pressure curve of liquid helium between 1.72° and 4.22° Abs., at which temperatures the vapour pressures are respectively 10 and 760 mm. The discontinuity in the curve due to the transformation of He I into He II is not evident from the results obtained, but is obvious in heating curves of liquid helium. The transition point lies between 2.16° and 2.21° Abs.

F. G. TRYHORN.

**Vapour pressure of bismuth chloride and bromide.** E. V. EVNEVITSCH and V. A. SUCHODSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1503—1512).—The vapour-pressure curves of bismuth chloride and bromide have been constructed. At 760 mm. the former substance boils at 440.1° and the latter at 460.9°. The latent heat of vaporisation of these substances and their Trouton constants have been calculated from vapour-pressure data for different pressures and temperatures.

R. TRUSZKOWSKI.

**Rate of attainment of vapour-pressure equilibrium in liquids.** W. A. WEST and A. W. C. MENZIES (J. Physical Chem., 1929, 33, 1893—1896).—Benzene, water, acetone, ethyl alcohol, acetic acid, and sulphur have been examined for a delay in the attainment of vapour-pressure equilibrium with a change in temperature. The temperatures of heating varied from 65° to 125° above the comparison temperature of 25°, and in no case was a delay distinguishable from the lag in thermal equilibrium observed. An explanation of Baker's results with acetic acid is advanced.

L. S. THEOBALD.

**Vapour pressures of sulphur between 100° and 550° with related thermal data.** W. A. WEST and A. W. C. MENZIES (J. Physical Chem., 1929, 33, 1880—1892).—The vapour pressure of sulphur between 104° and 543° has been measured by the static isotenoscope, the vaporisation temperatures being determined by means of a protected platinum resistance thermometer. The commercial roll sulphur was purified either by distillation in a vacuum or in nitrogen. The values found for the vapour pressures are well represented by Biot's equation  $\log p = a + \frac{b}{T} + cT$  and the results of previous investigators are compared with those given by this equation. The interpolated value of the latent heat of vaporisation of sulphur at the b. p. is 69.5 g.-cal./g. The curve connecting heat of vaporisation with temperature

falls rapidly to a minimum at 365°. The calculated entropies of vaporisation indicate marked association, possibly to  $(S_8)_2$ , in the liquid phase.

L. S. THEOBALD.

**Increase of density of glasses on solidification under high pressure, and reversion to the normal value on heating.** G. TAMMANN and E. JENCKEL (Z. anorg. Chem., 1929, 184, 416—420).—The density variations of a number of vitreous substances during solidification under 5700 kg./cm.<sup>2</sup> pressure have been determined by the pyknometer. The solidification temperature has less influence on the density increase  $\Delta d$  than has the chemical composition of the glass; for boron trioxide and vanadium pentoxide containing 12—25% of phosphorus pentoxide  $\Delta d$  is 5—8%, for phenolphthalein about 0.6%, whilst for sodium metaphosphate, arsenic trioxide, and colophony the effect is very small. The manner in which the normal density is re-attained on heating is described.

H. F. GILLBE.

**Plasticity of solids.** W. P. DAVEY (J. Rheology, 1929, 1, 45—48).—Plastic flow of solids involves the break-up of each single crystal into a group of smaller grains without affecting the continuity of the solid. Gradual stressing of a single crystal leads only to elastic deformation up to a critical value of the stress, above which permanent deformation and fragmentation occur simultaneously. That the elastic limit is a definite quantity shows that actual solids in the crystalline state do exist, and that all substances do not flow "more or less slowly." The critical stress is independent of the size and dimensions of the crystal. A sheared heated crystal of rock salt or of zinc undergoes plastic deformation in a series of jumps, of constant magnitude for any one experiment, the time intervals between them being at first regular and then increasing gradually and regularly. The magnitude of the jumps is the greater the higher is the temperature. Cold-working of metals must involve a similar process.

C. W. GIBBY.

**Theory of plastic flow in the rotation viscosimeter.** M. REINER (J. Rheology, 1929, 1, 5—10).—Mathematical.

C. W. GIBBY.

**Measurements of viscosity with colloids.** H. KROEPFELIN (Ber., 1929, 62, [B], 3056—3060).—The causes of apparent anomalies in the determinations of the viscosities of colloidal solutions are discussed. It is possible to compare viscosity measurements of colloids showing abnormal behaviour even when they are determined with capillaries of differing length and diameter. It is necessary in this case that the mean velocity should be stated or the half-measurement of the capillary and the mean velocity of outflow, or that the time of outflow and the volume should be cited.

H. WREN.

**Thermodynamical calculation of the compressibility of water.** W. JAZYNA (Z. Physik, 1929, 58, 858—860).—The first two laws of thermodynamics and Thomson's experiments on the lowering of the m. p. give a mean (interval 1—129 atm.) compressibility in agreement with the results of other workers.

A. B. D. CASSIE.

**Compressibility of ethylene.** H. DANNEEL and H. STOLTZENBERG (Z. angew. Chem., 1929, 42, 1121—1123).—The pressure-temperature curves of ethylene at pressures up to 200 atm. and temperatures up to 45° have been constructed. The coefficient  $dp/dt$  increases rapidly as the density rises.

S. I. LEVY.

**Variation with temperature of thermal separation in gaseous mixtures.** J. W. H. LUGG (Phil. Mag., 1929, [vii], 8, 1019—1024).—Using the apparatus of Elliott and Masson (cf. A., 1925, ii, 763) the thermal separation of hydrogen and carbon dioxide has been studied with the cold bulb at 29° and the hot bulb between 100° and 464°. Results indicate that the separation at higher temperatures is greater than expected from Chapman's logarithmic formula. The relation between composition difference and temperature difference is more nearly linear.

N. M. BLIGH.

**Micro-method for measuring diffusion of colourless substances.** R. ZUBER (Physikal. Z., 1929, 30, 882—884).—A small vessel contains layers of solution and solvent separated by a thin removable partition. Fürth has shown (A., 1926, 21) that when the layers come into contact the diffusion of coloured solutions can be followed colorimetrically by a micro-method. An arrangement has now been devised for adapting Fürth's method to colourless solutions, using the refractive index for measuring the rate of diffusion. The method has been tested on aqueous solutions of potassium chloride, the results indicating a pronounced variation of the diffusion coefficient ( $D$ ) with the concentration. Extrapolating to  $c=0$ ,  $D=17.1 \times 10^{-6}$ , whereas the values of the ionic mobilities indicate  $D=16.9 \times 10^{-6}$ .

R. A. MORTON.

**Theory of mixtures as a problem in probability.** K. LICHTENECKER (Physikal. Z., 1929, 30, 805—809; cf. *ibid.*, 1927, 28, 417; A., 1927, 189).—An extension of the logarithmic mixture rule is made to further types of mixtures, the treatment being theoretical throughout.

R. A. MORTON.

**Internal friction of binary liquid systems containing allylthiocarbimide and dimethyl-, diethyl-, or ethyl-aniline.** N. A. TRIFONOV and K. I. SAMARINA (Bull. inst. recherches biol. Univ. Perm, 1929, 6, 291—302).—The systems are classified as ideal, semi-ideal, and rational.

CHEMICAL ABSTRACTS.

**Viscosity and diffusion in glycerol-water mixtures.** Z. V. VOLKOVA (Z. physikal. Chem., 1929, 145, 200—206).—The diffusion coefficient of potassium iodide in highly viscous glycerol-water mixtures has been measured and found to be related to the specific volume of the mixture in the same way as the fluidity.

F. L. USHER.

**Viscosity of viscous liquids.** M. VOLAROVICH (J. Appl. Phys. Moscow, 1928, 5, 53—63).—Viscosity-temperature curves were obtained for solutions of sugar in glycerol by Margules' method in the ranges 17—65° and 3930—2.5 units.

CHEMICAL ABSTRACTS.

**Viscous liquids.** B. V. DERYAGIN and I. M. KHAVANOV (J. Appl. Phys. Moscow, 1928, 5, 65—

79).—The viscosities of solutions of sugar in glycerol and of potato molasses were determined over the range 14—70° by the falling-sphere method.

CHEMICAL ABSTRACTS.

**Dielectric constants of binary mixtures. II. Alcohols in benzene.** P. C. MAHANTI (J. Indian Chem. Soc., 1929, 8, 743—747; cf. A., 1929, 994).—The dielectric constants of the following alcohols dissolved in benzene have been measured by the method previously described, and the dipole moments calculated: *isopropyl*, *isobutyl*, *isoamyl*, *n*-undecyl, *n*-dodecyl,  $\beta$ -phenylethyl, and  $\gamma$ -phenylpropyl alcohols. For the primary alcohols the dipole moment is practically constant and has a mean value of  $1.63 \times 10^{-18}$  c.g.s.u., whilst for the *iso*-alcohols it is  $1.8 \times 10^{-18}$  c.g.s.u. These results are explained as follows: Hydrocarbons themselves are non-polar, the dipole moment of the alcohol being due to the introduction of the polar hydroxyl group. In view of the constancy of the dipole moment for the same type of alcohol, it seems reasonable to assume that the displacement of the electric charge which gives rise to the dipole takes place mainly in the group itself and in the part of the molecule adjacent to it, the existence of non-polar groups at a greater distance having practically no influence.

M. S. BURR.

**Effect of heating on the triboelectricity of liquid potassium and zinc amalgams. V.** POLARA (Nuovo Cim., 1929, 6, 78—83; Chem. Zentr., 1929, ii, 392).—Experiments on the behaviour of liquid zinc amalgam towards glass show that the amalgam becomes negatively charged, but not if the temperature is above 70—80°. Potassium amalgam exhibits no triboelectricity in the cold; negative triboelectricity appears when the material is heated, and becomes maximal at 50—70°.

A. A. ELDRIDGE.

**Prediction of binary azeotropism.** M. LECAT (Compt. rend., 1929, 189, 990—992).—Azeotropism occurs when the vapour pressure-temperature curves of a binary system intersect. The limitations of this rule, which is shown to be non-reciprocal, and the influence on azeotropism of various chemical groupings are discussed. (Cf. A., 1929, 955.)

J. GRANT.

**Vapour pressures and other physical constants of methylamine and methylamine solutions.** W. A. FELSING and A. R. THOMAS (Ind. Eng. Chem., 1929, 21, 1269—1272).—The vapour pressure ( $p$  mm.) of pure methylamine between  $-80^\circ$  and  $-10^\circ$  is given by  $\log_{10} p = -138.60647/T + 38.730167 \log_{10} T - 6.600156 \times 10^{-2}T + 3.870056 \times 10^{-5}T^2 - 75.7030015$ ; with less accuracy this reproduces Berthoud's data (A., 1917, ii, 237) up to the critical point. The density between  $-83^\circ$  and  $20^\circ$  is given by  $d = 0.93249 - 6.09221 \times 10^{-4}T - 106.443 \times 10^{-8}T^2$  to within 1 part in 5400 parts. These data are used to calculate heats of vaporisation of methylamine between  $-70^\circ$  and  $30^\circ$  by the Clapeyron-Clausius equation.

Total pressures of aqueous methylamine solutions have been determined over a wide range of concentrations. Partial pressures of dilute aqueous solutions and total heats of solution of gaseous methylamine are recorded.

J. G. A. GRIFFITHS.

**Vapour pressure of solutions of potassium in liquid ammonia.** W. C. JOHNSON and A. W. MEYER (J. Physical Chem., 1929, 33, 1922—1930).—The vapour pressures of solutions of potassium in liquid ammonia have been determined for different concentrations at 0°, -33.5°, and -50.38° by the method previously used for lithium (A., 1925, ii, 389). The form of the vapour-pressure curves corresponds closely with those of lithium and sodium in ammonia, and the vapour pressure remains constant so long as any potassium is present in equilibrium with the saturated solution. The vapour pressures of the saturated solutions at 0°, -33.5°, and -50.38° are 750, 162, and 62 mm., respectively. The solubility of potassium in liquid ammonia increases with a rise in temperature, since 1 g.-at. of potassium dissolves in 4.68, 4.95, and 5.05 g.-mols. of ammonia at 0°, -33.5°, and -50.38°, respectively. The smooth curves give no indication of the formation of a compound at these temperatures.

L. S. THEOBALD.

**Concentrated solutions. VII. Application of thermal analysis to binary mixtures of organic compounds melting at very low temperatures.** S. SAPIER (Bull. Soc. chim. Belg., 1929, 38, 392—408; cf. Timmermans, A., 1929, 254).—Using a resistance thermometer, heating and cooling curves have been obtained for mixtures of isopentane with pentane, carbon disulphide, ethyl bromide, and acetone, of methylal with ethylal, of methyl ethyl ketone and acetone, of methyl alcohol with ethyl alcohol, of ether with ethyl alcohol, methyl alcohol, carbon disulphide, acetone, and isopentane, of acetone with methyl alcohol and ethyl alcohol, of ethyl acetate with carbon disulphide and ethyl alcohol, of methylal with carbon disulphide, and of chloroform with methyl alcohol. The latent heats of fusion have been calculated.

C. W. GIBBY.

**Binary systems of transition elements with boron, carbon, and nitrogen.** G. HÄGG (Z. physikal. Chem., 1929, B, 6, 221—232).—A discussion of the properties of the various phases indicated by X-ray examination of the systems formed by elements in the transition series with hydrogen, boron, carbon, and nitrogen. These phases all have a typically metallic character, and show certain regularities in their physical and chemical properties, which are probably due to the small size of the metalloid atoms. These regularities are not shown in the binary phases of metals with other metalloid atoms. In a large number of phases formed by boron, carbon, and nitrogen with transition elements the metallic atoms are arranged in lattices of closest spherical packing, and the conditions necessary for the formation of such structures are discussed.

O. J. WALKER.

**X-Ray investigations on the system cadmium-antimony.** F. HALLA and J. ADLER (Z. anorg. Chem., 1929, 185, 184—192; cf. A., 1928, 1190).—X-Ray diagrams of 50 at.-% mixtures of cadmium and antimony indicate the existence of the compound  $\text{Cd}_3\text{Sb}_2$  as an unstable phase, which in the course of time gives place to  $\text{CdSb}$ . The unit cell of the latter compound has  $a$  6.52,  $b$  8.60,  $c$  4.16 Å.,

and contains 4 mols. The substance previously regarded by Insküll as  $\text{Cd}_3\text{Sb}_2$  is shown, by the agreement of the axial ratio determined by him goniometrically with that now found, to have been  $\text{CdSb}$ .

F. L. USHER.

**Complex systems with iron. II. System chromium-carbon.** R. KRAICZEK and F. SAUERWALD (Z. anorg. Chem., 1929, 185, 193—216; cf. A., 1927, 517).—The system chromium-carbon between 0 and 13.3% C has been investigated by means of heating and cooling curves, examination of microscopic texture, and density measurements. In the interval 8.32—9.9% C there occurs a series of mixed crystals, which undergoes a transformation of undetermined character at 1465°. There is evidence of the existence of two carbides,  $\text{Cr}_5\text{C}_2$  and  $\text{Cr}_3\text{C}_2$ , but not of  $\text{Cr}_4\text{C}$  or  $\text{Cr}_4\text{C}_2$ .

F. L. USHER.

**Formation of the  $\gamma$ -phase in silver-zinc alloys.** G. J. PETRENKO and B. G. PETRENKO (Z. anorg. Chem., 1929, 185, 96—100; cf. A., 1926, 229).—Cooling and heating curves of silver-zinc alloys containing from 38 to 55% Zn show that the  $\gamma$ -phase is formed peritectically at 665° according to the scheme:  $\beta$ -mixed crystals (45% Zn) + liquid (49% Zn) =  $\gamma$ -mixed crystals (47.61% Zn). The latter undergo a transition at 225°, below which they form the compound  $\text{Ag}_2\text{Zn}_3$ .

F. L. USHER.

**Electrical conductivity of silver-zinc alloys in the annealed condition.** G. J. PETRENKO (Z. anorg. Chem., 1929, 184, 376—384).—The composition-electrical conductivity curves of the silver-zinc alloys confirm the existence of the nine groups of alloys previously indicated by thermal analysis. The compound  $\text{AgZn}$ , assumed to exist in the  $\beta_1$ -solutions below the transition temperature in the crystalline state, is not indicated by electrical measurements. A sharp maximum on the temperature coefficient diagram demonstrates the presence of  $\text{Ag}_2\text{Zn}_3$  as a true chemical compound, whilst  $\text{Ag}_2\text{Zn}_5$  is indicated by a deep minimum; both compounds are indicated also by breaks in the conductivity curve.

H. F. GILLBE.

**Formation of the  $\beta$ -phase of silver-zinc alloys.** B. G. PETRENKO (Z. anorg. Chem., 1929, 184, 369—375).—The existence of a compound  $\text{AgZn}$  in the  $\beta$ -phase of silver-zinc alloys has been demonstrated by thermal analysis; during the transition of the  $\beta$ -phase in the crystalline state partial dissociation of the compound occurs, as evidenced by the heating curve.

H. F. GILLBE.

**Hardness, microstructure, and temperature coefficients of conductivity of platinum-iron alloys.** V. A. NEMLOV (Ann. Inst. Platine, 1929, 7, 1—13).—The curve connecting the hardness of rapidly cooled alloys with their composition shows the presence of two solid solutions, one containing from 0 to 35 at.-% and the other from 35 to 100 at.-% Pt, maxima occurring at 10 and 50 at.-%. Reheated alloys have points of maximum hardness at 40 and at 60 at.-%, and a sharp minimum at 50 at.-%, corresponding with the formation of a compound,  $\text{FePt}$ . The temperature coefficient of electrical conductivity curve has a sharp maximum at 50 at.-% for reheated alloys, and a minimum at 73 at.-% Pt

for both supercooled and reheated alloys. Numerous photomicrographs confirming the conclusions reached from the above curves are given. R. TRUSZKOWSKI.

**Platinum-iridium alloys.** V. A. NEMLOV (Ann. Inst. Platine, 1929, 7, 14—20).—The curve connecting the hardness of reheated alloys with their composition is continuous, with a maximum at 45% Ir, pointing to the presence of an unbroken series of solid solutions. A study of the photomicrographs of etched alloys and of the temperature coefficient of electrical conductivity curve confirms this view.

R. TRUSZKOWSKI.

**Rhodium-bismuth alloys.** E. J. RODE (Ann. Inst. Platine, 1929, 7, 21—31).—The m. p. diagram has a eutectic point at 0.7% Rh and 260°; at higher concentrations of rhodium a compound,  $\text{RhBi}_4$ , separates, which at 433° is converted into  $\text{RhBi}_2$ , and this, in turn, dissociates above 772° to yield  $\text{RhBi}$ . Above 995°, the last-named compound also dissociates, yielding probably a rhodium-bismuth solid solution.  $\text{RhBi}_2$  is insoluble in boiling concentrated nitric acid, and the relatively smaller solubility of rapidly cooled alloys is ascribed to the presence of this compound. Alloys containing more than 18.3% Rh cannot be dissolved without residue in aqua regia.

R. TRUSZKOWSKI.

**Palladium-antimony alloys.** A. T. GRIGORIEV (Ann. Inst. Platine, 1929, 7, 32—44).—The m. p. diagram suggests the existence of the compounds  $\text{PdSb}_2$ , m. p. 680° (decomp.),  $\text{PdSb}$ , m. p. 799°, and  $\text{Pd}_3\text{Sb}$ , m. p. 1182°, and of the eutectic alloys—1.13—32.68 at.-% Pd (594°), 51.13—60.92 at.-% Pd (730°), and 79—82 at.-% Pd (1069°). The compound  $\text{Pd}_3\text{Sb}$  forms solid solutions with excess both of antimony and of palladium. An apparent transition point corresponding with a compound  $\text{Pd}_5\text{Sb}_3$  appears at 62.5 at.-% Pd and 825°; the existence of this compound is, however, excluded by a study of the microcrystalline structure of the alloy of this composition and by the shape of the temperature coefficient of electrical conductivity curve.

R. TRUSZKOWSKI.

**Gold-antimony alloys.** A. T. GRIGORIEV (Ann. Inst. Platine, 1929, 7, 45—51).—The m. p. diagram is identical with that obtained by Vogel (A., 1906, ii, 679). Both this and the variation of the temperature coefficient of electrical conductivity indicate the presence of a compound,  $\text{AuSb}_2$ , m. p. 460° (decomp.).

R. TRUSZKOWSKI.

**Iron-beryllium and iron-boron alloys, and the structure of iron boride.** F. WEVER (Z. tech. Physik, 1929, 10, 137—138; Chem. Zentr., 1929, ii, 345).—The equilibrium diagrams for the systems iron-carbon, iron-boron, and iron-beryllium show with increasing atomic radius a gradual transition from the group with extended  $\gamma$ -field (iron-carbon) to that with a closed  $\gamma$ -existence region (iron-beryllium). Boron (with lattice parameter  $2.854 \times 10^{-8}$  cm.) forms a true substitution mixed crystal with  $\alpha$ -iron; this is probably also the case with the  $\gamma$ -iron-boron and the  $\gamma$ -iron-beryllium systems. A structure analysis of the compound  $(\text{Fe}_2\text{B})_x$  is given, the relation between  $\gamma$ -iron,  $\text{Fe}_4\text{N}$ , and  $\text{Fe}_3\text{B}_2$  being considered.

A. A. ELDRIDGE.

**Measurement of the elastic constant, lattice constant, and density of binary alloys in the range of solid solution.** Z. NISHIYAMA (Sci. Rep. Tōhoku Imp. Univ., 1929, 18, 359—400).—The values of Young's modulus,  $E$ , the lattice parameter,  $a$ , and the density,  $d$ , of a series of solid solution alloys of iron, nickel, copper, and aluminium have been determined. The value of  $d$  obtained by direct measurement in all cases agrees reasonably well with that calculated from  $a$  on the assumption that the atomic arrangement in the solid solution is of the simple substitution type. Although the hardness of a metal is increased by the presence of solute atoms the value of  $E$  for solid solution alloys is only slightly smaller or greater than that for the pure metal. With a few exceptions the value of  $E$  for a solid solution is inversely proportional to the  $n$ th power of the atomic volume; for  $\alpha$ -solid solutions of copper  $E = k(1 - 0.823T/T_m)V^{1.5}$ , where  $V$  is the atomic volume,  $T$  the temperature, and  $T_m$  the m. p. on the absolute scale.

A. R. POWELL.

**Röntgenographic examination of the iron-manganese system.** W. SCHMIDT (Arch. Eisenhüttenw., 1929—1930, 3, 293—300; Stahl u. Eisen, 1929, 49, 1696—1697).—Examination of alloys of the iron-manganese system by X-ray analysis shows that the  $\alpha$ -solid solution is present up to 20% Mn, the lattice parameter increasing from 2.857 Å. for pure iron to 2.871 Å. for the alloy with 20.1% Mn. Alloys with 16—60% Mn contain the  $\gamma$ -solid solution with a cubic face-centred lattice,  $a$  3.586 Å. with 15.7% Mn to  $a$  3.616 Å. with 55.85% Mn. Alloys with 60—98% have the structure of  $\beta$ -manganese, the lattice parameter increasing from 6.24 Å. with 62.7% Mn to 6.28 Å. with 87.25% Mn, and alloys with more manganese have the structure of  $\alpha$ -manganese. In addition there is, in alloys containing 12—29% Mn, a new phase,  $\epsilon$ , having a hexagonal close-packed lattice,  $a$  2.532—2.543,  $c$  4.061—4.082 Å. according to the manganese content. The linear increase in the parameters with increasing content of manganese shows that there is no iron-manganese compound present with a stoichiometric formula. As the  $\alpha$ ,  $\gamma$ , and  $\epsilon$  phases can coexist in the same alloy it follows that one of these is metastable in the range 12—29% Mn, but no evidence has yet been obtained to indicate which one it is. No transformation points have been observed by dilatometric or thermal analysis.

A. R. POWELL.

**Properties of nickel-copper alloys at low temperatures. Thermo-electric and dilatation determinations with nickel-copper at low temperatures.** A. KRUPKOWSKI and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 912—920, 921—929).—I. The electrical conductance curve at 0° of copper-nickel alloys, vacuum-annealed at 750—780°, is characteristic of pure mixed crystals and shows no appreciable curvature at the transition from ferro- to para-magnetic alloys. It shows a wide rounded minimum at a composition near to 55% Ni. In the temperature-conductance curves for some alloys a point of curvature occurs which corresponds exactly with the Curie points of the alloys, which, for alloys containing 43.45, 48.40, and 57.54% Ni

are respectively  $-247^{\circ}$ ,  $-196^{\circ}$ , and  $-97^{\circ}$ . A strong increase in the resistance coefficient occurs with those alloys in which the transition from the ferro- to the para-magnetic state takes place. Negative resistance coefficients between  $-258.4^{\circ}$  and  $-252.5^{\circ}$  were obtained with alloys containing between 12 and 35% Ni.

II. The thermo-electric coefficients of these alloys show two minima in the temperature ranges  $-205^{\circ}$  to  $-252.5^{\circ}$  and  $-183^{\circ}$  to  $-0^{\circ}$ , and one minimum in the range  $-205^{\circ}$  to  $-183^{\circ}$ . The maximum occurring between the two minima corresponds exactly with the Curie point. The thermo-electric coefficient decreases markedly at low temperatures and seems to approach zero at  $0^{\circ}$  Abs. The linear dilatation coefficient curves of these alloys show slight maxima, which with decreasing temperature occur at increasingly small percentages of nickel. The inflexion points of the resistance curves and the maxima of the thermo-electric coefficient curves meet with decreasing temperature on the curve of magnetic transition, which is a straight line which on extrapolation cuts the composition axis at a point corresponding with an alloy containing 41% Ni.

F. G. TRYHORN.

**Determination of the limits of solid solubility in silver-copper alloys by X-ray analysis.** O. WEINBAUM (*Z. Metallk.*, 1929, 21, 397—405).—The lattice parameter of copper is increased by alloying with silver from 3.605 to a maximum of 3.612 Å. with 3% Ag, after which it remains constant, whilst that of silver decreases with addition of copper from 4.078 to a constant minimum of 4.049 Å. with 5% Ag. The value for the lattice parameter of solid solutions of silver in copper increases with the annealing temperature from 3.612 for the alloy with 3% Ag to 3.622 Å. for the same alloy annealed at  $800^{\circ}$ . This alloy has also the maximum hardness and tensile strength of the copper-rich alloys; alloys with more silver undergo slight age-hardening after quenching from  $800^{\circ}$  and tempering for short periods. The hardness and tensile strength of annealed copper-silver alloys rise to maxima at 5% Cu, then remain constant up to 9% Ag. These results indicate that the solid solubility of silver in copper is about 3% and that of copper in silver 5% at the ordinary temperature.

A. R. POWELL.

**Structure of the mixed crystal series CuI-AgI.** G. LUNDE and P. ROSBAUD (*Z. physikal. Chem.*, 1929, B, 6, 115—117; cf. A., 1927, 97).—A series of seven specimens of mixed crystals of cuprous iodide and silver iodide has been submitted to X-ray analysis. In all cases the crystals were of the zinc blende type, thus confirming the statement of Barth and Lundé (cf. A., 1926, 895). In no case were hexagonal  $\beta$ -crystals found as reported by Reichel (cf. A., 1926, 562).

F. L. USHER.

**Existence of a new type of mixed crystal of the type  $\text{BaSO}_4$  and  $\text{KMnO}_4$ .** Employment of radioactive indicator method. V. CHLOPIN and B. NIKITIN (*Z. physikal. Chem.*, 1929, 145, 137—151).—An attempt has been made to decide on the validity of Grimm and Wagner's views as to the formation of a new type of mixed crystal by barium

sulphate and potassium permanganate (A., 1928, 356; 1929, 245; cf. Balarev, A., 1927, 721; 1928, 223, 356). Determinations have been made of the distribution of active lead or radium-D sulphate between potassium chlorate crystals and potassium chlorate solution and of radium sulphate between crystals of potassium, rubidium, and caesium chlorates and potassium permanganate in their respective solutions in absence and in presence of excess of sulphate ions introduced by magnesium or nickel sulphates. The solid perchlorates do not take up sulphate to any appreciable extent, whilst the large amount of radium sulphate taken up by permanganate can be explained as due to the adsorption of radium by hydrated manganese dioxide formed by the partial reduction of the potassium permanganate. The latter is, therefore, not suitable for the study of the new type of mixed crystals. The results show that, at concentrations of radium-D sulphate and radium sulphate between  $10^{-5}$  and  $10^{-6}\%$ , these compounds form no mixed crystals with the salts considered. If the new type of mixed crystals exists there must be a lower mixing limit for its formation, and it must be formed, not by the molecular interchange of isomorphous ions, but by the accumulation of several  $\text{M}^{++}$  and  $\text{SO}_4^{--}$  ions on the surface of the increasing  $\text{MXO}_4$  crystals. That is, the crystal structure must be made up of elementary crystalline micelles of both components. The new type of mixed crystal would, therefore, form a connecting link between true mixed crystals and layer crystals.

M. S. BURR.

**Optical striations.** F. EMICH (Mohnatsh., 1929, 53 and 54, 312—360; cf. A., 1929, 24). [With H. HÄUSLER, R. RASIN, and E. SCHALLY.]—The application of striation methods to the determination of the purity of liquids or soluble substances is described. Striation methods give a ready means of determining reactions between liquids, and details of control experiments with binary mixtures of organic liquids are given.

[With H. ALBER.]—An investigation of the action of pepsin on fibrin or on coagulated white of egg shows that striation methods provide an easy means of studying fermentation processes in which a sparingly soluble substrate is rendered soluble, and the activity of different pepsin preparations has been compared.

[With E. SCHALLY.]—Striations arising at the zone of mixing of liquids or solutions of the same refractive index have been investigated for strong electrolytes (acid and alkalis), on the one hand, and organic liquids, on the other. These striations have been named "*D*-Schlieren" and are attributed to changes taking place at the zone of mixing.

L. S. THEOBALD.

**Solubility of potassium selenate in water between  $0^{\circ}$  and  $100^{\circ}$ .** J. A. N. FRIEND (J.C.S., 1929, 2782—2783).—The solubility of potassium selenate in water has been determined between  $0^{\circ}$  and  $100^{\circ}$ . The results are in agreement with those of Tutton (J.C.S., 1897, 71, 846) but not with those of Etard (A., 1894, ii, 442).

C. W. GIBBY.

**Solubilities of *o*- and *p*-nitrophenols in aqueous methyl-alcoholic solutions at  $25^{\circ}$  and  $40^{\circ}$ .**

**Formation of  $\beta$ -*p*-nitrophenol.** J. C. DUFF (J.C.S., 1929, 2789—2796).—The solubilities of *o*- and *p*-nitrophenols in aqueous methyl-alcoholic solutions (100% water to 100% alcohol) have been determined at 25° and 40°. The  $\beta$ -form of *p*-nitrophenol may be prepared by slow cooling of an oily saturated solution of *p*-nitrophenol in aqueous methyl alcohol.

C. W. GIBBY.

**Solubility of arsenious oxide in ethyl malonate and its volatility in the vapour.** E. V. ZAPPI and A. MANINI (Anal. Asoc. Quím. Argentina, 1929, 17, 90).—The solubility of arsenious oxide in ethyl malonate is 0.058 g. in 100 g. at 15° and 0.061 g. in 100 g. at 100°. Arsenious oxide is volatile in ethyl malonate vapour; 0.090 g. is carried over in the distillation of 100 g. of ester.

R. K. CALLOW.

**Solubility product of extremely insoluble salts.** V. CHLOPIN (Naturwiss., 1929, 17, 959).—Salts of very low solubility do not crystallise at high degrees of supersaturation unless the solid phase is present, even if non-isomorphous salts are crystallised from the solution. The solubility product in such cases has no meaning in the absence of the solid phase.

J. A. V. BUTLER.

**Solubility of quartz and clay in felspar.** C. W. PARMELEE and C. R. AMBERG (J. Amer. Ceram. Soc., 1929, 12, 699—710).—A brief review of the literature on the subject shows wide discrepancies. Increasing amounts of kaolin and of clay were added to fixed amounts of felspar and the fired mixtures were examined microscopically by the immersion method. Three types of felspar were used. The presence of undissolved kaolin was shown by the presence of mullite crystals, the presence of undissolved quartz by cristobalite. Soda felspar is a better solvent for quartz and clay than potash felspar. Quartz begins to dissolve in soda felspar at about 1350° and the solubility increases with temperature until at 1425° 32 parts per 100 are soluble. In high-potash felspar dissolution of quartz begins only at 1400° and only 4 parts are soluble at 1425°. Clay begins to dissolve in soda felspar at 1225° and 36 parts per 100 are dissolved at 1425°, whereas in potash felspar dissolution begins at 1250° and 20.5 parts are dissolved at 1425°. Quartz begins to dissolve in porcelain bodies at the same temperature as in the felspar contained in the body, but the degree of dissolution per unit of felspar is much greater. The general trend of one of the boundary lines in the ternary system  $K_2O-Al_2O_3-SiO_2$  has been found. It is suggested that the comparatively low strength of soda felspar porcelains is due to the greater solubility of the quartz.

F. SALT.

**Salting-out effect with dichloro-ethanes and -propanes.** P. GROSS (Z. physikal. Chem., 1929, B, 6, 215—220).—The solubilities of  $\alpha\alpha$ - and  $\alpha\beta$ -dichloroethane,  $\alpha\beta$ -dichloropropane, and carbon tetrachloride in water and in 0.5*M*-potassium chloride and magnesium sulphate at 25° have been determined. There is apparently no connexion between the solubilities, the salting-out effects, and the dipole moments of the respective molecules. In the case of the symmetrical carbon tetrachloride molecule the salting-out effect is practically the same as for the other substances.

O. J. WALKER.

**Distribution ratios of organic acids between water and organic liquids.** H. W. SMITH and T. A. WHITE (J. Physical Chem., 1929, 33, 1953—1974).—The distribution ratios and association constants of many organic acids in the systems water-toluene, water-benzene, and water-chloroform at  $25 \pm 0.5^\circ$  are recorded.

L. S. THEOBALD.

**Salt action.** P. GROSS (Monatsh., 1929, 53 and 54, 445—453; cf. Debye, A., 1927, 1141).—Theoretical. The salting-out effect and neutral salt action are discussed. No simple relation between activity and velocity of reaction is to be generally expected. The magnitude of the activity coefficient of a neutral substance is considered in relation to the reaction between an ion and a non-electrolyte. The action of the ions is to bring about a weakening of the electrical salting-out effect.

L. S. THEOBALD.

**Adsorption of a gas.** Y. KOBAYASHI (Bull. Inst. Phys. Chem. Res. Tokyo., 1929, 8, 562—572).—The Langmuir adsorption isotherm has been deduced on the assumption that the adsorbed gas behaves as a two-dimensional gas the molecules of which have also a vibration perpendicular to the surface of the adsorbent. The equation has been applied to Homfray's data for the adsorption of argon on charcoal. The specific area of the charcoal is estimated to be  $3.9 \times 10^6$  sq. cm. per g. and the vibration frequency of the adsorbed argon  $2.5 \times 10^{12}$  per sec.

F. J. WILKINS.

**Adsorption of carbon dioxide and ammonia on charcoal and graphite.** A. MAGNUS and H. KRATZ (Z. anorg. Chem., 1929, 184, 241—271; cf. A., 1927, 928).—The adsorption of carbon dioxide on beechwood and coconut charcoal and on Ceylon and Acheson graphite at pressures from 0.01 to 700 mm. has been investigated at eight different temperatures. For ash-containing adsorbents there is no region where Henry's law can be applied, and the heats of adsorption calculated from the Clausius-Clapeyron equation decrease with increasing gas pressure. For pure charcoal and graphite Henry's law holds until about 25 micromols. of gas per g. have been adsorbed, showing that the deviations found with unpurified adsorbents are due to oxidic substances reacting with the carbon dioxide and forming places of high potential. Charcoal and graphite which have undergone similar previous treatment show heats of adsorption of the same order of magnitude. The adsorption isotherms and the heats of adsorption vary greatly with the temperature at which the charcoal is prepared, and these variations are traced to completion of carbonisation which leads to increase of the surface by roughening and to a decrease by graphitisation. Similar investigations with ammonia (as typical of a gas with a high dipole moment) reveal no region of proportionality between gas pressure and quantity adsorbed, even when the adsorbents are pure.

F. L. USHER.

**Adsorption phenomena with the platinum metals.** A. GUTHRIE and W. SCHIEFERDECKER (Z. anorg. Chem., 1929, 184, 305—332).—The isotherms and isobars of the palladium-hydrogen system have been determined; they correspond approximately with those obtained by other observers. The small



discrepancies observed are ascribed to variations in the method of preparation of the metal and of its particle size. The isobars of the system hydrogen-iridium (grey powder or iridium-black) from 20° to 190° are smooth, nearly straight lines of negative slope; the adsorptive power of the metal is diminished by strong ignition, but by heating the metal for a long period at a temperature not exceeding 350° its adsorptive power at lower temperatures is increased. Very little of the adsorbed gas is removed at 18° in a vacuum, but at 50° practically the whole is driven off. For the system iridium-carbon monoxide the isobars are similar to those of the iridium-hydrogen system, and by heating the metal in an atmosphere of carbon monoxide for a prolonged period the adsorptive power at low temperatures is considerably increased. The ruthenium-hydrogen isobars are also linear, and indicate but very slight adsorption, although the gas is driven off only by heating to about 650°. Osmium closely resembles iridium in its adsorptive power. H. F. GILLBE.

**Adsorption of nitrogen peroxide by colloidal silicic acid.** A. V. SAPOSHNIKOV, A. P. OKATOV, and M. A. SUSAROV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1353—1368).—Colloidal silicic acid is a satisfactory adsorbent for nitrogen peroxide; the degree of adsorption diminishes with diminishing concentration of adsorbent and with rise of temperature. The velocity of adsorption isotherm at 0° is flattened by reducing the rate of flow of gas from 200 to 100 c.c./min. The process of adsorption proceeds according to the Freundlich equation. About 95—99% of the adsorbed nitrogen can be recovered. The recovery of oxides of nitrogen from moist air can be effected by the use of silica sol. R. TRUSZKOWSKI.

**Adsorption measurements with an improved micro-balance.** R. STRÖMBERG (Kungl. Svenska Vetenskapsakad. Handl., 1928, **6**, [2], 1—122).—The balance is an improved form of that of Pettersson (A., 1920, ii, 482). The beam consists of two isosceles triangles, made of quartz, on a common vertical. In the middle of this is a quartz transverse axis, carrying a mirror and suspended at its ends by quartz fibres, fused on. The bodies to be weighed are suspended by quartz fibres, contact with the ends of the beam being made by small cones moving in an eye which has a circular cross-section. The balance is mounted in a vacuum case and its sensitivity is  $3-4 \times 10^{-6}$  mg. per scale division. A method of determining the thickness of quartz fibres from their colour is described.

The adsorption of water vapour by glass, quartz, platinum, and gold was observed by hanging thin plates of these materials from one beam of the balance by means of a long quartz fibre in a vessel in which the pressure of water vapour is fixed by the presence of a solution of sulphuric acid of known composition. In the case of glass the adsorbed film was removed before each experiment by heating to 145° in a vacuum. With a water vapour pressure of 3.83 mm. of mercury at 18.1°, the weight adsorbed reached a maximum within an hour and then diminished slightly, until after 15 hrs. the thickness of the adsorbed layer was 73 Å. or 28.2 molecular diameters. With saturated water vapour (15.58 mm.) the adsorption continued over a long

period and a thickness of 737 Å. (283 molecular diameters) was reached in about 250 hrs. Measurements with intermediate pressures were also made. The rate of increase of the amount adsorbed with the vapour pressure is small at low pressures, but becomes very great in the vicinity of the saturation pressure. On reducing the vapour pressure from a higher to a lower value, the amount adsorbed decreases and becomes constant at a considerably greater value than that adsorbed directly at the same pressure by a water-free surface. This hysteresis effect is exhibited only by glass.

Similar results were obtained at quartz, platinum, and gold surfaces, but these materials lose their adsorbed water easily when exposed to dry air. Platinum and gold absorb water quickly, constant weight being reached in a few hours. The thickness of the adsorbed films obtained with saturated water vapour at glass, quartz, platinum, and gold were approx. 740, 135, 380, 64 Å., respectively. (The real surface areas of platinum and gold were estimated to be respectively 40% and 100% greater than those measured.) The nature of the surface has therefore a specific effect on the adsorption. The results do not support theories of the unimolecular nature of adsorbed films. J. A. V. BUTLER.

**Statistical basis for the Langmuir adsorption formula.** K. KAR and A. GANGULI (Physikal. Z., 1929, **30**, 918—920).—Langmuir's formula  $c = k_1 \eta / (1 - \eta \beta)$  (where  $c$  is volume concentration,  $\eta$  surface concentration,  $\beta$  and  $k_1$  are constants) has been placed on a statistical basis. The following expression for  $k_1$  is shown to be supported by the experimental data:  $k_1 = (2\pi mkT)^{1/2} / h \cdot e^{-\alpha kT}$  ( $m$  is the mass of the molecule,  $k$  the Boltzmann constant,  $T$  the absolute temperature,  $h$  Planck's constant, and  $\alpha$  the adsorption potential per molecule). The experimental data refer to the adsorption of various gases on carbon at temperatures between -185° and +100°. It is assumed that the adsorbed gas exists as a solid. Volmer's treatment of the problem is criticised.

R. A. MORTON.

**Anomalies in weak adsorption.** M. DUNKEL and H. MARK (Monatsh., 1929, **53** and **54**, 764—778).—The authors discuss the dependability of phase volume on adsorption potential, the adsorption of gases at higher temperatures, the increase in heat of adsorption with temperature when the thickness of the adsorbed layer is small, and the decrease in phase volume with activation of the adsorbent.

L. S. THEOBALD.

**Slow adsorption of acetic acid, benzoic acid, and crystal-violet from aqueous solution by carbon.** W. KRESTINSKAJA (Kolloid-Z., 1929, **49**, 395—406).—Acetic acid, benzoic acid, and crystal-violet in aqueous solution are taken up slowly by charcoal. Experiments carried out with different concentrations of solution, studying the effects of varying the amount of charcoal, the volume of solution, and the reaction time, have established that the phenomenon is not due to a chemical reaction or to the formation of a solid solution, but is a true slow adsorption process. The low velocity of adsorption is due to the difficulty of diffusion of the substance into the narrow capillary spaces of the adsorbent. An adsorption

equilibrium is not observed with benzoic acid, which is adsorbed irreversibly. Acetic and benzoic acids are adsorbed in equivalent amounts by wood charcoal.

E. S. HEDGES.

**Chemical sorption. III. Heterogeneous chemical equilibrium.** S. LIEPATOV (Z. anorg. Chem., 1929, **184**, 232—236; cf. A., 1927, 16).—The results recorded in earlier papers are summarised and a distinction is drawn between two types of reactions in heterogeneous systems (solution-solid). In the case of a macrocrystalline solid, such as barium sulphate, reaction is homogeneous, entry of the solute into the solid being prevented by the crystal lattice, whereas in the case of an amicrocrystalline solid, such as the barium salt of nitroalizarin, reaction is heterogeneous and takes place within the solid phase. The reason for such reactions being attributed to adsorption is that the equilibrium is displaced owing to changes in the concentration of the solid phase.

F. L. USHER.

**Adsorption of complex platinum compounds on charcoal.** I. I. SHUKOV and O. P. SCHUPULINA (J. Russ. Phys. Chem. Soc., 1929, **61**, 1485—1496).—A number of complex platinum compounds, such as  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ ,  $(\text{NH}_4)_2\text{PtCl}_6$ ,  $\text{enNH}_3\text{Cl}_2(\text{NO}_2)_2\text{PtCl}$ , etc., decompose on adsorption on wood charcoal. The extent of adsorption depends on the arrangement of the electrical charges in the given complex, and only in so far as this is affected do stereoisomeric differences affect adsorption. Non-electrolytic compounds are more powerfully adsorbed than electrolytes. Optical isomerides cannot be separated from one another by differential adsorption on charcoal. No direct relationship appears to exist between the solubility of a compound and the extent to which it undergoes adsorption.

R. TRUSZKOWSKI.

**Absorption of liquids by disperse materials and its relation to hydrophilic properties, swelling, and sedimentation.** H. FREUNDLICH and W. SACHS (Z. physikal. Chem., 1929, **145**, 177—199).—A modification of the experimental arrangement devised by Joffe and McLean (cf. A., 1925, i, 1372) for following the process of absorption is described. The materials investigated fall into three classes, the first of which comprises highly lyophobic substances which take up very little liquid, an intermediate class in which more liquid is absorbed at considerable velocities, and a third consisting of lyophilic materials such as kaolin or fuller's earth, where the amount absorbed at the end-point is very large, but where absorption is relatively slow. In the last class the absorption velocity is in many cases calculated by the same formula as the swelling velocity. The slower is the absorption the greater is the degree of swelling. Experiments on the absorption by kaolin of various electrolytes show that the absorption velocity decreases with increasing concentration of electrolyte, but that the amount absorbed increases to a limiting value. For very low concentrations the absorption velocity is higher than for distilled water. This increase is attributed to the coagulating effect of the electrolyte, and the decrease at high concentrations to increased viscosity. In parallel experiments on the sedimentation of the same

kaolin in the same solutions both the rate of fall and the volume of the sediment increase with increasing concentration of electrolyte. The results of both series of experiments are explained by the hypothesis that a maximum amount of water is bound when each particle carries a certain quantity of electrolyte.

F. L. USHER.

**Adsorption of ferric chloride by crystallised barium sulphate.** L. DE BROUCKÈRE (Rev. gén. Colloid., 1929, **7**, 251—260).—See A., 1928, 357.

**Interfacial adsorption as a function of the concentration of colloidal solutions.** J. M. JOHLIN (J. Biol. Chem., 1929, **84**, 543—551).—The surface tension of solutions of sodium oleate from 0.0000003N to about 0.00003N concentration, as measured by the sessile bubble method, bears a linear relationship to the logarithm of the normality; with increasing concentration up to 0.019N a gradual deviation from linearity is observed, and with still further increase in concentration the surface tension rises and approximates gradually to a constant value at 0.059N. The results indicate that throughout the range of more dilute solutions the sodium oleate adsorbed at the interface is in equilibrium with the bulk of the solution. Maximal stability of foam is observed in those solutions which have the lowest surface tension; the capacity to foam is lost when the concentration falls below 0.000059N.

C. R. HARRINGTON.

**Hydrolytic adsorption at colloid surfaces.** S. W. PENNYCUICK (Nature, 1929, **124**, 987).—When barium chloride is added to a platinum sol, distribution of the barium hydroxide between the hydrochloric acid and the "acid" surface of the colloid takes place; the effect, which is not negligible when compared with the cationic interchange, plays an important part in coagulation and reversal phenomena.

A. A. ELDRIDGE.

**Sorption phenomena in chemical processes. V. Theory of heterogeneous chemical equilibria.** S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1259—1266).—The equilibrium constants for the heterogeneous reaction: barium salt of 3-nitroalizarin + acetic acid  $\rightleftharpoons$  3-nitroalizarin + barium acetate have been determined. The reaction in question follows the law of mass action, whence it would appear that the whole of the solid phase takes part in the reaction, and not only its surface.

R. TRUSZKOWSKI.

**Experimental tests of the Gibbs adsorption theorem. Structures of the surface of ordinary solutions.** J. W. McBAIN and R. DU BOIS (J. Amer. Chem. Soc., 1929, **51**, 3534—3549).—The adsorption of the following substances at an air-solution interface was measured by the bubble method of McBain and Davies (A., 1927, 1022): phenol, *p*-toluidine, isoamyl alcohol, resorcinol, thymol, acetic acid, butyric acid, hexoic acid, nonoic acid, and sodium chloride. The adsorption as calculated from the "approximate" Gibbs equation (involving concentration terms) increases rapidly with concentration, attains a maximum while the solution is fairly dilute and the surface tension is still decreasing, and then decreases. The final decrease is eliminated by using

the modified Gibbs equation (involving activity terms). Generally speaking, the amount of substance actually adsorbed may be up to eight times the amounts predicted by the Gibbs equation. The amounts of substance carried by a bubble from a solution are up to four times those which can be accommodated in a unimolecular film of closely packed, vertically oriented molecules. The results support McBain's conclusions regarding the structure of layers adsorbed at liquid surfaces. An electric bubble counter is described.

S. K. TWEEDY.

**Reversibility of the adsorption process and the thickness of the adsorption layer.** J. C. PHILIP (Inst. Chem. Eng., Dec. 5, 1929, Advance copy; 1—9).—Hysteresis effects, *i.e.*, the failure of sorption and desorption pressure-concentration curves to coincide, have been definitely proved to occur in the systems ferric oxide gel-benzene and dye-water vapour. Amongst possible explanations are delayed equilibrium and the presence of water vapour, but these are not adequate in all cases. The conflicting evidence as to whether the thickness of the adsorbed layer is unimolecular or multimolecular is summarised. It is possible that although the limit of adsorption normally corresponds with the completion of the unimolecular layer, special circumstances might favour the formation of a thicker film. If a unimolecular layer is assumed in the case of charcoal it should be possible to determine the "specific surface" experimentally. Results, however, vary widely with different substances adsorbed by the same charcoal. They agree in general with calculations based on the capillary condensation theory of adsorption. There is a good deal of evidence that adsorptive power may be unevenly distributed over the adsorbent surface. C. IRWIN.

**Desorption of electrolytes from suspended particles on coagulation.** S. A. VOSNESSENSKI, V. A. LAZAREV, and T. V. PEREVERZEVA (J. Russ. Phys. Chem. Soc., 1929, 61, 1411—1420).—The electrical conductivity of suspensions of clay to which electrolytes have been added rises sharply at the moment of coagulation. This effect, which is ascribed to elution, is more pronounced in the presence of hydrochloric acid or calcium chloride than of aluminium salts; the difference is attributed to hydrolysis of the aluminium salts. R. TRUSZKOWSKI.

**Sedimentation and wetting. Artificial inversion of the heating effect in wetting and the problem of heat of wetting in physico-chemical analysis.** B. ILJIN (Physikal. Z., 1929, 30, 880—882).—The heats of wetting of a typical sample of carbon by alcohols were found to be 10.8, 11.7, 13.0 kg.-cal. per g. of powder for ethyl, isopropyl, and isoamyl alcohols, whilst a specially prepared sample of carbon gave the values 5.6, 1.8, and 1.0 for the same series of alcohols. The reversal constitutes an "artificial" change in the normal series. When the heat of wetting is determined for ordinary carbon in contact with acetic anhydride or water the respective values are 13.0 and 5.8, but if various proportions of the two liquids are taken the value reaches a maximum of 19.1 at 50 mol.-% and the same value is obtained with glacial acetic acid. The phenomenon appears to provide a general method for the investigation of

compound formation in solution by means of the detection of maxima or minima in the heat of wetting.

R. A. MORTON.

**Surface tension of solutions. IV. Reciprocal influence of urethane and salts on their solution volume and solubility in water.** S. PALITZSCH (Z. physikal. Chem., 1929, 145, 97—108).—Density measurements have been made at 25° on the 400 salt-urethane solutions of which the surface tensions had previously been determined (*cf.* A., 1929, 257). The solution volume of the urethane is found to increase approximately linearly with the concentration, but in the case of the mixed solutions neither constituent has any appreciable effect on the solution volume of the other. There thus appears to be no connexion between surface tension and solution volume. The influence of urethane on the solubility of the salts in water at 25° has also been determined, and conversely. The binodal curve has been found for magnesium sulphate, but only its end-points for the other salts. The salting-out coefficients, or activity coefficients, have been calculated, and again there appears to be no marked connexion between solubility changes and changes of surface tension. A modification of the Kjeldahl method permitting an exact determination of urethane is described.

M. S. BURR.

**Viscosity coefficients and surface layers. II.** J. TRAUBE and S. H. WHANG (Z. physikal. Chem., 1929, 145, 257—264; *cf.* A., 1929, 129).—A reply to the criticism by Tausz and von Körösy and by Erk (*cf.* A., 1929, 499, 500). The application of the authors' results to the question of the permeability of living cells is discussed.

F. L. USHER.

**"Chemical theory" of antagonistic effect of ions in solution and at an interface. General theory of such mutual effects.** I. N. MUKHERJEE (Kolloid-Z., 1929, 49, 362—371).—A lecture in which the chemical theory of the mutual influence of ions at an interface is compared with the physical theory. The theories of surface dissociation and ion adsorption are explained.

E. S. HEDGES.

**Structure of surface films. XIII.** O. ROSENHEIM and N. K. ADAM. See this vol., 257.

**Membrane and osmosis. I.** F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 837—844).—Theoretical. A discussion of the bearing of the adsorption of one or more substances by a membrane on the problem of osmosis. Five possible types of system differing according to the nature of the adsorption complex are postulated.

F. G. TRYHORN.

**Measurements by the dialysis method. System electrolyte-water.** H. BRINTZINGER and B. TROEMER (Z. anorg. Chem., 1929, 184, 97—120; *cf.* A., 1928, 121, 833; 1929, 1003).—The method of dialysis described in previous papers has been applied to the investigation of electrolytes in aqueous solution. At a constant temperature and an external concentration approaching zero, the relation between log (concentration in dialyser) and time of dialysis is linear for alkali and alkaline-earth chlorides. The coefficients of dialysis decrease in the order caesium, rubidium, potassium, sodium, lithium, barium, strontium, calcium, and bear a linear relation to the

strength of the electric field at the surface of the cations, but do not run parallel with the equivalent conductivity. Electrolytes with the same cation but different anions give coefficients which decrease in a linear manner with increase in the electric field round the anion. Addition of a foreign electrolyte (*B*) with a common ion increases the rate of dialysis of another electrolyte (*A*), but if the added electrolyte has no common ion, the dialysis of one of the ions of *A* is accelerated or retarded according as the oppositely charged ion of *B* has a higher or lower mobility than the corresponding ion of *A*. The alkali and alkaline-earth chlorides have the same temperature coefficient of dialysis, viz., 0.022. The dialysis coefficients of chlorides of trivalent and quadrivalent cations are not constant, and the course of dialysis is represented by separate curves for the cation and anion, these curves being inclined to each other at an angle which increases with the degree of hydrolysis and with the rate of ageing of the resulting hydroxide.

F. L. USHER.

**Dialysis, ultrafiltration, and coagulation of molybdic acid.** L. S. BHATIA, S. GHOSH, and N. R. DEAR (Z. anorg. Chem., 1929, 184, 135—144).—Experiments on the dialysis and ultrafiltration of molybdic acid solutions indicate that a large proportion of the acid is in the molecular condition in the freshly-prepared solution, and that the amount of colloidal molybdic acid increases with time. These conclusions are supported by conductivity measurements. Addition of acids increases the amount of colloidal molybdic acid, and that of alkalis diminishes it. Dilution of the solutions stabilises them towards electrolytes, and ultrafiltration shows that dilution diminishes the proportion of colloidal acid.

F. L. USHER.

**Collodion membranes. III. Dialysis through collodion membranes and the relation between dialysis, diffusion, and membrane structure.** E. MANEGOLD (Kolloid-Z., 1929, 49, 372—395; cf. A., 1927, 727, 1022).—Experiments on the rate of dialysis of substances through collodion membranes have led to the calculation of a "dialysis constant," which is defined as the number of g.-mol. of a substance diffusing through 1 cm.<sup>2</sup> of the membrane surface in 24 hrs. under a concentration gradient of 1 mol. per litre and at a given temperature. The dialysis constant of a collodion membrane depends on its water content, its thickness, and the ease of penetration by water. The relation between the dialysis constant and the membrane structure is treated mathematically and the influence of the size and shape of the particles on filtration is considered. The results are applied to the processes occurring at membranes in the living organism.

E. S. HEDGES.

**Determination of the porosity of heteroporous membranes. II.** A. V. DUMANSKI and A. P. DUMANSKAJA (J. Russ. Phys. Chem. Soc., 1929, 61, 1243—1250).—A method for the measurement of the diameter and the number of the pores of heteroporous membranes is based on the principle that at any given pressure only pores of a certain diameter will allow gas to pass through them into a liquid. Measurement of the volume of gas passing through different mem-

branes in unit time at a number of different pressures is used to determine the number of pores of each diameter in the given membrane.

R. TRUSZKOWSKI.

**Electrometric behaviour of artificial membranes composed of selectively cation- and anion-permeable portions of surface.** R. HÖBER and F. HOFFMANN (Pflüger's Archiv, 1928, 220, 558—564; Chem. Zentr., 1929, ii, 435).—The membranes were composed of dried collodion and rhodamine-collodion portions respectively. Determinations of the chemical potentials between 0.1*N*-potassium and sodium chlorides, sodium chloride and thiocyanate, sodium chloride and potassium thiocyanate, and the concentration potentials between potassium chloride, potassium ferrocyanide, and barium chloride solutions of various concentrations showed that each portion of surface exhibited independently its characteristic membrane potential. The concentration effect for a rhodamine-collodion membrane between potassium chloride solutions of various concentrations is of opposite sign to that with a collodion membrane, and falls (in contradistinction to the latter) with increasing dilution of one solution. The plasma membrane of *Valonia* probably behaves like such a composite membrane.

A. A. ELDRIDGE.

**Theory of electro-osmosis. I.** S. KOMAGATA (Bull. Chem. Soc. Japan, 1929, 4, 255—264).—Mathematical. Equations are derived for the distribution of potential and of electric charge in a capillary, and for the flow of liquid and of electric current.

O. J. WALKER.

**Compressibility of aqueous solutions.** E. P. PERMAN and W. D. URRY (Proc. Roy. Soc., 1929, A, 126, 44—78).—Details are given of an apparatus, constructed of steel and designed to work up to pressures of 250 atm., by means of which accurate measurements have been made of the compressibilities of aqueous solutions of sucrose, carbamide, potassium chloride, and calcium chloride at temperatures ranging from 30° to 80° and pressures from 1 to 200 atm. The results are discussed with regard to (a) compressibility in equimolecular solutions and (b) the variation of compressibility with concentration. The compressibility-concentration curves indicate that the lowering of the compressibility at any given concentration is much greater in the case of the large sucrose molecule than in that of the carbamide molecule. Calcium chloride, however, causes a lowering of the compressibility nearly equal to, and at temperatures higher than 50° greater than, that due to sucrose, the calcium chloride curve first crossing the sucrose curve at 50° at about  $n/N=0.063$ , and at 80° at  $n/N=0.017$ . The lowering of compressibility does not depend directly on the mol. wt. of the solute, but on the changes in the cohesive and chemical intrinsic pressures of the system. Mean values of the compressibilities of the various solutions have been calculated by means of the formula  $c=100Mc_d/[100M-x(M-18n)d_s]$ , where  $c$  is the molecular compressibility of the solution,  $d$  the density of the pure solvent,  $d_s$  that of the solution,  $M$  the mol. wt. of the solute,  $x$  the weight in g. of solute per 100 g. of solution,  $n$  the dissociation factor, and  $C$  the mean compressibility. The agree-

ment between the calculated and experimental values is extremely good, and suggests that dissociation is complete in the electrolyte solutions.

Osmotic pressures of solutions of sucrose, carbamide, potassium chloride, and calcium chloride are calculated from the experimental data by means of a modification of Porter's general equation. For sucrose, carbamide, and potassium chloride solutions, the osmotic pressures on the whole increase with rising temperature. The same behaviour is shown by dilute calcium chloride solutions, but with solutions more concentrated than 30% the osmotic pressure decreases above 50°.

L. L. BIRCUMSHAW.

**Internal friction of mixed solutions.** W. HERTZ and F. HIEBENTHAL (*Z. anorg. Chem.*, 1929, **184**, 409—415).—The comparative influence of sodium chloride at various concentrations on the viscosity of water and of aqueous carbamide and dextrose solutions has been determined; the percentage difference of viscosity is greater at 70° than at 25°, and is greater for the solutions of non-electrolytes than for water. The chlorides of barium, calcium, and magnesium exert a similar influence, although for magnesium the temperature effect is reversed. The depressor action of the potassium halides on water is apparent in its influence on the viscosity of solutions of non-electrolytes.

H. F. GILBE.

**Viscosity, conductivity, and diffusion of aqueous solutions of isomorphous salts.** S. G. MOKRUSCHIN and E. I. KRILOV (*J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1285—1293).—The viscosity of solutions of isomorphous salts should be constant for any given concentration, assuming that the heat of dilution and the volumes of hydrated molecules are the same for all members of a series of isomorphous salts. Further, on the assumption that the heat of ionisation of all such salts is the same, and that its value varies in the same way with the degree of ionisation for all isomorphous salts, the conductivity of their solutions should be the same at any given concentration. Finally, if the viscosities and molecular and ionic volumes of isomorphous salts in solution are the same for all such salts, the coefficients of diffusion should also be equal. The validity of this theoretical reasoning was confirmed by experiment.

R. TRUSZKOWSKI.

**Colorimetric standards II. Relation of colour to concentration for aqueous solutions of certain inorganic salts.** M. G. MELLON (*J. Physical Chem.*, 1929, **33**, 1931—1940).—Numerical values for the colour of solutions of copper sulphate, copper ammonio-sulphate, ammonium chromate, ferric and cobalt chlorides, potassium dichromate, and pentammino-cobalt chloride have been derived from previous data (*A.*, 1927, 329) and the effect of dilution is considered.

L. S. THEOBALD.

**Ebullioscopic study of the molecular equilibria of resorcinol in solutions of calcium chloride.** F. BOURION and E. ROUYER (*Compt. rend.*, 1929, **189**, 1081—1082; cf. *A.*, 1929, 729).—For concentrations of resorcinol of 0.5—2.0 in both 0.25*M* and 0.6125*M* solutions of calcium chloride, equilibria between simple and double or triple molecules are indicated. The ebullioscopic constant of calcium chloride solution

increases with the concentration; it is greater than that of potassium chloride solution or of water, and of the same order as that of sodium chloride solutions of equivalent concentration. There is therefore evidence of adsorption of water by the ions of the salt.

J. GRANT.

**Square-root law of viscosity of strong electrolytes.** H. FALKENHAGEN and M. DOLE (*Z. physikal. Chem.*, 1929, **B**, **6**, 159—162; cf. Jones and Dole, *A.*, 1929, 1385).—Preliminary. The square-root law  $\eta_c = \eta_0(1 + A\sqrt{c})$ , where  $c$  is the normality of the solution,  $\eta_c$  and  $\eta_0$  are the coefficients of viscosity of solution and solvent, respectively, and  $A = 0.491 \times 10^{10} \epsilon z / 60 \eta_0 \sqrt{DkT} z$  ( $\epsilon$  is the charge,  $z$  the valency and  $\rho$  the frictional resistance of an ion,  $D$  the dielectric constant, and  $k$  the Boltzmann constant), is deduced from the Debye-Hückel conception of the ionic atmosphere, and values of  $A$  are calculated for a number of uni-univalent electrolytes. The expression in the form given above applies only to electrolytes in which the mobilities of the ions are equal.

F. L. USHER.

**Dependence of rotatory power on chemical constitution. XXXIV. Borotartaric acid.** S. G. BURGESS and H. HUNTER (*J.C.S.*, 1929, 2838—2852).—The system boric acid-*d*-tartaric acid-water has been investigated at 0°, 25°, and 50°. No borotartaric acid exists as a solid phase, but there is some evidence for the combination of the acids in the liquid phase. The  $p_H$  of solutions of mixtures of boric and tartaric acids has been measured. Borotartaric acid is comparable in strength with sulphuric acid. It is suggested that borotartaric acid contains a semipolar double linking between the boron atom and one of the oxygen atoms of the tartaric acid.

C. W. GIBBY.

**Grain size and grain-boundaries.** F. SKAUPY (*Monatsh.*, 1929, **53** and **54**, 73—82).—The significance of these factors is discussed in relation to ductility and hardness, conductivity and light-absorbing capacity.

L. S. THEOBALD.

**Preparation of metal sols in organic dispersion media by electrical disintegration.** E. BERL, K. BARTH, and K. WINNACKER (*Z. physikal. Chem.*, 1929, **145**, 298—302).—Apparatus is described for the preparation of sols of magnesium, zinc, lead, tin, copper, and iron in organic liquids, whereby the excessive development of gas bubbles and the separation of carbon associated with Svedberg's original method are avoided. The dispersions obtained are stable in oxygenic solvents, but the addition of rubber as protective is necessary when hydrocarbons are used.

F. L. USHER.

**Bredig silver hydrosol.** R. J. BEST and A. B. COX (*J.C.S.*, 1929, 2727—2732).—Silver sols obtained by arcing under water of specific conductivity 0.4—0.5  $\times 10^{-6}$  mho are most stable if the temperature during preparation is kept between 15° and 40°. Arcing for periods greater or less than 40—55 min. gave sols which were not permanently stable. Conductimetric titrations showed that the electrolyte produced is silver hydroxide. The clear liquid obtained by thawing a frozen sol contains more silver hydroxide than the original sol.

C. W. GIBBY.

**Preparation of concentrated silicic acid sols.** A. A. CHALIZEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1233—1237).—Potassium tartrate is precipitated on the addition of tartaric acid to potassium silicate solutions; the filtrate is a stable silicic acid sol, and may contain to 5%  $\text{SiO}_2$ , with not more than 0.03—0.04*M*-potassium hydrogen tartrate present. Such silica sols are very stable, often not coagulating for several months. R. TRUSZKOWSKI.

**Potassium chloride in fibrous form.** A. KUTZELNIGG (Kolloid-Z., 1929, 49, 439—441).—When saturated solutions of potassium ferrocyanide and ferric chloride are mixed and the gel of Prussian-blue so obtained is allowed to dry, an efflorescence appears, consisting of fibrous crystals of potassium chloride. After a few weeks these fibres may attain a length of a few cm. and a breadth of 1 mm. Most of the fibres contain enclosed Prussian-blue. Similar fibres of potassium chloride were obtained by drying the gel obtained by mixing saturated solutions of ferric chloride and potassium phosphate. E. S. HEDGES.

**Method of determining concentrations of colloidal solutions. (Use of Tyndall effect.)** O. EINSTEIN and H. BORCHERT (Naturwiss., 1929, 17, 997).—The principle of the method depends on the extinction of the Tyndall effect. A series of solutions of decreasing concentration was made, and the amount of dispersion medium required to make the Tyndall effect disappear was found. Two quantities can be distinguished: (1) a number which expresses the concentration at which the Tyndall effect is just not extinguished; (2) a number which gives the concentration when the Tyndall effect no longer occurs. Inside this range standard curves can be drawn from which the concentration can readily be derived. A. J. MEE.

**Law of particle projection.** A. Soós (Kolloid-chem. Beih., 1929, 30, 109—112).—The author has previously shown (*ibid.*, 1927, 24, 123; A., 1926, 575) that the intensity of light which has passed through a colloidal solution is a stepwise function of the thickness of the layer of sol. Certain inconsistencies in the former results are now explained. E. S. HEDGES.

**Temperature at which glass containing gold becomes red, and the temperature at which induced birefringence in glass disappears.** G. TAMMANN and H. SCHRADER (Z. anorg. Chem., 1929, 184, 293—294).—Finely-divided gold dissolved in a molten silicate glass imparts no colour to the latter when rapidly cooled, since the gold is present in the atomic state. Experiments in which glasses containing 0.4—2.0% Au are maintained at different constant temperatures for 6 hrs. show that a deep red colour is developed in every case at and above 390°; hence at this temperature the gold atoms possess sufficient mobility to unite to form ultramicroscopic particles. When specimens of the same glass are suddenly chilled after being heated at various temperatures, it is found that a temperature of 385° is required to produce double refraction. The temperature at which the latter vanishes depends on the temperature from which the glass has been chilled; e.g., the double refraction due to chilling from 388° disappears when the glass is subsequently heated to 388°, whereas that due to

chilling from 650° vanishes at 351°. These results indicate that the reddening of glass containing gold and the production of double refraction by chilling are both processes requiring a certain freedom of movement of the glass molecules. F. L. USHER.

**Relation between dielectric constant of emulsions, volume concentration of the dispersed phase, and degree of dispersion.** A. PIEKARA (J. Phys. Radium, 1929, [vi], 10, 360—369).—See A., 1929, 27.

**Dielectric polarisation and structure of hydrophilic colloids.** N. MARINESCO (Compt. rend., 1929, 189, 1274—1276).—Debye's theory of the dielectric polarisation of solutions is used to determine micelle size and to explain the author's observations on the inductive powers of colloids (A., 1929, 646, 1142). It is shown that 1 g. of substance fixes dielectrically  $(V_E - V_S)/M$  c.c. of water, where  $V_E$  and  $V_S$  are the mol. volumes in solution and in the solid state, respectively, and  $M$  is the mol. wt. The polarity of the solution and the electric moment are then deduced. The hydrophilic coefficients of crystalline haemoglobin, gelatin, and ovalbumin are 15, 8—10, and 11—13 c.c. of water per gram of dry substance, respectively, and are minimal at the isoelectric points. J. GRANT.

**Internal friction and the structure of "solvated colloids."** E. O. KRAEMER and R. V. WILLIAMSON (J. Rheology, 1929, 1, 76—92).—A model of a solvated colloid particle is discussed, and applied qualitatively to the consideration of internal friction and other physical properties. C. W. GIBBY.

**Thermodynamic analysis of the observed osmotic pressures of protein salts in solutions of finite concentration.** G. S. ADAIR (Proc. Roy. Soc., 1929, A, 126, 16—24).—The partial osmotic pressure of the protein ions ( $p_p$ ) may be calculated from the observed osmotic pressure ( $p$ ) of a solution of a protein salt, measured with membranes permeable to water and other crystalloids but impermeable to the protein, by the formula  $p = p_p + p_i$ , where  $p_i$  is the diffusible ion pressure difference, or the pressure due to the excess of diffusible ions inside the membrane. In order to confirm the provisional estimates (cf. A., 1928, 1326) of  $p_p$  and  $p_i$  and to interpret the osmotic pressures of concentrated protein solutions a more general method, based on the fundamental equations of Gibbs, is now developed. The following formula is derived:  $p_i = RT \int_0^c m_p n_p du$ , where  $m_p$  = g.-mol. of protein per litre of solvent,  $n_p$  = the mean value of the electric charge or valency of the protein ions in the assemblage of protein ions of different valencies, and  $u = EF/RT$ ,  $E$  being the membrane potential of the protein salt, measured under conditions where the activities of the diffusible salts have been kept constant by the equilibration of protein solutions of different concentrations with a standard solution of diffusible electrolytes. Both methods have been applied to a system composed of haemoglobin, water, potassium chloride, disodium phosphate, and potassium dihydrogen phosphate; the values of  $p_p$  are found to be almost identical in the case of dilute protein solutions, whilst with concentrated solutions the error in the provisional value is about 6%. L. L. BIRCUMSHAW.



**Plasticity of solvated colloids.** S. E. SHEPPARD and R. C. HOUCK (J. Rheology, 1929, 1, 20—30).—Measurements of the thickness of the thinnest coherent films of substances such as cellulose acetates and nitrate on mercury probably give the transverse dimensions of long-chain molecules, a conclusion in agreement with X-ray measurements. In solutions of cellulose and its derivatives the micelles may be chain- or leaf-like structures, of molecular dimensions transversely, produced by inter-crystallite swelling and complete solvation. The peptisation of many solvated colloids, particularly of cellulose derivatives, is often more effective in mixtures of two or more solvents. Evidence regarding the production of homogeneous solutions of solvated colloids has been sought by investigating the influence of solvent composition on the viscosity of a cellulose ester solution. The character of the curve obtained depends on the nature of the ester, the viscosity sometimes passing through a minimum. The sols of minimum viscosity behave as homogeneous liquids, showing no plasticity. Plastic sols containing greater or smaller amounts of water than those of minimum viscosity show diminished plasticity after shearing. It is considered that plastic flow in solutions of solvated colloids is evidence of incipient gel formation or incomplete dispersion.

C. W. GIBBY.

**Galvano-colloids. II. Formation of aluminium hydroxide.** A. V. DUMANSKI and Z. P. TSCHESCHEVA (J. Russ. Phys. Chem. Soc., 1929, 61, 1345—1351).—The process of formation of alumina sol by the addition of water to aluminium amalgam or to aluminium-platinum couple is accelerated by increase in the reacting surface, and by the addition of aluminium chloride or potassium hydroxide. Sols containing up to 2.3% of alumina can be prepared in this way in about 2 hrs. Sols so prepared are often dark in colour, due to the presence of particles of colloidal aluminium. The particles of alumina in these sols are charged positively. The above process consists first in the formation of hydroxide, and then in its peptisation by aluminium chloride; the former process is 1.4 times as fast as the latter, so that alumina gel is formed simultaneously with sol. An alumina sol can also be prepared by dissolving aluminium foil in boiling 0.01N-potassium hydroxide solution containing 2% of mannitol, when a yellow alumina gel and a white sol are obtained, showing that in this case, too, the process of peptisation is slower than that of hydroxide formation. Aluminium plates attacked by acids have a spongy surface, whilst alkalis produce a pitted surface. Alumina gel is exclusively obtained by the anodic oxidation of aluminium anodes in water, whilst alumina sol is formed when the medium contains aluminium chloride. After protracted passage of the current the presence of particles of colloidal aluminium can be observed. The rate of dissolution of the anode is constant. Sol formation does not take place in the electrolysis of potassium hydroxide-mannitol solutions; this is ascribed to passivation of the aluminium anode. Aluminium cathodes were amalgamated by passing a current through aluminium chloride solution, with a mercury anode; on breaking the current, the cathode began to dissolve with the formation of alumina sol.

R. TRUSZKOWSKI.

**Time-changes of emulsoids. Theory of syneresis.** S. LIEPATOV (Kolloid-Z., 1929, 49, 441—450).—Sols of viscose are very unstable and change with time; the viscosity falls during the first few days and afterwards rises rapidly, and the position of the viscosity minimum falls earlier for more dilute solutions. Finally, the sols set to gels and this change occurs more readily in the more dilute sols. The presence of electrolytes accelerates both the viscosity change and the sol-gel transformation, but the effect of electrolytes is less marked in concentrated viscose sols. The viscosity minimum and the sol-gel transformation appear earlier at higher temperatures. The lowering of viscosity is considered to be due to hydrolytic chemical changes occurring in the colloid particles. Syneresis appears in the gels the earlier, the more dilute is the gel and the higher is the temperature. The processes of gelation and syneresis are discussed in relation to the experimental results reported and it is maintained that gelation and syneresis depend on the approximation and mutual binding of hydrated particles through the operation of molecular attractive forces.

E. S. HEDGES.

**Stability of the sols of tungstic, vanadic, and silicic acids.** S. GHOSH and N. R. DHAR (J. Physical Chem., 1929, 33, 1905—1921).—The influence of electrolytes on the stability and viscosity of sols of tungstic, vanadic, and silicic acids has been investigated. Tungstic acid conforms to the Schulze-Hardy law and concentrated sols require more of an electrolyte than dilute sols for coagulation. The effect of a mixture of the chlorides of potassium and barium necessary for coagulation is additive. As compared with sodium chloride and potassium nitrate, larger quantities of acids and smaller amounts of the salts of weak acids are required to coagulate sols of vanadic and tungstic acids, and, like silicic acid, these sols are stabilised by hydrogen ions and sensitised by hydroxyl ions. The viscosities of these sols are increased by traces of an alkali and decreased by small amounts of acid. Ageing is accompanied by an increase in viscosity and by a decrease in specific conductance in the case of vanadic and tungstic acids, but with silicic acid viscosity and conductivity both increase. Boiling favours instability, and sols of tungstic and vanadic acids become more conducting but less viscous.

L. S. THEOBALD.

**Factors influencing precipitation of colloidal lead.** H. Q. WOODWARD (J. Cancer Res., 1929, 13, 173—179).—The coagulation of Bredig lead sols is greatly accelerated by rise of temperature; up to 37° it is retarded by addition of formaldehyde or dextrose (forming soluble compounds), and hastened by that of hydrogen peroxide.

CHEMICAL ABSTRACTS.

**Colloidal platinum in general colloid theories.** S. W. PENNYCUICK (Kolloid-Z., 1929, 49, 407—412).—The author's work on colloidal platinum is reviewed in the light of Pauli's theory, which it is shown to support. Part of the surface of colloidal platinum consists of a strong platonic acid—probably  $\text{H}_2\text{Pt}(\text{OH})_6$ —and the hydrogen ions of this acid are replaceable by the cations of added salts. The acid contained in the surface is responsible for the negative charge and the stability of the sol. The surface of the particles also

contains a feebly acidic oxide, which is held responsible for the protective effect of univalent bases on colloidal platinum and also for the peptising action of univalent bases on the coagulum. In the preparation of colloidal platinum sols by Bredig's method, the presence of oxygen is not necessary for the stability of the sol; the momentarily high temperature of the platinum particles and the electrolysis of the solution are sufficient factors for the formation of stabilising oxidation products. E. S. HEDGES.

**Colloid solubility.** I. N. JERMOLENKO (Kolloid-Z., 1929, 49, 424—433).—The factors determining the solubility of colloids are discussed and compared with those affecting molecular solubility. In particular, the effect of ageing and the influence of the amount of solid phase are discussed. Experiments have been directed to establishing the validity of the solid-phase rule for the dissolution of copper carbonate by ammonia in presence of ammonium chloride. The relation between the amount peptised and the amount of solid phase shows that the process is an example of dissolution-peptisation in Wo. Ostwald's classification. The chemical nature of the solid phase is not altered by peptisation with dilute electrolytes. The solubility of copper carbonate in ammonia is increased, not only by ammonium chloride, but also by addition of potassium nitrate. E. S. HEDGES.

**Unequal distribution of stabilising factors on the surface of colloidal particles.** H. R. KRUYT (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 857—863).—The behaviour of colloidal particles in cataphoresis and coagulation is discussed on the assumption that the stabilising factor, *e.g.*, electric charge, is distributed unequally on the surface. In such a case the coagulation probability of aggregated particles becomes less than that of the individual particles, owing to the screening of the uncharged surfaces in the aggregate by the charged surfaces. F. G. TRYHORN.

**Coacervation. (Partial miscibility in colloid systems.)** H. G. B. DE JONG and H. R. KRUYT (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 849—856, and Kolloid-Z., 1930, 50, 39—48).—The term "coacervation" is applied to the process of the visible separation into its component phases of a quasi-homogeneous lyophilic colloid. At temperatures between 40° and 50° coacervation occurs in iso-stable protein sols on the addition of aliphatic alcohols, simple and poly-phenols, and many inorganic and organic salt solutions. As for flocculation, a decrease in the charge and the hydration in the colloid systems are necessary for coacervation, but in the latter phenomenon the water in the coacervate is in a condition in which it is not miscible with the rest of the water in the system. In coacervation the original particles are regarded as having united so far as their solvation layers are concerned, with the result that the coacervate has the nature of a liquid, the solvate liquid having in some degree lost its mobility. The initial stages of coacervation are brought about by desolvation through a change in the constitution of the dispersion medium produced by the addition of the coacervating agent. F. G. TRYHORN.

**Action of solutions of electrolytes on kaolin suspensions.** I. I. SHUKOV, E. A. KREMLEV, and I. P. PROMAS (J. Russ. Phys. Chem. Soc., 1929, 61, 1329—1338).—The increase in the velocity of filtration of Gluchov kaolin suspensions caused by the addition of electrolytes is a function of the valency of the cation but not of the anion of the given electrolyte. An exception to this is, however, the stabilising action of hydroxyl ions. The process of coagulation of Gluchov kaolin suspensions is determined both by the action of cations and by the increase in size of coagulate particles; with Gluchovietz kaolin the second factor is absent. For this reason, the coagulative action of electrolytes on suspensions of the former kaolin cannot be estimated by measuring the bulk of coagulate formed. R. TRUSZKOWSKI.

**Formation of periodic structures by salting-out and by coagulation.** E. S. HEDGES (J.C.S., 1929, 2779—2782).—Periodic precipitation of sodium chloride may be obtained by allowing hydrogen chloride to diffuse into a horizontal capillary tube containing the salt solution. The spacing increases in a manner similar to that of the ordinary Liesegang effect. Similar results were obtained with potassium chloride, and with barium nitrate and nitric acid. These results cannot be explained by the present theories of the Liesegang phenomenon. When 1—30% ferric chloride solution diffuses into 0.1% arsenious sulphide sol in capillary tubes, definite bands are not formed, but the coagulum consists of an undulatory band. C. W. GIBBY.

**Hydrates and hydrogels.** H. KRAUT (Kolloid-Z., 1929, 49, 353—361).—An attempt is made to devise a method for the comparison of hydrogels, particularly those of aluminium hydroxide and stannic hydroxide, by consideration of their colour, surface, solubility in acids or bases of given concentration, water content under given drying conditions, and adsorptive capacity towards enzymes. The properties of gels of aluminium hydroxide prepared under different conditions of concentration and temperature are described, and in the case of stannic hydroxide it is shown that the division into  $\alpha$ - and  $\beta$ -stannic acid is not satisfactory. Changes in the properties of chromium hydroxide gel on ageing are described. E. S. HEDGES.

**Hydrogels. VI. Conversion of water of hydration into water of adsorption in the mechanical disintegration of hydrated crystals.** A. SIMON and O. FISCHER. **VII. Hydrates of chromic oxide.** A. SIMON, O. FISCHER, and T. SCHMIDT. **VIII. Hydrates of zirconium dioxide.** A. SIMON and O. FISCHER (Z. anorg. Chem., 1929, 185, 101—106, 107—129, 130—143; cf. Hagiwara, A., 1923, ii, 234; Simon and others, A., 1927, 510, 511, 730; 1929, 27; Hüttig, Magierkiewicz, and Fichmann, A., 1929, 511).—VI. Hagiwara's experiments on the effect of fine grinding on the condition of the water in aluminium hydroxide have been repeated with adequate precautions to secure the establishment of equilibrium. A crystalline hydroxide of the composition  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , after being ground under water to colloidal dimensions, had a water content of 2.78 mols., thus showing that the treatment had effected a chemical change, probably due to local heating. Comparison of the

dehydration isobars of this and the untreated hydroxide shows that, apart from this partial decomposition, their behaviour is identical. Hagiwara's conclusions are not substantiated.

VII. Hydrated chromic oxide was prepared by slow precipitation in the cold from dilute solution (*A*), by rapid precipitation from hot concentrated solution (*B*), by slow dialysis of 1% chromic nitrate solution (*C*), by precipitation from solution in alkali (*D*), and by prolonged heating of a precipitated specimen with water under pressure (*E*). Isobaric dehydration curves were determined for the different preparations, and in the cases of (*A*) and (*E*) evidence of the presence of a monohydrate, and less certainly of trihydrate, was obtained. X-Ray diagrams showed definite interference lines only with (*E*). The heat of formation calculated by means of Nernst's approximation formula was greatest for (*E*) and least for (*B*), whence it is inferred that water is more firmly combined in the former. Experiments on the peptisation or dissolution of preparations of different ages in various solutions lead to the same classification as do the other methods of investigation. It is concluded that freshly-prepared specimens are always amorphous and that the water is held mainly by capillarity. The process of ageing is extremely slow and consists in the combination of water to a monohydrate, and possibly to a trihydrate. Specimens prepared under conditions of slow molecular aggregation are of a more advanced "age" than those in which the aggregation was rapid.

VIII. Experiments with zirconium dioxide similar to those described for chromic oxide indicate that no definite hydrate is formed under any conditions, and that the final result of ageing is the production of the anhydrous oxide + water. Little difference was observed between specimens prepared under conditions of rapid and of slow aggregation. F. L. USHER.

**Solid-phase rule. II. Dissolution and peptisation of oxides and hydroxides.** WO. OSTWALD and W. RÖDIGER (Kolloid-Z., 1929, 49, 412—423; cf. this vol., 34).—The validity of the solid-phase rule has been investigated for several metallic hydroxides. The variation of the amount of substance peptised with the amount of the solid phase present has been established by means of quantitative experiments on the peptisation of stannic acid by hydrochloric acid and by potassium hydroxide at 10° and at 100°, aluminium hydroxide by hydrochloric acid, zinc hydroxide by sodium hydroxide, and bismuth hydroxide by lactose and by sucrose. Exceptions to the solid-phase rule appear in the systems zinc hydroxide-hydrochloric acid and zinc hydroxide-acetic acid, where the solubility is independent of the amount of the solid phase. It is held that in the exceptional cases molecular chemical reaction is chiefly concerned, whilst the solid-phase rule applies where colloid-chemical processes are mainly involved. The four types of peptisation curve (previously reported) are further discussed. E. S. HEDGES.

**Electrokinetic potential and its relation to the rate of coagulation of colloids. I.** B. N. GHOSH (J.C.S., 1929, 2693—2703).—The electrokinetic potentials of arsenious sulphide and ferric hydroxide sols in the zone of rapid coagulation have been investig-

ated. The potential is the higher the greater is the coagulating concentration of a univalent cation. The zone of rapid coagulation is variable. Addition of potassium or lithium chloride to salts of multivalent cations raises the potential at which coagulation takes place, the rise increasing with the amount of potassium chloride present. The rate of coagulation of arsenious sulphide sol by these mixtures does not depend on the electrokinetic potential. Ferric hydroxide sol is coagulated by various electrolytes at a potential of about 32 millivolts, in agreement with the conception of a critical potential. Its rate of coagulation is accelerated by the addition of thymol, urethane, and methyl alcohol, with corresponding lowerings of potential. The coagulation of arsenious sulphide sol by potassium chloride is accelerated by the addition of phenol and amyl alcohol, which retard coagulation by strontium chloride, in both cases without change in the potential. The anomalous behaviour of arsenious sulphide sol can be explained if there is an attractive force between the particles varying as a higher power of the distance than that involved in the electrical repulsion of the double layers, and if there is strong preferential adsorption of the ion having the same charge as that of the colloid. C. W. GIBBY.

**Precipitation of mercuric iodide in gels and in glycerol.** B. KIRSCH (Kolloid-Z., 1929, 49, 433—435).—Further experiments (cf. A., 1929, 1382) on the interaction of mercuric chloride and potassium iodide in media of gelatin and agar are described; the formation of precipitation rings is complicated by the fact that mercuric iodide is soluble in excess of either of the reagents. When mercuric iodide is precipitated in a viscous medium such as gelatin or glycerol, the yellow form is produced and is unusually stable at the ordinary temperature. Contrary to the accepted view, this phenomenon is not directly connected with the viscosity of the medium. The stability of the yellow modification is favoured by a hygroscopic medium and by a low content of water. The transformation of the yellow form into the red is accelerated by light and by rise of temperature.

E. S. HEDGES.

**Electrophoresis of protein sols in the presence of gold sols. Albumin, gelatin, and casein.** E. B. R. PRIDEAUX and F. O. HOWITT (Proc. Roy. Soc., 1929, A, 126, 126—137).—The macro- and micro-methods for the determination of electrophoretic velocities in an electric field are reviewed and compared, and reasons are advanced for considering the macro-method to be the more exact. Details are given of an improved U-tube apparatus by means of which the electrophoretic motion of gold sol boundaries has been measured, and results are recorded for the following solutions: gold 0.01—0.015%, albumin 0.05—0.1%, acetate buffer 0.02N; gold 0.01%, gelatin 0.1%, acetate buffer 0.002—0.02N; gold, casein, and acetate buffer. The agreement between the results of different investigators using different methods is best in the case of albumin. The curve representing the variation of the velocity with  $p_H$ , obtained in the present investigation, is almost exactly a straight line which cuts the axis of

zero velocity at  $p_H$  4.95. In the case of gelatin, the results show a want of symmetry in the cataphoresis, but the points down to  $p_H$  5.5 lie almost on a straight line which makes about the same angle with the abscissa as the corresponding line for albumin, and cuts the line of zero velocity at the same point,  $p_H$  4.95. From  $p_H$  6.0 onwards, the velocity appears to remain fairly constant. With casein two sets of results are obtained, according as velocities are taken on the upward or downward moving sides. The minimum  $p_H$  at which a stable solution and a definite negative velocity could be obtained was 4.75, and an isoelectric zone is indicated within the limit  $p_H$  3.65–4.75.

L. L. BIRCUMSHAW.

**Formation of pectin jellies by sugar.** G. SPENCER (J. Physical Chem., 1929, 33, 1987–2011).—The conditions underlying gelation in the system acid(or alkali)-pectin-sugar have been investigated using a method for the preparation of gels in the cold. The minimum concentrations of acid and sugar necessary to form a gel when plotted against each other give two fields in which gelation occurs on the acid and alkaline side of neutrality and which enclose a pectin sol region. With other precipitating agents, such as alcohol or glycerol, the boundary line becomes continuous with a maximum near the neutral point. In the case of sugar the field of gelation on the acid side is enlarged by an increase in concentration of pectin. Further experiments support the hypothesis that pectin sol is stabilised by adsorbed water and anions, and the soluble organic compounds which destabilise the sol do so by lowering the vapour pressure of the dispersion medium and in some cases by neutralising the negative charge resulting from anion adsorption. An increase in hydrogen or hydroxyl ions on either side of the maximum of the boundary curve decreases the amount of adsorbed water and hence the amount of precipitant required. The practical application of this hypothesis in jelly-making is discussed.

L. S. THEOBALD.

**Effect of salts on sugar-pectin jelly-formation.** G. SPENCER (J. Physical Chem., 1929, 33, 2012–2020; cf. preceding abstract).—Mainly a discussion of the results of previous investigators. Salts generally precipitate pectin more readily in alkaline than in acid solutions. The gel-sol boundary line is slightly depressed by the addition of salts in alkaline solution and raised in acid solution.

L. S. THEOBALD.

**Antagonistic action of ions on gelatin.** R. LABES and H. ZAIN (Arch. exp. Path. Pharm., 1929, 146, 63–77).—The precipitation of gelatin from aqueous solution by alcohol which in the absence of salt reaches a maximum at the isoelectric point of gelatin ( $p_H$  4.7) is affected in such a way by the presence of small quantities of calcium chloride that the maximum precipitation occurs on the alkaline side of the isoelectric point. In the presence of sodium chloride the maximum is displaced towards the acid side, but in this case considerably larger concentrations of the salt are required to effect the same degree of displacement. When both salts are simultaneously present they oppose each other's action, but the effect of a given quantity of calcium chloride is neutralised only by a considerably larger quantity of sodium

chloride. These observations explain the apparent antagonistic action of these two salts in relation to their action on gelatin described by Fenn (Proc. Nat. Acad. Sci., 1916, 2, 534). W. O. KERMACK.

**Influence of alkaloids on the flocculation optimum of lecithin.** H. ZAIN (Arch. exp. Path. Pharm., 1929, 146, 78–83).—Suspensions of Merck's commercial egg-lecithin in buffer solutions of various  $p_H$  values show maximum flocculation at  $p_H$  1.9–2.4, but when alkaloid salts are present in suitable concentrations (morphine hydrochloride, cocaine hydrochloride, atropine sulphate, strychnine nitrate, or quinine hydrochloride) the zone of flocculation is displaced to a less acid reaction and becomes broadened. Very little effect is noticed with concentrations of alkaloids 1 in 20,000. The effect is quite marked with concentrations 1 in 2000, whilst at concentrations 1 in 200 the zone of flocculation is much displaced and very broad. The above salts are in the order of their activity, morphine hydrochloride being the least and quinine hydrochloride the most active.

W. O. KERMACK.

**Dissociation of acids in methyl and in ethyl alcohol.** D. M. MURRAY-RUST and (SIR) H. HARTLEY (Proc. Roy. Soc., 1929, A, 126, 84–106).—With the object of determining whether acids which behave as strong electrolytes in water retain this property in alcoholic solution, as was found by Goldschmidt (A., 1925, ii, 128) to be the case for the halogen hydracids, measurements have been made of the electrical conductivity at 25° of solutions of the following acids in methyl and ethyl alcohol over the range 0.0001–0.002N: hydrochloric, chloric, perchloric, ethylsulphuric, benzenesulphonic, nitric, iodic, and thiocyanic acids. The measurements were carried out by the Kohlrausch method as described by Frazer and Hartley (A., 1925, ii, 1163), with two modifications suggested by Ulich (A., 1925, ii, 671). The results indicate that the first five acids are strong electrolytes in alcoholic solution; there is probably more association in ethyl than in methyl alcohol. The mobility of the hydrogen ion is calculated to be 142.0 in methyl alcohol and 59.5 in ethyl alcohol. The remaining three acids—nitric, iodic, and thiocyanic—behave as weak electrolytes in alcoholic solutions, the calculated dissociation constants for nitric and thiocyanic acids in ethyl alcohol being of the same order as that of benzoic acid in water. It is suggested that the addition of water could be used as a qualitative test to distinguish between strong and weak acids in alcoholic solution, since by adding about 0.5% of water to the alcoholic solution (about 0.001N) of a strong acid, the conductivity is decreased by about 25–30%, whilst a similar addition to a solution of a weak acid causes an increase of 20–30%.

L. L. BIRCUMSHAW.

**Activity of sulphuric acid in mixed solvents.** I. J. S. PRZEBOROVSKI, V. I. GEORGIEVSKI, and N. D. FILIPPOVA (Z. physikal. Chem., 1929, 145, 276–282; cf. A., 1928, 23).—Densities, viscosities, and conductivities of solutions of sulphuric acid in alcohol-water mixtures have been determined, and the potential of a hydrogen electrode has been measured in the same solutions. The activity of the

sulphuric acid passes through a minimum, and is higher in the presence of 70% and more of alcohol than in aqueous solution. Decrease of viscosity is not invariably accompanied by increase in conductivity. An attempt is made to establish a connexion between the hydrogen electrode potential and conductivity and viscosity.

F. L. USHER.

**Influence of intensive drying on inner equilibria.** V. A. SMITS, E. SWART, and P. BRUIN (J.C.S., 1929, 2712—2723).—Experiments are described which show that an apparent effect of drying on the vapour pressure of hexane can be obtained with moist liquid. The influence of the velocity of heating, and of the degree of admixture of the phosphoric oxide with the liquid, are discussed. The observed increases in the vapour pressure of nitrogen pentoxide on intensive drying may be due to the production of oxygen by the interaction of phosphoric oxide with traces of nitric acid. The m. p. of ammonia is not appreciably altered by drying for 5 years over phosphoric oxide.

C. W. GIBBY.

**Influence of an indifferent gas under pressure on the vapour pressure of water.** J. J. VAN LAAR (Z. physikal. Chem., 1929, 145, 207—219).—A formal deduction from thermodynamical theory of the fact, established experimentally by Bartlett (A., 1927, 207), that the vapour pressure is increased four-fold when an indifferent gas such as nitrogen under a pressure of the order of 1000 atm. is mixed with water vapour.

F. L. USHER.

**Transition temperature of carbon tetrachloride as a fixed point in thermometry.** E. L. SKAU and H. F. MEIER (J. Amer. Chem. Soc., 1929, 51, 3517—3519; cf. McCullough and Phipps, A., 1928, 1094).—The value  $-47.55 \pm 0.12^\circ$  was found; appreciable supercooling occurs and the transition temperature is unsuitable as a thermometric fixed point.

S. K. TWEEDY.

**Dehydration of calcium sulphate.** S. YAMANE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 12, 126—131).—The hemihydrate and dihydrate of calcium sulphate retain water at all temperatures between  $200^\circ$  and  $700^\circ$ ; the quantity of water thus bound is constant for each temperature, and diminishes progressively as the temperature rises. This phenomenon is ascribed to adsorption.

R. TRUSZKOWSKI.

**System copper-zinc.** R. RUER and K. KREMERS (Z. anorg. Chem., 1929, 184, 193—231; cf. Bauer and Hansen, B., 1927, 939).—The liquidus and solidus curves of copper-zinc alloys have been redetermined, and the solidification interval of the  $\alpha$ -series, and still more of the  $\beta$ -series of mixed crystals is found to be far smaller than has been hitherto assumed. Liquid alloys containing 62.1 and 40.2% Cu solidify at constant temperature. Changes taking place in the solid phase have been examined by means of heating and cooling curves for  $\beta$  mixed crystals. A simple transition  $\beta = \beta'$  occurs at  $444^\circ$  in the case of mixtures containing 61—55% Cu, whereas those containing 51—43% Cu undergo a double transition at  $464^\circ$  ( $\beta = \beta'$ ) and  $454^\circ$  ( $\beta' = \beta''$ ). The character of the  $\beta$ -phase has been further examined by determination of the specific heats of copper, zinc, and

mixtures containing 80—45% Cu over the temperature range  $850$ — $200^\circ$ , heats of transition being calculated on the assumption that the atomic heats are additive. The maximum heat of transition is given by a regulus with 51.81% Cu, the thermal behaviour of which closely resembles that of iron at the temperature of its magnetic transformation. The transformation of  $\beta$ -brass does not occur exclusively in a homogeneous phase, but involves the appearance of at least one new phase, although no change in the lattice structure can be detected. The nature of the compounds formed between zinc and copper is critically discussed. Evidence afforded by the thermal behaviour can be reconciled with the results of X-ray examination and electrical conductivity measurements if the formulæ of the two compounds are assumed to be  $\text{Cu}_{21}\text{Zn}_{31}$  and  $\text{Cu}_{14}\text{Zn}_{13}$ .

F. L. USHER.

**System copper-oxygen.** R. VOGEL and W. POCHER (Z. Metallk., 1929, 21, 333—337, 368—371).—Thermal analysis and microscopical examination of copper containing oxygen have shown that many of the results previously obtained for the equilibria in this system are incorrect. Prolonged annealing in nitrogen at  $950^\circ$  followed by slow cooling results in the retention of 0.8%  $\text{Cu}_2\text{O}$  (0.08% O) in solid solution. If copper containing more than 0.08% O is annealed for a long time below  $375^\circ$  decomposition of the cuprous oxide takes place with the formation of cupric oxide and the saturated solid solution of oxygen in copper. Cuprous oxide itself decomposes similarly so that it must be regarded as metastable below  $275^\circ$ . Above  $1230^\circ$  there is a region of immiscibility in mixtures containing 8—50%  $\text{Cu}_2\text{O}$ . Cuprous oxide melts at  $1230^\circ$  and forms a eutectic with cupric oxide containing 32%  $\text{CuO}$ , m. p.  $1075^\circ$ . Mixtures containing more than 34%  $\text{CuO}$  become completely liquid at  $1110^\circ$  with the evolution of oxygen until the eutectic composition is reached; this temperature must be regarded therefore as the m. p. of cupric oxide. The effect of variations in the partial pressure of oxygen on the equilibria in the system  $\text{Cu}_2\text{O}$ — $\text{CuO}$  is considered and pressure-temperature composition curves are given showing the relations in this system.

A. R. POWELL.

**Titanium and hydrogen.** L. KIRSCHFELD and A. SIEVERTS (Z. physikal. Chem., 1929, 145, 227—240; cf. A., 1926, 356, 810).—The isobar at atmospheric pressure and the isotherms at  $1000^\circ$ ,  $800^\circ$ ,  $640^\circ$ ,  $600^\circ$ , and  $500^\circ$  have been determined for the system titanium-hydrogen, and the results are shown in a space diagram. The curves are similar to those obtained with zirconium and thorium.

F. L. USHER.

**System  $\text{N}_2\text{O}_5$ — $\text{HNO}_3$ .** E. BERL and H. H. SAENGER (Monatsh., 1929, 53 and 54, 1036—1056).—The relation between the density ( $d_4^{25}$ ) and the percentage composition of mixtures of nitrogen pentoxide and nitric acid is represented by a smooth curve without maximum or minimum. The electrical conductivity rises to a maximum at 88.88%  $\text{N}_2\text{O}_5$  (100%  $\text{HNO}_3 = 85.71\%$   $\text{N}_2\text{O}_5$ ), corresponding with a compound  $\text{N}_2\text{O}_5 \cdot 6\text{HNO}_3$ . The b. p. decreases linearly with increasing concentration of the oxide, whilst the

f.-p. diagram shows a minimum ( $-69^\circ$ ) at a concentration of 88.9%  $\text{N}_2\text{O}_5$  (i.e.,  $\text{N}_2\text{O}_5 \cdot 6\text{HNO}_3$ ). A minimum value for the specific heat is found at 87.5%  $\text{N}_2\text{O}_5$ , whilst the heat of dissolution increases almost linearly with the concentration. The behaviour of mixtures towards wrought and cast iron and Krupp's steel V2A is investigated; with the exception of protected cast iron, for which the action is approximately constant with 85.93–90.1%  $\text{N}_2\text{O}_5$ , it is found that the chemical action increases with increased oxide concentration. Crystalline nitrogen pentoxide has  $d$  2.05.

H. BURTON.

**Hydrated oxides. XVII. System cobaltic oxide-water.** G. F. HÜTTIG and R. KASSLER (Z. anorg. Chem., 1929, **184**, 279–288; cf. Veil, A., 1927, 614).—Isobaric dehydration curves have been determined for specimens of hydrated cobaltic oxide prepared in various ways. When the molecular ratio of water to oxide is less than 3 the water is held more tenaciously than would be expected on the assumption of adhesion or capillarity. Dehydration between the limits 3 : 1 and 1 : 1 increases smoothly with rise of temperature, and the ease with which the water can be removed varies with the mode of preparation. No evidence of the existence of a definite compound intermediate between a mono- and a tri-hydrate has been obtained. Removal of water from a product having the composition  $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$  takes place at constant temperature, and is usually accompanied by the formation of cobalto-cobaltic oxide. The existence of a definite monohydrate is indicated, and this is supported by the appearance of X-ray spectrograms of products of varying composition. A comparison is drawn between this system and the system ferric oxide-water. F. L. USHER.

**Ceramics of refractory substances. IV. System zirconium dioxide-beryllium oxide.** O. RUFF, F. EBERT, and E. STEPHAN (Z. anorg. Chem., 1929, **185**, 221–224; cf. A., 1929, 766).—The fusion curve of mixtures of the above substances shows a eutectic at about  $2180^\circ$  and 40–45 mol.-%  $\text{BeO}$ . X-Ray examination shows the reversible transformation of zirconium dioxide into the tetragonal modification, and the normal lattice of beryllium oxide persists unchanged over the entire range of temperature employed. Beryllium oxide volatilises readily from the mixture, the m. p. of which after prolonged heating reaches that of pure zirconium dioxide.

F. L. USHER.

**Fusion curve of the system  $\alpha$ -naphthylamine- $\beta$ -naphthylamine.** I. GUBELMANN and H. J. WEILAND (Ind. Eng. Chem., 1929, **21**, 1239–1241).—The f.-p. curve for mixtures containing 0–10% of  $\beta$ -naphthylamine has been determined. Pure  $\alpha$ -naphthylamine has m. p.  $49.3^\circ$ . J. G. A. GRIFFITHS.

**Dissociation of the compounds  $\text{HgBr}_2 \cdot 2\text{NH}_3$  and  $\text{HgCl}_2 \cdot 2\text{NH}_3$ .** FRANÇOIS (Bull. Soc. chim., 1929, [iv], **45**, 1008–1013).—See A., 1929, 1388.

**Hydration of aluminates of calcium. II. Hydration products of tricalcium aluminate.** T. THORVALDSON, N. S. GRACE, and V. A. VIGFUSSON (Canad. J. Res., 1929, **1**, 201–213).—In a further study of tricalcium aluminate (cf. *ibid.*, 36), it has

been found that exposure of lime and alumina in the correct proportions to steam at  $150^\circ$  gives the hexahydrate, which on ignition at  $1100^\circ$  yields the anhydrous compound. The solubility of the hexahydrate as determined by gravimetric methods is 0.0246 and 0.0268 g. per 100 c.c. at  $21^\circ$  and  $40^\circ$ , respectively, whilst the density as determined by displacement in kerosene is 2.522 g. per c.c. X-Ray data are tabulated and the crystal structure is described, the lattice constant being  $12.576 \text{ \AA} \pm 0.02$ , with 8 mols. in the unit cube. By exposing the anhydrous aluminate to atmospheres of different humidities at temperatures below  $21^\circ$ , evidence was obtained of the formation of a series of higher hydrates crystallising in hexagonal plates and containing from 8 to 12 mols. of water, but the water is very loosely held and adsorption of water by the finely-crystalline hydrate makes the exact formulæ uncertain. The heats of dissolution in dilute hydrochloric acid (1 : 200) at  $20^\circ$  of the hydrates corresponding with 6, 8, 10, and  $12\text{H}_2\text{O}$  were 519, 498, 482, and 472 g.-cal. per g., respectively, and these differences support the view that a series of hydrates exists, as do the changes in refractive index with degree of hydration. Dehydration of the hexagonal plates at  $21^\circ$  produces no change of shape, however, and the X-ray diffraction patterns of the hydrates with 8, 10, and  $12\text{H}_2\text{O}$  are almost identical.

H. J. DOWDEN.

**System potassium metasilicate-silica.** F. C. KRACEK, N. L. BOWEN, and G. W. MOREY (J. Physical Chem., 1929, **33**, 1857–1879; cf. Morey and Fenner, A., 1917, ii, 370).—By means of the quenching method, the differential thermocouple method, and hydrothermal crystallisation, a study of the system potassium metasilicate-silica has been made. Three compounds  $\text{K}_2\text{O} \cdot \text{SiO}_2$ ,  $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ , and  $\text{K}_2\text{O} \cdot 4\text{SiO}_2$ , m. p.  $976^\circ$ ,  $1036^\circ$ , and  $765^\circ$ , respectively, occur in this system and the eutectics are at  $775^\circ$  and 45.5%  $\text{SiO}_2$  (by weight) and  $752^\circ$  and 69.0%  $\text{SiO}_2$ . The liquidus curve of  $\text{K}_2\text{O} \cdot 2\text{SiO}_2$  is of an unusual type, in that solid solutions are formed with excess of both potassium oxide and silica; the solid solutions decompose into the pure compound and melt at  $814^\circ$  and  $993^\circ$ , respectively. An enantiotropic inversion is found in  $\text{K}_2\text{O} \cdot 2\text{SiO}_2$  at  $590^\circ$ . The compound  $\text{K}_2\text{O} \cdot 4\text{SiO}_2$  is apparently biaxial and positive with  $\alpha$  1.477 and  $\gamma$  1.482. Temperature-composition diagrams are reproduced.

L. S. THEOBALD.

**Studies of  $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  and  $\text{ZnO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  separately with eutectics,  $\text{KNaO}$ -felspar eutectic, and  $\text{CaO} \cdot \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  eutectic.** D. C. ZIMMER and J. M. NEFF (J. Amer. Ceram. Soc., 1929, **12**, 746–749).—The purpose of the investigation was to determine the deformation eutectic of the above system, and to study the effect of variations in alumina and silica on these eutectics when applied to glazes. The results are given in diagrams and the formulæ of the two best glazes obtained are quoted.

F. SALT.

**Influence of alumina and silica on the  $(\text{K}_2\text{O} \cdot \text{Na}_2\text{O}) \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  eutectic.** W. N. BUTTERWORTH and P. KATES (J. Amer. Ceram. Soc., 1929, **12**, 750–752).—The influence of alumina and silica on the  $(\text{K}_2\text{O} \cdot \text{Na}_2\text{O}) \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  eutectic has been studied. The mixtures were made up into small



cones of the standard pyrometric type. Reduction of silica lowers the deformation temperature of the  $\text{KNaO-Al}_2\text{O}_3\text{-SiO}_2$  eutectic; reduction of alumina causes little change. It is concluded that the deformation eutectic is approximately  $(0.78\text{Na}_2\text{O}, 0.22\text{K}_2\text{O}), 0.204\text{Al}_2\text{O}_3\text{-}3.43\text{SiO}_2$ .

## F. SALT.

**Equilibrium in the reduction of silver chloride by hydrogen.** F. ISHIKAWA and M. WATANABE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 552—561).—The equilibrium has been studied statically over the temperature range  $456\text{--}710^\circ$  for liquid silver chloride and  $383\text{--}417^\circ$  for the solid. The equilibrium constants have been calculated and fitted to the reaction isochore.

## F. J. WILKINS.

**Action of hydrogen fluoride on compounds of selenium and tellurium. III. Solubilities of tellurium dioxide and oxyfluoride.** E. B. R. PRIE-DEAUX and J. O'N. MILLOTT (J.C.S., 1929, 2703—2709).—The system  $\text{H}_2\text{O-HF-TeO}_2$  has been investigated at  $10^\circ$  and the conditions of existence of the oxyfluorides have been defined. A saturated solution of tellurium dioxide in hydrogen fluoride contains about 81% of the latter. The presence of dissolved tellurous acid does not affect the hydrogen-ion activity of hydrofluoric acid as measured by the quinhydrone electrode.

## C. W. GIBBY.

**Equilibrium in the molten state between potassium, sodium, and their iodides.** E. RINCK (Compt. rend., 1929, 189, 1272—1274).—The mean value of the equilibrium constant for the reaction  $\text{Na} + \text{KI} \rightleftharpoons \text{K} + \text{NaI}$  at  $800^\circ$  is 56. The ratios of the values for the other halides (A., 1929, 993) approximate closely to the ratios of the at. wts. of the corresponding anions.

## J. GRANT.

**Reciprocal salt-pair  $\text{MgSO}_4\text{-Na}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ . III, IV, V.** W. SCHRÖDER (Z. anorg. Chem., 1929, 184, 63—76, 77—89; 185, 153—166; cf. A., 1929, 267).—III. Isotherms of the system  $\text{Mg}(\text{NO}_3)_2\text{-MgSO}_4\text{-H}_2\text{O}$  have been determined at three additional temperatures between  $0^\circ$  and  $100^\circ$ . The triple salt points  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O-MgSO}_4\cdot 6\text{H}_2\text{O-MgSO}_4\cdot \text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O-MgSO}_4\cdot 6\text{H}_2\text{O-MgSO}_4\cdot 7\text{H}_2\text{O}$  lie slightly above  $35^\circ$  and at nearly  $25^\circ$ , respectively. A space diagram of the system is given.

IV. Existing data relating to the  $25^\circ$  and  $50^\circ$  isotherms of the system  $\text{MgSO}_4\text{-}2\text{NaNO}_3\text{-H}_2\text{O}$  have been corrected and amplified, and the isotherm of the system  $\text{MgSO}_4\text{-Na}_2\text{SO}_4\text{-H}_2\text{O}$  at  $63^\circ$ , at which temperature vanthoffite, astrakhanite, löweite, and magnesium sulphate hexahydrate can coexist as stable phases, has been investigated. Previous work on this system (cf. Blasdale and Robson, A., 1928, 243) is critically reviewed, and a space diagram embodying the most trustworthy data is given.

V. Existing data relating to the systems  $\text{NaNO}_3\text{-H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2\text{-}2\text{NaNO}_3\text{-H}_2\text{O}$ , and  $\text{Na}_2\text{SO}_4\text{-}2\text{NaNO}_3\text{-H}_2\text{O}$  between  $0^\circ$  and  $100^\circ$  are critically reviewed, and amended space diagrams of the last two are given.

## F. L. USHER.

**Reciprocal salt pair  $\text{MgSO}_4 + 2\text{KNO}_3 \rightleftharpoons \text{Mg}(\text{NO}_3)_2 + \text{K}_2\text{SO}_4$ .** I. A. BENRATH and H. BENRATH [with H. WAZELLE] (Z. anorg. Chem., 1929, 184, 359—368).—Complete phase diagrams are given

for the reciprocal pair system  $\text{MgSO}_4\text{-KNO}_3$  at  $25^\circ$  and  $50^\circ$ . At  $25^\circ$  the leonite field does not appear, whilst that of  $\text{MgSO}_4\cdot 6\text{H}_2\text{O}$  is very small; at  $50^\circ$  neither  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$  nor schönite exists. Levi's observation of the transition of schönite into leonite above  $50^\circ$  could not be confirmed. H. F. GILLBE.

**Equilibria between water and the nitrates, chlorides, and sulphates of sodium and potassium.** E. CORNEC and H. KROMBACH (Ann. Chim., 1929, [x], 12, 203—295).—A more detailed account of work already abstracted (A., 1929, 1388).

**Quaternary system  $\text{K}_2\text{O-N}_2\text{O}_5\text{-H}_2\text{Cl}_2\text{-H}_2\text{O}$ .** V. I. NIKOLAEV and N. S. DOMBROVSKAJA (J. Russ. Phys. Chem. Soc., 1929, 61, 1251—1257).—At lower temperatures potassium is present chiefly as chloride, the proportion of nitrate increasing with rise of temperature.

## R. TRUSZKOWSKI.

**Displacement of heterogeneous equilibrium of two molten metals with their salts by a third indifferent substance.** J. J. VAN LAAR (Z. anorg. Chem., 1929, 185, 35—48; cf. A., 1926, 35).—Mathematical.

## F. L. USHER.

**Double decomposition in the absence of a solvent.** X. A. G. BERGMAN and N. S. DOMBROVSKAJA (J. Russ. Phys. Chem. Soc., 1929, 61, 1451—1478).—A scheme for the classification of reciprocal systems is given.

## R. TRUSZKOWSKI.

**Free energy of formation in fused salts. III. Bismuth halides.** G. DEVORO and A. GUZZI (Gazzetta, 1929, 59, 708—712; cf. A., 1928, 955, 1096).—The free energy of formation of bismuth chloride, bromide, and iodide has been calculated from measurements of the decomposition potential of the fused salts at temperatures between  $250^\circ$  and  $500^\circ$ . At  $350^\circ$  the free energies of formation of bismuth chloride and bromide are respectively 67,600 and 48,100 g.-cal. The discrepancy between the decomposition potential (0.95 volt) for bismuth chloride at its m. p. calculated from thermal data and that found by experiment (1.09 volts) may be due to the formation of a subchloride of bismuth. Extrapolation of the free energy-temperature curve for bismuth iodide indicates a dissociation of about 65% at  $700^\circ$ .

## F. G. TRYHORN.

**Elimination of systematic errors in older thermochemical data.** P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1929, 48, 1267—1271).—Polemical.

## R. J. W. LE FÈVRE.

**Thermochemistry of chlorine and hypochlorous acid.** W. A. ROTH (Z. physikal. Chem., 1929, 145, 289—297).—The hydrolysis constant for chlorine in dilute aqueous solution calculated from cryoscopic measurements is in agreement with the accepted value,  $1.5\text{--}1.6 \times 10^{-4}$ . The heat of dissolution of chlorine gas in water without hydrolysis, deduced from data by Jakowkin (cf. A., 1899, ii, 736) and by Neumann and Müller (cf. A., 1929, 1238), is  $+6.9$  kg.-cal. at  $18^\circ$ . Distribution experiments at  $0^\circ$  and measurement of the heat of dilution at  $19^\circ$  lead to the same result for the ratio  $[\text{HOCl}]/[\text{Cl}_2\text{O}]$  in aqueous solution. The high hydration constant (115 at  $19^\circ$ ) obtained by combining the two series of experiments

corresponds with the high heat of hydration, 8.0 kg.-cal., for the reaction  $\text{Cl}_2\text{O aq.} + \text{H}_2\text{O} = 2\text{HOCl aq.}$

F. L. USHER.

**Thermochemistry of the double salts formed by one molecule of cupric chloride with two molecules of the chlorides of potassium, rubidium, or caesium.** A. BOUZAT and E. CHAUVENET (Bull. Soc. chim., 1929, [iv], 45, 913—922; cf. A., 1924, ii, 19).—A discussion of results which have been previously abstracted.

F. L. USHER.

**Dependence on temperature of the rate of formation of cupric sulphide and the heat of loosening [of the crystal lattice].** K. FISCHBECK and O. DORNER (Z. anorg. Chem., 1929, 184, 167—179; cf. A., 1929, 1250).—The absorption of sulphur from solution by cuprous sulphide proceeds at a conveniently measurable speed, which increases 3.5 times for a rise of  $10^\circ$  at the ordinary temperature. The rate of growth of the cupric sulphide layer is proportional to the concentration gradient of the diffusing sulphur atoms and to the number of mobile sulphur atoms in the lattice, both factors being expressible in the form of equilibrium constants. By determining the quantity log (rate of formation) at different temperatures and applying van 't Hoff's formula, the heat equivalent of the complete process has been calculated. The heat equivalent of the second of the two factors is the heat of dissolution of sulphur in cupric sulphide, which can be evaluated from data already available, and the heat of loosening is then found by difference to be 14.75 kg.-cal. per g.-atom. The corresponding value for silver sulphide is 14 kg.-cal., whereas the value calculated from the variation of the ionic mobility with temperature is 52.6 kg.-cal. It follows that the mobilisation of ions in the lattice represents a condition of the crystal different from that in which uncharged atoms are mobilised. In cupric sulphide also the heat of loosening is not directly related to the (metallic) electrical conductivity.

F. L. USHER.

**Heat of combustion of ergosterol, isoergosterol, and cholesterol.** C. E. BILLS, W. M. COX, jun., and G. E. STEEL (J. Biol. Chem., 1929, 84, 655—656).—The heats of combustion of the three compounds are 10,053, 10,050, and 10,289 g.-cal. per g., respectively.

C.-R. HARRINGTON.

**Sensitive method for comparing the resistances of electrolytes to high frequencies.** A. DEUBNER (Physikal. Z., 1929, 30, 946—948).—A preliminary description of a new method and its application to copper sulphate solutions.

R. A. MORTON.

**Non-validity of Ohm's law for alternating-current circuits containing capacity and resistance.** O. FRANKE and O. RIEDIGER (Z. Elektrochem., 1929, 35, 914—919).—Contrary to the statements of Ahmadi and Tandon (A., 1929, 1014), Ohm's law is rigidly valid for circuits of the above type.

R. CUTHILL.

**Validity of Ohm's law in the case of strongly conducting solid electrolytes.** W. JOST (Z. physikal. Chem., 1929, B, 6, 210—214).—Measurements of the conductivity of solid silver iodide at  $218^\circ$  and silver chloride at  $300^\circ$  show that Ohm's law

is obeyed over the range 0.03 to 9 volts/cm. The mean values of the respective conductivities are 1.49 and  $1.95 \times 10^{-3}$ .

O. J. WALKER.

**Nitro-derivatives of platinum. VIII. I. I. TSCHERNABEV and S. I. CHORUNZHENKOV (Ann. Inst. Platine, 1929, 7, 98—112).**—Solutions of *trans*-nitrochlorides of bivalent platinum exhibit a fairly high electrical conductivity, the value of which does not alter on keeping and varies with dilution according to the Ostwald law; the Ostwald constants are of the order  $10^{-4}$ . *cis*-Nitrochlorides have a much lower conductivity; this is practically independent of concentration, and increases rapidly with time.

R. TRUSZKOWSKI.

**Electrochemistry of solutions of antimony trichloride in bromine.** W. A. PLOTNIKOV and O. K. KUDRA (Z. physikal. Chem., 1929, 145, 265—275).—Specific and molar conductivities of solutions of antimony trichloride in bromine have been determined. The specific conductivity reaches a maximum at 97%  $\text{SbCl}_3$ . During electrolysis bromine and chlorine are liberated simultaneously at the anode, whilst crystals of antimony trichloride and tribromide are found on the cathode. The results are explained by assuming the dissociation  $\text{Sb}_2\text{Cl}_6 = \text{Sb}_2\text{Cl}_3^{+++} + 3\text{Cl}^-$ . The specific conductivity is proportional to the concentration of the double molecule.

F. L. USHER.

**Complex lead salts.** (MME.) N. DEMASSIEUX (Bull. Soc. chim., 1929, [iv], 45, 989—1001).—Conductivity measurements have been made during the addition of sodium carbonate solution to solutions of various lead salts. With 0.02M-lead chloride two discontinuities are found, which are said to indicate the formation of phosgenite,  $\text{PbCl}_2\text{CO}_3$ , and of lead carbonate. Similar compounds are formed with lead bromide and iodide, but no complex is formed in the case of lead nitrate. The action of sodium oxalate on lead chloride and bromide is said to give rise to the compounds  $\text{PbCl}_2\text{C}_2\text{O}_4$  and  $\text{PbBr}_2\text{C}_2\text{O}_4$ . Oxalic acid reacts in solution with lead chloride, bromide, iodide, and nitrate, giving the same compounds in the first two cases, and only lead oxalate in the last two.

C. W. GIBBY.

**Basicity and constitution of some inorganic acids from electrical conductivity and coagulation experiments.** W. V. BHAGWAT and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 781—791).—Electrical conductivity measurements of sodium hypophosphite solutions of different concentrations, and comparison of the coagulating power of the salt with that of potassium chloride on ferric, ceric, and zirconium hydroxide sols suggest that hypophosphorous acid is monobasic with a slight tendency to be dibasic. Similarly, phosphorous acid is mainly dibasic with a slight tendency to be tribasic. The latter, however, does not appear to form the polymerised molecule  $(\text{H}_3\text{PO}_3)_2$  ionising to form  $\text{H}_4\text{P}_2\text{O}_6$  as suggested by Italiener ("Beiträge zur Kenntnis der phosphorigen Säure und ihrer Salze," Freiburg, 1917). Iodates exist in a partly polymerised state. Coagulation experiments with sodium and potassium salts show that the antimonite, titanite, boric, vanadic, tungstic, and molybdic ions are bivalent, and also that chromic

acid exists in solution mainly as  $\text{H}_2\text{CrO}_4$  and potassium dichromate as  $\text{KHCrO}_4$ . The coagulating power of potassium hydroxide for ferric hydroxide sols does not change appreciably on the addition of the hydroxides of zinc, tin, lead, chromium, or aluminium. This supports the view that these hydroxides are present in solution as negatively charged sols and do not form zincates, stannates, etc. M. S. BURR.

**Determination of absolute potential.** J. BILLITER (Monatsh., 1929, 53 and 54, 813—821).—A discussion of methods previously employed.

L. S. THEOBALD.

**Electrochemical properties of polonium.** F. JOLIOT (Compt. rend., 1929, 189, 986—988).—The oxidation and reduction reactions of polonium compounds have been studied by observing the changes in the deposition curve on the addition of a reagent to a standard solution of polonium electrolysed in the author's apparatus (A., 1927, 633). The critical deposition potentials (*C.D.P.*) of the constituent ions on the addition of hydrogen peroxide, oxalic, sulphurous, tellurous, and chromic acids, together with the analogy between the chemical properties of tellurium, polonium, and bismuth, suggest the existence of cations (*C.D.P.* 0.37 and 0.02 volt) corresponding with  $\text{PoO}^{++}$  and a suboxide or metal ion, respectively, and an anion,  $\text{PoO}_3^{--}$  (*C.D.P.* 1.1 volts), produced by hydrolysis. J. GRANT.

**Oxidation-reduction. XV. Potentiometric studies of the aminoindophenols: phenol-blue, *m*-tolylenediamine-indophenol, and *o*-toluidine-indophenol.** B. COHEN and M. PHILLIPS (U.S. Public Health Rep., Suppl. 74, 1929, 32 pp.).—The equilibrium potentials of mixtures of phenol-blue, *m*-tolylenediamine-indophenol, *o*-toluidine-indophenol, and their leuco-compounds, respectively, have been determined potentiometrically in buffers of various concentrations at 30°. The electrode equations for the three systems, involving the dissociation constants of the oxidants and the reactants, have been deduced and the constants evaluated. The values of the constants for the oxidants were checked by colorimetric and spectrophotometric measurements. Phenol-blue is slowly decomposed to indophenol in alkaline solution, and to dimethyl-*p*-phenylenediamine and benzoquinone in acid solution. *m*-Tolylenediamine-indophenol is sufficiently stable to be used as an indicator.

A. I. VOGEL.

**Variations in potential at a metal-air boundary.** M. ANDAUER (Z. physikal. Chem., 1929, 145, 220—226; cf. A., 1929, 144).—The *P.D.* between a metal surface and air is changed when any part of the metal is charged electrolytically with hydrogen or oxygen. By means of apparatus previously described such variations of potential have been observed with platinum, silver, mercury, nickel, and iron, but not with palladium, copper, or aluminium. The effect, which is of the order 0.1 volt, is considered to be due to the formation of a conducting film of gas over the entire surface of the metal. F. L. USHER.

**Volta effect. Influence of oxidation of the electrodes.** E. DUBOIS (Compt. rend., 1929, 189, 1260).—Metal electrodes immersed in pure oxygen at low pressure for a few minutes in the cold become

electronegative, a maximum variation in the Volta effect of 0.8 volt (for palladium) being obtained. The effect is increased at high temperatures, and in all cases the electrode returns to the electropositive state if subsequently heated in a vacuum. J. GRANT.

**Electrolysis by means of an asymmetrical alternating current.** F. HALLA (Z. Elektrochem., 1929, 35, 838—847).—The theory of electrolysis by a direct current with a superimposed alternating current is discussed in relation to the current density-voltage curves for electrolysis with direct current. A bibliography of electrolysis with symmetrical and asymmetrical alternating currents is appended.

R. CUTHILL.

**Moto-electrical effect [of various metals].** W. J. MÜLLER and K. KONOPICKY (Monatsh., 1929, 53 and 54, 707—720).—The current produced in a short-circuited cell consisting of two similar electrodes in the same electrolyte by the movement of one electrode (moto-electric effect) has been investigated for copper, zinc, iron, nickel, lead, and silver in a saturated, acid, or alkaline solution of sodium chloride, with or without the addition of a ferric salt or hydrogen peroxide as an oxidising agent. The moto-electric effect occurs only with electrodes which can react in some way with the electrolyte; ideal, unattackable electrodes show no effect. The small negative effect shown by copper and lead is independent of the concentration of hydrogen ions; a further, larger effect of opposite sign is superimposed on this in the case of metals such as zinc which react with the electrolyte and this effect is markedly affected by the hydrogen-ion concentration. In the presence of oxidising agents a third effect appears which is larger than either of the other two effects and is negative in alkaline and positive in acid solution. The results are discussed in terms of the changes in concentration arising at the diffusion layer around the electrode and the influence of movement on these changes.

L. S. THEOBALD.

**Theory of the valve electrode. Anodic behaviour of aluminium.** W. J. MÜLLER and K. KONOPICKY (Z. physikal. Chem., 1929, 145, 241—255; cf. A., 1929, 770).—A reply to Günther-Schulze (cf. *ibid.*, 1247). Further evidence is recorded in support of the authors' theory.

**Anodic behaviour of aluminium.** A. GÜNTHER-SCHULZE, W. J. MÜLLER, and K. KONOPICKY (Z. physikal. Chem., 1929, 145, 256; cf. preceding abstract).—Objections to the experiments of Müller and Konopicky are withdrawn. F. L. USHER.

**Becquerel effect. II.** C. WINTHER (Z. physikal. Chem., 1929, 145, 81—96; cf. A., 1928, 247).—The potential changes of the copper oxide electrode under different conditions have been followed. The electrode consists of oxidised copper on copper or platinum. Its potential varies with the oxygen concentration of the solution. When immersed in potassium chloride solution, consumption of oxygen by the electrode appears to proceed indefinitely. It is therefore an irreversible oxygen electrode. The potential of the electrode depends on its nearness to the walls of the electrode vessel, diminishing as the thickness of the layer of solution in front of it diminishes.

This phenomenon makes it possible to construct a galvanic "position" element. On the basis of this and previous work (*loc. cit.*) the origin of the Becquerel effect is stated to be as follows. The copper plate is an oxygen electrode with an oxygen pressure far smaller than that at the surface of the oxide layer. In the dark there is a continual consumption of oxygen by the copper and replacement of this by diffusion in the liquid until a steady state is reached. On irradiation the copper oxide becomes a conductor and the whole thus forms an oxygen concentration cell. The potential of the copper electrode then rises, whilst that of the copper oxide falls until they are both the same. The rise of potential of the copper is the positive Becquerel effect. An artificial Becquerel electrode may be constructed by connecting a quinhydrone electrode and a copper electrode by a selenium cell. When the latter is irradiated the potential of the copper electrode rises (positive Becquerel effect) and that of the quinhydrone electrode falls (negative Becquerel effect).

M. S. BURR.

**Influence of the medium on the photovoltaic effect of copper iodide.** (MLLE.) M. QUINTIN (*Compt. rend.*, 1929, 189, 1268—1269).—The photo-potential of copper covered electrolytically with a layer of iodide is made up of an instantaneous effect and a potential varying as a function of time. In solutions of copper salts the former is positive and almost zero and then becomes increasingly negative, although the darkness potential remains constant. In neutral electrolytes it is positive and decreases with time. In solutions of alkali iodides it is also positive and increases to a value which remains constant, and within a certain concentration range is characteristic of an iodine electrode. The phenomena indicate the production of cupric ions and the simultaneous action of light on the liquid medium and on the photosensitive substance (cf. Athanasia, A., 1929, 514).

J. GRANT.

**Method for investigating the course of the reaction in the formation of molecular hydrogen from atoms.** H. SENFTLEBEN and O. RIECHEMEIER (*Physikal. Z.*, 1929, 30, 745—750).—Hitherto it has been possible to follow the formation of molecules from atomic gases only in a qualitative manner. Quantitative work has been hindered by difficulties relating to the nature and surface condition of the walls of the containing vessel, the purity of the gas, etc. Details are given of methods for eliminating various disturbing influences; the causes of certain difficulties have been traced and other suggestions have been disposed of. The rate of recombination of hydrogen atoms (produced by the action of mercury exposed to the light of the resonance line) has been followed, the results indicating that triple collisions play an important part in the recombination.

R. A. MORTON.

**Velocity of unimolecular decomposition of a simple gas.** H. J. SCHUMACHER and G. SPRENGER (*Naturwiss.*, 1929, 17, 997).—The velocity of decomposition of nitrogen pentoxide at low pressures is discussed. The velocity is not dependent on the pressure, below 0.5 mm., which is in contradiction

to theory. The theory of unimolecular reactions having been developed from the side of complicated organic molecules, it is important to ascertain whether it holds for simple inorganic gases. It does not appear to do so for nitrogen pentoxide. It has been found that the decomposition of nitryl chloride,  $\text{NO}_2\text{Cl}$ , is also unimolecular. The velocity of decomposition of this compound was investigated within the temperature range 100—150°, and with pressures varying from 10,000 to 15 mm. The velocity was found to be dependent on the pressure of nitryl chloride. The addition of inactive gases, e.g., oxygen and nitrogen, causes an increase in the velocity, which is in accordance with the theory. The velocity of decomposition of nitrogen pentoxide was also investigated at very low pressures, and it was found that down to 0.08 mm. the reaction proceeded with normal velocity, but below this pressure the velocity became progressively smaller and smaller, so that complete decomposition could never be obtained. These results show without doubt that the explanation of the unimolecular decomposition of nitrogen pentoxide requires some special mechanism, whereas the decomposition of nitryl chloride is according to theory. A. J. MEE.

**Gaseous combustion.** W. T. DAVID and W. DAVIES (*Nature*, 1930, 125, 127—128).—Intensity of the luminosity in an exploded gaseous mixture is practically completely dependent on temperature and the amount of chemical combination has little, if any, effect on intensity of emission. Flame photographs, therefore, merely indicate temperature and not the chemical condition of gases behind the wave front. Chemical combination in the gaseous phase appears to result in the formation of long-lived, abnormal molecules which are more easily excited to give luminous vibrations. Correlation of temperature and pressure records when thin platinum or rhodium wires were immersed in the exploding gases indicates that the gaseous molecules after combination contain an excess of internal energy which can be readily communicated to a hot surface. L. S. THEOBALD.

**Explosion of hydrogen-air mixtures in a closed vessel.** I, II. B. H. THORP (*Phil. Mag.*, 1929, [vii], 8, 813—824, 824—833).—I. A diaphragm indicator suitable for measurements of pressure in gaseous explosions in closed vessels is described. A flat invar diaphragm, 0.75 mm. thick, is clamped firmly on to a seating turned in the wall of the explosion vessel, and on it is mounted a light pillar carrying a light mirror. By using a long beam of light the deflexion can be measured to 1 in 500. The results are compared with those of Pier (A., 1909, ii, 789), Maxwell and Wheeler (A., 1928, 248), Siegel (A., 1914, ii, 528), Bone (A., 1925, ii, 800), and others, and it is concluded that the differences between them are connected with differences in size and shape of explosion vessel. The use of vessels of different shapes and sizes has a marked effect on the maximum pressure developed by a given mixture of gases, which cannot be due to heat loss before maximum pressure, as the rate of attainment of the latter varies directly as the diameter, whilst the rate of heat loss varies inversely as the diameter. The cause of the differences is probably a time lag in the combustion.

II. Six series of explosions are recorded, at initial pressures of 1 atm., the ratios of nitrogen to oxygen being 0, 2, 3.9, 4.9, 6.1, and 6.8, respectively, and the ratios to hydrogen being over as wide a range as possible. In mixtures containing excess of oxygen there is extensive incomplete combustion at maximum pressure, and to a smaller extent in the presence of excess of hydrogen. The values for the specific heat of steam calculated from maximum pressure measurements must consequently always be too high. The extent of incomplete combustion can be calculated by taking the lowest apparent specific heat as true; it varies from about 3% to 0 in the presence of excess of hydrogen, and from about 5 to 11% in excess of oxygen. It is increased by replacement of excess hydrogen by nitrogen, and decreased by replacement of excess oxygen by nitrogen. C. W. GIBBY.

**Spark ignition of low inflammable gas mixtures.** K. YUMOTO (Proc. Imp. Acad. Tokyo, 1929, 5, 318—321; cf. A., 1929, 403).—Experiments on the ignition of carbon monoxide-air and ethyl bromide-air mixtures in a wide spark gap are described. Under certain conditions ignition takes place at two positions, each separated from the anode and cathode by a quarter of the width of the spark gap. The flame at the anode moves towards the anode, but the cathode flame remains stationary.

J. A. V. BUTLER.

**Effects of temperature and pressure on upper explosive limit of methane-oxygen mixtures.** C. M. COOPER and P. J. WIEZEVICH (Ind. Eng. Chem., 1929, 21, 1210—1214).—Upper explosive limits of oxygen-methane mixtures at total pressures from 1 to 229 atm. and at temperatures between 10° and 530° have been investigated. The mixtures were ignited by sparks from a device of the make-and-break type. Explosion did not result in complete consumption of oxygen in mixtures at high pressure. At 20°, as the total pressure was increased from 1 to 170 atm. the proportion of oxygen in the limit mixture decreased from 39 to 11%. Rise of temperature was accompanied by decrease in the proportion of oxygen necessary for ignition. Above 400° spontaneous reaction became prominent. J. G. A. GRIFFITHS.

**Temperature of spontaneous inflammation of gaseous mixtures of air and saturated hydrocarbons. Influence of pressure and preliminary heating.** P. MONDAIN-MONVAL and B. QUANQUIN (Compt. rend., 1929, 189, 917—919; cf. Dumanois and Mondain-Monval, this vol., 57).—Varying quantities of air and pentane vapour, previously separately heated to a known temperature, were passed together through a tube, 80×2 cm., maintained at that temperature, the product being passed into a condenser and then through various reagents. Towards 200° a slight coloration occurs in Schiff's reagent, becoming well marked at 270°, at which temperature carbon dioxide is also detected. At 325° white fumes are formed with sudden rise of temperature, and formaldehyde, various fatty acids, and small quantities of acetaldehyde and butaldehyde appear in the condenser. Increase in the amount of air stops the fumes and lowers the temperature. Similar results are obtained with hexane at 330°, heptane at 325—

330°, octane at 269°, and petrol (*d* 0.72) at 330°. The temperature is uninfluenced by the presence of a catalyst as copper, or by the concentration of the hydrocarbon, but is lowered by increased pressure. The production of fumes is accompanied by the appearance of a faint blue light.

C. A. SILBERRAD.

**Spontaneous ignition of mixtures of air and hydrocarbons. Influence of concentration.** P. MONDAIN-MONVAL and B. QUANQUIN (Compt. rend., 1929, 189, 1194—1196).—The authors' conclusions (cf. preceding abstract) are confirmed for pentane, hexane, heptane, octane, and petrol. The rapid increase in pressure observed in the bomb in cases where flame production does not occur cannot be distinguished from that associated with true combustion and is probably promoted by exothermic reaction without flame. Ethylene and a small but constant quantity of carbon dioxide were detected in the zone of oxidation without flame. J. GRANT.

**Combustion limits at high pressures of mixtures of air with inflammable gases. II.** E. BERL and H. BAUSCH (Z. physikal. Chem., 1929, 145, 347—359; cf. B., 1927, 546).—The effect of increased pressure on the limiting composition of explosive mixtures has been studied in mixtures of air with commercial and pure carbon monoxide, water-gas, ammonia, and ammonia "contact gas." A considerable extension of both upper and lower limits occurs with commercial and pure carbon monoxide and with ammonia. With water-gas the upper limit is raised whilst the lower is scarcely affected, and in the case of "contact gas" the upper limit is nearly independent of pressure. The presence of a small quantity of hydrogen in carbon monoxide leads to a marked extension of the limiting composition on both sides. On the other hand, addition of 5% of methane to "contact gas" narrows the limits of combustion, especially at the normal pressure. F. L. USHER.

**Gaseous explosions. VII. Effect of lead tetraethyl on rate of rise of pressure.** M. S. CARR and G. G. BROWN.—See B., 1929, 1037.

**Gaseous explosions. VIII. Effect of lead tetraethyl, hot surfaces, and spark ignition on flame and pressure propagation.** M. SOUDERS, jun., and G. G. BROWN (Ind. Eng. Chem., 1929, 21, 1261—1267; cf. Brown and Watkins, B., 1927, 322).—The effect of lead tetraethyl, both in the vapour phase and when thermally decomposed, on flame speeds and the rate of rise of pressure following ignition was determined for explosive mixtures of benzene, pentane, isohexane, and heptane in air. Lead tetraethyl vapour was ineffective in retarding combustion until decomposed by the burning mixture, whereas decomposed lead tetraethyl introduced before firing the charge retarded both flame speed and rate of rise of pressure. The introduction of a hot surface into the bomb in order to produce auto-ignition of the charge ahead of the advancing flame resulted in an unusually high rate of rise of pressure. Decomposed lead tetraethyl prevented or delayed the auto-ignition and retarded the resulting combustion. High-frequency pressure waves ordinarily present in the explosions were eliminated by decreasing the number

of sparks in the igniting discharge. A shock wave is developed from the mutual influence of pressure waves and a high rate of release of energy. With the paraffins the acceleration of the rate of rise of pressure in and by the waves is very rapid, but with benzene it is relatively moderate. With auto-ignition the rate of rise of pressure was often as high as that produced by the high-frequency waves just before the appearance of the shock wave. Auto-ignition did not produce a shock wave unless waves of high amplitude were present, but the latter did not develop into shock waves unless considerable energy was released by auto-ignition or by the after-burning following normal combustion. H. S. GARLICK.

**Oxidation processes in motor fuels. II.** E. BERL and K. WINNACKER (Z. physikal. Chem., 1929, **145**, 161—176; cf. B., 1929, 158).—The influence of commercial anti-detonators (lead tetraethyl, iron pentacarbonyl), of equivalent amounts of colloiddally dispersed heavy metals, and of their oxides on the oxidation of hexane has been compared. The metals were dispersed either electrically in the hydrocarbon or as a cloud in nitrogen, and the oxides were obtained by dispersion of the metal in oxygen. Since the metals exercise retarding effects on the combustion similar to those observed with the commercial organo-metallic compounds, whilst the oxides have no influence, it is inferred that the metal particles do not merely interrupt the reaction "chains," but that they probably form intermediate compounds with the hydrocarbon radical or with a peroxide.

F. L. USHER.

**Reaction velocity and activity of hydrochloric acid in water-alcohol mixtures.** S. KILPI and U. H. PURANEN (Z. physikal. Chem., 1929, **145**, 109—136; cf. A., 1929, 888, 1017).—The equilibrium coefficients and velocity coefficients of the reaction between hydrochloric acid and alcohol in alcohol-water mixtures containing 25, 49.5, 64.2, and 80.2 mol.-% of alcohol, respectively, have been determined at approximately 96.5° and 110°. The dependence of reaction velocity on concentration in all cases may be represented by the Debye-Hückel formula. The coefficients  $A'$  and  $a'$  in this formula, calculated from either the equilibrium coefficients or from the velocity coefficients, agree with the theoretical values. In dilute solutions, when  $B'c$  in the formula is of minor importance in comparison with the expression  $2.4'\sqrt{c}/(1+a'\sqrt{c})$ , the electrolyte influences to the same extent the reaction velocity and the activity determined electrometrically at 25°. It is not easy to make the comparison in more concentrated solutions because the calculation of  $B'$  is difficult, but the effect of electrolyte on reaction velocity in these appears, on the whole, to be greater than the effect on electromotive activity. On the assumption that dissolution work depends on ionic changes the activity of hydrochloric acid should, according to Born's expression for heat of dissolution, as far as can be determined from the approximate nature of the formula, increase with increase in alcohol content in the same way as the reaction velocity has already been shown to do. The temperature coefficient of  $C_1$ , the velocity coefficient of the direct reaction, is inde-

pendent of the composition of the alcohol-water mixture at the temperatures considered, but the temperature coefficient of  $C_2$ , for the reverse reaction, is markedly diminished by increase of alcohol content. Changes of concentration due to expansion of the solution with rise of temperature have no appreciable influence on the results. M. S. BURR.

**Initial inertia in chemical reactions.** E. PUXEDDU (Gazzetta, 1929, **59**, 687—694; cf. A., 1928, 484).—No relationship was found between the strength of the acid and the induction period in the decomposition of sodium thiosulphate in acid solution. The acids used were sulphuric, hydrochloric, nitric, acetic, and formic at concentrations from 0.2N to N, and at temperatures from 0° to 45°. The period of induction with formic acid was approximately the same as with the mineral acids. The effect of temperature and concentration on the initial inertia of the reaction between potassium iodate and sulphur dioxide in aqueous solution confirms previous work on the influence of these factors. F. G. TRYHORN.

**Chemical kinetics in highly dilute solution. Bromoacetate and thiosulphate ions in the presence of sodium ion at 25°.** V. K. LA MER (J. Amer. Chem. Soc., 1929, **51**, 3341—3347).—Krapivin's kinetic experiments on the reaction  $\text{CH}_2\text{Br}\cdot\text{CO}_2' + \text{S}_2\text{O}_3'' \rightarrow \text{S}_2\text{O}_3\cdot\text{CH}_2\cdot\text{CO}_2'' + \text{Br}'$  in presence of sodium ions (A., 1913, ii, 310) are continued in the range 0.01—0.0005N. Brönsted's theory of reaction velocity is fully supported by the results; the latter conform to Debye's theory at the highest dilutions only (below 0.001N). Peculiar advantages of reactions of this type for studying theories of catalysis etc. are pointed out (cf. Kappanna, A., 1929, 516). S. K. TWEEDY.

**Kinetics of the cell reaction. I.** J. WEICHERTZ (Z. physikal. Chem., 1929, **145**, 330—346; cf. A., 1929, 1397).—The course of a unimolecular reaction in a cell bounded by a porous membrane of finite thickness is calculated on the basis of a number of simplifying assumptions, and the rates thus calculated are compared with results of experiments on the decomposition of dextrose by living yeast-cells. Satisfactory agreement is found when the concentration of dextrose is small, and the deviations observed with higher concentrations are attributed partly to the fact that under these conditions the reaction is not strictly unimolecular, and also to osmotic effects. From the initial acceleration of fermentation it is calculated that the degree of permeability of the membrane of the yeast-cell is about  $4 \times 10^{-5}$ . It is concluded that the membrane has a simple porous structure. F. L. USHER.

**Mechanism of oxidative processes. XX. Succinic acid-dehydrogenase.** H. WIELAND and K. FRAGE (Annalen, 1929, **477**, 1—32).—The kinetics of the dehydrogenation of succinic acid in presence of various hydrogen acceptors have been studied. The enzyme preparation used was obtained from the muscle of the left ventricle of horse's heart by Fischer's method (A., 1928, 89). In presence of oxygen, optimum activity is at  $p_{\text{H}}$  7.3—7.8. The initial course of dehydrogenation of succinate is more rapid



with oxygen than with air, but after 75 min. the same volume of oxygen is consumed. The rate of oxygen uptake, which is constant for the first three quarters of the reaction, is considerably retarded by small amounts of hydrogen cyanide. Further retardation occurs with increasing amount of the acid. The velocity of dehydrogenation with methylene-blue is about one half of that with oxygen (cf. Bach and Michlin, A., 1927, 591), but the course of the reaction is similar in each case. Hydrogen cyanide has no retarding action in presence of methylene-blue. Using oxygen and methylene-blue (0.0002—0.004*N*) together, the oxygen consumption is approximately the same as with oxygen alone (cf. Wieland and Bertho, A., 1929, 219). Addition of hydrogen cyanide causes a powerful retardation (increasing with diminishing amount of the dye), which, however, is not so pronounced as that of hydrogen cyanide on oxygen dehydrogenation.

Crystal-violet is not a hydrogen acceptor and it has no retarding action on the absorption of oxygen. With hydrogen cyanide and crystal-violet together, retardation is more pronounced than with the cyanide alone. Benzoquinone is not an acceptor; it exerts a powerful retarding action on the dehydrogenation with oxygen. Quinol is dehydrogenated by the enzyme preparation at  $p_H$  6.8, and lactonitrile is as strong in its retarding action as is hydrogen cyanide. The dry enzyme preparation is about twice as reactive as the moist material which was used throughout the investigation. All experiments were carried out at 37°.

H. BURTON.

**Kinetics of electro-deposition of hydrogen and oxygen.** F. P. BOWDEN (Proc. Roy. Soc., 1929, A, 126, 107—125; cf. Bowden and Rideal, A., 1928, 1088).—Using the method previously described (*loc. cit.*) a study has been made of the kinetics of the electro-deposition of hydrogen and oxygen on metallic electrodes. The theory is developed that the evolution of hydrogen or oxygen may be regarded as a surface reaction involving the evaporation of adsorbed gas dipoles from the electrode surface to form neutral molecules, and that the magnitude of the *P.D.* across the metal/electrolyte interface is controlled by the number and electric moment of these adsorbed dipoles. Only those dipoles which possess a certain energy of activation can leave the surface, the number *N* capable of escaping being given by  $N = N_0 e^{-(w-\alpha V)/RT}$ , where  $w-\alpha V$  is a measure of the necessary energy of activation. It is found experimentally that, for each surface investigated,  $\alpha$  is a constant over a wide range of current density and temperature. For hydrogen on mercury and oxygen on platinum  $\alpha=0.5$ ; for hydrogen on other pure metals  $\alpha$  has approximately the same value, but if the surface is contaminated by another metal the value falls considerably.

The variations of reaction velocity and electrode potential with temperature are expressed by means of the formulæ  $2.3d \log i/dT = (w-\alpha V)/RT^2$  and  $dV/dT = (w-\alpha V)/\alpha T$ . These are investigated experimentally for hydrogen and oxygen on a number of metallic electrodes, and are found to hold with considerable accuracy. The energy of activation when

the electrode potential is zero is calculated from the temperature coefficient of the reaction velocity or of the potential, and found to be 15,000 g.-cal. for hydrogen on mercury, 23,000 g.-cal. for oxygen on bright platinum, and 7000—9000 g.-cal. for hydrogen on bright platinum, according to the state of activity of the surface. Theories of hydrogen overpotential are discussed, and evidence is adduced in favour of the view that "transfer resistance" is a secondary effect occurring only at high current densities (cf. Newbury, A., 1925, ii, 405; 1928, 958).

L. L. BIRUMSHAW.

[Rate of] drying of solids. II. P. K. SHERWOOD.—See B., 1929, 1035.

**Velocity of dissolution of zinc-tin alloys in acids.** R. VONDRÁČEK (Coll. Czech. Chem. Comm., 1929, 1, 627—637).—The relation between the composition of zinc-tin alloys and their rates of dissolution in *N*-hydrochloric acid at 23° has been investigated. Generally, the velocity increased during the initial stages of reaction, due to multiplication of local elements, and then decreased owing to the formation of a coating of tin. Alloys containing less than 4% of tin exhibited the first phenomenon only and those with more than 30% showed no initial acceleration and, in general, were attacked less readily in proportion as the tin content was increased. Alloys with less than 10% of tin had an initial rate of dissolution approximately proportional to the square root of the tin content.

From the behaviour of alloys containing up to 0.2% of tin it is suggested that the limit of solubility of this metal in solid zinc lies between 0.1 and 0.2%. Support for this view was derived from a microscopical examination of these alloys. J. G. A. GRIFFITHS.

**Rate of oxidation of ferrous hydroxide and ferrous sulphide to ferric hydroxide.** W. GLUUD and W. RIESE (Gas- u. Wasserfach, 1929, 72, 1251—1253).—The rate of oxidation of suspensions of ferrous hydroxide and ferrous sulphide in various solutions by a current of air was investigated. In solutions of sodium or ammonium hydrogen carbonate increase of alkalinity favours oxidation of ferrous hydroxide. With the former, however, increase of salt concentration reduces the oxidation rate. The addition of sodium sulphate or other neutral salt renders it more difficult to remove the carbon dioxide by air-blowing the sodium hydrogen carbonate solution. Ammonium sulphate facilitates the removal of both carbon dioxide and ammonia. Ferrous sulphide is much more slowly oxidised, and increasing alkalinity in sodium carbonate solutions retards oxidation. It is accelerated by rise of temperature from 20° to 40°. Ferrous sulphide precipitated from ferric oxide suspensions is more readily oxidised than that made from ferrous oxide, perhaps owing to the presence of ferric sulphide. C. IRWIN.

**Temperature of inflammation of combustible solids.** W. SWIENTOSLAWSKI, B. ROGA, and M. CHORAZY.—See B., 1930, 42.

**Chemical resistance of aluminium coated with anodic films.** S. SETOH and A. MIYATA.—See B., 1930, 16.

**Combustion of charcoal in oxygen, nitric oxide, and nitrous oxide. I. Adsorption of oxygen. II. Effect of temperature.** M. S. SHAH (J.C.S., 1929, 2661—2676, 2676—2692).—I. The amounts of oxygen, nitric oxide, nitrous oxide, carbon dioxide, and carbon monoxide adsorbed by charcoal at 0° and the composition of the gases evolved in a vacuum at various temperatures have been determined. Whilst the adsorption of oxygen and nitric oxide increases steadily with time, for the other gases a state of equilibrium is reached within a few hours. The greater part of the oxygen adsorbed at 0° is evolved in a vacuum at this temperature, whilst the remainder is liberated as carbon monoxide and dioxide at or above 280°. Nitric oxide is partly decomposed on adsorption at 0° and the gas evolved contains a large amount of nitrogen with some carbon dioxide. Between 0° and 125° the gas evolved consists of nitric oxide with nitrogen and carbon dioxide. Above 280° a mixture of oxides of carbon only is obtained. Adsorbed nitrous oxide, carbon dioxide, and carbon monoxide are liberated almost completely in a vacuum at 0°.

At 470°, nitrous oxide reacts with charcoal and all its nitrogen is liberated in a vacuum at this temperature. The oxygen is liberated as oxides of carbon, partly at 470° and partly at higher temperatures. Adsorbed carbon dioxide and carbon monoxide are recovered unchanged at 470°.

It is concluded that the combustion of charcoal in oxygen, nitric oxide, and nitrous oxide proceeds by the fixation of oxygen on the charcoal, forming some surface compound which breaks down at and above 280° with the formation of carbon monoxide and dioxide.

II. The decomposition of nitrous oxide in silica vessels and in the presence of thoria, alumina, platinum-black, titania, platinum foil, and silica has been studied. A surface action takes place, the catalytic activity of these substances being in the order stated (thoria greatest). It is now found (cf. I.) that in the presence of charcoal the formation of nitrogen is perceptible at 100° and increases with rise of temperature. Below 300° oxygen is retained by the charcoal; above this temperature carbon monoxide is produced in small and fairly constant amount, whilst the amount of carbon dioxide increases steadily with rise of temperature. The amount of oxygen fixed by the charcoal increases to a maximum at 500° and then decreases, and it is estimated that it would become zero at about 700°. When the same charcoal is repeatedly treated with nitrous oxide, the fraction of the nitrous oxide decomposed diminishes progressively at first and remains constant after five successive treatments. The fraction of oxygen fixed in charcoal in each treatment diminishes at first and remains constant at about 20%. The total amount fixed increases steadily and showed no signs of reaching a limit in fifteen successive experiments.

[With R. H. PURCELL].—The flame spectra of charcoal and carbon monoxide burning in nitrous oxide are identical, showing that the flame combustion of charcoal above 710° proceeds through the formation of carbon monoxide at the surface and its subsequent combustion.

At -78° and -190° the amount of adsorbed oxygen which reacts with charcoal is very small. Nitric oxide is reduced by charcoal at all temperatures above -78°, most of the oxygen remaining fixed on the charcoal. Some nitric oxide is retained by charcoal, the amount decreasing with rise of temperature. At low temperatures some nitrogen peroxide is formed and, combining with nitric oxide, appears as nitrogen trioxide. No carbon monoxide is formed below 500°. It is suggested that nitric oxide is held on the surface of charcoal by an intermediate layer of oxygen. The mechanisms of these reactions are discussed.

J. A. V. BUTLER.

**Influence of the azide ion on the catalysis of the decomposition of hydrogen peroxide by colloidal platinum.** E. OLIVIERI-MANDALÀ (Gazzetta, 1929, 59, 699—702).—Although azoimide is not decomposed by colloidal platinum, the acid and its salts act as strong negative catalysts in the decomposition of hydrogen peroxide by colloidal platinum. The rate of decomposition of the peroxide is reduced to less than half in the presence of azoimide, or its ammonium, lithium, sodium, or potassium salts in 0.0003*N*-concentration. The decomposition is accelerated by traces of ferrous azide by reason of the strong positive catalytic effect of the ferrous ion.

F. G. TRYHORN.

**Liquid partial oxidation. I. [Oxidation of acetaldehyde and ethylbenzene.]** E. P. KING, S. SWANN, jun., and D. B. KEYES (Ind. Eng. Chem., 1929, 21, 1227—1231).—Catalysis of liquid-phase oxidation, by oxygen, of acetaldehyde to acetic acid and of ethylbenzene to acetophenone has been investigated. Two-stage oxidation of ethyl alcohol gave a 90% yield of acetic acid. The oxidation of acetaldehyde in concentrated aqueous solutions of acetic acid is catalysed by the acetates of cobalt, nickel, manganese, vanadium (brown), cerium, vanadium (green), iron, and chromium, named in order of decreasing catalytic activity. The rate of oxidation is retarded by decreasing the concentration of acetic acid. The more rapid is the reaction, the higher is the yield of acetic acid. Ethylbenzene is oxidised more rapidly in the presence of manganese acetate than in that of acetic anhydride (Stephens, A., 1928, 1233). Metallic oxides and acetates of other metals have negligible catalytic action. Stirring facilitates the absorption of oxygen.

J. G. A. GRIFFITHS.

**Factors influencing the activity of aluminium and ferric chlorides in the Friedel and Crafts reaction.** M. C. BOSWELL and R. R. McLAUGHLIN (Canad. J. Res., 1929, 1, 400—404).—Aluminium chloride made by the action of hydrogen chloride on aluminium contains adsorbed hydrogen chloride to the extent of 9 c.c. per g.; this adsorbed gas cannot be removed by a stream of nitrogen at the ordinary temperature, but the capacity of the compound to adsorb hydrogen chloride is reduced considerably by repeated sublimation in nitrogen. The catalytic activity of aluminium chloride in the Friedel and Crafts reaction is diminished by the presence of adsorbed hydrogen chloride, but is increased by admixture with an equimolecular amount of ferric chloride, although the latter alone has only about

one third the activity of the aluminium compound. Aluminium chloride made by the action of chlorine on aluminium and mixtures of aluminium and ferric chloride which have been partly reduced are much less active than pure aluminium chloride.

A. R. POWELL.

**Mechanism of catalytic hydrogenation.** M. BOURGUEL and (Mlle.) V. GREY (Compt. rend., 1929, 189, 909—911; cf. A., 1928, 28).—If the colloidal palladium preparation is shaken in an atmosphere of hydrogen, preliminarily if the liquid to be reduced is miscible therewith (otherwise irregular results are obtained), preliminarily or not if immiscible, the initial velocity of hydrogenation is given by the equation  $V = aP(1 - 10^{-bc})/C$ , where  $P$  is the weight of palladium present,  $C$  its concentration, and  $a$  and  $b$  are constants, of which  $a$  depends on the substance to be reduced, and  $b$  solely on the particular sample of colloidal palladium used. These results are consistent only with the preliminary formation of a complex  $Pd_nH_2$ ,  $n$  depending on the value of  $C$ , and this complex being the actual catalysing agent.

C. A. SILBERRAD.

**Mechanism of catalytic hydrogenation.** M. BOURGUEL and (Mlle.) V. GREY (Compt. rend., 1929, 189, 1083—1085).—The activity in litres per hr. of catalytic hydrogenation of phenylacetylene by colloidal palladium is given by the expressions: (1)  $[\alpha(1 - 10^{-\beta\pi})/\pi] + \gamma$ , where  $\pi$  is the pressure of hydrogen in mm. of mercury (between 2.6 and 760 mm.), and  $\alpha$ ,  $\beta$ , and  $\gamma$  are constants which for 2.85 mg. of colloidal palladium per 100 c.c. of water are 2.07, 0.158, and 1200, respectively; (2)  $a(1 - 10^{-bc})/C$ , where  $C$  is the concentration of catalyst in mg. per litre,  $a = 138$ , and  $b = 0.00435$  at 760 mm. pressure. The analogy between these expressions confirms the authors' theory (cf. preceding abstract) of the existence of a compound  $Pd_nH_2$  in which  $Pd_n$  and  $H_2$  play the same rôle.

J. GRANT.

**Catalysis of reactions between solids.** Catalytic formation of stannate from lime and stannic oxide. S. TAMARU and N. ANDO (Z. anorg. Chem., 1929, 184, 385—408).—By heating a mixture of stannic oxide and calcium oxide at 850—900° for 30 min. complete conversion into an acid-soluble product takes place if a trace of some foreign material, especially a reducing agent, be present. The reaction, which takes place on the surface of the calcium oxide particles, is strongly retarded if water be absent. The reaction product has the composition  $2CaO, SnO_2$  and the probable mechanism involves the reduction of part of the stannic oxide to stannous oxide, which then reacts according to the equation  $SnO + 2CaO + H_2O \rightarrow 2CaO, SnO_2 + H_2$ . On account of the volatility of stannous oxide the reaction proceeds if the two oxides be heated out of contact with one another in an enclosed space.

H. F. GILLBE.

**Historical development and theory of the ammonia catalysis.** A. MITTASCH and W. FRANKENBURGER [with SCHWAMBERGER and HODLER] (Z. Elektrochem., 1929, 35, 920—927).—The development of the ammonia synthesis is reviewed. Iron obtained in the state of free atoms by vaporisation and condensation in presence of a substance which

prevents the atoms coalescing will combine directly with nitrogen. In the catalytic decomposition of ammonia at 360—750° in presence of tungsten, a tungsten imide is an intermediate product in the formation of nitride, and at 250—360° the imide is quite stable, practically no nitride being formed. The amount of imide formed is never greater than corresponds with a unimolecular layer of NH groups on the metal surface.

R. CUTHILL.

**Formation of hydrazine during the oxidative degradation of ammonia and by degradation in the flame.** K. A. HOFMANN and J. KORPIUN (Ber., 1929, 62, [B], 3000—3007; cf. A., 1929, 1400).—The probability that the first step in the oxidation of ammonia at an alkaline surface in presence of metallic oxides consists in dehydrogenation to imide and hydrogen is strengthened by the observation that the catalysts are active in the same sequence in the oxidation of molecular hydrogen by air. The intermediate formation of imide is rendered probable, since hydrazine is produced when mixtures of ammonia and nitrogen are passed over nickel gauze or lime activated with nickel or copper at 340—355°. Hydrazine is also formed when ammonia containing a small proportion of oxygen is passed over a contact of fine copper gauze at 340—400°/5—7 mm. In its initial stages, the combustion of ammonia in the flame follows the same course provided that the ammonia is in excess with respect to oxygen. When oxygen burns at a narrow quartz tube in excess of ammonia and the products are very rapidly cooled the ratio of hydrogen to nitrogen is almost exactly 1:1 if the volume of ammonia is at least twice that of the oxygen. The yield of hydrazine depends greatly on the cooling of the flame.

The yield of ammonia obtained by burning an excess of hydrogen in a mixture of nitrogen and oxygen is an almost linear function of the amount of oxygen and is independent of the quantity of nitrogen within wide limits. The yield of hydrazine is irregular and appears to be subject to catalytic influences.

H. WREN.

**Mechanism of the oxidation of mercury vapour.** IV. Reaction outside the platinum catalyst. V. Oxidation velocity of platinum. Y. OKAYAMA (J. Soc. Chem. Ind. Japan, 1929, 32, 202B—204B, 205B).—IV. Theoretical. If the platinum catalyst is at such a temperature that the decomposition velocity of mercuric oxide exceeds the vaporisation velocity from the platinum, then the oxidation of the mercury must occur outside the catalyst. The various ways in which reaction could occur under these conditions are given and the velocity equations are deduced. The vapour pressure of the mercury has a much greater influence on the velocity than when the reaction occurs on the catalyst surface.

V. The fall in pressure observed when a platinum filament is heated in oxygen at 0.1 mm. in presence of a little mercury is due to oxidation of the mercury and oxidation of the platinum, the velocity of the latter reaction being less than 1% of that of the former.

S. K. TWEEDY.

**Oxidation of mercury vapour.** VI, VII, VIII. Y. OKAYAMA (J. Soc. Chem. Ind. Japan, 1929, 32,

219B—220B).—The velocity of oxidation of mercury vapour by gaseous oxygen in presence of a heated platinum filament (catalyst) was measured. The vapour tension of the mercury was kept constant, but it has only a very small influence on the velocity, indicating that the reaction occurs on the platinum surface. The results indicate that molecules and atoms of oxygen are simultaneously present on the platinum surface and that both react with impinging mercury atoms. The proportion of atomic oxygen present increases as the filament temperature rises.

S. K. TWEEDY.

Decomposition of methyl alcohol by catalysts composed of oxides of zinc and chromium. J. R. HUFFMANN and B. F. DODGE.—See B., 1930, 49.

Catalysts for formation of alcohols from carbon monoxide and hydrogen. V. Decomposition and synthesis of methyl alcohol with a zinc-copper-chromium oxide catalyst. M. R. FENSKE and P. K. FROLICH.—See B., 1930, 49.

Effect of poisons on the velocities of dehydrogenation of methyl alcohol and formaldehyde at a surface of copper catalyst activated with ceria as promoter. J. C. GHOSH and J. B. BAKSHI (J. Indian Chem. Soc., 1929, 6, 749—761; cf. B., 1927, 426).—A method has been described by which the velocity coefficients for the two consecutive reactions  $\text{CH}_3\text{OH} \rightarrow \text{H}\cdot\text{CHO} + \text{H}_2$  and  $\text{H}\cdot\text{CHO} \rightarrow \text{CO} + \text{H}_2$  at the surface of the copper catalyst activated by ceria can be separately determined. The velocity of the second reaction is considerably smaller than that of the first. The inhibiting effect of the following poisons on the two reactions has been investigated: carbon disulphide, carbon tetrachloride, chloroform, acetonitrile, bromine, and mercuric iodide. Iodine increases the velocity of reaction in each case. Observations with carbon disulphide, chloroform, and bromine indicate that amounts of these substances containing an atom of sulphur, an atom of chlorine, and an atom of bromine, respectively, possess identical inhibiting power on the dehydrogenation of methyl alcohol. The amount required for complete inhibition is directly proportional to the activity of the catalyst as measured by the velocity coefficient. These results are in agreement with Taylor's hypothesis (A., 1925, ii, 562) that catalytic action will occur only on those "active" points of the surface where the extent of valency saturation is least. In very small doses chloroform and carbon disulphide increase the velocity of dehydrogenation of methyl alcohol at the beginning, but diminish very considerably, from the beginning, the velocity of decomposition of formaldehyde. Mercuric iodide in very small doses reduces very markedly the velocity of dehydrogenation of methyl alcohol, but the velocity of decomposition of formaldehyde is only very slightly affected. These facts suggest that the two reactions occur at different points of the catalytic surface with different chemical and adsorptive properties. The poisonous effect of mercuric iodide cannot be due to iodine, as shown by experiment, so it must be due to mercury vapour. A much smaller quantity of mercury is sufficient for complete inhibition than is required of sulphur etc., and it is suggested that the probable cause of inhibition

is to be found in the destruction of the non-homogeneity of the copper surface by condensation of mercury vapour on an active area, which it dissolves and spreads out as a smooth inactive layer, after which it re-evaporates and condenses on another active area. The inhibiting effect of carbon tetrachloride and acetonitrile increases with time. This behaviour cannot readily be explained. Acetonitrile is a very active poison.

M. S. BURR.

Catalytic oxidation of alcohol. L. Y. KARPOV.—See B., 1930, 7.

Pyrogenic decomposition of aromatic compounds under pressure by means of hydrogen in presence of a mixed catalyst. II. V. IPATIEV and N. ORLOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1295—1300).—See A., 1929, 548.

Catalytic reduction of geraniol and citronellal by means of platinum-black. K. SUZUKI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 573—589).—The reduction of geraniol by hydrogen in the presence of platinum-black is more rapid than when nickel is also present, but the same product is obtained. A small quantity of ferrous sulphate decreases the velocity of reduction considerably. Citronellal is reduced to dihydrocitronellal in the presence of platinum-black. In presence of ferrous sulphate the addition to the double linking is prevented and the product obtained is citronellol.

F. J. WILKINS.

Luminous effect on mercury electrodes during electrolysis. A. V. DUMANSKI, Z. P. TSCHESCHEVA, and A. V. BANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1239—1241).—When a current of 0.04—0.08 amp. at 60—70 volts, passing through a solution of an electrolyte from a mercury anode to a platinum cathode, is broken, the surface of the mercury luminesces for some time. The most intense luminescence is observed with 0.1N-sodium chloride, potassium bromide, or aluminium chloride solutions; using less concentrated solutions the effect is weaker, whilst with greater concentrations its duration is shorter. Sodium carbonate, sulphate, and oxalate solutions also give the effect, which was not, however, observed with sodium nitrate, sulphite, or acetate, potassium chlorate or hydroxide, or nitric acid solutions. The spectrum of the luminescence consisted of a diffuse, unbroken band between 510 and 617  $\mu\mu$  for aluminium chloride, and 510—607  $\mu\mu$  for sodium chloride.

R. TRUSZKOWSKI.

Cathodic disintegration of alloys. I. Alloys of zinc and copper. L. BELLADEN and L. SCRRA (Gazzetta, 1929, 59, 785—795).—The delay in the cathodic disintegration of zinc in air and in hydrogen is due to the presence of a film of oxide. Increase in the voltage of the spark ruptures this film and allows the disintegration of the metal to proceed. In air the film thickens through the action of oxygen ions. Similar behaviour is shown by alloys of zinc and copper. With low voltage and current density the amount dissipated decreases with increase in the percentage of zinc. At high voltages alloys rich in zinc undergo the greatest disintegration. The amount of disintegration is greater in hydrogen than in air. The metal dissipated always contains a lower per-

tage of copper than the alloy, and in hydrogen this percentage is slightly less than in air.

F. G. TRYHORN.

**Polarographic studies with the dropping mercury cathode. VII. Maximum of current occurring in electrolysis of mercuric cyanide solutions.** M. DILLINGER (Coll. Czech. Chem. Comm., 1929, 1, 638—647; cf. Demassieux and Heyrovský, A., 1929, 269).—The electro-reduction of mercuric cyanide at the dropping mercury cathode in oxygen-free dilute aqueous solutions of electrolytes leads to discontinuous maxima in electro-capillary and current-voltage curves closely analogous to those obtained in the electro-reduction of oxygen (A., 1929, 1241, 1393). The concentration of electrolyte necessary to evoke the greatest maximum is independent of the rate of dropping of the mercury and is directly proportional to the concentration of mercuric cyanide, and for a 0.001*M*-solution of the cyanide must be such as to give rise to a conductivity equal to that of 0.0025*N*-hydrochloric acid. Potassium cyanide gives anomalous results. It is suggested that at the maximum of current, the mercuric cyanide is reduced as fast as it is adsorbed at the mercury-solution interface and the greatest maximum occurs when the electrolyte and the cyanide are adsorbed at equal rates.

J. G. A. GRIFFITHS.

**Effects of electrodeless discharge on potassium chlorate, bromate, and iodate.** S. D. MAHANT (J. Indian Chem. Soc., 1929, 6, 705—709).—The apparatus employed was similar to that described by Bhatnagar and others (A., 1928, 814). The effect of the electrodeless discharge on potassium chlorate, bromate, and iodate is quite different from that of heat or ultra-violet radiations, no oxygen being produced in the first case in sufficient amount to measure quantitatively, and no persalts being formed. The chlorate forms small quantities of potassium chloride and hypochlorite, and the bromate, bromide and hypobromite, but the iodate gives only iodine. In one case, where water was present and the pressure of the system was 13—15 mm., the iodate remained white and was found at the end to contain hypoiodite and no iodine. The results cannot be repeated quantitatively, owing to the large number of different factors which affect them, such as (1) voltage at which discharge passes, (2) length of exposure, (3) extent of surface exposed to discharge and rate of its renewal by shaking, since it is evidently a surface phenomenon, and (4) the pressure in the system.

M. S. BURR.

**Production of hydroxyl by water vapour discharge.** G. I. LAVIN and F. B. STEWART (Proc. Nat. Acad. Sci., 1929, 15, 829—832; cf. A., 1929, 520).—An arrangement by which the amount of hydrogen peroxide formed when a discharge is passed through water vapour can be compared with the intensity of the hydroxyl bands produced at the same time is described. There is an approximate proportionality, and the maximum proportion of water passing through the discharge tube converted into peroxide is at least 3.9%.

C. A. SILBERRAD.

**Photolysis of water and the photovoltaic effect of gold and platinum electrodes.** R. AUDUBERT (Compt. rend., 1929, 189, 1265—1267).—Whatever

the sense and intensity of the photovoltaic effect in the author's experiments (this vol., 38), the sensitiveness of the gold, or platinum electrodes in contact with different electrolytes increases with the frequency of the exciting radiation, whilst the inversion potential is independent of the frequency. The relation  $v_0 = A - \alpha V_0$ , where  $v_0$  is the initial frequency,  $V_0$  the darkness potential in volts,  $\alpha$   $2.24 \times 10^{14}$ , and  $A$   $5.88 \times 10^{14}$  for platinum and  $5.7 \times 10^{14}$  for gold, has been verified. The explanation of the phenomena by the photolysis of water into hydrogen and oxygen is supported by the values of the *E.M.F.* of decomposition obtained from the formula  $h\nu_0/\nu$ .

J. GRANT.

**Photochemical dissociation. Decomposition of gaseous hydrogen chloride in total and monochromatic ultra-violet light. II.** C. T. SCHULTZ (J. Chim. phys., 1929, 26, 506—541; cf. this vol., 46).—As hydrogen chloride shows an absorption band beginning at about 2200 Å. the varieties of radiation used were: (1) the total emission of a very strong condensed spark between zinc electrodes; (2) the same filtered through (a) chlorine, (b) a sheet of glass, (c) quartz (which left practically only radiation of 2025.5—2138.6 Å.), and (3) the total emission with aluminium electrodes. Full details are given of the method whereby the hydrogen chloride was prepared and exposed to these sources of radiation in a quartz vessel of 15.4 c.c. capacity, under pressures of 50—400 mm., for periods of 15—285 min. The total impurities in the hydrogen chloride were less than 1 in  $10^4$ , and the chlorine produced by the photochemical action was so dry that it did not act on potassium hydroxide or mercury. It was further shown that the resultant mixture of hydrogen chloride, hydrogen, and chlorine, alone or in contact with potassium hydroxide or mercury, undergoes no further change in ordinary light. Measurement of decomposition was therefore made by determining the reduction in pressure consequent on absorption of undecomposed hydrogen chloride. The results obtained showed that: (i) only the ultra-violet radiation absorbed by hydrogen chloride effects its decomposition. (ii) The amount of decomposition increases with, although not proportionately to, the time of exposure. (iii) Total decomposition and velocity of reaction increase, whilst percentage decomposition decreases, with increased pressure, although always at a smaller rate. (iv) A preliminary estimate shows that when acted on by radiation (2c) not more than 5 mols. of hydrogen chloride are decomposed per quantum. Numerous tables, and photographs showing absorption are given.

C. A. SILBERRAD.

**Photochemical combination of hydrogen and chlorine at low pressures.** A. TRIFONOV [in part with G. RJABININ] (Z. physikal. Chem., 1929, B, 6, 118—126; cf. A., 1929, 776).—The photochemical reaction between hydrogen and chlorine has been studied for equimolecular mixtures at pressures between 0.1 and 0.8 mm. Above 0.2 mm. the velocity of the reaction is proportional to the cube of the pressure, in agreement with Semenov's theoretical formula; below this pressure the reaction either ceases abruptly or proceeds very slowly. Alteration

of the moisture content of the reactants does not affect the limiting pressure of 0.2 mm. The possibility of the phenomenon being due to a reaction with the tap grease has not been eliminated. F. L. USHER.

**Temperature coefficients of some photochemical reactions in various solvents in the dark and in the light.** N. A. YAJNIK and H. L. UPPAL (J. Indian Chem. Soc., 1929, 6, 729–741).—The following reactions have been studied at different temperatures in presence and in absence of light: (1) The oxidation of hydrogen sulphide in aqueous solution by oxygen (in excess). (2) Bromination of lactic acid in water, chloroform, and carbon tetrachloride, using equimolecular concentrations of the reactants. (3) Bromination of cinnamic acid in carbon disulphide, carbon tetrachloride, and chloroform, again using equimolecular concentrations. In all cases the formula for a unimolecular reaction gave sufficiently constant values for the velocity coefficient. In general, the temperature coefficient of the velocity coefficient is greater in the dark than in the light. No definite relationship can be traced between the dielectric constants of the solvents, on the one hand, and either the velocity coefficients or the temperature coefficients on the other. M. S. BURR.

**Law of blackening of the photographic plate by electron streams.** W. SEITZ and G. HARIO (Physikal. Z., 1929, 30, 758–760).—The darkening of Agfa-Kontrast plates and films has been determined for electrons ranging in velocity from 1.5 to 18.5 kilovolts. The curve,  $\log it$  ( $i$ =electron density,  $t$ =time of exposure) plotted against darkening  $S$  ( $S=\log I_0/I$ ,  $I_0$  being the light intensity through clear plate,  $I$  through darkened plate) at first exhibits a linear course, then reaches apparent saturation, and later exhibits a very rapid increase in  $S$  with increasing values of  $\log it$ . The saturation region is very evident for velocities corresponding with 5–12 kilovolts, much less evident for 1.5 kilovolts, and for 15–18.5 kilovolts the rapid rate of increase of  $S$  sets in so soon that the saturation cannot be detected for values of  $S<1.5-2.5$ . Two darkening effects appear to be superimposed, one due to the direct action of the electrons and the other due to the X-rays generated at the film surface. The saturation effect represents a stage at which the maximum number of grains become developable as a result of the primary process, the effect of the X-rays becoming important for large values of  $it$ . With very rapid electrons the X-rays become more important. These views have been tested by photographing sections of films darkened under defined conditions, the magnification (760) demonstrating that the depth of the darkening process conforms with the hypothesis advanced.

R. A. MORTON.

**Photochemical oxidation and reduction from an electronic point of view. II.** A. STEIGMANN (Z. wiss. Phot., 1929, 27, 268–272; cf. A., 1929, 1152).—The chromophoric groups in dyes are the seat of their light-sensitivity, but many dyes are quite fast to light. This results from an "electron-screening" action, consisting of either (1) preferential action of other light-sensitive groups present ("intramolecular desensitising"), as in alizarin, or (2) an

inhibitory action exerted by other groups, linkings, or configurations present in the molecule of the dye, as the result of which no photochemical action occurs even although light is absorbed. The manner of transformation of the absorbed energy is obscure in the latter case. The author suggests bleaching experiments to show the relative screening effects of various substituents and of constitutional differences, taking, e.g., dyes of the indanthrene or flavanthrene types. L. V. CHILTON.

**Eberhard effect in relation to photographic photometry.** N. VALENKOV (Z. wiss. Phot., 1929, 27, 236–267).—The Eberhard effect is the increased density obtained at the sharp edge of a uniformly illuminated field. It is appreciable only in the case of coarse-grained emulsions exposed to visible light (and then only for extremely sharp images), and is of the same character whether ferrous oxalate or metol-quinol be employed as developer. It is of no consequence either in astrophotometry or in spectrophotometry, in which images of the requisite sharpness are rarely obtained. L. V. CHILTON.

**Rôle of sensitisers in photography, and the latent image.** F. E. E. GERMAN and D. K. SHEN. —See B., 1930, 83.

**Behaviour of nickel carbonate in relation to photosynthesis.** R. EMERSON (J. Gen. Physiol., 1929, 13, 163–168).—The effect of illumination on purified nickel carbonate in carbon dioxide was examined by the manometer and by testing for the production of oxygen and carbohydrate. No evidence was obtained for the photosynthetic activity of this preparation as claimed by Baly (A., 1927, 1040, 1041; 1929, 408). K. V. THIMANN.

**Photochemical reaction between cyclohexane and chlorine in carbon tetrachloride solutions.** K. P. BASU (J. Indian Chem. Soc., 1929, 6, 691–703; cf. A., 1929, 1023).—The photochemical reaction between cyclohexane and chlorine in solution in dry carbon tetrachloride, irradiated by either white or monochromatic light, is unimolecular with respect to chlorine. The velocity coefficient is directly proportional to the intensity of the incident radiation, is independent of the concentration of the chlorine, and increases slightly with the concentration of the cyclohexane. The coefficient diminishes a little as the reaction proceeds, apparently due to the retarding influence exercised by the chlorocyclohexane formed. The quantum efficiency is 19 at 436  $\mu$ , 30 at 404  $\mu$ , and 41 at 366  $\mu$ . The temperature coefficients for the same wave-lengths are 1.5, 1.29, and 1.26, respectively. In explanation of the observed facts a mechanism is suggested which may be represented as follows: (1)  $\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$ . (2)  $\text{C}_6\text{H}_{12} + \text{Cl} \rightarrow \text{C}_6\text{H}_{11}\text{Cl} + \text{H}$ . (3)  $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$ . (4)  $\text{H} + \text{C}_6\text{H}_{11}\text{Cl} \rightarrow \text{C}_6\text{H}_{12} + \text{Cl}$ . (5)  $\text{H} + \text{Cl} \rightarrow \text{HCl}$ . Equation (4) explains the diminution in the velocity coefficient as the reaction proceeds. M. S. BURR.

**Photochemical decomposition of benzoquinone in water and in alcohol.** P. A. LEIGHTON and G. S. FORBES (J. Amer. Chem. Soc., 1929, 51, 3549–3559).—The photochemical reduction of benzoquinone in water, the temperature coefficient of which



is approximately unity, exhibits an induction period during which a dimeride is probably formed (cf. Hartley and Leonard, J.C.S., 1909, 95, 34); there is no inhibition when 50% alcohol is used as the solvent. Below  $\lambda 4350 \text{ \AA}$ . the quantum efficiency in pure and aqueous alcoholic solutions is constant at 0.5 independent of the wave-length and, in aqueous-alcoholic solutions, of the concentration also; at higher wave-lengths the efficiency decreases, indicating the existence of a definite threshold region inside the first absorption band. The threshold value is displaced towards shorter wave-lengths with progressive decrease in alcohol concentration. Possibly every absorbed quantum produces activation, a secondary reaction having an efficiency of 50% producing the observed yields. S. K. TWEEDY.

**Effects of cathode rays on the proteins of serum.** L. E. BAKER and R. P. COREY (J. Exp. Med., 1929, 50, 439—444).—A large proportion of the albumin and globulin suffers denaturation with the formation of products soluble at the  $p_H$  of the serum, whilst an insoluble substance is formed on the window of the cell. Slight hydrolytic fission takes place with formation of small quantities of ammonia and of products precipitable and non-precipitable, respectively, with trichloroacetic acid.

#### CHEMICAL ABSTRACTS.

**Photochemical reaction between oxalic acid and chlorine in presence of hydrochloric acid.** A. K. BHATTACHARYA and N. R. DHAR (J. Chim. phys., 1929, 26, 556—564; cf. A., 1929, 37).—The reaction between oxalic acid and chlorine in presence of hydrochloric acid (in absence thereof it is immeasurably rapid) is bimolecular in the dark, with temperature coefficient 2.95. In radiation of wave-lengths 4725, 5650, and  $7304 \text{ \AA}$ . the coefficients are respectively 2.3, 2.4, and 2.5 with yields per quantum at  $25^\circ$  of 8.6, 7.2, and 4.9. (It is to be noted that the radiation capable of splitting the molecule of chlorine into atoms has  $\lambda = 5220 \text{ \AA}$ .) Absorption of incident radiation is almost directly proportional to its intensity. The ratio (ratio of velocities of reaction for two intensities of incident radiation)/(ratio of those intensities) varies from 1.68/6.25 to 7.3/6.25, and is closely connected with the ratio of the velocities of reaction in light and in darkness. The bearing of these results on the divergent results reported as to the relation between intensity of radiation and velocity of reaction in the case of hydrogen and chlorine is discussed. C. A. SILBERRAD.

**Bromination of cinnamic acids.** J. MEYER and K. PUKALL (Z. physikal. Chem., 1929, 145, 360—392).—The rates of bromination in chloroform solution of the individual cinnamic acids have been measured both in the dark and in light of various colours. The velocity coefficient for *trans*-cinnamic acid in either daylight or artificial light did not give reproducible values, and the reaction proceeded after removal of the source of light. This effect was traced to the action of a catalyst or catalysts which are not all due to impurities in the bromine used. In yellow, blue, or nearly white light the coefficient exhibited a drift which could be abolished by allowing the reaction to take place in light of wave-length not photo-

chemically absorbed by bromine. Important differences were observed in the behaviour of *allocinnamic* acid, m. p.  $68^\circ$ , the bromination of which proceeds considerably faster than that of the *trans*-acid under similar conditions. The effect of yellow light in accelerating the reaction in the case of *allocinnamic* acid is only  $1/8$  of that obtained with the *trans*-acid. The rate of addition of bromine to the three *cis*-acids of m. p.  $68^\circ$ ,  $58^\circ$ , and  $42^\circ$  was observed to increase in the order named. The conclusion reached is that these acids are to be regarded as isomeric, and not merely as polymorphic. F. L. USHER.

**Photochemical reactions of ergosterol.** E. H. REERINK and A. VAN WIJK (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 845—848).—The two wave-length ranges  $300\text{--}270 \mu$  and about  $250 \mu$  have different actions on ergosterol. In the first period of reaction with the longer wave-length less than about 60% of the ergosterol undergoes change, and the absorption spectra can be interpreted by the assumption of the presence of only one substance, apart from the ergosterol, with a broad band having a maximum at about  $265 \mu$ . By precipitation of the unchanged ergosterol with digitonin, the reaction product, vitamin-D, was obtained as lozenge-shaped transparent plates, m. p.  $0^\circ$ . The absorption curves of ergosterol after long irradiation cannot be calculated from those of ergosterol and vitamin-D, in consequence of a photochemical change in the reaction product. With short-wave irradiation it is impossible to obtain more than a 15% yield of vitamin-D, since there are formed by-products which produce a maximum in the absorption spectrum with an absorption coefficient of about twice that of ergosterol. As the reaction proceeds the absorption falls to almost zero with the destruction of the vitamin-D. F. G. TRYHORN.

**Chemical action of  $\alpha$ -rays on nitric oxide.** W. MUND and R. GILLEROT (Bull. Soc. chim. Belg., 1929, 38, 343—359).—Under the action of  $\alpha$ -particles nitric oxide gives rise to nitrogen peroxide and trioxide, in equilibrium with excess of nitric oxide. Each pair of ions produced in the mixture causes the formation of at least 0.78 mol. of nitrogen. C. W. GIBBY.

**Argentothiosulphuric acids and their derivatives. I. Preparation of sodium salts and isolation of monoargentomonothiosulphuric acid.** H. BAINES (J.C.S., 1929, 2763—2769).—Previous analyses of the sodium argentothiosulphates do not agree. Salts having the following compositions have been obtained: sodium monoargentomonothiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{Ag}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$  or  $\text{Na}(\text{AgS}_2\text{O}_3) \cdot \text{H}_2\text{O}$ ; sodium triargentotetrathiosulphate,  $\text{Na}_3[\text{Ag}_3(\text{S}_2\text{O}_3)_4] \cdot 2\text{H}_2\text{O}$ . Crystal data for these salts are given. Evidence is advanced for the existence of sodium monoargentodithiosulphate,  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$ , in solution. Monoargentomonothiosulphuric acid,  $\text{H}(\text{AgS}_2\text{O}_3) \cdot \text{H}_2\text{O}$ , was obtained as an unstable white precipitate by acidifying with nitric acid an ammoniacal solution of the sodium salt. Aqueous solutions of triargentotetrathiosulphuric acid have been obtained. J. A. V. BUTLER.

**Triple compounds of gold bromide and rubidium [bromide] with bromides of other metals.** E. S. BURKSER, S. G. RUBLOV, and A. M.

SCHARNOVSKY (Z. anorg. Chem., 1929, **185**, 144—152; cf. A., 1927, 1155).—The preparation and properties of the following compounds are described:  $\text{Rb}_{21}\text{M}^{\text{III}}\text{Br}_4$ ,  $\text{RbAuBr}_4$ , where  $\text{M}^{\text{II}}$  is copper, cadmium, or mercury, and  $\text{M}^{\text{III}}$  is thallium, and  $\text{Rb}_3\text{M}^{\text{III}}\text{Br}_6$ ,  $2\text{RbAuBr}_4$ , where  $\text{M}^{\text{III}}$  is bismuth or antimony. They differ from the triple iodide salts in containing no univalent gold. Metals belonging to the same family give compounds of analogous composition and of the same crystal system.

F. L. USHER.

**Production of pure beryllium oxide from beryllium ores.** H. A. SLOMAN.—See B., 1929, 1043.

**Base exchange in artificial autunites.** J. G. FAIRCHILD (Amer. Min., 1929, **14**, 265—275).—Calcium, potassium, barium, manganese, copper, cobalt, nickel, lead, and magnesium autunites were prepared by treating sodium (or calcium) autunite with a concentrated solution of the chloride. Most of the compounds contained less than  $8\text{H}_2\text{O}$ .

#### CHEMICAL ABSTRACTS.

**Hydrates of bleaching powder.** B. NEUMANN and H. HAEBLER (Z. Elektrochem., 1929, **35**, 909—914; cf. B., 1926, 190; O'Connor, B., 1928, 88).—By the chlorination of calcium hydroxide at 35—40° there are formed the hydrates  $3\text{CaOCl}_2 \cdot \text{CaO} \cdot 4\text{H}_2\text{O}$  and  $3\text{CaOCl}_2 \cdot \text{CaO} \cdot 6\text{H}_2\text{O}$ , the latter corresponding with ordinary bleaching powder. Chlorination at about —15° gives a hydrate,  $\text{CaOCl}_2 \cdot \text{CaO} \cdot 2\text{H}_2\text{O}$ . In all these hydrates one molecule of water is firmly held, presumably as calcium hydroxide. The compositions have been established both by direct analysis and by isothermal dehydration experiments.

R. CUTHILL.

**Phosphorescent compounds of temporary action.** L. VERNITZ (Trans. State Inst. Appl. Chem., Moscow, 1927, No. 8, 46—59).—The conditions necessary for producing alkaline-earth sulphide luminophores with maximum luminescence and duration of light were investigated. Calcium sulphide must be prepared from oxide, and barium or strontium sulphide from the carbonate; other metals (except the excitators added) must be absent.

#### CHEMICAL ABSTRACTS.

**Action of ferric chloride on zinc.** E. BEUTEL and A. KUTZLNIGG (Monatsh., 1929, **52**, 339—342).—Ferric chloride solutions containing less than 100 g. per litre have no effect on a bright zinc surface, but more concentrated solutions give a deposit which contains iron, the velocity of deposition increasing with the concentration of the solution; the optimum concentration is 500 g. per litre. A matte zinc surface which has been treated with the sand-blast is slowly darkened by solutions containing 50 g. of  $\text{FeCl}_3$  per litre. The deposit forms a spongy, non-adherent, grey layer with a metallic lustre, and consists of irregular, microscopic granules containing zinc as well as iron. The thickness of the deposit formed in 0.5 hr., using ferric chloride solution containing 300 g. per litre, is about  $3 \times 10^{-4}$  mm. Extended treatment of the deposit with distilled water furnishes no rust, but leads to the formation of minute filaments of zinc hydroxide. Exposure of sheet zinc

for a long period to the action of ferric chloride solutions containing 500—1000 g. per litre converts the primary iron coating into a compact deposit of dark brown ferric hydroxide. Hydrolysis of ferric chloride affords hydrochloric acid, which attacks the zinc, with ultimate precipitation of a quantity of ferric hydroxide corresponding with the acid which has formed zinc chloride; by treatment for 48 hrs. with solutions of ferric chloride containing 5, 20, and 200 g. per litre, zinc loses 0.38, 1.3, and 7%, respectively, of its weight. Extensive reduction of ferric chloride to ferrous chloride also occurs.

The primary iron deposit formed in concentrated ferric chloride solutions appears to undergo, more or less rapidly according to the degree of concentration, a change giving a brilliant, lustrous, but extremely brittle metallic layer, which breaks up spontaneously on reaching a certain thickness; this is found to be about  $9 \times 10^{-3}$  mm. The deposit contains zinc, and its composition varies with concentration of the ferric chloride solution. Grey deposits are also obtained with alcoholic ferric chloride solution, and with dilute or concentrated aqueous ferrous sulphate. A coherent, tenacious, dove-grey deposit is similarly produced in the presence of fluoride ions, whilst addition of a colloid (glue) yields a solution which appears to contain iron as a dispersed phase, since after removal of a black deposit it possesses a dull grey colour.

C. W. SHOPPEE.

**Yellow luminous phosphorescence.** L. VANINO and F. SCHMID (J. pr. Chem., 1929, [ii], **124**, 52—54).—A mixture of barium oxide (40.0 g.), sulphur (9.0 g.), lithium phosphate (0.7 g.), and 0.4% alcoholic copper nitrate (3.0 c.c.) gives a yellow luminous product but of feeble light intensity. Better results are obtained by the use of barium carbonate and strontium hydroxide, and it is important to add a reducing agent. The most satisfactory results were obtained from (a) for a golden-yellow phosphorescence: barium carbonate 25.0 g., strontium hydroxide 15.0 g., sulphur 10.0 g., starch 3.0 g., lithium sulphate 1.0 g., magnesium oxide 1.0 g., 0.5% thorium sulphate solution 2 c.c., and 0.4% cupric sulphate solution 3 c.c.; (b) for a lemon-yellow phosphorescence: barium carbonate 24.0 g., strontium hydroxide 17.0 g., sulphur 10.0 g., starch 3.0 g., lithium sulphate 1.0 g., magnesium oxide 1.0 g., thorium sulphate (2 c.c.), and cupric sulphate (3 c.c.) solutions of the concentrations given under (a). The intimately mixed masses are strongly heated for 40 min.

A. I. VOGEL.

**Chemically pure powdered mercury.** F. KRAUSS and K. MÄHLMANN (Z. anorg. Chem., 1929, **184**, 298—302; cf. A., 1908, ii, 193, 500).—Early work on the preparation of mercury in the powdered form is criticised and the products are considered to have been contaminated with basic salts. Light grey powders containing 99.8% Hg have been obtained under definite conditions from solutions of mercuric and mercurous nitrate by precipitation with hydrazine hydrate, sulphur dioxide, ferrous sulphate, stannous chloride, or phosphorous acid. The powdered mercury is liquefied by rubbing or shaking, and probably consists of microscopic particles of the metal sur-

rounded by an extremely thin layer of a basic salt which, however, cannot be detected analytically.

F. L. USHER.

#### Reduction of mercuric chloride by glycerol.

M. N. GOSWAMI and P. N. GANGULI (J. Indian Chem. Soc., 1929, 6, 711—715).—On heating an aqueous solution of glycerol with mercuric chloride the latter is reduced to mercurous chloride. The amount of reduction reaches a maximum of 88—90% at 180—182°. The glycerol appears to be first oxidised to glyceraldehyde, which is then split up into formaldehyde, probably by way of glycollic acid. Glycerol is also dehydrated to acetaldehyde. No carbon dioxide is formed. A determination of total aldehyde by the hydrogen sulphite method gave 11.17%, calculated as formaldehyde, on the amount of glycerol, whilst a determination of formaldehyde alone by Romijn's cyanide method gave 5.6%. These results can be only approximate.

M. S. BURR.

**Intermetallic compounds in mercury.** A. S. RUSSELL (Nature, 1930, 125, 89).—A preliminary report of the formation in liquid mercury of intermetallic compounds other than with mercury. The empirical formulae of the complexes so far obtained are  $\text{SnCu}_2$ ,  $\text{SnCu}_3$ ,  $\text{SnCu}_4$ ,  $\text{ZnCu}$ ,  $\text{ZnFe}$ ,  $\text{ZnFe}_8$ , and  $\text{CuFe}$ .

L. S. THEOBALD.

**Measurements with bi- and quadri-valent compounds of the rare earths. II. Classification of the rare earths based on periodic variations of the properties of their ions.** W. KLEMM. **III. Ytterbium dichloride.** W. KLEMM and W. SCHÜTH (Z. anorg. Chem., 1929, 184, 345—351, 352—358).—II. The rare earths may be classified in seven groups by consideration of the periodic variations of the magnetic properties of the ions, of the colour of the tervalent compounds, and of the stability of the dioxides and trichlorides.

**III. Ytterbium trichloride** is reduced to the dichloride by heating for 6 hrs. in an atmosphere of hydrogen at 600—620° and finally for about 30 min. at 850—900°. The almost colourless dichloride has  $d_{25}^{20}$  5.08, and dissolves in water without decomposition to a yellow solution, from which hydrogen is readily evolved on addition of acid. Although the material as ordinarily prepared (98% pure) exhibits feeble paramagnetic properties, the pure compound is probably diamagnetic. The compound  $\text{YbCl}_2 \cdot 8\text{NH}_3$  is reddish-yellow, whilst  $\text{YbCl}_2 \cdot 2\text{NH}_3$  and  $\text{YbCl}_2 \cdot \text{NH}_3$  are yellow.

H. F. GILLBE.

#### Extraction of the rare earths from gadolinite.

D. W. PEARCE and J. A. HARRIS (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 61—66).—Five wet and five dry methods for the decomposition of gadolinite were investigated and their efficiencies compared. For the maximum extraction of the rare-earth content, concentrated hydrochloric acid or saturated sodium hydroxide solution in the wet, and a mixture of sodium carbonate and borax in the dry, gave the best results.

N. M. BLIGH.

**Reaction between titanium sesquioxide and iron oxides.** F. HALLA (Z. anorg. Chem., 1929, 184, 421—427).—By reduction of hydrated titanous acid an apparently new form of titanium sesquioxide, which when heated with ferrous oxide at 1000° forms

a spinel  $\text{FeO} \cdot \text{Ti}_2\text{O}_3$  having  $d$  4.68 and  $\alpha$   $8.47 \pm 0.02 \text{ \AA.}$ , has been prepared. The reactions between  $\alpha$ -titanium sesquioxide and ferrous and ferric oxides, and between the new material and ferric oxide have been studied by X-ray examination of the reaction products.

H. F. GILLBE.

**Germanic oxide and oxalic acid.** J. BARDET and A. TCHAKIRIAN (Compt. rend., 1929, 189, 914—915).—Germano-oxalic acid is prepared by treating such an excess of germanic oxide with boiling solution of oxalic acid that oxide is deposited on cooling the filtered solution after concentration as far as possible. On concentration an uncrystallisable syrup is obtained in which neither alcohol nor ether produces a precipitate; it decomposes after a few hours with deposition of germanic oxide. The ratio  $\text{Ge} : \text{H}_2\text{C}_2\text{O}_4$  indicates the formula  $\text{H}_2\text{Ge}(\text{C}_2\text{O}_4)_3$ . The germanium and oxalic acid are partly in the form of a complex ion; neutralisation with soda occurs with an amount corresponding with 0.75 of the oxalic acid present. Addition of mannitol allows partial neutralisation of the germanic acid also. Similarly potassium iodate and iodide react with only part of the oxalic acid. Germanic oxide dissolves much more readily in ammonium hydrogen oxalate solution; the solution, after all that is possible has crystallised, leaves an uncrystallisable syrup of composition  $\text{Ge}(\text{C}_2\text{O}_4)_2 \cdot \text{GeO}(\text{C}_2\text{O}_4) \cdot x\text{H}_2\text{O}$ , which is not decomposed by hydrogen sulphide and is attacked by sulphuric acid at a high temperature only with production of germanic oxide.

C. A. SILBERRAD.

#### Lower oxygenated compounds of nitrogen.

L. CAMBI (Gazzetta, 1929, 59, 770—784).—Analysis of the decomposition products of metallic hyponitrites (sodium, copper, silver, cadmium, lead, and thallium) indicates that in acid solutions scission occurs mainly to nitrogen and nitric acid, and in some degree to nitrogen and nitrous acid. The nature and valency of the metallic ion influence the course of the reaction. It is suggested that decomposition may occur to give the following groups of compounds;  $\text{N}_2\text{O} + \text{H}_2\text{O}$ ,  $\text{NO} + \text{NO}_2 + 2\text{N}_2 + \text{H}_2\text{O}$ ,  $\text{HNO}_3 + 2\text{N}_2 + 2\text{H}_2\text{O}$ . Mixed solutions of sodium hyponitrite and ferrous and ferric salts were used in place of ferrous and ferric hyponitrites. The decomposition of ferrous hyponitrite solution is remarkable in giving unusually large amounts of nitrous oxide, whilst with the ferric salt the products are chiefly nitrogen and nitric acid. By oxidation with alkaline potassium permanganate solution the hyponitrites are converted into nitrites, but in acid solution nitric acid is formed, together with the autoreduction of some of the hyponitrite to nitrogen,  $(\text{HNO}) + 2\text{O} \rightarrow \text{HNO}_3$ ,  $5(\text{HNO}) \rightarrow 2\text{N}_2 + \text{HNO}_3 + 2\text{H}_2\text{O}$ . The course of the oxidation of sodium and silver hyponitrites by iodine depends on the hydrogen-ion concentration of the solution and on the conditions of the experiment. In the presence of excess of alkali oxidation is chiefly to nitric oxide and nitrite: in neutral or slightly acid solution (acetic or carbonic) nitrite and nitric oxide, together with some free nitrogen and nitrous oxide, are formed. Oxidation by potassium ferricyanide is slow; nitrous oxide is evolved and much of the hyponitrite is converted into nitrite. Excess of ferricyanide oxidises the nitrite to nitrate with evolution of nitric oxide. The

complexity of the reactions rules out the occurrence of the intermediate products previously suggested by Raschig. The decomposition of hyponitrites by iodine in alkaline solutions suggests that the free acid reacts in the form  $\text{HO}\cdot\text{N}:\text{N}\cdot\text{OH}$ , and a comparison of the behaviour of the hyponitrites on oxidation with that of nitrohydroxylamine indicates that the properties of the  $\text{N}\cdot\text{OH}$  group differ in the two classes of compound. The structure and reactions of the metallo-nitrosyl compounds formed by direct union of nitric oxide and a metal or a reducing salt are discussed in relation to the decomposition of the hyponitrites.

F. G. TRYHORN.

**Nitrogen sulphide.** III. S. A. VOSNESSENSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1317—1322).—The blue sublimate obtained by Usher (A., 1925, ii, 581) by heating nitrogen sulphide under reduced pressure at 100—140° in the presence of silver gauze is probably not a polymorph of nitrogen sulphide, but finely-divided sulphur. Nitrogen sulphide gives a blue coloration in the presence of alkali in organic solvents, and this phenomenon may be employed in the titration of organic acids by alcoholic sodium or potassium hydroxide.

R. TRUSZKOWSKI.

**Nitrides.** S. A. VOSNESSENSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1323—1328).—Methods for the preparation of nitrides are reviewed. The densities of the nitrides of sulphur, copper, zinc, and barium are respectively 2.63, 5.80, 5.40, and 6.46, and the decomposition points of the nitrides of barium, chromium, and copper are respectively above 1000°, above 900°, and 300°. A comparison of the densities of a number of nitrides shows that these vary periodically with the at. wt. of their constituent elements. The decomposition temperatures of nitrides are the higher the smaller is the atomic volume of their constituent nitrogen, and the simpler their structure.

R. TRUSZKOWSKI.

**Action of iodine vapour on phosphorus vapour.** Volatility product. H. PÉLABON (Compt. rend., 1929, 189, 1085—1087).—It has been shown qualitatively that Tian's conception of the volatility product (A., 1929, 1014) may be applied to the reaction  $\text{P}_4 + 6\text{I}_2 = 4\text{PI}_3$ .

J. GRANT.

**Preparation and properties of the borides of tantalum and of niobium.** L. ANDRIEUX (Compt. rend., 1929, 189, 1279—1281).—*Tantalum* and *niobium borides* ( $\text{TaB}_2$ ,  $d^{15}$  11.0, and  $\text{NbB}_2$ ,  $d^{15}$  6.4) were prepared as small, hard grey crystals by the electrolysis of fused mixtures of alkali or alkaline-earth borates and fluorides with tantalic or niobic oxide (cf. A., 1927, 216, 844), any amorphous boron and calcium boride being removed from the mixture in dilute nitric acid. The crystals resist nitric or hydrochloric acid or aqua regia, but are readily oxidised and slowly attacked in the cold by hydrofluoric and sulphuric acids and by fused alkalis. For analysis they may be decomposed by fused potassium hydrogen sulphate in the presence of sulphuric acid, and the insoluble pentoxide weighed.

J. GRANT.

**Action of air on flowers of sulphur and ground sulphur.** J. E. STEPHENSON and S. W. BRIDGE (Analyst, 1929, 54, 737; cf. A., 1929, 1253).—

The use of flowers of sulphur 100% of which passed a 300-mesh sieve gave results identical with those previously obtained when only 98.5% passed the 300-mesh sieve.

H. D. HEWER.

**Preparation of large crystals of chrome alum, and explanation of corrosion figures.** F. A. ROHRMAN and N. W. TAYLOR (J. Chem. Educ., 1929, 6, 473—478; Chem. Zentr., 1929, ii, 378).

**Complex compounds. I. Removal of ammonia from the co-ordination sphere.** H. I. SCHLESINGER and (MISS) R. K. WORNER (J. Amer. Chem. Soc., 1929, 51, 3520—3523).—Chloropentamminechromic chloride is converted into insoluble *chromium trichlorotriammine*,  $\text{Cr}(\text{NH}_3)_3\text{Cl}_3$ , by heating at 270° in hydrogen chloride until the salt turns from pink to green. This substance reacts slowly with liquid ammonia to yield the original pentammine; it is possibly a polynuclear compound and its properties are quite different from those of the substance of the same composition described by Werner (A., 1910, ii, 960). If it is heated at 175° in hydrogen chloride hygroscopic crystalline *ammonium chromic hexachloride*,  $(\text{NH}_4)_3[\text{CrCl}_6]$ , is produced; this substance reacts rapidly with gaseous ammonia with production of the original pentammine. It is apparently not a double compound; the chromium has taken up hydrogen chloride rather than changed its co-ordination number as a result of the removal of ammonia from the co-ordination sphere. If the triammine salt is heated at 270° in hydrogen chloride a salt having the composition  $2\text{CrCl}_3 \cdot 3\text{NH}_4\text{Cl}$  is formed, and is further slowly decomposed to anhydrous chromic chloride. Insoluble *chromium chloro-oxalatotriammine* is formed when the above triammine is heated with solutions containing oxalate ions. The original triammine is recovered if the compound is heated with hydrochloric acid, and if heated at 190° in hydrogen chloride a polynuclear compound of composition corresponding with  $2\text{CrCl}_3 \cdot (\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot 4\text{NH}_4\text{Cl}$  is formed; this substance has properties similar to those of ammonium chromic chloride.

S. K. TWEEDY.

**Complex compounds. II. Preferential removal of bromide ion from the co-ordination sphere.** H. I. SCHLESINGER and D. N. RICKLES (J. Amer. Chem. Soc., 1929, 51, 3523—3527).—By thermal decomposition at 175° of the appropriate pentammines (cf. preceding abstract) the following "triammines" were prepared: (I)  $[\text{Br}_3(\text{NH}_3)_3\text{Cr}]_x$ , (II)  $[\text{ClBr}_2(\text{NH}_3)_3\text{Cr}]_x$ , (III)  $[\text{Cl}_2\text{Br}(\text{NH}_3)_3\text{Cr}]_x$ . The properties of these compounds resemble those of the chromium trichlorotriammine previously described. Compounds of this type containing iodo-, nitrate-, or nitrito-groups could not be prepared by thermal decomposition or by removing water from aquotriammines. By boiling chromium chloro-oxalatotriammine with hydrobromic acid, *chromium dichlorotetrammine bromide* (probably a *cis*-compound) was obtained, which is converted by heat into *chromium dichlorobromotriammine* and a purple substance, which reacts with ammonium oxalate to give the original oxalato-triammine and yields the *chloride*, *iodide*, etc. by double decomposition. Treatment of chromium bromo-oxalatotriammine with hydrobromic acid

yields (?cis) *dibromotetramminechromic bromide*,  $[\text{Br}_2(\text{NH}_3)_4\text{Cr}]\text{Br}$ , a green compound which yields a red aqueous solution from which, after a few days, alcohol and ether or hydrobromic acid precipitates red *diaquotetramminechromic bromide*. When (I) is heated with hydrobromic acid a mixture of a *tetrammine*,  $[\text{Br}_2(\text{NH}_3)_4\text{Cr}]\text{Br}$ , and a *pentammine* is obtained, the latter being insoluble in ice-water. This *tetrammine*, probably a *trans*-compound, gives a red aqueous solution from which, however, the original substance and not the aquo-compound is precipitated by alcohol and ether; it does not yield a chromium bromo-oxalatotriammine, neither can it be formed from this compound. The structure of the triammines is discussed briefly. If III is heated with ammonium oxalate the salt  $[\text{ClC}_2\text{O}_4(\text{NH}_3)_3\text{Cr}]_2$  is obtained; treatment of II in a similar manner yields mixtures. Dry ammonia reacts with these triammines at  $200^\circ$  to produce mixtures of pentammines; if the partial pressure of the ammonia is reduced to 182 mm. only II reacts to give appreciable quantities of pentammine.

S. K. TWEEDY.

**Salts of the complex hexacarbamidochromic cation.** E. WILKE-DÖRFURT and K. NIEDERER (Z. anorg. Chem., 1929, 184, 145—166; cf. A., 1927, 120).—An examination of salts of this cation reveals a close resemblance to the hexa-aquo- and hexammino-compounds of the metal. The salts are usually bluish-green, dichroic, and contain water of crystallisation. The cation is green. Heating, or the addition of strong acids or alkalis, destroys the complex. Physical constants have been determined for hexacarbamidochromic salts already described in the literature. The following compounds are described: *chlorate*, explodes on heating; *thiosulphate* ( $+3\text{H}_2\text{O}$ ); *dichromate*,  $d$  1.781; *fluosilicate* ( $+6\text{H}_2\text{O}$  and  $3\text{H}_2\text{O}$ ); *manganicyanide* ( $+4\text{H}_2\text{O}$ ); *cobalticyanide* ( $+4\text{H}_2\text{O}$ ); *nitroprusside* ( $+3.5\text{H}_2\text{O}$ ); *cobaltinitrite* ( $+0.5\text{H}_2\text{O}$ ); *naphthalene-2-sulphonate* ( $+2.5\text{H}_2\text{O}$ ); *toluenesulphonate* ( $+2.7\text{H}_2\text{O}$ ); *o-dichlorobenzenesulphonate* ( $+2.7\text{H}_2\text{O}$ ); *disflavinate-flavianate* ( $+4\text{H}_2\text{O}$ ). The following, in which the cation forms salts with mixed anions, are also described: *sulphate-perchlorate* ( $+ \text{H}_2\text{O}$ ), explodes on heating; *sulphate-fluoborate* ( $+ \text{H}_2\text{O}$ ); *sulphate-permanganate* ( $+3\text{H}_2\text{O}$ ); *sulphate-fluosulphonate* ( $+3\text{H}_2\text{O}$ ); *sulphate-iodide* ( $+2\text{H}_2\text{O}$ ); *sulphate-bromide* ( $+2\text{H}_2\text{O}$ ); *sulphate-nitrite* ( $+2\text{H}_2\text{O}$ ), unstable in solution; *sulphate-nitrate* ( $+4\text{H}_2\text{O}$ ); *sulphate-chlorate* ( $+3\text{H}_2\text{O}$ ); *sulphate-benzenesulphonate*; *dichromate-bromide* ( $+ \text{H}_2\text{O}$ ); *dichromate-nitrate* ( $+ \text{H}_2\text{O}$ ); *dichromate-perchlorate*,  $d$  1.802; *dichromate-permanganate*; *dichromate-tetrafluoborate*,  $d$  1.764; *dichromate-disulphate* ( $+5\text{H}_2\text{O}$ ); *platinocyanide-chloride* ( $+3\text{H}_2\text{O}$ ); *nickelocyanide-chloride* ( $+2\text{H}_2\text{O}$ ). The solubilities of a number of the compounds are recorded.

F. L. USHER.

**Tervalent manganese.** VII. J. MEYER and R. KANTERS (Z. anorg. Chem., 1929, 185, 177—183; cf. A., 1927, 33).—A new method of preparing hydrated manganese dioxide consists in passing sulphur dioxide into a solution of potassium permanganate at  $75^\circ$  and washing the resulting precipitate with dilute sulphuric acid and with water. After drying at  $100$ — $105^\circ$  the composition corresponds with

the formula  $\text{MnO}_2 \cdot \text{H}_2\text{O}$ . When heated at  $200$ — $225^\circ$  some oxygen is lost, but the water content is not reduced below 3.74%. Manganic oxide prepared by precipitation is more reactive than that made by heating the dioxide at  $700^\circ$ . From the behaviour of manganic oxide and of trimanganese tetroxide towards dilute and concentrated acids it is inferred that tervalent manganese is present in each; the latter is therefore to be regarded as  $\text{MnO} \cdot \text{Mn}_2\text{O}_3$ , not as  $2\text{MnO} \cdot \text{MnO}_2$ . A method for the determination of the three oxides in mixtures is given.

F. L. USHER.

**Solubility of manganese dioxide under the influence of metallic mercury.** J. MEYER and R. KANTERS (Z. anorg. Chem., 1929, 185, 172—176).—When manganese dioxide and metallic mercury are placed in dilute solutions of sulphuric or nitric acid both substances are attacked, manganous and basic mercurous sulphate being formed in the first case and manganous and mercurous nitrate in the second. If a 25% solution of ammonium, calcium, or magnesium chloride is used in place of the acid, the mercury is dissolved, although to a much smaller extent, in the form of mercuric chloride. The results are considered to bear on the deterioration on keeping of electric dry cells.

F. L. USHER.

**High-temperature products of iron with hydrogen sulphide, carbon disulphide, and hydrogen selenide.** J. B. PEEL and P. L. ROBINSON (Proc. Univ. Durham Phil. Soc., 1929, 8, 153—154).—Pure iron reacts slowly with hydrogen sulphide at  $350$ — $900^\circ$ , but is converted rapidly at  $1000^\circ$  into a silver-white, crystalline non-magnetic substance of the composition  $\text{FeS}$ ,  $d$  4.630. The material falls to a powder when touched, is reduced by hydrogen at  $800^\circ$ , and does not precipitate copper or bismuth from solutions of their salts. In these respects it differs considerably from the usual form of ferrous sulphide. When iron is heated in carbon disulphide at  $1000^\circ$  a greyish-white, crystalline, magnetic substance having the empirical composition  $\text{Fe}_2\text{S}_6$  is obtained.

[With C. L. MAVIN.]—A fused mass solidifying to a silver-white, crystalline, magnetic product,  $d$  6.211, is obtained by heating iron in hydrogen selenide at  $750^\circ$ . Analysis shows 3% more selenium than corresponds with the formula  $\text{FeSe}$ . The substance does not react with hydrochloric acid unless metallic iron or a similar metal is present.

A. R. POWELL.

**Influence of temperature on precipitation of nickel carbonate.** M. SERGEEV (Masloboino Zhir. Delo, 1928, No. 11, 15).—Precipitation is best effected at the b. p. with excess of sodium carbonate.

CHEMICAL ABSTRACTS.

**Oxidation reactions of complex platinum compounds.** II. **Oxidation by persulphate and free oxygen.** L. A. TSCHUGAEV and I. I. TSCHERNAEV (Ann. Inst. Platine, 1929, 7, 124—137).—See A., 1929, 1157.

**Nitro-derivatives of platinum.** V. I. I. TSCHERNAEV (Ann. Inst. Platine, 1929, 7, 52—72).—Reduction of nitrites or hydroxylamines of bivalent platinum by means of zinc in acid solution leads to the production of amines, i.e., Zinin's reaction is applicable to such compounds. Platinum is com-

combined with the nitrogen of the nitro- or hydroxylamino-groups, and this arrangement is not affected by the number of groups in the inner sphere or by their stereochemical arrangement. The products of reduction of *cis*-platinonitrites are, however, different from those obtained by the reduction of the *trans*-isomerides. In mixed hydroxylamino-nitroplatinum compounds the hydroxylamino-groups are reduced before the nitro-groups. The positions of amino-groups are identical with those of the hydroxylamino-groups present before reduction. R. TRUSZKOWSKI.

**Nitro-derivatives of platinum. VI. I. I.** TSCHERNAIEV and A. N. FEDOROVA (Ann. Inst. Platine, 1929, 7, 73—82).—Two stereoisomeric forms of ethylenediaminodinitrodichloroplatinum have been prepared;  $\text{en}(\text{NO}_2)_2\text{Cl}_2\text{Pt}$  by addition of chlorine to  $\text{en}(\text{NO}_2)_2\text{Pt}$ , and  $\text{enNO}_2\text{ClNO}_2\text{ClPt}$  by the action of sodium nitrite on the corresponding trichloride. Ammonia replaces only one chlorine atom of each isomeride, to yield respectively  $\text{en}(\text{NO}_2)_2\text{NH}_3\text{ClPtCl}$  and  $\text{enNO}_2\text{ClNO}_2\text{NH}_3\text{PtCl}$ . The preparation of the isomeric *trans*-dinitrotriammine by the action of sodium nitrate on  $\text{enClNH}_3(\text{NO}_2)_2\text{Pt}$  did not succeed, the sole product being an amidodiammine, corresponding with the original mononitrotriammine. R. TRUSZKOWSKI.

**Nitro-derivatives of platinum. VII. I. I.** TSCHERNAIEV and F. M. KLATSCHKIN (Ann. Inst. Platine, 1929, 7, 84—97).—A third stereoisomeride of platinum ethylenediaminodinitrochloroammine (see above),  $\text{enNO}_2\text{NH}_3\text{NO}_2\text{ClPtCl}$ , is prepared by the action of sodium nitrate on  $\text{enNO}_2\text{NH}_3\text{Cl}_2\text{PtCl}$ . This triammine is converted by alkalis into  $\text{enNO}_2\text{NH}_2\text{NO}_2\text{ClPt}$ , which is also produced by addition of excess of ammonia; as the ammonia evaporates, however, the compound is converted into the *cis*-dinitrotetrammine. This tetrammine, like the pyridino-derivative,  $\text{enNO}_2(\text{C}_5\text{H}_5\text{N})\text{NO}_2\text{NH}_3\text{Pt}$ , is a weak base, readily forming chlorohydroxy-salts, whilst the corresponding methylamino-compound gives a normal chloride. Ammonia in the *trans*-position to a nitro-group is very readily replaced by negative groups, and the lability of one of a pair of *trans*-nitro-groups would be even greater; the failure to prepare the *trans*-dinitrotriammine (above) is ascribed to this circumstance. R. TRUSZKOWSKI.

**Derivatives of tetramminoplatinum chloride.** N. S. KURNAKOV and I. A. ANDREJEVSKI (Ann. Inst. Platine, 1929, 7, 161—169).—The yellow double salt  $\text{PtCl}_2 \cdot 2\text{NH}_3 \cdot 4(\text{PtCl}_2 \cdot 4\text{NH}_3)$  is isomorphous with tetramminoplatinous chloride hydrate,  $\text{PtCl}_2 \cdot 4\text{NH}_3 \cdot n\text{H}_2\text{O}$ , and the coloured product obtained by the repeated crystallisation of the latter salt is a solid solution of the two salts. R. TRUSZKOWSKI.

**Methods of quantitative analysis for nearly pure gases. I—III.** M. TRAUTZ and others.—See B., 1930, 56.

**Limit of separation of dissolved substances by fractional precipitation.** O. RUFF (Oesterr. Chem.-Ztg., 1929, 32, 199—200).—The influence of inter-reaction, mixed crystal formation, adsorption, and complex and double salt formation on the possibility of separation of various metals by fractional

precipitation, e.g., as sulphides, is discussed in relation to the mass action law. Experiments on a number of individual separations are described.

H. F. GILLBE.

**Azo-dyes of phenolphthalein as indicators in acidimetry and alkalimetry.** I. H. EICHLER (Z. anal. Chem., 1929, 79, 81—90).—Attempts have been made to obtain an improved indicator by the introduction of the azo-group into the phenolphthalein molecule. Phenolphthalein has been coupled with various diazo-compounds, and the resulting substances have been employed as indicators in acidimetric titrations. The most satisfactory of these is the compound  $\text{C}_{20}\text{H}_{12}\text{O}_4(\text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H})_2$ , prepared from phenolphthalein and diazotised sulphanilic acid. This compound is deep yellowish-brown in alkaline and light yellow or almost colourless in acid solutions; it is suitable for the titration of both strong and weak acids and bases.

H. F. HARWOOD.

**$\alpha$ -Naphthaflavone as indicator in iodometry.** J. F. REITH (Pharm. Weekblad, 1929, 66, 1097—1110).—In macro-analysis, the corrections to be made when  $\alpha$ -naphthaflavone is used as indicator are given for various iodide contents of the end solution; the colour change when iodides are present is from blue to violet, and very sharp, whilst when iodides are absent it is from blue to colourless and less sharp. A small correction is necessary in the latter case also. The indicator is suitable for the colorimetric determination of small quantities of iodine, and will detect 5 mg. when iodides are present; the reaction may be employed for determination of free chlorine in water. The influence of acidity is discussed. S. I. LEVY.

**Analysis of photographic products and raw materials. I. Determination of iodide in mixtures of halides. II. Determination of halide impurities in potassium iodide. III. Conversion of silver halides into alkali halides. IV. Rapid complete analysis of iodobromide emulsions. V. Stop-watch method for rapid determination of traces of copper in silver nitrate.** H. BAINES.—See B., 1929, 1050.

**Determination of fluorine as calcium fluoride.** E. CARRIÈRE and ROUANET (Compt. rend., 1929, 189, 1281—1282).—A solution of the fluoride (0.3—0.4 g.) in 25 c.c. of water is boiled with 5 c.c. of ammonia solution and 10 c.c. of 0.5*M*-calcium chloride solution, the precipitate filtered, washed with boiling 6% ammonia solution until the filtrate gives no chloride reaction, dried, and weighed. If the quantity of calcium chloride solution added is known, the total filtrate and washings may be collected, and the excess of calcium precipitated as oxalate and titrated with potassium permanganate solution. The recorded error with sodium or potassium fluoride is 0.1% for both methods. J. GRANT.

**Determination of fluorine by conversion into silicon fluoride.** J. CASARES (Anal. Fis. Quím. [tecn.], 1929, 27, 290—301).—Earlier methods are criticised on account of the time required for the operation and the necessity of using very pure silica. If the fluoride be heated with ordinary glass powder and sulphuric acid at 160°, silicon fluoride is quanti-



tatively evolved within a few minutes, the error being 0.1—0.5%.

H. F. GILLBE.

**Determination of fluorine in phosphorite.** S. N. ROSANOV.—See B., 1930, 55.

**Colorimetric micro-method for the determination of sulphur in sulphides, sulphates, etc.** I. S. LORANT (*Z. physiol. Chem.*, 1929, 185, 245—266).—A method for micro-determination of sulphur depends on the blue colour produced by the action of hydrogen sulphide on dimethyl-*p*-phenylenediamine sulphate (Caro's reaction). A measured amount of the solution is placed in a glass-stoppered 50-c.c. cylinder containing 20 c.c. of a zinc acetate solution (50 g. of zinc acetate, 10 g. of sodium acetate, and 0.05 g. of sodium chloride per litre). Water is added to the 35 c.c. mark followed by 7.5 c.c. of the reagent solution (1 g. of dimethyl-*p*-phenylenediamine sulphate in 100 c.c. of water treated with 400 c.c. of sulphuric acid and made up to 2 litres) and 2 c.c. of a solution of 25 g. of ferric ammonium sulphate and 5 c.c. of sulphuric acid made up to 200 c.c. with water. The whole is shaken and compared with the standard after 1 hr.

For the determination of sulphates the sulphate is reduced with hydriodic acid in presence of formic acid and red phosphorus in a modified Zeisel apparatus. The hydrogen sulphide is swept out by nitrogen or air and is washed by means of sodium dihydrogen phosphate and pyrogallol solution and absorbed in the zinc acetate solution, where it is determined as before. The method determines 5  $\gamma$  with an error of less than 5%.

J. H. BIRKINSHAW.

**Test for thiosulphates.** E. E. JELLEY and W. CLARK.—See B., 1930, 55.

**Preparation and determination of hyposulphites.** A. MCGLYNN and O. W. BROWN.—See B., 1930, 55.

**Colour reaction between naphthol-yellow and hyposulphites.** E. E. JELLEY (*Analyst*, 1930, 55, 34—35; cf. B., 1927, 922).—Two drops of concentrated ammonia solution are added to a few c.c. of the very dilute dye (diluted to the same depth of shade as a 0.02% solution of naphthol-yellow which is used as a check), a very small amount of solid hyposulphite is added, and the colour noted. Alternatively, to detect hyposulphite a few mg. of the solid substance or 1 c.c. of solution are added to a few c.c. of *N*-ammonia containing 0.02% of naphthol-yellow. A rose colour is formed in the presence of hyposulphite. With this test Manchester-yellow and naphthol-yellow give a rose; 2 : 4 : 5- and 2 : 4 : 7-trinitro- $\alpha$ -naphthol a pale salmon-pink; Victoria-yellow an orange; picric acid a brown; dinitrosoresorcinol a purple; and aurantia a pale brown colour;  $\alpha$ -nitroso- $\beta$ -naphthol and  $\beta$ -nitroso- $\alpha$ -naphthol show fading; and quinoline-yellow S, tartrazine, chrysophenine, auramine, acid-yellow, chrysoidine, and fluorescein show no change. Sodium formaldehydesulphoxylate, sodium sulphide, sulphurous acid and its salts, thiosulphate, polythionates, salts of hydroxylamine or hydrazine, stannous, titanous, or ferrous salts, or sodium amalgam show no rose colour.

D. G. HEWER.

**Detection of nitrites in water.** S. VERGNOUX.—See B., 1930, 38.

**Determination of arsenic in sulphuric acid.** H. A. J. PIETERS and M. J. MANNENS.—See B., 1929, 1043.

**Separation and determination of arsenic [in metals].** B. S. EVANS.—See B., 1929, 1046.

**Determination of silica in presence of fluor-spar.** W. T. SCHRENK and W. H. ODE.—See B., 1930, 55.

**Volumetric determination of carbon in difficultly combustible iron and steel alloys.** E. ZINDEL.—See B., 1930, 14.

**Use of cerium dioxide as contact substance in micro-elementary analysis.** P. HAAS and F. RAPPAPORT (*Mikrochem.*, 1929, 7, 327—333).—Micro-determinations of carbon and hydrogen may be carried out using as a catalyst layers of cerium dioxide-pumice and plugs of cerium dioxide-asbestos (prepared by soaking the materials in a concentrated solution of ceric nitrate and igniting) in the combustion tube, together with the customary lead dioxide and silver wire. This arrangement possesses the advantage that the attack on the tube is much less than when copper oxide and lead chromate are used, and the progress of the combustion can be followed and controlled by the change in appearance of the cerium dioxide-pumice layer next to the boat containing the substance. The statement of Bekk (cf. A., 1913, ii, 981) that it is necessary to re-ignite the cerium dioxide-asbestos strongly after the combustion of substances containing sulphur could not be substantiated; 40 successive analyses of such substances were satisfactorily carried out. When used for the combustion of sulphur-free compounds, 200 or more analyses can be carried out with the same tube, the time required for each being 30—40 min. The results of a number of analyses are given and compared with those obtained by the usual Pregl method.

H. F. HARWOOD.

**Determination of carbon monoxide [in gases].** P. SCHLÄPFER and E. HOFMANN.—See B., 1930, 5.

**Detection of small traces of carbon monoxide in ethylene.** B. S. WALKER and O. E. ALLEY.—See B., 1930, 36.

**Apparatus for determination of carbon dioxide in water supersaturated with the gas.** ANON.—See B., 1929, 1043.

**Test-paper for detection of small amounts of carbonyl chloride.** A. SUCHIER (*Z. anal. Chem.*, 1929, 79, 183—185).—Test-papers prepared by treating filter-paper with a mixture of solutions of 1 g. of dimethyl-*p*-aminobenzaldehyde in 5 c.c. of alcohol and of 1 g. of diphenylamine in 5 c.c. of alcohol and drying in a current of carbon dioxide are turned from pale yellow to brown by air containing as little as 0.004 g. of carbonyl chloride per m.<sup>3</sup> The papers are also affected by chlorine and hydrogen chloride, but are not so sensitive to the latter as is moist litmus paper.

R. CUTHILL.

**Microchemical detection of sodium with zinc uranyl acetate.** V. P. MALITZKY and V. A. TUBA-

KATIEV (Mikrochem., 1929, 7, 334—336).—The use of zinc uranyl acetate as a microchemical reagent for sodium is recommended. A drop of the reagent added to a drop of the neutral test solution gives characteristic microscopic crystals of sodium zinc uranyl acetate,  $\text{NaOAc} \cdot \text{Zn}(\text{OAc})_2 \cdot 3\text{UO}_2(\text{OAc})_2 \cdot 6\text{H}_2\text{O}$ . The reaction is very sensitive, and 0.01  $\gamma$  of sodium can be detected, even in the presence of potassium, ammonium, the alkaline earths, and many other metals. Phosphates if present give an amorphous precipitate, which, however, does not interfere with the detection of the crystals. The solution of the reagent should either be freshly made or preserved in a silica container. H. F. HARWOOD.

**Stability of 0.1N-sodium chloride, and other matters pertaining to volumetric analysis.** VASTERLING (Pharm. Ztg., 1930, 75, 58—59).—A 0.1N-sodium chloride solution which had been kept in a stoppered bottle unopened for 10 years was found to have lost only 0.6% in concentration. Camphoric acid is recommended as a standardising medium for alkalis, and the conclusion is reached that sodium chloride, potassium dichromate, silver nitrate, potassium hydrogen carbonate, and potassium bromate are all suitable for use as standards in pharmaceutical volumetric determinations. H. F. HARWOOD.

**Titrimetric determination of calcium in phosphorites.** F. KAMINSKI.—See B., 1930, 55.

**Determination of strontium and barium in presence of one another. Separation of barium as chromate.** L. SZEPELLÉDY (Magyar chem. Fol., 1929, 35, 77—80; Chem. Zentr., 1929, ii, 770—771).—Potassium chromate solution (10%, 10 c.c.) is added dropwise to a boiling solution containing the salt (0.3 g.), ammonium chloride (5 g.), and acetic acid (15 g.) in presence of small pieces of nickel; the liquid is filtered after 24 hrs., and the precipitate is washed with cold water (50 c.c.) and dried for 2 hrs. at 132°. The filtrate and washings are evaporated to 100 c.c. with 10 c.c. of N-ammonia solution, and the strontium is determined as oxalate by Winkler's method.

A. A. ELDRIDGE.

**Iodometric determination of zinc.** R. LANG (Z. anal. Chem., 1929, 79, 161—170).—Zinc may be determined by adding potassium iodide to the solution, which should be neutral or only slightly acid with sulphuric acid, and should contain not more than 0.45 g. of zinc per 100 c.c., then adding 0.2M-potassium ferri-cyanide solution about 2 c.c. at a time until in excess, the iodine liberated by the reaction  $3\text{Zn}^{++} + 2\text{K}' + 2\text{Fe}(\text{CN})_6''' + 2\text{I}' = \text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2 + \text{I}_2$  being titrated with thiosulphate after each addition. In order so to accelerate this reaction that the reaction  $2\text{Fe}(\text{CN})_6''' + 2\text{I}' = 2\text{Fe}(\text{CN})_6''' + \text{I}_2$  does not occur to any appreciable extent, 5—10 g. of potassium sulphate per 100 c.c. of solution must be added before titration. It is found empirically that under these conditions 1 litre of 0.1N-thiosulphate solution is uniformly equivalent to 9.97 g. of zinc. The titration may be carried out in presence of ferric salts by adding sufficient potassium hydrogen fluoride to prevent iron being precipitated. In mixed solutions of copper and zinc salts, the copper is determined iodometrically first. Manganese, cobalt, nickel, cadmium, tartrates,

ammonium sulphate and nitrate, and large amounts of alkali chlorides, phosphates, normal fluorides, acetates, and oxalates interfere with the determination. R. CUTHILL.

**Determination of cadmium.** V. EYVARD (Natuurwetensch. Tijds., 1929, 11, 191—193).—The compound of allyl iodide with hexamethylenetetramine, obtained by boiling equimolecular proportions of the reagents in chloroform solution, is a colourless, crystalline substance, readily soluble in water, behaving as the iodide of a strong base; with cadmium salts it gives a characteristic crystalline precipitate of the double iodide of cadmium and the base,  $\text{CdI}_2 \cdot 2[(\text{CH}_2)_6\text{N}_4\text{C}_3\text{H}_5]\text{I}$ , containing only 11.44% Cd. The precipitate is very stable, and may be dried at 100°; it is slightly soluble in water, but insoluble in presence of excess of precipitant, and in alcohol. By microchemical reaction, less than 0.1 mg. of cadmium may be detected. The reaction may be used for determination of cadmium, the precipitate being merely washed with 96% alcohol, dried, and weighed. Zinc, even in large excess, does not interfere.

S. I. LEVY.

**Two "spot reactions" for lead.** F. PAVELKA (Mikrochem., 1929, 7, 301—304).—0.001 Mg. of lead can be detected by placing a drop of the nearly neutral solution to be tested on filter-paper which has been previously soaked in a 0.5% ammoniacal solution of carminic acid, then exposing to ammonia fumes, and again drying. If lead be present a violet spot is produced. An excess of copper prevents the reaction, but by suitable modification of the test lead may be detected in the presence of silver, bismuth, or cadmium. An alternative test is to place a drop of the test solution on filter-paper, and add a drop of dilute pyridine solution, followed by a 0.1% solution of gallo-cyanine. The spot is washed with successive drops of 1% pyridine, when a violet stain is formed in presence of lead. The lead may also be first precipitated on the paper as sulphate, and the above test then applied, this method permitting the detection of lead in the presence of silver, copper, cadmium, and bismuth. H. F. HARWOOD.

**Microchemical reactions of copper, nickel, and cobalt with dithio-oxamide.** P. RÁV (Z. anal. Chem., 1929, 79, 94—101).—The compounds of copper, nickel, and cobalt with dithio-oxamide are very insoluble, and can be utilised in microchemical tests for these metals. From 0.002 to 0.01  $\mu\text{g}$ . of the three metals can thus be detected, the sensitivity of the reaction varying slightly with the particular microchemical method employed. Complex compounds of the above metals (e.g., nickel dimethylglyoxime) are also converted into the dithio-oxamides when warmed with a solution of the reagent. Dithio-oxamide in presence of acetic acid may be used to detect small amounts of copper in presence of a large excess of cadmium, but the method cannot be employed for the detection of traces of cadmium in presence of excess of copper, as the copper precipitate carries down the cadmium under these conditions.

H. F. HARWOOD.

**Iodometric determination of copper.** E. H. SMITH (Chemist-Analyst, 1929, 18, No. 4, 6—7).—

The end-point is sharpened by using sufficient potassium iodide to dissolve the cuprous iodide.

#### CHEMICAL ABSTRACTS.

**Electro-analysis of copper without platinum electrodes.** J. GUZMÁN and A. RANCAÑO (Anal. Fis. Quím. [tecn.], 1929, 27, 269—289).—A copper cathode and stainless steel anode may be employed for the quantitative deposition of copper from solutions containing nitrate, sulphate, phosphate, formate, acetate, tartrate, or citrate; the error does not exceed 2% except when citrate or tartrate is present, when the error may reach 4.5%. In each case the loss of weight of the anode does not exceed 1—2 mg., and this is ascribed to the action of the potassium ferrocyanide employed to indicate the completion of the electrolysis. H. F. GILLBE.

**Potentiometric titration of ceric sulphate.** K. SOMEYA (Z. anorg. Chem., 1929, 184, 428; cf. A., 1929, 1032).—Furman's observations (*ibid.*, 669) have been confirmed. H. F. GILLBE.

**Determination of alumina in aluminoborosilicates.** O. V. KRASNOVSKI (Z. anal. Chem., 1929, 79, 175—183).—Alumina can be determined by Blum's method (A., 1916, ii, 493) in aluminoborosilicates containing up to 30% of boric oxide without previous removal of the boron being necessary. Silicates containing more than 10% of alumina require double precipitation. R. CUTHILL.

**Spectroscopic analysis of Spanish manganese ores.** S. PIÑA DE RUBIES and J. DORRONSORO (Anal. Fis. Quím., 1929, 27, 778—786).—The arc spectra of a number of Spanish manganiferous minerals have been studied: apart from obvious impurities, elements found to enter into the constitution of the minerals are cobalt, nickel, lead, phosphorus, titanium, and vanadium, of which the last two have not been previously observed.

H. F. GILLBE.

**Determination of manganese and iron by successive titration with permanganate.** I. S. TELETOV and N. N. ANDRONNIKOVA.—See B., 1930, 15.

**Chancel's method for the separation of iron and aluminium.** P. L. L. ROBINSON and W. E. SCOTT (Proc. Univ. Durham Phil. Soc., 1929, 8, 155—159).—The quantity of aluminium precipitated by boiling a neutral solution of the sulphate with a large excess of sodium thiosulphate depends on the rate of evaporation of the liquid during boiling and on the time of boiling. Even after vigorous boiling for 10 hrs. about 2% of the total alumina fails to be precipitated. The presence of ferrous sulphate in the solution does not affect the results and only minute traces of iron are occluded in the precipitate, which, however, invariably contains sodium sulphate and is hygroscopic after ignition. A minimum amount of about 8 g. of sodium thiosulphate is necessary for the precipitation of 0.2 g. of aluminium.

A. R. POWELL.

**Application of ammonium oxalate to the qualitative analysis of the first three groups in presence of phosphoric acid.** M. O. CHARMAN-DARJAN (Z. anal. Chem., 1929, 79, 90—94).—A new

scheme of separation of the metals of the iron, zinc, barium, and alkali groups in presence of phosphates has been devised. The alkaline earths are first removed by treating the solution successively with ammonium sulphate and ammonium oxalate, the remaining metals together with the phosphoric acid passing into solution. After removal of the excess of oxalate from the filtrate, the alkalis are separated by treatment with barium hydroxide, phosphoric acid and the other metals being precipitated. The precipitate is dissolved in dilute sulphuric acid and treated with sodium hydroxide and hydrogen peroxide, whereby magnesium, iron, manganese, nickel, and cobalt are precipitated and aluminium, zinc, phosphate, and chromate remain in solution; suitable tests for the above metals are described.

H. F. HARWOOD.

**Titration of cobalt in presence of nickel and iron.** V. CUVELIER (Natuurwetensch. Tijds., 1929, 11, 163—169).—The method of Willard and Hall (A., 1922, ii, 874) is modified by titrating the excess of stannous chloride directly with potassium dichromate, employing diphenylamine as internal indicator, instead of using excess of the dichromate and titrating with a ferrous salt. The titration with dichromate gives accurate results only in a solution acidified with Knop's phosphoric acid mixture, and at about 35°.

S. I. LEVY.

**Determination of small amounts of nickel in steel.** B. JONES.—See B., 1930, 61.

**Colour reactions of molybdenum.** S. L. MALOWAN (Z. anal. Chem., 1929, 79, 201—204).—Potassium benzylxanthate gives a reddish-violet colour with ammonium molybdate. The test is not so delicate, however, as that with potassium ethylxanthate (A., 1920, ii, 59), and the colour is transient. Ethyl ethylxanthate and acetylated potassium ethylxanthate give no colour unless free alkali is present; benzyl ethylxanthate does not react even then.

R. CUTHILL.

**Determination of tungsten by means of phenylhydrazine hydrochloride in hydrochloric acid solution.** G. DOTREPPE (Bull. Soc. chim. Belg., 1929, 38, 385—386).—A solution containing about 0.004 g. of tungstic oxide is added to one of 1 g. of phenylhydrazine hydrochloride in 50 c.c. of 8N-hydrochloric acid. After heating on a water-bath for 1 hr. the precipitate is washed by decantation, filtered, and ignited to tungstic oxide.

C. W. GIBBY.

**Determination of tungsten by stannous chloride.** G. DOTREPPE (Bull. Soc. chim. Belg., 1929, 38, 375—384).—Details are given of a method for the determination of tungsten in tungstates, tungsten steels, and ferrotungsten. The solution is reduced by stannous chloride, and the tungsten weighed as tungstic oxide.

C. W. GIBBY.

**Use of phenolic acids in the detection, separation, and determination of metals. II. Colorimetric detection and determination of uranium. III. Gravimetric determination of uranium.** R. N. DAS-GUPTA (J. Indian Chem. Soc., 1929, 6, 763—776, 777—779).—II. Methods for the colorimetric detection and determination of small quantities of uranium in solution, by tannic gallic, and resoreylic

acids in presence of sodium acetate, have been worked out and compared with the sodium salicylate method (Müller, A., 1920, ii, 60). The sensitiveness of the reagents is found to be in the order tannic acid > gallic acid > sodium salicylate > resorcylic acid. With tannic acid there is a tendency for the coagulation of a colloidal product of reaction, so that, on the whole, the gallic acid method appears to be the most satisfactory. The limit of sensitivity with gallic acid is 0.023 g. per litre. Addition of ammonium chloride increases the sensitivity, but the same amount must be added in each case.

III. From a neutral or faintly acid solution, or from a solution containing suspended  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ , uranium can be quantitatively precipitated by the addition of tannic acid followed by a solution of sodium acetate and ammonium chloride or nitrate, or of a slightly ammoniacal ammonium acetate solution sufficient to neutralise any mineral acidity which may be liberated and to coagulate the precipitate. The precipitate is ignited in air to form  $\text{U}_3\text{O}_8$ . The precipitate thus obtained from uranyl nitrate solution is free from nitrate and acetate and is very stable in alkaline solution, but readily soluble in dilute mineral acids and excess of dilute acetic acid, giving colourless solutions. Accurate results are obtained. Even with small amounts of uranium the results are fairly good.

M. S. BURR.

**Wood's metal as cathode material in electroanalysis.** H. PAWECK (Z. anal. Chem., 1929, 79, 113—114).—Polemical. (Cf. A., 1929, 161.)

H. F. HARWOOD.

**Electroanalytical method with a cathode of Wood's [fusible] metal.** H. PAWECK and W. STRICKS (Z. anal. Chem., 1929, 79, 115—134).—The above method of electroanalysis (A., 1928, 143) has now been extended to include the determination of tin, silver, iron, nickel, cobalt, and thallium, full details for the individual depositions being given. Attempts to determine antimony by this method have proved unsuccessful. Experiments made to ascertain if the potential altered during electrolysis showed that in the case of nickel, cobalt, iron, and tin there was no change up to the point when 10% of its weight of metal had been taken up by the cathode. When this stage is reached the cathodic alloy is solid, even at  $80^\circ$ , so that no further measurements are possible. In the case of mercury the potential remained constant until 15.26% of mercury had been taken up by the cathode, when a steady decrease in the value set in until 39.25% of mercury was present; subsequent increases in the mercury content caused no further alteration in the potential. The final alloy containing 47.97% of mercury was liquid at the ordinary temperature. Photomicrographs of etched surfaces of the cathodic alloy after having taken up other metals accompany the paper.

H. F. HARWOOD.

**Determination and separation of zirconium and beryllium.** O. RUFF and E. STEPHAN (Z. anorg. Chem., 1929, 185, 217—220).—The application of a correction factor in determining zirconium as pyrophosphate is unnecessary, and theoretical values are obtained, if the platinum derived from the crucible

in which the hydrogen sulphate fusion is carried out is removed by means of hydrogen sulphide prior to precipitation. In the determination of beryllium as pyrophosphate the factor 0.255 should be used instead of the theoretical factor  $\text{Be}_2\text{P}_2\text{O}_7/2\text{BeO}=0.260$ . Good values are obtained in the separation of the metals by the pyrophosphate method if the above precautions are observed.

F. L. USHER.

**Volumetric determination of vanadium, iron, and uranium with titanium salts.** V. G. CHLOPIN and L. E. KAUFMAN.—See B., 1929, 1046.

**Rapid micro- and macro-determination of bismuth.** G. SPACU and G. SUCIU (Z. anal. Chem., 1929, 79, 196—201).—Bismuth can be quantitatively precipitated as the compound  $(\text{BiI}_4)_2(\text{Co en}_3)\text{I}$  (reddish-yellow) from a solution containing 2 c.c. or less of hydrochloric acid of  $d$  1.19 per 100 c.c. by adding an excess of potassium iodide and then, at the b. p., a very slight excess of a hot concentrated solution of ethylenediaminecobaltic chloride,  $(\text{Co en}_3)\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ , containing sufficient potassium iodide to form the corresponding iodide. The mixture is boiled for a few minutes, then filtered, the precipitate being washed with a solution of 0.1 g. of potassium iodide and 0.1 g. of ethylenediaminecobaltic chloride in 100 c.c. of water, then with 96% alcohol and ether, and dried and weighed. Nitric acid, if present, must be removed at the outset by evaporating the solution with hydrochloric acid. The method is also suitable for use in micro-analysis.

R. CUTHILL.

**Analysis of sodium bismuthate by the gas-volumetric method.** T. SOMIYA and K. KAWAI (J. Soc. Chem. Ind. Japan, 1929, 32, 249B).—Sodium bismuthate in the presence of cobalt nitrate is decomposed by sulphuric acid as follows:  $2\text{NaBiO}_3 + 4\text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{Bi}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O} + \text{O}_2$ . This reaction appears to be quantitative and can be used successfully for analytical purposes employing 1 g. of the sample, 30 c.c. of 1:9 sulphuric acid, and 0.2 c.c. of saturated cobalt nitrate solution. The gas evolved contains carbon dioxide derived from carbonates in the material and this must be absorbed.

C. IRWIN.

**Determination of minute quantities of bismuth.** A. PORTNOV and V. SKVORZOV (Farm. Zhur., 1928, 534—539).—The organic substances are destroyed by ignition, the product is dissolved in hydrochloric acid, and the excess of acid removed on the water-bath. The chloride is converted into the compound  $\text{K}_2\text{BiI}_5 \cdot 4\text{H}_2\text{O}$  (free iodine being removed with chloroform, although little is formed in presence of glycerol) and the bismuth is determined colorimetrically. The sensitiveness is 0.0025 mg. per c.c.

CHEMICAL ABSTRACTS.

**Analytical chemistry of tantalum, niobium, and their mineral associates.** XVI. Tartaric hydrolysis. XVII. Quantitative precipitation of the earth acids and certain other oxides from tartrate solution. W. R. SCHOELLER and H. W. WEBB (Analyst, 1929, 54, 704—715).—XVI. A study of the quantitative course of the tartaric hydrolysis of the earth acids in the presence of some of their mineral associates shows that (a) earth-acid recovery is not quite quantitative; (b) the behaviour of the

tartaric solutions of tungsten, tantalum, and niobium towards nitric acid is similar, and with hydrochloric acid precipitation is incomplete at higher, and may not take place at lower, concentrations; (c) an approximate separation from titania is achieved; (d) zirconia creates a marked disturbance in the quantitative course of the reaction; (e) thoria (rare earths) interferes very slightly, reflecting the progressive change of chemical behaviour of the elements of the group IV; (f) the common metals and beryllium interfere still less. (a) may be overcome as follows.

**XVII. Quantitative recovery of the earth acids** may be ensured by the use of either tannin or cupferron subsequently to the tartaric hydrolysis. The hydrolysis filtrate is heated with 1 g. of tannin and titrated with 1:1 ammonia solution and the precipitate is purified exactly as the earth acid precipitates. Alumina is also precipitated and the method affords a means of separating it from iron. Precipitation with cupferron is also satisfactory with a slight tendency to a negative error, and aluminium is not precipitated. Zirconia and titania are quantitatively precipitated from tartrate solutions after neutralisation as well as with acids, but accurate neutralisation after addition of the tannin is required.

D. G. HEWER.

**Drop method of qualitative analysis for gold, palladium, and platinum present together and in the presence of other elements encountered in ordinary qualitative analysis.** N. A. TANANAEV and K. A. DOLGOV (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 1377—1384).—A drop of solution is placed on filter-paper and a drop of a solution of benzidine in acetic acid is added. A blue or green coloration is given if the drop contains not less than 0.00035 mg. of gold. Palladium can be detected by wetting filter-paper with a drop of saturated thallium nitrate solution, adding gold chloride solution, and then the solution under examination, when the spot darkens if 0.00035 mg. of palladium is present. Platinum is detected by placing a drop of thallium nitrate solution on the paper, then a drop of the unknown solution, and then another drop of thallium nitrate, excess of which is removed by applying a drop of ammonia to the centre of the spot, which is then treated with stannous chloride; an orange or a yellow coloration appears in the presence of not less than 0.001 mg. of platinum. Should this reaction be masked by the presence of larger quantities of gold or palladium, these metals may be removed by precipitation with hypophosphorous acid. Should the above three metals be present simultaneously, the following procedure may be adopted: a drop of mercuric cyanide solution is placed on filter-paper, then the solution, and then another drop of mercuric cyanide solution, excess of which is washed off by water. A capillary tube containing stannous chloride is now drawn across the spot, when a rose-yellow coloration at the centre indicates palladium and a yellow coloration at the peripheries indicates platinum (0.003 mg.). A capillary tube containing benzidine dissolved in acetic acid is now drawn across the spot at right angles to the first, when a blue coloration at the peripheries indicates gold (0.0005—0.001 mg.).

R. TRUSZKOWSKI.

**Extraction apparatus with [fritted] glass filter-plates.** W. SCHÖBEL (*Pharm. Ztg.*, 1930, 75, 56—58).—Filter-plates of fritted glass can be advantageously introduced into many forms of apparatus employed for the preparation of extracts and a number of types of these are described. The above may work either on the Soxhlet principle or by direct percolation, the latter having the advantage that a much smaller quantity of solvent is necessary. The results of comparative tests with a number of types showed that with small quantities (30 g.) of material direct percolation (a glass filter-plate being used to support the substance) gave an extraction after 10 hrs. equal to that obtained from the ordinary Soxhlet apparatus, whilst with larger quantities (up to 1000 g.) an 80% extraction was reached in the same time. Two forms of perforator containing glass filter-plates and designed for the continuous extraction of a solution by a liquid of lower density are also described.

H. F. HARWOOD.

**Immersion filter for phosphorus, calcium, and crude fibre determinations.** R. H. SIMON (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 442—443).—Glass filter-plates with a porosity of 4—5  $\mu$  are recommended as immersion filters (cf. Nette, B., 1925, 340) for dealing with fine precipitates of phosphorus and calcium, whilst those with larger pores are suitable for the separation of crude fibre. The filter must be of zero capacity and the vacuum should be regulated to avoid destroying the continuity of the film in the disc. Dissolution of the precipitate may be effected by pumping solvent, and, if required, washing water through the stem of the filter. The accuracy of the plates with phosphorus precipitates is not so great as when Shimer tubes are used (cf. B., 1929, 625), but there is considerable economy of time. The device is particularly valuable for the filtration of plant-residues from cellulose-dissolving liquids, where the use of filter-paper or asbestos is impracticable.

H. J. DOWDEN.

**Measurements of temperature at working electrodes.** B. BRUŽS (*Z. physikal. Chem.*, 1929, 145, 283—288).—Apparatus is described by means of which temperature changes at the surfaces of working electrodes can be measured. When a current is passed between nickel electrodes in a solution of a nickel salt the anode is at a higher temperature than the cathode, and the difference is directly proportional to the current density up to a certain value of the latter, at which there is a sudden increase in the temperature difference, attributed to the evolution of oxygen at the anode. If two nickel electrodes through which a small current has been passed for a few minutes are short-circuited through a milliammeter a chemically induced current, in the same direction as the impressed current, is observed when the polarisation has been dissipated. This induced current is ascribed to disintegration of the lattice giving rise to enhanced activity of the loosened lattice atoms.

F. L. USHER.

**Exact determination of vapour tensions.** A. SMITS and E. SWART (*J.C.S.*, 1929, 2724—2726).—The filling of an apparatus with a pure volatile substance, by cooling the latter and evacuating the

apparatus, while melting and solidifying the substance several times, does not ensure that no appreciable amount of gas is left. A procedure which enables volatile substances to be completely freed from gases is described.

J. A. V. BUTLER.

**Radioactive recoil in the study of diffusion.** G. VON HEVESY and W. SEITH (Ber. Naturforsch. Ges. Freiburg, 1928, 28, 6 pp.; Chem. Zentr., 1929, ii, 527).—A sensitive radioactivity method for the study of diffusion in the solid state is described.

A. A. ELDRIDGE.

**Laboratory generator for making hypochlorite.** R. E. GOODE (Chemist Analyst, 1929, 18, 18).

CHEMICAL ABSTRACTS.

**Continuous circulator for a corrosion test or continuous filter.** J. M. W. BROWN (Chemist Analyst, 1929, 18, 16—17).

CHEMICAL ABSTRACTS.

**Corrosion testing apparatus.** D. F. OTHMER.—See B., 1930, 61.

**Apparatus for determination of moisture content of solids and the sorption of gases and vapours by solids at elevated temperatures.** W. E. KUENTZEL (J. Amer. Chem. Soc., 1929, 51, 3560—3561).—The apparatus, for a description and diagram of which the original must be consulted, is such that the determination may be interrupted periodically and the rate of sorption etc. can therefore be measured.

S. K. TWEEDY.

**Hydrogen microelectrode.** R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1929, 17, 91—94).—The platinum electrode is contained in a small vessel the lower part of which is drawn out to a capillary (to which the needle of a hypodermic syringe may be attached), and with a side tube for sucking the liquid up the capillary. The liquid is saturated with hydrogen before the determination, and a bubble of hydrogen is in contact with the electrode. The circuit is completed through the capillary, which dips into potassium chloride solution.

R. K. CALLOW.

**Accurate Cochiu viscosimeter.** H. J. SCHULZ (Chem. Fabrik., 1929, 497).—It is now possible to obtain glass tubes of which the internal diameter is constant within 0.01 mm. throughout the length; with these tubes, remarkable accuracy is obtained in the measurement of viscosities by the Cochiu method.

S. I. LEVY.

**Simple volumenometer.** R. WASMUTH.—See B., 1930, 86.

**Correction of thermo-elements for temperature variations of the cold junction.** U. RETZOW (Z. tech. Physik, 1929, 10, 164—168; Chem. Zentr., 1929, ii, 604).—Theoretical.

A. A. ELDRIDGE.

**Modification of the registering mercury manometer.** A. TEITEL-BERNARD (Pflüger's Archiv, 1929, 222, 242—244; Chem. Zentr., 1929, ii, 604—605).

**Hygroscopic properties of glass.** N. A. SHISKAKOV (J. Appl. Phys. Moscow, 1927, 4, 37—46).—The velocity of adsorption of water is smaller for a glass surface covered with an alkaline film than for a clean glass surface. Glass vessels for high vacua should be blown with a compressor, immediately evacuated

and sealed, and should not be long exposed to atmospheric air. Adhering gas is rapidly removed by boiling with dilute acid. Glass dust treated for a short time at 250—300° with acid vapours and steam readily adsorbs water at the ordinary temperature.

CHEMICAL ABSTRACTS.

**Claisen fractionating apparatus with replaceable sections.** F. FRIEDRICH (Chem.-Ztg., 1929, 53, 910).—A connecting section for joining the distillation flask to the fractionating column comprises a wide tube bent so that the upper and lower portions are parallel and the intermediate section is inclined at an angle of about 30° to the vertical. An opening in the bend is provided for the introduction of the steam tube, which is replaceable, being held in position by a rubber connexion. The bend prevents spray entering the fractionating column and, owing to its small volume as compared with the usual bulb, the distillation is rendered more efficient.

A. R. POWELL.

**Photographic method of measuring refractive indices.** T. M. LOWRY and C. B. ALLSOPP (Proc. Roy. Soc., 1929, A, 126, 165—169).—An apparatus is described by means of which measurements of refraction can be carried into regions of selective absorption right up to the point where the light is stopped completely even by a thin film of liquid; within this wide region the refractive index of a liquid can be recorded for scores of different wave-lengths in the course of a few seconds. The method consists essentially in the focussing of the interference fringes from a thin film of liquid on the slit of a spectrograph, the refractive index of the liquid being deduced from comparative measurements of the number of fringes contained in a given width of the slit, as shown on successive lines of the image of the slit in the spectrograph. The film of liquid, which can be made either parallel-faced or wedge-shaped, is contained in a quartz etalon cell of very small capacity. The sources of error in the method are discussed, together with suggestions for their elimination, and the possibilities of the method are illustrated by the reproduction of an uncorrected curve for nicotine.

L. L. BIRCHMUNSHAW.

**Micro-sublimation under reduced pressure.** M. WAGENAAR (Pharm. Weekblad, 1929, 66, 1121—1124).—An apparatus in which heating is effected by a micro-burner, the material being contained in a platinum tray suspended from the thermometer bulb, is described. The sublimate is received on a plate attached to a thick brass rod, the other end of which may be cooled. With effective cooling and prolonged time, sublimation may be effected at very low temperatures.

S. I. LEVY.

**Apparatus for tracing the change in moisture content of small quantities of powder.** L. H. LAMPITT and J. H. BUSHILL (J. Sci. Instr., 1929, 6, 369—373).—The change in moisture content of a powder may be followed by observing the deflexion of a torsion micro-balance on the pan of which is a layer of the powder one particle thick.

C. W. GIBBY.

**Automatic pipette.** A. HENDERSON and J. ROBERTS (Analyst, 1929, 54, 737—739).—An automatic pipette for filling by means of air pressure, and for fitting to the stopper of large storage bottles, is



illustrated by six diagrams showing all the effects of turning the single key which controls all the movements. Pressure is produced by a small hand bellows or a small mechanical blower. D. G. HEVER.

**Luminescence microscope.** G. KÖGEL (Mikrochem., 1929, 7, 305—313).—The construction and use of the luminescence microscope and its auxiliary apparatus are described. The name "dispersion fluorescence" is proposed for the type of fluorescence in which the emitted secondary rays lie close to the primary ones, irrespective of the portion of the spectrum in which the latter occur. This phenomenon is of importance in connexion with the chemical constitution of substances; thus a series of compounds containing the CH group all exhibit a line in the region  $\nu=20,000$ , which is not present in the corresponding spectrum of such a substance as carbon tetrachloride, where the CH group is absent. H. F. HARWOOD.

**Technique of fluorescence analysis.** M. HAITINGER and V. REICH (Chem. Fabr., 1929, 529).—By the use of a small glass flask filled with distilled water as concentrator for filtered ultra-violet light an ordinary microscope can be used for the study of fluorescence. Magnifications of up to 400 in reflected light and 6000 in transmitted light can be used and the ultra-violet light itself does not reach the eye of the observer. A system of two flasks allows even greater magnifications to be used. Care must be taken that the glass used is not itself fluorescent.

C. IRWIN.

**Epidiastroscope for lecture experiments.** A. STOCK and H. RAMSER (Z. angew. Chem., 1929, 42, 1165—1169).—A new epidiastroscope, and a number of lecture demonstrations of chemical processes which may be carried out with it, are described.

J. A. V. BUTLER.

## Geochemistry.

**Isotope of oxygen, mass 17, in the earth's atmosphere.** W. F. GIAUQUE and H. L. JOHNSTON (J. Amer. Chem. Soc., 1929, 51, 3528—3534).—The existence of the above isotope was demonstrated from a study of atmospheric absorption spectra. The abundance of oxygen isotopes in the atmosphere is estimated. S. K. TWEEDY.

**Sub-soil water of the Zagreb district.** G. JANEČEK (Arh. Hemiju, 1929, 3, 178—179).—The sub-soil water of Zagreb has during the past 50 years been found to be of constant chemical composition, in disagreement with Iveković's theory (*ibid.*, 113).

R. TRUSZKOWSKI.

**Constancy of chemical composition of Zagreb sub-soil water.** H. IVEKOVIĆ (Arh. Hemiju, 1929, 3, 179—182).—A reply to Janeček's criticism (cf. preceding abstract).

R. TRUSZKOWSKI.

**Mineral waters of Sardinia.** I. E. PUXEDDU and G. SANNA (Giorn. Chim. Ind. Appl., 1929, 11, 438—442).—Physical constants are given for the waters of eight thermal springs in Sardinia. All the waters are alkaline and some contain dissolved carbon dioxide, although in most the only gases in solution are oxygen and nitrogen; the proportion of the latter is the same in each of the eight waters. In one instance almost pure nitrogen, with possibly a rare gas, is liberated from the water. T. H. POPE.

**Hydrogen-ion concentration of sea-water off the coast of S. California.** E. G. MOBERG (Proc. III Pan-Pacific Sci. Cong., 1926 (1928), I, 221—228).

CHEMICAL ABSTRACTS.

**Phosphate, silica, and fixed nitrogen content of sea-water.** E. G. MOBERG (Proc. III Pan-Pacific Sci. Cong., 1926 (1928), I, 229—232).—Colorimetric methods are described.

CHEMICAL ABSTRACTS.

**Analysis of mineral springs in the Upper Chechnya (Caucasus).** A. P. POPOV and V. A. KARNITZKI (J. Appl. Chem. Russia, 1928, 1, 291—299).

CHEMICAL ABSTRACTS.

**Quality of the surface waters of N. Carolina.** E. E. RANDOLPH (J. Elisha Mitchell Sci. Soc., 1928, 44, 70—74).

CHEMICAL ABSTRACTS.

**Iodine in N. Carolina water supplies.** J. W. PERRY (J. Elisha Mitchell Sci. Soc., 1928, 44, 87—89).

CHEMICAL ABSTRACTS.

**Geochemistry of iodine.** S. S. MIHOIĆ (XIth Ann. Rep. Jugoslav. Med. Soc., 1929, Preprint, 49 pp.).—The different layers of the earth contain the following amounts of iodine in parts per million: atmosphere 0.0004, hydrosphere 0.04, biosphere 20, lithosphere 0.3, chalcosphere, 0.2, siderosphere 0.15. Iodine minerals being scarce, and the possibility of an inorganic concentration of iodine small, all economically important sources of iodine are due to biochemical processes by which iodine was concentrated in the past. The connexion between the distribution of iodine in the soil and the incidence of goitre is discussed.

C. W. GIBBY.

**Capsular silica.** F. A. BURT (Amer. Min., 1929, 14, 222—226).—The material from Brazos County, Texas, is described.

CHEMICAL ABSTRACTS.

**Weathering of Jugoslavian granites.** L. MARIĆ (Arh. Hemiju, 1929, 3, 183—187).—The contents of the following constituents respectively in intact and weathered andalusite granite from Jelenski Dol are as follows:  $\text{Fe}_2\text{O}_3$  1.17, 1.38;  $\text{FeO}$  0.63, 0.22;  $\text{Na}_2\text{O}$  3.33, 2.87;  $\text{K}_2\text{O}$  3.76, 4.58;  $\text{H}_2\text{O}$  0.73, 1.35.

R. TRUSZKOWSKI.

**Mineralogy of the precious stones.** A. SCHOEP (Natuurwetensch. Tijds., 1929, 11, 180—190).—A résumé of a lecture delivered at Ghent, September 1929.

S. I. LEVY.

**Radioactive platinum concentrates.** W. F. SEYER (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 75—76).—The presence or absence of platinum and radioactive properties in a number of specimens of black sand from various localities is tabulated, and their composition is given. Boiling water removed

26% of the activity, treatment with hydrochloric acid 2%, and treatment with aqua regia 93%.

N. M. BLIGH.

**Coloured clays of the Olonetz region, U.S.S.R.** I. LILEEV (Trans. State Inst. Appl. Chem., Moscow, 1927, No. 8, 74—98).—A chemical, mineralogical, and geological description is given. The high silica content detracts from their covering capacity as pigments, their value depending on the ferric oxide content.

#### CHEMICAL ABSTRACTS.

**Analyses of some pure [cobalt] compounds, technical products, and cobalt minerals.** V. CUVELIER (Natuurwetensch. Tijds., 1929, 11, 170—179).—Results are given of analyses of pure laboratory preparations, of commercial cobalt, and compounds marketed by the Union Minière, of various steels, and of some minerals from the Belgian Congo. Among the latter is a new variety from Mindingi (Katanga), which is crystalline and has  $d$  4.317. Analyses gave the composition  $(\text{Fe}, \text{Co}, \text{Al})_2\text{O}_3 \cdot \text{H}_2\text{O}$ , with cobalt predominating (Co 68.4—68.9%); small proportions of copper and silica are regarded as adventitious. The new mineral has been named stainierite. The discovery of a specimen of heterogenite containing no copper affords grounds for the belief that the latter and the new mineral are respectively colloidal and crystalline forms of the same individual. S. I. LEVY.

**Glaucinite in the pliocene sands of Brittany.** Y. MILON (Compt. rend., 1929, 189, 1004—1005).—The glaucinite occurs in grains 2—4  $\mu$  in size covered with a pellicule of iron oxide which may be removed by acid. The sands owe their red colour to the altered condition of the glaucinite. J. GRANT.

**Origin of zinc deposits at Franklin and Sterling Hill, New Jersey.** W. A. TARR (Amer. Min., 1929, 14, 207—221).

**Distribution of rare elements in the Japanese islands.** S. KÔZU and W. WATANABE (Proc. III Pan-Pacific Sci. Cong., 1926 (1928), I, 839—852).—Rare earths, rare acid earths, lithium, beryllium, tungsten, molybdenum, thorium, and uranium are found chiefly in the outer zone of N.E. and the inner zone of S.W. Japan. Radioactive minerals are found in the inner zone of N.E. Japan. Platinum, iridium, and osmium are most abundant in Hokkaido. The maximum helium content of natural gas is 0.2%.

#### CHEMICAL ABSTRACTS.

**Characteristics of "terra rossa" from the vicinity of Rome.** B. FILOSOFOV (Glinka Mem. Vol. Leningrad Agric. Inst., 1928, 191—207).—Native rock and weathered material contained, respectively:  $\text{H}_2\text{O}$  (hygroscopic) 1.17, 8.7;  $\text{SiO}_2$  47.53, 43.2;  $\text{Al}_2\text{O}_3$  14.85, 19.46;  $\text{FeO}$  5.32, 7.21;  $\text{MnO}$  0.27, 0.13;  $\text{MgO}$  8.18, 9.08;  $\text{CaO}$  12.66, 11.74;  $\text{K}_2\text{O}$  5.59, 0.51;  $\text{Na}_2\text{O}$  2.15, 1.41;  $\text{CO}_2$  0, 0.01;  $\text{H}_2\text{O}$  1.28, 4.42; organic material 0, 0.55%. Weathering in the Mediterranean region is similar to that of laterisation in the tropics. The intensity of the red colour is determined by the presence of calcium, but its presence is not a necessary attribute of the formation of "terra rossa."

#### CHEMICAL ABSTRACTS.

**Structure of lublinitite.** S. MIZGIER (Z. Krist., 1929, 70, 160—162; Chem. Zentr., 1929, ii, 544).—Lublinitite is identical with calcite. A. A. ELDRIDGE.

**Petrochemical characters of the Santorin caldera.** C. KTÉNAS (Compt. rend., 1929, 189, 996—998).—The lavas are acid or basic hornblende dacitoides and are usually oligoclasic but sometimes andesinic. Mineralogically and chemically they belong to the calco-alkaline series, being distinguished by the high sodium content (3.06—3.81%  $\text{Na}_2\text{O}$ , 59.2—65.6%  $\text{SiO}_2$ ) characteristic of South Ægean volcanic formations. J. GRANT.

**Limits of the mixed Ægean region. Attempts at geological synthesis.** C. KTÉNAS (Compt. rend., 1929, 189, 1196—1198; cf. preceding abstract).—An attempt is made to trace the limits of the mixed alkali region and to determine their general geological relations. The chemical compositions of five lavas are given. The free silica varies between 5.76 and 17.64%, and the virtual plagioclase is always basic and andesinic (39—46% of anorthite). Of the alkali metals, sodium and potassium are present in predominating and often equal amounts, and it is concluded that the mixed alkali region is enclosed by a semicircle of calco-alkali lavas, the actual chemical compositions of the magmas having been modified by metamorphic agents. J. GRANT.

**Variation of optical properties with chemical composition in the rhodonite-bustamite series.** M. H. HEY (Min. Mag., 1929, 22, 193—205).—A pale pink mineral from Franklin Furnace, New Jersey, remarkable for the bright brick-red fluorescence it displays in ultra-violet rays, is found by analysis I ( $d$  3.302) to be bustamite. Intimately associated with it are hardystonite and willemite, which fluoresce with violet and brilliant green colours, respectively. This property was made use of in selecting pure material for analysis. Analysis II ( $d$  3.418) is of a cleavage mass of brownish-red rhodonite from Långban, Sweden, and III ( $d$  3.615) of small bright red crystals of rhodonite from Harstig mine, Pajsberg, Sweden.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{ZnO}$	$\text{MgO}$	$\text{CaO}$	Ign.	Total.
I.	47.68	0.23	0.06	27.65	0.26	0.03	24.86	0.06	100.85
II.	47.69	0.43	0.05	32.93	0.07	0.02	15.24	0.29	98.63*
III.	46.33	0.26	0.83	44.28	0.07	0.04	8.02	0.22	100.05

\* Including  $\text{FeO}$  1.92; also alkalis, not determined.

These minerals are all anorthic, but with cleavages rather different. The optical orientation and constants are determined in detail.

	$\alpha$	$\beta$	$\gamma$	2V.	Opt. sign.
I.	1.664	1.675	1.679	50—55°	negative
II.	1.695	1.703	1.710	84°	negative
III.	1.720	1.725	1.733	75°	positive

These and previously determined values are plotted against the chemical composition, and it is seen that in this isomorphous series of calcium manganese metasilicates the density and refractive indices show a regular increase with the molecular percentage of manganese oxide. At 30 mol.-% of  $\text{CaO}$  there is a change over in the optical sign, and this gives a convenient division between rhodonite and the calcium-bearing bustamite variety. This division falls at  $d$  3.47 and refractive index ( $\beta$ ) 1.709.

L. J. SPENCER.

**Bismutotantalite, a new mineral, from Uganda.** E. J. WAYLAND and L. J. SPENCER (Min. Mag., 1929,

22, 185—192).—The mineral was found in a pegmatite vein at Gamba Hill in Busiro County. The large rough crystals, up to several pounds in weight, somewhat resemble columbite. They are pitch-black with sub-metallic lustre, black streak, and  $H\ 5-5\frac{1}{2}$ . Very thin splinters are transparent and smoke-grey to colourless;  $n > 2.2$ , birefringence  $0.1-0.15$ . The mineral is not attacked by acids, including hydrofluoric. Analyses I and II, by W. O. R. WYNN, and III give the formula  $\text{Bi}_2\text{O}_3 \cdot (\text{Ta}, \text{Nb})_2\text{O}_5$ . Frequently the crystals are altered to a pinkish-yellow material which gave analyses IV—VI by M. H. HEY. This is finely granular and consists of a mixture of optically isotropic and strongly birefringent materials. It is decomposed by hydrofluoric acid, the bismuth going into solution, and the tantalum acid remaining insoluble.

	$\text{Ta}_2\text{O}_5$	$\text{Nb}_2\text{O}_5$	$\text{Bi}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{SiO}_2$	$\text{H}_2\text{O}$	Total	d.
I.	40.12	6.63	52.26	0.11	0.12	—	0.33	99.61*	8.44
II.	41.15	6.46	49.86	0.30	0.12	—	1.05	98.94	8.03
III.	31.14	14.75	50.46	1.36		2.16	—	99.88	—
IV.	64.31	—	32.93	0.42	—	1.19	2.01	100.86	—
V.	52.13	—	42.82	0.64	—	0.62	2.10	98.31	—
VI.	62.88	—	24.05	0.71		2.00	8.65	98.29	6.29

\* Including  $\text{SnO}_2 + \text{Sb}_2\text{O}_3\ 0.01$ .

The crystals are orthorhombic with  $a:b:c = 0.7813:1:1.1363$ . They often show good parting planes parallel to (011), and less prominent (100). When (011) is given the indices (043) the mineral shows a relation to tantalite, but the pyramid planes then have high indices.

$a:b:c$ .

Bismutotantalite, $\text{Bi}_2\text{O}_3 \cdot \text{Ta}_2\text{O}_5$ .....	0.7813:1:0.8522
Stibiotantalite, $\text{Sb}_2\text{O}_3 \cdot \text{Ta}_2\text{O}_5$ .....	0.7995:1:0.8448
Tantalite, $\text{FeO} \cdot \text{Ta}_2\text{O}_5$ .....	0.8285:1:0.8898

L. J. SPENCER.

**Fülöppite**, a new Hungarian mineral of the *plagionite-šemseyite* group. I. DE FINÁLY and S. KOCH (Min. Mag., 1929, 22, 179—184).—The mineral was found at Nagybánya, Hungary [now Baia Mare, Romania], as small lead-grey monoclinic crystals of the *plagionite* habit; hardness rather greater than 2,  $d_{100}^{20} 5.23$ . Analysis I shows the mineral to be an acid member of the *plagionite* group with the formula  $2\text{PbS}_2\text{Sb}_2\text{S}_3$ .

	S.	Sb.	Pb.	Fe.	$\text{SiO}_2$	Total
I. ...	24.10	47.50	28.29	—	0.19	100.08
II. ...	23.10	46.17	29.33	0.08	0.94	99.62

The figures of the analysis are, however, equally near to a formula  $3\text{PbS}_2\text{Sb}_2\text{S}_3$ , and the mineral then fits into the following morphotropic series, which with increasing lead shows an increase in the  $c$ -axis, whilst the  $a$ -axis remains practically unchanged.

$a:b:c$ .

$\beta$ .

Fülöppite, $3\text{PbS}_2\text{Sb}_2\text{S}_3$ .....	1.1087:1:0.7011	$85^\circ 15' 5''$
Plagionite, $5\text{PbS}_2\text{Sb}_2\text{S}_3$ .....	1.1305:1:0.8422	$72^\circ 45'$
Heteromorphite, $7\text{PbS}_2\text{Sb}_2\text{S}_3$ .....	—	—
Semseyite, $9\text{PbS}_2\text{Sb}_2\text{S}_3$ .....	1.1356:1:1.0218	$74^\circ 14'$

Intimately associated with the *fülöppite* is another lead-antimony mineral, which forms radiating groups of fine needles of a steel-grey to black colour.  $H\ 2$ ,  $d_{100}^{20} 5.22$ . Analysis II gives the formula  $3\text{PbS}_2\text{Sb}_2\text{S}_3$ , and this mineral is referred to *keeleite*. Other minerals present on the specimens are zinc-blende, quartz, dolomite, and a few minute crystals of sulphur.

L. J. SPENCER.

**Boehmite from bauxites.** R. HOCART and J. DE LAPPARENT (Compt. rend., 1929, 189, 995—996).—The boehmite ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) occurring as symmetric orthorhombic micro-crystals in certain bauxites (A., 1927, 748) has been shown by X-ray analysis to be identical with Boehm's bauxite (A., 1926, 113). Boehmite is homologous with *lepidocrocite* ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and *diaspore* with *goethite*. J. GRANT.

**Partly fused quartz-felspar-rock; glomero-granular texture.** L. HAWKES (Min. Mag., 1929, 22, 163—173).—A unique specimen of a granitic rock from Iceland shows areas of quartz and of felspar sharply separated by a narrow band of microcrystalline material. The suggestion is made that by the later lava flows the temperature of the rock was raised above the eutectic point but below the m. p. of the constituent minerals. Under these conditions a granite of the quartz-orthoclase-albite eutectic composition should melt completely in the dry state below  $970^\circ$ . Experiments on heating quartz and felspar in close contact at about  $1000^\circ$  were, however, without result. The areas of quartz and of felspar in the Icelandic rock each consist of a number of individuals; such an aggregation of grains of the same mineral in coarse-grained granites from other localities is described. A rock texture of this type is named "*glomero-granular*." L. J. SPENCER.

**Mineral hitherto unrecognized in the phonolites of Dunedin, New Zealand.** P. MARSHALL (Min. Mag., 1929, 22, 174—178).—A mineral present in these rocks as small irregular grains and as minute (0.15 mm.) hexagonal crystals has previously been taken to be *nepheline*. It, however, shows a lower refractive index and a lower birefringence than *nepheline*, and it also gives different staining reactions. The mineral is readily decomposed by dilute acids, and even when boiled in water some chlorine goes into solution. Analyses of the portion (12.5% in I, 25.65% in II, and 21.35% in III) of the powdered rock soluble in warm dilute hydrochloric acid gave:

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	Cl.	Total
I.	36.67	34.70	1.80	24.18	0.86	2.15	100.66*
II.	36.40	34.70	2.49	24.90	0.96	3.15	102.60
III.	35.96	34.11	2.12	23.03	0.53	1.58	97.33

\* Including  $\text{SO}_3\ 0.30$ .

These results approximate to a formula  $12\text{SiO}_2 \cdot 6\text{Al}_2\text{O}_3 \cdot 9\text{Na}_2\text{O} \cdot 0.5\text{NaCl}$ , and show that this mineral, to which the name *ameletite* is given, is distinct from the related minerals *nepheline*, *davyne*, *microsommit*, and *sodalite*. *Ameletite* quickly stains a deep violet when a thin section of the rock is treated with a dilute solution of silver nitrate, and it often shows natural staining with iron compounds. The mineral has been also found in the phonolites of the Pacific Islands and it is perhaps of wide distribution.

L. J. SPENCER.

**Tungsten-bearing minerals of Galicia.** I. WOLFRAMITES from La Brea, Corpiño, and Carboeiro. I. P. PONDAL and J. VÁZQUEZ-GARRIGA (Anal. Fis. Quím., 1930, 28, 79—82).—See A., 1929, 1418.

**Rocks of the Katmai region (Alaska).** W. F. GISOLF (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 930—939; cf. *ibid.*, 1927, 31, 660).—Modified

Nigglian parameters have been calculated from the molecular quotients for the rocks of the Katmai region. The poles in the aluminium-alkali field, and also those in the silica field, lie in almost straight lines. The rocks of this region may be considered as heteromorphic rocks of diorites composed of plagioclase, amphibole, and free quartz. The suggested composition of the amphibole is  $AT_5M_{14}SiO_2$  ( $A=Na_2O+K_2O$ ,  $T=Al_2O_3$ ,  $M=CaO+MgO+FeO+2Fe_2O_3$ ). The problems of the differentiation of the Katmai region rocks and of those of the Katmai volcano from the same original magma are discussed. It is suggested that the different nature of the two sets of rocks may be traced to the effect of pressure differences on crystallisation of a huge quantity of magma at uniform temperature. F. G. TRYHORN.

[Origin of] coal and petroleum. G. STADNIKOV (Brennstoff-Chem., 1929, 10, 477—480).—Although a distinction can be drawn between "humus coals," e.g., the brown coals and bituminous coals, which have been formed from plant residues rich in lignin, and the cannel and boghead coals, which are polymerisation products of the fatty acids of algae and similar micro-organisms (cf. B., 1929, 1002; this vol., 57), true humus or boghead coals seldom occur naturally. Most coal seams are heterogeneous in respect of both

composition and origin. The boghead coals are characterised by high hydrogen and volatile matter contents, and by the very low proportion of phenols in the tar produced on carbonisation. The durain of bituminous coals appears to be related to the boghead coals. Detailed examination of the Sumpfowey seam shows this to comprise a series of coals intermediate in character between humus and boghead coals. Coorongite contains less oxygen than the boghead coals, from which it differs also in containing some unsaponifiable constituents resembling crude petroleum. The fats of the original algae from which coorongite has been formed must therefore have been partly reduced, probably by the action of anaerobic bacteria while the material lay at the bottom of salt water containing hydrogen sulphide; the partly reduced material must then have been brought to the surface by some movement of the water, its further transformation having subsequently taken place in the presence of air. This theory also accounts for the formation of petroleum, which, it is assumed, is produced by the continued anaerobic decomposition of the same original material. A. B. MANNING.

Ions and electrical currents in the upper atmosphere. E. O. HULBURT (Science, 1929, 70, 216).

## Organic Chemistry.

Gradual combustion of hydrocarbons. S. LANDA (Paliva a topeni, 1929, 11, 1—4).—On oxidation, paraffin yielded propaldehyde, formaldehyde, acetaldehyde, hexaldehyde, and octaldehyde, methyl and ethyl alcohols, acetone, and methyl ethyl ketone. Triacotane (prepared by electrolysis of potassium palmitate and from a Japanese wax) gave formaldehyde, heptaldehyde, octaldehyde, formic, butyric, and valeric acids, but acetaldehyde, methyl or ethyl alcohol, acetic or propionic acid were not detected. The formation of aldehyde on gradual oxidation is used as a test for paraffin in petroleum oils. CHEMICAL ABSTRACTS.

Stereochemistry of derivatives of methane and ethylene. A. SEMENTZOV (J. Russ. Phys. Chem. Soc., 1928, 61, 1125—1129).—Weissenberg's theories, that the carbon atoms in substituted methane and ethylene compounds possess the pyramidal and not the van 't Hoff tetrahedral configuration, were investigated. Attempts to resolve the mono-amide of maleic acid into optically active isomerides were, however, unsuccessful. Experiments are at present in progress to prepare dimethoxyisobutyric acid by two methods, which should give, respectively, the *cis*- and *trans*-isomerides, resolution of which into optically active constituents should tend to confirm Weissenberg's views. M. ZVEGINTZOV.

Chlorination of methane. M. C. BOSWELL and R. R. McLAUGHLIN (Canad. J. Res., 1929, 1, 240—255; cf. A., 1919, i, 565).—In the production of methyl chloride the degree of chlorination under various conditions was studied, using a catalyst of pumice impregnated with cupric chloride solution,

dried at 110° and partly reduced by heating in moist nitrogen for 9 hrs. at 450°. The optimum conditions for the exclusive production of methyl chloride are that the ratio of nitrogen : methane : chlorine is 70 : 7 : 1, the gases should be moist, and a temperature of 450° be used; the yield is then 75—80%. When the hydrogen content was 8%, the proportion of chlorine in the reaction mixture could be more than doubled, the chlorine being completely utilised in the formation of methyl chloride and hydrogen chloride. A mixture of methane and chlorine in the ratio 1 : 4, without nitrogen when passed for 6 hrs. at a rate of 2500 c.c. per hr. gave a yield of more than 90% of carbon tetrachloride, with no loss of chlorine, but doubling the rate of flow caused explosions, which could be suppressed only by diluting very largely with nitrogen. With a nitrogen : methane ratio of 7 : 1, the yield of carbon tetrachloride was somewhat more than 80.2%. With considerably modified apparatus, preliminary experiments on the chlorination of ethane gave yields of more than 75% of ethyl chloride. H. J. DOWDEN.

Chemical effects of electrical discharge in butane. IV. Fractionation of the liquid product. S. C. LIND and G. GLOCKLER (J. Amer. Chem. Soc., 1929, 51, 3655—3660).—The liquid product formed during the subjection of butane to the electric discharge (cf. A., 1929, 1264) has been obtained using an all-glass apparatus, whereby formation of solid products is at a minimum. The amount of liquid obtained corresponds with 15.37% of the weight of butane used. Fractionation of the liquid into light (b. p. 0—160°/740 mm.), middle (b. p. 78—112°/5 mm.), and heavy (b. p. 230°/10<sup>-4</sup> mm.) oils and

further fractionation of the light oil affords a fraction, b. p. 110—113°/744 mm.,  $d$  0.708,  $n$  1.4021, which probably consists of a mixture of octanes and octenes. The formation of octanes is explained thus:  $C_4H_{10} \rightarrow C_4H_{10}^+ + E^-$ ;  $C_4H_{10} + C_4H_{10}^+ \rightarrow (C_4H_{10} \cdot C_4H_{10})^+ \xrightarrow{E^-} C_8H_{18} + H_2$ . H. BURTON.

**Pyrolysis of hydrocarbons: isobutene.** C. D. HURD and L. U. SPENCE (J. Amer. Chem. Soc., 1929, **51**, 3561—3572).—Decomposition of isobutene in a pyrex glass tube is slow at 600°, but increases rapidly up to 700°. Dilution with nitrogen or hydrogen or increasing the surface of the reaction tube does not affect the percentage decomposition; the reaction is, therefore, unimolecular and homogeneous. The decomposition products obtained at 700° are propylene, methane, isobutane, hydrogen, acetylene, ethylene, and oil; the amount of oil is diminished by diluting the isobutene with nitrogen or hydrogen. The oil contains benzene, toluene, and higher hydrocarbons. *iso*Butene is more stable than *isobutane* (cf. this vol., 58). It is suggested that radicals of the type  $\dot{C}Me_2\dot{C}H_2$  are built up into aromatic hydrocarbons.

Bromination of isobutene at 0—5° gives about 25% of tribromoisobutane and 9% of higher brominated compounds in addition to the dibromide (cf. Mereshkovski, A., 1923, i, 527). H. BURTON.

**Fixation of acetylene by magnesium phenyl bromide in presence of ferric chloride.** A. JON and G. CHAMPETIER (Compt. rend., 1929, **189**, 1089—1091).—When a mixture of magnesium phenyl bromide (3 mols.) and a benzene solution of acetylene is treated slowly below 6° with ethereal ferric chloride (1 mol.) the acetylene is absorbed. The amount of acetylene absorbed varies with the experimental conditions, and the reaction product is a thick, brown magma, which when freed from solvent alters rapidly on exposure to air; the product contains all the iron. Absorption of acetylene is probably due to the formation of an unstable, intermediate organo-iron compound. When the Grignard reagent is shaken with ferric chloride in an atmosphere of nitrogen the following change occurs:  $6MgPhBr + 2FeCl_3 = 3Ph \cdot Ph + 2Fe + 6MgClBr$ ; the resultant product does not absorb acetylene. H. BURTON.

**Action of ozone on ethers and alcohols.** F. G. FISCHER (Annalen, 1929, **476**, 233—249).—Treatment of *diisoamyl* ether with dry ozonised oxygen at 0° gives hydrogen peroxide as an initial product. Subsequent treatment of the reaction mixture with water and zinc dust affords (a) *isovaleraldehyde* (small amount), (b) *isoamyl formate*, and (c) *isoamyl isovalerate* (main product). The reactions occurring are:  $(CH_3R)_2O + O_3 \rightarrow (a) 2R \cdot CHO + H_2O_2$ ; (b)  $H \cdot CO_2CH_2R$ ; (c)  $R \cdot CO_2CH_2R + H_2O_2$ . Similar treatment of dimethyl ether (cooled in acetone and solid carbon dioxide) gives dihydroxydimethyl peroxide (from formaldehyde and hydrogen peroxide), formaldehyde, and formic acid. Diethyl ether furnishes acetaldehyde and ethyl acetate: free hydrogen peroxide could not be detected. Dibutyl ether affords butaldehyde, butyl formate, and butyl butyrate. Ethyl *isoamyl* ether yields acetaldehyde, *isovaleraldehyde*, and ethyl *isovalerate*, whilst dibenzyl ether

furnishes benzoic acid, benzyl benzoate, and benzaldehyde. Treatment of methyl, ethyl, and *isoamyl* alcohols gives varying amounts of the corresponding aldehydes and acids. The various modes of formation of the above decomposition products are discussed. H. BURTON.

**Catalytic oxidation of alcohol.** L. Y. KARPOV.—See B., 1930, 7.

**Amyl alcohols from the pentanes.** E. E. AYRES.—See B., 1929, 1008.

**Decomposition of  $\beta$ -methylhexan- $\beta$ -ol.** C. D. HURD and C. W. BENNETT (J. Amer. Chem. Soc., 1929, **51**, 3675—3676).—When  $\beta$ -methylhexan- $\beta$ -ol is refluxed for several hours, dehydration to  $\beta$ -methyl- $\Delta^{\beta}$ -hexene,  $n_D^{20}$  1.4040 (dibromide, b. p. 99—100°/27 mm.,  $n_D^{20}$  1.5020), occurs. Dehydration proceeds more readily when iodine is used (cf. Edgar, Calingaert, and Marker, A., 1929, 789), but some  $\beta$ -methyl- $\Delta^{\alpha}$ -hexene is formed in addition to the above hydrocarbon. H. BURTON.

**Reactions relating to carbohydrates and polysaccharides. XXIV. Ring migration in glycerol cyclic acetals. Behaviour of *p*-nitrobenzylideneglycerol. XXV. Methylation processes and tendency toward ring shift in glycerol cyclic acetals.** H. HIBBERT, M. E. PLATT, and N. M. CARTER (J. Amer. Chem. Soc., 1929, **51**, 3641—3644, 3644—3648).—XXIV. When  $\alpha\gamma$ -*p*-nitrobenzylideneglycerol is heated with 0.01% of its weight of hydrogen chloride at 100°, rearrangement into the  $\alpha\beta$ -isomeride occurs and an equilibrium mixture of 1 part of the former and 2 parts of the latter is obtained. When the  $\alpha\gamma$ -derivative is treated with 8% of its weight of 0.1N-hydrochloric acid at 100°, an equilibrium mixture of 0.37 part of the  $\alpha\gamma$ - and 1 part of the  $\alpha\beta$ -derivatives is formed after 1 hr. Some hydrolysis occurs during the experiments.

XXV. Methylation of  $\alpha\gamma$ -benzylideneglycerol with methyl sulphate and sodium hydroxide solution under alkaline conditions at 30° affords, in addition to unchanged material and hydrolytic products, the corresponding  $\beta$ -methyl ether. Methylation does not occur when the reaction mixture is kept acid; some fission of the acetal occurs. No  $\alpha\beta$ -benzylideneglycerol  $\gamma$ -methyl ether is formed in the experiments. H. BURTON.

**Polyhydric alcohols. I. Constitution of the dibenzoylmannitol of Einhorn and Holland.** H. OHLE, H. ERLBACH, H. HEPP, and G. TOUSSAINT (Ber., 1929, **62**, [B], 2982—2990).—Mannitol, suspended in anhydrous pyridine, is converted by gradual addition of benzoyl chloride at 10° into a mixture of mannitol  $\delta\epsilon$ -dibenzoate, m. p. 183°,  $[\alpha]_D^{20} +16.20^\circ$  in pyridine,  $[\alpha]_D^{20} +22.42^\circ$  in acetone, and *d*-mannitol tribenzoate, m. p. 162°,  $[\alpha]_D^{20} -18.0^\circ$  in acetone,  $[\alpha]_D^{20} -44.0^\circ$  in pyridine; the isolation of the dibenzoate is best effected by partial alcoholysis of the crude product with boiling ethyl alcohol in presence of anhydrous copper sulphate. Further benzylation of the tribenzoate gives the hexabenzoate, m. p. 149°. The dibenzoate is converted by acetone containing sulphuric acid into much syrupy material and  $\alpha\beta$ -*isopropylidenemannitol*  $\delta\epsilon$ -dibenzoate, m. p. 96.5°,  $[\alpha]_D^{20} +41.36^\circ$  in acetone, obtained as sole product, but in

very bad yield when anhydrous copper sulphate is used as catalyst. Further benzoylation converts the compound into  $\alpha\beta$ -isopropylidenemannitol  $\gamma\delta\epsilon$ -tetra-benzoate, m. p. 123°, from which d- $\alpha\beta$ -isopropylidene-mannitol, m. p. 86°, is readily obtained (cf. Irvine and Paterson, J.C.S., 1914, 105, 898). Condensation of the dibenzoate with benzaldehyde gives d- $\alpha\beta$ -benzylidenemannitol  $\delta\epsilon$ -dibenzoate, m. p. 117°,  $[\alpha]_D^{20} +28.04^\circ$  in chloroform, hydrolysed by methyl-alcoholic ammonia to  $\alpha\beta$ -benzylidenemannitol, m. p. 136°,  $[\alpha]_D^{20} +28.83^\circ$  in water. Acetic anhydride transforms d- $\alpha\beta$ -isopropylidenemannitol dibenzoate into d- $\alpha\beta$ -isopropylidenemannitol  $\gamma\delta$ -diacetate  $\delta\epsilon$ -dibenzoate, m. p. 75°,  $[\alpha]_D^{20} +21.22^\circ$  in chloroform, whereas *p*-toluenesulphonyl chloride and pyridine afford d- $\alpha\beta$ -isopropylidenemannitol  $\delta\epsilon$ -dibenzoate  $\zeta(?)$ -*p*-toluenesulphonate, m. p. 132°,  $[\alpha]_D^{20} +40.0^\circ$  in chloroform; prolonged action of *p*-toluenesulphonyl chloride at 37° appears to afford an unstable di-*p*-toluenesulphonyl derivative. Similarly, mannitol dibenzoate affords d-mannitol  $\alpha\beta\gamma\delta$ -tetra-acetate  $\delta\epsilon$ -dibenzoate, m. p. 126°,  $[\alpha]_D^{20} +41.35^\circ$  in chloroform (also a hexabenzoate), but only d-mannitol  $\delta\epsilon$ -dibenzoate di-*p*-toluenesulphonate, m. p. 137°,  $[\alpha]_D^{20} +43.14^\circ$  in chloroform. Final proof of the position of the acyl groups is afforded by the oxidation of d-mannitol  $\delta\epsilon$ -dibenzoate or its  $\alpha\beta$ -isopropylidene derivative to dibenzoylmesotartaric acid, identified further as calcium mesotartarate. H. WREN.

**Action of sulphuric acid on mercaptans.** S. F. BIRCH and W. S. NORRIS.—See B., 1929, 1004.

**Derivatives for identification of mercaptans.** E. WERTHEIM (J. Amer. Chem. Soc., 1929, 51, 3661—3664).—Mercury salts of the following mercaptans are obtained by interaction with mercuric cyanide in alcoholic solution: propyl, m. p. 71—72° (lit. 68°); isopropyl, m. p. 62—63° (lead salt, m. p. 91—92°); butyl, m. p. 85—86° (lead salt, m. p. 80—81°); isobutyl, m. p. 94—95°; amyl, m. p. 74—75°, and heptyl, m. p. 76—77° (lead salt, m. p. 94—95°). 3:5-Dinitrobenzoyl derivatives of the following mercaptans are prepared by heating the mercaptan (1.5 mols.) with 3:5-dinitrobenzoyl chloride (1 mol.) and a few drops of pyridine until evolution of hydrogen chloride ceases: ethyl, m. p. 61—62°; propyl, m. p. 51—52°; isopropyl, m. p. 83—84°; butyl, m. p. 48—49°; isobutyl, m. p. 63—64°; amyl, m. p. 39—40°; isoamyl, m. p. 42—43°; heptyl, m. p. 52—53°; phenyl, m. p. 148—149° (benzoyl derivative, m. p. 56°), and benzyl, m. p. 119—120° (benzoyl derivative, m. p. 30°). The use of 3-nitrophthalic anhydride is recommended for the identification of mercaptans. When this is heated with a mercaptan and the product formed treated successively with sodium hydroxide solution and hydrochloric acid, crystalline esters are obtained. The following are described: ethyl, m. p. 148—149°; propyl, m. p. 136—137°; isopropyl, m. p. 144—145°; butyl, m. p. 143—144°; isobutyl, m. p. 135—136°; amyl, m. p. 131—132°; isoamyl, m. p. 144—145°; heptyl, m. p. 131—132°; phenyl, m. p. 130—131°, and benzyl, m. p. 136—137°; these m. p. are obtained with a bath previously heated to 100°, and the majority of the esters show slight decomposition at the m. p.

H. BURTON.

**Preparation, properties, and reactions of lead mercaptides.** P. BORGSTROM, L. M. ELLIS, jun., and E. E. REID (J. Amer. Chem. Soc., 1929, 51, 3649—3651).—Lead salts of the following mercaptans are prepared by treating an alcoholic solution with a 0.25*M*-solution of lead acetate in 50% alcohol: ethyl; *n*- and iso-propyl; *n*- and iso-butyl; isoamyl; benzyl; phenyl, and  $\gamma$ -hydroxypropyl. Recrystallisation of some of the lead compounds reduces their stability; the m. p. could not be obtained constant. Titration of the compounds with a benzene solution of iodine is not practicable. Black colorations are observed with the ethyl, *n*-butyl, *n*-amyl, and benzyl derivatives, and sulphur or hydrogen sulphide, in presence of benzene. H. BURTON.

**Transformation of the fatty acids during geological periods.** III. G. STADNIKOV and A. WEIZMANN.—See B., 1929, 1002.

**[Refractometric determination of formic acid in the presence of acetic acid.]** J. BULIŘ (Chem. Listy, 1929, 23, 610).—Polemical.

R. TRUSZKOWSKI.

**[Refractometric determination of formic acid in the presence of acetic acid.]** J. STASTNÝ (Chem. Listy, 1929, 23, 608—610).—Polemical, in reply to Buliř's criticism.

R. TRUSZKOWSKI.

**Microchemical detection of acetic acid.** D. KRÜGER and E. TSCHIRCH (Mikrochem., 1929, 7, 318—326).—Acetic acid can be detected in its salts by evaporating a drop of the solution on a microscope slide and adding a drop of a reagent containing 1 g. of uranium formate, 1 g. of sodium formate, and 1 c.c. of 50% formic acid in 7 c.c. of water; in the presence of acetate characteristic crystals of sodium uranyl acetate are formed, and 0.09 mg. of acetic acid can thus be detected. Free acetic acid can be detected by a slight modification of the test, but this is then less sensitive. Sulphates have no appreciable effect on the reaction, but chlorides, nitrates, and phosphates interfere. The above test also permits the detection of acetic acid in the presence of its homologues; the alternative methods for the microchemical recognition of acetic acid by the formation of its lead, silver, copper, or mercurous salt are all less satisfactory than the test described above. H. F. HARWOOD.

**Determination of acetic acid in normal and basic copper acetates.** E. I. SPITALSKI, I. S. KACEN, and L. L. KLATSCHKO (J. Russ. Phys. Chem. Soc., 1929, 61, 1497—1502).—A sample of copper acetate solution containing about 0.3 g. of acetic acid is diluted with 100 c.c. of hot water, standard alkali is added with shaking, keeping the temperature at about 70°, until the solution is alkaline to phenolphthalein, when it is brought to boiling, and filtered hot into an excess of standard acid. The residue of copper oxide is washed three times with hot water to remove adsorbed alkali, and the washings are added to the filtrate. Excess of acid is then determined.

R. TRUSZKOWSKI.

**Evaluation of acetic anhydride.** E. TERLINCK.—See B., 1929, 1007.

**Organic salts of bismuth: preparation of easily decomposed compounds.** M. PICON (J.



Pharm. Chim., 1929, viii, 10, 481—496, and Bull. Soc. chim., 1929, [iv], 45, 1056—1066).—The salts have been prepared either by the direct interaction of the acid with bismuth oxide in the presence of water at 100° or by double decomposition of solutions of the sodium salts of the acid and of bismuth nitrate in glycerol. The normal bismuth octoate and palmitate were obtained by treating the initial products prepared by the first method for a longer time in the absence of water. The following compounds are described. Almost pure basic bismuth carbonate is prepared by passing carbon dioxide through a suspension of bismuth oxide in water at 100°. *Bismuth octoate*, a viscous liquid, soluble in oxygen-free organic solvents and completely decomposed in methyl alcohol; and the basic salt,  $C_7H_{15}CO_2BiO$ ; *bismuth palmitate*, m. p. 82°; basic *palmitate*,  $C_{16}H_{31}O_2BiO$ ; *bismuth ricinoleate*, a viscous, pale yellow liquid which solidifies slowly, and is completely decomposed in methyl alcohol, yielding the basic salt,  $C_{18}H_{33}O_2BiO$ . Double decomposition yields a mixture of normal *bismuth sulphoricinate*,  $(C_{18}H_{33}O_6S)_2Bi$ , and the basic *dibismuthyl* compound,  $C_{18}H_{33}O_6S(BiO)_2$ ; *bismuth pinonate*; *bismuth cyclohexylacetate*; *bismuth camphoroxalate*.

C. C. N. VASS.

**Derivatives of fatty acids. Preparation of stearolic acid.** K. KINO (J. Soc. Chem. Ind. Japan, 1929, 32, 187—188B).—Dibromostearic acid and sodium hydroxide (4 mols.) are heated in the presence of amyl alcohol for 2 hrs. at 120—125°. After removal of the amyl alcohol, the residue is acidified and extracted with ether. The product, after distillation and recrystallisation from alcohol, has m. p. 46—46.5°. A. A. GOLDBERG.

**Alleged formation of optically active lactic acids from carbohydrates under the influence of sunlight.** K. P. JACOBSON (Biochem. Z., 1929, 215, 216—221).—The lactic acid prepared from maltose and laevulose by the action of barium or calcium hydroxide solution in presence of sunlight is optically inactive. This contradicts Duclaux's finding (Ann. Inst. Pasteur, 1893, 7, 751). His observed rotation may have been due to saccharic acid.

J. H. BIRKINSHAW.

**Reaction of pyruvic acid with glycerol.** P. BRIGL, M. SCHÜTZE, and K. HARTUNG [with G. MATSCHENZ] (Annalen, 1929, 476, 214—232).—Treatment of a mixture of glycerol and ethereal pyruvic acid with

thionyl chloride affords the lactonic ether

$$\begin{array}{c} \text{CH}_2\text{O} \\ \diagup \quad \diagdown \\ \text{CH}-\text{O} > \text{CMe} \\ \diagdown \quad \diagup \\ \text{CH}_2\text{O}-\text{CO} \end{array}$$

(I) (designated the  $\alpha$ -lactone), b. p. 129°/17 mm., m. p. 84—85°, together with a *dimeride* (II), m. p. 244°; I is identical with the pyruvin of Erhart (A., 1885, 1201) and Jowanowitsch (*ibid.*, 1125). Hydrolysis of I with *N*-hydrochloric acid gives glycerol and pyruvic acid, but with cold aqueous-alcoholic sodium hydroxide fission of the lactone ring occurs, giving the *hydroxy-acid* [ $+H_2O$ ] (III),  $\begin{array}{c} \text{CH}_2\text{O} \\ \diagup \quad \diagdown \\ \text{CH}(\text{CH}_2\text{OH})-\text{O} > \text{CMe} \cdot \text{CO}_2\text{H} \end{array}$ , m. p. 74—75°, m. p. (anhydrous) 100° (silver salt, decomp. 173—174° after darkening at 160°). The *amide* (IV), m. p. 139° (*monobenzoyl* derivative, m. p. 125°; *mono-p-toluenesulphonyl* derivatives, m. p. 94° and 139°), of

III is obtained from I and 1% alcoholic ammonia, whilst I and hydroxylamine afford the corresponding *hydroxamic acid* (V), decomp. 122—122.5°.

When glycerol and pyruvic acid are heated at 100—120°, the main product formed is a  $\beta$ -lactone (VI), m. p. 61—62°, isomeric with I. This is hydrolysed by acid and alkali in a manner similar to I. Treatment of VI with hydroxylamine gives a *hydroxamic acid*, decomp. 142—143°, isomeric with V, whilst with alcoholic ammonia an *amide*, m. p. 91° (*monobenzoyl* derivative, m. p. 121°), isomeric with IV, is produced. The last-named amide is also formed when II is treated with concentrated aqueous ammonia. H. BURTON.

**Asymmetric synthesis and the existence of racemic compounds in solution.** A. COTTON (Compt. rend., 1929, 189, 1211—1213).—The results of Kuhn and Braun (A., 1929, 522) are discussed. When equal amounts of solutions of copper *d*- and *l*-tartrates are mixed the resulting solution is deeper coloured and has a different absorption than either of the original solutions, thus indicating racemate formation. H. BURTON.

**Polarimetric determination of tartaric acid and malic acid by the formation of "emetics" with antimony salts.** H. BESSON (J. Pharm. Chim., 1929, [viii], 10, 536—548).—A method based on the determination of the rotatory power of a solution of an "emetic" formed by the addition of oxalates of sodium and antimony to solutions of tartaric acid and its derivatives has been successfully applied to the determination of *d*- and *l*-tartaric acid, alkali and alkaline-earth tartrates, and alkali tartrates in presence of citric acid and/or other optically active substances. E. H. SHARPLES.

**Condensation of pyruvic acid with formaldehyde in the presence of sulphuric acid. II. So-called "tetramethylenedioxalylic acid."** V. V. FEOFLAKTOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1145—1176; cf. A., 1927, 132).—The preparation, properties, and structure of the acid  $C_9H_8O_6$ , obtained as one of the products of the condensation of pyruvic acid and paraformaldehyde and erroneously described by Kaltwasser as tetramethylenedioxalylic acid (A., 1896, i, 670), are examined in detail and compared with other lactone-forming acids. The acid is dibasic, and exists in the dilactone form,  $\text{CH}_2 \cdot \text{C} \begin{array}{l} \diagup \text{C}(\text{OH}) \cdot \text{CO} \\ \diagdown \text{CH}_2 - \text{O} \end{array} \cdot \text{C} \begin{array}{l} \diagup \text{C}(\text{OH}) \cdot \text{CO} \\ \diagdown \text{CH}_2 - \text{O} \end{array} \cdot \text{CH}_2$ .

The di-enolic structure is given, since the lactone readily gives a bright coloration with ferric chloride and tartrates as a dibasic acid. Only a monoacetyl derivative, m. p. 135°, is obtained, but benzoylation gives a dibenzoyl derivative, m. p. 122°. Silver oxide gives both a mono- and a di-salt, whilst potassium hydroxide and ammonia yield only the mono-salts. The enolic form is much more stable than the keto-form, since of all the ketonic reactions, only the hydrazone could with difficulty be obtained.

Treatment with sulphuric acid eliminated water from the two hydroxyl groups, giving the *anhydro-acid*, m. p. 300°. Bromine gave a *bromide*, m. p. 157—158°. When oxidised successively with silver oxide, nitric acid, and potassium permanganate, closure of the trimethylene ring occurs, and trimethylene-1 : 1 : 2 : 2-tetracarboxylic acid is obtained as a final product.

As an intermediate step the monolactone of 1:2-di-(hydroxymethyl)trimethylene-1:2-dicarboxylic acid,  $\text{CH}_2\text{C}(\text{CH}_2\text{OH})\text{CO}\text{O}$ , m. p.  $186^\circ$ , is formed; when heated at  $190^\circ$  it passes into the dilactone, m. p.  $84-87^\circ$ . The monolactone on oxidation with nitric acid yields the lactone of 1-hydroxymethyltrimethylene-1:2:2-tricarboxylic acid, m. p.  $216^\circ$ , and this is oxidised by potassium permanganate to trimethyl-1:1:2:2-tetracarboxylic acid. M. ZVEGINTZOV.

**Physical constants of *d*-gluconic acid and several of its salts.** O. E. MAY, S. M. WEISBERG, and H. T. HERRICK (J. Wash. Acad. Sci., 1929, 19, 443-447).—Composition, solubilities in water at  $25^\circ$ , specific rotation, and degree of hydration of sodium, potassium, ammonium, barium, calcium, magnesium, nickel, manganese, zinc, and lead *d*-gluconates have been determined. The acid has  $[\alpha]_D^{20} +7.3^\circ$  in water, and the dissociation constant is about  $1.65 \times 10^{-4}$ .

C. W. GIBBY.

**$\alpha$ -Seleninopropionic acid and its optical resolution.** H. J. BACKER and W. VAN DAM (Rec. trav. chim., 1929, 48, 1287-1298).—Treatment of potassium diselenide solution (prepared directly, using an improved technique for the production of hydrogen selenide) with  $\alpha$ -bromopropionic acid gave  $\alpha$ -diselenodipropionic acid,  $[\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{Se}]_2$ , which by oxidation with dilute nitric acid formed  $\alpha$ -seleninopropionic acid,  $\text{SeO}_2\text{H}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$  (lead salt; barium salt dihydrate, decomp.  $150-160^\circ$ ; calcium salt dihydrate).

Resolution of the *r*-acid by quinine led to the isolation of the tetrahydrated quinine salt of the *l*-acid, m. p. about  $128^\circ$  (decomp.) after softening at  $115^\circ$ , whence the *l*-acid,  $[\text{M}]_D -110^\circ$ , for the undissociated compound in water. Treatment of the acid in solution with hydrochloric or hydriodic acid caused development of dextrorotation owing to the formation of *d*-diselenodipropionic acid,  $[\text{M}]_D +932^\circ$  (quinine salt, m. p.  $164^\circ$ ).

The dissociation constants of  $\alpha$ -seleninopropionic acid were ascertained by electrometric titration to be  $k_1 3.36 \times 10^{-3}$ ;  $k_2 3.28 \times 10^{-6}$ .

R. J. W. LE FÈVRE.

**Condensation of hippuric acid with aldehydes. Test for aldehydes.** W. M. RODIONOV and A. J. KOROLEV (Z. angew. Chem., 1929, 42, 1091-1092).—The production of azlactones from hippuric acid is a characteristic reaction of aldehydes and is not given by ketones (except pyruvic acid). The substance to be tested is added to a little hippuric acid mixed with anhydrous sodium acetate and a few drops of acetic anhydride; a yellow coloration or precipitate on warming for 5-10 min. on the water-bath shows the presence of an aldehyde. The precipitate dissolves in concentrated sulphuric acid to a blood-red solution, becoming yellow on dilution.  $\alpha$ -*n*-Amylcinnamaldehyde gives the azlactone, 2-phenyl-4- $\alpha$ -*n*-amylcinnamylidene-5-oxazolone, m. p.  $97-98^\circ$ . The azlactone from perillaldehyde, 2-phenyl-4-perillylidene-5-oxazolone, has m. p.  $137-138^\circ$ . C. HOLLINS.

**Solid compounds of aldehydes with monochlorocarbamide.** R. OTTENSOOSER (Bull. Soc. chim., 1929, [iv], 45, 1013-1015).—The solution of

monochlorocarbamide, obtained by passing chlorine into a mixture of carbamide (1 part) and water (1 part) until the weight is increased by 1 part (cf. Béhal and Detœuf, A., 1911, i, 957), with *n*-butaldehyde and isovaleraldehyde yields *n*-butylidenechlorocarbamide, m. p.  $144^\circ$ , and isoamylchlorocarbamide, m. p.  $173.5^\circ$ , respectively. Propaldehyde yields propylidenechlorobiuret,  $\text{CHET}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHCl}$ , m. p.  $140^\circ$  (cf. Béhal and Detœuf, A., 1912, i, 73), and isobutaldehyde gives isobutylidenechlorodibutylidene,  $\text{CHMe}_2\cdot\text{CH}(\text{NH}\cdot\text{CO}\cdot\text{NHCl})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $151^\circ$ , converted by 5% alcoholic potassium hydroxide into the cyclic dicarbamide,  $\text{CHMe}_2\cdot\text{CH}\begin{matrix} \text{NH}\cdot\text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO}\cdot\text{NH} \end{matrix}$ , m. p.  $229-230^\circ$ . R. BRIGHTMAN.

**Determination of hexamethylenetetramine.** E. E. REBAGLIATI.—See B., 1930, 50.

**Compounds of the thioparaldehyde type derived from chloral.** F. D. CHATTAWAY and E. G. KELLETT (J.C.S., 1929, 2908-2916).—The product of the action of sulphuric acid on chloral sulphhydrate,  $[\text{CCl}_3\cdot\text{CH}(\text{OH})]_2\text{S}$ , m. p.  $138-139^\circ$  (diacetyl derivative, m. p.  $84^\circ$ ), is separated by fractional crystallisation into trithioparachloral [2:4:6-tristrichloromethyl-1:3:5-trithian], m. p.  $181^\circ$ , and two forms of dithioparachloral [2:4:6-tristrichloromethylcyclo-1:3:5-oxadithia-2:4:6-trimethylene],  $\alpha$ -modification, m. p.  $236^\circ$ ,  $\beta$ -, m. p.  $108^\circ$  (cf. A., 1928, 1357). The mixed product of the action of sulphuric acid on chloral sulphhydrate yields on dry distillation a mixture of chloral and trichloroethylene and a residue of sulphur.

None of the thioparachlorals is oxidised by 30% hydrogen peroxide; potassium permanganate in cold acetone causes disruption of the molecule. They do not form additive compounds with halogens or with mercuric chloride. This inertness of the bivalent sulphur atoms is accompanied by enhanced reactivity of the chlorine atoms (cf. Bennett and Hock, A., 1926, 146); thus from thioparachloral, 3 mols. of hydrogen chloride are readily eliminated by a cold alcoholic solution of potassium acetate, giving 2:4:6-trisdichloromethylene-1:3:5-trithian, m. p.  $126^\circ$ . Under similar conditions the dithioparachlorals lose hydrogen chloride only from the group in the 4-position, each yielding a corresponding form of 2:6-bistrichloromethyl-4-dichloromethylenecyclo-1:3:5-oxadithia-2:4:6-trimethylene,  $\alpha$ -form, m. p.  $97^\circ$ ,  $\beta$ -form, m. p.  $92^\circ$ . In the presence of alkalis stronger than potassium acetate, both forms of dithioparachloral lose 3 mols. of hydrogen chloride and are converted into the same 2:4:6-trisdichloromethylenecyclo-1:3:5-oxadithia-2:4:6-trimethylene, m. p.  $89^\circ$ . Trithioparachloral on treatment with dry gaseous ammonia loses hydrogen chloride as with other alkalis, and does not yield a thialdine.

The foregoing unsaturated compounds do not combine directly with bromine, but readily add chlorine. From trisdichloromethylenetrithian is obtained 2:4:6-trichloro-2:4:6-tristrichloromethyl-1:3:5-trithian, m. p.  $175^\circ$ ; and from 2:4:6-trisdichloromethylenecyclo-1:3:5-oxadithia-2:4:6-trimethylene two of the possible forms of 2:4:6-trichloro-2:4:6-tristri-

*chloromethylcyclo-1:3:5-oxadithia-2:4:6-trimethylene*,  $\alpha$ -modification, m. p. 175°,  $\beta$ -modification, m. p. 157°, and no trace of a third isomeride. Addition of chlorine to  $\alpha$ - and  $\beta$ -2:6-bis(trichloromethyl)-4-dichloromethylenecyclo-1:3:5-oxadithia-2:4:6-trimethylene leads to corresponding forms of 4-chloro-2:4:6-tris(trichloromethyl)cyclo-1:3:5-oxadithia-2:4:6-trimethylene,  $\alpha$ -form, m. p. 136°,  $\beta$ -form, m. p. 98–99°, both of the latter crystallising as pure compounds; these two isomerides show a difference in reactivity of the chlorine atom in the 4-position; when the  $\alpha$ -compound is boiled with alcohol this chlorine atom is replaced by an ethoxy-group, 4-ethoxy-2:4:6-tris(trichloromethyl)cyclo-1:3:5-oxadithia-2:4:6-trimethylene, m. p. 137°, resulting; the use of sodium ethoxide leads to 4-ethoxy-4-trichloromethyl-2:6-bis(dichloromethylenecyclo-1:3:5-oxadithia-2:4:6-trimethylene), m. p. 94°. The  $\beta$ -compound may be boiled with alcohol without change and on treatment with cold sodium ethoxide loses hydrogen chloride and is converted into 4-chloro-4-trichloromethyl-2:6-bis(dichloromethylenecyclo-1:3:5-oxadithia-2:4:6-trimethylene), m. p. 88°. R. CHILD.

**Keten from acetic acid.** C. D. HURD and K. E. MARTIN (J. Amer. Chem. Soc., 1929, 51, 3614–3617).—During the decomposition of acetic acid at 800° (no change occurs below this temperature) some keten is produced (by dehydration) in addition to methane and carbon dioxide. The formation of acetic anhydride (cf. Peytral, A., 1922, i, 219) and ethylene are explained thus:  $\text{Me}\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot\text{CO} \longrightarrow \text{Ac}_2\text{O}; 2\text{CH}_3\cdot\text{CO} \longrightarrow 2\text{CO} + \text{C}_2\text{H}_4$ . H. BURTON.

**Keto-enol transformation of dihydroxyacetone.** W. A. ROTH (Naturwiss., 1929, 17, 960).—The author's observations of the heat effect (A., 1929, 655), which indicate that the reaction is unimolecular, are in agreement with the observations of Virtanen, Karström, and Turpeinen (this vol., 114) on the fermentation of dihydroxyacetone by *B. coli*.

J. A. V. BUTLER.

**Compounds of nickel, cobalt, and copper which contain the *O*-monomethyl ether of diacetyldioxime.** E. THILO and K. FRIEDRICH (Ber., 1929, 62, [B], 2990–3000).—Methylation of nickel diacetyldioxime cannot be effected with diazomethane on account of the sparing solubility of the compound. A suspension of nickel diacetyldioxime in boiling ethyl alcohol is converted by sodium ethoxide into the salt,  $\text{C}_8\text{H}_{13}\text{O}_4\text{N}_4\text{NiNa}$ , whereas lithium ethoxide yields exclusively the normal lithium compound,  $\text{C}_8\text{H}_{12}\text{O}_4\text{N}_4\text{NiLi}$ ; similar salts of potassium, calcium, and, probably, ammonium may be prepared. The lithium and sodium compounds are completely decomposed by methyl sulphate or iodide, with production of the dimethyl ether of diacetyldioxime. The monomethyl ether of diacetyldioxime is converted by anhydrous nickel chloride in boiling ethyl alcohol (but not acetone) into the compound  $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_4\text{NiCl}_2$ , which is partly decomposed into nickel chloride and diacetyldioxime monomethyl ether in boiling acetone and completely converted by water or ammonia into the mono-ether. It is not decomposed by hydrogen chloride, but is transformed by the aqueous acid into nickel diacetyldioxime and diacetyldioxime di-

methyl ether. Cobalt chloride and the mono-ether in boiling acetone or ethyl alcohol give red and green isomeric compounds,  $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_4\text{CoCl}_2$ . The red substance is stable in alcohol or acetone, but otherwise resembles closely the green nickel derivative (see above). The green cobalt salt is stable towards cold water, slowly decomposed by boiling water. It is not decomposed by ammonia or hydrochloric acid and reacts only slowly with silver nitrate in water, acetone, or alcohol. Even with a large excess of the mono-ether in boiling acetone, anhydrous copper chloride gives exclusively the compound  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_2\text{CuCl}_2$ ; it is decomposed by water, ammonia, or hydrochloric acid, but not by hydrogen chloride. In boiling alcohol the mono-ether and copper chloride afford the di-ether and the copper chloride compound of diacetyldioxime. The dimethyl ether of diacetyldioxime appears incapable of uniting with nickel, cobalt, or copper chloride.

If an alcoholic solution of the compound  $\text{C}_{10}\text{H}_{20}\text{O}_4\text{N}_4\text{NiCl}_2$  is treated with 2 mols. of sodium ethoxide, the unstable, red base,  $\text{C}_{10}\text{H}_{18}\text{O}_4\text{N}_4\text{Ni}$ , is obtained, converted into the original material by hydrogen chloride without formation of water.

H. WREN.

**Analytical study of the reactions of oximes.** J. V. DUBSKÝ and M. KURAŠ (Publ. Fac. Sci. Univ. Masaryk, 1929, No. 114, 1–43).—Various salts of the oximes of hippuramide, potassium oxaldiaminoacetate, potassium oxamethaneaminoacetate, semioxamide, hippuronitrile, oxalhydrazide, diacetoxalhydrazide, benzamide, and of benzhydroxamic acid have been prepared and described. The copper salts of all oximes examined ranged in colour from light to dark green, and were deposited as amorphous precipitates. Benzoxamidoxime gives a blue coloration with ferric chloride, which gives an intense red coloration with all other oximes. Hippuramidioxime dicobalt salt was isolated; the metal is in this case tervalent. Of the nickel salts prepared, that with benzamidoxime contains tervalent nickel. No relationship exists between the composition of an oxime and its tendency to form basic or normal salts. *Hippuramidioxime*, m. p. 100°, and *semioxamidioxime*, m. p. 220°, are described.

R. TRUSZKOWSKI.

**Classification of the sugars.** II. J. G. MALTBY (J.C.S., 1929, 2769–2771).—An amplification of previous work (A., 1926, 822). A modified system of nomenclature for the groups is suggested whereby the corresponding groups in the oxide rings of the aldoses and the ketoses have the same designation. The middle group will have the same configuration in the *d*-pyranoses as in dextrose, and *l*-xulose and  $\alpha$ -glucoheptose are accordingly placed in the *l*-series; the relative configuration of the reducing group and the middle group decides the classification into  $\alpha$ - and  $\beta$ -series. The consideration of the effect of the configuration of the middle group on the relative proportions of the two products of the cyanohydrin synthesis (*loc. cit.*) is extended to include further examples.

R. CHILD.

**Precipitation of sugars and polyhydric alcohols as copper-barium hydroxide complexes.** P.

FLEURY and P. AMBERT (Compt. rend., 1929, 189, 1282—1285).—When aqueous solutions of dextrose are treated with copper sulphate and barium hydroxide solutions, the amount of dextrose precipitated as a complex increases gradually with increasing amount of the alkali and reaches a maximum (96%) with a very large excess of the alkali. With sodium hydroxide solution the amount of sugar precipitated increases rapidly to a maximum (78%) and then decreases with increasing amounts of alkali. The amount of dextrose precipitated is also related to the concentration of copper sulphate; maximal separation occurs with 2 mols. of the sugar and 3 mols. of the salt. Lævulose, galactose, arabinose, sucrose, lactose, maltose, raffinose, and stachyose behave similarly to dextrose, whilst mannitol, erythritol, glycerol, ethylene glycol, and inositol are incompletely precipitated. H. BURTON.

Oxidation of sugars with atmospheric oxygen and hydrogen peroxide. I. F. M. KUEN (Biochem. Z., 1929, 215, 12—25).—Oxidation of lævulose by atmospheric oxygen commences at  $p_H$  9.8 and increases rapidly with  $p_H$ . Phosphate is without effect. Dextrose is more strongly oxidised by hydrogen peroxide at  $p_H$  7 than is lævulose. Phosphate greatly increases the velocity of oxidation. Iron catalyses the oxidation by hydrogen peroxide; when present along with phosphate, the action of the latter is not observed. Dextrose oxidised by hydrogen peroxide and iron gives carbon dioxide, formic, oxalic, lactic, and polyhydroxy-acids, and, in traces, acetic acid, acetaldehyde, and carbon monoxide. Formaldehyde is probably the precursor of the hydrogen obtained. J. H. BIRKINSHAW.

Degradation of dextrose by oxidation. IV. B. BLEYER and W. BRAUN (Biochem. Z., 1929, 216, 224—227; A., 1929, 297).—The analytical data previously given have been confirmed, but it has been found that 60% of the dextrose is oxidised to lactic acid and 40% to formic acid and carbon dioxide. W. MCCARTNEY.

Reaction between sugars and boric acid. F. J. BERENSTEIN (Biochem. Z., 1929, 215, 344—349).—When solutions of boric acid and lævulose are mixed, hydrogen ions are liberated. A smaller effect is obtained with galactose, whilst with dextrose, lactose, and maltose the effect is very small. Whereas in the titration of boric acid with sodium hydroxide using phenolphthalein as indicator only 10% of the acid is neutralised at the colour change, in presence also of sufficient galactose, 40%, and of dextrose and lactose, 25%, but of lævulose (as with mannitol and glycerol) 100%, of the acid is neutralised. P. W. CLUTTERBUCK.

Interconversion of hexoses by means of phosphates: formation of glucose. H. A. SPOEHR and H. H. STRAIN (J. Biol. Chem., 1929, 85, 365—384).—When kept for 166—168 days at 37° in a solution of sodium phosphate of initial  $p_H$  8.16—8.28, dextrose yielded 22% of ketoses, *d*-mannose 32% of ketoses, and lævulose 39% of aldoses; the final  $p_H$  was 7.1—7.4, indicating some acid formation. Lævulose afforded 28% of aldoses when kept for 165 days at 37° in a phosphate mixture of  $p_H$  6.69. The glucose of

Lobry de Bruyn and van Ekenstein (A., 1898, i, 227) can be obtained by the action of sodium phosphate on hexoses. Glucose is not a homogeneous substance; the osazone, m. p. 165° (*loc. cit.*), can be separated into fractions with m. p. ranging from 150° to 207°; on keeping in alkaline solution it yields small amounts of fermentable hexoses, and its oxidation by bromine indicates that it contains some aldoses. When glucose was treated with hydrocyanic acid and ammonia a calcium glutohexonate could be prepared from the solution, which, with hydriodic acid and phosphorus, gave  $\alpha$ -methyl-*n*-hexoic acid, and must therefore have been derived from a 2-ketohexose.

C. R. HARRINGTON.

Mercaptals of sugars. III. *iso*Butylmercaptals of sugars. Y. UYEDA (Bull. Chem. Soc. Japan, 1929, 4, 264—265).—The *isobutylmercaptals* of the following sugars have been prepared, the figures in parentheses giving the m. p. and values of  $[\alpha]_D^{15-14}$ , respectively: glucose (130°; +40.0°); galactose (129°; +41.2°); mannose (111°; +16.4°); rhamnose (112°; +14.0°); arabinose (123°; +20.0°); maltose (140°; +13.2°), and sucrose (138°; +9.6°).

A. I. VOGEL.

Isolation of crystalline  $\alpha$ - and  $\beta$ -ethylglucofuranosides ( $\gamma$ -ethylglucosides) and other crystalline derivatives of glucofuranose. W. N. HAWORTH and C. R. PORTER (J.C.S., 1929, 2796—2806).—The formulation of  $\gamma$ -glucose as a glucofuranose requires the possibility of two forms of the sugar and of its derivatives; two crystalline forms of ethylglucofuranoside are described.

1:2-*isopropylideneglucose* 5:6-*monocarbonate* (by the action of carbonyl chloride on dextrose or *isopropylideneglucose* in acetone), m. p. 223—224° (decomp.) after softening at 215°,  $[\alpha]_D^{20}$  -36° (*p*-toluenesulphonyl derivative, m. p. 103—105°,  $[\alpha]_D^{20}$  -36° in acetone), is converted by alcoholic hydrogen chloride under stated conditions into  $\beta$ -ethylglucofuranoside 5:6-*monocarbonate*, m. p. 164—165°,  $[\alpha]_D^{19}$  -50.6° in water [2:3-*diacetyl* derivative, m. p. 79—81°,  $[\alpha]_D^{21}$  -39° in acetone], yielding on hydrolysis with sodium hydroxide  $\beta$ -ethylglucofuranoside,  $[\alpha]_D^{20}$  -86° in water. The mixture from the mother-liquors when acetylated and fractionated affords, besides the above diacetyl derivative, 2:3-*diacetyl*- $\alpha$ -ethylglucofuranoside 5:6-*monocarbonate*, m. p. 159—160° after softening at 155°,  $[\alpha]_D^{21}$  +143° in acetone, which when hydrolysed with barium hydroxide gives  $\alpha$ -ethylglucofuranoside, m. p. 82—83°,  $[\alpha]_D^{20}$  +98° in water. Both  $\alpha$ - and  $\beta$ -ethylglucofuranosides are unaffected by Fehling's solution or cold dilute permanganate over a period of several hours; they are stable to alkalis but are rapidly hydrolysed by 0.01*N*-hydrochloric acid at 95°. These properties are comparable with those of Fischer's  $\gamma$ -methyl glucoside.

$\beta$ -Methylglucofuranoside 5:6-*monocarbonate*, m. p. 143—145° (efferv.),  $[\alpha]_D^{20}$  -66° in water, is prepared from *isopropylideneglucose* carbonate and methylalcoholic sulphuric acid.

Glucofuranose 5:6-*monocarbonate*, m. p. 182—183° after softening at 170°, results from the acid hydrolysis of *isopropylideneglucose* carbonate,  $\beta$ -ethyl- or  $\beta$ -methyl-glucufuranoside 5:6-*monocarbonate*; it reduces Fehling's solutions actively, decolorises cold

permanganate but does not restore the colour to Schiff's reagent; its *phenylosazone*, m. p. 202—203°, has  $[\alpha]_{D}^{20} -103^{\circ}$  to  $+48^{\circ}$  in pyridine in 4 days. Elimination of the carbonate residue from the latter and from the *anilide*, decomp.  $180^{\circ}$  after softening at  $175^{\circ}$ , by means of barium hydroxide leads respectively to ordinary glucosazone and glucosyanilide.

The structures of the foregoing derivatives are referred back to *diisopropylidenglucose*, which has been shown (Anderson, Charlton, and Haworth, A., 1929, 1044) to possess a butylene-oxide ring. *p*-Toluenesulphonylisopropylidenglucose carbonate, on elimination of the carbonate residue by means of barium hydroxide, followed by the introduction of a second acetone residue, gives *p*-toluenesulphonyldiisopropylidenglucose, m. p. 120—121° (Freudenberg and Ivers, A., 1922, i, 524). Further independent evidence of the ring structure of the glucofuranosides is provided by the oxidation of the methylated methylglucufuranoside to 2:3:5:6-tetramethyl- $\gamma$ -gluconolactone, and finally to *d*-dimethoxysuccinic acid (Haworth, Hirst, and Miller, A., 1927, 1173).

The results are discussed in their bearing on the validity of the recent views of Hudson (A., 1926, 714).

R. CHILD.

**Acetone [isopropylidene] compounds of the mercaptals of monosaccharides. III. Derivatives of *d*-galactose.** E. PASCU and A. LÖB (Ber., 1929, 62, [B], 3104—3107; cf. this vol., 70).—*d*-Galactose benzylmercaptal, m. p.  $144^{\circ}$ , is converted by acetone in presence of anhydrous copper sulphate into a mixture of di- and mono-2:3-isopropylidene-*d*-galactose benzylmercaptal, m. p. 102—103°,  $[\alpha]_{D}^{20} +8.76^{\circ}$  in *s*-tetrachloroethane. In presence of sulphuric acid the non-crystalline 2:3:5:6-diisopropylidene derivative is the sole product; it is also obtained from acetone and the mono-compound in presence of sulphuric acid or copper sulphate. When treated with methyl sulphate it affords a non-crystalline 4-methyl-2:3:5:6-diisopropylidene-*d*-galactose benzylmercaptal, hydrolysed by alcoholic hydrochloric acid to 4-methyl-*d*-galactose benzylmercaptal, m. p. 130—131°,  $[\alpha]_{D}^{20} -27.55^{\circ}$  in pyridine. Removal of the mercaptal residue by mercuric chloride in alcohol affords 4-methyl- $\alpha$ -*d*-galactose, m. p. (indef.)  $118^{\circ}$ ,  $[\alpha]_{D}^{20} +117.05^{\circ}$  to  $+67.77^{\circ}$  in water during 3 hrs. (*osazone*, decomp.  $194$ — $195^{\circ}$  after darkening at  $190^{\circ}$ ,  $[\alpha]_{D}^{20} +130.7^{\circ}$  in pyridine), which does not yield silver methoxyacetate when oxidised with silver oxide.

H. WREN.

**Sugars with branched carbon-chains. I. Constitution of the sugar from hamameli-tannin.** O. T. SCHMIDT (Annalen, 1929, 476, 250—271).—The crystalline and gelatinous forms of hamameli-tannin obtained by Freudenberg and Blümmel (A., 1925, i, 51) show no chemical differences. The crystalline tannin contains nine hydroxyl groups (Zerevitinov) and on *p*-bromobenzoylation affords an amorphous octa-*p*-bromobenzoyl derivative, m. p. 128—135°. Prolonged treatment of the crystalline tannin with methyl alcohol containing 0.25% of hydrogen chloride causes a change in the rotatory power (*d* to *l*) and after 6 days at  $37^{\circ}$  reaction is complete. Neutralisation of the mixture with methyl-

alcoholic potassium hydroxide, evaporation in a vacuum, and subsequent extraction of the residue with acetone afford the *tannin methyl semiacetal*. This is hydrolysed by dilute sodium hydroxide in an atmosphere of hydrogen to gallic acid and methylhamameloside (I),

$C_7H_{14}O_6$ , a syrup,  $[\alpha]_{D}^{20} -75^{\circ}$  in methyl alcohol (*triacetate*, m. p.  $72.5^{\circ}$ ,  $[\alpha]_{D}^{20} -34.8^{\circ}$  in alcohol). The inversion constant of methylhamameloside as determined by Freudenberg's method (A., 1928, 1222) is  $35-36 \times 10^{-4}$ .

Reduction of the ammonium hexonate (Freudenberg and Blümmel, *loc. cit.*) obtained from the hamamelihexose (now termed hamamelose) with red phosphorus and hydriodic acid (*d* 2.0) affords 3.5—5% of  $\alpha$ -methylvaleric acid (*p*-iodophenacyl ester, m. p.  $66^{\circ}$ ), thus determining the position of the aldehyde group (*cf. loc. cit.*). The *p*-iodophenacyl esters of  $\alpha$ -ethylbutyric and  $\alpha\beta$ -dimethylbutyric acids have m. p.  $54^{\circ}$  and  $66^{\circ}$ , respectively.

H. BURTON.

**Condensation of dextrose and  $\gamma$ -fructose. Conversion of sucrose into isosucrose.** (SIR) J. C. IRVINE and J. W. H. OLDHAM (J. Amer. Chem. Soc., 1929, 51, 3609—3612).—Sucrose octa-acetate is converted into an equimolecular mixture of glucose tetra-acetate and  $\gamma$ -fructose tetra-acetate by treatment with acetyl bromide in acetic acid solution at the ordinary temperature. Condensation of the above mixture under the conditions previously described (A., 1929, 683) gives as the only crystallisable product isosucrose octa-acetate (occasionally isotrehalose octa-acetate is isolated). Anhydrofructose triacetate (*loc. cit.*) is converted by treatment with acetyl and hydrogen chlorides into  $\gamma$ -fructose tetra-acetate. Condensation of this with glucose tetra-acetate also furnishes isosucrose octa-acetate. As isosucrose is less stable than sucrose it is improbable that sucrose octa-acetate is first formed.

H. BURTON.

**Preparation of alkylglucosides from mercaptals of monosaccharides.** E. PASCU and N. TICHARICH (Ber., 1929, 62, [B], 3008—3012; cf. A., 1925, i, 515).—The dibenzylmercaptals of the aldmonoses are converted into simple  $\alpha$ -alkylglucosides when heated with mercuric chloride dissolved in the requisite alcohol. The  $\beta$ -form is produced only in minor amount. The following transformations are recorded. *l*-Arabinose benzylmercaptal, m. p.  $144^{\circ}$ ,  $[\alpha]_{D}^{20} -18.86^{\circ}$  in pyridine (*cf. Lawrence, A., 1896, i, 272*), into  $\beta$ -methyl-*l*-arabinoside, m. p.  $169$ — $170^{\circ}$ ,  $[\alpha]_{D}^{20} +246.1^{\circ}$  in water; *l*-rhamnose benzylmercaptal, m. p.  $125^{\circ}$ ,  $[\alpha]_{D}^{20} +35.28^{\circ}$  in pyridine (*cf. Lawrence, loc. cit.*), into  $\alpha$ -methyl-*l*-rhamnoside, isolated as the triacetate, m. p.  $86$ — $87^{\circ}$ ,  $[\alpha]_{D}^{20} -53.7^{\circ}$  in *s*-tetrachloroethane; *d*-galactose benzylmercaptal, m. p.  $144^{\circ}$ ,  $[\alpha]_{D}^{20} -26.36^{\circ}$  in pyridine, into  $\alpha$ -methyl-*d*-galactoside, m. p.  $111^{\circ}$ ,  $[\alpha]_{D}^{20} +177.6^{\circ}$  in water,  $\alpha$ -ethyl-*d*-galactoside, m. p.  $139$ — $140^{\circ}$ ,  $[\alpha]_{D}^{20} +186.8^{\circ}$  in water, and  $\alpha$ -allyl-*d*-galactoside, m. p.  $138$ — $142^{\circ}$ ,  $[\alpha]_{D}^{20} +171.7^{\circ}$  in water.

H. WREN.

**Rotatory power and structure in the sugar group. XXI.  $\beta$ -Phenylthioglucosides of dex-**

trose, xylose, lactose, and cellobiose. XXII. Evidence concerning the ringed structure of  $\beta$ -phenylthio-cellobioside and -lactoside. XXIII. Preparation and structure of  $\beta$ -phenylthiomaltoside and its hepta-acetate. C. B. PURVES (J. Amer. Chem. Soc., 1929, **51**, 3619—3627, 3627—3631, 3631—3636).—XXI. The following compounds are prepared by condensing bromoaceto-sugars (prepared from the fully acetylated sugar by the action of hydrogen bromide in acetic acid and chloroform solution) with potassium phenyl sulphide in alcoholic chloroform solution:  $\beta$ -phenylthioxyloside triacetate, m. p. 78°,  $[\alpha]_D^{20}$  —58.9° in chloroform;  $\beta$ -phenylthiocellobioside hepta-acetate, decomp. about 295°  $[\alpha]_D^{20}$  —28.5° in chloroform;  $\beta$ -p-tolylthiocellobioside hepta-acetate, m. p. 217°,  $[\alpha]_D^{20}$  —28.0° in chloroform;  $\beta$ -phenylthiolactoside hepta-acetate, m. p. 155—156°,  $[\alpha]_D^{20}$  —19.6° in chloroform (cf. Fischer and Delbrück, A., 1909, i, 365); and  $\beta$ -phenylthioglucoside tetra-acetate, m. p. 117°,  $[\alpha]_D^{20}$  —17.5° in chloroform (cf. *loc. cit.*). Hydrolysis of these acetates with methyl-alcoholic ammonia affords  $\beta$ -phenylthioxyloside, m. p. 144°,  $[\alpha]_D^{20}$  —70.8° in water;  $\beta$ -phenylthiocellobioside, m. p. 230°,  $[\alpha]_D^{20}$  —59.3° in water;  $\beta$ -phenylthiolactoside, m. p. 220°,  $[\alpha]_D^{20}$  —39.3° in water (cf. *loc. cit.*), and  $\beta$ -phenylthioglucoside, m. p. 133°,  $[\alpha]_D^{20}$  —70.5° in water. The molecular rotation of the  $C_{50}$  atom in the acetylated derivatives is calculated from the above and Hudson's results (A., 1924, i, 371) to be approximately 30,500. Deviations from this value are similar in magnitude but opposite in sign to those for the corresponding chloro-sugar acetates (Hudson, *loc. cit.*). No such agreement is found for the non-acetylated derivatives.

XXII. Partial hydrolysis of  $\beta$ -phenylthio-lactoside and -cellobioside with *N*-sulphuric acid at 100° gives  $\beta$ -phenylthioglucoside in each case. The oxygen bridge linking is concluded to be normal in the disaccharides.

XXIII.  $\beta$ -Phenylthiomaltoside hepta-acetate, m. p. 93—95°,  $[\alpha]_D^{20}$  +49.0° in chloroform, is obtained with difficulty by the general method. When hydrolysed with aqueous-alcoholic sulphuric acid at 90°,  $\beta$ -phenylthioglucoside is obtained, indicating that the maltoside has the normal ring structure. Hydrolysis of the acetate with alcoholic ammonia or dilute methyl-alcoholic sodium methoxide affords amorphous  $\beta$ -phenylthiomaltoside,  $[\alpha]_D^{20}$  +38.12° in water. H. BURTON.

Flavanone glucosides. V. Reduction of flavone and flavanone derivatives. Y. ASAHINA, G. NAKAGOME, and M. INUBUSE (Ber., 1929, **62**, [B], 3016—3021; cf. A., 1928, 1256).—Acacetin and eriodictol suspended in water are reduced by sodium amalgam to acacetidin and luteolinidin respectively, identical with the compounds described by Robinson and co-workers (A., 1924, i, 305; 1925, i, 825). Homoeeriodictol similarly affords luteolinidin 3'-methyl ether, m. p. 255° (decomp.). Quercetin pentamethyl ether is reduced to the pseudo-base of cyanidin pentamethyl ether [picrate,  $C_{26}H_{23}O_{13}N_3$  (also hemihydrate), m. p. 202—203°; chloride,  $C_{15}H_{10}O(OMe)_5Cl \cdot H_2O$ , m. p. 158—159°] (cf. Pratt and Robinson, A., 1925, i, 422). Apiin, naringin, sakuranin, and hesperidin are also reduced by sodium

amalgam giving compounds which yield red or violet-red dyes when acidified. H. WREN.

Inulin. H. VOGEL (Ber., 1929, **62**, [B], 2980—2981).—Inulin is converted when heated in glycerol at 90—95°/12—13 mm., into an isodiffructosan,  $(C_6H_{10}O_5)_2 \cdot H_2O$ ,  $[\alpha]_D^{20}$  —34.01° in water. The mol. wt. of the compound increases rapidly when it is preserved, whilst the initial free solubility in cold water diminishes until a depression of the f. p. is not observed. The final product, isoinulin, is a voluminous, non-hygroscopic powder,  $[\alpha]_D^{20}$  —34.38° in water, which lacks the ash content characteristic of natural inulin. H. WREN.

Composition of alkali-cellulose from cotton. B. RASSOW and L. WOLF (Ber., 1929, **62**, [B], 2949—2953; cf. Rassow and Wadewitz, A., 1924, i, 374).—Repeated treatment of mercerised cotton with absolute alcohol until an aliquot portion (35 c.c.) of the liquid is just rendered acid to phenolphthalein by addition of 0.05 c.c. of 0.1*N*-hydrochloric acid leads to the isolation of the compound  $C_6H_{10}O_5 \cdot NaOH$  (*loc. cit.*). If, however, the treatment is continued until the washings show a similar behaviour in presence of alizarin-yellow (cf. Schwarze, Diss., Leipzig, 1929), the compound  $C_{12}H_{20}O_{10} \cdot NaOH$  is obtained. H. WREN.

Lignin and cellulose. XII. Cellobiosan and cellulose. K. FREUDENBERG, E. BRUCH, and H. RAU (Ber., 1929, **62**, [B], 3078—3083; cf. A., 1929, 1046).—Re-examination of the behaviour of cellobiosan acetate in freezing glacial acetic acid shows that the process is not suitable for the determination of mol. wt., since the apparent f. p. of the solvent shows a small but measurable dependence on the temperature of the cooling bath. In the presence of the biosan acetate the duration of the rise in temperature is about three times as great as with the solvent alone and the depression increases with falling bath temperature. The measurements can be reconciled only with a very high mol. wt. of the biosan. H. WREN.

Cellobiosan and cellulose. K. FREUDENBERG (Naturwiss., 1929, **17**, 959).—See preceding abstract.

Characterisation of cellulose preparations. K. HESS (Annalen, 1929, **476**, 298—299).—The author's previous work (A., 1925, i, 1246; 1928, 1360) and the results of Hägglund and Klingstedt (B., 1928, 119) are discussed. H. BURTON.

Characterisation of cellulose preparations by the rotation method. II. E. HÄGGLUND and F. W. KLINGSTEDT (Annalen, 1929, **476**, 286—297; cf. B., 1928, 119).—The results of Hess and Ljubitsch (A., 1928, 1360) are criticised. H. BURTON.

Lignin. K. KÜRSCHNER [with WOLLMARKER] (Tech. u. Chem. Pap. Zellstoff-Fabr., 1929, **26**, 53—66; Chem. Zentr., 1929, ii, 414—415).—The constitution of wood is discussed. Treatment with perbenzoic acid at the ordinary temperature resulted in an increase in weight of 7.5—12% owing to decomposition of lignin, pure cellulose similarly gaining 1.7—2.2%. The carbon content of oxidised wood is smaller than the normal. The action of other hydrolytic and hydrolytic-oxidative reagents on wood increases the reducing substance produced by subsequent hydrolysis



with sulphuric acid. In the "pre-hydrolysis" first hexosans and then pentosans are hydrolysed. Barium carbonate is unsuitable for the neutralisation of the hydrolysis mixture.

A. A. ELDRIDGE.

**Identification of amines. V. Derivatives of tertiary amines.** C. S. MARVEL, E. W. SCOTT, and K. L. AMSTUTZ (J. Amer. Chem. Soc., 1929, **51**, 3638—3641).—The quaternary ammonium chlorides from benzyl chloride and diethylaniline, dimethyl-*p*-toluidine, 6-methylquinoline, and tri-*n*-butylamine have m. p. 104°, 171°, 209°, and 185°, respectively. Quaternary ammonium *p*-toluenesulphonates are obtained from methyl *p*-toluenesulphonate and the following bases in benzene solution, the m. p. of the salt being given in parentheses: pyridine (138—139°); 2-methylpyridine (149—150°); 2-chloropyridine (119—120°); quinoline (125—126°); 2-methyl- and 6-methyl-quinolines (161° and 153—154°, respectively); 6-chloroquinoline (142—143°); 6-bromoquinoline (150—152° after softening at 95°); 2:6-dimethyl-quinoline (175°); isoquinoline (163°); dimethyl-aniline (161°); dimethyl-*p*-toluidine (85°); di-*n*-butylaniline (180°); tri-*n*-amylamine (76—80°). Phenyltrimethylammonium *p*-bromobenzenesulphonate and methanesulphonate have m. p. 218—220° and 192° (decomp.), respectively. *p*-Nitrobenzyl and phenacyl chlorides are unsatisfactory reagents for tertiary amines.

H. BURTON.

**Preparation of glucosamine hydrochloride.** J. VAN ALPHEN (Chem. Weekblad, 1929, **26**, 602).—The chitin prepared from the shells of shrimps by successive treatments with sodium hydroxide and dilute hydrogen chloride solutions is odourless and colourless, and can be kept indefinitely if dry. Boiling with concentrated hydrochloric acid gives a good yield of the hydrochloride.

S. I. LEVY.

**Preparation of aminoacetal.** J. S. BUCK and S. N. WRENN (J. Amer. Chem. Soc., 1929, **51**, 3612—3613).—Aminoacetaldehyde diethylacetal is obtained in good yield from the iodoacetal and an excess of alcoholic ammonia at 110—125°. Low yields and tarry products are formed from chloro- and bromoacetals.

H. BURTON.

**Complex compounds of platinum with aminoacetal.** L. A. TSCHUGAIEV and B. P. ORELKIN (Ann. Inst. Platine, 1929, **7**, 118—123).—See A., 1913, i, 23.

**Synthesis of betainealdehyde (synthetic muscarine?).** R. VOET (Bull. Soc. chim., 1929, [iv], 45, 1016—1022).—Chloroacetaldehyde diethylacetal (1 mol.) and trimethylamine (1 mol.) when heated in 33% alcoholic solution at 125—130° for 8—10 hrs., after elimination of unchanged trimethylamine with barium hydroxide (cf. Brabant, A., 1913, i, 956), and treatment of the product with hydrochloric acid, yields a mixture of equal parts of the monomeric and polymeric forms of betainealdehyde. The monomeric form,  $\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CHO}$ , gives a semicarbazone, m. p. 305°, and a chloroplatinate,  $(\text{NMe}_3\cdot\text{CH}_2\cdot\text{CHO})_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$ . The same semicarbazone is formed more slowly from the trimeric form, decomp. 100° [chloroplatinate,  $(\text{NMe}_3\cdot\text{CH}_2\cdot\text{CHO})_6\text{Pt}_2\text{Cl}_{12}\cdot 4\text{H}_2\text{O}$ ]. Similarly,  $\beta$ -tri-

methylaminopropaldehyde dimethylacetal hydrochloride yields a mixture of equal parts of monomeric  $\beta$ -homomuscarine hydrochloride [chloroaurate, decomp. 153°; chloroplatinate,  $(\text{NMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO})_2\text{PtCl}_6\cdot \text{H}_2\text{O}$ ; semicarbazone, m. p. 304.5—305°], and the trimeric form, decomp. 60° yielding acraldehyde, which gives the same semicarbazone as the monomeric but more slowly; the chloroaurate, decomp. 193°, and chloroplatinate are described.

R. BRIGHTMAN.

**Biochemistry of sulphur. II. Distinctive reaction for cysteine and cystine.** M. X. SULLIVAN. **III. Groups involved in the naphthaquinone reaction for cysteine and cystine.** M. X. SULLIVAN and W. C. HESS (U.S. Pub. Health Rep., 1929, **44**, 1421—1428, 1599—1608).—I. The colour test for cysteine previously described (A., 1926, 1266) is modified to include cystine. Solutions of the last-named acid are reduced with sodium cyanide, and then treated successively with sodium 1:2-naphthaquinone-4-sulphonate, alkaline sodium sulphite, and sodium hyposulphite. Although the reduction to cysteine is incomplete, the method can be applied to the determination of the cystine content of proteins, provided pure cystine is used as a standard. Ferrous sulphate (4% of wt. of cystine used) and ferric chloride (1—8%) do not interfere with the reaction, but heavy metal salts should be avoided. Haemoglobin (1%) has no effect on the determination of cysteine. Negative reactions were given by ergothioneine,  $\alpha$ -amino- $\beta$ -phenylpropionic acid 4:4'-disulphide, methionine (Barger and Coyne, A., 1929, 175),  $\beta\beta$ -diaminodiethyl disulphide, furfuraldehyde, lævulinic and pyruvic acids, and reduced glutathione. The test is more specific than either the Folin-Looney (A., 1922, ii, 539) or Okuda tests (A., 1926, 190).

II. The colour reaction for cysteine is not given by compounds containing the thiol or amino-group alone, the amino- and disulphide groups together, or the thiol and amino-groups together, if far apart in the molecule. Mixtures of amino-acids and thiol compounds give a negative reaction. Since  $\beta\beta$ -diaminodiethyl disulphide also gives a negative reaction, it appears that the amino-, thiol, and carboxyl groups are necessary for the reaction, and they must possess the same orientations as in cysteine. 2:2'-Diaminodiphenyl disulphide and *o*-aminothiophenol (improved methods of preparation given) do not give the reaction.

H. BURTON.

**Glutathione. I. Preparation in crystalline form; identification.** E. C. KENDALL, B. F. MCKENSIE, and H. L. MASON.—See this vol., 113.

**Formation of thiocarbamates in aqueous solution.** B. HOLMBERG (Svensk Kem. Tidskr., 1929, **41**, 249—257).—A 93% yield of trithiocarbo-diglycollic acid is obtained by shaking carbon disulphide with *N*-potassium hydroxide for 24 hrs. In the presence of varying amounts of ethyl alcohol the formation of xanthate continues even after 24 hrs.; this is ascribed to the interaction of already formed trithiocarbonate with potassium ethoxide. A number of amido-derivatives (thiocarbamides) have been prepared by shaking an aqueous 12% solution of potassium hydroxide with carbon disul-



give marked amounts of ether only with *cyclopentyl* bromide; the other compounds mainly lose hydrogen bromide. In general, reaction occurs less completely than with water and sodium acetate. With metallic sodium, methylcyclohexyl bromide and cycloheptyl bromide react to the extent of 79.2% and 71.6%, respectively, giving 42.9% and 43.3% of dimethyldicyclohexyl and dicycloheptyl. In contrast, cyclohexyl bromide gives only 12% change, resulting exclusively in the production of cyclohexene. With potassium phenoxide, the elimination of hydrogen bromide is less marked and, with extensive total change, the phenyl esters are produced in considerable amount; the most favourable results are obtained with *cyclopentyl* bromide and least reaction occurs with *cyclohexyl* bromide (involving only loss of hydrogen bromide). With potassium hydrogen sulphide and potassium sulphide extensive change occurs, *cyclopentyl* bromide being most reactive. Primary amines react readily with *cyclopentyl*, methylcyclohexyl, and *cycloheptyl* bromides, but piperidine gives little difference in total change with the three halides.

The following compounds are described: *cyclopentyl methyl ether*, b. p. 105—106.5° (corr.), *benzyl ether*, b. p. 96—97°/12 mm., 226—227°/atm. pressure, *phenyl ether*, b. p. 109.5—112°/12 mm., 239° (corr.) (atm. pressure),  $\beta$ -naphthyl ether, b. p. 187°/12 mm., and  $\alpha$ -naphthyl ether, b. p. 185—186°/12 mm. [*picrate*, m. p. 113.2° (corr.)]; *cyclopentyl benzoate*, b. p. 144.5—145.5°/12 mm.; *cyclopentyl mercaptan*, b. p. 131.5—132° (mercury and lead salts); *cyclopentyl methyl sulphide*, b. p. 158—159°, and *ethyl sulphide*, b. p. 176—177°; *dicyclopentyl sulphide*, b. p. 129.5—130.5°/24 mm. (additive compound with mercuric chloride); *dicyclopentyl sulphoxide*, m. p. 71.5°; *dicyclopentylmethylsulphonium iodide*, m. p. 88.7°; additive compound of mercuric chloride and *cyclopentyl ethyl sulphide*; *cyclopentyl ethyl sulphoxide*, m. p. 43°; *cyclopentylmethylsulphonium iodide*, m. p. 65.5°; *cyclopentylidiphenylcarbinol*, m. p. 122°, from *cyclopentyl* bromide and benzophenone in presence of sodium and ether; *cyclopentylaniline*, b. p. 137°/12 mm., 266°/atm. pressure (*hydrochloride*; *sulphate*; *hydrogen oxalate*; *acetyl derivative*, m. p. 96°); *cyclopentyltoluidine*, b. p. 142.5—143.5°/12 mm. (*hydrochloride*; *sulphate*; *acetyl derivative*, m. p. 61°); *cyclopentyl-1:3:4-xylylidine*, b. p. 150—151°/12 mm. (*hydrogen oxalate*, m. p. 134°); *cyclopentyl-p-phenetidine*, b. p. 179.5—180.5°/12 mm.; *cyclopentyl- $\beta$ -naphthylamine*, m. p. 177°; *cyclohexylpiperidine*, b. p. 86.5—87°/12 mm. (*hygroscopic hydrochloride*; *sulphate*; *hydrogen oxalate*, m. p. 186.5°); *cyclohexyl- $\beta$ -naphthylamine*, m. p. 168°; *3-methylcyclohexyl phenyl ether*, b. p. 132—134°/12 mm.; *3-methylcyclohexyl benzoate*; *3:3'-dimethyldicyclohexyl sulphide*, b. p. 165—168°/11 mm.; *3-methylcyclohexyl ethyl sulphide*; *3-methylcyclohexylaniline*, b. p. 151—152.5°/11 mm., *-o-toluidine*, b. p. 161.5—162°/12 mm., *-1:3:4-xylylidine*, b. p. 170—172.5°/11 mm., *-p-phenetidine*, b. p. 194—196°/11 mm., *- $\beta$ -naphthylamine*, m. p. 172°, and *-piperidine*, b. p. 114—115°/13 mm.; *cycloheptyl phenyl ether*, b. p. 143—144°/12 mm.; *cycloheptyl mercaptan*, b. p. 74°/11 mm.; *dicycloheptyl sulphide*, b. p. 174°/11 mm.; *cycloheptyl-aniline*, b. p. 156—157°/11 mm.,

*-o-toluidine*, b. p. 169—170°/11 mm., *- $\beta$ -naphthylamine*, m. p. 170—171°, and *-piperidine*, b. p. 124—125°/11 mm. H. WREN.

**Decomposition of phenyl iodide dichloride.** E. V. ZAPPI and V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1929, 17, 81—89).—See this vol., 79.

**Aromatic compounds of fluorine. V. Difluorobenzenes.** Analytical observations. G. SCHIEMANN and R. PILLARSKY [in part with W. SCHÜTH] (Ber., 1929, 62, [B], 3035—3043; cf. A., 1929, 1051, 1052).—*m*-Phenylenediamine is converted into the corresponding *diazonium fluoborate*, decomp. 206°, which yields *m*-difluorobenzene, b. p. 82—83°/752 mm., m. p. —59°,  $d_4^{20}$  1.1552,  $n_D^{20}$  1.44035, when heated. Similarly, *p*-phenylenediamine is transformed successively into a *diazonium fluoborate*, decomp. 186°, and *p*-difluorobenzene, b. p. 88.4—88.6° (corr.)/767 mm., m. p. —13°,  $d_4^{20}$  1.1684,  $n_D^{20}$  1.44225, which is also obtained from *p*-fluorophenyl-*diazonium fluoborate*, decomp. 154.5°.

Nitration of fluorobenzene with acetyl nitrate affords *p*-fluoronitrobenzene, b. p. 95—97.5°/22 mm., m. p. 26.5°, and a fraction rich in *o*-fluoronitrobenzene. Similar fractions are obtained by the action of nitric acid ( $d$  1.52) on fluorobenzene in presence of phosphoric oxide. The preparation of the fluoronitrobenzenes is accomplished by the thermal treatment of the requisite nitrophenyldiazonium fluoborates (cf. *loc. cit.*) mixed with sand; the following constants (among others) are recorded: *p*-compound, b. p. 86.6° (corr.)/14 mm.,  $d_4^{20}$  1.3300,  $n_D^{20}$  1.53156; *m*-compound, b. p. 86°/19 mm.,  $d_4^{20}$  1.3254,  $n_D^{20}$  1.53622; *o*-compound, b. p. 86—87°/11 mm. Reduction of *p*-fluoronitrobenzene with stannous chloride and hydrochloric acid or with iron filings affords *p*-fluoroaniline, b. p. 184—186°/767 mm.,  $d_4^{20}$  1.1725,  $n_D^{20}$  1.51954 [acetyl derivative, m. p. 150—151°; *benzoyl* compound, m. p. 185°; *p*-nitrobenzoyl derivative, m. p. 180.5° (corr.); *picrate*, decomp. 214° after darkening at 198°]. *o*-Fluoroaniline, b. p. 58°/11 mm., is converted through the corresponding *diazonium fluoborate*, decomp. 159°, into *o*-difluorobenzene, b. p. 91—92°/751 mm., m. p. —34°,  $d_4^{20}$  1.1599,  $n_D^{20}$  1.44506.

Nitrogen in diazonium fluoborates is determined by decomposition of the compounds with sulphuric acid and measurement of the liberated nitrogen (cf. Wilke-Dörfurt and Balz, A., 1927, 238). For the determination of carbon and hydrogen the combined use of lead chromate and copper oxide is recommended. H. WREN.

**Reduction of the nitro-group as a function of polarity.** R. H. CLARK and E. G. HALLONQUIST (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 71—74).—A quantitative method of analysis for nitro-groups (Callan and Henderson, A., 1922, ii, 524) has been found to apply to the determination of all nitro-groups, regardless of polarity. The fact that the method holds for such compounds as *o*- and *p*-dinitrobenzene proves that the reduction of positive and negative nitro-groups to amino-groups is not parallel to the behaviour of the positive and negative halogens with stannous chloride. R. K. CALLOW.

**Sulphonic acids of *m*- and *p*-xylenes and mesitylene and their derivatives.** A. F. HOLLEMAN (Rec. trav. chim., 1929, 48, 1075—1083).—See this vol., 80.

**Structure and spectrochemical behaviour of triphenylmethane and acetylene derivatives.** K. VON AUWERS and F. BERGMANN (Annalen, 1929, 476, 272—279).—Spectrochemical data are recorded for triphenylmethane, glycol di(triphenylmethyl) ether, glycerol  $\alpha$ -di(triphenylmethyl) ether, phenylacetylene, *s*-diphenylacetylene, tetraphenylbutinene, hexaphenylbutinene (I) (Wieland and Kloss, A., 1929, 1053),  $\alpha$ -phenyl- $\beta$ -diphenylmethylacetylene,  $\alpha$ -phenyl- $\beta$ -triphenylmethylacetylene, and  $\alpha$ -phenyl- $\beta$ -tri-*p*-tolylmethylacetylene. The determinations were carried out mainly in 1-methylnaphthalene solution, and the results show that I is probably correctly represented as  $\text{CPh}_3\text{:C}\equiv\text{CPh}_3$  (cf. *loc. cit.*).

The ketone,  $\text{C}_{39}\text{H}_{30}\text{O}$ , formulated by Wieland and Kloss (*loc. cit.*) as *p*-triphenylacetyltriphenylmethane, shows an exaltation, indicating that the assigned structure is the correct one. H. BURTON.

**[Association and solvation of polystyrenes.]** H. KROEPFELIN (Ber., 1929, 62, [B], 3061—3063; cf. this vol., 145).—In connexion with the viscosity measurements of Staudinger and Heuer (this vol., 78), it is shown that the influences of the length of the capillary on the apparent viscosity of the abnormal colloidal solutions are attributable in part to the mode of presentation of the experimental results and are partly explicable by known reasons when the outflow process is more closely examined. The introduction of special hypotheses is unnecessary.

H. WREN.

**2 : 3-Dimethylnaphthalene from coal tar.** O. KRUBER (Ber., 1929, 62, [B], 3044—3047).—The initial material is a coal-tar oil, b. p. 265—267°, from which the main quantity of the 1 : 6-, 2 : 6-, and 2 : 7-dimethylnaphthalenes has been removed. The oil is treated with sulphuric acid (96%) at 40—50° and the viscous mixture of sulphonic acids is heated at 160°, whereby 2 : 3-dimethylnaphthalene-6-sulphonic acid is produced; the monohydrated sodium salt and the corresponding amide, m. p. 228—229°, are described. Treatment of the sodium salt with 70% sulphuric acid and steam at 180—190° affords 2 : 3-dimethylnaphthalene, b. p. 265—266°/767 mm. It appears to be present to the extent of 5—7% in the initial material. Oxidation of the hydrocarbon with chromic acid in glacial acetic acid yields 2 : 3-dimethyl- $\alpha$ -naphthaquinone, m. p. 127°, oxidised by aqueous permanganate to *o*-phthalic acid. Fusion of the sodium sulphonate with potassium hydroxide gives 2 : 3-dimethyl-6-naphthol, m. p. 160°, coupled to benzeneazo-2 : 3-dimethyl-6-naphthol, m. p. 154—155°. Treatment of the dye with stannous chloride and hydrochloric acid followed by oxidation of the product affords 2 : 3-dimethyl- $\beta$ -naphthaquinone, m. p. 146—147°.

H. WREN.

**2-Iodo-dichloride, 2-iodoso-, and 2-iodoxy-derivatives of fluorene and fluorenone.** P. CHANUSSOT (Anal. Assoc. Quím. Argentina, 1929, 17, 71—80).—2-Iodofluorene yields, by Willgerodt's method, 2-iodofluorene dichloride, decomp. 70—75°,

giving (?) 2-chloro-7-iodofluorene, m. p. 118—120°. 2-Iodofluorenone dichloride is obtained similarly. The iodoso- and iodoxy-derivatives are not formed by Willgerodt's methods, but are readily obtained by decomposition of the iodide dichlorides by aqueous pyridine, and by the action of chlorine on the iodides dissolved in the same medium, respectively (cf. Ortoleva, A., 1900, i, 592). 2-Iodosofluorene, decomp. 150—160° (acetate, decomp. 180—190°), 2-iodosofluorenone, m. p. 175° (acetate), 2-iodoxyfluorene, explodes 185—186°, and 2-iodoxyfluorenone, explodes 170—173°, are described.

These derivatives appear less stable than the corresponding phenyl compounds; the iodine atom is less prone to pass into the multivalent state owing to its firmer attachment to the nucleus.

R. K. CALLOW.

***ms*-Alkylanthracenes and "transannular tautomerism."** VII. E. DE B. BARNETT and J. L. WILTSHIRE (Ber., 1929, 62, [B], 3063—3072; cf. A., 1929, 1289).—To account for the profound influence of chlorine atoms in the  $\alpha$ -position on the properties of substituents attached to the meso-carbon atom of the anthracene nucleus, the possibility of the existence of a co-ordinative linking between the chlorine and meso-hydrogen atom, thus leading to a stabilisation of the latter, is discussed in detail.

1 : 8-Dichloroanthrone is converted by acetic anhydride and pyridine into 1 : 8-dichloro-9-anthranyl acetate, m. p. 186°; 4 : 5-dichloro-9-anthranyl acetate, m. p. 163°, is prepared similarly. 1 : 8-Dichloro-9-anthrone with methyl iodide and potassium hydroxide affords 1 : 8-dichloro-10-methyl-9-anthrone, m. p. 204°, whereas 4 : 5-dichloro-9-anthrone appears to yield the anthranyl methyl ether; 1 : 8-dichloro-10-methyl-9-anthranyl acetate, m. p. 210°, is described. 1 : 8-Dichloro-10-benzyl-9-anthrone, m. p. 218°, is converted by pyridine and acetic anhydride into 1 : 8-dichloro-10-benzyl-9-anthranyl acetate, m. p. 176°, whereas, under like conditions, 4 : 5-dichloro-10-benzyl-9-anthrone, m. p. 148°, remains unchanged. With magnesium methyl iodide, 1 : 8-dichloro-10-benzyl-9-anthrone affords 1 : 8-dichloro-9-methyl-10-benzyl-9 : 10-dihydroanthran-9-ol, m. p. 119°, converted by acetic acid containing a little hydrochloric acid into 1 : 8-dichloro-9-methylene-10-benzyl-9 : 10-dihydroanthracene, m. p. 116°, oxidised by chromic acid to 1 : 8-dichloro-10-benzyl-9-anthrone. 4 : 5-Dichloro-9-methyl-10-benzyl-9 : 10-dihydroanthran-9-ol, m. p. 141°, with acetic and hydrochloric acids yields 4 : 5-dichloro-9-methylene-10-benzyl-9 : 10-dihydroanthracene, m. p. 114°. 1 : 8-Dichloro-9 : 10-dibenzyl-9 : 10-dihydroanthran-9-ol, m. p. 195°, with acetic and hydrochloric acids at 100° gives 4 : 5-dichloro-10-benzyl-9-benzylidene-9 : 10-dihydroanthracene, m. p. 151° (oxidised to 4 : 5-dichloro-10-benzylanthrone), also prepared from 4 : 5-dichloro-9 : 10-dibenzyl-9 : 10-dihydroanthran-9-ol, m. p. 191°.

H. WREN.

***ms*-Alkylanthracenes and "transannular tautomerism."** VIII. E. DE B. BARNETT and J. L. WILTSHIRE (Ber., 1929, 62, [B], 3072—3077; cf. preceding abstract).—Anthrone is converted by magnesium *p*-chlorobenzyl chloride followed by dehydra-

tion of the product into 9-*p*-chlorobenzylanthracene, m. p. 129°, transformed by bromine in carbon disulphide into 10-bromo-9-*p*-chlorobenzylanthracene, m. p. 199°, in which the bromine atom is not reactive. 1:5-Dichloroanthrone affords 1:5-dichloro-9-*p*-chlorobenzylanthracene, m. p. 175°, brominated to 1:5-dichloro-10-bromo-9-*p*-chlorobenzylidene-9:10-dihydroanthracene, m. p. 175° after softening (also +0.5C<sub>6</sub>H<sub>6</sub>), in which the bromine atom is readily replaced, yielding the corresponding 10-methoxy-, m. p. 192°, 10-ethoxy-, m. p. 219°, and 10-acetoxy-, m. p. 240°, derivatives. The 10-methoxy-compound is converted by methyl-alcoholic hydrogen chloride into 1:5-dichloro-9-*p*-chloro- $\alpha$ -methoxybenzylanthracene, m. p. 240°. 1:5-Dichloroanthrone, *p*-chlorobenzyl chloride, and potassium hydroxide give 1:5-dichloro-10-*p*-chlorobenzylanthrone, m. p. 184°, converted by magnesium benzyl chloride into 1:5-dichloro-9-benzyl-10-*p*-chlorobenzyl-9:10-dihydroanthran-9-ol, m. p. 155°, according to the rate of heating; 1:5-dichloro-10-*p*-chlorobenzyl-9-benzylidene-9:10-dihydroanthracene, m. p. 168°, is described. 1:5-Dichloro-10-benzyl-9-*p*-chlorobenzyl-9:10-dihydroanthran-9-ol, m. p. 194°, is slowly dehydrated to 1:5-dichloro-10-benzyl-9-*p*-chlorobenzylidene-9:10-dihydroanthracene, m. p. 226°.

H. WREN.

**Hydrocarbons from ergosterol.** O. RYGH (Z. physiol. Chem., 1929, 185, 99—104).—When ergosterol is treated with phosphoryl chloride in pyridine solution, the main product formed is *ergotetraene A*, C<sub>27</sub>H<sub>40</sub>, m. p. 97°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +177° in chloroform. When this is heated with acetic anhydride isomerisation occurs and *ergotetraene B*, m. p. 105°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +93.5° in chloroform, results. Reduction of isomeride *A* with sodium and alcohol affords a dihydro-derivative, m. p. 98°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +121.7° in chloroform; *B* is unaffected by similar treatment. Reduction of *B* with hydrogen in presence of platinum-black and acetic acid at 70°/150 atm. gives a saturated hydrocarbon, C<sub>27</sub>H<sub>48</sub>, m. p. 82—83°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +21.6° in chloroform, similar to the *allo*- $\alpha$ -ergostane of Reindel and Walter (A., 1928, 295). Similar reduction of *A* gives an ill-defined, unsaturated substance. Both *A* and *B* show absorption maxima at 260 m $\mu$ .

H. BURTON.

**Pyrogenic decomposition of chrysene with hydrogen at high pressures.** N. A. ORLOV and N. D. LICHATSCHEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1181—1184).—Chrysene was treated with hydrogen at 450°/100 atm. for 17 hrs. in the presence of anhydrous ferric chloride, yielding a mixture of tetrahydrochrysene, phenanthrene, tetrahydrophenanthrene, naphthalene and its homologues, in accordance with the anticipated mechanism of the reaction. The applicability of this mechanism to the chemistry of coal distillation is discussed. M. ZVEGINTZOV.

**Polynuclear aromatic hydrocarbons and their derivatives.** V. Naphthoanthracenes, the products of their oxidation and a new class of deeply coloured hydrocarbons. E. CLAR and F. JOHN (Ber., 1929, 62, [B], 3021—3029; cf. A., 1929, 922).—The products obtained by the oxidation of 2':3'-naphtho-1:2-anthracene and its homologues, regarded tentatively as phthalylanthrones (cf. A., 1929,

689), are shown to be probably molecular compounds of 1:2-phthalylanthracenes and 1:2:3:4-diphthalylbenzenes. These homogeneous, crystalline compounds, which readily separate from the products of the oxidation of *ang*-naphthoanthracenes and obstinately resist further oxidation, can be separated from one another by reduction with alkali hyposulphite, which does not act on *ang*-phthalylanthracenes. The additive compounds are also prepared by crystallisation of mixtures of their components (1:1). The mol. wt. in freezing anthracene in absence of air is half the expected value. The compound, m. p. 332°, described (*loc. cit.*) as 1'(?4)-keto-7:7'-dimethyl-1':4'-dihydro-2':3'-naphtho-1:2-anthraquinone is derived from 1:4-diketo-7:7'-dimethyl-1:4-dihydro-2':3'-naphtho-1:2-anthracene, m. p. 376°, and 1':4'-diketo-7:7'-dimethyl-1':4'-dihydro-2':3'-naphtho-1:2-anthraquinone, m. p. 334°. 1:4-Diketo-6':7'-dimethyl-1:4-dihydro-2':3'-naphtho-1:2-anthracene, m. p. 376°, is described.

The action of benzoyl chloride and aluminium chloride on *m*-xylophenone affords a mixture of 2:4-dibenzoyl-*m*-xylene and 4:6-dibenzoyl-*m*-xylene, m. p. 104°. The last-named compound condenses when treated as described previously (*loc. cit.*) to aromatic hydrocarbon and a *lin*-dihydronaphthanthracene, C<sub>22</sub>H<sub>16</sub>, m. p. 273°. If the mixture of *lin*-naphthanthracene and its dihydro-derivative is oxidised with chromic acid, 2:3:6:7-dibenzanthraquinone, m. p. 370—371°, is obtained (cf. Mills and Mills, J.C.S., 1912, 101, 2194). Passage of *lin*-naphthanthracene or its dihydro-derivative over metallic copper in a current of carbon dioxide at 370—400°/12—20 mm. yields a dark blue linear hydrocarbon, C<sub>22</sub>H<sub>14</sub>, which when oxidised yields only a monoquinone. A red linear hydrocarbon, C<sub>22</sub>H<sub>16</sub>, m. p. 270°, invariably accompanies the crude mixture of *lin*-naphthanthracene and its dihydro-compound. *ang*-Naphthanthracene when passed over copper as described above affords a stable, blue hydrocarbon, C<sub>24</sub>H<sub>18</sub>, m. p. 360°.

H. WREN.

**General method for preparation of primary and secondary amines.** A. GUYOT and M. FOURNIER (Compt. rend., 1929, 189, 927—929).—When a mixture of an alcohol and ammonia or a primary amine is passed over heated nickel or heated under pressure with this catalyst at 150—200°, almost theoretical yields of the corresponding primary or secondary amine are obtained. *cyclo*Hexanol and ammonia at 150° give *cyclo*hexylamine, whilst at 190° *dicyclo*hexylamine is exclusively formed. Finely-divided cobalt, iron, and copper act in a similar manner.

A. A. GOLDBERG.

**Reaction of magnesium phenyl bromide with hydroxylamine.** A. WEISSBERGER, K. FASOLD, and H. BACH (J. pr. Chem., 1929, [ii], 124, 29—32).—The formation of aniline occurs only to a small extent, alternative reactions predominating. Thus after 30 min. contact there were obtained diphenyl (13%), phenol (4%), unchanged bromobenzene (16—25%), aniline (2—4%), and only 4—6% of the theoretical yield of ammonia. In an atmosphere of nitrogen the yield of aniline was not improved, the products being the same as those given by

magnesium phenyl bromide in absence of hydroxylamine.

R. J. W. LE FÈVRE.

**4 - p - Bromophenylsemicarbazide.** A. S. WHEELER (J. Amer. Chem. Soc., 1929, **51**, 3653—3655).—*p*-Bromophenylcarbamide, m. p. 220°; resolidifying at 225° and decomp. 296° when heated rapidly, or decomp. 296° when heated slowly (cf. Pinnow, A., 1892, i, 460), is obtained by brominating phenylcarbamide in alcohol or acetic acid solution, or from *p*-bromoaniline hydrochloride and aqueous potassium cyanate. Treatment of the above bromocarbamide with hydrazine hydrate in boiling alcohol affords 4-*p*-bromophenylsemicarbazide, decomp. 254°. 4-*p*-Bromophenylsemicarbazones of the following are described: acetone, m. p. 174° (corr.); methyl ethyl ketone, m. p. 175° (corr.); chloroacetone, m. p. 182° (decomp.; corr.);  $\alpha$ -dichloroacetone, m. p. 196° (decomp.; corr.); acetophenone, m. p. 218°, and benzophenone, m. p. 205° (corr.). H. BURTON.

**Formation of N-nitrosoamines from tertiary amines. I. Conversion of derivatives of dimethylaniline by nitrous acid into the corresponding nitrosoamines and monomethylanilines.** W. G. MACMILLAN and T. H. READE (J.C.S., 1929, 2863—2867).—The interaction between nitrodimethylanilines in hydrochloric acid and 50% aqueous sodium nitrite at the ordinary temperature leads to nitrosoamine formation in every case, accompanied frequently by nuclear nitro-compounds, the quantity increasing if the temperature be allowed to rise. Nitrosoamine formation cannot therefore be regarded as a distinctive property of secondary amines. Thus 3-nitrodimethylaniline gives  $\alpha$ -3:4-dinitrodimethylaniline, m. p. 176°, 3:6-dinitrodimethylaniline, m. p. 112°, and 3-nitrophenylmethylnitrosoamine, m. p. 77°; 4-nitrodimethylaniline yields 4-nitrophenylmethylnitrosoamine, m. p. 104°; 3:6-dinitrodimethylaniline gives 3:6-dinitrophenylmethylnitrosoamine, m. p. 128°; 4-bromo-3-nitrodimethylaniline affords 4-bromo-3-nitrophenylmethylnitrosoamine, m. p. 78°, and 4-bromo-3:6-dinitrodimethylaniline, m. p. 109°; and 4-bromo-2-nitrodimethylaniline gives 4-bromo-2-nitrophenylmethylnitrosoamine, m. p. 73°. If the reaction be carried out at 17°, no nuclear substitution occurs (except about 5% for 4-bromo-3-nitrodimethylaniline). The following monomethylanilines were prepared from the corresponding nitrosoamines by hydrolysis in the presence of carbamide and sulphuric acid: 3:6-dinitro-, m. p. 163°; 4-bromo-3-nitro-, m. p. 196°; 4-bromo-2-nitro-, m. p. 103°, and 4-bromo-2:6-dinitro-methylaniline, m. p. 106°.

A. I. VOGEL.

**Interaction of nitroamines with sulphonyl chlorides.** F. BELL (J.C.S., 1929, 2787—2789).—The difficulty experienced in the preparation of disulphonamido-derivatives directly from the nitroamines and arylsulphonyl chlorides, and the ease of conversion of the mono- into the di-sulphonamido-derivatives is attributed to some combination between the nitro- and amino-groups in the former case, and to the greater tendency towards ionisation of the amino-hydrogen of the monosulphonamido-derivatives owing to the presence of the positive nitro-group, in the latter. Interaction of equimolecular quantities of

*m*-nitrobenzenesulphonyl chloride and *o*-nitroaniline in pyridine solution gives *m*-nitrobenzenesulphon-*o*'-nitroanilide, m. p. 165°, and *di-m*-nitrobenzenesulphon-*o*'-nitroanilide, m. p. 179°, separated by crystallisation from benzene. *Di-p*-toluenesulphon-*o*'-nitroanilide, m. p. 191°, and *di-p*-toluenesulphon-*p*'-nitroanilide, m. p. 219°, respectively, were obtained from *p*-toluenesulphonyl chloride and the corresponding toluenesulphon-nitroanilides. *m*-Nitrobenzenesulphon-*p*'-nitroanilide has m. p. 180°. 1:8-Dinitro- $\beta$ -naphthylamine and *p*-toluenesulphonyl chloride give *p*-toluenesulphon-1:8-dinitro- $\beta$ -naphthalide, m. p. 221°, and *di-p*-toluenesulphon-1:8-dinitro- $\beta$ -naphthalide, m. p. 258° (decomp.), separated by crystallisation from acetic acid.

*Di-m*-nitrobenzenesulphon-*o*'-nitroanilide is unaffected by nitric acid (*d* 1.5), and *m*-nitrobenzenesulphon-*p*'- and -*o*'-nitroanilide yield *m*-nitrobenzenesulphon-*o*'*p*'-dinitroanilide, m. p. 210°. *p*-Toluenesulphon-*p*'- and -*o*'-nitroanilide give *p*-toluenesulphon-*o*'*p*'-dinitroanilide, m. p. 161°, with nitric acid (*d* 1.42), converted by nitric acid (*d* 1.5) into *m*-nitro-*p*-toluenesulphon-*o*'*p*'-dinitroanilide, m. p. 220°.

A. I. VOGEL.

**Nitration of *o*-toluidine.** F. GOVAERT (Bull. Soc. chim. Belg., 1929, **38**, 372—374).—When aceto-*o*-toluidide in glacial acetic acid solution is nitrated with acetyl nitrate, the product hydrolysed with hydrochloric acid, and then distilled in steam, 3-nitro-*o*-toluidine, m. p. 95°, is obtained in 53% yield. A poorer yield results if the crude nitration product is crystallised from acetic acid, and the resultant 3-nitroaceto-*o*-toluidide, m. p. 158°; hydrolysed. Nitration with concentrated nitric acid gives erratic results.

A. I. VOGEL.

**3:5:6-Trichloro-*p*-xylylidine and some derivatives.** E. BUREŠ and T. RUBEŠ (Coll. Czech. Chem. Comm., 1929, **1**, 648—657).—See A., 1929, 1057.

**Nitration of  $\beta$ -naphthylamine.** F. BELL (J.C.S., 1929, 2784—2787).—Treatment of *p*-toluenesulphon- $\beta$ -naphthalide in acetic acid solution with nitric and acetic acids gives the 1:6-dinitro-derivative, m. p. 204° (cf. Morgan and Micklethwait, J.C.S., 1912, **101**, 148), hydrolysed by cold sulphuric acid to 1:6-dinitro- $\beta$ -naphthylamine, m. p. 245° (*mono*- and *di*-acetyl derivatives, m. p. 230° and 185°). Dinitration of aceto- $\beta$ -naphthalide (cf. Vesely and Jakes, A., 1923, i, 918) yielded 1:8- and 1:6-dinitroaceto- $\beta$ -naphthalide, m. p. 230°, whilst nitration of *p*-toluenesulphon-5-nitro- $\beta$ -naphthalide, m. p. 158°, afforded *p*-toluenesulphon-1:5-dinitro- $\beta$ -naphthalide, m. p. 182°, hydrolysed by sulphuric acid into 1:5-dinitro- $\beta$ -naphthylamine, m. p. 191°. Nitration of *p*-toluenesulphon-8-nitro- $\beta$ -naphthalide, m. p. 139°, gave *p*-toluenesulphon-1:8-dinitro- $\beta$ -naphthalide, m. p. 221° (decomp.).

*m*-Nitrobenzenesulphon- $\beta$ -naphthalide, m. p. 167—169°, on nitration yields *m*-nitrobenzenesulphon-1:6-dinitro- $\beta$ -naphthalide, m. p. 252° (decomp.), giving by further nitration *m*-nitrobenzenesulphon-1:6:8-trinitro- $\beta$ -naphthalide, m. p. 227° (*pyridine* additive compound, m. p. 212°), converted by sulphuric acid into 1:6:8-trinitro- $\beta$ -naphthylamine, m. p. 300°



(decomp.), and also obtained by nitration of *m*-nitrobenzenesulphon-8-nitro- $\beta$ -naphthalide, m. p. 196°.

A. I. VOGEL.

**Diphenyl and its derivatives.** V. L. MASCARELLI and D. GATTI [with E. JONA and C. F. CAPELO] (Gazzetta, 1929, 59, 858—866).—Partial reduction of 2:2'-dinitrodiphenyl with alcoholic ammonium sulphide yields 2-nitro-2'-aminodiphenyl, an oil [*monoacetyl* derivative, m. p. 151—152° (from aqueous alcohol) or 158° (from benzene); *diacetyl* derivative, m. p. 121—122° and 125°; *picrate*, m. p. 167.5° (darkens at 163°)]. 2:2'-Dinitro-4:4'-dimethyldiphenyl yields similarly the 2-nitro-2'-amino-derivative, an oil [*hydrochloride*, m. p. 129—130°; *monoacetyl* derivative, m. p. 145—146°; *diacetyl* derivative, m. p. 116—117° (sinters at 105°)]. 3:3'-Dinitrodiphenyl, reduced in alcoholic toluene solution, yields 3-nitro-3'-aminodiphenyl, an oil [*hydrochloride*, m. p. 275—276° (decomp.; darkens at 230°, sinters at 250°); *sulphate*, m. p. 156—157°; *nitrate*; *picrate*, decomp. 220° (darkens 192—204°); *chloroplatinate*, darkens 200°, decomp. 260—288°; *acetyl* derivative, m. p. 156—157° (sinters at 115—120°)].

The solubilities of 2:2'-, 3:3'-, and 4:4'-dinitrodiphenyl in alcohol at 20° are, respectively, 0.039, 0.059, and 0.146%.

Attempts to diazotise partly 2:2'-diaminodiphenyl and prepare an iodo-compound by Sandmeyer's reaction have been unsuccessful, a mixture of decomposition products from the tetrazo-compound being obtained.

R. K. CALLOW.

**Reaction of *o*-aminoazo-derivatives with phthalic anhydride.** G. B. CRIPPA and P. GALIMBERTI (Gazzetta, 1929, 59, 825—829).—The reaction previously investigated (A., 1929, 181), in which the benzeneazo-group is eliminated when an *o*-aminoazo-derivative is heated with phthalic anhydride, does not occur with lightly substituted benzene derivatives. Thus *o*-aminoazobenzene yields *o*-phthalimidoazobenzene (I), m. p. 140°, and 2:4-diaminoazobenzene yields 2:4-diphthalimidoazobenzene (II), m. p. 200°. However, 4:6-dibenzeneazo-*m*-phenylenediamine yields *m*-diphthalimidobenzene. Reduction of I yields benzoylenebenziminazole, accompanied by benziminazole-2-benzoic acid, which is converted into benzoylenebenziminazole by heating with acetic anhydride. Similarly II yields 6-phthalimidobenzoylenebenziminazole, m. p. 295°. Hydrolysis of I and II by potassium hydroxide solution yields, respectively, azobenzene-2-phthalamic acid and azobenzene-2:4-diphthalamic acid (*barium* salt), which are dehydrated when heated.

R. K. CALLOW.

**Condensation of 2-benzeneazo-1-naphthylamine-4-sulphonic acid.** G. CHARRIER (Atti R. Accad. Lincei, 1929, [vi], 10, 189—193).—Dehydrogenation of 2-benzeneazo-1-naphthylamine-4-sulphonic acid, suspended in nitrobenzene, by means of an acetic acid solution of chromic anhydride gives a condensation product containing sulphur, m. p. above 300°, exhibiting the characters of a poly-condensed dinitrazole derivative. This compound is provisionally given a constitution analogous to that of dinaphthylene dioxide, from which it may theoretically be derived

by replacing the two oxygen atoms by two SO<sub>2</sub> groups.

T. H. POPE.

**Azo-dyestuffs and their intermediates. I. Constitution and degradation of nitrated 1-diazo-2-naphthol-4-sulphonic acid.** P. RUGGLI, F. KNAPP, E. MERZ, and A. ZIMMERMANN (Helv. Chim. Acta, 1929, 12, 1034—1051).—Decomposition of the nitro-1-diazo-2-naphthol-4-sulphonic acid described in G.P. 164,655 with cuprous oxide in boiling alcohol affords 6-nitro-2-naphthol-4-sulphonic acid (I), oxidised by potassium permanganate solution to 4-nitrophthalic acid (also formed by similar oxidation of the original diazo-derivative). Reduction of I with zinc dust and hydrochloric acid gives 6-amino-2-naphthol-4-sulphonic acid, which on desulphonation by Friedländer and Lucht's method (A., 1894, i, 138) yields 6-amino-2-naphthol, decomp. 212—213° (lit. 190—195°) [dibenzoyl derivative, m. p. 228—230° (lit. 233.5°)]. The dibenzoyl derivative of 5-amino-2-naphthol has m. p. 223° (lit. 223° and 233°). 6-Chloro-2-naphthol-4-sulphonic acid is desulphonated to 6-chloro-2-naphthol, m. p. 115° (cf. Claus and Zimmermann, A., 1881, 915). Diazotisation of the above aminonaphtholsulphonic acid, subsequent decomposition by boiling with dilute sulphuric acid, and final desulphonation of the product formed, affords 2:6-dihydroxynaphthalene. Chlorination of 6-chloro-2-naphthol in acetic acid solution in sunlight gives 1:6-dichloro-2-naphthol, m. p. 119.5°.

1-Diazonaphthalene-4-sulphonic acid is not nitrated under the conditions for the preparation of 6-nitro-1-diazo-2-naphthol-4-sulphonic acid. H. BURTON.

**Reduction of normal diazo-hydrates.** A. ANGELI and Z. JOLLES (Atti R. Accad. Lincei, 1929, [vi], 10, 141—144).—The transformation of normal diazo-hydrates into the corresponding hydrocarbons by means of feeble reducing agents is readily explainable by the formation of an unstable intermediate compound such as phenyldi-imide, NPh:NH, which subsequently decomposes into nitrogen and hydrocarbon (cf. A., 1926, 947). The accuracy of this view is shown by the formation of *s*-benzoylphenylhydrazine when an alkaline solution of benzene-diazonium chloride is reduced by means of sodium stannite in presence of benzaldehyde. A number of other reactions, such as the formation of azoimide and ammonia by the action of dilute sulphuric acid on potassium azodicarboxylate, are similarly explainable by the intermediate formation of unsaturated compounds. The conversion of the normal diazo-hydrate into NPh:NH by reduction renders it highly probable that the oxygen atom is present in the oxide form, O:NPh:NH. Since the action of nitroxyl on the normal diazo-hydrate yields nitrosobenzene and nitrogen, it is possible to remove either the iminic residue or the oxygen atom from the diazo-hydrate. These results support the authors' views concerning the structure of the diazo-hydrates. T. H. POPE.

**Action of aromatic diazo-compounds on lignin and cellulose.** W. KÜSTER and R. DAUR (Cellulosechem., 1930, 11, 4—6).—The coupling of benzenediazonium chloride with primary lignin yields a brown product of azo-character. Repeated treatment of beech-wood meal, free from resins and hemi-

celluloses, with diazobenzene-*p*-sulphonic acid and sodium hydroxide results in the dissolution of all the lignin and the greater portion of the cellulose, leaving a gelatinous and structureless residue. Addition of  $\beta$ -naphthylamine to the solution precipitates a lignin derivative, the analytical data of which suggest that one azobenzenesulphonic acid and one phenol-sulphonic acid group have been attached to a lignin complex containing about 40 carbon atoms. The action of diazo-salts on cellulose (filter-paper) affords a product of increased reducing power and solubility in sodium hydroxide.

T. H. MORTON.

#### *cis-trans*-Isomerism and steric hindrance.

**XI. 2-Ethylcyclohexanols.** G. VAVON and V. M. MITCHONITCH (Bull. Soc. chim., 1929, [iv], 45, 961—972).—Hydrogenation of 2-ethylcyclohexanone, b. p. 67°/13 mm.,  $d_4^{20}$  0.9224,  $n_D^{20}$  1.4528 (*semicarbazone*, m. p. 101°, hydrogenated in aqueous alcohol in presence of hydrochloric acid to 2-ethylcyclohexylsemicarbazide, m. p. 149°; *oxime*, m. p. 60°, yielding 2-ethylcyclohexyl- $\beta$ -hydroxylamine, m. p. 66°, when hydrogenated in aqueous alcohol in presence of hydrochloric acid and platinum-black), in presence of platinum-black in acetic and hydrochloric acids yields *cis*-2-ethylcyclohexanol, b. p. 74°/12 mm.,  $d_4^{20}$  0.9274,  $n_D^{20}$  1.4655 (3 : 5-dinitrobenzoate, m. p. 99°; *phenylurethane*, m. p. 101.5°; *hydrogen phthalate*, m. p. 102—103°). *trans*-2-Ethylcyclohexanol, b. p. 79°/12 mm.,  $d_4^{20}$  0.9193,  $n_D^{20}$  1.4640 (3 : 5-dinitrobenzoate, m. p. 105°; *phenylurethane*, m. p. 82—83°; *hydrogen phthalate*, m. p. 97°), is obtained by hydrogenation with sodium and alcohol (yield 85%) or by heating the sodium derivative of the *cis*-isomeride in hydrogen at 170—180° for 15 hrs. In the absence of a catalyst at 100° the *cis*- and *trans*-alcohols are esterified at approximately the same rate, but in presence of sulphuric acid at 0° and 39° the *trans*-alcohol is esterified about 1.5 times as rapidly as the *cis*-isomeride. Similarly, the *cis*-hydrogen phthalate, which is two to three times as soluble as the *trans*-isomeride, is hydrolysed more slowly, the ratio of the velocity coefficients, *trans/cis*, being 3.7 in water at 39° and 3.5 in 75% alcohol at 69° (cf. Vavon and Callier, A., 1927, 761).

Hydrogenation of *o*-ethylphenol, b. p. 200—201° (*phenylurethane*, m. p. 141°; 3 : 5-dinitrobenzoate, m. p. 108°; *p*-nitrobenzoate, m. p. 56—57°), in acetic acid in presence of platinum-black affords a mixture of *cis*- and *trans*-2-ethylcyclohexanols, b. p. 76—79°/12 mm. (yield 80%), giving 82% of 2-ethylcyclohexanone on oxidation. The *o*-ethylphenol was obtained from the mixture of *o*- (2 parts) and *p*-nitroethylbenzene (1 part) obtained (yield 90%) by nitrating ethylbenzene in sulphuric acid at -5° to 0° with ethyl nitrate (cf. Béhal and Choay, A., 1894, i, 280). *o*-Ethylaniline (yield 77%) and *p*-ethylaniline (yield 87%) were obtained by reduction of the nitroethylbenzene in acetic acid in presence of platinum-black. *p*-Ethylphenol (yield 80% from the amine) has b. p. 214—215°, m. p. 45—46° (*phenylurethane*, m. p. 120°; 3 : 5-dinitrobenzoate, m. p. 132—133°; *p*-nitrobenzoate, m. p. 80—81°). Hydrogenation in presence of platinum-black of 2-ethylidenecyclohexanone, b. p. 77—79°/10 mm.,  $d_4^{20}$  0.9807,  $n_D^{20}$  1.4963 [*semicarbazone*, m. p. 192° (decomp.)], obtained from acetaldehyde and

cyclohexanone in presence of 4—15% sodium hydroxide solution (yield 17%) and dehydration of the ketol by distillation over oxalic acid or potassium hydrogen sulphate, yields the same 2-ethylcyclohexanone. Propaldehyde similarly affords 15% of 2-propylidenecyclohexanone, hydrogenated to 2-propylcyclohexanone (A., 1928, 166). 2-Chlorocyclohexanone and magnesium ethyl bromide when heated at 60—80° after distilling off the ether (cf. Bouveault and Chereau, A., 1906, i, 513) give 50—60% of a mixture of 2-ethylcyclohexanone and ethyl cyclopentyl ketone, b. p. 174—175°,  $d_4^{20}$  0.9177,  $n_D^{20}$  1.4506 (*semicarbazone*, m. p. 134°; *semicarbazide*, m. p. 139—140°; *oxime*, b. p. 106—107°/10 mm.), yielding when hydrogenated in acetic acid in presence of platinum-black ethylcyclopentylcarbinol, b. p. 70°/10 mm.,  $d_4^{20}$  0.9257,  $n_D^{20}$  1.4662 (3 : 5-dinitrobenzoate, m. p. 88—89°; *phenylurethane*, m. p. 56—57°; *hydrogen phthalate*, m. p. 91—92°), this rupture of the six-membered ring taking place even if the reaction is effected in the cold (cf. A., 1928, 634).

R. BRIGHTMAN.

Changes in molecular structure during chemical reactions. I. Thermal decomposition of esters and rearrangements occurring thereby. W. HÜCKEL, A. NEUNHOEFFER, A. GERCKE, and E. FRANK (Annalen, 1929, 477, 99—160).—I. Elimination of water from *cis*- and *trans*-2-cyclohexylcyclohexanols (supposed isomerism of dicyclohexyl).—Reduction of 2-cyclohexylcyclohexanone with sodium and alcohol affords *trans*-2-cyclohexylcyclohexanol, b. p. 265—268°/748 mm., m. p. 52° (lit. 53—54°) [*phenylcarbimide* derivative, m. p. 136° (lit. 132°); *p*-toluenesulphonate, m. p. 122°; *oxalate*, m. p. 80°], formed also by catalytic reduction of *trans*-2-cyclohexenylcyclohexanol, m. p. 42° (lit. 34—35°) (*hydrogen phthalate*, m. p. 168°), in presence of methyl alcohol and palladised charcoal. Reduction of 2-cyclohexylcyclohexanone by Skita's method, or of 2-hydroxydiphenyl by Adams' method, gives *cis*-2-cyclohexylcyclohexanol, b. p. 264—267°/748 mm., m. p. 63° (lit. 60°) [*phenylcarbimide* derivative, m. p. 153° (lit. 148°)]. Dehydration of the last-named alcohol with zinc chloride at 180—190° (cf. Schrauth and Görig, A., 1923, i, 1084) furnishes a quantitative yield of nearly pure  $\Delta^1$ -cyclohexylcyclohexene, b. p. 234°/748 mm., m. p. -41°,  $d_4^{20}$  0.9071,  $n_D^{20}$  1.49556 (nitroschlorides, m. p. 115° and 140°), reduced catalytically (palladised charcoal) to dicyclohexyl, b. p. 232.5°/736 mm., m. p. 0°. The dicyclohexyl obtained by catalytic reduction (Adams) of diphenyl (prepared by the Fittig reaction) has b. p. 233°/736 mm., m. p. 2.25°,  $d_4^{20}$  0.8862,  $n_D^{20}$  1.47977; if the dicyclohexyl contains moisture, a well-defined fraction b. p. 227—229°, is also obtained. Oxidation of  $\Delta^1$ -cyclohexylcyclohexene with alkaline potassium permanganate yields adipic acid, whilst treatment with ozone in acetic acid solution and subsequent oxidation with permanganate affords  $\epsilon$ -keto- $\epsilon$ -cyclohexylhexoic acid. Similar dehydration of *trans*-2-cyclohexylcyclohexanol furnishes a mixture of unsaturated hydrocarbons, b. p. 231—234°/736 mm., m. p. -50°, hydrogenated to a mixture of hydrocarbons, b. p. 230—233°/736 mm. Ozonisation of the unsaturated hydrocarbons and subsequent oxidation with permanganate affords  $\epsilon$ -keto- $\epsilon$ -cyclohexylhexoic acid and

oily products. Oximation of the aldehyde mixture obtained from the ozonisation, rearrangement of the oximes with phosphorus pentachloride in ether, and subsequent hydrolysis affords, in addition to adipic acid, hexahydrobenzoic acid, cyclohexylamine, and some cyclohexylacetic acid (amide, m. p. 167—168°), thus showing that  $\Delta^1$ -cyclohexylcyclohexene and  $\Delta^1$ -hexahydrobenzylcyclopentene are present in the original mixture. The cyclopentene derivative is formed by a ring contraction similar to that described by Vavon and Mitchovitch (A., 1928, 516). No evidence was obtained for the presence of a third substance in the unsaturated hydrocarbon mixture. Contrary to the statement of Schrauth and Görig (*loc. cit.*) there appears to be only one dicyclohexyl.

**II. Elimination of water from *cis*- and *trans*-2-cyclopentylcyclopentanol.**—Reduction of 2-cyclopentylcyclopentanone with sodium and alcohol gives mainly the *trans*-alcohol, whilst catalytic reduction (Skita) affords mainly the *cis*-alcohol. The mixtures obtained are purified through the hydrogen phthalates, yielding *cis*-, b. p. 113°/13 mm., m. p. 23°,  $d_4^{25}$  0.9730,  $n_D^{25}$  1.48772 (*phenylcarbimide* derivative, m. p. 86°; *p*-toluenesulphonate, m. p. 51°; *hydrogen phthalate*, m. p. 93—95°), and *trans*-2-cyclopentylcyclopentanol, b. p. 112—113°/12 mm.,  $d_4^{25}$  0.9792,  $n_D^{25}$  1.48878 (*phenylcarbimide* derivative, m. p. 92.5°; *p*-toluenesulphonate, m. p. 44—47°, and *hydrogen phthalate*, m. p. 111°). Dehydration of either of the alcohols with zinc chloride at 140° affords 1:2:3:4:5:6:7:8-octahydronaphthalene (blue nitrosochloride, m. p. 91°) as the main product (cf. Zelinski, Titz, and Fatejev, A., 1927, 47); a small amount of a second hydrocarbon [colourless nitrosochloride, m. p. 111° (cf. Wallach, A., 1912, i, 568)] is also obtained from the *cis*-derivative. The changes occurring during the dehydration are probably (i) a ring enlargement, (ii) a pinacol change, and (iii) elimination of water from the formed pinacol-alcohol.

**III. Behaviour of esters of secondary alcohols on hydrolysis and thermal decomposition.**—cycloHexyl *p*-toluenesulphonate, m. p. 44—45°, is hydrolysed by prolonged treatment with water, dilute hydrochloric acid, concentrated sodium or copper acetate solution, and concentrated barium hydroxide solution at 100° to cyclohexene; some cyclohexyl acetate is also obtained if hydrolysis is carried out with concentrated lead acetate solution and 5% acetic acid. The *p*-toluenesulphonate, m. p. 97—98°, of *l*-fenchyl alcohol is hydrolysed by 15% sodium hydroxide solution at 125—130° to 96% of  $\alpha$ -fenchene and 4% of a fenchyl alcohol, the *p*-nitrobenzoate, m. p. 123°, of which is not identical with the  $\alpha$ - and  $\beta$ -esters described by Kenyon and Priston (A., 1925, i, 941). The *p*-toluenesulphonate, m. p. 96°, of *cis*- $\alpha$ -decahydronaphthol, m. p. 93°, is decomposed by boiling with methyl alcohol to 1:2:3:4:5:6:7:8-octahydronaphthalene. Oxidation of this hydrocarbon with alkaline potassium permanganate affords a glycol, m. p. 68—69°, succinic acid, and oily acids; distillation of the oil with acetic anhydride gives a ketone (semicarbazone, m. p. 189°). Reduction of *trans*- $\alpha$ -ketodecahydronaphthalene with hydrogen in presence of acetic acid, colloidal platinum, chloroplatinic and hydrochloric acids at 50°, and purifica-

tion of the alcohol formed through the hydrogen phthalate and hydrogen oxalate, gives a new *trans*- $\alpha$ -decahydronaphthol, b. p. 232.5° (corr.)/745 mm., m. p. 49°, the *p*-toluenesulphonate, m. p. 68—69°, of which is also decomposed by boiling with methyl alcohol. The *p*-toluenesulphonates of *trans*- $\alpha$ -, m. p. 63°, *cis*- $\beta$ -, m. p. 105°, *trans*- $\beta$ -, m. p. 75°, and *trans*- $\beta$ -decahydronaphthols, m. p. 53°, have m. p. 99—100°, 77—78°, 63°, and 111°, respectively; these esters are all stable towards boiling methyl alcohol. The above esters containing two adjacent methylene groups are all stable, as are the esters containing a *trans*-alkyl group adjacent to the ester group. An adjacent *cis*-alkyl group, however, renders the ester unstable, and fission to the acid and hydrocarbon readily occurs.

Treatment of the potassium derivatives of *l*-fenchyl alcohol and *trans*- $\beta$ -decahydronaphthol, m. p. 75°, with phosphoryl chloride in toluene affords the corresponding neutral phosphates, m. p. 160° and 159°, respectively. These esters are unaffected by prolonged treatment with alcoholic potassium hydroxide at 160—170°. Hydrolysis of the phosphites of *cis*- $\beta$ -, m. p. 105°, and *trans*- $\beta$ -decahydronaphthol, m. p. 75°, and *l*-menthol regenerates the original alcohol. Similar results are found for the oxalates, m. p. 100°, 111°, and 142°, respectively, of *cis*- $\alpha$ -, m. p. 93°, *trans*- $\alpha$ -, m. p. 63°, and *trans*- $\alpha$ -, m. p. 49°-decahydronaphthols, respectively (cf. A., 1927, 238). Fenchyl alcohol and boric acid react at 125°, yielding the borate,  $C_{30}H_{51}O_3B$ , m. p. 147°. The borate, m. p. 155°, of *trans*- $\alpha$ -decahydronaphthol, m. p. 63°, is only slowly hydrolysed by alkali, regenerating the original alcohol. cycloHexanol, *cis*- $\alpha$ -, m. p. 93°, *trans*- $\beta$ -, m. p. 75°, and *cis*- $\beta$ -, m. p. 105°-decahydronaphthols do not react with boric acid. The following orthosilicates are prepared by heating the alcohol with silicon tetrachloride in absence of moisture, the m. p. of the ester being given in parentheses: *l*-menthol (102—103°); *cis*- $\alpha$ -, m. p. 93 (116—118°); *trans*- $\alpha$ -, m. p. 63° (105°); *cis*- $\beta$ -, m. p. 105° (97—98°), and *trans*- $\alpha$ -, m. p. 75°-decahydronaphthols (124—125°). All the silicates are extraordinarily stable towards boiling 50% potassium hydroxide solution, but are rapidly hydrolysed by acids; this indicates fission of the silicon-oxygen linkings.

The reactions described support Skita's conclusions (A., 1920, i, 832) that a stable alcohol (*trans*) is formed during alkaline reduction of a ketone, whilst the unstable (*cis*) form is produced by catalytic reduction in acid media. Isomerides prepared under similar experimental conditions show similar reactivity, and it is thought that the instability of the *cis*-esters is related to the polar forces (as measured by the dipole moment) in the molecule. It is suggested that both *cis*- and *trans*-elimination of water occurs during the dehydration of alcohols.

H. BURTON.

**Chlorination of phenol with dichlorocarbamide.** M. V. LICHOSCHERSTOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1019—1023).—*s*-Dichlorocarbamide chlorinates phenol in aqueous alkaline solutions, but considerable oxidation occurs, and the yields are low. In the presence of hydrochloric acid, however, the reaction proceeds smoothly, *o*- and *p*-chloro-, 2:4-dichloro-, and 2:4:6-trichloro-phenols being

obtained, and carbamide regenerated. The chlorination can be easily controlled. M. ZVEGINTZOV.

**Bromination of phenol with dichlorocarbamide and potassium bromide.** M. V. LICHOSCHERSTOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1025—1028; cf. preceding abstract).—*s*-Dichlorocarbamide reacts in aqueous solution with potassium bromide, liberating bromine and regenerating carbamide. The bromine can be used quantitatively to brominate phenol, *o*- and *p*-bromophenols being obtained. M. ZVEGINTZOV.

#### Halogenation of phenolic ethers and anilides.

**I. Bromination of ethers in 50% acetic acid.** A. E. BRADFIELD, B. JONES, and K. J. P. ORTON (J.C.S., 1929, 2810—2817).—A study has been made of the rates of interaction of bromine and certain *p*-chloro- and *p*-bromo-phenyl ethers in the presence of 5 and 10 mols. of hydrobromic acid in a medium consisting of equal volumes of glacial acetic acid and water ("50% acetic acid") at 20°. A constant value for the velocity coefficient is not obtained when, in the application of the mass law expressions, the concentration of the bromine is placed equal to that of the titratable bromine (cf. Bradfield and Jones, A., 1928, 628), since only that portion of the bromine "unfixed" as perbromide in the reaction  $\text{Br}_2 + \text{Br} = \text{Br}_3'$  is active in substitution reactions. By assuming that the concentration of the "unfixed" bromine is always at the equilibrium value and the relation between the "unfixed" and the total bromine concentrations is given by  $K = [\text{Br}_2][\text{Br}]/[\text{Br}_3']$ , an expression for the velocity coefficient,  $k'$ , has been deduced, from which  $K$  has been computed to be 0.021, in good agreement with values deduced by other methods (cf. W. J. Jones, J.C.S., 1911, 99, 392). The velocity coefficients found with 10 mols. of hydrobromic acid (with 5 mols. there is a small but regular downward drift as the reaction progresses) were: *p*-chloro-, 0.665, and *p*-bromo-anisole, 0.715; *p*-chloro-, 1.51, and *p*-bromophenetole, 1.66; *p*-chloro-, 4.77, and *p*-bromo-phenyl isopropyl ether, 5.06. The relative directive effects of the groups OR and of chlorine and bromine in these halogenophenyl ethers have been calculated; the effects of the methyl, ethyl, and isopropyl groups are independent of the nature of the *p*-substituent, and those of the *p*-chloro- and *p*-bromo-groups are independent of the nature of the alkyl group.

The velocity of bromination of ethers increases rapidly with increasing water content of the medium.

A. I. VOGEL.

**Halogenation of anisole derivatives.** H. H. HODGSON and A. KERSHAW (J.C.S., 1929, 2917—2923).—Reduction of 3-chloro-2-nitroanisole with tin and hydrochloric acid gives 3:5-dichloro-*o*-anisidine, from which is prepared 2:3:5-trichloroanisole (I), m. p. 84°. This was synthesised by nitrating *m*-chloroacetanilide in glacial acetic acid solution with nitric (*d* 1.5) and sulphuric acids, hydrolysing the 3-chloro-4- and -6-nitroacetanilides produced with hydrochloric acid, and separating the two amines by distillation in steam (the 3-chloro-6-nitroaniline is volatile) or by crystallisation from alcohol (3-chloro-4-nitroaniline is less soluble). The last-named com-

pound was converted by potassium chlorate and concentrated hydrochloric acid at 50° into 2:3:6-trichloro-4-nitroaniline, m. p. 143°, then by the diazo-reaction into 2:3:5-trichloronitrobenzene, m. p. 45° (also obtained from 2:4-dichloroaniline through 2:4-dichloro-6-nitroacetanilide, and 2:4-dichloro-6-nitroaniline), 2:3:5-trichloroaniline, m. p. 73°, by iron and acetic acid, 2:3:5-trichlorophenol, m. p. 62°, and finally by methyl sulphate and alkali into I.

3-Chloro-2-iodoanisole dichloride, m. p. 72°, passes spontaneously on keeping into 3:4-dichloro-2-iodoanisole (II), m. p. 84°. This was synthesised by successive conversion of *o*-dichlorobenzene into 1:2-dichloro-4-nitrobenzene, 3:4-dichloroaniline (with iron and acetic acid), 3:4-dichlorophenol, m. p. 65°, 3:4-dichloro-2-nitrophenol, m. p. 76° [with nitric acid (*d* 1.5) and fuming sulphuric acid], 3:4-dichloro-2-nitroanisole, m. p. 126°, and II. 3:6-Dichloro-2-iodoanisole, m. p. 21°, was prepared from 2:5-dichlorophenol through 3:6-dichloro-2-nitrophenol, m. p. 70° (by sulphonation and hydrolysis with steam), 3:6-dichloro-2-nitroanisole, m. p. 70°, and 3:6-dichloro-*o*-anisidine (hydrochloride).

3-Chloroanisole-2-diazoperbromide yields 3-chloro-2:4-dibromoanisole and not the 2:6-compound as previously described (Hodgson and Kershaw, A., 1928, 284). Sulphonation of *m*-chlorophenol at 100° occurs almost entirely in the *p*-position, since on dibromination and subsequent desulphonation 3-chloro-2:4-dibromophenol is obtained.

An electronic interpretation of these results on the basis of current electronic theories is given, 3:*N*-dichloro-*o*-anisidine and 3-chloro-2-iodoanisole being assumed as intermediate products for 3:5-dichloro-*o*-anisidine and 3:4-dichloro-2-iodoanisole, respectively. A. I. VOGEL.

**Supposed 3-nitro-4-ethanesulphonamidophenetole of Autenrieth and Bernheim.** F. REVERDIN (Helv. Chim. Acta, 1929, 12, 1051—1052).—The substance, m. p. 179°, described by Autenrieth and Bernheim (A., 1905, 1, 47) as the mononitro-derivative of 4-ethanesulphonamidophenetole, is shown to be identical with 3:5-dinitro-4-ethanesulphonamidophenetole, m. p. 182° (A., 1929, 310).

H. BURTON.

**Nitration of aromatic compounds in alcoholic solution.** F. REVERDIN (Helv. Chim. Acta, 1929, 12, 1053—1059; cf. A., 1929, 1289).—Nitration of *p*-chloroacetamidobenzene with nitric acid (*d* 1.4) in alcoholic solution at 56° affords 3-nitro-4-chloroacetamidobenzene, m. p. 104° (A., 1923, i, 320). With acid of *d* 1.18 in presence of boiling alcohol, nitration and hydrolysis occurs. 3-Nitro-4-chloroacetamidophenetole, m. p. 95°, is obtained by both the above methods, but some hydrolysis occurs with the acid of *d* 1.18. Methanesulphon-*p*-anisidine, m. p. 115°, is converted by nitric acid (*d* 1.18) in hot alcoholic solution into 3-nitro-4-methanesulphonamidobenzene, m. p. 125°; with acid of *d* 1.4, 3:5-dinitro-4-methanesulphonamidobenzene, m. p. 183°, results. Similarly, ethanesulphon-*p*-anisidine, m. p. 69°, yields 3-nitro-, m. p. 95°, and 3:5-dinitro-4-ethanesulphonamidobenzene, m. p. 163°; benzenesulphon-*p*-anisidine gives 3-nitro-, m. p. 87°, and 3:5-dinitro-4-benzene-

*sulphonamidoanisoles*, m. p. 176°; benzenesulphon-*p*-phenetide, m. p. 142° (lit. 136°), furnishes 3-nitro-, m. p. 75° (lit. 72°), and 3:5-dinitro-4-benzenesulphonamidophenoles, m. p. 174–175°. Attempted nitration of form-*p*-anisidide, m. p. 81°, and form-*p*-phenetide, m. p. 68.5°, under similar conditions, causes hydrolysis. The results now and previously obtained (*loc. cit.*) are reviewed briefly.

H. BURTON.

**Oxidation of arylthiolarlydes.** III. E. GEBAUER-FÜLNEGG and E. RIESZ (Monatsh., 1929, 52, 365–371).—4-Chloro-2-nitro-1-chlorothiobenzene condenses in ethereal or in benzene solution with various primary and secondary aromatic amines. Ethylaniline in ether gives 4-chloro-2-nitro-1-phenyl-ethylaminothiobenzene, m. p. 74°, converted by oxidation with potassium dichromate or hydrogen peroxide in boiling glacial acetic acid into a compound,  $C_{14}H_{13}O_4N_2S$ , m. p. 110–120°, the identity of which with 4-chloro-2-nitrobenzenesulphon-N-ethylanilide, m. p. 122°, prepared from 4-chloro-2-nitrobenzenesulphonyl chloride and ethylaniline, is uncertain; *p*-chloroaniline in ether affords 4-chloro-2-nitro-1-*p*-chloroanilinothiobenzene, m. p. 172°; *o*- and *p*-toluidine in benzene furnish, respectively, 4-chloro-2-nitro-1-*o*-tolylaminothiobenzene, m. p. 123°, and 4-chloro-2-nitro-1-*p*-tolylaminothiobenzene, m. p. 137°; 4-chloro-2-nitro-1-(2':4'-dichloroanilino)thiobenzene, m. p. 154°, is oxidised by hydrogen peroxide in boiling acetic acid to an amorphous product; 4-chloro-2-nitro-1- $\alpha$ -naphthylaminothiobenzene, m. p. 180°, and 4-chloro-2-nitro-1- $\beta$ -naphthylaminothiobenzene, m. p. 176°, yield amorphous products by oxidation; mesidine affords 4-chloro-2-nitro-1-(2':4':6'-trimethylanilino)thiobenzene, m. p. 178°, which by oxidation with hydrogen peroxide in boiling glacial acetic acid gives a water-soluble product, thereby differing from the foregoing compounds, and by use of milder conditions yields the starting material; 4-chloro-2-nitro-1-*p*-phenetidinothiobenzene, m. p. 86°, is converted into amorphous products by oxidation; *s*-di-4-chloro-2-nitrophenylthiol-*m*-phenylenediamine, decomp. 70–80°, gives a brownish-black, amorphous substance by oxidation. With di-*o*-substituted amines, *e.g.*, trichloro- or tribromo-aniline, or 2:4-dichloro-1-naphthylamine, 4-chloro-2-nitro-1-chlorothiobenzene does not condense either in high-boiling media or in the presence of aluminium chloride. C. W. SHOPPEE.

**Stereoisomeric resorcitols [cyclohexane-1:3-diols] and phloroglucitols [cyclohexane-1:3:5-triols].** H. LINDEMANN and H. BAUMANN (Annalen, 1929, 477, 78–98).—Reduction of resorcinol with hydrogen in presence of water, alcohol, or decalin and a nickel-cobalt-copper catalyst at 100–125° affords a mixture, b. p. 140–150°/13 mm., of *cis*- and *trans*-cyclohexane-1:3-diols; relatively small amounts of cyclohexane and cyclohexanol are formed as by-products. The above mixture is converted by hydrobromic acid into *cis*-, m. p. 112°, and *trans*-1:3-dibromocyclohexanes, b. p. 116°/16 mm., m. p. 1°. Acetylation of the above mixture affords the inseparable mixture of acetates, whilst benzylation (pyridine method) furnishes *cis*-, m. p. 65°, and *trans*-cyclohexane-1:3-diol dibenzoates, m. p. 121–123°, separable through their differing solubilities in alcohol.

Treatment of the above *trans*-dibromide with silver acetate gives *trans*-cyclohexane-1:3-diol diacetate, b. p. 95°/0.4 mm., together with the acetate, b. p. 35°/0.3 mm., of  $\Delta^3$ -cyclohexenol, b. p. 61°/19 mm. (phenylcarbimide derivative, m. p. 83°;  $\alpha$ -naphthylcarbimide derivative, m. p. 127°). Treatment of the diol mixture with phenylcarbimide yields the *cis*-bisphenylcarbimide derivative, m. p. 213° (corresponding *bis*- $\alpha$ -naphthylcarbimide derivative, m. p. 245°); the *trans*-isomeride could not be obtained pure. Triphenylmethylation of the diol mixture affords the *cis*-, m. p. 144°, and *trans*-di(triphenylmethyl) ethers, m. p. 199°, separable by their differing solubilities in warm ethyl acetate. Hydrolysis of the former ether with hydrochloric acid in acetone solution gives *cis*-cyclohexane-1:3-diol, b. p. 141°/13 mm., m. p. 83°, also obtained by distillation of its bisphenylcarbimide derivative with potassium hydroxide. *trans*-cyclohexane-1:3-diol, b. p. 142–143°/20 mm., is prepared by similar hydrolysis of the above ether. The *bis*-1-menthylcarbimide derivative, m. p. 157°,  $[\alpha]_D^{25}$  –64.73° in alcohol, of the *cis*-diol is hydrolysed by methyl-alcoholic potassium hydroxide solution at 100°, regenerating the inactive *cis*-diol.

Similar hydrogenation of phloroglucinol in presence of decalin affords 30% of a mixture of  $\alpha$ - (+2H<sub>2</sub>O), m. p. about 110°, m. p. (anhydrous) 184° (cf. Wislicenus, A., 1894, i, 235) (triacetate, m. p. 79°; trisphenylcarbimide derivative, m. p. 245°), and  $\beta$ -cyclohexane-1:3:5-triols, m. p. 145° (trisphenylcarbimide derivative, m. p. 160°).

H. BURTON.

**Nitrosation of phenols.** VII. Resorcinol monomethyl ether and *m*-cresol. H. H. HODGSON and H. CLAY (J.C.S., 1929, 2775–2778).—Contrary to Henrich and Rhodius (A., 1902, i, 447) and in agreement with Henrich and Eisenach (A., 1904, i, 1007), it is shown that nitrosation of resorcinol monomethyl ether yields almost exclusively 6-nitroso-3-methoxyphenol, since oxidation with dilute nitric acid gave a nearly quantitative yield of 6-nitro-3-methoxyphenol, m. p. 95° (also produced with hydrogen peroxide and with alkaline potassium ferricyanide). The constitution of the latter was proved by heating with potassium carbonate and methyl sulphate in xylene solution at 140° for 8 hrs., when 4-nitroresorcinol dimethyl ether, m. p. 74°, identical with the substance prepared from 3-chloro-4-nitro-anisole or by the action of excess of methyl-alcoholic sodium methoxide on 1:3-dichloro-4-nitrobenzene, was produced. Nitration of resorcinol monomethyl ether in glacial acetic acid solution with nitric acid (*d* 1.5) below 0° afforded chiefly 6-nitro-3-methoxyphenol, together with a small quantity of 4-nitro-3-methoxyphenol, m. p. 144°, separable by distillation in steam. Nitrosation of *m*-cresol yielded 6-nitroso-*m*-cresol (oxidised to 6-nitro-*m*-cresol), together with a small quantity of 4-nitro-*m*-cresol. An explanation of these results on the basis of current electronic theories is given.

A. I. VOGEL.

**Aromatic allyl and propenyl compounds.** H. I. WATERMAN and R. PRIESTER (Rec. trav. chim., 1929, 48, 1272–1277).—A study of the interactions of eugenol and isoeugenol and their benzoates in carbon tetrachloride solution with iodine showed that

(as with safrole and isosafrole) the allyl compounds can absorb more iodine than the corresponding propenyl compounds (cf. A., 1929, 999). During the iodination of eugenol isomerisation to isoeugenol must therefore occur.

The setting and melting point of pure isosafrole is 6.7° to 6.8° and of eugenol, -9.2° to -9.1°.

R. J. W. LE FÈVRE.

**Aromatic allyl and propenyl compounds. Geometrical isomerides of isoeugenol.** H. I. WATERMAN and R. PRIESTER (Rec. trav. chim., 1929, 48, 1278—1279).—Liquid commercial isoeugenol does not contain a geometrical isomeride of isoeugenol, since when dissolved in benzene and shaken with mercuric acetate solution (to remove contaminating eugenol) it gave, after distillation in a cathode vacuum, only crystalline isoeugenol, m. p. 29.4—29.8°,  $n_D^{20}$  1.5777. It is, therefore, merely a mixture of eugenol and isoeugenol. R. J. W. LE FÈVRE.

**Rupture of naphthylmethane derivatives by hydrogenation under pressure.** W. N. IPATIEV and B. N. DOLGOV (Bull. Soc. chim., 1929, [iv], 45, 950—961; cf. A., 1926, 949; 1927, 866, 1060).—When hydrogenated under pressure dihydroxydinaphthyl- and phenyldihydroxydinaphthyl-methanes are converted into the corresponding xanthen by elimination of water, the xanthen subsequently undergoing further hydrogenation and yielding by fission of the molecule in two directions hydrogenated naphthalenes or naphthols. Thus,  $\beta\beta'$ -dihydroxydi- $\alpha$ -naphthylmethane, m. p. 192—193°, in cyclohexane at 250—260°/80—100 atm. in presence of nickel oxide yields tetrahydronaphthalene,  $\beta$ -decahydronaphthol, a mixture of hydrogenated naphthols, methyl- $\beta$ -naphthol, possibly partly hydrogenated, and a viscous oil, b. p. 255—270°/18 mm., probably an octahydrobenzoxanthen,  $C_{10}H_{10}<\begin{smallmatrix} CH_2 \\ O \end{smallmatrix}>C_{10}H_{10}$ . The intermediate 2-hydroxydi- $\alpha$ -naphthylmethane has not been isolated, although its existence is indicated by earlier work (Ipatiev and Orlov, A., 1927, 251), but this decomposes in two ways, yielding 1-methylnaphthalene and  $\beta$ -naphthol or naphthalene and 1-methyl- $\beta$ -naphthol. Similarly, phenyl- $\beta\beta'$ -dihydroxydinaphthylmethane, m. p. 197°, at 250—280° yields 1—3% of gaseous hydrocarbons, a crystalline product, m. p. 167—168°, probably a phenyloctahydrodibenzoxanthen, naphthalene and hydrogenated naphthalenes,  $\beta$ -decahydronaphthol, a fraction, b. p. 193—199°/18 mm.,  $d_4^{15}$  0.9738, probably a mixture of highly hydrogenated xanthen, and a fraction, b. p. 185—186°/18 mm.,  $d_4^{15}$  0.9806,  $n_D^{20}$  1.5249, representing the hydrogenation product of 1-benzyl-naphthalene, fission of the intermediate phenol into naphthalene and benzyl- $\beta$ -naphthol being the main, and into benzyl-naphthalene and  $\beta$ -naphthol the side reaction. Diphenyl- $\alpha$ -naphthylcarbinol, m. p. 133°, when hydrogenated at 250° yields diphenyl- $\alpha$ -naphthylmethane, m. p. 149.5°; at 280—290° the latter is converted into dicyclohexylmethane, b. p. 246—252°,  $d_4^{25}$  0.882,  $n_D^{20}$  1.4822, and hydrogenated naphthalenes, a result indicating that the methane carbon atom is much more firmly attached to the benzene than to the naphthalene nuclei. These results confirm previous observations (Kauffmann and Egner, A., 1914, i, 39;

Wolff, A., 1893, i, 222) that the presence of naphthalene rings promotes the formation of xanthen.

R. BRIGHTMAN.

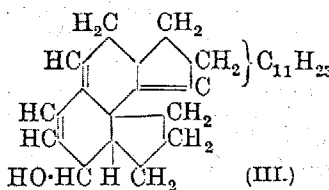
**Trimercapto- $\beta$ -naphthol.** E. BLUMENSTOCK-HALWARD and E. RIESZ (Monatsh., 1929, 52, 377—378).—By reduction in acetone solution with zinc dust and concentrated hydrochloric acid  $\beta$ -naphthol-3:6:8-trisulphonyl chloride (I) yields 3:6:8-trithiol- $\beta$ -naphthol, which is very sensitive to oxidation and is isolated as the tri-lead salt by treatment with lead acetate, or as the tripicryl derivative by heating its alcoholic solution with picryl chloride and sodium acetate. By simultaneous reduction and acetylation I affords 3:6:8-triacetylthiol- $\beta$ -naphthyl acetate, m. p. 134°.

C. W. SHOPPEE.

**Configuration of inactive inositol.** S. POSTERNAK and T. POSTERNAK (Helv. Chim. Acta, 1929, 12, 1165—1181).—A more detailed account of work previously reviewed (A., 1929, 807). H. BURTON.

**Sterol group. VIII. Reactions of isoergosterol.** I. M. HEILBRON and F. S. SPRING (J.C.S., 1929, 2807—2810).—Reindel, Walter, and Rauch's isoergosteryl acetate (A., 1927, 241), obtained from ergosteryl  $\beta$ -acetate and dry hydrogen chloride, is shown to be a mixture separable by fractional crystallisation from benzene and alcohol (1:2) of  $\alpha$ -isoergosteryl acetate, m. p. 139°,  $[\alpha]_D^{25}$  -90.3° in chloroform, and  $\beta$ -isoergosteryl acetate, m. p. 111—112°,  $[\alpha]_D^{25}$  -58.9° in chloroform. Both isomerides exhibit an absorption band at 247  $\mu$ , but a slight difference exists in their molecular extinction coefficients. Hydrolysis with 5% alcoholic potassium hydroxide gives  $\alpha$ -isoergosterol (I), m. p. 143—144°,  $[\alpha]_D^{25}$  -134.2° in chloroform, yielding a deep yellow colour with antimony trichloride and a pink colour with the Rosenheim reagent, and also obtained in nearly quantitative yield by refluxing ergosterol with 10% alcoholic sulphuric acid for 1 hr., and  $\beta$ -isoergosterol (II), m. p. 135°,  $[\alpha]_D^{25}$  -95° in chloroform, respectively. Four atoms of hydrogen are absorbed on hydrogenation in ethereal solution in the presence of palladium of both I and II,  $\alpha$ -ergosterol, m. p. 130—131°, being formed. Reindel, Walter, and Rauch's statement (*loc. cit.*) that three ethylenic linkages are saturated on hydrogenation with platinum is erroneous. Reduction of I with sodium and amyl alcohol yielded dihydroisoergosterol, m. p. 181—182°,  $[\alpha]_D^{25}$  -77.7° in chloroform (acetate, m. p. 183°). The mechanism of the conversion of ergosterol into isoergosterol is discussed and it is concluded that the isomerisation is due to a shift of the 6:7 double linking. Reindel and others' suggestion (*loc. cit.*) of the production of a conjugated system during the isomerisation has been confirmed by the formation of an additive compound of  $\beta$ -isoergosteryl acetate and

maleic anhydride, m. p. 159° (cf. Diels and Alder, A., 1928, 1018); no condensation is obtained with  $\alpha$ -isoergosteryl acetate, this being attributed to a difference in spatial positions of the respective ring systems. If one of





the double linkings in ergosterol occupies the  $\Delta^{1:13}$  position, the shift takes place to position  $\Delta^{2:3}$ , the isergosterols being formulated as III.

A. I. VOGEL.

**Action of thionyl chloride on cholesterol and other alcohols.** P. J. DAUGHENBAUGH and J. B. ALLISON (J. Amer. Chem. Soc., 1929, **51**, 3665—3667).—When cholesterol is treated with the theoretical amount of thionyl chloride in pyridine solution, *cholesteryl sulphite*, m. p. 186.5—187°, is obtained. Sulphites are obtained similarly from ethyl and butyl alcohols, and phenol. Cholesteryl sulphite is stable to aqueous acid or alkali but is hydrolysed by boiling with 30% alcoholic potassium hydroxide solution. Similar treatment of glucose diisopropylidene ether in ethereal pyridine solution affords a *sulphite*. When cholesterol is treated with an excess of thionyl chloride and a small amount of pyridine, and the mixture boiled, a quantitative yield of cholesteryl chloride results. With the sugar derivative in ethereal pyridine, little or no sulphur dioxide is eliminated when the reaction mixture is boiled. The product formed is hydrolysed to the original sugar. Cholesterol, under similar conditions, yields about 80% of the chloride and 20% of the sulphite.

H. BURTON.

**Nor-*d*- $\psi$ -ephedrine, a convenient base for the resolution of externally compensated acids. Resolution of *dl*-benzenesulphonylalanine and of *dl*-*N*-phenylalanineamide-4-arsinic acid.** C. S. GIBSON and B. LEVIN (J.C.S., 1929, 2754—2758).—Nor-*d*- $\psi$ -ephedrine, m. p. 77°,  $[\alpha]_D^{25} +37.5^\circ$  in methyl alcohol,  $+24.7^\circ$  in water (sulphate,  $[\alpha] +48.7^\circ$  in water; *d*- $\psi$ -methylephedrine methiodide,  $[\alpha] +42.3^\circ$  in water; nor-*d*- $\psi$ -ephedrine hydrogen tartrate,  $[\alpha] +49.5^\circ$  in water; dibenzoylnor-*d*- $\psi$ -ephedrine,  $[\alpha] +32.8^\circ$  in methyl alcohol; *N*-benzoylnor-*d*- $\psi$ -ephedrine,  $[\alpha] +67.2^\circ$  in methyl alcohol; *O*-benzoylnor-*d*- $\psi$ -ephedrine hydrochloride,  $[\alpha] -37.6^\circ$  in water), has been employed in the resolution of *dl*-benzenesulphonylalanine, a substance not previously resolved (cf. J.C.S., 1912, **101**, 939; A., 1915, i, 801; 1925, i, 137; 1928, 287), and of *dl*-phenylalanineamide-4-arsinic acid. When warm solutions of *dl*-benzenesulphonylalanine, m. p. 124—125°, in aqueous sodium hydroxide and of nor-*d*- $\psi$ -ephedrine in water are mixed, the *dAdB salt*, m. p. 147—148°,  $[\alpha] +46.6^\circ$  in water, is obtained, converted by ammonia into *d*-benzenesulphonylalanine, m. p. 126—127°,  $[\alpha]$  of sodium salt  $-33.4^\circ$  in water. The mother-liquor yielded the *l*-base, m. p. 126—127°,  $[\alpha]$  of sodium salt,  $-33.1^\circ$  in water (also obtained in 65% yield from *d*-alanine, benzenesulphonyl chloride, and sodium hydroxide, followed by acidification;  $[\alpha]$  of sodium salt,  $-10.5^\circ$  in ethyl alcohol). *dl*-Benzenesulphonylalanine methyl ester, and *dl*-benzenesulphonylalanineamide have m. p. 52° and 179—180°, respectively. The corresponding derivatives of the *d*- and *l*-acids are described: *methyl esters*, both m. p. 65—67°, *d*-ester,  $[\alpha] +42.6^\circ$  in ethyl alcohol, *l*-ester,  $-42.3^\circ$ ; *amides*, both m. p. 211—212°, *d*-amide,  $[\alpha] +41.3^\circ$  in ethyl alcohol, *l*-amide  $-41.9^\circ$  ( $-75.0^\circ$  in water).

The *lAdB salt*, m. p. 217—223° (decomp.),  $[\alpha] +8.97^\circ$  in water, was similarly prepared from *dl*-phenylalanineamide-4-arsinic acid and nor-*d*- $\psi$ -

ephedrine, and afforded the *l*-acid, m. p. 247°,  $[\alpha]$  of sodium salt  $-18.6^\circ$  in water; the *d*-acid,  $[\alpha]$  of sodium salt  $-17.12^\circ$ , was isolated from the mother-liquors. All the rotations are for the mercury green line ( $\lambda$  5461) at 20°. The rotations given by Smith (A., 1928, 309) are for the mercury yellow line ( $\lambda$  5790).

A. I. VOGEL.

**Stereochemical structure. I. Optically active glycols derived from *d*(-)-mandelic acid.** R. ROGER (Helv. Chim. Acta, 1929, **12**, 1060—1067).—Magnesium phenyl bromide reacts with ethyl  $\alpha$ -hydroxybutyrate, forming *r*- $\alpha$ -*diphenyl-n-butane- $\alpha\beta$ -diol*, m. p. 115—116°, which is dehydrated by boiling 20% sulphuric acid to benzhydryl ethyl ketone. The above glycol differs from both the isomeric  $\alpha$ - and  $\beta$ -ethylhydrobenzoin described by Tiffeneau and Lévy (A., 1927, 1184), showing that no change in structure of propionylphenylcarbinol occurs during its reaction with magnesium phenyl bromide (cf. Tiffeneau and Lévy, *loc. cit.*).

Magnesium ethyl bromide and *d*(-)-mandelamide afford *d*(-)-*propionylphenylcarbinol*, m. p. 39—40°,  $[\alpha]_D^{25} -455^\circ$  in benzene, which with magnesium phenyl bromide yields the  $\alpha$ -form, m. p. 89—90°,  $[\alpha]_D^{25} +35^\circ$  in benzene, of *d*(+)-ethylhydrobenzoin. This differs from the  $\beta$ -form,  $[\alpha]_D^{25} +21.7^\circ$  in benzene (McKenzie and Wren, J.C.S., 1910, **97**, 473; McKenzie and Roger, A., 1925, i, 25). Magnesium benzyl chloride and *d*(-)-mandelamide give *d*(-)-*phenylacetylphenylcarbinol*, m. p. 128—129°,  $[\alpha]_D^{25} -122.3^\circ$  in acetone, which is converted by magnesium phenyl bromide into  $\beta$ -*d*(+)-*benzylhydrobenzoin*, m. p. 125—126°,  $[\alpha]_D^{25} +106.7^\circ$  in chloroform. This is not identical with  $\alpha$ -*d*(-)-*benzylhydrobenzoin* [Roger and McKenzie, A., 1929, 317; from magnesium benzyl chloride and *d*(-)-benzoin]. Both forms give the same colour reaction with sulphuric acid.

H. BURTON.

**Chaulmoogryl-bromo- and -chloro-phenols.** P. SANTILLAN and A. P. WEST (Philippine J. Sci., 1929, **40**, 493—497).—*Chaulmoogrates* of the following phenols have been prepared by condensation of the phenol with chaulmoogryl chloride in presence of phosphorus trichloride: *o*-bromophenol, m. p. 51.5—53°; *o*-chlorophenol, m. p. 48—50°; *p*-chlorophenol, m. p. 53—55°; and tribromophenol, m. p. 54—56°.

E. H. SHARPLES.

**Colour reaction of oximes.** I. DE PAOLINI (Gazzetta, 1929, **59**, 816—819).—The statement of Raikowa (A., 1929, 911) that only those oximes capable of isomerisation to the  $\psi$ -oxime [ $\text{C}(\text{CH}_2)_2\text{NH}\cdot\text{OH}$ ] give red colorations with ferric chloride is untrue, for the following amidoximes are recorded in the literature as reacting with ferric chloride: formanilideoxime, benzanilideoxime, benz-*o*-toluidideoxime, and, in particular, benzopiperidoxime (Ley, A., 1907, i, 301). The coloration with ferric chloride is attributed to formation of complex salts with the tautomeric form  $\text{CRR}'\cdot\text{CH}\cdot\text{NO}$ , the existence of which is indicated, whilst the  $\psi$ -oxime form is excluded, by the direct formation of bromonitroso-compounds. The intense colorations given by  $\alpha$ - and  $\beta$ -oximino-acids are probably due to the formation of complex salts analogous to those of the amino-acids.

R. K. CALLOW.

**Action of potassium hypobromite on *o*-benzamidophenylbutyramide.** S. J. KANEVSKAJA (J. pr. Chem., 1929, [ii], **124**, 33—47).—*o*-Benzamidophenylbutyramide, m. p. 139—140°, prepared in 90% yield by heating the nitrile with sulphuric acid at 100° for 10 min., reacts with 1 mol. of potassium hypobromite to give a non-homogeneous product which when extracted with chloroform, evaporated, treated with 5% hydrochloric acid, and again extracted with chloroform gave a substance,  $C_{34}H_{34}O_4N_4$ , m. p. 145—146°, probably a ureido-compound. The acid extract when precipitated with alkali followed by extraction with chloroform yielded  $\gamma$ -*o*-benzamidophenylpropylamine, m. p. 126—127°, soluble in water (hydrochloride, m. p. 276—277°; benzoyl derivative, m. p. 158—159°), and  $\gamma$ -5-bromo-2-benzamidophenylpropylamine, m. p. 169—170°, insoluble in water [hydrochloride, m. p. 243° (decomp.); benzoyl derivative, m. p. 180—181°]. The bromo-compound was oriented by oxidation with 5% aqueous potassium permanganate to 5-bromobenzoylanthranilic acid, m. p. 248—249°, further converted by concentrated hydrochloric acid at 130—140° into *p*-bromoaniline. *o*-Benzamidophenylbutyric acid, m. p. 156°, and its 5-bromo-derivative, m. p. 178—179°, were also isolated.

$\gamma$ -*o*-Aminophenylpropylamine hydrochloride, m. p. 228—230° (decomp.) (base, b. p. 165°/16 mm.), and the corresponding 5-bromo-derivative, m. p. 226°, are produced by heating  $\gamma$ -*o*-benzamidophenylpropylamine and its bromo-derivative respectively with hydrochloric acid. *o*-Benzamidophenylbutyric acid and potassium hypobromite yield the 5-bromo-compound.

A. I. VOGEL.

**Attempts to synthesise disubstituted derivatives of naphthalene.** A. ANGELETTI (Gazzetta, 1929, **59**, 851—858).—Attempts to bring about ring-closure in *p*-substituted phenylparaconic and  $\beta$ -benzylidenepropionic acids with the object of preparing 1:7-disubstituted naphthalenes have resulted in the separation of very small quantities of phenolic products.  $\beta$ -Anisylidenepropionic acid is unchanged by distillation under reduced pressure or by treatment with sulphuric acid. When distilled under atmospheric pressure a small amount of phenolic product may be separated from which (?) 1-hydroxy-7-methoxynaphthalene, m. p. 122—124° (darkens at 60°), is isolated. *p*-Nitrophenylparaconic acid yields a trace of phenolic substance when distilled.  $\beta$ -4-Hydroxybenzylidenepropionic acid, m. p. 192—193° (decomp. from 186°) (calcium salt,  $+H_2O$ , decomp. 230°), is prepared by the condensation of *p*-hydroxybenzaldehyde with sodium propionate and acetic anhydride. The acid distils under reduced pressure with slight and under atmospheric pressure with considerable decomposition. No trace of 1:7-dihydroxynaphthalene is recognisable in this product or the product of treatment with acids.

R. K. CALLOW.

**Catalytic reduction of hydroxybenzoic acids.** F. BALÁŠ and L. ŠROL (Coll. Czech. Chem. Comm., 1929, **1**, 658—667).—The reduction of a series of hydroxybenzoic acids and their derivatives in alcoholic solution with platinum-black and hydrogen

at the ordinary temperature is described. Salicylic acid yields 1-hydroxycyclohexane-2-carboxylic acid, m. p. 111°; acetylsalicylic acid gives hexahydrobenzoic acid, m. p. 32°, and acetic acid; phenyl salicylate affords dodecahydrosalol, b. p. 145°/12 mm.,  $d_4^{25}$  1.0100,  $n_D^{25}$  1.4642; *m*-hydroxybenzoic acid gives *cis*-3-hydroxycyclohexane-1-carboxylic acid, m. p. 132°; and *p*-hydroxybenzoic acid yields *cis*-4-hydroxycyclohexane-1-carboxylic acid, m. p. 152° (lactone, m. p. 109—110°), and a small quantity of the *trans*-acid, m. p. 119—120°.

A. I. VOGEL.

**Synthesis of *i*-surinamine.** S. J. KANEVSKAJA (J. pr. Chem., 1929, [ii], **124**, 48—51).—A mixture of an ethereal solution of *p*-methoxyphenylacetaldehyde, an aqueous solution of methylamine hydrochloride, and a saturated aqueous solution of potassium cyanide is vigorously stirred for 3 hrs. when an 80% yield of  $\alpha$ -methylamino- $\beta$ -*p*-methoxyphenylpropionitrile hydrochloride, m. p. 152—153° (darkening at 140°), is obtained. The latter on keeping with excess of concentrated hydrochloric acid for 48 hrs. and then heating for 5—6 hrs. at 130—140°, gave an 85—87% yield of *i*-surinamine (*N*-methyltyrosine), m. p. 265—320° according to rate of heating.

A. I. VOGEL.

**Preparation of ethyl benzoylacetate.** R. L. SHRINER and A. G. SCHMIDT (J. Amer. Chem. Soc., 1929, **51**, 3636—3638).—Ethyl benzoylacetate is conveniently prepared from ethyl sodioacetoacetate and benzoyl chloride in benzene solution. The above ester (0.25 mol.) is hydrolysed to ethyl benzoylacetate (78% yield) by adding it to a mixture of water (8.3 mols.), ammonia (*d* 0.9; 0.1 mol.), and ammonium chloride (0.6 mol.) at 40°, and keeping the mixture at 40° for 10 min. (cf. Claisen, A., 1896, i, 557).

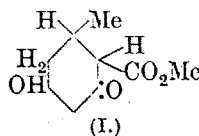
H. BURTON.

**Lichin substances. VII. Synthesis of methyl  $\beta$ -orcinolcarboxylate and new synthesis of rhizonic acid.** A. SONN (Ber., 1929, **62**, [B], 3012—3016; cf. A., 1917, i, 143).—Ethyl methyl dihydroresorcyate is converted by potassium hydroxide and methyl iodide followed by bromination of the product into ethyl 6-bromo- $\beta$ -orcinolcarboxylate, m. p. 112—113°, transformed by hydrogen in presence of palladised calcium carbonate or by palladised asbestos at 150° into ethyl  $\beta$ -orcinolcarboxylate, m. p. 128°.

Methyl acetoacetate and methyl crotonate in presence of sodium methoxide afford methyl methyl dihydroresorcyate (I), m. p. 125—126° after softening, converted successively into methyl 1:4-dimethylhydroresorcyate, m. p. 158—159° after softening, and methyl  $\beta$ -orcinolcarboxylate, m. p. 141°. Hydrolysis of the respective ethyl esters with cold, concentrated sulphuric acid yields 6-bromo- $\beta$ -orcinolcarboxylic acid, decomp. 204—205°, and  $\beta$ -orcinolcarboxylic acid, m. p. 185° (decomp.). Treatment of ethyl  $\beta$ -orcinolcarboxylate with ethereal diazomethane affords ethyl rhizonate, m. p. 81° (cf. Pfau, A., 1928, 1241), whence rhizonic acid, m. p. about 210° when rapidly heated.

H. WREN.

**Acetyl migration during partial hydrolysis of mixed acylated caffeic acid.** E. PACSU and C.



STIEBER (Ber., 1929, 62, [B], 2974—2979).—Protocatechualdehyde is converted by sodium acetate and acetic anhydride into 3:4-diacetoxycinnamic acid (methyl ester, m. p. 119—120°), hydrolysed by cold sodium hydroxide to 3:4-dihydroxycinnamic acid, m. p. 200°. The last-named acid is converted by aqueous sodium hydroxide and ethereal acetic anhydride at 0° into 4-hydroxy-3-acetoxycinnamic acid, m. p. 179—180°, in which the position of the acetyl group is established by conversion into methyl 4-methoxy-3-acetoxycinnamate, m. p. 116°, identical with the compound derived from acetylisoferulaic acid; methyl 3-methoxy-4-acetoxycinnamate has m. p. 124°. 4-Hydroxy-3-acetoxycinnamic acid, benzoyl chloride, and sodium hydroxide at -15° afford 3-acetoxy-4-benzoyloxycinnamic acid, m. p. 164°, hydrolysed by hydrochloric acid in acetic acid to 4-hydroxy-3-benzoyloxycinnamic acid, m. p. 223°, yielding on re-acetylation 4-acetoxy-3-benzoyloxycinnamic acid, m. p. 150°. Treatment of 4-hydroxy-3-benzoyloxycinnamic acid with ethereal diazomethane affords methyl 4-methoxy-3-benzoyloxycinnamate, m. p. 120°, hydrolysed to isoferulaic acid.

H. WREN.

**Reaction of phthalyl chloride with amides.** T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1929, 51, 3651—3652).—When phthalyl chloride is heated with an amide in presence or absence of toluene until evolution of hydrogen chloride ceases good yields of *N*-acylphthalimides are obtained (cf. Titherley, J.C.S., 1904, 85, 1679; 1906, 89, 708). The following are new: *N*-benzenesulphon-, m. p. 205°; *N*-*o*- and -*p*-toluenesulphon-, m. p. 182° and 231°, respectively; *N*-3-nitro-*p*-toluenesulphon-, m. p. 247°, and *N*-2:5-dichlorophenyl-phthalimide, m. p. 185—190°.

H. BURTON.

**Condensation of aldehydes with hydrazones.** I. Condensation of benzaldehyde with benzaldehydephenylhydrazone. A. GIACALONE (Gazzetta, 1929, 59, 702—707).—Benzaldehyde (1 mol.) condenses with benzaldehydephenylhydrazone (2 mols.) at 100° in presence of zinc chloride to yield *pp'*-dibenzylidenedihydrazinotriphenylmethane,  $\text{CHPh}(\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{CHPh})_2$ , m. p. 196° (diacetyl derivative, m. p. 164°). *pp'*-Diaminotriphenylmethane yields on diazotisation and reduction with sodium sulphite the unstable *pp'*-dihydrazine, m. p. about 45°, which condenses with benzaldehyde in acetic acid to give a substance identical with the above.

R. K. CALLOW.

**Photochemical reactions in the *o*-nitrobenzylidenacetals.** *o*-Nitrobenzylidene- $\alpha\beta$ -glyceride. I. TANASESCU and E. MACOVSKI (Bull. Soc. chim., 1929, [iv], 45, 1022—1030; cf. A., 1926, 726).—*o*-Nitrobenzaldehyde and glycerol when heated in a current of dry hydrogen chloride yield *o*-nitrobenzylidene- $\alpha\beta$ -glyceride, b. p. 221—223°/13 mm., 239—240°/25 mm., the  $\alpha\beta$ -structure of which is based on its synthesis (cf. Hibbert, A., 1929, 47, 170) and the formation of a benzoate, phenylurethane, and 1-naphthylurethane. When insolated alone or in benzene solution *o*-nitrobenzylidene- $\alpha\beta$ -glyceride is converted into the *o*-nitrosocarboxyl derivative,  $\text{CH}_2\cdot\text{O}-\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NO}$  (I) (dibenzoate), which,

unlike the *o*-nitrobenzylidenacetals, yields no indigotin with acetone after acid hydrolysis. The benzoate, phenylurethane, and 1-naphthylurethane are similarly isomerised to the corresponding *o*-nitrosocarboxyl derivatives, but *m*-nitrobenzylidene- $\alpha\beta$ -glyceride, b. p. 230—232°/13—14 mm., similarly prepared, its benzoate, phenylurethane, and 1-naphthylurethane do not undergo such photochemical isomerisation.

R. BRIGHTMAN.

#### Substituted benzyl alkyl ketones,

$\text{CHRP}\cdot\text{CO}\cdot\text{R}'$ . (MILE.) J. LÉVY and P. JULLIEN (Bull. Soc. chim., 1929, [iv], 45, 941—950).—The following have been obtained by the action of magnesium alkyl halides on substituted phenylacetone nitriles:  $\alpha$ -phenyldiethyl ketone, m. p. 225—228° (semicarbazone, m. p. 136°); benzyl  $\alpha$ -phenylethyl ketone, b. p. 205—206°/40 mm. (semicarbazone, m. p. 143—145°; oxime, m. p. 82—83°);  $\alpha$ -phenylpropyl methyl ketone, b. p. 220—225° (semicarbazone, m. p. 189—190°);  $\alpha$ -phenyldipropyl ketone, b. p. 242—245° (semicarbazone, m. p. 106—107°);  $\gamma$ -phenyloctan- $\delta$ -one, b. p. 160—165°/20 mm. (semicarbazone, m. p. 98—99°);  $\gamma$ -phenylhexan- $\beta$ -one, b. p. 235—236°,  $d_4^{20}$  0.970 (semicarbazone, m. p. 130—131°; oxime, m. p. 42—43°);  $\delta$ -phenylheptan- $\gamma$ -one, b. p. 240—245° (semicarbazide, m. p. 108—109°);  $\delta$ -phenylnonan- $\epsilon$ -one, b. p. 175°/25 mm. (semicarbazone, m. p. 109°);  $\alpha\beta$ -diphenylbutan- $\gamma$ -one, b. p. 188—189°/20 mm. (semicarbazones, m. p. 144—145° and 168°; oxime, m. p. 134°), and  $\alpha\beta$ -diphenylpentan- $\gamma$ -one, b. p. 190—193°/15 mm. (semicarbazone, m. p. 215—216°; oxime, m. p. 106—107°).  $\beta$ -Phenylhexan- $\gamma$ -one,  $\alpha\gamma$ -diphenylbutan- $\beta$ -one,  $\gamma$ -phenylheptan- $\delta$ -one, and  $\gamma$ -phenyloctan- $\delta$ -one have also been prepared by oxidation of the secondary alcohol ( $\beta$ -phenylhexan- $\gamma$ -ol has b. p. 150—155°/20 mm.;  $\alpha\gamma$ -diphenylbutan- $\beta$ -ol, m. p. 73°,  $\gamma$ -phenylheptan- $\delta$ -ol, b. p. 145—147°/20 mm.,  $\gamma$ -phenyloctan- $\delta$ -ol, m. p. 45°).  $\beta$ -Phenyl- $\delta$ -methylpentan- $\gamma$ -one, b. p. 256—257° (semicarbazone, m. p. 129—130°);  $\beta$ -phenylheptan- $\gamma$ -one, b. p. 256—257° (semicarbazone, m. p. 129°);  $\beta$ -phenyl- $\epsilon$ -methylhexan- $\gamma$ -one, b. p. 237—240° (semicarbazone, m. p. 147.5—148°);  $\gamma$ -phenyl- $\epsilon$ -methylhexan- $\delta$ -one, b. p. 253—254° (semicarbazone, m. p. 158—159°), and  $\epsilon$ -phenyl- $\beta$ -methylheptan- $\delta$ -one, b. p. 242—243° (semicarbazone, m. p. 141—142°), are similarly obtained from  $\beta$ -phenyl- $\delta$ -methylpentan- $\gamma$ -ol, b. p. 156—160°/30 mm.,  $\beta$ -phenylheptan- $\gamma$ -ol, b. p. 156—160°/30 mm.,  $\beta$ -phenyl- $\epsilon$ -methylhexan- $\gamma$ -ol, b. p. 135—137°/21 mm.,  $\gamma$ -phenyl- $\epsilon$ -methylhexan- $\delta$ -ol, b. p. 155—158°/20 mm., and  $\epsilon$ -phenyl- $\beta$ -methylheptan- $\delta$ -ol, b. p. 153—155°/23 mm., respectively.  $\alpha\gamma$ -Diphenylpentan- $\beta$ -one is also obtained from  $\alpha\gamma$ -diphenylpentan- $\beta$ -ol, m. p. 74—76° (from magnesium benzyl chloride and  $\gamma$ -phenylbutaldehyde), and by the action of magnesium benzyl chloride on  $\beta$ -phenylbutyramide. The following are also obtained by the action of magnesium alkyl halides on disubstituted amides:  $\gamma$ -phenyloctan- $\delta$ -one,  $\epsilon$ -phenyl- $\beta$ -methylheptan- $\delta$ -one,  $\alpha\delta$ -diphenylhexan- $\gamma$ -one, b. p. 220—230°/24 mm. (semicarbazone, m. p. 129—130°);  $\epsilon$ -phenyl- $\beta$ -methylheptan- $\delta$ -one, b. p. 150—154°/24 mm., 252—255°/760 mm. (semicarbazone, m. p. 106—107°);  $\gamma$ -phenyl- $\beta$ -methylheptan- $\delta$ -one, b. p. 263—267° (semicarbazone, m. p. 128°);  $\delta$ -phenyloctan- $\gamma$ -one, b. p. 268°/760 mm., 147—150°/16 mm.

(semicarbazone, m. p. 104–105°) (from  $\beta$ -phenylhexylamide, m. p. 96°);  $\epsilon$ -phenylnonan-8-one, b. p. 275–277° (semicarbazone, m. p. 100–101°);  $\delta$ -phenyl- $\beta$ -methyloctan- $\epsilon$ -one, b. p. 172–175°/25 mm. (semicarbazone, m. p. 137–138°), and  $\alpha$ -diphenylhexan-8-one, b. p. 207–208°/18 mm. (semicarbazone, m. p. 134°).  $\gamma$ -Phenylhexan- $\beta$ -one,  $\gamma$ -phenyl- $\delta$ -methylpentan- $\beta$ -one, b. p. 115–118°/28 mm. (semicarbazone, m. p. 153–154°), and  $\delta$ -phenylheptan- $\zeta$ -one, b. p. 250–251°,  $d_4^{20}$  0.960 (semicarbazone, m. p. 156–158°; oxime, m. p. 63–66°), are obtained by alkylation of phenylacetone.  $\alpha\beta$ -Diphenylpentan- $\gamma$ -one,  $\alpha\beta$ -diphenylhexan- $\gamma$ -one, b. p. 210–212° (semicarbazone, m. p. 184–184.5°; oxime, m. p. 116–117°), and  $\alpha\beta$ -diphenyl- $\delta$ -methylpentan- $\gamma$ -one, b. p. 195–200°/27 mm. (semicarbazone, m. p. 205–206°; oxime, m. p. 122–123°), are similarly obtained by benzylation of the corresponding phenyl-butanone or -pentanone.

R. BRIGHTMAN.

**Pyrochemical decomposition of azibenzil.** J. J. RITTER and G. M. WIEDEMANN (J. Amer. Chem. Soc., 1929, 51, 3583–3586).—Diphenylketen is obtained in 45% yield when a suspension of azibenzil (benzoylphenylazomethylene) in light petroleum (b. p. 60–90°) is boiled until the solid disappears. A small amount of bisbenzilketazine, m. p. 202° (corr.), is formed during the reaction. When this ketazine is distilled, benzoic acid and benzonitrile are produced. The supposed additive compound, m. p. 201°, of diphenylketen and azibenzil (Staudinger, A., 1911, i, 650) is probably the above ketazine. H. BURTON.

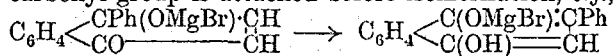
**[Action of hydrazine hydrochloride on aromatic ketones.] Anisilketazine.** J. VAN ALPHEN (Ber., 1929, 62, [B], 3029–3030).—The compound described by Schapiro (A., 1929, 1302) as anisilhydrazone is anisilketazine (cf. van Alphen, this vol., 91). The action of hydrazine hydrate on anisil in alcohol gives anisilhydrazone, m. p. 143° (decomp.) (*loc. cit.*).

H. WREN.

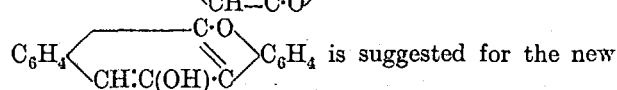
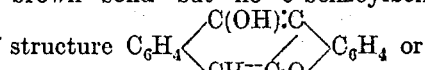
**Ketonic amines and local anæsthetics.** L. BERMEJO and L. BLAS.—See this vol., 247.

**Action of Grignard reagents on naphthaquinones. II. Action of magnesium phenyl bromide on  $\alpha$ - and  $\beta$ -naphthaquinones.** A. FRANSSEN (Bull. Soc. chim., 1929, [iv], 45, 1030–1044).—Further fractionation of the reaction products from magnesium phenyl bromide and  $\alpha$ -naphthaquinone (A., 1925, i, 1146) affords, in addition to 1:4-dihydroxydiphenyl-1:4-dihydronaphthalene, a bluish-grey substance, decomp. at 230°, a reddish-brown substance, decomp. 150°, and a black, tarry residue from which indefinite products are obtained. The two new products have a composition intermediate between that of  $\alpha$ -naphthaquinone and -quinol,  $C_{16}H_{12}O_2$ , and are regarded as complex quinhydrones resulting from isomerisation of the quinols first formed, or condensation with a further molecule of naphthaquinone. If the Grignard reagent solution is added dropwise to the  $\alpha$ -naphthaquinone the coloured substances constitute the main reaction product and only traces of 1:4-dihydroxydiphenyl-1:4-dihydronaphthalene are obtained. If, however, the Grignard reagent is kept in excess and the  $\alpha$ -naphthaquinone added gradually with continuous agitation, 1:4-di-

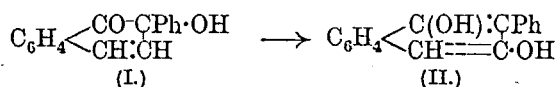
hydroxydiphenyl-1:4-dihydronaphthalene is formed almost exclusively; under these conditions the second carbonyl group is attacked before isomerisation, e.g.,



can take place. With excess of magnesium phenyl bromide  $\beta$ -naphthaquinone gives no diquinol, but 25% of a substance,  $C_{16}H_{10}O_2$ , m. p. 187°, yielding a monoacetate, m. p. 70–71°, which does not react with *p*-nitrophenylhydrazine or alcoholic hydriodic acid and on oxidation with chromic and acetic acids yields a brown solid but no *o*-benzoylbenzoic acid. The



product; it may result from loss of hydrogen from the intermediate product II, which is produced by iso-



merisation of I, formed by hydrolysis of the Grignard reaction product.

R. BRIGHTMAN.

**Rearrangement of naphthaquinonephenylhydrazones.** R. WILLSTÄTTER, E. ULBRICH, L. POCÁNY, and C. MAMMERI (Annalen, 1929, 477, 161–194).—Ethyl chloroformate and  $\beta$ -formylphenylhydrazine react in boiling benzene forming  $\alpha$ -carbomethoxy- $\alpha$ -phenylhydrazine, m. p. 69–70°, which condenses with 1:4-naphthaquinone in cold acetic acid solution yielding methyl 1:4-naphthaquinonephenylhydrazone-*N*-carboxylate, m. p. 181–182° (corresponding ethyl ester, m. p. 149–150°, hydrolysed by 20% sulphuric acid to 4-benzeneazo- $\alpha$ -naphthol). The migration of the acyl group from nitrogen to oxygen is not observed when the ethyl ester is treated with potassium hydroxide in ether (cf. Willstätter and Veraguth, A., 1907, i, 453); an additive compound,  $C_{19}H_{16}O_3N_2 \cdot KOH$ , is obtained, and when an ethereal suspension of this is shaken for some time the potassium salt of 4-benzeneazo- $\alpha$ -naphthol is produced. Treatment of the above naphthaquinonephenylhydrazone-*N*-carboxylates with cold methyl-alcoholic barium hydroxide solution gives, in addition to the benzeneazonaphthol, rearrangement products, in which the carbalkoxy-group has migrated to the naphthalene ring; methyl and ethyl 8-benzeneazo-5-hydroxy-1-naphthoate, m. p. 223° (decomp.) and 224–225°, respectively, are thus obtained. Reduction of either of these esters with a solution of stannous chloride in methyl-alcoholic hydrochloric acid affords the lactam, m. p. 170°, of 8-amino-5-hydroxy-1-naphthoic acid. The free amino-acid is oxidised with lead dioxide and dilute sulphuric acid to 1:4-naphthaquinone-5-carboxylic acid, darkens at 164° and blackens at 170–185° without melting (lead salt; methyl ester, m. p. 115–116°; ethyl ester, m. p. 79.5–80°), also formed by similar oxidation of 5-amino-1-naphthoic acid. Hydrolysis of the benzeneazohydroxynaphthoates with a mixture of acetic and hydrobromic acids gives the lactam, m. p. 202.5–203° [1:8-phenylpyridazone-

4-naphthaquinone (Dziewoński, Galitzerówna, and Kocwa, A., 1927, 359)], of 1:4-naphthaquinone-5-carboxylic acid-4-phenylhydrazine, also obtained in small amount from 5-hydroxy-1-naphthoic acid and benzenediazonium chloride, and from phenylhydrazine and 1:4-naphthaquinone-5-carboxylic acid. The main product of the last-named reaction is 5-benzeneazo-8-hydroxy-1-naphthoic acid, m. p. 214° (decomp.) [methyl ester, m. p. 179.5—180° (decomp.)], formed also from benzenediazonium chloride and 8-hydroxy-1-naphthoic acid. Ethyl 4-benzeneazo- $\alpha$ -naphthol-O-carboxylate, m. p. 78° (corresponding dimethylamide, m. p. 107—108°), is prepared from 4-benzeneazo- $\alpha$ -naphthol and ethyl chloroformate in pyridine at 0°, whilst ethyl 5-hydroxy-1-naphthoate couples with benzenediazonium chloride forming ethyl 8-benzeneazo-5-hydroxy-1-naphthoate, m. p. 161—162° (the free acid, m. p. 251°, is the main product of the coupling reaction with 5-hydroxy-1-naphthoic acid). Ethyl 4-benzeneazo-1-hydroxy-2-naphthoate, m. p. 94.5° [free acid, m. p. 209° (decomp.; lit. 194°) (acetyl derivative, m. p. 191°)], and ethyl 4-benzeneazo- $\alpha$ -naphthol-2'-(+0.5C<sub>6</sub>H<sub>6</sub>), m. p. 181.5°, -3', m. p. 200°, and -4'-carboxylates, m. p. 239.5°, are prepared by the usual coupling reactions.

$\beta$ -Phenylsemicarbazide (Busch and Walter, A., 1903, i, 522) reacts with *p*-benzoquinone in aqueous alcoholic solution at 0° only, forming the  $\beta$ -phenylsemicarbazone, m. p. 114—115°. This is decomposed readily by warming with solvents to 4-hydroxyazobenzene. 4-Hydroxyazobenzene-O-carboxyl chloride, m. p. 86—87° (corresponding dimethylamide, m. p. 152°), is prepared from the hydroxy-derivative and carbonyl chloride in presence of benzene and dimethylaniline. The  $\beta$ -phenylsemicarbazone, m. p. 172—173° (decomp.), of 1:4-naphthaquinone is converted into benzeneazonaphthol by the action of boiling alcohol or acetic acid, or by shaking with potassium hydroxide in dry ether; the diphenylhydrazine, m. p. 186—187°, is stable to alkali treatment.

7-Hydroxy-1-naphthonitrile, m. p. 195—196° (8-benzeneazo-derivative, m. p. 206°), is hydrolysed by 50% alcoholic potassium hydroxide solution to 7-hydroxy-1-naphthoic acid. The 8-benzeneazo-derivative of this is converted into the lactam, m. p. 237—238° [1:8-phenylpyridazone-2-naphthaquinone (Dziewoński, *loc. cit.*)], of 1:2-naphthaquinone-8-carboxylic acid-1-phenylhydrazine by heating at 185°, dissolution in sulphuric acid, long boiling with alcohol, or by acidification of a hot alkaline solution. 4-Hydroxyazobenzene-3-carboxylic acid eliminates water when boiled with acetic anhydride forming the lactam, m. p. about 181°, of *p*-benzoquinone-3-carboxylic acid-4-phenylhydrazine. H. BURTON.

#### Additive compounds of phenols and ammonia.

V. Ammoniation of derivatives of phenol, naphthols, and hydroxyanthraquinones. E. BRINER and H. KUHN (Helv. Chim. Acta, 1929, 12, 1067—1095; cf. A., 1926, 1241; 1927, 1181; 1928, 1238).—Using the methods previously described (*loc. cit.*) proof of the formation of the following compounds is obtained (the numbers in parentheses are heats of ammoniation in kg.-cal.): *p*-cresol monoammoniate; *o*-4-xylenol monoammoniate; *m*-aminophenol mono-

ammoniate, greenish-brown; *m*-aminophenol diammoniate; 3-nitro-*p*-cresol mono-, red, and di-ammoniates, yellow; 2:6-dihydroxynaphthalene mono- (5.5) and di-ammoniates (1.3); 1:2-aminonaphthol semi- (2.8), mono- (1.2), and di-ammoniates, brownish-black; 2:7- (4.6), 1:5- (6.7), dark brown, and 2:8-aminonaphthol monoammoniates (8.2); alizarin mono- (5), violet, and di-ammoniates, bluish-violet; quinizarin mono-, dark violet, and di-ammoniates, violet-red; anthrapurpurin mono-, violet, and tri- (di?)-ammoniates; 1-nitro-2-hydroxyanthraquinone mono- (3.8), ochre, and di-ammoniates (0.4), reddish-brown; 1-nitro-4-hydroxyanthraquinone monoammoniate (3.7), carmine-red; 3-nitroalizarin mono- (6.8), brown, and tri- (di?)-ammoniates, greenish-brown; 4-nitroalizarin mono- (6), reddish-brown, and di-ammoniates, dark brown; 1-amino-5-hydroxyanthraquinone monoammoniate, dark red; 3-aminoalizarin diammoniate, dark violet. The position of the amino-group in the aminonaphthols has a large influence on ammoniation. Diammoniation occurs only when the amino-group is *ortho* to the hydroxyl. When a nitro-group is *ortho* to the hydroxyl, diammoniation is again favoured (*cf. loc. cit.*). H. BURTON.

Action of aromatic sulphonyl chlorides on  $\beta$ -aminoanthraquinone. New vat dyes. E. RIESZ and R. FERKS (Monatsh., 1929, 52, 372—376).—The purity of the products obtained by condensation of *p*-toluenesulphonyl chloride and  $\beta$ -aminoanthraquinone in nitrobenzene (Truttwin, B., 1923, 89A) is improved by removal of the medium with steam; the alkali-insoluble dye, C<sub>19</sub>H<sub>9</sub>O<sub>3</sub>N<sub>2</sub>S, m. p. 310—320° (decomp.), obtained in addition to  $\beta$ -*p*-toluenesulphonamidoanthraquinone, m. p. 289°, is probably *N*-*p*-toluenesulphonyl-2:7-di- $\beta$ -anthraquinonylaminoanthraquinone (I). The same products are obtained in the presence of anhydrous sodium acetate or cuprous chloride, or by the method of Ullmann and Medenwald (A., 1913, i, 735). With sodium hyposulphite and alkali I gives an orange-red vat, which dyes cotton a fast violet-brown. A series of compounds analogous to I, prepared by the above method using various sulphonyl chlorides, has the same tinctorial properties; an accumulation of substituents, especially methyl groups, in the sulphonyl residue leads to a deeper shade, but sulphonic acid groups appear to be without influence. C. W. SHOPPEE.

Resins. II. Preparation of pure  $\alpha$ - and  $\beta$ -amyrin and their constitution. P. HORRMANN (Arch. Pharm., 1930, 268, 64—76).—The conversion of amyirin (from Manila-elemi, containing approximately 75% of  $\alpha$ - and 25% of  $\beta$ -amyrin) into its pure  $\alpha$ - and  $\beta$ -benzoates in much better yields than have hitherto been obtained, is described. The purified amyirin, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +84.3°, is benzoylated with benzoyl chloride and pyridine (92.7% yield). Separation of the mixed benzoates is effected by shaking with pentane, in which the  $\alpha$ -benzoate is much more soluble (1:20) than the  $\beta$ -compound (1:150). The residue of undissolved  $\beta$ -benzoate is again treated with pentane and the insoluble residue crystallised from benzene to give the pure  $\beta$ -benzoate, m. p. 230—231°. The residue from the evaporated pentane solutions (mainly  $\alpha$ -benzoate together with a little of the  $\beta$ -benzo-

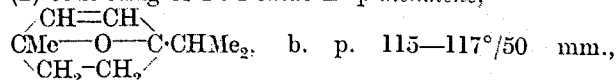
ate and some unchanged amyirin) is crystallised from benzene to give the pure  $\alpha$ -benzoate, m. p. 194–195°. The combined residues from the mother-liquors are re-benzoylated and the separation process is repeated, the ultimate yields being  $\alpha$ -, 62%,  $\beta$ -benzoate, 22.5%, and loss 15.5%. By hydrolysis of the pure benzoates with aldehyde-free alcoholic potassium hydroxide pure  $\alpha$ -amyrin, m. p. 183–184°, b. p. 243°/0.74 mm., and  $\beta$ -amyrin, m. p. 193–194°, b. p. 259.5°/0.8 mm., are obtained and are converted by oxidation with chromic and acetic acids into  $\alpha$ -amyrone, m. p. 125–126°, b. p. 249°/0.3 mm. (semicarbazone, decomp. 205–206°; oxime, m. p. 240–241°), and  $\beta$ -amyrone, m. p. 177–178°, b. p. 254°/0.3 mm. [semicarbazone, m. p. 244–245° (decomp.); oxime, m. p. 269–270°], the m. p. of these derivatives generally being higher than those previously recorded in the literature. Oxidation of  $\alpha$ -amyrone with absolute nitric acid in acetic acid gives a small quantity of a crystalline substance,  $C_{10}H_{16}O_5$ , m. p. 209–210°, whilst evaporation of the mother-liquor yields an amorphous residue separated by sodium carbonate into an acidic, amorphous substance,  $C_{28}H_{40}O_9N_2$ , decomp. 220–225° (equivalent, by titration, 261), and an amorphous substance,  $C_{29}H_{45}O_9N_3$ , decomp. 220°, which is insoluble in sodium carbonate and is the main product of the oxidation process. The two last-named substances seem also to be obtained by similar oxidation of  $\beta$ -amyrone, although absolute identity cannot be established owing to the failure to obtain them in crystalline form. Attempts to prepare sulphonic acid derivatives of amyirin, to convert amyrone oximes into isooximes, or to prepare an isonitroso-derivative of the ketones were all unsuccessful.

J. W. BAKER.

**Rotenone, the active constituent of *Derris* root.** III. **Tubaic acid.** S. TAKEI and M. KOIDE (Ber., 1929, 62, [B], 3030–3034).—Mainly a more detailed account of work published previously (cf. A., 1929, 933). The preparation of tubaic acid from rotenone is fully described. *Thallium tubate*, m. p. 169°, *methyl tubate*, m. p. 52°, and the *p*-toluene-sulphonyl derivative of hydrotubaic acid, m. p. 70°, have been prepared.

H. WREN.

**Oxidation of  $\alpha$ -terpinene with perbenzoic acid.** L. A. ELSON, C. S. GIBSON, and J. L. SIMONSEN (J.C.S., 1929, 2732–2735).—A specimen of  $\alpha$ -terpinene of b. p. 173–180°,  $d_4^{25}$  0.8529,  $n_D^{25}$  1.4748, was added to an ice-cold solution of perbenzoic acid in chloroform. The product was separated by distillation etc. into three fractions: (1) containing mainly *p*-cymene present in the original oil, (2) consisting of 1:4-oxido- $\Delta^2$ -*p*-menthene,



$d_4^{25}$  0.9281,  $n_D^{25}$  1.4728, oxidised by potassium permanganate in alkaline solution to 1:4-cineolic acid, and (3) an unidentified complex mixture. Oxygen addition to  $\alpha$ -terpinene therefore occurs in the 1:4-positions and the projected synthesis of the compound obtained by heating ascaridole to 150° cannot be realised.

R. J. W. LE FÈVRE.

**Derivatives of pinonic acid.** O. FERNÁNDEZ and M. M. CASTILLA (Anal. Fís. Quím., 1929, 27, 659–662).—*Pinononitrile*, b. p. about 140°/12 mm., is prepared by heating zinc pinonate with lead thiocyanate. It is impracticable to prepare it by way of the *amide*, m. p. 179°, because of the low yield of the latter. Reduction of the nitrile by sodium and alcohol yields the unstable *amine*,  $C_{10}H_{17}O(NH_2)$  (*hydrochloride*), whilst boiling with hydroxylamine in alcohol yields the *amine oxime*,  $NH_2 \cdot C_{10}H_{15} \cdot N \cdot OH$ . Interaction of pinonic acid with sodium or amyl nitrite gives *pinoylformaldoxime*, from which the *aldehyde*, b. p. 162°/15 mm. (*quinoxaline* derivative, decomp. without melting, with *o*-phenylenediamine) is obtained by hydrolysis.

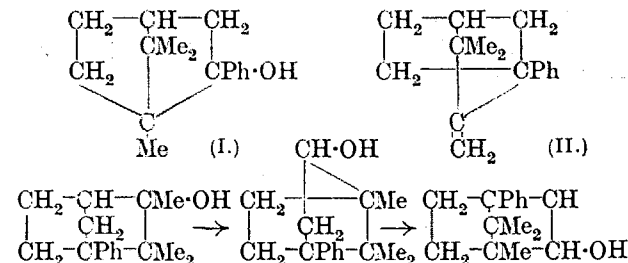
R. K. CALLOW.

**Transformations of ethylene oxides in the terpene series.** M. FAIDUTTI (Compt. rend., 1929, 189, 854–856).—Distillation over silica or pumice-stone of camphene oxide, b. p. 90–92°/20 mm., prepared by the action of perbenzoic acid on camphene, gives camphenylaldehyde (semicarbazide, m. p. 191–192°). Treatment of nopinene with perbenzoic acid gives an *oxide*, b. p. 98–99°/33 mm.,  $d_4^{25}$  0.963,  $n_D^{25}$  1.47576, which, by similar distillation or by treating with zinc chloride in ethereal solution, gives an *aldehyde*, b. p. 207–208°/755 mm.,  $d_4^{25}$  0.977,  $n_D^{25}$  1.47703, regarded as possibly identical with dihydromyrtanal.

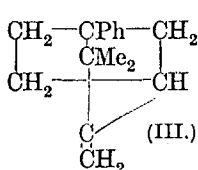
A. A. GOLDBERG.

**Phenyl-substituted camphor and its derivatives.** S. S. NAMETKIN, A. S. KITCHKIN, and D. N. KURSANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1065–1079).—Tertiary phenylbornyl alcohol (I),  $\alpha$ -phenylcamphene (II), phenylisoborneol from  $\alpha$ -phenylcamphene,  $\beta$ -phenylcamphene, phenylcamphor, and phenylcamphane were investigated with the view of determining the position of the phenyl group in phenylisoborneol and its derivatives.

Phenylcamphane, b. p. 147.5–148°/14 mm., m. p. 13.5°,  $d_4^{25}$  0.9817,  $n_D^{25}$  1.5387, was obtained from the hydrazone of phenylcamphor, m. p. 67.5–68°, by heating with sodium ethoxide in a sealed tube. The hydrocarbon, on nitration with dilute nitric acid, gave only a compound containing a secondary nitro-group, and no trace of a tertiary one, thus indicating the absence of a tertiary hydrogen atom, and of the grouping :CHPh. The position of the phenyl group is thus determined and the mechanism of the dehydration of tertiary phenylbornyl alcohol to  $\alpha$ -phenylcamphene and hydration of the latter to phenylisoborneol, m. p. 115.5–116°, elucidated, and shown to be similar to the transformation of  $\alpha$ -methylcamphene into 4-methylisoborneol (Nametkin and Briusova, A., 1928, 182).







During the process of dehydration, however, a pinacol-pinacolin rearrangement may partly take place, with the formation of  $\beta$ -phenylcamphene (III), m. p. 32–5°, b. p. 128–129°/7 mm.,  $d_4^{20}$  0.9919,  $n_D^{20}$  1.5449, which was isolated from the reaction mixture. M. ZVEGINTZOV.

**Optically active pinocarveol.** H. SCHMIDT (Ber., 1929, 62, [B], 2945–2949).—Distillation of the residues from the fractionation of the oil from *Eucalyptus globulus* discloses the presence of terpinol, identified as terpin hydrate. A portion, b. p. 207–209°,  $d_4^{20}$  0.965,  $\alpha_D$  –42°, when treated successively with boric acid and phenylcarbimide affords the phenylurethane of pinocarveol, m. p. 84–85°, from which pinocarveol, b. p. 208–209°/750 mm., m. p. 7°,  $d_4^{20}$  0.981,  $n_D^{20}$  1.49961,  $[\alpha]_D^{20}$  –62.19° ( $\alpha$ -naphthylurethane, m. p. 95°), is derived. It is converted quantitatively by sodium acetate and acetic anhydride into the acetate, b. p. 227–228°/760 mm.,  $d_4^{20}$  0.997,  $\alpha_D$  +15.8°, and by dilute sulphuric acid into a bimolecular hydrate, (C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>)<sub>2</sub>,  $\alpha_D^{20}$  –30.15° in alcohol. Bromination of pinocarveol in chloroform or alcohol yields a compound (C<sub>10</sub>H<sub>16</sub>OBr)<sub>2</sub>, m. p. 160°, stable towards permanganate. Oxidation with chromic acid gives mainly cuminaldehyde with some pinocaryone. H. WREN.

**Bromination of desylacetophenone.** C. F. H. ALLEN and E. F. HERRMANN (J. Amer. Chem. Soc., 1929, 51, 3591–3594).—Bromination of desylacetophenone in chloroform or acetic acid solution gives a quantitative yield of 4-bromo-2 : 3 : 5-triphenylfuran (A., 1927, 971). Bromination of small amounts of the diketone in acetic acid containing a large amount of potassium acetate affords  $\alpha$ -bromo- $\alpha\beta$ -dibenzoyl- $\beta$ -phenylethane, m. p. 119°, decomp. 130°, in 25% yield. This is converted by alcoholic potassium hydroxide into  $\alpha\beta$ -dibenzoylstyrene and by boiling acetic acid into the above furan.  $\alpha$ -Benzoyl- $\beta$ -p-toluoyl- $\alpha$ -phenylethane, m. p. 122°, and 2- $\beta$ -benzoyl- $\beta$ -phenylpropionylthiophen, m. p. 126°, are prepared by Smith's method (J.C.S., 1890, 57, 649).

H. BURTON.

**Catalytic hydrogenation of the pyrone nucleus.** J. P. DÁVILA (Anal. Fis. Quím., 1929, 27, 637–646).—Catalytic hydrogenation of ethyl chelidonate (ethyl 1 : 4-pyrone-2 : 6-dicarboxylate) in acetic acid in presence of platinum oxide–platinum-black yields a mixture of ethyl tetrahydropyran-2 : 6-dicarboxylate, b. p. 170°/20 mm. [acid, m. p. 188°; amide (+H<sub>2</sub>O), m. p. 262° (decomp.)], and a fraction of b. p. 180–220°/20 mm. The latter probably consists of a mixture of ethyl 4-hydroxytetrahydropyran-2 : 6-dicarboxylate, m. p. 52° (+H<sub>2</sub>O), (I), and the lactone ester, the former of which yields 4-hydroxytetrahydropyran-2 : 6-dicarboxylamide, m. p. 288° (decomp.). I is obtained as the chief product of hydrogenation in decalin solution and is isolated in the pure state from the reaction mixture. R. K. CALLOW.

**Phosphoryl chloride as a condensing agent in the synthesis of coumarin derivatives.** K. G. NAIK, R. D. DESAI, and R. K. TRIVEDI (J. Indian Chem. Soc., 1929, 6, 801–802).—The authors have

been unable to effect condensation of  $\alpha$ -naphthol and ethyl benzylacetoacetate with sulphuric acid as described by Jacobson and Ghosh (J.C.S., 1915, 107, 424). With phosphoryl chloride, condensation occurs readily. Ethyl benzylacetoacetate condenses with resorcinol, pyrogallol, and phloroglucinol in presence of phosphoryl chloride (cf. *loc. cit.*). H. BURTON.

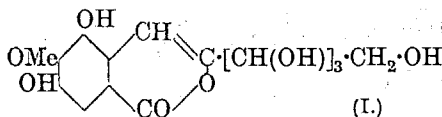
**Orienting influence of oxonium oxygen.** The nitration of 2-phenylbenzopyrylium perchlorate and ferrichloride. R. J. W. LE FÈVRE (J.C.S., 1929, 2771–2774).—2-Phenylbenzopyrylium ferrichloride and perchlorate, m. p. 178–179°, gave by nitration at the ordinary temperature 3'-nitro-2-phenylbenzopyrylium ferrichloride, m. p. 145–147°, and perchlorate, m. p. 239–241° after softening at about 230°. The yield of the latter salt after 40 hrs.' nitration using nitric acid of  $d$  1.5 was 86%. The 14% deficiency may have been due to destruction of the initial salts by nitric acid, or to formation and destruction of isomeric 2'- or 4'-nitrophenylbenzopyrylium salts. 4'-Nitro-2-phenylbenzopyrylium perchlorate (obtained from salicylaldehyde,  $p$ -nitroacetophenone, formic acid, and hydrogen chloride) had m. p. about 220°, decomp. about 225°, and was destroyed by nitric acid in 2 days. The above 3'-nitrophenylbenzopyrylium perchlorate was synthesised similarly using  $m$ -nitroacetophenone. Salicylidene- $m$ - and  $p$ -nitroacetophenones (?) have m. p. 252° and 297–298°, respectively.

R. J. W. LE FÈVRE.

**Colloidal phenoxides. I. Relation between constitution and colloidal properties in benzoyl-pyrones.** W. BAKER and F. M. EASTWOOD (J.C.S., 1929, 2897–2907).—In an attempt to discover any relationship between constitution and the ability to form gels in dilute alkali hydroxide solution such as is shown by 7-hydroxy-2 : 3-diphenylbenzo- $\gamma$ -pyrone (A., 1925, i, 1299) a number of closely-related benzoyl-pyrones have been prepared. Although no simple relationship exists, the following substituents must be present for the formation of a colloidal phenoxide : (1) a hydroxyl group in position 7 with or without a second hydroxyl group in position 5; (2) a phenyl,  $p$ -methoxyphenyl, or styryl group in position 2, further substitution in these groups not necessarily being excluded; (3) a phenyl group in position 3 except when a styryl group occupies position 2, in which case a  $p$ -methoxyphenyl group may replace the phenyl group. The following are prepared, the formation of a gel being indicated by the letter (g) after the compounds concerned. 7-Hydroxy-3-phenyl-2-styrylbenzo- $\gamma$ -pyrone, m. p. 298° (slight decomp.) (g), is obtained by hydrolysis of the corresponding 7-cinnamoyloxy-derivative (Baker and Robinson, *loc. cit.*) with aqueous-alcoholic potassium hydroxide and precipitation with carbon dioxide. The following are obtained by fusion of the appropriate  $o$ -hydroxyphenyl benzyl ketone with a mixture of the anhydride and the sodium salt of the appropriate aromatic acid : 5 : 7-dihydroxy-2 : 3-diphenylbenzo-, m. p. 252° (g), methylated with methyl sulphate to 5-hydroxy-7-methoxy-2 : 3-diphenylbenzo-, m. p. 193–194° (together with a little of the dimethyl ether); 5 : 7-dihydroxy-3-phenyl-2-styrylbenzo-, m. p. 281° (slight decomp.)

(g), through the intermediate 5-hydroxy-7-cinnamoyloxy-compound, m. p. 232°; 7-hydroxy-3-p-methoxyphenyl-2-styrylbenzo-, m. p. 304° (g), through the intermediate 7-cinnamoyloxy-derivative, m. p. 221° (the required 2:4-dihydroxyphenyl p-methoxybenzyl ketone, m. p. 159°, being obtained by hydrolysis of the ketimine obtained by the action of dry hydrogen chloride and zinc chloride on an ethereal solution of p-methoxyphenylacetonitrile and resorcinol at 0°); 7-hydroxy-2-phenyl-3-p-methoxyphenylbenzo-, m. p. 264°; 5:7-dihydroxy-2-phenyl-3-p-methoxyphenylbenzo-, m. p. 230—231° (acetyl derivative, m. p. 196—197°); 7-hydroxy-3-phenyl-2-p-methoxyphenylbenzo-, m. p. 288° (g); 7-hydroxy-2:3-di-p-methoxyphenylbenzo-, m. p. 271—272° (dimorphous); 7-hydroxy-3-phenyl-2-(3:4-dimethoxyphenyl)benzo-, m. p. 240° (the preparation of which requires carefully controlled conditions which are described) (properties of its alkali salts are peculiar owing to its marked basic, oxonium properties), methylated with methyl sulphate in aqueous-acetone potassium hydroxide solution to its methyl ether, m. p. 181°; and 6-hydroxy-2:3-diphenylbenzo-, m. p. 258—260° (slight decomp.) (sodium salt), - $\gamma$ -pyrone. The 2:5-dihydroxyphenyl benzyl ketone, m. p. 109.5°, required for the preparation of the last-named pyrone is obtained by demethylation of the corresponding 2:5-dimethoxy-derivative (Kauffmann, A., 1906, i, 283) with a mixture of hydriodic and glacial acetic acids, the substance, m. p. 170°, described by Finzi (A., 1905, i, 906) as this ketone probably being unchanged quinol, since this is the only phenolic product which could be isolated by the interaction of quinol with phenylacetic acid and zinc chloride or phenylacetyl chloride and aluminium chloride. Derivatives with a benzyl group in position 2 could not be prepared, since 2:4-dihydroxyphenyl benzyl and  $\beta$ -phenylethyl ketones condense with phenylacetic anhydride and sodium phenylacetate to give, respectively, 7-hydroxy-3-phenyl-4-benzyl-, m. p. 232° (methyl ether, m. p. 183—184°), and 7-hydroxy-3:4-dibenzyl-, m. p. 220° and 210° (dimorphous) (methyl ether, m. p. 144°). -coumarin. The ketonic intermediates required for the preparation of 8-hydroxybenzo- $\gamma$ -pyrones could not be prepared, since magnesium benzyl cyanide would not react with 2:3-dimethoxybenzaldehyde, nor with 2:3-dimethoxybenzonitrile, m. p. 47° (prepared by dehydration of the corresponding benzaldoxime). Similarly, condensation of guaiacol with ethyl  $\alpha$ -phenylacetoacetate gives only a trace of an unidentified substance, C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>, m. p. 203°. J. W. BAKER.

**Non-tannin substance of extract of *Saxifraga crassifolia*.** I. Bergenin. A. E. TSCHITSCHIBABIN, A. V. KIRSANOV, A. I. KOROLEV, and N. N. VOROSHOV (Bull. Acad. Sci. U.S.S.R., 1929, 323—354). —An exhaustive study of the constitution of bergenin [cf. Garrau and Machelart, Compt. rend., 1880, 91, 942; Morelli, A., 1882, 159; Povarnin, Vestnik Tanning Ind. (Russ.), 1921, No. 13, 13; Sadikov and Guthner, A., 1928, 207]. Bergenin is shown to be 5:7-dihydroxy-6-methoxy-3- $[\alpha\beta\gamma\delta$ -tetrahydroxybutyl]isocoumarin (I), the evidence for this structure being as follows.



Although bergenin, C<sub>14</sub>H<sub>16</sub>O<sub>9</sub>, m. p. 233° (uncorr.),  $[\alpha]_D^{25}$  -37.25°, contains six hydroxyl groups, as is shown by Zerevitinov's method (A., 1912, i, 841), it yields only a penta-acetyl derivative, m. p. 199—203°. Two of the hydroxyl groups are phenolic in character, since, with sodium ethoxide in absolute alcoholic solution, bergenin gives a monosodium salt or, with a large excess of the ethoxide, a disodium salt, and when methylated by means of diazomethane it forms dimethylbergenin, C<sub>13</sub>H<sub>11</sub>O<sub>6</sub>(OMe)<sub>3</sub>, m. p. about 80° (+2H<sub>2</sub>O) or 194—196° (anhydrous). Bergenin contains no aldehydic or ketonic carbonyl grouping and no free carboxyl group, but the presence of a lactonic grouping is shown by the results of the slow titration of the solution of either bergenin or its penta-acetyl compound with aqueous alkali hydroxide in presence of phenolphthalein.

Oxidation of dimethylbergenin with alkaline permanganate solution yields a number of products, of which three were investigated: (1) 5:6:7-trimethoxyisocoumarin, (OMe)<sub>3</sub>C<sub>6</sub>H< $\begin{smallmatrix} \text{CH}:\text{CH} \\ \text{CO}\cdot\text{O} \end{smallmatrix}$ >, m. p. 84°, which on dissolution in the theoretical quantity of boiling 0.1N-sodium hydroxide and subsequent acidification gives the compound (OMe)<sub>3</sub>C<sub>6</sub>H(CO<sub>2</sub>H)·CH<sub>2</sub>·CHO [or (OMe)<sub>3</sub>C<sub>6</sub>H(CO<sub>2</sub>H)·CH:CH·OH], m. p. 129°, this remaining unchanged when boiled with dilute acid and yielding trimethoxyisocoumarin when distilled in a vacuum. Like isocoumarin (Bamberger and Frew, A., 1894, i, 192), the compound of m. p. 129° gives an uncrystallisable resin with phenylhydrazine. The action of excess of boiling aqueous sodium hydroxide decomposes trimethoxyisocoumarin more profoundly, giving a crystalline compound, C<sub>24</sub>H<sub>26</sub>O<sub>11</sub>, which does not exhibit acid properties and is analogous in composition to the compound

C<sub>6</sub>H<sub>4</sub>< $\begin{smallmatrix} \text{CH}:\text{CH}\cdot\text{O}\cdot\text{CH}:\text{CH} \\ \text{CO}\text{---}\text{O}\text{---}\text{CO} \end{smallmatrix}$ >C<sub>6</sub>H<sub>4</sub> similarly obtained from isocoumarin (Bamberger and Frew, loc. cit.).

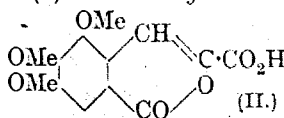
Alkali permanganate oxidises 5:6:7-trimethoxyisocoumarin to 3:4:5-trimethoxyhomophthalic acid, CO<sub>2</sub>H·C<sub>6</sub>H(OMe)<sub>3</sub>·CH<sub>2</sub>·CO<sub>2</sub>H, m. p. 145—146°, which forms an anhydride, m. p. 124—125°, when distilled in a vacuum, and may be synthesised according to the following scheme: gallic acid  $\rightarrow$  3:4:5-trimethoxybenzoic acid  $\rightarrow$  syringic acid  $\rightarrow$  trichloromethylhydroxydimethoxyphthalide

OH·C<sub>6</sub>H(OMe)<sub>2</sub>< $\begin{smallmatrix} \text{CH}(\text{CCl}_3) \\ \text{CO} \end{smallmatrix}$ >O  $\rightarrow$  4-hydroxy-3:5-dimethoxyphthalidecarboxylic acid  $\rightarrow$  3:4:5-trimethoxyhomophthalic acid  $\rightarrow$  3:4:5-trimethoxyhomophthalic acid.

(2) Trimethoxyisocoumarincarboxylic acid (II), m. p. 254°, which loses carbon dioxide, giving 5:6:7-trimethoxyisocoumarin.

(3) 3:4:5-Trimethoxyphthalic acid (cf. Alimchandani and Meldrum, J.C.S., 1920, 117, 968).

The positions of the methoxyl groups in bergenin are



shown by the fact that bergenin yields 3 : 5-dihydroxy-4-methoxybenzoic acid when fused with potassium hydroxide. Bergenin may be coupled with either one or two molecules of a diazonium salt: the orange-red compound,  $C_{14}H_{15}O_9 \cdot N_2Ph$ , decomposes at about  $200^\circ$ , and the cinnamon compound,  $C_{14}H_{14}O_9(N_2Ph)_2$ , dyes wool in an acid bath. In the formation of the second class of compounds it is possible either that the second diazophenyl group enters the pyrone ring of the isocoumarin nucleus or that a hydrazone is formed after rupture of the pyrone ring. *Aminobergenin*,  $C_{14}H_{17}O_9N + 3H_2O$ , m. p. (decomp.)  $224^\circ$  (anhydrous), forms a *diazo-oxide*,  $C_{14}H_{17}O_9N_2 + 2H_2O$ , decomposing from about  $180^\circ$  onwards.

The action of ammonia on 5 : 6 : 7-trimethoxyisocoumarin yields the compound  $(OMe)_3C_6H < \begin{smallmatrix} CH=CH \\ C(OH):N \end{smallmatrix}$  and that on 5 : 6 : 7-trimethoxyisocoumarincarboxylic acid the compound  $(OMe)_3C_6H < \begin{smallmatrix} CH=CH \\ C(OH):N \end{smallmatrix} CO_2H$ . Bergenin and dimethylbergenin also react with ammonia, the product probably being  $(OR)_3C_6H < \begin{smallmatrix} CH=CH \\ C(OH):N \end{smallmatrix} [CH \cdot OH]_3 \cdot CH_2 \cdot OH$ .

T. H. POPE.

**Coumaro- $\alpha$ -pyrones.** R. N. SEN and D. CHAKRAVARTI (J. Indian Chem. Soc., 1929, 6, 793—800).—Hydroxycoumarins usually condense readily with malic acid or ethyl acetoacetate in presence of sulphuric acid, yielding coumaro- $\alpha$ -pyrones. Thus, umbelliferone and malic acid give a *coumaro- $\alpha$ -pyrone*,  $CH:CH > C_6H_2 < \begin{smallmatrix} CH:CH \\ CO-O \end{smallmatrix}$ , m. p.  $245-250^\circ$  (the methyl derivative, m. p.  $304-305^\circ$ , is obtained similarly from 4-methylumbelliferone). Homoumbelliferone and malic acid afford a *methylcoumaro- $\alpha$ -pyrone*, m. p.  $318-320^\circ$ ; with ethyl acetoacetate a *dimethylcoumaro- $\alpha$ -pyrone* is produced. 4-Methylumbelliferone and ethyl acetoacetate furnish a *dimethylcoumaro- $\alpha$ -pyrone*, identical with the dimethyldi-coumarin of Hantzsch and Zürcher (A., 1887, 830); similarly, 4-methylhomoumbelliferone gives a *trimethylcoumaro- $\alpha$ -pyrone*. Daphnetin and malic acid yield a *hydroxycoumaro- $\alpha$ -pyrone* [methyl derivative (*monoacetate*), prepared similarly from 4-methyldaphnetin]. 5 : 7-Dihydroxy-4-methylcoumarin and malic acid afford a *hydroxycoumaro- $\alpha$ -pyrone*, decomp.  $320^\circ$  (*acetate*). Alternative formulæ are suggested for the above compounds.

H. BURTON.

**Penthian series. II. Penthian-4-one. III. Stereoisomeric derivatives of some penthianols.** G. M. BENNETT and W. B. WADDINGTON (J.C.S., 1929, 2829—2832, 2832—2838).—II. Penthian-4-one reacts with the appropriate arylhydrazine in ethyl-alcoholic solution to yield the *phenylhydrazone*, m. p.  $119^\circ$  (converted by boiling acetic acid into *penthienindole*, I, m. p.  $157^\circ$ ), the *p-nitrophenylhydrazone*, m. p.  $156^\circ$  (unaffected by boiling acetic acid), and the *p-bromophenylhydrazone*, m. p.  $144^\circ$  (giving with acetic acid, 8-bromopenthienindole, m. p.  $162^\circ$ ).

Penthianone gives with one equivalent of hydrogen peroxide an impure *sulphoxide* (?), m. p.  $113^\circ$ , and

with 2.5 equivalents the corresponding *sulphone*, m. p.  $170^\circ$ . Treatment of an aqueous solution of penthianone with potassium cyanide in presence of sodium hydrogen sulphite gives *penthianone cyanohydrin*, m. p.  $63^\circ$ , which is hydrolysed by warming with hydrochloric acid to *penthianolcarboxylic acid*, m. p.  $133^\circ$  (corresponding *sulphone*, m. p.  $208^\circ$ ). Penthianone reacts with magnesium phenyl bromide in ethereal solution, forming *4-phenylpenthian-4-ol*, m. p.  $78^\circ$  (corresponding *phenylurethane*, m. p.  $186.5-188^\circ$ ; *sulphone*, m. p.  $197^\circ$ ). Magnesium benzyl chloride similarly gives *4-benzylpenthian-4-ol*, m. p.  $51^\circ$  (*phenylurethane*, m. p.  $194-195.5^\circ$ ; corresponding *sulphone*, m. p.  $152.5^\circ$ ).

Crystallographic data for penthianone are recorded.

II. Oxidation of the three penthianols (see above) by hydrogen peroxide gives, in each case, a mixture of two stereoisomeric oxides as required by theory. Thus phenylpenthianol gives *4-phenylpenthian-4-ol  $\alpha$ -oxide*, m. p.  $187-187.5^\circ$ , and  *$\beta$ -oxide*, m. p.  $199-200^\circ$ ; their crystalline forms are orthorhombic and monoclinic, respectively, and their solubilities in ethyl acetate at  $20^\circ$  are 0.422 and 0.475 g., respectively, per 100 g. of solvent. From benzylpenthianol are derived *4-benzylpenthian-4-ol  $\alpha$ -oxide*, m. p.  $186^\circ$  (orthorhombic), and  *$\beta$ -oxide*, m. p.  $150.5-152.5^\circ$  (monoclinic); their solubilities in ethyl acetate (100 g.) at  $20^\circ$  are 0.297 g. and 0.872 g., respectively. Penthianolcarboxylic acid yields *penthian-4-ol-4-carboxylic acid  $\alpha$ -oxide*, m. p.  $222^\circ$  (decomp.; bath preheated to  $210^\circ$ ), and  *$\beta$ -oxide*, m. p.  $182-184^\circ$  (decomp.); their solubilities in 100 g. of methyl ethyl ketone at  $21.5^\circ$  are 0.25 g. and 0.30 g., respectively.

Phenylpenthianol, when boiled with an excess of ethyl-alcoholic methyl iodide, gives only *4-phenyl-1-methylpenthian-4-olsulphonium  $\alpha$ -iodide*, m. p.  $182.5^\circ$  (decomp.), when the crude product is crystallised from 90% alcohol. The crude iodides are therefore converted by aqueous sodium picrate into picrates from which are isolated *4-phenyl-1-methylpenthian-4-olsulphonium  $\alpha$ -picrate*, m. p.  $158^\circ$ , and  *$\beta$ -picrate*, m. p.  $146-148^\circ$ ; these, by acidification with hydrochloric acid etc., give  *$\alpha$ - and  $\beta$ -chloroplatinates*, m. p.  $190-200^\circ$  and m. p.  $165-194^\circ$ , respectively. Addition of aqueous "chloramine-T" to alcoholic phenylpenthianol yields *4-phenylpenthian-4-ol-1-p-toluenesulphonylimine*, m. p.  $217^\circ$ , in an apparently uniform condition.

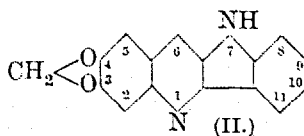
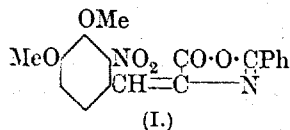
Full crystallographical data for the first three pairs of isomerides are recorded. R. J. W. LE FÈVRE.

**6 : 7-Dimethoxyisatin, 5 : 6-methylenedioxyisatin, and the nuclear degradation of 3 : 4-methylenedioxyquinoline.** J. M. GUILLAND, R. ROBINSON, J. SCOTT, and S. THORNLEY (J.C.S., 1929, 2924—2941).—The results of four series of exploratory researches in various syntheses are described. (A) Unsuccessful attempts to prepare 4 : 7-dimethoxyisatin by ring closure of derivatives of 2 : 5-dimethoxyaniline. The last-named substance, prepared in 82% yield by reduction of nitroquinol dimethyl ether under prescribed conditions, is converted by the action of sulphuric acid on its mixture with chloral hydrate, hydroxylamine hydrochloride, and water at its b. p. into *di-(2 : 5-dimethoxyanilino)-aceto-2 : 5-dimethoxyanilide*,

$[C_6H_3(OMe)_2 \cdot NH]_2CH \cdot CO \cdot NH \cdot C_6H_3(OMe)_2$  (?), m. p. 210°, isolated as its *sulphate*, m. p. 298° (decomp.). Gradual addition of 2:5-dimethoxyaniline, with heating, to mixed solutions of formaldehyde and sodium hydrogen sulphite gives 2:5-dimethoxyanilinoacetoneitrile, m. p. 113.5°, separated from the by-product, 4:4'-di(cyanomethylamino)-2:5:2':5'-tetramethoxydiphenylmethane,  $CN \cdot CH_2 \cdot NH \cdot C_6H_2(OMe)_2 \cdot CH_2 \cdot C_6H_4(OMe)_2 \cdot NH \cdot CH_2 \cdot CN$ , m. p. 236°, by its solubility in hot 95% alcohol. The nitrile is hydrolysed by cold concentrated sulphuric acid to 2:5-dimethoxyanilinoacetamide, m. p. 164°. When 2:5-dimethoxyaniline is heated with anhydrous oxalic acid at a temperature not exceeding 130°, *or*-2:5-dimethoxyanilic acid, m. p. 138°, is obtained, whilst by heating with acetic anhydride and glacial acetic acid and subsequent addition of bromine, *aceto*-4-bromo-2:5-dimethoxyanilide, m. p. 123°, is obtained. This is hydrolysed by boiling concentrated hydrochloric acid to 4-bromo-2:5-dimethoxyaniline, m. p. 107°, and is converted by nitric (*d* 1.42) and acetic acids into *aceto*-4-nitro-2:5-dimethoxyanilide by replacement of the bromine atom.

(B) Reduction of 6-nitro-3:4-methylenedioxy-mandelic acid (prepared from crude 6-nitropiperonal; Robinson and Robinson, J.C.S., 1914, 105, 1466) by ferrous sulphate and ammonia followed by atmospheric oxidation of the solution affords 5:6-methylenedioxyisatin, which with dilute nitric acid at 60° undergoes smooth fission to *or*-6-nitro-3:4-methylenedioxyanilic acid, m. p. 183° (decomp.), hydrolysed by hot aqueous sodium carbonate to 5-nitro-4-amino-pyrocatechol methylene ether.

(C) The azlactone (I), obtained in 75% yield when 2-nitroveratraldehyde and hippuric acid are condensed with fused sodium acetate and acetic anhydride, has m. p. 170° (Bain, Perkin, and Robinson, J.C.S., 1914,

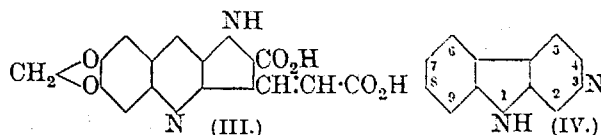


105, 2403, give 145°), is converted by short hydrolysis with 10% sodium hydroxide or dilute alcoholic hydrochloric acid into 2-nitro- $\alpha$ -benzamido-3:4-dimethoxycinnamic acid, m. p. 224—225° (decomp.) (*loc. cit.*, m. p. 228°), but by prolonged hydrolysis with boiling dilute aqueous-alcoholic sodium hydroxide is converted into 6:7-dimethoxyisatin, m. p. 212—213° [*semicarbazone*, m. p. 254° (decomp.)], and 2-aminoveratric acid. The former is also obtained, together with a larger relative amount of an acid, m. p. 178° (decomp.), possibly *azodimethoxyphenylglyoxylic acid*.

$(MeO)_2C_6H_3(CO \cdot CO_2H) \cdot N_2 \cdot C_6H_3(OMe)_2 \cdot CO \cdot CO_2H$ , by sodium amalgam reduction of an aqueous suspension of 2-nitro-3:4-dimethoxymandelic acid, m. p. 127° (prepared by hydrolysis of the nitrile obtained by the action of powdered potassium cyanide and glacial acetic acid on 2-nitroveratraldehyde). 6:7-Dimethoxyisatin is reduced by sodium hyposulphite in boiling water to 6:7-dimethoxydioxindole, m. p. 200° (decomp., after softening from 170°), further reduced by sodium amalgam in neutral solution to 6:7-dimethoxyoxindole, m. p. 192—193°. The last-named

is also obtained when 2-nitro-3:4-dimethoxyphenylacetic acid (Kay and Pietet, J.C.S., 1913, 103, 947) is reduced with tin and hydrochloric acid, or is reduced by ferrous sulphate and ammonia to 2-amino-3:4-dimethoxyphenylacetic acid, m. p. 154° (decomp.), and this is dehydrated by heating at 160°.

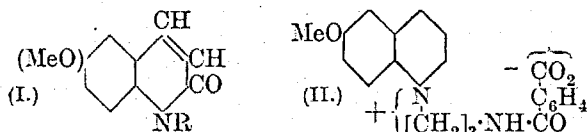
(D) Condensation of 6-aminopiperonal (Rilliet and Kreitmann, A., 1921, i, 567) with technical indoxyl fusion in boiling 95% alcoholic solution in a coal gas atmosphere gives 3:4-methylenedioxyquinoline (II), m. p. 280°, which, however, could not be degraded to  $\delta$ -carboline (for nomenclature, see below). Rapid oxidation with the minimum quantity of chromic acid in glacial acetic acid gives only a small yield of an acid, m. p. 312° (decomp.), which probably has the structure III, whilst nitration with nitric acid (*d* 1.42) gives the 10-nitro-derivative, decomp. 360° without melting, with previous colour changes. Oxidation of this nitro-compound with 47% nitric acid



gives traces of the acid obtained by the action of boiling 29% or 47% nitric acid on 3:4-dihydroxyquinoline, isolated as its *hydrochloride* + 2.5H<sub>2</sub>O, darkening at 273°, not melting at 308° (*sulphate*, decomp. 268°), obtained from 3:4-methylenedioxyquinoline by application of the method of Späth and Lang (A., 1922, i, 166). Oxidation of this base with nitric acid gives a mixture of (probably) 7-nitro- $\delta$ -carboline-3:4-dicarboxylic acid, and 7-nitro- $\delta$ -carboline-3-carboxylic acid, m. p. 338—339° (decomp.), into which the whole product was converted by heating with acetic acid. Reduction of this acid with ferrous sulphate and ammonia gives a substance, not melting at 360°, which is probably the corresponding 7-azoxyacid. In numbering the carboline it is suggested that, in conformity with other condensed nuclear types, the substances originally known as 3-, 4-, 5-, and 6-carbolines should be renamed 2-, 3-, 4-, and 5-carbolines, or, better, to avoid confusion,  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -carboline, respectively,  $\beta$ -carboline being represented by IV. J. W. BAKER.

Attempts to find new anti-malarials. II. Aminoalkylquinolinium salts and some related substances. T. R. SESHADRI (J.C.S., 1929, 2952—2959).—Gabriel's method (A., 1921, i, 58) for the preparation of quaternary pyridonium salts has been extended to the preparation of similar derivatives of quinoline, 6-methoxyquinoline, and isoquinoline. When quinoline is heated with  $\beta$ -bromoethylphthalimide, m. p. 83°, at 100° it gives  $\beta$ -phthalimidoethylquinolinium bromide, m. p. 264—265° (*picrate*, m. p. 216—218°), hydrolysed to  $\beta$ -aminoethylquinolinium bromide hydrobromide, m. p. 275—277°, by boiling aqueous hydrobromic acid. The corresponding chloride hydrochloride has m. p. 270—271° (*picrate*, m. p. 238—239°). Oxidation of the quaternary bromide with alkaline potassium ferricyanide affords 1- $\beta$ -o-carboxybenzamidoethyl-2-quinolone (as I, R =  $[CH_2]_3 \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H$ ), which could not be puri-

fied, since it is easily converted by dehydration into the second product of the reaction, 1- $\beta$ -phthalimidoethyl-2-quinolone, m. p. 272—273°. Either of these products is hydrolysed by boiling dilute hydrochloric acid to 1- $\beta$ -aminoethyl-2-quinolone hydrochloride, m. p. 245—246° [picrate, m. p. 225° (decomp.)]. Similarly, from  $\gamma$ -bromopropylphthalimide are obtained



$\gamma$ -phthalimidopropylquinolinium bromide, m. p. 259—260°, hydrolysed to  $\gamma$ -aminopropylquinolinium bromide hydrobromide, m. p. 271—273° (chloride hydrochloride, m. p. 267—268°), and oxidised to 1- $\gamma$ -o-carboxybenzamidopropyl-2-quinolone, m. p. 153—154° (decomp.), hydrolysed to 1- $\gamma$ -aminopropyl-2-quinolone hydrochloride, m. p. 217—218°. By similar methods from 6-methoxyquinoline are obtained:  $\beta$ -phthalimidoethyl-6-methoxyquinolinium bromide +  $H_2O$  and anhydrous, m. p. 248—250° (decomp.) (picrate, m. p. 199—200°);  $\beta$ -aminoethyl-6-methoxyquinolinium chloride hydrochloride, m. p. 264—265° (decomp.) (picrate, m. p. 203—205°), demethylated by heating with concentrated hydrochloric acid at 150—160° to the corresponding -6-hydroxy-derivative, m. p. 267—269° [picrate, m. p. 248—249° (decomp.)]; 1- $\beta$ -o-carboxybenzamidopropyl-, m. p. 144—145° (decomp.), converted by heating at 140—145° into 1- $\beta$ -phthalimidoethyl-, m. p. 188—189°, -6-methoxy-2-quinolones; 1- $\beta$ -aminoethyl-6-methoxy- and -6-hydroxy-2-quinolone hydrochlorides, m. p. 266—267° and 281—282° (decomp.), respectively (picrates, m. p. 237° and 254—256°, respectively);  $\gamma$ -phthalimidopropyl-6-methoxyquinolinium bromide, +0.5 $H_2O$ , m. p. 125—127° (decomp.), and anhydrous, m. p. 198—200° (picrate, m. p. 208—210°), converted by the action of silver oxide on its hot aqueous solution into the betaine anhydro- $\gamma$ -o-carboxybenzamidopropyl-6-methoxyquinolinium hydroxide (II), sinters 140°, decomp. 198—199°;  $\gamma$ -aminopropyl-6-methoxy- and -6-hydroxy-quinolinium chloride hydrochlorides, m. p. 259—261° (decomp.), and 274—276°, respectively; 1- $\gamma$ -o-carboxybenzamidopropyl-, m. p. 164—165° (decomp.), and 1- $\gamma$ -phthalimidopropyl-, m. p. 149—150°, -6-methoxy-2-quinolones; 1- $\gamma$ -aminopropyl-6-methoxy-, and -6-hydroxy-2-quinolone hydrochlorides, m. p. 239—240° and 277—279°, respectively. From isoquinoline are obtained  $\beta$ -phthalimidoethylisoquinolinium bromide, m. p. 291—292°;  $\beta$ -aminoethylisoquinolinium bromide hydrobromide, m. p. 286—288° [chloride hydrochloride, m. p. 273—275°, also obtained through the betaine, m. p. 186—189° (decomp.)]; 2- $\beta$ -o-carboxybenzamidopropyl-, m. p. 167—168° (decomp.), and 2- $\beta$ -phthalimidoethyl-, m. p. 185—186°, -isoquinolones; 2- $\beta$ -aminoethylisoquinolone hydrochloride, m. p. 237—239°;  $\gamma$ -phthalimidopropylisoquinolinium bromide, m. p. 243—245°;  $\gamma$ -aminopropylisoquinolinium bromide hydrobromide, m. p. 228—229°;  $\gamma$ -aminopropylisoquinolinium chloride hydrochloride, m. p. 236—237° (sintering 135°); 2- $\gamma$ -phthalimidopropylisoquinolone, m. p. 157—158°; and 2- $\gamma$ -aminopropylisoquinolone hydrochloride, m. p. 189—191°.

J. W. BAKER.

**Condensations of benzaldehyde and ethyl acetoacetate with carbamide and thiocarbamide.** L. E. HINKEL and D. H. HEY (Rec. trav. chim., 1929, 48, 1280—1286).—Benzaldehyde, carbamide, and ethyl acetoacetate reacted together, either alone or in hot alcoholic solution, to give ethyl benzuramidocrotonate, m. p. 206° [dibromo-derivative, m. p. 182—183° (decomp.)], and ethyl 4-phenyldihydrolutidine-3:5-dicarboxylate, m. p. 156° (tetrabromo-derivative, m. p. 131°).

Ethyl  $\beta$ -uramidocrotonate reacted with benzaldehyde in alcoholic solution to form ethyl benzuramidocrotonate; with the addition of ethyl acetoacetate higher yields were experienced and some ethyl 4-phenyldihydrolutidine-3:5-dicarboxylate was also formed. The last-named compound was mainly formed when molecular proportions of benzaldehyde, ethyl acetoacetate, and ethyl  $\beta$ -amino- $\beta$ -uramidobutyrate were heated in alcoholic solution.

Benzylidenediureide, ethyl acetoacetate, and alcohol gave chiefly ethyl benzuramidocrotonate accompanied by a little ethyl 4-phenyldihydrolutidine-3:5-dicarboxylate.

Ethyl  $\beta$ -uramidocrotonate has m. p. 171° (lit. 147°, 165—166°), but the m. p. varies according to the crystallisation solvent used, evidently owing to the occurrence of the prototropic change:  $C:C:N \rightleftharpoons C:C:N$ , since alkaline hydrolysis etc. of the ester of m. p. 171° gives methyluracil quantitatively, whilst similar treatment of the lower-melting varieties gives only small amounts of this substance.

[With O. SAMUEL].—Benzaldehyde, thiocarbamide, and ethyl acetoacetate, when heated in presence or absence of alcohol as solvent, gave ethyl benzthiouramidocrotonate, m. p. 205°, along with an isomeric compound, m. p. 203°. The ester, m. p. 205°, when boiled with aqueous-alcoholic chloroacetic acid, formed ethyl benzuramidocrotonate, but the isomeric compound gave a new compound,  $C_{14}H_{18}O_3N_2$ , m. p. 203.5°. R. J. W. LE FÈVRE.

**Condensation of 2-aminopyridine with formaldehyde.** A. E. TSCHITSCHIBABIN and I. L. KNUNJANZ (Ber., 1929, 62, [B], 3048—3053).—2-Aminopyridine reacts readily with formaldehyde, yielding non-crystalline products converted by excess of the aldehyde in presence of boiling formic acid into tetramethyl-2-aminodi-5-pyridylmethane, b. p. 252—254°/11 mm., m. p. 85° [picrate, m. p. 227° (decomp.)]. Under similar conditions, 2-dimethylaminopyridine does not react with formaldehyde. When heated with sulphur at 190° the methane derivative is converted into tetramethyl-2-aminodi-5-pyridyl thioketone, m. p. 196° (decomp.), transformed by boiling 10% hydrochloric acid into tetramethyl-2-aminodi-5-pyridyl ketone, m. p. 169—170°; the oxime, m. p. 207°, of the ketone is isomerised by sulphuric acid monohydrate to a compound,  $C_{15}H_{19}ON_5$ , m. p. 244—245°, hydrolysed to 2-dimethylaminopyridine-5-carboxylic acid, m. p. 222°, identical with the acid prepared from 2-chloropyridine-5-carboxylic acid and dimethylamine at 180° (potassium salt). Treatment of tetramethyl-2-aminodi-5-pyridylmethane with nitric acid (d 1.52) in presence of sulphuric acid (d 1.84) at 0° yields (?) di-3-nitrotetramethyl-2-aminodi-5-pyridylmethane, m. p.

105°, which cannot be nitrated further. When heated with sodamide, tetramethyldi-2-aminodi-5-pyridylmethane loses dimethylamine. Reduction of tetramethyldiaminodipyridyl ketone with sodium amalgam affords *tetramethyldi-2-aminodi-5-pyridyl-carbinol*, m. p. 150—151°.

5-Nitro-2-aminopyridine is converted by boiling formaldehyde into a compound,  $C_{11}H_{10}O_4N_6$ , m. p. 262—264° (decomp.), which yields a *hydrochloride* and *sulphate* sparingly soluble in water. H. WREN.

**Products of the nitration of 2-dimethylaminopyridine.** A. E. TSCHITSCHIBABIN and I. L. KNUNJANZ (Ber., 1929, 62, [B], 3053—3054).—Under the conditions described previously (A., 1928, 427), 3-nitro-2-dimethylaminopyridine, m. p. 31°, is formed by the nitration of 2-dimethylaminopyridine; it is isolated by steam-distillation of the mother-liquors obtained after removal of the crude nitro-product.

Replacement of methyl sulphate by methyl iodide in the treatment of 2-aminopyridine results in a 65% yield of 2-dimethylaminopyridine. H. WREN.

**Indole halogeno-ketones. II.** G. SANNA (Gazzetta, 1929, 59, 838—850).—3- $\omega$ -Iodoacetyl-2-methylindole, m. p. 185° (decomp.) (N-silver derivative), is obtained in poor yield by the method previously described (A., 1929, 825), but is formed quantitatively by heating the bromo- or chloro-compound with potassium iodide in alcohol. The keto-alcohol (Mingoia, A., 1929, 579) is formed by treatment with 2-5% potassium hydroxide solution, but more concentrated alkali yields a mixture of condensation products. When the bromo- and iodo-compounds are warmed with phenylhydrazine acetate in aqueous solution the *phenylhydrazones*, m. p. 209—211° and 179°, respectively, are formed, accompanied in the latter case by a halogen-free substance, m. p. 200°. 2-Methyl-3-indacylpyridinium bromide, m. p. 291°, and iodide, m. p. 255°, are formed with pyridine, and are decomposed by 50% potassium hydroxide.

The following analogous derivatives of indole have been prepared by similar methods: 3- $\omega$ -Chloroacetylindole (3-indacyl chloride) (Majima and Kotake, A., 1923, i, 150) (N-silver derivative; *phenylhydrazone*, m. p. 130°, accompanied by a substance, m. p. 220°); *indacylpyridinium chloride*, m. p. 268°; 3- $\omega$ -bromoacetylindole (3-indacyl bromide), m. p. 230° (decomp.) (N-silver derivative); *indacylpyridinium bromide*, m. p. 256°; 3- $\omega$ -iodoacetylindole (3-indacyl iodide), m. p. 211° (N-silver derivative); *indacylpyridinium iodide*, m. p. 235°. The action of dilute potassium hydroxide solution on 3- $\omega$ -chloroacetylindole yields a substance, m. p. 90°, and (2) 3- $\omega$ -hydroxyacetylindole (+H<sub>2</sub>O), m. p. 160°.

The m. p. of the series of phenacyl, indacyl, methylindacyl, and methylindacylpyridinium chlorides are higher than those of the iodides, and the m. p. of the bromides are intermediate, with the exception of indacyl bromide, which has a higher m. p.

R. K. CALLOW.

**Doebner's reaction. IX.** R. CIUSA and L. MUSAJO (Gazzetta, 1929, 59, 796—804).—On the basis of previous work (A., 1921, i, 195; 1922, i, 1062) and the work of other authors, a mechanism for Doebner's reaction is proposed. The primary reaction

between benzylideneaniline and pyruvic acid, for example, is condensation to give the compound  $NHPh \cdot CHPh \cdot CH_2 \cdot CO \cdot CO_2H$  (I) (cf. Carrara, A., 1928, 1024). In the main reaction (cf. Borsche, A., 1909, i, 52) water is eliminated from I with the formation of the dihydrocinchonic acid, which reacts with benzylideneaniline to give the cinchonic acid and benzylideneaniline. The first side-reaction is the elimination of water from I to give 4:5-diketo-1:2-diphenylpyrrolidine, which is converted into the 4-anil by intermolecular decomposition. Secondly, a certain amount of the dihydrocinchonic acid yields directly the cinchonic and tetrahydrocinchonic acids, the latter losing carbon dioxide to give 2-substituted quinoline derivatives. The intermediate compound I is analogous to that isolated by Simon and Maguin (A., 1908, i, 296) from ethyl oxalacetate and benzylidene- $\beta$ -naphthylamine. Confirmation of the reducing action of the Schiff's base is afforded by a series of experiments in which it is found that as the proportion of benzylidene-, anisylidene-, or piperonylidene- $\beta$ -naphthylamine, or benzylideneaniline to pyruvic acid is increased, the yield of cinchonic acid increases. This does not accord with Carrara's mechanism (*loc. cit.*). The 4-anil of 4:5-diketo-1:2-diphenylpyrrolidine is formed when the latter is boiled in alcoholic solution with acetic acid and benzaldehyde, acetic acid alone, aniline, or benzylideneaniline. In the last reaction 2-phenylquinoline-4-carboxylic acid is formed in 10% yield (cf. Carrara, *loc. cit.*), probably by way of the compound I with a reversal of the normal reactions.

R. K. CALLOW.

**Attempts to find new anti-malarials. III. Substituted aminoalkylaminoquinolines.** A. W. BALDWIN (J.C.S., 1929, 2959—2965).—Acetylation of 5-amino-6-methoxyquinoline (Jacobs and Heideberger, A., 1921, i, 44) gives 5-acetamido-6-methoxyquinoline, m. p. 193°, converted by sulphuric and nitric (d 1.42) acids below 15° into its 8-nitro-derivative, m. p. 265° (decomp.), which is reduced by iron and dilute alcoholic hydrochloric acid to 8-amino-5-acetamido-6-methoxyquinoline, m. p. 207—208°. This is butylated by heating with *n*-butyl iodide and excess of sodium carbonate in boiling xylene to the corresponding 8-*n*-butylamino-derivative, m. p. 136°. 8-Amino-6-methoxy- and -6-ethoxy-quinolines are converted by boiling with *n*-butyl iodide and sodium carbonate in water into 8-*n*-butylamino-6-methoxy-, m. p. 45°, and 8-*n*-butylamino-6-ethoxy-, m. p. 38—39°, -quinolines, isolated as their sparingly soluble *hydrochlorides*, m. p. 159—160° and 171—172°, respectively, whilst under similar conditions, using trimethylene bromide, is obtained  $\alpha\gamma$ -di-(6-methoxy-8-quinolylamino)propane,  $(MeO \cdot C_6H_5N \cdot NH \cdot CH_2)_2CH_2$ , m. p. 131—132° (*hydrochloride*, m. p. 222°). The introduction of further basic centres into 8-aminoquinoline derivatives is best effected by interaction with bromoalkylphthalimides, subsequent hydrolysis giving an amino-group, which can be alkylated, in the side-chain and thus from the appropriate starting materials are obtained: 8- $\beta$ -phthalimidoethylamino-6-methoxyquinoline *hydrobromide*, m. p. 246—247°, hydrolysed with hydrazine hydrate and subsequent treatment with hydrochloric acid to the *dihydrochloride*, m. p. 263—264°, of the corresponding 8- $\beta$ -aminoethyl-



amino-derivative,  $\text{MeO}\cdot\text{C}_9\text{H}_5\text{N}\cdot\text{NH}_2\cdot[\text{CH}_2]_2\cdot\text{NH}_3\cdot\text{Cl}_2$  (N-n-butyl derivative); 8- $\gamma$ -phthalimidopropylamino-6-methoxyquinoline, m. p. 101–102°, and 8- $\gamma$ -aminopropylamino-6-methoxyquinoline dihydrochloride, m. p. 251–252° (N-n-butyl and N-isoamyl derivatives of the base).  $\alpha$ -Dibromopentane in boiling xylene condenses with phthalimide in the presence of potassium carbonate to give  $\epsilon$ -bromo-n-amylphthalimide (Gabriel, A., 1902, i, 401) and  $\alpha$ -diphthalimidopentane, m. p. 188°, which is similarly condensed with 8-amino-6-methoxyquinoline to give 8-( $\epsilon$ -phthalimido-n-amylamino)-6-methoxyquinoline,  $\text{MeO}\cdot\text{C}_9\text{H}_5\text{N}\cdot\text{NH}\cdot[\text{CH}_2]_5\cdot\text{N}:(\text{CO})_2\cdot\text{C}_6\text{H}_4$ , m. p. 117–118° (hydrobromide, m. p. 101–103°), hydrolysed to 8-( $\epsilon$ -amino-n-amylamino)-6-methoxyquinoline dihydrochloride,  $+3\text{H}_2\text{O}$ , m. p. 83° (N-n-butyl derivative). 8- $\gamma$ -Phthalimidopropylamino-6-methoxyquinoline, m. p. 127°; 8- $\gamma$ -aminopropylamino-6-methoxyquinoline dihydrochloride, m. p. 242° (N-n-butyl derivative); 8- $\gamma$ -phthalimidopropyl-6-methylquinoline, m. p. 123°, and 8- $\gamma$ -aminopropylamino-6-methylquinoline dihydrochloride, m. p. 262° (N-n-butyl derivative), are prepared by similar methods. J. W. BAKER.

**New product derived from pyramidone.** R. CHARONNAT and R. DELABY (Compt. rend., 1929, 189, 850–852).—The action of cold hydrogen peroxide on pyramidone gives dioxypyramidone (pyramidone  $+2\text{O}$ ), m. p. 105.5°, b. p. 194–201°/2 mm., a non-basic substance which, however, forms a hydrochloride in ethereal solution. Alkaloids which precipitate both pyramidone and antipyrine do not precipitate “dioxypyramidone.” Various colorimetric reactions are given and a comparison is made between its physiological properties and those of pyramidone and antipyrine. A. A. GOLDBERG.

**Synthesis of 1-phenyl-2-methyl-3:4-cyclotrimethylene-5-pyrazolone.** C. MANNICH (Arch. Pharm., 1929, 267, 699–702).—The condensation product of ethyl cyclopentanone-2-carboxylate and phenylhydrazine, when heated with dry sodium ethoxide (2 mols.) in a hydrogen atmosphere, gives 1-phenyl-3:4-cyclotrimethylene-5-pyrazolone,

$\text{CH}_2\text{--}\begin{array}{c} \text{CH}_2\cdot\text{C}\cdot\text{NH} \\ \text{CH}_2\cdot\text{C}\cdot\text{CO} \end{array}\text{--NPh}$ , m. p. 183–184° (sodium or sodamide in toluene may also be used). This substance is converted by methyl sulphate and alkali into 1-phenyl-2-methyl-3:4-cyclotrimethylene-5-pyrazolone, m. p. 128°. The antipyretic properties of this substance exceed those of antipyrine. A. I. VOGEL.

**Stereoisomeric 2:3:5:6-tetramethylpiperazines.** I. F. B. KIPPING (J.C.S., 1929, 2889–2897).—Pure tetramethylpyrazine, m. p. 85–86°, b. p. 189–190° (anhydrous hydrochloride, m. p. 156°; Wolff, A., 1887, 464, gives 91°), has been reduced with a number of different reducing agents in an attempt to prepare the five possible stereoisomeric 2:3:5:6-tetramethylpiperazines. Reduction with sodium and alcohol gives only the  $\alpha$ - and  $\beta$ -compounds, thus confirming Stoehr's results (A., 1897, i, 298). Reduction of the anhydrous hydrochloride with hydrogen and a platinum oxide-platinum catalyst in alcoholic acetic acid is not quantitative, but affords the  $\beta$ -base (regenerated from its purified isonitroso-derivative obtained from the more soluble hydriodide fraction

after crystallisation from aqueous alcohol mixtures) and the new  $\gamma$ -2:3:5:6-tetramethylpiperazine, m. p. 67–68°, b. p. 195–196° [dihydrochloride  $+ \text{H}_2\text{O}$  and anhydrous, not melting below 300°; dihydriodide; dinitroso-derivative, m. p. 173–174°; monobenzoyl, m. p. 85° (hydrochloride, not melting at 300°); dibenzoyl, m. p. 163–164°; and mono-p-toluenesulphonyl, m. p. 332° (decomp.), derivatives], from the less soluble hydriodide fraction. Reduction of tetramethylpyrazine hydrate with aluminium amalgam in 95% alcohol at 50° gives a mixture of  $\alpha$ - $\beta$ -, and  $\gamma$ -bases, whilst sodium amalgam in aqueous acetic or hydrochloric acid affords only the  $\alpha$ - and  $\beta$ -isomerides. With tin and hydrochloric acid the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -bases are obtained together with a small quantity of  $\delta$ -2:3:5:6-tetramethylpiperazine, m. p. 53–55° (probably the hydrate) (dihydrochloride, not melting below 300°), isolated as its dinitroso-derivative, m. p. 189–190°. The properties of the isomerides are similar except with regard to their behaviour with p-toluenesulphonyl chloride. The  $\alpha$ -base (anhydrous) gives only a di-p-toluenesulphonyl derivative, m. p. 308–309°, the  $\beta$ -base (anhydrous) both mono-p-toluenesulphonyl, m. p. 81–82° [hydrochloride, m. p. 278° (decomp.)], and di-p-toluenesulphonyl, m. p. 222°, derivatives, whilst the  $\gamma$ -base gives only a mono-derivative (above). J. W. BAKER.

**Molecular compounds of diketopiperazine with certain heavy metals.** T. ASAHINA and T. DÔNO (Z. physiol. Chem., 1929, 186, 133–136; cf. A., 1928, 1025).—The following compounds are described: diketopiperazine mercuric chloride,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\cdot 2\text{HgCl}_2$ ; diketopiperazine uranyl chloride,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\cdot \text{UO}_2\text{Cl}_2\cdot 1.5\text{H}_2\text{O}$ ; diketopiperazine uranyl nitrate,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\cdot \text{UO}_2(\text{NO}_3)_2$ , and diketopiperazine cadmium chloride,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\cdot \text{CdCl}_2$ . These compounds may have a bearing on the ability of protein to combine with heavy metals. W. O. KERMACK.

**Pyrazine salts.** IV. C. GASTALDI and E. PRINCIVALLE (Gazzetta, 1929, 59, 751–757).—In the preparation of 6-keto-1:2:5-trimethyl-1:6-dihydro-pyrazine 4-methiodide, m. p. 220° (A., 1928, 1027), a pyrazine salt, m. p. 245°, is obtained as a by-product. Treatment of the methiodide with potassium hydroxide solution yields the unstable 6-keto-5-methylene-1:2:4-trimethyl-1:6:4:5-tetrahydropyrazine, probably by way of the  $\psi$ -base. It is converted by hydriodic acid into the original methiodide, and by hydrochloric acid into the methochloride, m. p. 203° (decomp.). It reacts with diazonium salts (cf. A., 1929, 197), with phenylhydrazine to give a compound, m. p. 201° (decomp.), and with benzoyl chloride to give 6-keto-5-benzoylmethylene-1:2:4-trimethyl-1:6:4:5-tetrahydropyrazine, m. p. 165°. The benzoyl compound is decomposed by boiling water into acetophenone and 5:6-diketo-1:2:4-trimethyl-1:6:4:5-tetrahydropyrazine, m. p. 170°, and it reacts with semicarbazide to give, by a secondary hydrolysis, benzoylsemicarbazide, m. p. 225°, and the original 5-methylene derivative. R. K. CALLOW.

**1-Substituted benziminazoles.** M. A. PHILLIPS (J.C.S., 1929, 2820–2828).—Treatment of 4-nitro-2-aminodiphenylamine with hot 4N-hydrochloric and formic acids or of 4-nitro-2-formamidodiphenylamine

with boiling 2*N*-hydrochloric acid gave 5-nitro-1-phenylbenziminazole, reduction of which with stannous chloride and hydrochloric acid gave the corresponding 5-amino-compound (also obtained from 2:4-diaminodiphenylamine, formic acid, and 4*N*-hydrochloric acid). 2:4-Diaminodiphenylamine, acetic anhydride, and 3*N*-hydrochloric acid when refluxed together or 2:4-diacetamidodiphenylamine (or 4-amino-2-acetamidodiphenylamine) when boiled with 4*N*-hydrochloric acid afforded 5-amino-1-phenyl-2-methylbenziminazole, m. p. 145–146° (also prepared by iron-hydrochloric acid reduction of the analogous 5-nitro-compound) (acetyl derivative, m. p. 230°). Similarly, 1-phenylbenziminazole and 1-phenyl-2-methylbenziminazole were obtained from 2-aminodiphenylamine by boiling with 4*N*-hydrochloric acid and formic acid or acetic anhydride, respectively. 2-Aminodiphenylamine-4-arsinic acid, 4*N*-hydrochloric acid, and formic acid, when boiled together, formed 1-phenylbenziminazole-5-arsinic acid; substitution of acetic anhydride for formic acid led to the isolation of 1-phenyl-2-methylbenziminazole-5-arsinic acid, and of lactic acid for formic acid, to 1-phenyl-2- $\alpha$ -hydroxyethylbenziminazole-5-arsinic acid.

*o*-Nitromethylaniline, acetic anhydride, and sulphuric acid reacted to give *o*-nitroacetomethylanilide, m. p. 70°, which was reduced as for 4-amino-2-acetamidodiphenylamine to the corresponding amine, m. p. 67–68°. By the action of acetic anhydride on either the last-named compound or on *o*-aminomethylaniline, diacetyl-*o*-aminomethylaniline, m. p. 172°, was formed.

The interaction of *o*-aminomethylaniline with 4*N*-hydrochloric acid and formic acid gave 1-methylbenziminazole, m. p. 30° (forming with methyl sulphate 1-methylbenziminazole methosulphate, m. p. 128°). Similarly, 5-dimethylamino-1:2-dimethylbenziminazole methosulphate had m. p. 225° (decomp.). 1:2-Dimethylbenziminazole was isolated as the trihydrate, m. p. 65° (dehydrated at 50° giving the anhydrous base, m. p. 112°), from the reaction between diacetyl-*o*-aminomethylaniline and 4*N*-hydrochloric acid or between *o*-aminoacetomethylanilide dihydrochloride, acetic anhydride, and 4*N*-hydrochloric acid; using lactic acid, 1-methyl-2- $\alpha$ -hydroxyethylbenziminazole, m. p. 80°, was obtained.

Acetic anhydride and 3-nitro-4-aminophenylarsinic acid yielded in the cold 3-nitro-4-acetamidophenylarsinic acid, m. p. above 300°, reduction of which by ferrous sulphate and sodium hydroxide solution gave 3-amino-4-acetamidophenylarsinic acid, m. p. 275°. By the action of nitrous acid the last-named compound formed 1-acetyl-1:2:3-benzotriazole-5-arsinic acid, m. p. above 300°.

4-Chloro-3-nitrophenylarsinic acid was heated under pressure with aqueous ammonia (*d* 0.88) and the 4-nitro-3-aminophenylarsinic acid, m. p. above 300° (acetyl derivative), so formed reduced with ferrous sulphate and alkali producing 4-amino-3-acetamidophenylarsinic acid, which gives with nitrous acid 1-acetyl-1:2:3-benzotriazole-6-arsinic acid. 3:5-Dinitro-4-acetamidophenylarsinic acid and 4-amino-2-acetamidodiphenylamine (obtained from the corresponding nitro-compound by acetic acid-water-iron reduction) had m. p. above 300° and 165°, respectively.

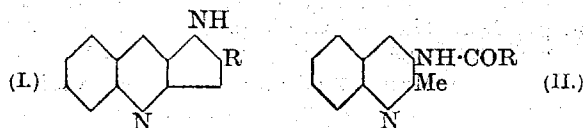
*Picrates* of the following bases are also described: benziminazole, m. p. 220°; 2-methyl-, m. p. 207–208°; 2-ethyl-, m. p. 137°; 1-methyl-, m. p. 248°; 1:2-dimethyl-, m. p. 238°; and 1-methyl-2- $\alpha$ -hydroxyethyl-benziminazole, m. p. 210°.

R. J. W. LE FÈVRE.

Attempts to find new anti-malarials. IV.  $\beta$ -Benziminazolylethylamine and  $\beta$ -5(or 6)-ethoxybenziminazolylethylamine. B. CHATTERJEE (J.C.S., 1929, 2965–2968).—*o*-Phenylenediamine and succinic anhydride (2 mols.) when boiled together in xylene yield the succinate, m. p. 182°, of benziminazole-2-propionic acid, m. p. 228° (Meyer and Lüders, A., 1918, i, 450, give 236°) [hydrochloride, m. p. 236–237°; amide, m. p. 259–260° (*loc. cit.*, m. p. 254°); hydrazide, m. p. 268° (decomp.)]. The amide is converted by the Hofmann reaction into  $\beta$ -benziminazolylethylamine dihydrochloride, decomp. 270–272° (*picrate*, m. p. 193°; free base is a viscous liquid). By boiling 3-nitro-*p*-phenetidine and succinic anhydride in xylene 2-nitro-4-ethoxysuccinanic acid, m. p. 172–173°, is obtained, but this is reduced to ethoxybenziminazolepropionic acid only in very poor yields, whilst 5(or 6)-ethoxybenziminazole-2-propionic acid, m. p. 181° (hydrochloride, m. p. 221°; methyl ester, m. p. 103°; amide, m. p. 189°), is similarly obtained from 3-amino-*p*-phenetidine (best prepared by reduction of the corresponding nitro-compound with stannous chloride and hydrochloric acid) and is converted into  $\beta$ -5(or 6)-ethoxybenziminazolylethylamine dihydrochloride, m. p. 251–252° (decomp.).

J. W. BAKER.

Attempts to find new anti-malarials. Introduction. G. BARGER and R. ROBINSON. I. Some pyrroloquinoline derivatives. (Mrs.) G. M. ROBINSON (J.C.S., 1929, 2947–2951).—The initial paper of a series in which substances with constitutions similar to those of (a) the *Cinchona* alkaloids, (b) the *Harmala* alkaloids, and (c) synthetic plasmoquine [8-(diethylaminoisopentylamino)-6-methoxyquinoline] are prepared. The method of Koenigs and Fulde (A., 1927, 1205) for the preparation of methylpyrindole has been extended to obtain derivatives of 2:3-pyrrolo-(4':5')-quinoline (I) from 3-acylamido-2-methylquinolines of type II; the yields are poor unless the materials are mixed with copper powder to facilitate rapid heat conduction throughout the mass.



3-Amino-2-methylquinoline with anhydrous formic acid gives 3-formamido-2-methylquinoline, m. p. 163°, dehydrated by heating with dry sodium ethoxide and copper powder in hydrogen at 270° to 2:3-pyrrolo-(4':5')-quinoline (I, R=H), m. p. 226° (hydrochloride). Acetylation of 3-amino-2-methylquinoline gives the 3-acetamido-compound (Stark, A., 1907, i, 973), dehydrated to 2:3-(2'-methylpyrrolo)(4':5')-quinoline (I, R=Me), m. p. 262°, whilst benzoylation with benzoyl chloride, glacial acetic acid, and excess of potassium acetate affords 3-benzamido-2-methylquinoline, m. p. 161°, converted into 2:3-(2'-phenylpyrrolo)-

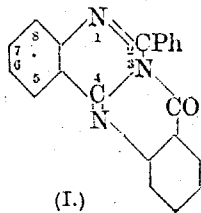
(4' : 5')-quinoline (I, R=Ph), m. p. 268° (*hydrochloride*; *acetate*). The *methosulphate*, m. p. 345° (decomp.), in contrast to the behaviour of quindoline *methosulphate* (Armit and Robinson, J.C.S., 1922, 121, 827), is converted by hot aqueous sodium hydroxide into *anhydro-2 : 3-(2'-phenylpyrrolo)(4' : 5')-quinoline methohydroxide*, which shrinks to a resin above 100°, and with dry methyl sulphate in dry toluene gives the *methosulphate* of the *anhydro-base*.

J. W. BAKER.

**Quinazolines. II.** J. S. AGGARWAL, R. S. DAS, and J. N. RAY (J. Indian Chem. Soc., 1929, 6, 717—722).—Phenylacetanilide condenses with ethyl aminofornate in presence of phosphoric oxide and xylene (cf. A., 1929, 939), forming 4-*keto-2-benzyl-3 : 4-dihydroquinazoline*, m. p. 247° (3-*methyl* derivative, m. p. 95°; *picrate*, m. p. 170°). Similarly, phenylacet-*o*-toluidide, -*m*-toluidide, m. p. 75°, and -*p*-toluidide give 4-*keto-2-benzyl-8-methyl*-, m. p. 198° (*picrate*, m. p. 153°), 4-*keto-2-benzyl-7-methyl*-, m. p. 230° (*picrate*, m. p. 168°), and 4-*keto-2-benzyl-6-methyl-3 : 4-dihydroquinazoline*, m. p. 239° (*picrate*, m. p. 194°; 3-*methyl* derivative, m. p. 116°), respectively. From phenylacet-*o*-anisidide, m. p. 84°, -*p*-anisidide, m. p. 124°, -*o*-xylylidide, m. p. 158°, - $\alpha$ -naphthalide, m. p. 175°, and - $\beta$ -naphthalide, m. p. 158°, the following substituted 4-*keto-2-benzyl-3 : 4-dihydroquinazolines* are obtained : 8-*methoxy*-, m. p. 257° (*picrate*, m. p. 191°; 3-*methyl* derivative, m. p. 138°); 6-*methoxy*-, m. p. 241°; 7 : 8-*dimethyl*-, m. p. 189° (*picrate*, m. p. 165°); 7 : 8-*benzo*-, m. p. 265°, and 6 : 7 (or 5 : 6)-*benzo*-, m. p. 278°, respectively. No *isoquinoline* derivatives are formed during the above reactions and the yield of quinazoline varies from 3 to 36·7%.

H. BURTON.

**Quinazolines. III. Synthesis of 3 : 4-quinazolinylquinazolines.** J. S. AGGARWAL and J. N. RAY (J. Indian Chem. Soc., 1929, 6, 723—728).—Anthranelic acid condenses with 4-*keto-2-phenyl-3 : 4-dihydroquinazoline* in presence of phosphorus trichloride forming 2-*phenyl-3 : 4-quinazolinylquinazoline* (I), m. p. 241—242°. Using the appropriate substituted 4-*keto-3 : 4-dihydroquinazoline*, the following are prepared similarly : 2 : 7-*dimethyl*-, m. p. 285°; 6-*methoxy-2-methyl*-, m. p. 240°; 2-*benzyl*-, m. p. 243—244°; 2-*benzyl-7-methyl*-, m. p. 213°; 2-*benzyl-6-methyl*-, m. p. 235—236°; 8-*methoxy-2-benzyl*-, m. p. 254°, and 6-*methoxy-2-benzyl-3 : 4-quinazolinylquinazoline*, m. p. 244°.



The colour reactions of the above substances with acetic-sulphuric acid, Mandeline's reagent, and alcoholic potassium hydroxide are similar to those of rutæcarpine, but differ from those of oxyberberine.

H. BURTON.

**Chlorophyll series. I. Thermal decomposition of magnesium-free compounds.** J. B. CONANT and J. F. HYDE (J. Amer. Chem. Soc., 1929, 51, 3668—3674).—When phæophorbide *a* and methyl phæophorbide *a* are heated at 200—250° in dilute diphenyl solution, 1 mol. of carbon dioxide is eliminated and 23% of pyrophæophorbide *a*, m. p. (block) between 210° and 220°, and 21% of methyl pyro-

phæophorbide *a*, m. p. (block) 220—225°, respectively, are obtained. Chlorin *e* eliminates 2 mols. of carbon dioxide, yielding a mixture of pyrochlorin *e*, green, m. p. 165—170°, and pyrochlorin *e*-porphyrin. Pyrochlorin *e* is unstable and on keeping for some months furnishes a small amount of a red substance similar to, but not identical with, the above porphyrin. The trimethyl ester of chlorin *e* does not eliminate carbon dioxide when heated, indicating that the loss of carbon dioxide from methyl phæophorbide *a* is not due to decomposition of an ester grouping. Pyrophæophorbide *a* is an acid, indicating that the acid group in phæophorbide *a* is unaffected. The elimination of carbon dioxide from the above derivatives is probably due to the decomposition of a lactone grouping.

Phæophorbide *b* and methyl phæophorbide *b* lose 1 mol. of carbon dioxide, whilst rhodin *g* loses 2 mols. when heated at 220—250° in diphenyl solution.

H. BURTON.

**Fluorescence of porphyrins and hydrogen-ion concentration.** H. FINK and K. WEBER (Naturwiss., 1930, 18, 16—17).—The relationship between the fluorescence of porphyrins and hydrogen-ion concentration was investigated for coproporphyrin, uroporphyrin, and hæmatoporphyrin. For the first compound, which has four carboxyl groups, the minimum fluorescence occurred at  $p_H$  3·9; for the second, which has eight carboxyl groups, it occurred at  $p_H$  3·3; for the third, which has two carboxyl groups, at  $p_H$  4·4. If the relative intensity of the fluorescence is plotted against hydrogen-ion concentration, a curve is obtained which resembles in form the dissociation curve of ampholytes with acid and alkaline branches. These fluorescence curves are characteristic for each porphyrin, and may be used in a similar way to other physical properties for determining the presence of any particular one. The minimum fluorescence lies in a different place on the graph for each compound, and the forms of the curves are different for different porphyrins. It is possible to re-classify the blood- and plant-porphyrins on this basis. The position of the side-chains with respect to each other in the porphyrin molecule and the degree of saturation appear to play a great part in the determination of the curve. The isomeric porphyrins can be distinguished by the form of these curves.

A. J. MEE.

**Ketophenmorpholine synthesis from 5-amino-eugenol. II.** E. PUXEDDU and G. SANNA (Gazzetta, 1929, 59, 733—741).—8-Methoxy-3-*keto-6-allyl-2 : 3-dihydro-1 : 4-benzoxazine* (A., 1929, 1317) is also obtained from 5-chloroacetamidoeugenol by the action of diethylamine in pyridine. Under various conditions of reaction none of the glycino- (aminoacetamido-) derivative can be recognised in the product. The bromination products of the benzoxazine derivative, m. p. 183° (previously given as 175°) and 125°, are regarded as isomeric 6-*dibromopropyl* derivatives, one keto- and two enol forms being possible. The compound of m. p. 183° is also obtained by the action of diethylamine on 5-chloroacetamidoeugenol dibromide. The interaction of 5-amino-eugenol and oxalyl chloride yields two compounds, m. p. 228° and 233°, the latter insoluble in benzene,

which are regarded as *cis*- and *trans*-isomerides of *dieugenol*-5 : 5'-*oxamide*. R. K. CALLOW.

**Dioximes. LVIII.** I. DE PAOLINI and A. CASTIGLIONI (Gazzetta, 1929, 59, 723—728).—The work described is a further extension of the method of preparing derivatives of trioxime,  $\text{HON}:\text{CH}:\text{C}(\text{NOH})\cdot\text{CH}:\text{NOH}$  (A., 1928, 620). The action of hydroxylamine on ethyl dioximinobutyrate in methyl-alcoholic solution yields *methylhydroxytrioxime*,  $\text{HON}:\text{CMe}:\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{OH}$ , isolated as the *sodium* salt, which yields the *tetra-acetyl* derivative, m. p. 153—154° (decomp.), with acetic anhydride. When the base is liberated from the sodium salt by acid, hydroxylamine is eliminated with the formation of 4-oximino-3-methyl-1 : 2 : 5-*isooxazolone*, m. p. 147° (lit. 141—142°) (*benzoyl* derivative, m. p. 194°). This reaction is reversed under certain conditions, and the action of hydroxylamine on the *isooxazolone* in methyl alcohol yields *methylhydroxytrioxime*, identified as the acetate. Analogously, 3-amino-4-oximino-1 : 2 : 5-*isooxazolone* and hydroxylamine yield *aminohydroxytrioxime*, isolated as the acetate, by way of the ammonium salt, and 4-oximino-3-phenyl-1 : 2 : 5-*isooxazolone* yields the unstable *phenylhydroxytrioxime*, of which the *ammonium* salt was isolated. A preliminary notice is given of the preparation of dihydroxytrioxime from ethyl *isonitrosomalonalate*. R. K. CALLOW.

**Indole derivatives of coumarone.** G. SANNA (Gazzetta, 1929, 59, 694—698).—2-Methyl-3-indacyl bromide (3- $\omega$ -bromoacetyl-2-methylindole) (A., 1929, 825) reacts with the potassium derivative of salicylaldehyde in boiling alcoholic solution to give 2-methyl-3-indolyl 2-coumaronyl ketone, m. p. 182° [picrate, m. p. 193°; phenylhydrazine, m. p. 95°; oxime, m. p. 138—143° (possibly a mixture of isomerides)]. Fusion with potassium hydroxide yields coumarone and 2-methylindole-3-carboxylic acid. R. K. CALLOW.

**Dioximes. LVI.** G. PONZIO (Gazzetta, 1929, 59, 713—717).—Further work on the transformation of furoxan derivatives into dioxdiazines (glyoxime peroxides) by heating in various solvents (cf. A., 1928, 888) shows that the reaction, contrary to the first conclusion, is reversible. Thus an equilibrium mixture of *p*-anisylmethylfuroxan (65%) and 4-*p*-anisyl-5-methyl-1 : 2 : 3 : 6-dioxdiazine (*p*-anisylmethylglyoxime peroxide) (35%) is obtained from either compound by boiling in acetic acid (4 hrs.), propionic acid (1 hr.), butyric acid (30 min.), phenol (5 min.), or quinoline (1 min.). Propionic acid is conveniently substituted for acetic anhydride in the preparation of the peroxides.

Further evidence is adduced in support of the furoxan and dioxdiazine structures assigned to the two classes of glyoxime peroxides. Position isomerism in arylalkylfuroxans as an explanation of the differences is excluded by the fact that symmetrical diphenyl- and di-*p*-anisyl-furoxans react with phosphorus pentachloride, and failure to react cannot, therefore, be attributed to the adjacency of an aryl group to the extranuclear oxygen. The mol. wt. of *p*-anisylmethylfuroxan, determined cryoscopically in *p*-anisylmethylglyoxime peroxide, is normal (cf. A., 1929, 334, 1072).

Di-*p*-anisylfuroxan is converted by heating at 120—130° with phosphorus pentachloride into *p*-anisyl-(chloro-*p*-anisyl)furoxan, m. p. 128°. Naphthaquinonedioxime yields a peroxide which is unaffected by phosphorus pentachloride. R. K. CALLOW.

**Dioximes. LIX.** G. PONZIO (Gazzetta, 1929, 59, 810—816).—Phenylmetazonic acid is readily prepared from oximinophenylacetonitrile oxide by warming it in dilute acetic acid with sodium acetate, and is separated by way of the nickel salt (cf. A., 1926, 1159). Phenylmetazonic acid is isomerised rapidly by concentrated, slowly by dilute hydrochloric acid to phenylhydroxyglyoxime, and it is converted by benzoyl chloride at 100° into dibenzoylphenylhydroxyglyoxime (A., 1926, 825). Treatment with hot sodium hydroxide solution yields 3-hydroxy-5-phenyl-1 : 2 : 4-oxadiazole, probably by isomerisation to a labile form of phenylhydroxyglyoxime and a Beckmann transformation of the latter followed by loss of water (cf. A., 1926, 1159; 1927, 470). The *sodium* salt is precipitated by the addition of sodium hydroxide to the alcoholic solution. Treatment with acetic anhydride yields a *triacyl* compound, m. p. 86°, which yields on hydrolysis 3-hydroxy-5-phenyl-1 : 2 : 4-oxadiazole, accompanied by the 5 : 3-isomeride. Phenylmetazonic acid is also obtained by the action of hydroxylamine on benzoylformhydroxamic acid, which evidently reacts in the form  $\text{CHBz}:\text{NO}_2\text{H}$ . In presence of sodium acetate and acetic acid the product is a mixture of phenylhydroxyglyoxime and phenylmetazonic acid, from which the former separates first. Hydroxylamine hydrochloride in water, however, gives phenylhydroxyglyoxime alone as a result of isomerisation by the acid present. Phenylmetazonic acid is stable in neutral aqueous solution. The reported decomposition of phenylloximinooacetonitrile oxide (phenylglyoxime peroxide, "phenylfuroxan"; Wieland and Semper, A., 1908, i, 108) to benzonitrile oxide and formhydroxamic acid is improbable, and cannot, in fact, be confirmed. The action of bromine water on phenylmetazonic acid yields 3-hydroxy-5-phenyl-1 : 2 : 4-oxadiazole, probably through phenylbromoglyoxime and the labile form of phenylhydroxyglyoxime, and this fact is used as an additional argument in favour of regarding the substance obtained by the action of alkali on the oxide of oximinocynoacetic acid as  $\text{CO}_2\text{H}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CH}:\text{NO}_2\text{H}$ , which, by a reaction analogous to that of phenylmetazonic acid, yields dibromoglyoxime with bromine (cf. Wieland, Semper, and Gmelin, A., 1909, i, 609; Ponzio and de Paolini, A., 1926, 825).

*p*-Tolylmetazonic acid is prepared similarly to the phenyl compound from oximino-*p*-tolylacetonitrile oxide (Avogadro, A., 1928, 637), and is transformed by 20% sodium hydroxide solution into 3-hydroxy-5-*p*-tolyl-1 : 2 : 4-oxadiazole, by hydrochloric acid into *p*-tolylhydroxyglyoxime, and by acetic anhydride into a *triacyl* compound, m. p. 107—109°.

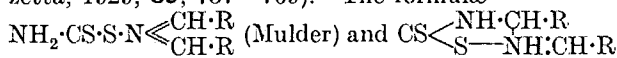
R. K. CALLOW.

**Dioximes. LX.** M. MILONE (Gazzetta, 1929, 59, 829—838; cf. Ponzio, above).—The equilibria between phenylmethylfuroxan (I) and 4-phenyl-5-methyl-1 : 2 : 3 : 6-dioxdiazine (II) and between *p*-anisylmethylfuroxan (III) and 4-*p*-anisyl-5-methyl-

1 : 2 : 3 : 6-dioxdiazine (IV) at 110° and 126° have been studied by constructing the f.-p. diagrams for each pair of substances and determining the m. p. of the mixtures obtained by heating the components for varying periods. In each case the reaction is unimolecular and reversible. The points of equilibrium are at 59% of I and at 62% of III, and the values of  $K'/K$  are 1.439 and 1.634, respectively. The velocities of reaction increase with rise of temperature, but the points of equilibrium are unchanged. The hypothesis of desmotropism suggested by von Auwers (A., 1927, 1123) for dimethylglyoxime peroxide is not applicable to these arylmethylglyoxime peroxides.

R. K. CALLOW.

"Carbothialdines" and alkylidenethiocarbamic acids. T. G. LEVI and L. GIMIGNANI (Gazzetta, 1929, 59, 757—769).—The formulæ



(Delépine) for "carbothialdines" are discussed, preference being given to the former. In particular, the argument of Delépine based on the existence of the compound  $\text{CS} \begin{smallmatrix} \text{NMe} \cdot \text{CH}_2 \\ \text{S} \text{---} \text{NMe} \cdot \text{CH}_2 \end{smallmatrix}$  is invalid, for the existence of a dimethyl derivative of the other formula is not excluded. Both carboacetothialdine and carbobenzothialdine undergo decomposition when treated with methyl iodide, yielding the compound  $(\text{SMe})_2\text{C} \cdot \text{NH} \cdot \text{HI}$ , which was also obtained by Delépine from the above dimethylcarboacetothialdine, but the reaction can be represented by the scheme:  $\text{NH}_2 \cdot \text{CS} \cdot \text{SN}(\text{CHR})_2 + 4\text{EtOH} = \text{NH}_2 \cdot \text{CS} \cdot \text{SNH}_4 + 2\text{R}(\text{OEt})_2$ , followed by  $\text{NH}_2 \cdot \text{CS} \cdot \text{SNH}_4 + 2\text{MeI} = \text{I} \cdot \text{SMe} \cdot \text{C}(\text{NH}_2) \cdot \text{SMe} + \text{NH}_4\text{I}$  and  $\text{I} \cdot \text{SMe} \cdot \text{C}(\text{NH}_2) \cdot \text{SMe} \rightarrow (\text{SMe})_2\text{C} \cdot \text{NH} \cdot \text{HI}$ . Preliminary results indicate that products which are probably identical ( $[\text{CH}_2 \cdot \text{N} \cdot \text{CS} \cdot \text{SN}(\text{CHMe})_2]_3$ ), are obtained by condensation of acetaldehyde with ammonium methylenedithiocarbamate (this vol., 75) or from carboacetothialdine and formaldehyde.

Carboacetothialdine has m. p. 118° (decomp.). Pure carbobenzothialdine, m. p. 127° (decomp.), is prepared by the interaction of benzaldehyde and pure ammonium dithiocarbamate in hot alcoholic solution. Like the aliphatic compounds, it is decomposed to give carbon disulphide, benzaldehyde, and ammonium thiocyanate by hot water, and analogously by dilute acids. The interaction of carbothialdines with salts of heavy metals gives not only dithiocarbamates (Mulder, *loc. cit.*), but also alkylidene- or arylidene-dithiocarbamates, which are unstable, slowly liberating the corresponding aldehyde. The silver salts, which have been examined, have not been separated from the mixtures obtained.

R. K. CALLOW.

Determination of nicotine. F. D. CHATTAWAY and G. D. PARKES (J.C.S., 1929, 2817—2820).—For the determination of nicotine in tobacco the following method is recommended: the evaporated extract obtained by ethereal extraction in a Soxhlet apparatus is steam-distilled. The distillate is saturated with hydrogen chloride and a solution made by saturating with chlorine a suspension of iodine in hydrochloric acid then added. Nicotine tetrachloriodide (containing 23.077% of nicotine) is collected on a tared

Gooch crucible. The precipitates obtained with the above reagent are more tractable than those produced with silicotungstic acid and the method can be employed when the nicotine exists in the presence of ammonia or pyridine.

The tetrachloriodide reagent will detect nicotine present to the extent of 1 part in 100,000 parts of water and can be employed accurately to determine the base in solutions containing 1 part in 5000 parts.

R. J. W. LE FÈVRE.

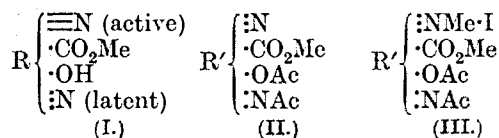
Alkaloids of *Anabasis aphylla*. A. ORÉKHOFF (Compt. rend., 1929, 189, 945).—A new alkaloid, *anabesine*,  $\text{C}_{10}\text{H}_{16}\text{N}_2$ , has been isolated from *Anabasis aphylla*, a plant indigenous to the Turkestan and Caspian regions. It is a water-soluble, steam-volatile oil, b. p. 145—146°/15 mm.,  $d_4^{20}$  1.044,  $[\alpha]_D^{20}$  -47° 21' (picrate, m. p. 205—207°; picrolonate, m. p. 235—237°). Solutions of *anabesine*, even when extremely dilute, give a precipitate with silicotungstic acid.

A. A. GOLDBERG.

Alkaloids of *Fritillaria verticillata*, Willd., var. *Thunbergii*, Baker. I. M. FUKUDA (Sci. Rep. Tôhoku Imp. Univ., 1929, [i], 18, 323—327).—From the alcoholic extract of the rhizomes of the plant a mixture of alkaloids is isolated as the partly crystalline hydrochlorides. The bases from the crystalline fraction can be separated by crystallisation into *verticine*,  $\text{C}_{18}\text{H}_{33}\text{O}_2\text{N}$  or  $\text{C}_{19}\text{H}_{35}\text{O}_2\text{N}$ , m. p. 224—224.5°,  $[\alpha]_D^{20}$  -10.66° in alcohol (*chloroplatinate* described), which possibly contains one methoxyl group, and *verticilline*,  $\text{C}_{19}\text{H}_{33}\text{O}_2\text{N}$ , m. p. 148—150° (sinters at 130°), resolidifying at 157—159°, remelting at 212—213° (*chloroplatinate*). The bases from the non-crystalline fraction, separated as the perchlorates, yield a non-crystalline substance and *fritillarine*,  $\text{C}_{19}\text{H}_{33}\text{O}_2\text{N}$ , m. p. 130—131° (*chloroplatinate*).

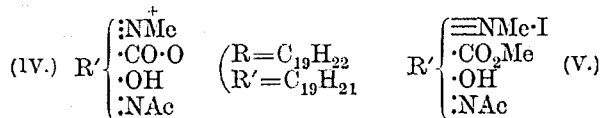
R. K. CALLOW.

Yohimba alkaloids. V. Acetylation of *isoyohimbine*. G. HAHN and W. SCHUCH (Ber., 1929, 62, [B], 2953—2974; cf. A., 1928, 432).—*iso*Yohimbine is converted by sodium acetate and boiling acetic anhydride into *diacetyliso-yohimbine* (II), m. p. 185° (decomp.),  $[\alpha]_D^{20}$  -20.8° in ethyl alcohol, in 70—80% yield, which is quantitatively hydrolysed by alcoholic potassium hydroxide to *isoyohimboic acid*, yielding *isoyohimbine* when esterified. The possibility that oxidative acetylation has occurred is excluded by analytical results, as is the production of a mixed anhydride, since ethyl *isoyohimboate* yields a different *diacetyl* compound,  $\text{C}_{22}\text{H}_{26}\text{O}_3\text{N}_2\text{Ac}_2$ , m. p. 173—174°,  $[\alpha]_D^{20}$  +9.0° in pyridine.

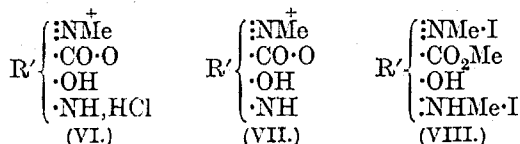


The second acetyl group is therefore considered to be attached to one of the nitrogen atoms and since *isoyohimbine* behaves as a monacid base the union of the acetyl group to the "latent" nitrogen atom (cf. I) is deduced in the following manner. The diacetyl derivative gives a non-crystalline *methiodide*, III, converted by alcoholic potassium ethoxide into the *methylbetaine* of *N-acetyliso-yohimboic acid*, IV,

m. p. 205–206° (decomp.),  $[\alpha]_D^{25} + 78.6^\circ$  in water, which affords a *methiodide* V, decomp. 248° after



darkening,  $[\alpha]_D^{25} + 38.3^\circ$  in pyridine, converted by potassium ethoxide into the betaine IV. The last-



named compound yields a crystalline *hydrochloride*, VI,  $[\alpha]_D^{25} + 60.1^\circ$  in water, which is converted by potassium ethoxide into a *betaine*, VII, m. p. 199–200° (decomp.) after darkening at 170°,  $[\alpha]_D^{25} + 48.9^\circ$  in water, re-converted by 2*N*-hydrochloric acid into the labile *hydrochloride*; the *dimethiodide* of the betaine, VIII (+4H<sub>2</sub>O), is described. Elimination of the *N*-acetyl group of diacetyl*isoyohimbine* can be effected by boiling 2*N*-hydrochloric acid, thus giving an *O*-monoacetyl compound, C<sub>21</sub>H<sub>25</sub>O<sub>3</sub>N<sub>2</sub>Ac, H<sub>2</sub>O, m. p. 196° (decomp.) after loss of water of crystallisation at 132°,  $[\alpha]_D^{25} + 39.6^\circ$  in pyridine, with a secondary latent nitrogen atom. *isoyohimbine* therefore appears to contain a 1 : 2 : 3 : 4-tetrahydroisoquinoline ring, fission of which leaves a double linking in diacetyl*isoyohimbine* as demonstrated by its absorption of 2 atoms of hydrogen, whereas *isoyohimbine* is indifferent towards the gas in presence of palladium. *alloyohimbine* yields only a normal *O*-monoacetyl*alloyohimbine*, decomp. 175–176° after loss of 1MeOH at 131°,  $[\alpha]_D^{25} - 33.9^\circ$  in pyridine.

Treatment of the hydrochloride, VI, with concentrated potassium hydroxide affords a well-defined amino-acid isolated as the *hydrochloride*, C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>·HCl·H<sub>2</sub>O,  $[\alpha]_D^{25} + 94^\circ$  in water. Since the same product is derived from the betaine,  $[\alpha]_D^{25} + 48^\circ$ , and from *isoyohimboic acid methylbetaine A* (see later), the reaction appears specific to the betaine group of the active nitrogen atom.

*isoyohimbine* is converted by methyl iodide in acetone into the *methiodide*, C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>·MeI·H<sub>2</sub>O, decomp. 243°,  $[\alpha]_D^{25} + 67.5^\circ$  in methyl alcohol, which when treated with alcoholic potassium ethoxide affords *isoyohimboic acid methylbetaine A*, which cannot be crystallised from water or freed readily from traces of alkali. Its constitution is elucidated by its conversion by methyl-alcoholic hydrogen chloride into *isoyohimbine methochloride*, decomp. 272°,  $[\alpha]_D^{25} + 114.1^\circ$  in water,  $[\alpha]_D^{25} + 64.4^\circ$  in methyl alcohol, also derived from *isoyohimbine methiodide* and silver chloride in methyl alcohol. Treatment of *isoyohimboic acid* with methyl sulphate and potassium hydroxide affords an isomeric *isoyohimboic acid methylbetaine* (lat.), C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>·5H<sub>2</sub>O,  $[\alpha]_D^{25} + 84.6^\circ$  in water,  $[\alpha]_D^{25} + 42.2^\circ$  in methyl alcohol, readily crystallised from water. With 2*N*-hydrochloric acid it yields a very stable *hydrochloride*, C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>·HCl, decomp. 272°,  $[\alpha]_D^{25} + 132.5^\circ$  in water,  $[\alpha]_D^{25} + 72.3^\circ$  in methyl alcohol, reconverted by 2*N*-sodium hydroxide into the betaine.

With methyl-alcoholic hydrogen chloride it gives a *methochloride*, C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>·MeCl·H<sub>2</sub>O, decomp. 296°,  $[\alpha]_D^{25} + 155.4^\circ$  in water,  $[\alpha]_D^{25} + 98.6^\circ$  in methyl alcohol [re-transformed by 2*N*-sodium hydroxide into the betaine (lat.)], which, with methyl iodide in acetone gives the corresponding *methiodide*,

C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>·MeI·H<sub>2</sub>O, decomp. 263°,  $[\alpha]_D^{25} + 75.4^\circ$  in methyl alcohol. The betaine (lat.) does not suffer the Hofmann degradation with potassium hydroxide.

The *methiodide* of the *O*-monoacetyl compound, C<sub>21</sub>H<sub>25</sub>O<sub>3</sub>N<sub>2</sub>Ac·MeI, and the corresponding *betaine*, decomp. 182°,  $[\alpha]_D^{25} + 108.8^\circ$  in water, are incidentally described.

H. WREN.

**Hypaconitine, a new *Aconitum* alkaloid.** R. MAJIMA and S. MORIO (Annalen, 1929, 476, 171–181).—Fractional precipitation of the mixed hydrobromides of alkaloids obtained from *Aconitum hakusanense*, *A. callianthum*, or *A. tortuosum* led to the isolation of *hypaconitine*, C<sub>23</sub>H<sub>30</sub>O<sub>6</sub>(OMe)<sub>4</sub>(NMe<sub>3</sub>), decomp. 197–198°,  $[\alpha]_D^{25} + 22.4^\circ$  in chloroform (*hydrobromide*, m. p. 178–179°, also *hydrobromide hydrate*, 2·5H<sub>2</sub>O; *perchlorate*, decomp. 178–180°; *chloroaurate*, decomp. 243–245°), which by boiling with an equi-volume mixture of sulphuric acid and water gave *benzhypaconine* (*hydrochloride*, 3·5H<sub>2</sub>O, and *anhydrous*, decomp. 242–244°,  $[\alpha]_D^{25} - 6.5^\circ$  in water) and by heating with water under pressure formed acetic and benzoic acids along with *hypaconine* (*tetra-acetyl derivative*, decomp. 182–184°).

*Hypaconitine*, heated under reduced pressure in a current of hydrogen, formed *pyrohypaconitine*, m. p. 119–120°,  $[\alpha]_D^{25} + 21.7^\circ$  (from *A. hakusanense*), +18.1° (from *A. senanense*) (both in chloroform) (*hydrobromide*; *perchlorate*, decomp. 268–269°; *chloroaurate*, decomp. 216–217°), whilst potassium permanganate in acetone solution (containing acetic acid) gave by oxidation *hypoxonitine*, decomp. 267–268°,  $[\alpha]_D^{25} - 63.1^\circ$  (in chloroform). R. J. W. LE FÈVRE.

**Mesaconitine, a second new *Aconitum* alkaloid.** S. MORIO (Annalen, 1929, 476, 181–193).—Following the usual procedure with the alkaloids from *Aconitum manschuricum*, *mesaconitine*, decomp. 208–209°,  $[\alpha]_D^{25} + 25.4^\circ$  (in chloroform) (*hydrobromide*, m. p. 172–173°,  $[\alpha]_D^{25} - 24.8^\circ$ , and *hydrobromide hydrate* with 3·5H<sub>2</sub>O; *chloroaurate*, decomp. 224–226°; *perchlorate*, decomp. 217–225°), was obtained. Hydrolysis with dilute sulphuric acid gave *benzmesaconine* [*hydrochloride monohydrate*, decomp. 255–257°,  $[\alpha]_D^{25} - 24.0^\circ$  (in water); *hydrobromide trihydrate*, decomp. 245–246°,  $[\alpha]_D^{25} - 21.8^\circ$  (in water)], whilst warming with alcoholic potassium hydroxide afforded *mesaconine* (identified as *tetra-acetyl derivative*, decomp. 228–229°). On a boiling dimethyl-aniline bath *mesaconitine* decomposed into acetic acid and *pyromesaconitine* [*hydrobromide*, decomp. 226° after sintering at 222°,  $[\alpha]_D^{25} - 40.5^\circ$  (in water); *chloroaurate monohydrate*, decomp. 180–181°; *perchlorate*, decomp. 285–287°], accompanied by some *pyromesaconitine-γ*, decomp. 169–170°,  $[\alpha]_D^{25} - 107^\circ$  (in alcohol) [*hydrobromide*, decomp. 240–241°,  $[\alpha]_D^{25} - 102^\circ$  (in water), *chloroaurate*, decomp. 193–194°]. Acetone-potassium permanganate oxidation of *mesaconitine* yielded oxonitine, decomp. 282°.

R. J. W. LE FÈVRE.



**Identity of aconitine-A, japaconitine-A, and japaconitine-A<sub>2</sub>.** R. MAJIMA and S. MORIO (Annalen, 1929, 476, 194—203).—From comparisons of carefully purified specimens of japaconitine-A and aconitine-A (and their respective hydrobromides, perchlorates, and chloroaurates) it is concluded that these substances are identical. Japaconitine-A or -A<sub>2</sub>, or aconitine-A, by heating on a boiling dimethyl-aniline bath and treatment of the product with hydrobromic acid, all gave pyraconitine  $\alpha$ -bromide, decomp. 271—272° (perchlorate, decomp. 153—154°).

From pure aconitine-A or japaconitine-A three chloroaurates were obtained:  $\alpha$ -, m. p. 138—140° (lit. 135°, 231°);  $\beta$ -, m. p. 157—158° (lit. 152°);  $\gamma$ -, m. p. 177° (lit. 176°). Crystallisation of the  $\alpha$ -form from chloroform or ether transformed it into the  $\beta$ - and  $\gamma$ -forms.

Aconitine from *A. napellus* was transformed into the hydrobromide and aconitine-A bromide removed; from the mother-liquors (previously considered to contain aconitine-C bromide only) the perchlorates of mesaconitine and hyphaconitine were isolated.

R. J. W. LE FÈVRE.

**Summarised observations on Aconitum alkaloids.** R. MAJIMA and S. MORIO (Annalen, 1929, 476, 203—214).—Crystallographic data are given for aconitine, mesaconitine, and hyphaconitine; the remaining matter is adequately described by the title.

R. J. W. LE FÈVRE.

**Harmine and harmaline. X. Synthesis of 7- and 8-methoxyketotetrahydro- $\beta$ -carbolines and the constitution of acetylharmaline.** H. S. B. BARRETT, W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1929, 2942—2946).—Ethyl cyclopentanone-carboxylate couples with *p*-methoxybenzenediazonium chloride in alkaline solution to give the *p*-methoxyphenylhydrazones, m. p. 97°, of ethyl hydrogen  $\alpha$ -keto-adipate. This is converted by boiling alcoholic sulphuric acid into ethyl  $\beta$ -2-carbethoxy-5-methoxyindole-3-propionate, m. p. 110°, the corresponding dicarboxylic acid, m. p. 225° (decomp.), which is obtained on hydrolysis being converted, with loss of carbon dioxide, by heating in diphenylamine solution into  $\beta$ -5-methoxyindole-3-propionic acid, m. p. 136° (methyl ester, m. p. 100°). The hydrazide, m. p. 146° (obtained by heating the methyl ester and hydrazine hydrate at 150°), is converted by sodium nitrite and acetic acid into the azide, from which, by the action of dry hydrogen chloride in chloroform-toluene solution, is obtained 7-methoxy-2-keto-2:3:4:5-tetrahydro- $\beta$ -carboline, m. p. 280° (for nomenclature, cf. this vol., 220). By an exactly similar series of reactions starting with *m*-methoxybenzenediazonium chloride are obtained ethyl  $\beta$ -2-carbethoxy-6-methoxyindole-3-propionate, m. p. 109°;  $\beta$ -2-carboxy-6-methoxyindole-3-propionic acid, m. p. 221° (decomp.);  $\beta$ -6-methoxyindole-3-propionic acid, m. p. 165° (methyl ester, m. p. 69°, by the action of an ethereal solution of diazomethane; hydrazide, m. p. 143°), and, finally, 8-methoxy-2-keto-2:3:4:5-tetrahydro- $\beta$ -carboline, m. p. 198°, identical with the substance, to which this constitution was assigned, obtained previously from acetylharmaline (Nishikawa, Perkin, and Robinson, cf. A., 1924, i, 565). This synthesis therefore con-

firms the correctness of the structure assigned by these authors to acetylharmaline. J. W. BAKER.

**Microchemistry of brucine.** M. WAGENAAR (Pharm. Weekblad, 1929, 66, 1170—1176).—An account of an examination of known micro-tests. The most sensitive reagents are zinc and mercuric iodides, each of which will detect 0.5 mg. at a dilution of 1 in 1000.

S. I. LEVY.

**Brucine.** H. THOMS and J. GONEIN (Arch. Pharm., 1930, 268, 48—57).—By the interaction of brucine with various halogeno-ketones, halogeno-acids, and their derivatives in chloroform solution, a series of quaternary additive compounds of the type C<sub>23</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>·RCl(Br) (similar to those obtained from strychnine; Moufang and Tafel, A., 1899, i, 309, 310), has been prepared and converted into the corresponding bases and betaines. Thus with the appropriate halogeno-ketone are obtained *N*-acetylbrucinium chloride (R=·CH<sub>2</sub>Ac), m. p. 232—233° (decomp.), converted by the action of silver sulphate in hot aqueous solution into the corresponding sulphate and thence by the action of the theoretical quantity of baryta into the hydroxide [picrate, m. p. 250° (decomp., with previous darkening)]; *N*-phenacylbrucinium bromide (R=·CH<sub>2</sub>Bz), m. p. 230° (decomp.) [gold chloride double salt, m. p. 173—175° (decomp.)], converted into the hydroxide [chloroplatinate, decomp. 230°; picrate, m. p. 220° (decomp.)]; *N*-3:4-di-hydroxyphenacyl- + 1.5H<sub>2</sub>O [R=·CH<sub>2</sub>·CO·C<sub>6</sub>H<sub>3</sub>(OH)<sub>2</sub>], m. p. 250—251° (decomp.) (acetate; hydrochloride), and *N*-2:3:4-trihydroxyphenacyl-, m. p. 190° (decomp.), -brucinium chlorides. From various chloro-acids and their esters are similarly obtained: *N*-carb-ethoxymethylbrucinium chloride (R=·CH<sub>2</sub>·CO<sub>2</sub>Et), m. p. 251—252° (decomp.), converted by the action of sodium carbonate or ammonia on its aqueous solution into the betaine

+2H<sub>2</sub>O, C<sub>23</sub>H<sub>26</sub>NO<sub>4</sub>N<CH<sub>2</sub>>CO (I), m. p. 247° (decomp.), [ $\alpha$ ]<sub>D</sub><sup>20</sup> +25.26° (in acetic acid) (chloroplatinate, decomp. above 200°), whilst the hydrochloride, decomp. above 200°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -12.65° (in water), of the betaine is obtained by the action of chloroacetic acid on brucine at 110°; *N*- $\beta$ -carbethoxyethylbrucinium bromide (R=·CHMe·CO<sub>2</sub>Et), m. p. 201—204° (decomp.), converted by the action of the calculated quantity of absolute alcoholic potassium hydroxide on the solution of the corresponding nitrate into the methylbetaine +3H<sub>2</sub>O, m. p. 216—217° (decomp.); *N*-dicarbethoxymethylbrucinium chloride [R=·CH(CO<sub>2</sub>Et)<sub>2</sub>], m. p. 246—248° (decomp.), converted by sodium carbonate into the betaine I; *N*-chloro-carbethoxymethylbrucinium chloride (R=·CHCl·CO<sub>2</sub>Et), m. p. 151° (decomp.), reconverted into brucine by the action of aqueous sodium carbonate; and *N*-di-chlorocarbethoxymethylbrucinium chloride (R=·CCl<sub>2</sub>·CO<sub>2</sub>Et), m. p. 133° (decomp.).

J. W. BAKER.

**Strychnos alkaloids. III. Structural relationship between strychnine and brucine.** F. CORTESE (Annalen, 1929, 476, 280—285).—Oxidation of strychnine with chromic acid in dilute sulphuric acid solution gives the acids, C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub> (I) and C<sub>17</sub>H<sub>22</sub>O<sub>6</sub>N<sub>2</sub> (II), obtained previously by Wieland and

Münster (A., 1929, 707) from brucine (cf. Leuchs and Kröhnke, A., 1929, 1320). Similar oxidation of the acid  $C_{19}H_{22}O_6N_2$  (Hanssen, A., 1887, 505; cf. Leuchs, A., 1922, i, 1052) also affords I and II.

H. BURTON.

**Benzeneazomorphine.** G. CHARRIER and A. NERI (Gazzetta, 1929, 59, 804—810).—2-Benzeneazomorphine (Wieland and Kappelmeier, A., 1911, i, 743; Lautenschläger, A., 1919, i, 344) is converted into 2-benzeneazomorphine, decomp.  $200^\circ$ , when the solution in concentrated sulphuric acid is kept in the cold for 7 days or heated for a few hours. Pschorr's formula for morphine is considered to be in best accord with this ready transformation. The action of benzenediazonium chloride on *apomorphine* appears to yield a mixture of two substances, possibly the 1- and 2-azo-derivatives. R. K. CALLOW.

**Sinomenine and disinomenine. XI. Position of the double linking in sinomenine.** K. GOTO and H. SUDZUKI (Bull. Chem. Soc. Japan, 1929, 4, 244—254).—From a series of reduction experiments it is concluded that the double linking in sinomenine is situated in the  $C_7$ — $C_8$  position. Sinomenine is reduced by sodium amalgam in alkaline solution to *bis*-8 : 8'-dimethoxysinomenine, m. p.  $304^\circ$ ,  $[\alpha]_D^{25} -24.49^\circ$  in 1% aqueous hydrochloric acid (*methiodide*, m. p. above  $305^\circ$ ; *semicarbazone*, m. p. above  $300^\circ$ ), in 40% yield, whilst neutral reduction with sodium amalgam gives *dimethoxydihydrosinomenine*, m. p.  $138^\circ$ ,  $[\alpha]_D^{25} +59.17^\circ$  in alcohol,  $+48.88^\circ$  in 1% hydrochloric acid (*methiodide*, m. p.  $115^\circ$ ; *semicarbazone*, m. p.  $235^\circ$ ), in about 65% yield; the latter is probably *l*-dihydrothebaine. Reduction by Clemmensen's method affords a 20% yield of *demethoxydeoxydihydrosinomenine*, m. p.  $148^\circ$ ,  $[\alpha]_D^{25} +43.22^\circ$  in alcohol (*methiodide*, m. p.  $267^\circ$ ; *hydriodide*, m. p.  $245^\circ$ ) (a 30% yield is obtained if dihydrosinomenine is employed), which is probably *d*-tetrahydrodeoxycodine. Sinomenine with hydrochloric acid at  $100^\circ$  gives *bisdemethylsinomyliene*, m. p. above  $312^\circ$ ,  $[\alpha]_D^{25} +335.32^\circ$  in 1% hydrochloric acid (*methiodide*, m. p.  $285^\circ$ ; *dioxime*, m. p.  $315^\circ$ ; *semicarbazone*, m. p. above  $300^\circ$ ), in about 10% yield. With zinc and hydrochloric acid in the cold sinomenine gives rise to *hydrosinomenine*, m. p.  $196^\circ$ ; morphine and codeine are unaffected by this treatment. A. I. VOGEL.

**Qualitative reactions of primary arsines.** S. S. NAMETKIN and V. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1045—1050).—See A., 1929, 949.

**Compounds of tryparsamide type. II. Resolution of *dl*-2-*N*-methylphenylalanineamide-4-arsinic acid.** C. S. GIBSON and B. LEVIN (J.C.S., 1929, 2759—2763; cf. A., 1929, 584).—By boiling sodium 6-amino-*m*-tolylarsinate in aqueous solution with  $\alpha$ -bromopropionic acid, *dl*-*N*-2-methylphenylalanine-4-arsinic acid, m. p.  $170^\circ$  (decomp.) [*methyl* and *ethyl* esters, m. p.  $215^\circ$  (decomp.) and  $214$ — $216^\circ$  (decomp.), respectively], was obtained. *dl*-*N*-2-methylphenylalanineamide-4-arsinic acid, m. p.  $219^\circ$  (decomp.), was prepared either by treatment of the above methyl ester with concentrated ammonia solution or by the interaction of  $\alpha$ -bromopropionamide

and aqueous sodium 6-amino-*m*-tolylarsinic acid; unlike its ammonium, brucine, and nor-*d*- $\psi$ -ephedrine salts, the quinine and strychnine salts were not crystalline. Optical resolution was accomplished by nor-*d*- $\psi$ -ephedrine, the *lAdB* salt, m. p.  $205$ — $208^\circ$  (decomp.),  $[\alpha] -2.46^\circ$  (in aqueous solution), separating from a solution containing the amide-acid (2 equivs.), the *d*-base (1 equiv.), and sodium hydroxide (1 equiv.). *d*- and *l*-*N*-2-methylphenylalanineamide-4-arsinic acid had m. p.  $267^\circ$  and  $267$ — $268^\circ$  (decomp. after darkening from  $260^\circ$ ), and  $[\alpha]$  (as sodium salt)  $+33.4^\circ$  and  $-34.9^\circ$ , respectively. These optically active amide-acids on hydrolysis with an excess of sodium hydroxide yielded the sodium salts of the corresponding dibasic acids having opposite signs; apparently the hydrolysis of the amide-acids is accompanied by racemisation.

The results of an examination for therapeutical activity of compounds of the tryparsamide type described in Parts I and II are recorded. The following had no action: *d*- and *l*-phenylalanine-4-arsinic acids, *dl*-*N*-2-methylphenylalanine-4-arsinic acid, and the corresponding amide-acid; the following had definite but transient actions: *dl*-*N*-phenylalanine-4-arsinic acid, *d*- and *dl*-phenylalanineamide-4-arsinic acids; whilst *l*-*N*-phenylalanineamide-4-arsinic acid and *l*-*N*-2-methylphenylalanineamide-4-arsinic acid exhibited only slight actions.

R. J. W. LE FÈVRE.

**Monohalogenomononitrotoluenes. Arsenical compounds derived from 3-bromo-4-nitrotoluene.** L. A. ELSON, C. S. GIBSON, and J. D. A. JOHNSON (J.C.S., 1929, 2735—2742).—The remaining two bromonitrotoluenes have been synthesised. 5-Nitro-2-acetamidotoluene mixed with alcohol, water, and acetic acid, was treated at the b. p. with iron powder; 5-amino-2-acetamidotoluene, so obtained, had m. p.  $143^\circ$ . Diazotisation of 4-nitro-3-aminotoluene (obtained by heating aqueous ammonia, methyl alcohol, and 3 : 4-dinitrotoluene in an autoclave) gave 3-chloro-4-nitrotoluene, b. p.  $146^\circ/19$  mm., m. p.  $22^\circ$ , 3-bromo-4-nitrotoluene, b. p.  $156$ — $158^\circ/19$  mm., m. p.  $37^\circ$ , and 3-iodo-4-nitrotoluene, m. p.  $95$ — $97^\circ$  to a milky liquid becoming clear at  $104^\circ$  and melting after resolidification at  $103$ — $105^\circ$  with no preliminary change.

2 : 3-Dinitro-4-aminotoluene gave by diazotisation in hydrochloric acid 3-chloro-2-nitrotoluene, m. p.  $21$ — $22^\circ$ , and 3-bromo-2-nitrotoluene, b. p.  $129$ — $130^\circ/10$  mm., m. p.  $27^\circ$  (accompanied by a substance,  $C_{12}H_9O_4N_2Br_3$ , m. p.  $95$ — $96^\circ$ ). From 2 : 6-dinitro-4-aminotoluene, hydrobromic acid, etc., 4-bromo-2 : 6-dinitrotoluene, m. p.  $89$ — $90^\circ$ , was obtained.

A boiling mixture of 3-bromo-4-nitrotoluene, *o*-aminophenylarsinic acid, potassium carbonate, amyl alcohol, and a trace of copper powder yielded 2-nitro-5-methyldiphenylamine-6'-arsinic acid, m. p.  $228$ — $230^\circ$  (decomp.), reduction of which by sulphur dioxide in the presence of alcohol, iodine, and hydrochloric acid gave 2-nitro-5-methyldiphenylamine-6'-dichloroarsine, m. p.  $137^\circ$  (decomp.). The last-named substance was transformed by boiling acetic acid into 10-chloro-4-nitro-1-methyl-5 : 10-dihydrophenarsazine, m. p.  $198$ — $200^\circ$  (slight decomp.).

R. J. W. LE FÈVRE.

**2-Phenyl-4 : 5- $\alpha\beta$ -naphth-1 : 2 : 3-triazole-4'-arsinic acid.** G. CHARRIER and A. NERI (Gazzetta, 1929, 59, 742—750; cf. A., 1928, 187).—An improved method for the preparation of this compound is described. *p*-Aminophenylarsinic acid is diazotised and the product coupled with  $\beta$ -naphthylamine to give 2-amino-1-benzeneazonaphthalene-4'-arsinic acid, m. p. 285° [sodium salt (+0.5H<sub>2</sub>O), decomp. before m. p.], which is dehydrogenated by treatment with cuprammonium sulphate in alcoholic solution (cf. Schmidt and Hagenböcker, A., 1921, i, 897) to give 2-phenylnaphththiazole-4'-arsinic acid. (I) [sodium hydrogen and disodium (+7H<sub>2</sub>O) salts, decomp. before m. p.]. Oxidation of I by chromic acid in acetic acid yields an *o*-quinone, which gives with phenylhydrazine a  $\beta$ -hydroxy- $\alpha$ -benzeneazo-derivative (decomp. before m. p.). Oxidation of I by permanganate in alkaline solution yields 4-carboxy-2-phenyl-5-*o*-carboxyphenyl-1 : 2 : 3-triazole-4'-arsinic acid (+2.5H<sub>2</sub>O), decomp. above 305°. Reduction of I with sodium hyposulphite in alkaline solution yields a mixture of the corresponding arseno- and arsenoxy-derivatives.

R. K. CALLOW.

**10-Chloro-5 : 10-dihydrophenarsazine and derivatives.** XI. Mono-, di-, and tri-methyl derivatives. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 2743—2753).—*N*-*o*- and -*p*-Tolylbenziminoclorides, b. p. 164°/6 mm. and 186°/10 mm., respectively, reacted with ethereal *o*-, *m*-, and -*p*-cresols, sodium, and ethyl alcohol to give *N*-*o*-, -*m*-, and -*p*-tolylbenziminoc-*o*-tolyl ethers, m. p. 63—64°, 51—52°, and 54°, respectively, and similarly *N*-*m*-tolylbenziminoc-*p*-tolyl ether, m. p. 52—53°, *N*-*o*-tolylbenziminophenyl ether, m. p. 54—56°, and *N*-*o*-tolylbenziminoc-*m*-tolyl ether. Those compounds all isomerised completely to the benzoyl derivatives of the substituted diphenylamines by heating to 280—300°; the last-named ether gave benzoyl-*o*-tolyl-*m*-tolylamine, m. p. 103—104° (identical with the product of heating *N*-*m*-tolylbenziminoc-*o*-tolyl ether). Also described are: benzoylphenyl-*o*-tolylamine, m. p. 110—111°, benzoyldi-*o*-tolylamine, m. p. 114—115°, benzoyl-*m*-tolyl-*p*-tolylamine, m. p. 118—119°, *o*-tolyl-*p*-tolylamine, b. p. 183°/19 mm., and *o*-tolyl-*m*-tolylamine, b. p. 187°/22 mm.

A mixture of phenyl-*o*-tolylamine, arsenious chloride, and *o*-dichlorobenzene when boiled gave 10-chloro-4-methyl-5 : 10-dihydrophenarsazine, m. p. 191—192°, with hydrogen chloride evolution; 10-chloro-2 : 6-dimethyl-5 : 10-dihydrophenarsazine, m. p. indefinite about 226° (decomp.), was similarly prepared from *o*-tolyl-*p*-tolylamine. Oxidation of the preceding substance by hydrogen peroxide in boiling acetic acid solution gave 2 : 5-dimethylphenarsazinic acid, m. p. above 310° (sodium, barium, silver, and mercury salts; hydrochloride, 2C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>Na<sub>3</sub>·3HCl, decomp. at 266—268° after becoming green at 208°). *o*-Tolyl-*m*-tolylamine condensed with arsenious chloride in *o*-dichlorobenzene solution to give 10-chloro-1(or 3) : 6-dimethyl-5 : 10-dihydrophenarsazine, m. p. 216—218° (decomp.), oxidation of which afforded 1(or 3) : 6-dimethylphenarsazinic acid, m. p. above 309° (sodium and ammonium salts). The above work shows that the factors underlying the

condensations of substituted diphenylamines with arsenious chloride are different from those previously postulated (J.C.S., 1926, 2243, footnote).

4-Amino-*m*-xylene, *o*-bromophenylarsinic acid, amyl alcohol, and potassium carbonate reacted, when heated in the presence of copper powder, with formation of 2 : 4-dimethyldiphenylamine-6'-arsinic acid, m. p. 135° (sodium, calcium, and barium salts). This acid underwent reduction by sulphur dioxide in a mixture of alcohol, hydrochloric acid, and a trace of iodine to give 10-chloro-2 : 4-dimethyl-5 : 10-dihydrophenarsazine, m. p. 216—217° (corresponding 10-bromo-compound, decomp. 198° after softening at 195°). 2 : 4-Dimethylphenarsazinic acid, m. p. above 300° (hydrochloride, m. p. about 200°), was obtained by oxidation of the preceding 10-chlorodihydrophenarsazine with hydrogen peroxide in acetic acid. Boiling a mixture of 3-bromo-*p*-tolylarsinic acid, *p*-toluidine, potassium carbonate, amyl alcohol, and a trace of copper powder gave 4 : 3'-dimethyldiphenylamine-6'-arsinic acid, m. p. 153—154° (slight decomp.) (sodium and barium salts), reduction of which in the usual manner afforded 10-chloro-2 : 7-dimethyl-5 : 10-dihydrophenarsazine (+AcOH), decomp. 195—198° after turning green at 190—195°. The analogous bromo-compound had m. p. 179—180°. The 10-chloro-compound gave on oxidation 2 : 7-dimethylphenarsazinic acid, m. p. above 295° (ammonium, calcium, barium, and magnesium salts; hydrochloride, decomp. 219—221°).

3 : 3'-Dimethyldiphenylamine-6'-arsinic acid, m. p. 145—146° (ammonium, barium, and sodium salts) (prepared from 3-bromo-*p*-tolylarsinic acid and *m*-toluidine as for 4 : 3'-dimethyldiphenylamine-6'-arsinic acid), formed on reduction of 10-chloro-1(or 3) : 7-dimethyl-5 : 10-dihydrophenarsazine, decomp. 225—226° after turning green at 218° [corresponding bromo-compound had m. p. 255—256° (decomp.)], which, in turn, gave by oxidation 1(or 3) : 7-dimethylphenarsazinic acid, m. p. above 295° (hydrochloride, darkened and shrank at 217—219°). From a mixture of 3-bromo-*p*-tolylarsinic acid, 4-amino-*m*-xylene, potassium carbonate, amyl alcohol, and copper powder was obtained 10-chloro-2 : 4 : 7-trimethyl-5 : 10-dihydrophenarsazine, m. p. 220—222° (decomp.) (hydrochloride, decomp. 235—236° with generation of a green coloration). 10-Chloro-1 : 4 : 7-trimethyl-5 : 10-dihydrophenarsazine, prepared in the usual way from 3-bromo-*p*-tolylarsinic acid and 2-amino-*p*-xylene, had m. p. 200—202° after slight softening.

*N*-2 : 4-Dimethylphenylbenziminocloride (obtained by heating 4-benzamido-*m*-xylene with phosphorus pentachloride) had b. p. 175°/6 mm. and m. p. 42°.

R. J. W. LE FÈVRE.

**Salts of triphenylselenonium hydroxide.** H. M. LEICESTER and F. W. BERGSTROM (J. Amer. Chem. Soc., 1929, 51, 3587—3591).—Diphenyl selenide is converted by treatment with nitric and hydrochloric acids into diphenylselenium dichloride. This undergoes the Friedel-Crafts reaction with benzene, affording triphenylselenonium chloride, decomp. 230° 230° (all m. p. are corr.) (dihydrate; iodide, decomp. 237.5°; dichromate, decomp. 238°; picrate, m. p. 141—142°; nitrate, m. p. 107—108°). When the above chloride is dissolved in boiling ethylene dibromide

*triphenylselenonium bromide*, decomp.  $236^{\circ}$ , separates on cooling. Thermal decomposition of the three halides affords diphenyl selenide and chloro-, bromo-, or iodo-benzene, respectively.

The Grignard, Wurtz-Fittig, and Friedel-Crafts reactions with selenium tetrachloride give complex mixtures of products. H. BURTON.

**Alteration of the acidity of glycollic and thiol-acetic acid derivatives by replacement of oxygen and sulphur by selenium.** O. BEHAGHEL and M. ROLLMANN (Ber., 1929, 62, [B], 2693—2696; cf. A., 1927, 148).—Measurements of the conductivities of solutions of *o*- and *p*-methoxyphenyl-, *p*-methylthiolphenyl-, *o*- and *p*-tolyl-, *o*- and *p*-chlorophenyl-, and *o*- and *p*-nitrophenyl-selenolacetic acids shows that the introduction of the selenium atom causes an increase in acidity which is less than that induced by oxygen or sulphur. The decrease in effect from oxygen to sulphur is greater than that from sulphur to selenium. H. WREN.

**$\alpha$ - and  $\beta$ -Selenium derivatives of naphthalene.** J. LOEVENICH, H. FREMDLING, and M. FÖHR (Ber., 1929, 62, [B], 2856—2865).— $\alpha$ -Selenonaphthol is characterised by the preparation of its silver, lead, cupric, and mercuric salts.  $\alpha$ -Naphthyl methyl selenide, b. p.  $173^{\circ}/16$  mm., obtained in 46.9% yield from  $\alpha$ -selenonaphthol and methyl sulphate in alkaline solution, is oxidised to  $\alpha$ -naphthyl methyl selenone,  $C_{10}H_7 \cdot SeO_2 \cdot Me$ , b. p.  $290^{\circ}$ .  $\alpha$ -Naphthyl ethyl selenide, b. p.  $167$ — $168^{\circ}/13$  mm.,  $\alpha$ -naphthyl isopropyl selenide, b. p.  $165$ — $167^{\circ}/14$  mm., and  $\alpha$ -naphthyl *n*-butyl selenide, b. p.  $180^{\circ}/13$  mm., are prepared from the selenonaphthol, sodium alkoxide, and alkyl iodide. Treatment of  $\alpha$ -selenonaphthol with the appropriate acid chloride affords the acetyl derivative, b. p.  $167^{\circ}/18$  mm., and benzoyl compound, m. p.  $133^{\circ}$ . Paracet-aldehyde or pyruvic acid and selenonaphthol afford  $\alpha\alpha$ -di-1-naphthylselenolethane, m. p.  $89^{\circ}$ , whereas acetone gives  $\beta\beta$ -di-1-naphthylselenolpropane, m. p.  $130^{\circ}$ . Oxidation of  $\alpha\alpha'$ -dinaphthyl selenide with potassium dichromate in boiling aqueous acetic acid affords  $\alpha\alpha'$ -dinaphthyl selenoxide, m. p.  $105^{\circ}$ , converted by excess of permanganate into  $\alpha\alpha'$ -dinaphthyl selenone, m. p.  $106^{\circ}$ .

Addition of a diazotised solution of  $\beta$ -naphthylamine containing sodium acetate to aqueous potassium selenocyanate affords  $\beta$ -selenocyanonaphthalene, m. p.  $68^{\circ}$ , oxidised by boiling 20% nitric acid to naphthalene- $\beta$ -seleninic acid,  $C_{10}H_7 \cdot SeO_2H$ , m. p.  $156^{\circ}$  (silver and lead salts; methyl ester, m. p.  $106^{\circ}$ , from the sodium salt and methyl chloroformate in methyl alcohol; ethyl ester, b. p.  $65$ — $68^{\circ}/12$  mm.). Treatment of sodium naphthalene- $\beta$ -seleninate with boiling methyl iodide affords  $\beta$ -naphthyl methyl selenone, m. p.  $136^{\circ}$ , also obtained by oxidation of  $\beta$ -naphthyl methyl selenide with permanganate.  $\beta$ -Naphthyl ethyl selenone, m. p.  $40$ — $41^{\circ}$ , is obtained analogously.  $\beta$ -Selenonaphthol, m. p.  $72$ — $74^{\circ}$ , is prepared by hydrolysis of  $\beta$ -selenocyanonaphthalene by aqueous-alcoholic sodium hydroxide in presence of dextrose or by reduction of naphthalene- $\beta$ -seleninic acid by dextrose in alkaline solution. The lead salt is converted by methyl iodide into  $\beta$ -naphthyl methyl selenide, m. p.  $54^{\circ}$ ;  $\beta$ -naphthyl *n*-butyl selenide, m. p.  $137^{\circ}$ ; the

acetyl (m. p.  $132$ — $133^{\circ}$ ) and benzoyl (m. p.  $118^{\circ}$ ) derivatives of  $\beta$ -selenonaphthol;  $\alpha\alpha$ -di-2-naphthylselenolethane, m. p.  $134^{\circ}$ , and  $\beta\beta$ -di-2-naphthylselenolpropane, m. p.  $96^{\circ}$ , are described. Oxidation of an ethereal solution of selenonaphthol by exposure to air yields  $\beta\beta'$ -dinaphthyl diselenide,  $C_{10}H_7 \cdot Se \cdot Se \cdot C_{10}H_7$ , m. p.  $126$ — $127^{\circ}$ , whereas the isomeric *di*- $\beta$ -naphthyl selenoselenide,  $(C_{10}H_7)_2Se \cdot Se$ , m. p.  $112$ — $114^{\circ}$ , is prepared by the action of red selenium on di- $\beta$ -naphthyl selenide or from diazotised  $\beta$ -naphthylamine and potassium diselenide. The last-named compound loses selenium after long treatment with boiling alcohol, whereas the diselenide is completely stable under these conditions. The diselenide is not affected by oxidising agents which convert the selenoselenide into  $\beta\beta'$ -dinaphthyl selenoxide, m. p.  $134^{\circ}$ , and thence into  $\beta\beta'$ -dinaphthyl selenone, m. p.  $160$ — $161^{\circ}$ .

H. WREN.

**Valency. XIV. Optically active telluronium salt: phenyl-*p*-tolylmethyltelluronium iodide.** T. M. LOWRY and F. L. GILBERT (J.C.S., 1929, 2867—2876).—Phenyl-*p*-tolylmethyltelluronium bromide is converted by interaction with silver *d*-bromocamphor- $\pi$ -sulphonate in dry acetone into its bromocamphor- $\pi$ -sulphonate, which by fractional crystallisation from acetone and ethyl acetate (50%) gives 1-phenyl-*p*-tolylmethyltelluronium *d*-bromocamphor- $\pi$ -sulphonate, m. p.  $180$ — $181^{\circ}$ , which exhibits marked mutarotation in acetone or ethyl acetate (e.g.,  $[M]_{5461}^{19} + 262^{\circ}$  to  $[M]_{5461}^{18} + 347^{\circ}$ , the latter value being that of the bromocamphorsulphonic acid itself), indicating the presence of an unstable, levorotatory cation (at least  $[M] = 85^{\circ}$ ). In agreement with this view, addition of a cold dilute aqueous solution of potassium iodide to an acetone solution of the bromocamphor-sulphonate precipitates 1-phenyl-*p*-tolylmethyltelluronium iodide, which is initially levorotatory in acetone ( $[M]_{5461}^{19} - 67^{\circ}$ ), but rapidly mutarotates to a final value  $[M]_{5461}^{19} + 2^{\circ}$  (due to the presence of about 1% of the *d*-bromocamphorsulphonate). Similarly, the silver salt of Reychler's acid converts the original bromide into *d*-phenyl-*p*-tolylmethyltelluronium *d*-camphor- $\beta$ -sulphonate, which could not be crystallised, and exhibits only very slow mutarotation, the dispersion curves indicating the presence of a cation having  $[M]_{5461}^{19}$  about  $+72^{\circ}$ . The corresponding precipitated iodide is usually obtained inactive, but in two cases rapid mutarotation ( $[M]_{5461}^{19} - 67^{\circ}$  to  $+2^{\circ}$ ) was detected. These results definitely prove the optical activity of the cation  $[TePhMeC_7H_7]^+$  and hence quadrivalent tellurium must possess a tetrahedral configuration. The mutarotation curves are definitely not unimolecular and hence racemisation of the cation is not represented by the simple isomeric change  $lB \rightleftharpoons dB$ . J. W. BAKER.

**Aromatic aldehyde derivatives of proteins, peptides, and amino-acids.** H. D. DAKIN (J. Biol. Chem., 1929, 84, 675—682).—When heated with excess of benzaldehyde in presence of sodium acetate and acetic anhydride, alanine gives a compound,  $C_{10}H_{11}O_2N$ , m. p.  $185$ — $190^{\circ}$  after softening at  $175^{\circ}$ ; glycylglycine, glycyl-leucine, and alanyl-leucine, on similar treatment, react with 2 mols. of benzaldehyde with elimination of 1 mol. of water,

to give compounds  $C_{18}H_{18}O_4N_2$ ,  $C_{22}H_{26}O_4N_2$ ,  $C_{23}H_{28}O_4N_2$ , respectively, all melting indefinitely above  $200^\circ$ . Proteins, when treated in this manner, give derivatives with similar properties, the proportion of benzaldehyde (or other aromatic aldehyde) in the product being characteristic of the individual protein. The products are acidic substances which no longer give the protein reactions except the reaction with diazobenzenesulphonic acid; they are very resistant to acid or alkaline hydrolysis; they reduce permanganate immediately to manganate, and slowly to manganese dioxide with production of benzoic acid. They do not therefore possess the properties which would be expected were their formation due to condensation of the aldehyde with diketopiperazine groups in the protein molecule. Leucineimide gives with benzaldehyde, under the above conditions, a condensation product which is readily resolved into the starting materials by treatment with sodium hydroxide.

C. R. HARRINGTON.

**Mol. wt. of phycocyan and phycoerythrin from *Porphyra tenera* and of phycocyan from *Aphanizomenon flos aquæ*.** T. SVEDBERG and T. KATSURAI (J. Amer. Chem. Soc., 1929, **51**, 3573—3583).—The phycocyan from *P. tenera* and *Ceramium rubrum* (A., 1928, 533) show similar absorption spectra in the visible and ultra-violet; a similar relationship is observed for phycoerythrin from the same sources. The visible absorption of phycocyan from *A. flos aquæ* differs from the above phycocyan, but the ultra-violet absorption of all the specimens is similar. The specific volumes of all the proteins studied are identical and are independent of  $p_H$ .

Determinations of the mol. wt. of the three proteins mentioned in the title by the methods of sedimentation velocity (cf. A., 1927, 716) and sedimentation equilibrium (cf. A., 1926, 340) near the isoelectric point give a value of  $208,000 \pm 5000$  for all three. Solutions of the proteins decompose with increase in  $p_H$ . The phycoerythrin is the most stable, but at  $p_H$  11.0 it decomposes, yielding 25% of molecules of one sixth of the original size. The phycocyan from *Aphanizomenon* is completely disrupted at  $p_H$  12.0 into molecules of one sixth of the original size.

The phycoerythrins from *P. tenera* and *C. rubrum* are probably identical, as are the phycocyan from these algæ. These are designated *R*-phycoerythrin and *R*-phycocyan, respectively. The phycocyan from *A. flos aquæ* is designated *C*-phycocyan.

H. BURTON.

**Mol. wt. of Bence Jones protein.** T. SVEDBERG and B. SJÖGREN (J. Amer. Chem. Soc., 1929, **51**, 3594—3605).—Solutions of Bence Jones protein show an absorption maximum at about  $280 \mu\mu$  and a minimum at about  $255 \mu\mu$ ; these are independent of the  $p_H$  of the solution. An improved type of ultra-centrifuge is described for the determination of the mol. wt. of the protein by the methods of sedimentation equilibrium and sedimentation velocity. The determinations were carried out at various  $p_H$  values. Between  $p_H$  3.5 and 7.5 the protein is stable and has a mol. wt. of  $35,000 \pm 1000$ , which is identical with that of egg-albumin. At  $p_H < 3.5$  the molecule undergoes some change, giving a non-centrifugable

substance, whilst at  $p_H > 7.5$  hydrolysis into smaller molecules occurs.

H. BURTON.

**Action of alkali hydroxides at high temperatures on albuminous substances.** L. DUPONT (Compt. rend., 1929, **189**, 922—924).—The action of alkali hydroxide on egg-albumin and gelatin at  $325$ — $350^\circ$  causes evolution of all the nitrogen in the form of ammonia and gives the alkali salts of most of the lower monobasic aliphatic acids, oxalic and benzoic acids.

A. A. GOLDBERG.

**Reaction of proteins. II. Action of salts in the acetic acid—sodium chloride test. IV. Anion series.** S. OGATA (Hokkaido J. Med., 1928, **6**, 148—160, 567—576).—II. In presence of hydrogen chloride and salts, the quantity of ammonium sulphate necessary for the precipitation of gelatin becomes constant at  $p_H$  2.69. When disodium monohydrogen phosphate is added, hydrogen chloride of any concentration fails to precipitate the protein, the addition of sodium chloride being necessary.

IV. With horse serum the case of precipitation is in the reverse order of the lyotropic series; with glue, only a few potassium salts can cause precipitation, although the order is the same. The effect of addition of ferrocyanide is to give the solution a definite  $p_H$  value. The dissociation constant of hydroferrocyanic acid is  $10^{-3}$  to  $10^{-4}$ . The effect of the presence of ethyl alcohol on the precipitation caused by various chlorides and acetic acid cannot be attributed to interaction between the salts and the alcohol.

CHEMICAL ABSTRACTS.

**Nucleic acid-protein compounds.** E. HAMMARSTEN and G. HAMMARSTEN (Acta med. Scand., 1928, **68**, 6 pp.; Chem. Zentr., 1929, ii, 755—756).—Mutual precipitation of protein and thymonucleic acid takes place if the protein possesses a sufficient positive charge, giving with the nucleic acid anion an electrically neutral or relatively weakly charged complex. Precipitation by hydrogen ions depends on the  $p_H$ , the relative concentrations of nucleic acid and protein, and the presence of other electrolytes; the varying results are discussed. Solutions of crystallised egg-albumin and tetrasodium thymonucleate in varying ratios were treated with different quantities of hydrochloric acid and the composition of the mother-liquor was determined.

A. A. ELDRIDGE.

**Microchemical reactions. I. Compounds of dyes with protein-nucleic acid. II. Precipitation of protein-nucleic acid with lanthanum and sulphosalicylate ions.** E. HAMMARSTEN, G. HAMMARSTEN, and T. TEORELL (Acta Med. Scand., 1928, **68**, 219—238; Chem. Zentr., 1929, ii, 756).—Lanthanum salts precipitate protein-nucleic acid. The conditions for coloration of serum-albumin, thymonucleic acid, and mixtures of these substances by iodoeosin, light-green, safranin, rosaniline, malachite green, and methyl-violet have been examined. The precipitating effect of sulphosalicylic acid and lanthanum nitrate on solutions of electro-dialysed gelatin, thymonucleic acid, and mixtures of these substances was determined for different  $p_H$  values.

A. A. ELDRIDGE.

**Collagen.** Changes which collagen undergoes when treated with solutions of hydrochloric acid and sodium hydroxide. J. KNAGGS (Biochem. J., 1929, 23, 1308—1327).—Purified collagens derived from different mammalian tissues when treated with sodium hydroxide yield on hydrolysis a higher percentage of diamino-nitrogen than when treated with hydrochloric acid. Previous treatment of ash-free gelatin prepared from horn-piths affects its viscosity, drop number, and percentages of amino- and diamino-nitrogen. The viscosity curve is roughly the mirror image of the other three curves. The examination of the product obtained by removing elastin from collagen by tryptic digestion indicated that intramolecular changes took place in the protein molecule in the process. The swelling of collagen in hydrochloric acid and sodium hydroxide of different  $p_H$  values showed that: (a) previous treatment affects the degree of swelling, (b) around the point of maxi-

mum swelling the percentage of diamino-nitrogen is either at a maximum or a minimum, (c) collagen prepared from different tissues has not the same chemical constitution. S. S. ZILVA.

**Alkalimetric titration of aliphatic mercaptoacids.** E. LARSSON (Z. anal. Chem., 1929, 79, 170—175).—For the alkalimetric titration of  $\beta$ -thiomalamic acid, bromothymol-blue is the best indicator, whereas for thioglycolic acid and apparently also  $\alpha$ - and  $\beta$ -thiolactic acids neutral-red or phenol-red should be used. Phenolphthalein probably gives satisfactory results with  $\alpha$ -mercaptoisobutyric and thiomalic acids, provided that a considerable amount of indicator is used. R. CUTHILL.

**Determination of methylene-blue.** M. FRANÇOIS and L. SEGUIN (Ann. Falsif., 1929, 22, 547—550).—See A., 1929, 1084.

## Biochemistry.

**Microscopical, micro-spectroscopical, and quantitative examination of blood.** M. WAGENAAR (Z. anal. Chem., 1929, 79, 101—113).—Chemical and physical methods for the detection of blood in supposed blood-stains are discussed. In preference to Teichmann's hæmin reaction the hæmochromogen test is recommended, and a modified reagent containing lactose, sodium hydroxide, glycerol, and pyridine is proposed. The ratio of total protein to iron in the sample affords trustworthy information, a ratio of 360 : 1 being good evidence for the presence of blood. Blood is much more resistant to decomposition than is generally supposed; after being heated at 230° crystals of hæmochromogen could still be obtained, and even after heating for 15 min. at 250° the characteristic spectrum of this substance persisted. The results of tests on samples of blood of varying age (up to 3000 years) are enumerated; in every case one or more characteristic tests were obtained.

H. F. HARWOOD.

**Adsorption by erythrocytes. II. Adsorption of methylene-blue.** N. IVANOVSKI and M. ŠABOLOTOVA (Biochem. Z., 1929, 216, 130—135; cf. A., 1928, 1390).—Erythrocytes from the rabbit adsorb methylene-blue from solutions of the dye which contain sodium chloride. The adsorption is complete in 30 min. and the dye can be removed only with difficulty by washing with sodium chloride solution.

W. MCCARTNEY.

**Reaction of lead with the constituents of erythrocytes.** L. C. MAXWELL and F. BISCHOFF (J. Pharm. Exp. Ther., 1929, 37, 413—428).—When lead acetate is added to red-cell filtrates, deproteinised either by ultrafiltration or addition of trichloroacetic acid, the amount of inorganic phosphate removed is insufficient to account for the precipitation of the lead entirely as tertiary lead phosphates. On addition of lead acetate to the ultrafiltrate from hæmolyzed rabbit cells, the amount of organic phosphorus (0.61 mg.) precipitated with the lead (7.3 mg.) corresponds almost exactly with that

required for the formation of penta-lead diphosphoglycerate. Experiments *in vitro* with mixtures of potassium dihydrogen phosphate and diphosphoglyceric acid give similar results. The small amount of nitrogen in the lead precipitates is an occluded impurity. Pure lead diphosphoglycerate shows the same inhibition of hæmolysis as ionic lead, but this inhibition disappears on admixture with tertiary lead phosphate, although the mixture is found to be almost as toxic to rabbits as the pure diphosphoglycerate. Lead diphosphoglycerate appears to be considerably more soluble than lead phosphate. Ionic lead has no effect on the gas exchange of the red cells even when the hæmoglobin content falls 75%. As the inorganic phosphate of the red blood-corpuscle is low, when the lead ion reaches an erythrocyte lead diphosphoglycerate is formed almost exclusively and this toxic compound exerts its effect elsewhere in the body, whether in the bone-marrow or the liver is uncertain.

P. G. MARSHALL.

**Inorganic composition of blood. III. Influence of serum on permeability of erythrocytes to potassium and sodium.** S. E. KERR (J. Biol. Chem., 1929, 85, 47—64).—The permeability of red blood-corpuscles to sodium and potassium ions increases as the proportion of serum in the surrounding fluid is diminished. Penetration of the cells by potassium is obtained with lower concentrations of the latter when serum is absent than when it is present. A 0.85% solution of sodium chloride, which permits the transfer of inorganic ions across the cell membrane cannot therefore be described as physiological. The effect of serum is less evident with the relatively impermeable erythrocytes of the sheep and ox than with those of the dog.

C. R. HARRINGTON.

**Enzymes of leucocytes. II. Proteolytic activity. III. Enzymes of the salivary glands.** R. WILLSTÄTTER, E. BAMANN, and M. RÖHDEWALD (Z. physiol. Chem., 1929, 185, 267—280; 186, 85—96; cf. A., 1929, 354).—II. Leucocytes from horse's



blood obtained by sedimentation (Hamburger) and after destruction of the erythrocytes by acid hydrolysis (Szilárd) show a similar trypsin content, but the Szilárd preparation has a higher peptidase content. The tryptic action of the leucocytes of the horse, dog, and pig obtained by Szilárd's method was compared on caseinogen and clupein at varying  $p_H$ . The proteolytic action is strongest at neutral reaction. Addition of enterokinase produced no definite increase in acidity. In weakly alkaline media dipeptide and tripeptide are hydrolysed, the latter more strongly; the creptic is more marked than the tryptic action. The carboxy-peptidase action is small.

III. Extracts of the salivary glands of the dog, pig, and horse contain erepsin and proteinases—trypsin and cathepsin. The hydrolysis of caseinogen is slight but measurable; the ratio of tryptic to ereptic hydrolysis is less favourable than for leucocytes. The catheptic action is more pronounced. Human saliva hydrolyses caseinogen eight times as rapidly as the gland; the peptide hydrolysis is weaker. The peptidase action of saliva at neutral and alkaline reaction is weakened by removal of the cells and bacteria; the amylolytic action is unaffected. The bacteria showed ereptic and strong tryptic, but no catheptic action.

J. H. BIRKINSHAW.

**Catalytic oxidations with hæmin.** R. KUHN and K. MEYER (Z. physiol. Chem., 1929, 185, 193—216).—The velocity of oxygen uptake was determined for a new class of compounds capable of oxidation by hæmin and molecular oxygen, namely, those containing ethylene linkings. The rate of oxidation of unsaturated fatty acids depends on the position of the double linking and on changes in the carboxyl groups (e.g., esterification). The oxidation of olive oil was not inhibited by *N*/130-hydrocyanic acid. Ergosterol in cyclohexanol was oxidised in presence of hæmin; the oxidation by acetic anhydride-hæmin was strongly inhibited by hydrocyanic acid.

Oxidation of polyenes of the carotene series, bixin, norbixin, bixin methyl ester, and  $\alpha$ -crocetin was catalysed by hæmin in suitable solvents. The oxidation of norbixin, lycopin, xanthophyll, and physalien in dioxan was not catalysed, probably owing to unsuitability of the solvent. The reaction of plant polyenes is not of the order expected from the number of double linkings; this seems to be due to conjugation. The carbohydrates in slightly acid, slightly alkaline, or neutral solution are not oxidised by hæmin and oxygen.

J. H. BIRKINSHAW.

**Tryptophan content of the plasma-proteins and its relation to the sedimentation rate of Fåhræus.** E. OHLSSON, G. NORDH, and T. SWAETICHIN (Biochem. Z., 1929, 215, 443—451).—The sedimentation rate and the tryptophan content of the plasma-proteins of 117 clinical cases are tabulated and are shown to vary together. The correlation coefficients between tryptophan content and sedimentation rate after sedimentation for 1 and 2 hrs. are calculated to be 0.668 and 0.728, respectively. The albumin and globulin fractions individually show fairly constant tryptophan contents and a high sedimentation rate is accompanied with a high

globulin-albumin ratio and with a high tryptophan content of the total protein, the globulin and tryptophan contents of the serum being simultaneously increased.

P. W. CLUTTERBUCK.

**Influence of neutral salts on the separation of proteins by the acetone method.** M. PIETTRE (Compt. rend., 1929, 189, 1034—1036).—Precipitation of the proteins of blood-serum with 2.5 volumes of acetone in the cold frees it almost entirely from sodium chloride, and a further precipitation frees it from alkali hydrogen carbonate. This method has been applied to the purification of the globulins separated from plasma by precipitation with ammonium or magnesium sulphate. Direct treatment with acetone gives a mixture of globulins and fibrinogen, albumin alone being prepared in a pure state in this way. By initial dialysis followed by the acetone treatment, globulin, "myxoprotein," and albumin have been separated after centrifuging to remove the fibrinogen precipitated during dialysis. Dialysed plasma gives a protein sol with acetone which is precipitated only by prolonged contact with 4 volumes of acetone. "Myxoprotein" precipitated in this way becomes viscous and translucent and finally disperses on addition of sodium chloride to a concentration of 0.9%. After isolation, the proteins (except albumin) require the presence of ions to effect dissolution and the various physico-chemical phenomena can be explained by the adsorption of electrolytes on them.

P. G. MARSHALL.

**Precipitation reactions between salts of heavy metals and purified serum-proteins.** T. GEILL (Biochem. Z., 1929, 216, 165—178).—The precipitation reactions taking place between purified (electrodialysed) albumin and globulin from horse-serum and copper sulphate, cupric chloride, mercuric chloride, and silver nitrate have been studied. Precipitation took place in mixtures in which the concentration of protein was either 0.5% or 0.05%. In the cases of albumin and copper sulphate and of globulin and silver nitrate, two zones of precipitation (higher and lower zones of salt concentration) were observed. With albumin and silver nitrate there was precipitation in the higher zone only and with the other combinations in the lower zone only. The influence of the various ions, of the charge on the proteins and of their concentration, and of change in the  $p_H$  of the mixtures on the reactions was investigated. It was found that at low salt concentrations the reactions are reversible. The possible mechanism of the reactions is discussed.

W. MCCARTNEY.

**Influence of time of precipitation on determination of calcium in blood-serum, and magnitude of the dialysable and non-dialysable portions.** H. BÜLL (Biochem. Z., 1929, 216, 228—232).—The rate of precipitation of calcium as oxalate in blood-serum is greatly influenced by the protein content and viscosity of the serum, so that comparable results cannot be obtained for different sera if the time of precipitation is less than 16 hrs. Magnesium is present in some sera in amount sufficient to introduce error. Sera with less than the normal calcium content (10 mg. per 100 c.c.) contain very little non-dialysable calcium except where the ratio of albumin to globulin

is abnormal. In sera with normal or high calcium content the magnitude of the non-dialysable portion seems to be regulated by the extent of the ionisation caused by the organism. W. MCCARTNEY.

**Determination of total calcium content of blood-serum.** M. J. HENDRIKS (Biochem. J., 1929, 23, 1206—1211).—Fairly concordant values can be obtained in the determination of calcium in serum and ash according to the Trevan-Bainbridge method if the calcium oxalate is precipitated slowly in order to avoid the occlusion of magnesium. Standard solutions containing calcium only can be used. Clark and Collip's method gives generally somewhat higher and de Waard's method somewhat lower values than the Trevan-Bainbridge method. S. S. ZILVA.

**Inorganic constituents of the blood of normal and parathyroidectomised dogs.** W. K. WEAVER and C. I. REED (J. Biol. Chem., 1929, 85, 281—288).—The only alterations in the inorganic constituents of the blood of dogs following parathyroidectomy were a decrease in the calcium and an increase in the phosphorus. Tetany can become latent while the calcium : phosphorus ratio is still disturbed, so that this latency is not to be ascribed to the activity of accessory parathyroid tissue. C. R. HARRINGTON.

**Micro-determination of chloride in blood.** W. W. PRĄDZICZ-NEMINSKI (Biochem. Z., 1929, 215, 452—459).—The extraction of sodium chloride from blood, which had been collected in filter-paper as in Bang's method, is incomplete in 24 hrs., a second period of 24 hrs.' extraction yielding a further 11% of chloride. A modification of the Mohr-Bang method is described which permits a determination to be carried out in a few minutes and gives the higher results. P. W. CLUTTERBUCK.

**Determination of iron in blood by molybdo-manganometry.** P. FLEURY and J. MARQUE (Bull. Soc. Chim. biol., 1929, 11, 1123—1129).—The blood is incinerated with a little magnesium nitrate, and the finely-divided iron oxide dissolved in cold hydrochloric acid. The iron is reduced to the ferrous state by shaking with mercury in the cold, and titrated with potassium permanganate in presence of phosphomolybdate. K. V. THIMANN.

**Alkalinity of the blood of domestic animals.** F. LEUCHTENBERGER (Landw. Jahrb., 1929, 70, 1—29; Bied. Zentr., 1929, 58, 560—561).—The technique of sampling and the micro-titration with tartaric acid using litmus are described. The alkalinity of the blood of sheep and cows decreases with advancing age. Higher live weight is associated with lower blood alkalinity. Greater productivity of wool in sheep or of milk or fat in cows is accompanied by an increased alkalinity of the blood. A. G. POLLARD.

**Buffering power of serum.** W. ARCISZEWSKI and W. KOPACZEWSKI (Compt. rend., 1929, 189, 1029—1032).—Isotonic solutions of various inorganic salts have been compared in their action on the  $p_H$ , conductivity, and surface tension of human serum. Additions of an acid or a base in concentrations of about 0.0005*M* have no effect on the  $p_H$  of serum. Cations are buffered more effectively than anions, and

the surface tension (measured by a stalagmometric method) is but little affected by such compounds as lecithin, sodium glycocholate, sodium benzoate, or even saponin. P. G. MARSHALL.

**Relation between the hydrolytic power of horse-serum amylase and serum-protein.** BROcq-ROUSSEU, Z. GRUZEWSKA, and G. ROUSSEL (Compt. rend., 1929, 189, 1203—1205).—The ratio of the amylase activity to protein of the serum obtained from a horse at successive bleedings remains approximately constant. W. O. KERMACK.

**Colorimetric determination of phenols in sera.** A. GONZÁLEZ (Anal. Fis. Quím. [tecn.], 1929, 2, 219—226).—Details are given of a method by which the amount of phenols (including cresols) in antitoxic sera may be determined after removal of proteins, by comparison of the blue coloration, due to formation of brominated indophenol, produced by the addition of ammonia and bromine water. In order to avoid the loss of phenol which occurs when the proteins are precipitated by acid, coagulation is brought about by the addition of alcohol. R. K. CALLOW.

**Blood-fat. II. Acetone-ether-soluble fraction.** H. J. CHANNON and G. A. COLLINSON (Biochem. J., 1929, 23, 1212—1221; cf. A., 1929, 1189).—The fatty acids present in the fraction were arachidonic, linoleic, oleic, stearic, and palmitic acids. The fatty acids produced by hydrolysis of the fraction were considerably more unsaturated than those of the phosphatide fraction, 55% of these being present as cholesteryl ester. The amount of fatty acid in the fraction which is not in combination with cholesterol corresponds with no more than 15 mg. per 100 c.c. of blood. S. S. ZILVA.

**Determination of soap in blood.** C. P. STEWART and A. C. WHITE (Biochem. J., 1929, 23, 1263—1266).—The blood is extracted with a mixture of alcohol and ether. After evaporation of the solvents, 0.5 c.c. of *N*/350-sulphuric acid is added, and the mixture titrated with *N*/70-sodium hydroxide, using bromocresol-purple as indicator. The difference between a blank titration and the above gives the amount of alkali combined with fatty acid. For normal human blood the concentration calculated as oleic acid is 18—40 mg. per 100 c.c., for plasma 46.7—98.7 mg. per 100 c.c. S. S. ZILVA.

**Simplification of the determination of dextrose in blood by the Folin-Wu and Fontès-Thivolle methods.** M. M. IBÁÑEZ (Anal. Fis. Quím. [tecn.], 1929, 2, 227—232).—The Folin-Wu and Fontès-Thivolle methods give generally comparable results. The latter method is simplified, without any considerable loss in accuracy, by titrating without separating the cuprous oxide by centrifuging. R. K. CALLOW.

**Determination of dextrose in blood.** G. RODRÍGON (Bull. Biol. Pharm., 1929, 3, 242—244).—The blood is mixed with fluoride and precipitated with trichloroacetic acid; phenylhydrazine and acetic acid are added and the colour is compared with standard potassium chromate solutions containing a few drops of permanganate. The method is designed for rough clinical tests and occupies 15 min. K. V. THIMANN.

**Blood-sugar analysis by the method of Hagedorn and Jensen.** E. J. BIGWOOD and A. WUILLOT (Bull. Soc. Chim. biol., 1929, 11, 1204—1211).—A comparison of the use of hot zinc hydroxide and cold sodium tungstate as protein precipitants in the method of Hagedorn and Jensen (A., 1923, ii, 265, 440) for sugar in blood-serum. It is concluded that the reducing substance remaining after yeast fermentation is present beforehand in the serum and not derived from decomposition products of the yeast.

K. V. THIMANN.

**Can immediately-reducing carbohydrate of the blood be determined by Hagedorn and Jensen's method?** G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1929, 11, 1212—1218; cf. preceding abstract).—Using a copper tartrate solution to determine reducing power, in place of the ferricyanide recommended by Hagedorn and Jensen and used by the above authors, some reducing substance remains after flocculation of pure yeast suspensions by zinc hydroxide, but not if sodium tungstate is used as flocculant. The ferricyanide reagent is therefore considered to be too sensitive for dextrose determinations, whilst the use of zinc hydroxide introduces artefacts by acting on the yeast. No reducing substance, unfermentable by yeast, of a saccharide nature pre-exists in the serum. K. V. THIMANN.

**Blood-sugar analysis by the method of Hagedorn and Jensen.** E. J. BIGWOOD and A. WUILLOT (Bull. Soc. Chim. biol., 1929, 11, 1219—1222).—A reply to Fontès (preceding abstract), insisting that accurate results can be obtained with the authors' method by the use of blank determinations.

K. V. THIMANN.

**Blood-proteins.** T. MISAO (Japan. J. Med. Sci., VI, Bact. and Par., 1929, 1, 1—51).—The serological specificities of blood-proteins are recorded.

CHEMICAL ABSTRACTS.

**Anti-body formation by polysaccharides.** S. NISHIMURA (J. Exp. Med., 1929, 50, 419—429).—The sera of rabbits immunised with inulin, soluble starch, and dextrin contain specific antibodies. The polysaccharides gave no protein colour reaction, but all contained nitrogen; proteins may function as the vehicle.

CHEMICAL ABSTRACTS.

**Solid-phase rule in hæmolysis.** W. OSTWALD and W. RÖDIGER (Kolloid-Z., 1930, 50, 65—68).—An investigation of the influence of the concentration of blood-corpuscles on the degree of hæmolysis in sodium hydroxide solution has shown that a maximum effect is produced at medium concentrations of the corpuscles, thus following the solid-phase rule. Similar behaviour was observed in solutions of potassium thiocyanate with gelatin coloured with night-blue and fibrin coloured with carmine. E. S. HEDGES.

**Selachian yolk protein.** J. NEEDHAM (Biochem. J., 1929, 23, 1222—1224).—The main protein of the yolk of the dogfish, *Acanthias vulgaris*, is a phosphoprotein containing 0.62% of phosphorus and resembling in its general characters the vitellins. A second protein, to which the name "thulichthin" is given, accompanies ichthulin in this egg; it has the properties of a pseudoglobulin and is analogous to the livetin of avian egg-yolk.

S. S. ZILVA.

**Silkworm-pupa as fish food. I. Chemical composition. II. Digestion with protease of eels. III. Chemical change in stored pupæ.** O. SHINOBU (J. Imp. Fish. Inst., Japan, 1929, 23, 114—115, 115—116, 117).—I. The dry material contains (approx.): ash 4.3, ether extract 31, total nitrogen 8.8, non-protein nitrogen 1%. The protein of the Spring silkworm pupa contains: total 14.82, amide- 1.05, melanin- 0.27, monoamino- 9.64, diamino- 3.85, histidine- 0.87, lysine- 1.05, arginine- 1.88, and cystine-nitrogen 0.05%.

II. The protease of eels is most active between  $pH$  5.7 and 7.4 at 33.5—36°.

III. Dried pupæ decompose slowly, the acid value of the extracted oil increasing in 1 year from 24.43 to 71.58.

CHEMICAL ABSTRACTS.

**Carbohydrates of crab nerve.** E. G. HOLMES (Biochem. J., 1929, 23, 1182—1186).—The peripheral nerves and nerve ganglia of *Maia* and *Cancer* are extremely rich in carbohydrate, which is present as glycogen and as "free carbohydrate." In the case of the ganglia, some, at least, of the carbohydrate is present as di- or poly-saccharide, soluble in 60% alcohol and in Schenk's reagent. In nitrogen there is hydrolysis of glycogen and in the case of the ganglion of the soluble di- or poly-saccharide. There is also formation of lactic acid. In oxygen the formation of lactic acid is inhibited; the breakdown of glycogen is less than occurs in nitrogen. S. S. ZILVA.

**Occurrence of adenylic acid in brain.** K. POHLE (Z. physiol. Chem., 1929, 185, 281—283).—From horse brain adenosine-phosphoric acid was isolated; it appears to correspond with muscle-adenylic acid.

J. H. BIRKINSHAW.

**Function of cholesterol in the organism.** S. MINOVICI (Anal. Fis. Quim., 1929, 27, 431—438; cf. Bull. Soc. Chim. biol., 1927, 9, 1129—1164).—Views of the function of cholesterol are summarised. It is suggested that it plays the part of an insulator and protector of nerve substance.

R. K. CALLOW.

**Marine mammals. I. Adrenal of the whale. M. YAMAGAWA and S. NISHIMURA. II. Pancreas. M. YAMAGAWA and N. NAKAMURA** (J. Imp. Fish. Inst., 1926, 22, No. 2, 22—23, 26—28).—Adrenaline and insulin, respectively, were prepared.

CHEMICAL ABSTRACTS.

**Composition of bone skeletal substance.** T. GASSMANN (Z. physiol. Chem., 1929, 185, 234—236).—Various objections are advanced to Klement's formula (A., 1929, 1328).

J. H. BIRKINSHAW.

**Composition of bone skeletal substance.** R. KLEMENT (Z. physiol. Chem., 1929, 185, 237—238).—A reply to Gassmann (see preceding abstract).

J. H. BIRKINSHAW.

**Examination of the fine structure of wool by X-ray analysis.** J. EWLES and J. B. SPEAKMAN (Proc. Roy. Soc., 1930, B, 105, 600—607).—It is suggested that the wool cell starts as a spherical cell of gelatinous material, becoming gradually extended through an ellipsoidal form (Geelong 80's merino wool) to an elongated form (Cotswold wool) which gives the clearest evidence of an ordered structure. The most

striking point in the X-ray photographs of Cotswold wool is the existence of two equatorial spots with a spacing of 10.3 Å., which are due to planes parallel to the fibre axis, probably the cell-walls. All wools were first purified by extraction with alcohol and other following scouring with soap. P. G. MARSHALL.

**Distribution of hexosephosphoric acid in different muscles and organs of the animal organism.** O. FEINSCHMIDT (Biochem. Z., 1929, 215, 413—417).—The hexosemonophosphoric acid content of a number of voluntary, smooth and heart muscles, brain, and kidney are tabulated. White muscle both of rabbit and fowl contains more hexosemonophosphate than red muscle, heart contains more than smooth muscle, and brain contains about the same as red and heart muscle.

P. W. CLUTTERBUCK.

**Extractive purines of muscle.** I. A. DMOCHOWSKI (Biochem. J., 1929, 23, 1346—1352).—More than 50% of the purine-nitrogen of rabbit's or dog's muscle is found in the aqueous extract; the remainder cannot be removed even by prolonged extraction. The extract contains only traces of "free" purines precipitable as cuprous salts. The greater part of the extracted purines is precipitated only after hydrolysis of the aqueous extract with 4% sulphuric acid. About 75% of this fraction is precipitated by uranyl acetate as pentose-nucleotides, the filtrate containing, apart from "free" purines, probably also nucleosides. The distribution of the various purine fractions is independent of diet. Guanine is not present in the extract of rabbit's muscle, but the residue contains both guanine and adenine. Most of the adenine, however, is found in the nucleotide fraction of the extracts, whilst hypoxanthine is present in the nucleoside fraction, probably as the free purine. Xanthine was detected only in traces.

S. S. ZILVA.

**Sulphur content of rat's muscle and liver.** Y. KAMBAYASHI (Biochem. Z., 1929, 215, 402—405).—A table summarises the total, water-soluble, and sulphate-sulphur contents of a number of samples of rat's liver and muscle. The total sulphur contents of liver and muscle are almost identical and correspond with the value for human liver. The mean value for sulphate-sulphur is also almost identical for the two tissues, but the water-soluble sulphur for muscle is about 20% higher than for liver.

P. W. CLUTTERBUCK.

**Coagulation of muscle-plasma.** E. C. SMITH (Proc. Roy. Soc., 1930, B, 105, 579—599).—The relationship between *rigor mortis* and gelation of muscle-plasma is investigated by comparison of the hardness of the muscle with the strength of the gel, and an obvious connexion shown between the two. Both in *rigor* muscle and *in vitro* the gel can be liquefied by addition of salt. Change in acidity during gelation has no connexion with the latter. That it is due to some acid other than lactic acid is shown by the fact that it is independent of the glycogen content of the muscle even when this has been greatly reduced by administration of insulin. Addition of acetic acid to "Kühne" salt plasma ( $p_H$  6.6) produced increased opacity at  $p_H$  5.8 and a gelatinous precipitate at  $p_H$  5.4,

but gave no evidence of gel formation such as occurs on incubation of diluted salt plasma at 37° with a much smaller change in acidity. P. G. MARSHALL.

**Auriculoventricular junctional system of the heart. I. Glycogen content.** K. YAMAZAKI (J. Biochem. Japan, 1929, 10, 481—490).—The Tawara bundle of horse or ox heart contains more glycogen than heart muscle.

CHEMICAL ABSTRACTS.

**Determination of glycogen in small amounts of tissue.** A. E. OSTERBERG (J. Biol. Chem., 1929, 85, 97—108).—The tissue is heated on the steam-bath with 60% potassium hydroxide solution; glycogen is precipitated by addition of alcohol and sodium sulphate, and hydrolysed by heating with dilute hydrochloric acid. The dextrose formed is determined by the method of Folin (A., 1928, 786). The method is applicable to 5—15 mg. of tissue, the error being  $\pm 5\%$ .

C. R. HARRINGTON.

**Sperm of the marine animal. I.** M. YAMAGAWA, H. MIKAWA, and T. TOMIYAMA. **II.** M. YAMAGAWA and T. ITO. **III.** M. YAMAGAWA and B. IBUKA (J. Imp. Fish. Inst., Tokyo, 1926, 22, No. 2, 30—31, 32—33, 33—34).—The cystine, tryptophan (13 varieties) and arginine, histidine and lysine (4 varieties) contents of the milt of Japanese fish are recorded. The compound  $C_{29}H_{54}O_5N_{11}H_2PtCl_6$  was prepared from the sperm of *Amblygaster immaculatus*; for the related protamine the name "amblygine" is proposed. A histone,  $C_6H_{16}O_2N_3S$ , and a nucleic acid,  $C_{52}H_{55}O_{52}N_{14}P_4$ , are described.

CHEMICAL ABSTRACTS.

**Individuality of the mammary glands of the cow.** J. PROKS (Proc. VIII. World's Dairy Cong., 1928, 296—299).—Maximal differences in the constituents of milk from individual teats were: water 0.50—1.40, fat 0.35—1.35, protein 0.04—0.35, lactose 0.07—0.74, ash 0.01—0.07, solids not fat 0.13—0.71%; Reichert-Meissl value 0.8—1.8, Wauters-Polenske value 0.6—2.9, saponif. value 0.6—5.8, iodine value (Hübl) 0.49—1.61,  $n^{40}_{D}$  0.7—1.0.

CHEMICAL ABSTRACTS.

**Chemical composition of "histamine" gastric juice of man.** L. GRIMBERT and P. FLEURY (Bull. Soc. Chim. biol., 1929, 11, 1105—1122).—See A., 1929, 592.

**Gastric lipase in healthy breast-fed infants.** K. GONDO (Nagasaki J. Med., 1928, 6, 681—695).—After ingestion of milk the lipase action increases with time, but the individual variation is large.

CHEMICAL ABSTRACTS.

**Preparation of the unconjugated acids of ox-bile.** S. M. WHITE (Biochem. J., 1929, 23, 1165—1171).—In one method the conjugated bile acids are hydrolysed with sodium hydroxide and the sodium salts are separated by fractional precipitation with magnesium chloride, magnesium deoxycholate being much less soluble in water than magnesium cholate and more soluble than the magnesium salts of the higher fatty acids. In another method the hydrolysed bile acids are separated by utilising the fact that deoxycholic acid is comparatively insoluble in 60% acetic acid; the yield of deoxycholic acid thus obtained is rather less than that obtained

by the first method and also only a small amount of cholic acid is obtained.

The preparation of uncombined deoxycholic acid from acetic-choleic acid can be effected by digesting it in dilute sodium hydroxide solution or by distilling off the acetic acid in a current of steam.

S. S. ZILVA.

**Allantoin in dog's bile.** S. YOSHIMURA (J. Biochem. Japan, 1929, 10, 435—442).—In dogs the biliary uric acid is normally 0.55% of the urinary uric acid; administration of uric acid intravenously or orally increases the factor only to 2.3% and 1.3%, respectively, but causes a large increase in the allantoin in the bile (normally 18.9 mg. per 100 c.c.). Phosphorus poisoning diminishes the excretion of allantoin.

CHEMICAL ABSTRACTS.

**Nitrogen content of the bile and its relation to that of urine.** S. YOSHIMURA (Nagasaki J. Med., 1928, 6, 740—775).—Average values (dog) are for bile: residual nitrogen 8.45 mg. (accumulated in 1 day), 32.44% of which is urea-, 25.35% allantoin-, 6.7% amino-, 4.37% ammonia-, 0.88% creatinine-, and 0.28% uric acid-nitrogen; urine 0.9, 2.40, 10, 8.10, 2—20, 0.55%, respectively. In phosphorus poisoning biliary urea and allantoin decrease, whilst ammonia and uric acid increase.

CHEMICAL ABSTRACTS.

**Urobilin in urine.** R. DANET (Bull. Biol. Pharm., 1929, 3, 249).—The urine is shaken with amyl alcohol instead of chloroform. This gives a clear solution for examination of the fluorescence.

K. V. THIMANN.

**Determination of allantoin in animal urine.** M. CHAMPAGNE and G. MOURROT (Compt. rend., 1930, 190, 82—84).—Allantoin is precipitated with mercuric acetate, filtered after 30 min., and the nitrogen in the precipitate determined. The content of urea must be kept below 0.5%, chlorides below 0.2%, and the  $p_H$  adjusted to between 7.2 and 7.4.

K. V. THIMANN.

**Amylase in normal urine.** W. B. MAYER and H. FINKELSTEIN (Bull. Johns Hopkins Hosp., 1929, 45, 105—107).—Variations of 0.8—8.8 amylase units per c.c. of urine were observed in the same individual; daily variations of 1.4—5.7 and 7.4—12.3 units are recorded. The specimens could be kept over-night at 4° with or without toluene.

CHEMICAL ABSTRACTS.

**Determination of carbon in urine.** K. VOIT (Biochem. Z., 1929, 215, 418—421).—The urine is heated with chromic-sulphuric acid mixture in a stream of oxygen. The gases produced are passed over heated copper oxide and lead peroxide and the carbon dioxide is absorbed and weighed. Two determinations may be carried out in 3 hrs.

P. W. CLUTTERBUCK.

**Millon's reaction and its application to the examination of protein in urine.** P. FLEURY and P. DELAUNEY (J. Pharm. Chim., 1929, [viii], 10, 529—536).—The method of Florence (*ibid.*, 1925, [viii], 2, 97) for the detection of protein in urine has been modified as follows: 2.5 g. of sodium chloride are dissolved in 50 c.c. of the filtered urine and, after the addition of 10 drops of methyl-red solution, 10% acetic acid is added until the liquid reddens. After

filtering if necessary, it is heated at 100° for 20 min. The liquid is filtered through an 8—10 cm. filter-paper, which is then washed twice with boiling water and twice with boiling alcohol and dried. Millon's reaction (1 hr. contact in the cold) and the xanthoproteic reaction are carried out on strips of the paper, the strips for the former reaction being washed with 1% nitric acid, then distilled water, and dried before examination. This procedure gives positive results in certain cases where the normal treatment shows no trace of albumin and the sensitiveness of the reaction is about 0.015—0.020 g. of protein per litre. A stable Millon's reagent consists of a 30% solution of mercuric nitrate in 10% nitric acid ( $d$  1.39), to which is added, just before use, a 10% solution of sodium nitrite in the proportion of 2 drops per c.c. of reagent.

E. H. SHARPLES.

**Enzymic detection and determination of tyrosine in urine.** S. S. LIGHTMAN and H. SOBOTKA (J. Biol. Chem., 1929, 85, 261—273).—Potato press-juice is strained and precipitated with an equal volume of 95% alcohol; the precipitate is re-dissolved and re-precipitated and then dried in a vacuum; the resulting preparation of tyrosinase is standardised against solutions of tyrosine, the unit being defined as that amount which will give visible melanin formation in a 0.004% solution of tyrosine at  $p_H$  6.8 within 24 hrs.; a good preparation should contain 1 unit in 12.5 mg. The product of the concentrations of tyrosine and enzyme is constant for solutions containing 0.004—0.02% of tyrosine. For the determination of tyrosine in urine excess of the enzyme is employed and the melanin formation in different dilutions of the urine is compared with that in buffer solutions containing known amounts of tyrosine when treated under the same conditions. Owing to the presence in urine of an inhibitory factor, the smallest concentration of tyrosine which can be detected is 0.0125%. The reaction given by *p*-cresol may be distinguished from that of tyrosine by the persistence of the red colour in the former case.

C. R. HARRINGTON.

**Application of Van Slyke and Palmer's method for the titration of organic acids in liquids containing proteins. I. Titration of the organic acids in urine containing protein.** E. E. MARTINSON and A. A. MARKOVA (Biochem. Z., 1929, 216, 124—129).—The removal of protein from urine in which organic acids are to be determined by the method of Van Slyke and Palmer is conveniently carried out, without influence on the subsequent titration, by the addition of trichloroacetic acid. When the calcium hydroxide is added to the urine allowance must be made for the presence of this acid. At  $p_H$  2.7 not more than 1.55% of it takes part in the titration.

W. MCCARTNEY.

**Source of error in the determination of the organic acids of urine by the method of Van Slyke and Palmer.** E. M. P. WIDMARK and E. LJUNGBERG (Biochem. Z., 1929, 216, 1—3).—The acids of urine which form insoluble or sparingly soluble calcium salts are wholly or partly precipitated by the addition of calcium oxide. In the portion of the acids which is soluble in ether the loss due to the use of calcium

oxide amounts to 7—11%. The proportion of uric acid which escapes determination in the Van Slyke and Palmer method may amount to 25—35%.

W. MCCARTNEY.

**Determination of ether-soluble acids of urine by the rocking extraction method.** E. M. P. WIDMARK (Biochem. Z., 1929, 215, 434—439).—The method is described and a number of determinations are recorded. The amount of the acids excreted is much higher on a fat and vegetable diet than on a mixed diet.

P. W. CLUTTERBUCK.

**Ethyl alcohol in urine.** S. OTANI (Chiba J. Med., 1928, 6, 1715—1743).—Normal urine (nurses, abstainers, 16—27 years) contained 0.01114 vol. per 1000; the faeces contained none. The production of ethyl alcohol is increased in diseases of the liver and kidney; in tuberculosis the increase is due to imperfect excretion by the lungs.

CHEMICAL ABSTRACTS.

**Determination of isopropyl alcohol in presence of acetone in urine.** C. A. COOK and A. H. SMITH (J. Biol. Chem., 1929, 85, 251—260).—Urine is cleared with copper sulphate and calcium hydroxide and the filtrate is subjected to oxidation with potassium dichromate and sulphuric acid in presence of mercuric sulphate. The total acetone is determined from the weight of the precipitate formed. The preformed acetone is determined in another sample of urine by distillation into excess of hydroxylamine hydrochloride solution and titration of the acid liberated. The difference of the two determinations represents acetone which has been formed from isopropyl alcohol.

C. R. HARINGTON.

**Rapid distillation of lower volatile fatty acids from faeces.** W. H. OLMSTED, C. W. DUDEN, W. M. WHITAKER, and R. E. PARKER (J. Biol. Chem., 1929, 85, 115—126).—Faeces are collected in 10% sodium hydroxide solution, and nitrogenous material is removed by precipitation with mercuric chloride and calcium hydroxide; excess of mercury is removed with hydrogen sulphide and 100 c.c. samples of the filtrate are treated with magnesium sulphate and sulphuric acid and submitted to steam-distillation. Acetic, propionic, and butyric acids, when added to faeces, can be recovered almost quantitatively by this method, and formic acid to the extent of 85%. In faeces from normal adults, formic acid is present to the extent of about 10% of the total volatile acids, whilst 30—60% may be present as either acetic or butyric acid.

C. R. HARINGTON.

**Effect of diet and of catharsis on lower volatile fatty acids in faeces of normal men.** E. W. GROVE, W. H. OLMSTED, and K. KOENIG (J. Biol. Chem., 1929, 85, 127—136).—Change from a high-protein diet to one rich in carbohydrates caused an increase of 60—300% in the faecal elimination of lower volatile fatty acids in normal individuals, whilst catharsis produced 100% increase in the elimination. In the latter experiments the acetic acid eliminated corresponded with the fermentative degradation of 1—4% of the carbohydrate ingested.

C. R. HARINGTON.

- (i) Alkaptonuria with minimum protein intake.
- (ii) Alkaptonuria and carbohydrate withdrawal.

H. LIEB and F. LANYAR (Z. physiol. Chem., 1929, 186, 111—118, 119—123).—(i) In an experiment of 8 days' duration in which the protein in the diet of a 25-yr.-old female alkaptonuric was reduced from 70 to 13 g. per day, the calories required being supplied by additional fat and carbohydrate, the quantity of homogentisic acid excreted in the urine fell and the ratio of homogentisic acid to urinary nitrogen remained approximately constant. It therefore appears that in this patient the inability to metabolise tyrosine and phenylalanine is complete. (ii) In the same patient the withdrawal of carbohydrate from the diet so as to produce acetonuria had no effect on the amount of homogentisic acid excreted.

W. O. KERMACK.

**Inorganic elements of spinach in treatment of nutritional anaemia.** H. S. MITCHELL and L. MILLER (J. Biol. Chem., 1929, 85, 355—363).—An aqueous extract of dried spinach, administered in a daily dose containing 0.5 mg. of iron, 0.014 mg. of copper, and 0.012 mg. of manganese, was more effective in preventing nutritional anaemia in rats than the ash of the same extract or than a mixture of pure salts of iron, copper, and manganese in the same proportions.

C. R. HARINGTON.

**Intestinal calculus of medicinal origin.** R. GUYOT (J. Pharm. Chim., 1929, [viii], 10, 500—505).—A hard, solid mass possessing the appearance of a typical intestinal calculus, excreted following the intake of gelatinous barium sulphate (for X-ray examination), was composed chiefly of barium sulphate.

C. C. N. VASS.

**Porphyryns of salivary calculi.** E. DERRIEN and C. BENOIT (Arch. Soc. Sci. Méd. Montpellier, 1929, 9, 510—515).—Salivary calculi of human and animal origin contained coproporphyrin and protoporphyrin, to which their rose-red fluorescence in ultra-violet light is due. Copper is also present to the extent of about 0.3%.

K. V. THIMANN.

**Urine of cancer rats.** Y. KIMURA (Japan. J. Exp. Med., 1928, 7, 113—134).—Parallel with the growth of the transplanted tumour the destruction of the body-proteins is increased. In the urine the total nitrogen, urea-nitrogen, and allantoin are increased, the ratio ammonia-nitrogen : total nitrogen decreases, whilst the amino-acids at first decrease and later increase. The excretion of salts increases, and the normal salt ratios are disturbed. The excretion of neutral sulphur increases markedly and that of sulphuric acid slightly; the phosphate increase is parallel to that of allantoin.

CHEMICAL ABSTRACTS.

**Lactic acid formation in tumour tissue.** H. R. DOWNES (J. Cancer Res., 1929, 13, 268—282).—Human tumour tissue, when incubated with a nutrient solution containing dextrose, forms lactic acid generally in excess of the amount formed by normal muscle or embryo hash. The lactic acid-forming power of non-transplantable rat tumour tissue is unaltered. Irradiation does not affect the lactic acid-forming ability of animal tumours; the power is rapidly lost by transplantable rat tumours kept on ice. Dextrose, maltose, and mannose serve equally as lactic acid precursors, laevulose and hexosephosphate are less



readily available, whilst sucrose, lactose, galactose, and glycogen cannot be used.

#### CHEMICAL ABSTRACTS.

**Blood-cholesterol in cancer.** IV. W. L. MAT-  
TICK and K. W. BUCHWALD (J. Cancer Res., 1929, 13,  
157—166).—In cancer there is a tendency towards  
hypercholesterolaemia in the plasma, with little  
change in the corpuscles. The plasma-*lecithin* is  
slightly lowered. Total fatty acids are abnormally  
high in the plasma, and less markedly so in the  
corpuscles. It appears that in cancer there is either  
an increase in fat absorption or a decrease in utilisation.

#### CHEMICAL ABSTRACTS.

[Effect of] **folliculin and the hormone of the  
anterior pituitary lobe in cancer of mice.** E.  
HARDE and P. HENRI (Compt. rend. Soc. Biol.,  
1929, 100, 542—544; Chem. Zentr., 1929, ii, 442).—  
The effects of injection indicate that neither hormone  
is present in cancerous tissue. A. A. ELDRIDGE.

**Metabolism and deficiency diseases and their  
treatments by light and iron preparations.**  
N. R. DHAR (J. Physical Chem., 1929, 33, 1897—  
1904).—Speculative. Previous views are amplified,  
and it is emphasised that light and the use of prepa-  
rations containing iron should be of service in the  
treatment of metabolic and deficiency diseases.

#### L. S. THEOBALD.

**Carotinæmia and diabetes.** J. M. RABINOWITCH  
(Canad. Med. Assoc. J., 1928, 18, 527—530).—To test  
for xanthosis, plasma (3 c.c.) is made into a paste with  
plaster of Paris and shaken with 95% ethyl alcohol  
(3 c.c.); after addition of 3 c.c. of light petroleum  
(b. p. 30—50°), shaking for 10 min., and centrifuging,  
the upper layer containing carotene is compared  
colorimetrically with a solution of oleic acid in light  
petroleum. A 10% solution ( $\approx$  1 unit of pigment)  
gives a colour corresponding with the normal  
maximum.

#### CHEMICAL ABSTRACTS.

**Relation between blood-sugar and urinary  
sugar.** E. STEINITZ (Deut. med. Woch., 1929, 55,  
871—873; Chem. Zentr., 1929, ii, 446).—The blood-  
sugar threshold value in diabetes is subject to con-  
siderable variation, increasing with the severity.  
In severe and moderately severe cases it is nearly as  
high as normally, in mild cases it is lower.

#### A. A. ELDRIDGE.

**Utilisation of substitute carbohydrates by the  
diabetic organism.** A. GOTTSCHALK (Deut. Arch.  
klin. Med., 1929, 164, 87—95; Chem. Zentr., 1929, ii,  
589).—Tetra- $\alpha$ -glucosan is readily fermented by top  
or bottom yeast, and is prone to auto-oxidation. It  
does not suffer fission by the action of enzymes of the  
gastro-intestinal tract or tissue. Tetra- $\alpha$ -glucosan is  
probably converted first into glycogen. Taka-  
diastase contains no enzyme which attacks it.

#### A. A. ELDRIDGE.

**Possibility of using *d*-sorbitol in the treatment  
of diabetes mellitus.** H. REINWEIN (Deut. Arch.  
klin. Med., 1929, 164, 61—72; Chem. Zentr., 1929, ii,  
589—590).—A clinical study. A. A. ELDRIDGE.

**Acid-base equilibrium of the blood in eclamp-  
sia.** H. T. STAUDER, N. J. EASTMAN, E. P. H.  
HARRISON, jun., and J. F. CADDEN (J. Biol. Chem.,  
1929, 85, 233—243).—In normal pregnancy the total

base of the blood-serum is reduced by about 8 milli-  
mols. per 100 c.c.; there is coincident reduction in the  
protein and hydrogen carbonate, but no increase in  
organic acids, and the  $p_H$  is within normal limits. In  
eclampsia, on the other hand, the  $p_H$  is reduced to  
about 7.04 owing to a marked alkali deficit and to an  
accumulation of organic acids. C. R. HARINGTON.

**Rate of glycolysis in erythræmia (poly-  
cythæmia vera).** J. E. COOK and M. SOMOGYI  
(Arch. Int. Med., 1929, 44, 813—817).—The increased  
rate of glycolysis exhibited by blood from cases of  
polycythæmia vera is not altered when the number  
of red blood-cells is reduced by the administration of  
phenylhydrazine and it is not to be referred to an  
increase in the number of white blood-corpuscles.

#### W. O. KERMACK.

**Excretion of copper oxide-reducing substances  
in the urine of hypertonics and normal individ-  
uals.** E. WIECHMANN and J. ELZAS (Deut. Arch.  
klin. Med., 1929, 164, 50—60; Chem. Zentr., 1929, ii,  
590).—Fasting, as well as sugar-fed, normal subjects  
excrete copper oxide-reducing substances in the urine;  
the excretion is unchanged in hypertonics.

#### A. A. ELDRIDGE.

**Excretion of purine bases in the urine in  
chronic myelotic leucæmia.** H. TEITGE (Z.  
physiol. Chem., 1929, 186, 124—132).—Analysis of  
100 litres of urine from a case of chronic myelotic  
leucæmia showed the presence of 1.47 g. of hetero-  
xanthine, 0.1986 g. of 1-methylxanthine, 0.541 g. of  
paraxanthine, 0.080 g. of carnine, 0.03 g. of adenine,  
and 0.041 g. of hypoxanthine; xanthine could not  
be isolated.

#### W. O. KERMACK.

**Creatine metabolism in generalised myositis  
fibrosa.** M. BODANSKY, E. H. SCHWAB, and P.  
BRINDLEY (J. Biol. Chem., 1929, 85, 307—325).—  
In a case of generalised myositis fibrosa there was  
observed marked creatinuria; creatine administered  
by mouth was almost entirely excreted again after a  
short latent period during which a small fraction was  
converted into creatinine. The creatine content of  
the muscles was diminished, particularly where  
inflammatory changes were conspicuous.

#### C. R. HARINGTON.

**Urine and organs in acute porphyria.**  
E. DERRIEN and C. BENOIT (Arch. Soc. Sci. Méd.  
Montpellier, 1929, 8, 456—472).—The urine in the  
last ten days of a fatal case of porphyria in a  
female was rich in uroporphyrin and its zinc com-  
pound and poor in coproporphyrin. The bile con-  
tained a substance possibly identical with mesobili-  
violins, and the kidney coproporphyrin. It is suggested  
that the elimination of zinc is itself one of the most  
serious factors in the disease. K. V. THIMANN.

**Tryptophan content of Bence Jones protein.**  
E. ÖHLSSON and G. NORDH (Biochem. Z., 1929, 215,  
440—442).—A sample of Bence Jones protein con-  
tained 4.2% of tryptophan.

#### P. W. CLUTTERBUCK.

**Curative action of dried or sweetened con-  
centrated, cow's milk on experimental rickets  
of the rat.** L. RANDOIN and R. LECOQ (J. Pharm.  
Chim., 1929, [viii] 10, 496—500).—Both kinds of milk

when added to a rickets-producing diet show a marked curative action on young rats fed on this diet prior to the addition.  
C. C. N. VASS.

**Uptake and distribution of calcium and phosphorus in normal and rachitic animals.** E. HESSE (Arch. exp. Path. Pharm., 1929, 147, 173—192).—When calcium malonate or a mixture of calcium malonate and disodium hydrogen phosphate is fed to a dog, about 33% of the calcium and 50% of the phosphorus are absorbed from the gastro-intestinal tract within 24 hrs. When, however, the calcium salt is administered as an emulsion in gum arabic, the absorption of calcium within 24 hrs. rises to 75%. In a phosphatide emulsion the absorption of calcium amounts to 50%, whilst the phosphorus is completely taken up within 8 hrs. The uptake of calcium when administered in the form of certain commercial preparations has also been investigated. In experiments on normal rats, rachitic rats, and rats protected from rickets by irradiated ergosterol about 10% of the calcium administered was stored in the body.

W. O. KERMACK.

**Effect of heating syphilitic serum and its protein fractions on precipitation reaction.** M. NISHIO (J. Infect. Dis., 1929, 43, 148—155).—Globulin from syphilitic serum, whether heated (56°, 30 min.) or not, gives precipitation results by the Kahn test similar to those given by the serum after heating. Unheated, but not heated, albumin from the serum prevents or reduces the precipitation given by the globulin.  
CHEMICAL ABSTRACTS.

**Action of vitamin-D on a parathyroidectomised dog. (Treatment of Tetania parathyreoprivia.)** V. DEMOLE and A. CHRIST (Arch. exp. Path. Pharm., 1929, 146, 361—376).—Administration of irradiated ergosterol to a dog causes a rise in the blood-calcium both in the normal and the parathyroidectomised animal. In the latter, administration of irradiated ergosterol prevents the onset of tetany if it is administered before or soon after the operation, whilst it causes the symptoms of tetany to disappear if it is administered after these have set in.

W. O. KERMACK.

**Differentiation of the reducing substances in the urine during pregnancy.** R. ROCKWOOD and E. F. DODGE (Surg. Gyn. Obstet., 1928, 47, 660—664).—Of the samples 28% gave reduction by Benedict's test; lactosazone was isolated from only 50% of the non-fermentable specimens. Before breast engorgement the reducing substance is usually dextrose, whilst during that stage it is usually lactose.

CHEMICAL ABSTRACTS.

**Oxidation-reduction potentials in biological systems. I. Oxidation-reduction potentials in hen's eggs before and during development.** V. A. PALOV and M. M. ISSAKOVA-KEO (Biochem. Z., 1929, 216, 19—27).—The results of measurements of the oxidation-reduction potential of the whites and yolks of fertile and infertile eggs from various races of fowls show that the magnitudes of the potentials are related to the condition of the eggs. The potentials of unincubated non-developing eggs tend to move to the positive side; those of normally developing eggs become slowly more negative. The potentials of the

yolks seem to be always more positive than those of the whites.

W. MCCARTNEY.

**Behaviour of the hexone and purine bases present in the free state during incubation of the hen's egg.** M. TAKAHASHI (J. Biochem. Japan, 1929, 10, 451—455).—Purine bases are produced during the incubation of the hen's egg. The free histidine increases from 0.1 to 0.38 mg.; the arginine (1 mg.) also increases. Free lysine (6 mg.) reaches a maximum (27.4 mg.) in 19 days.

CHEMICAL ABSTRACTS.

**Determination of cholesterol by the digitonin method especially in hen's eggs and in chickens.** H. DAM (Biochem. Z., 1929, 215, 468—474).—By heating cholesterol at 109° with lipins, the amount of free cholesterol decreases. When cholesterol is treated with sodium ethoxide with exclusion of air, a loss of cholesterol could not be detected with certainty. In heating sterol digitonides with xylene it must be remembered that some commercial xylenes when boiled for a long time yield a difficultly volatile substance.

P. W. CLUTTERBUCK.

**Cholesterol metabolism in hen's eggs and chickens.** H. DAM (Biochem. Z., 1929, 215, 475—492).—It could not be confirmed that the cholesterol content of eggs decreases at the beginning of hatching. The ratio cholesteryl ester to total cholesterol increased by 10% at the beginning and by 40% at the end of hatching. A small amount of the cholesterol of egg-yolk is combined with protein and cannot be extracted without hydrolysis. By rearing chicks for 2 months on a diet of known small sterol content, the difference sterol (animal and faeces) — sterol (food) is more than double the sterol content of the egg.

P. W. CLUTTERBUCK.

**Effect of diet on iron and copper content of the egg.** C. E. ELVEHJEM, A. R. KEMMERER, E. B. HART, and J. G. HALPIN (J. Biol. Chem., 1929, 85, 89—96).—Egg-yolk contains on the average 0.0143% of iron and 0.00076% of copper; the white contains 0.00056% of copper. These amounts cannot be increased by daily administration to the hens of 50 mg. of iron and 0.5 mg. of copper.

C. R. HAREINGTON.

**Seasonal change in composition of carp muscle.** O. SHINOBU (J. Imp. Fisheries Inst., Japan, 1929, 23, 118—119).—Carp (August) contained; total solids 21.80, crude ash, 1.21, ether extract 2.30, total nitrogen 2.96%; seasonal variations were small.

CHEMICAL ABSTRACTS.

**Chemical change in fasting eels.** O. SHINOBU (J. Imp. Fisheries Inst., Japan, 1929, 23, 119—120).—In 50 days' fast at 8—18°, with loss of weight about 11%, the total solids decreased from 42 to 40, and the ether extract from 24 to 21%.

CHEMICAL ABSTRACTS.

**Change in the content of inorganic bases of blood and urine of dogs during activity of the digestive glands.** E. E. MARTINSON and S. SALASKINA (Biochem. Z., 1929, 216, 109—123).—During the period of activity of the digestive glands of dogs following normal consumption of food the total amount of inorganic bases in the blood first fell during 1 or 2 hrs. and then rose during the third hour

to a value higher than that before feeding. The amount of inorganic bases in their urine fell greatly during the normal period of digestion. In the case of dogs undergoing sham-feeding (Pavlov) the amount of inorganic bases in the blood increased during the first 2 hrs. During the third hour a decrease occurred, but the amount remained higher than it was before sham-feeding. During the period of intestinal secretion the amount of inorganic bases in the blood of a dog from which the stomach had been removed decreased. The changes which take place in the amount of inorganic bases in the blood during the normal period of digestion are governed by the regulatory activity of the kidneys and by the intestinal secretions. It is possible also that the gastric secretion influences the amount of inorganic bases in the blood by causing increased transference of salts from the tissues to the blood.

W. MCCARTNEY.

**Post-mortem formation of methæmoglobin in red muscle.** J. BROOKS (Biochem. J., 1929, 23, 1391—1400).—The red flexor muscle of the foreleg of the ox after remaining a few hours at 0° attained a "steady state" and the depth of oxygen penetration was approximately 2 mm. After 100 hrs. this depth increased linearly to approximately 4 mm. Freezing and thawing had no significant effect. Methæmoglobin is not formed in the absence of oxygen, but is formed slowly in the oxygen region of the tissue exposed to the air and most rapidly at some distance from the tissue-air interface. Freezing and thawing increased the rate of formation. The dependence of the rate on the position in the oxygen region was in qualitative agreement with the expected behaviour.

S. S. ZILVA.

**Effect of prolonged contractions on the content of phosphorus compounds of pigeon and rabbit muscle.** D. FERDMANN (Z. physiol. Chem., 1929, 185, 239—244).—The effect of muscle contraction produced electrically and by strychnine injection on the various phosphorus compounds of the muscle of pigeons and rabbits was studied. Strychnine injection in pigeons produces a decrease only in the amount of creatine-phosphoric acid and an increase in hexosephosphoric acid. Strong muscular contractions produced by either method in the rabbit cause a large decrease in creatine-, hexose-, and pyro-phosphoric acid.

J. H. BIRKINSHAW.

**Influence of prolonged muscular rest on metabolism.** D. P. CUTHBERTSON (Biochem. J., 1929, 23, 1328—1345).—Human subjects in nitrogenous equilibrium show within a day or two from the commencement of a period of muscle rest a rise in the excretion of sulphur, nitrogen, phosphorus, and calcium in that order of priority. This loss is maintained fairly steadily for a varying period, after which it gradually declines. The rise in the excretion of sulphur is due to a practically proportionate increase in inorganic sulphate. Ethereal sulphate tends to decrease, whilst neutral sulphur remains more constant. The rise in the excretion of nitrogen is mainly due to a proportionate increase in the amount of urea. Ammonia excretion also rises, but more slowly. Creatinine and uric acid are practically unaltered. The S:N ratio suggests a sulphur-rich

source of the excreted material, presumably for the most part muscle. The gaseous metabolism remains constant from day to day. Maxima and minima percentage day-to-day variations in the oxygen consumption gradually decrease as the experimental period lengthens from  $\pm 14\%$  to  $\pm 1.2\%$ .

S. S. ZILVA.

**Influence of protein metabolism on conversion of creatine into creatinine.** J. L. BOLLMAN (J. Biol. Chem., 1929, 85, 169—177).—Dogs on a low-protein diet showed no increased excretion of creatinine as the result of administration of creatine, much of which was excreted unchanged. On a high-protein diet, however, little of the creatine was excreted unchanged and after two weeks on such a diet the creatinine excretion showed an increase which continued after the cessation of the high-protein diet.

C. R. HAREINGTON.

**Creatine-creatinine metabolism.** J. L. BOLLMAN (Proc. Mayo Clinic, 1929, 4, 220—221).—On a low-protein diet free from creatine the daily excretion of creatinine is unchanged by oral or intravenous administration of creatine in amounts comparable to the daily excretion of creatinine. Casein (100 g., but not 10 g.) markedly increased the excretion of creatinine and reduced the urinary creatine.

CHEMICAL ABSTRACTS.

**Creatine metabolism in the nephrectomised white rat.** A. CHANUTIN and H. SILVETTE (J. Biol. Chem., 1929, 85, 179—193).—Subcutaneous administration of creatine to nephrectomised rats is followed by an increase in the creatine content of all organs examined, particularly of the liver, skin, and muscle. All of the creatine administered could not, however, be accounted for, which indicates the destruction of some of the compound in the organism. A close relationship is observed between changes in the blood-creatinine and in the muscle-creatinine.

C. R. HAREINGTON.

**Creatine and creatinine metabolism in the dog.** R. SCHUMANN (Z. physiol. Chem., 1929, 186, 104—110).—The administration of histidine by mouth to dogs does not increase the output of creatinine in the urine. The output is slightly increased by the administration of 5—10 g. of yeast-nucleic acid, but this result is probably brought about indirectly and it appears very improbable that the urinary creatinine is derived from purine bases.

W. O. KERMACK.

**Effect of pentose ingestion on uric acid excretion.** K. MADDERS and R. A. McCANCE (Biochem. J., 1929, 23, 1175—1177).—The ingestion of pentose has no influence on the excretion of uric acid.

S. S. ZILVA.

**Tryptophan and growth. II. Growth on a tryptophan-deficient diet supplemented with tryptophan derivatives. III.  $\beta$ -Indolylpropionic and  $\beta$ -indolylpyruvic acids as supplements to tryptophan-deficient diets.** C. P. BERG, W. C. ROSE, and C. S. MARVEL (J. Biol. Chem., 1929, 85, 207—218, 219—231).—II. *Acetyl-L-tryptophan*, m. p. 206—207° (decomp.), *benzoyl-L-tryptophan*, m. p. 104—105°, *methylenetryptophan* (cf. Homer, A., 1913, ii, 451), and *L-tryptophan ethyl ester hydrochloride*, m. p. 221° (decomp.), were administered to young

rats on a tryptophan-deficient diet. The acetyl derivative and the ester hydrochloride replaced tryptophan satisfactorily, whilst the benzoyl and methylene derivatives were unable to do so. Commercial pancreatin or fresh intestinal extracts liberated tryptophan from the ester hydrochloride, but not from the acetyl derivative; deacetylation of the latter appears therefore to take place subsequently to absorption.

III.  $\beta$ -Indolylpropionic acid failed to replace tryptophan in the diet of young rats, whilst  $\beta$ -indolylpyruvic acid (m. p.  $212^\circ$  after softening at  $204^\circ$ ) was dietetically equivalent to the amino-acid.

C. R. HARRINGTON.

**Fate of hippuric acid in the chicken organism.** M. TAKAHASHI (J. Biochem. Japan, 1929, 10, 457—461).—Of the hippuric acid fed to chickens 90% can be recovered in the excreta, 10% being found as benzoic acid. Hydrolysis in the kidney is more effective than in the liver or muscle.

CHEMICAL ABSTRACTS.

**Influence of the vegetative system on the deaminating function of the liver.** M. BUFANO (Arch. Farm. sperim., 1929, 47, 241—266).—In general, but by no means always, injection of glycine results in some increase in the amino-acid content of the blood in dogs, the variations in which, after injection of glycine and autonomic poisons, are not dependent on variations in the concentration of the blood. The course of the amino-acid curve is neither constantly nor usually parallel to that of the blood-sugar curve.

T. H. POPE.

**Conversion of cyanide into thiocyanate in man and in alkaline solutions of cystine.** M. BODANSKY (J. Pharm. Exp. Ther., 1929, 37, 463—474).—Administration by mouth of 10 mg. of potassium cyanide in a gelatin capsule produces a rise in the thiocyanate secreted in the saliva which corresponds with that produced when an equimolecular proportion of potassium thiocyanate (15 mg.) is given. Not more than 12% of the cyanide or thiocyanate ingested appears in four 15-min. specimens of saliva, but cyanide is largely if not completely converted into thiocyanate (cf. Voegtlin and others, A., 1926, 863); moreover, experiments *in vitro* on the action of cyanide on 1% solutions of cystine in 0.05M-sodium carbonate showed definitely the presence of thiocyanate and cysteine, whilst no cyanate could be detected at any stage. The time of heating the cystine solution before adding the cyanide materially affects the amount of thiocyanate formed, as does also the amount of cystine. Variation of the concentration of sodium carbonate or the amount of cyanide has no effect. Freshly-prepared solutions of cysteine yield no thiocyanate on treatment with cyanide. Using Mauthner's procedure (A., 1912, i, 335) it is possible to isolate  $\alpha$ -amino- $\beta$ -thiocyanopropionic acid from the mixtures from different experiments, thus indicating that a part of the thiocyanate formed remains in organic combination.

P. G. MARSHALL.

**Action of mineral substances on endogenous nitrogen metabolism.** E. F. TERROINE and T. REICHERT (Compt. rend., 1929, 189, 1019—1020).—

A mineral-free diet of demineralised rice flour 85%, malt extract 5, cod-liver oil 2, washed sawdust 8, together with a few drops of lemon juice, was given to adult rats for a week and then augmented for a further week by a mixture containing sodium chloride 11.6%, potassium chloride 10.4, dipotassium hydrogen phosphate 23.2, sodium hydrogen carbonate 2.9, potassium sulphate 1.8, calcium citrate 34.8, magnesium citrate 9.4, and ferric citrate 5.8. The results show that sodium chloride alone produces as much economy in nitrogen metabolism as the complete salt mixture (25—30%), whilst ferric citrate alone gives an increase of 7%.

P. G. MARSHALL.

**Relationship between serum-calcium and age.** E. M. GREISHEIMER, O. H. JOHNSON, and M. RYAN (Amer. J. Med. Sci., 1929, 177, 704—709).—Average values were: women,  $10.858 \pm 0.049$  mg.; men,  $10.746 \pm 0.045$  mg.; at 12 and 78 years, respectively: women, 11.8, 9.7 mg.; men 11.6, 10.0 mg. [per 100 c.c.].

CHEMICAL ABSTRACTS.

**Salt maintenance in the animal organism.** L. URBANEK (Mezőgazdasági Kutatások, 1928, 1, 1—20; Bied. Zentr., 1929, 58, 562—565).—The calculation of the salt supplement to foodstuffs is described. The alkaline-earth "salt ratio," i.e., necessary lime excess/total  $P_2O_5$ , varies considerably for the same foodstuff. In the case of mixed foods, values for the lime deficiency calculated from the individual constituents and those from the total analysis of the mixture may differ appreciably.

A. G. POLLARD.

**Passage of halogens through animal membranes.** W. LIPSCHITZ (Arch. exp. Path. Pharm., 1929, 147, 142—167).—Concentration of iodide ions is effected by the gastric and the parotid glands to an extent depending on their concentrations in the plasma. The concentration of iodide in the saliva and gastric juice may be 15 or 7 times, respectively, as great as that in the plasma, whilst with bromides the degree of concentration is considerably less (about 1.5 times) and independent of the concentration in the blood. The concentrations of bromide and chloride in the aqueous humour of the eye of the rabbit are greater than their concentrations in the blood-plasma, whilst the opposite is true of the concentration of iodide.

W. O. KERMAK.

**Influence of pyruvic acid and acetaldehyde on the iodic acid value of the blood-serum of hungry animals.** T. SUGITA (Osaka J. Med., 1929, 28, 151—164).—When acetaldehyde (5 g. per kg.) is administered to a fasting (8 days) dove or dog, the high iodic acid value of the serum exhibits a further increase followed by a decrease. With pyruvic acid the effect is similar, but more rapid. From the fact that only narcotic doses of acetaldehyde are effective, it is concluded that although the intermediate product of the sugar metabolism can accelerate the complete combustion of the product of the incomplete combustion which has been accumulated in the blood, its accelerating action is inferior to that of sugar, whilst such a lower oxidation product as acetaldehyde has no accelerating effect.

CHEMICAL ABSTRACTS.

**Fate of pyruvic acid in the autolysis of muscular tissue.** A. UTEVSKI (Biochem. Z., 1929, 125, 406—

412).—Sodium pyruvate added to a number of tissue pulps (muscle, liver, brain) disappeared during autolysis. It was not converted into malic or acetic acid, but chiefly into lactic acid.

P. W. CLUTTERBUCK.

**Conversion of pyruvic into lactic acid in the liver.** (MME.) Y. KHOUVINE, E. AUBEL, and L. CHEVILLARD (Compt. rend., 1929, 189, 1102–1104).—When a mixture of minced liver, sodium pyruvate, and Ringer's solution is incubated at 39° under anaërobic conditions, lactic acid and carbon dioxide are produced. The lactic acid:carbon dioxide ratio increases with the ratio of liver to pyruvate, to an almost constant value of 3.8–3.9:1. Reduction of the pyruvate probably occurs with hydrogen derived from dextrose:  $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$ . If this is so the above ratio should be 4.09. A small amount of acetaldehyde is produced from the pyruvate during the above change.

H. BURTON.

**Changes in lactic acid and dextrose in the blood on passage through organs.** H. E. HIMWICH, Y. D. KOSKOFF, and L. H. NAHUM (Proc. Soc. Exp. Biol. Med., 1928, 25, 347–349).—There appears to be a carbohydrate cycle between muscle and liver, the former sending lactic acid through the blood to the latter, which returns dextrose to the muscle.

CHEMICAL ABSTRACTS.

**Utilisation by the organism of energy liberated by oxidations, and the food value of alcohol.** E. F. TERROINE and R. BONNET (Bull. Soc. Chim. biol., 1929, 11, 1223–1253).—After a full discussion of the work done on this problem for the last 50 years, the authors conclude that the conflicting results obtained are due, in part at any rate, to a failure to take account of the heat produced as an immediate result of the ingestion of alcohol. In the pigeon, the rabbit, and in man, under conditions of thermal neutrality and at rest, the ingestion of alcohol is followed by an increase in the total metabolism, corresponding with 92.3–98% of the potential energy of the alcohol. In the pigeon at 12°, however, the heat produced by the injection of alcohol exactly replaces that produced by the normal consumption of reserves. Alcohol is, therefore, a thermogenic, but not a dynamogenic, substance, and distinction should be drawn between those oxidations which yield energy available for mechanical work or chemical synthesis and those which produce only heat.

K. V. THIMANN.

**Physiological acidosis in the dog.** F. MAIGNON and E. KNITHAKIS (Bull. Soc. Chim. biol., 1929, 11, 1170–1186).—The  $p_H$  of the blood of dogs in most cases falls by 0.1 on fasting, whilst the alkaline reserve remains unchanged. Ketosis is almost absent. In carbohydrate fasting the volume of urine falls to 65% of the normal, its acidity increases, and the ketone content remains almost unchanged, although higher per litre of urine.

K. V. THIMANN.

**Influence of sodium hydrogen carbonate on ketonic metabolism of the dog in physiological acidosis.** F. MAIGNON and E. KNITHAKIS (Bull. Soc. Chim. biol., 1929, 11, 1187–1203).—The administration of sodium hydrogen carbonate to dogs during inanition or carbohydrate fasting, in amount

sufficient to neutralise the acidity of the urine, reduced the excretion of acetone and  $\beta$ -hydroxybutyric acid. The same effect is observed on a diet free from carbohydrate, but it is complicated by temporary retention of these substances, and by adaptation of the animal to the diet. The latter results in a reduction in the acidity and ketone content of the urine. It is concluded that any disturbance in the acid-base equilibrium leads to production and excretion of ketonic substances. K. V. THIMANN.

**Demethoxylation of lignin in the animal body.**

M. PHILLIPS, H. WEIHE, D. B. JONES, and F. A. CSONKA (Proc. Soc. Exp. Biol. Med., 1929, 26, 320–321).—Loss of methoxyl content of lignin when ingested by dogs (15%) or cows (37%) is probably due to the action of an enzyme in the gastric juice.

CHEMICAL ABSTRACTS.

**Lignin metabolism.** F. A. CSONKA, M. PHILLIPS, and D. B. JONES (J. Biol. Chem., 1929, 85, 65–75).—Administration of lignin caused increased urinary excretion of hippuric acid in cows and dogs. The lignin excreted in the faeces had a lower methoxyl content than that which was administered; this demethylation is ascribed to the action of the gastric juice, since it could be brought about *in vitro* by digestion with gastric juice under aërobic conditions.

C. R. HARRINGTON.

**Relation between liver function and blood-sugar. III. Influence of parenteral administration of the hepatotoxin on the function of carbohydrate metabolism of liver.** M. SHINMEN (Japan. J. Exp. Med., 1928, 7, 67–85).—Small doses had no effect on the blood-sugar, dextrose or adrenaline hyperglycaemia, or the glycogen content of the liver of rabbits or rats. Successive large doses caused temporary hyperglycaemia and disturbed carbohydrate metabolism.

CHEMICAL ABSTRACTS.

**Behaviour of cholesterol within the animal body. II. Content of free and ester cholesterol in various tissues of normal rabbits. III. Influence of various autonomous nervous poisons on the cholesterol content of each organ and tissue. IV. Role of the thyroid gland in the cholesterol content.** J. ONIZAWA (J. Biochem. Japan, 1929, 10, 409–411, 413–424, 425–434).—II. The free cholesterol content of tissues, except the adrenal gland, varies much less than the cholesteryl ester content, which varies considerably in normal organs. The adrenal glands contain more than 5%, the spleen, liver, and kidney more than 0.5%, the skin, testicles, diaphragm, and brain more than 0.01%, and the heart and lung less than 0.01% of the ester. Blood-plasma exhibits great variations. The cholesterol content is greater in the autumn and winter than in the spring and summer.

III. Only those drugs acting on the sympathetic nerve have a marked effect on the free cholesterol content of tissues. Adrenaline raises the value, but not if ergotoxin has previously been administered.

IV. Extirpation of the thyroid gland only slightly affects the free cholesterol content of tissue; the cholesteryl ester content is unchanged except in the adrenals and the blood-plasma, where it is increased.

CHEMICAL ABSTRACTS.

**Cholesterol in the rabbit given lecithin.** C. KAMEDA (Osaka J. Med., 1929, 28, 35—66).—A rabbit given lecithin (0.5—1 g. per day) showed a temporary increase in weight. Subcutaneous injection of lecithin causes an increase in blood-cholesterol.

CHEMICAL ABSTRACTS.

**Fluctuation of the cholesterol content [of rabbit's blood] due to vegetable stimuli.** III. C. KAMEDA (Osaka J. Med., 1929, 28, 335—350).—Subcutaneous injection of choline into a rabbit generally decreases the blood-cholesterol. With atropine sulphate the decrease is slight. With choline chloride and adrenaline, or pilocarpine and insulin, independent effects are observed.

CHEMICAL ABSTRACTS.

**Blood-cholesterol, after fasting and after ingestion of cholesterol.** G. W. PUCHER and G. E. SLY (Bull. Buffalo Gen. Hosp., 1929, 7, 10—14).—Variations in the same individual are considerable. Administration of cholesterol appears to cause a small rise in blood-cholesterol.

CHEMICAL ABSTRACTS.

**Cholesterol content of the liver after administration of peptone.** H. SAKAI (Biochem. Z., 1929, 216, 28—31).—When rats are fed with peptone and boiled meat there is no increase in the cholesterol content of their livers or faeces.

W. MCCARTNEY.

**Cholesterol metabolism: its dependence on the thyroid gland and on the spleen.** H. SAKAI (Biochem. Z., 1929, 216, 32—44).—The cholesterol contents of the livers and of the suprarenal capsules of normal guinea-pigs are increased when suspensions of thyroid gland are orally injected. In guinea-pigs from which the spleens have been removed the cholesterol contents of the organs vary in a manner which indicates that two opposing factors are at work, one tending to increase the contents, the other tending to diminish them, and this is the case also when thyroid is administered to the animals. The body-weight of the animals has been found to have a considerable influence on the cholesterol contents of their livers and suprarenal capsules, particularly when the spleens have been removed or when thyroid has been administered.

W. MCCARTNEY.

**Influence of feeding either fat and lipase or lecithin on the sugar excretion of depancreatized dogs.** S. SOSKIN (Biochem. J., 1929, 23, 1385—1390).—In three totally depancreatized dogs the administration of fat was followed by an excretion of extra dextrose which could not be accounted for by the glycerol portion of the fat, the nitrogen excretion, and the carbohydrate stores of the animal. In an experiment where "intarvin" was the fat administered it failed to show its supposed antiketogenic action.

S. S. ZILVA.

**Nutritive significance of the fluorescing constituents of vinegar.** F. FLURY (Biochem. Z., 1929, 215, 422—433).—The residue obtained by evaporating vinegar in a vacuum at the ordinary temperature contains vitamins (A, B, C) and enzymes (catalase and diastase), but only in such small amounts that it is unlikely that they are of any physiological value. Lipases and proteases were not detected. The fluorescing substances are not identical with either the vitamins or the enzymes.

P. W. CLUTTERBUCK.

**Nutritional value of sprouting grain.** L. RAYBAUD (Compt. rend., 1929, 189, 1015—1017).—Feeding of germinating grain, which must be aseptic, has the same beneficial effect on human beings as on animals. The effective daily dose is 5—30 g., according to the age of the subject. In rachitic infants (3—8 years) the normal increase in weight is quickly restored by the vitamins, enzymes, and amino-acids which the grain contains, and resistance to infections is increased.

P. G. MARSHALL.

**[Physiological] action of metals.** II. K. WALTNER and K. WALTNER (Arch. exp. Path. Pharm., 1929, 146, 310—312; cf. A., 1929, 720).—Further observations have been made of the effect of the administration in the food of certain metals and their salts (in concentrations usually of 2%) on the growth, bones, and blood of young rats. Metallic aluminium and lead bring about a decrease in the number of red blood-corpuscles and haemoglobin. Calcium sulphate and calcium fluoride inhibit growth and the latter also causes a decrease in the number of red blood-corpuscles and haemoglobin. Lithium lactate is highly toxic and causes a fall in weight. Zinc carbonate markedly inhibits growth and causes osteoporosis, a decrease in the number of red blood-cells and haemoglobin. Smaltine ( $\text{CoAs}_2$ ) produces some inhibition of growth and signs of osteoporosis.

W. O. KERMACK.

**Action on muscle of perchlorates, fluoborates, and fluorosulphonates.** G. BOEHM (Arch. exp. Path. Pharm., 1929, 146, 327—346).—The action of solutions of potassium perchlorate, potassium fluoborate, and potassium fluorosulphonate and the corresponding sodium salts on the sartorius muscle of the frog has been further investigated, especially in relation to the effect of the simultaneous presence of calcium or of novocaine. The perchlorate and fluoborate ions which have a marked contracting action on the muscle are probably beyond the thiocyanate ion in the Hofmeister series.

W. O. KERMACK.

**Antagonisation of narcotic action of magnesium salts by potassium, sodium, and other univalent cations.** A. D. HIRSCHFELDER (J. Pharm. Exp. Ther., 1929, 37, 399—412).—Injection of  $M/6$ -potassium chloride kills rabbits anaesthetised with magnesium sulphate owing to the toxic action on the heart, but when this is diluted with 4 volumes of  $M/6$ -sodium chloride or when  $M/30$ -potassium chloride is used the animals are instantly awakened. Similar although less powerful effects can be obtained with the chlorides of rubidium, caesium, sodium, and lithium, in this order. The ratio of the effectiveness of sodium to potassium chloride is about 1:30, i.e., approximately the reverse of the proportions in blood-plasma; a similar relationship holds between potassium and calcium chlorides. From lithium to potassium the effectiveness increases with mol. wt. and ionic velocity, whilst ionic hydration decreases. Ammonium chloride is virtually ineffective, readily producing convulsions followed by death in rabbits. The anaesthetic action of magnesium sulphate appears to be due to its power of decreasing the permeability of the membranes of the nerve cells by increasing



the proportion of water-in-oil emulsion as opposed to oil-in-water emulsion. P. G. MARSHALL.

**Solubility of alkylethylbarbituric acids and the surface activity of their aqueous solutions in relation to their narcotic effects on fishes.** D. BROWN (Compt. rend. Soc. Biol., 1929, 100, 703—705; Chem. Zentr., 1929, ii, 595).—Solutions of such concentration that they have the same narcotic effect have also the same surface tension; with *n*-alkyl derivatives the solubility in water is inversely proportional to the narcotic strength.

A. A. ELDRIDGE.

**Methyl *p*-hydroxybenzoate (solbrol).** U. G. BIJLSMA (Arch. Int. Pharm. Ther., 1928, 34, 173—179; Chem. Zentr., 1929, ii, 438).—The biological and biochemical properties of methyl *p*-hydroxybenzoate have been compared with those of salicylic acid.

A. A. ELDRIDGE.

**Effect of tetronal on the production of hæmatorporphyrin in the urine.** F. G. GERMUTH (Indian Med. Gaz., 1929, 64, 491—492).—Acceleration in the ratio sulphonal 1·00, trional 1·34, tetronal 1·56 was observed.

CHEMICAL ABSTRACTS.

**Ketonic amines and local anæsthetics.** L. BERMEJO and L. BLAS (Anal. Fis. Quim., 1929, 27, 736—739).—In the course of an investigation of the effect on local anæsthetic activity of substituting the structure :N- . . . -C·CO·R for the usual types :N- . . . -C·O·CO·R and :N- . . . -C·O·C·R it has been found that  $\omega$ -aminoacetophenone and  $\beta$ -aminopropiophenone are inactive, triphenacylmethylamine is slightly active, and  $\beta\beta$ -dipropiophenonemethylamine, (COPh·CH<sub>2</sub>·CH<sub>2</sub>)<sub>2</sub>NMe, is highly active. The hydrochloride of this base, m. p. 162°, is formed by boiling under reflux a mixture of propiophenone, methylamine hydrochloride, and formaldehyde solution.

R. K. CALLOW.

**Physiology of amœboid movement.** V. Anaërobic movement. VI. Action of oxygen. VII. Action of anæsthetics. C. F. A. PANTIN (Proc. Roy. Soc., 1930, B, 105, 538—579).—Marine "Limax" amœbæ (100  $\mu$  × 25  $\mu$ ) are employed, their size prohibiting either measurement of their oxygen consumption or chemical analysis. Anaërobiosis is obtained by four methods and in all cases amœboid movement ultimately ceases, although it is recovered in presence of oxygen even after 48 hrs. Disodium hydrogen arsenate exerts no effect on movement, whether aerobic or anaërobic. In the case of oxygen deficiency without complete anaërobiosis the activity is gradually reduced, and the time required for recovery is more or less prolonged according to the degree of such deficiency. The critical oxygen pressure is 30—40 mm. In testing the action of cyanides and sulphides the sodium salts were used and the reaction of the strongly alkaline solutions was adjusted to  $p_H$  8·2—8·4, whilst the osmotic pressure was adjusted to that of sea-water. At concentrations greater than  $10^{-6}M$  the amœbæ are very sensitive to cyanide, and they show a similar sensitivity to sulphide at a concentration greater than  $10^{-4}M$ , although recovery may be complete even after immersion for 24 hrs. The effective concentrations

of alcohols required to produce anæsthesia follow the series, methyl<ethyl<butyl<amyl, which may be due to the varying permeability of the cell to these reagents. Alcohols do not act primarily on respiration, as evidenced by the fact that their effect is additive to that of anaërobiosis, whilst cyanides exert no effect in the absence of oxygen.

P. G. MARSHALL.

**Action of morphine on the distribution of sugar in the intermediate phases during the period of digestion.** N. KOTSCHNEFF (Arch. exp. Path. Pharm., 1929, 147, 168—172; cf. Arch. ges. Physiol., 1928, 220, 628).—After subcutaneous administration of morphine as after adrenaline the absorption of dextrose from the intestine is inhibited. The other effects of the action of adrenaline, such as the mobilisation of liver-glycogen and the uptake of blood-sugar by the lungs, are also brought about by morphine, which probably acts by mobilising adrenaline.

W. O. KERMACK.

**Opium addiction.** X. Excretion of morphine by human addicts. E. G. FRY, A. B. LIGHT, E. G. TORRANCE, and W. A. WOLFF (Arch. Int. Med., 1929, 44, 862—869).—In addicts accustomed to morphine, the administration of 0·97 g., 1·94 g., and 3·89 g. of morphine per day resulted in the elimination of 8·7, 9·8, and 10·7%, respectively, of the alkaloid in the urine, whilst much smaller quantities were eliminated in the faeces. After withdrawal of the drug the elimination in the urine fell rapidly during the first 4 hrs. and remained at a fairly constant low level during the following 26 hrs.

W. O. KERMACK.

**Effect of soaps on the toxicity of alkaloids (cryptoalkaloids).** L. VELLUZ (Compt. rend., 1929, 189, 1325—1327).—The toxic effect of strychnine sulphate (subcutaneously injected) is diminished by adding 1% of sodium oleate to a 0·2% solution of the salt with subsequent incubation at 37—38° for 24 hrs. At a concentration 0·05% of oleate the lethal dose is unaffected, whilst between 0·1 and 0·4% precipitation of the alkaloid occurs. When 0·1N-hydrochloric acid is added to the 1% oleate solution in amount sufficient to decompose half of the oleate, a colloidal solution is obtained which is still less toxic. The original toxicity reappears when the sodium oleate is decomposed entirely by acid or precipitated as the insoluble calcium salt. Sodium ricinoleate has a similar effect to that of the oleate. Alkaloidal salts (e.g., aconitine nitrate) which form soluble compounds with soaps retain their toxicity.

The name cryptoalkaloid is applied to any alkaloid the toxicity of which is diminished by combination with a soap or fatty acid.

H. BURTON.

**Elimination of alkaloids and genalkaloids in the bile.** H. HERMANN, E. CAUJOLLE, and F. JOURDAN (Compt. rend., 1930, 190, 78—79).—Alkaloids were injected into the veins of the dog and frog, and the bile was examined for their presence both by chemical methods and by injection or anastomosis into a second animal, in which the pharmacological effects were observed. Quinine was detected in the bile by the thalleioquinine reaction and fluorescence. Nicotine, strychnine, and genostychnine were rapidly eliminated and were found in large

quantities in the bile, atropine and genatropine less so.

K. V. THIMANN.

**Chemical action of specific diuretics and influence of the sex organs on it.** H. ZWYER (*Biochem. Z.*, 1929, 216, 45—65).—Euphyllin, euphyllin-calcium, and euphyllin-calcium iodide, in equivalent amounts, have been injected intramuscularly into male rabbits which were then castrated and again received injections of the same substances. As regards both the amount of urine secreted and its chloride content the euphyllin compounds act more powerfully than does euphyllin itself. Since the compounds are equally effective it follows that this difference in action is due to the calcium ion. The action of the diuretics is weaker after castration than before it.

W. MCCARTNEY.

**Digestive enzymes of invertebrates.** P. KRÜGER (*Sitzungsber. preuss. Akad. Wiss.*, Berlin, 1929, 548—564).—The digestive enzymes of the invertebrates exhibit relationships with the intracellular enzymes of the vertebrates and are also clearly related to the vegetable enzymes, especially those of yeast, so that still more primitive states are indicated. The experiments have been extended to organisms not previously studied.

R. A. MORTON.

**Enzyme problem and oxidation in the living organism.** O. WARBURG and E. NEGELEIN (*Z. Elektrochem.*, 1929, 35, 928—935).—A survey of past work on the mechanism of oxidation within the living cell.

R. CUTHILL.

**Pigment formation.** B. BLOCH (*Amer. J. Med. Sci.*, 1929, 177, 609—618).—The agent responsible for the specific "dopa" reaction is considered to be identical with the natural pigment-producing oxidase. Pyrocatechol is concerned in the formation of natural pigment.

CHEMICAL ABSTRACTS.

**Mechanism of oxidative processes. XXI. Dehydrogenating enzymes of milk.** H. WIELAND and B. ROSENFELD (*Annalen*, 1929, 477, 32—77; cf. A., 1914, i, 1007).—A stable, active enzyme preparation is obtained when cream is dried in a vacuum and then extracted thoroughly with ether and light petroleum. Further purification is effected by shaking a solution with a small amount of aluminium hydroxide-C at  $p_H$  8.0, whereby admixed protein is removed (if a large amount of the hydroxide is used, adsorption of the enzyme occurs). The activity of the preparation, measured in xanthine-dehydrogenase units (=X; the amount of enzyme which will decolorise 1 c.c. of 0.001N-methylene-blue solution in presence of 0.2 c.c. of 0.01M-xanthine, when the total volume is 5 c.c., at  $p_H$  8.0 and 37°, in 5 min.) and salicylaldehyde-dehydrogenase units (=S; as above but in presence of 0.2 c.c. of 0.02M-salicylaldehyde), as compared with the original milk, is about 100 times as active for X and about 20 times as active for S. The ratio X:S increases considerably from milk to cream, varies appreciably for milk collected at different times (in these cases the values for S are approximately constant), and is of the same order for milk and skim-milk. The total enzymic activity is greater for cream+skim-milk

than for the original milk by about 38% for X and 14% for S (cf. Dixon and Thurlow, A., 1924, i, 1380). The value of X for an enzyme solution is also increased by about 32% by the addition of a colloidal solution of cholesterol. Xanthine-dehydrogenase is adsorbed to a slightly greater extent than salicylaldehyde-dehydrogenase by aluminium hydroxide-C at  $p_H$  8.0; at  $p_H$  4.6, using skim-milk, the aldehyde-dehydrogenase is adsorbed preferentially. When whey ( $p_H$  4.5) is brought to  $p_H$  8.0 with sodium hydrogen carbonate instead of ammonia the X/S ratio is increased considerably. The aldehyde-dehydrogenase is also adsorbed on calcium oxalate (precipitation of calcium in whey by ammonium oxalate). Xanthine-dehydrogenase shows an optimum action at  $p_H$  8.0—9.0, but there is considerable action even at  $p_H$  12.0. For salicylaldehyde-dehydrogenase the optimum  $p_H$  is 8.0; the activity is also dependent on the concentration of the substrate, showing a maximum with formaldehyde and acetaldehyde at about 0.05M-concentration. Xanthine-dehydrogenase is destroyed by oxygen only during the course of dehydrogenation. This is due to the formation of hydrogen peroxide during the oxidation of xanthine. The enzyme loses its activity when treated with hydrogen peroxide in  $5 \times 10^{-4}M$ -concentration (cf. Bernheim and Dixon, A., 1928, 329). Hydrogen peroxide is also formed during the oxidation of hypoxanthine with oxygen and milk. When the reaction is carried out in presence of cerium(III) hydroxide, coloured cerium peroxide is produced. Dixon and Thurlow's statement (*loc. cit.*) that hypoxanthine reacts more quickly than xanthine could not be confirmed. In absence of oxygen the enzyme preparation cannot bring about any rearrangement of xanthine or hypoxanthine.

Oxidation of salicylaldehyde occurs to the extent of about 43% with oxygen and milk, but with an active enzyme preparation only 10—12% change occurs. When milk is coagulated with rennin the caseinogen which separates out contains 10% of the aldehyde-dehydrogenase. This enzyme causes a more complete oxidation of salicylaldehyde than the enzyme in the whey.

The previously described oxidase and reductase are considered to be identical.

H. BURTON.

**Inactivation of oxidising enzymes of gum arabic.** H. FLÜCK (*Pharm. Acta Helv.*, 1929, 4, 58—62; *Chem. Zentr.*, 1929, ii, 436—437).—Inactivation can usually be accomplished by heating the gum in the dry condition. Strychnine, hydrastine, atropine, morphine, codeine, ethylmorphine, diacetylmorphine, cocaine, hyoseyamine, digitalin, digitoxin, and digitalein are attacked by the active gum; slight turbidity with inactive gum is probably attributable to coagulation due to adsorption. Boiling a solution of the gum diminishes the viscosity more than inactivation by precipitation with boiling alcohol.

A. A. ELDRIDGE.

**Determination of oxidase activity; potato oxidase.** A. E. STEARN and A. A. DAY (*J. Biol. Chem.*, 1929, 85, 299—306).—The time required to produce a given rise of potential of a quinhydrone electrode in an oxidase solution when air is bubbled

through the solution affords a measure of the activity of the oxidase.

C. R. HARRINGTON.

**Oxidation of quinol at diminished oxygen tensions.** A. P. VINOGRADOV (Biochem. Z., 1929, 215, 350—358).—The oxidation of quinol in presence of phenolase and also in presence of iron in phosphate buffer at  $p_H$  7.6 is considerably retarded at low oxygen tensions, especially at a partial pressure of 30—40 mm.

P. W. CLUTTERBUCK.

**Oxidation of tyrosine at diminished oxygen tensions.** A. P. VINOGRADOV and I. M. DEDJULIN (Biochem. Z., 1929, 215, 359—365).—Two series of experiments are described on the oxidation of tyrosine by oxygen at reduced pressures in presence of tyrosinase, one at  $p_H$  6 and the other at  $p_H$  8. Oxidation in the former case is almost independent of, whilst in the latter it varies considerably with, the oxygen tension.

P. W. CLUTTERBUCK.

**Use of sulphur in biological chemistry.** DE REY-PAILHADE (Bull. Soc. Chim. biol., 1929, 11, 1143—1145).—Hydrogen sulphide is evolved when certain biological materials are mixed with sulphur at 40°, even if the nitroprusside reaction is not given.

K. V. THIMANN.

**Malt amylase. VIII. Identity of the dextrinising and saccharifying enzymes.** T. SABALITSCHKA and R. WEIDLICH (Biochem. Z. 1929, 215, 267—278).—The ratio of saccharification and dextrination constants in 15 experiments with amylase and diastase preparations which had received different pre-treatments was  $1.28 \pm 0.17$ , and was not changed when the enzyme was concentrated 15—17 times by adsorption and elution, 6.6 times by dialysis, and 4.5 times by precipitation with alcohol. The constancy of this ratio supports the view that one and the same enzyme is responsible for both dextrination and saccharification (cf. A., 1929, 721, 1197).

P. W. CLUTTERBUCK.

**Potato amylase.** J. BURGER (Magyar Chem. Fol., 1928, 34, 120—128, 135—140, 150—154).—The hydrolysis of starch by potato amylase is optimal at  $p_H$  7.0; salts activate in the order: sodium, potassium, ammonium; sulphate, chloride, bromide, fluoride, nitrate. In autolysis (optimum  $p_H$  7.0) the order of activating influence is: potassium, sodium, ammonium; fluoride, chloride, sulphate, nitrate, bromide. On storage zymogen is converted into amylase. The  $p_H$  of the potato, which after harvesting is 5.8—5.9, reaches after 2—3 weeks a constant value 6.3—6.4. CHEMICAL ABSTRACTS.

**Enzymic hydrolysis of glycogen.** A. D. BARBOUR (J. Biol. Chem., 1929, 85, 29—45).—Glycogen was incubated at 37° for 5 hrs. with a glycerol extract of liver or muscle, the optimum  $p_H$  for the reaction being 6.3; the digestion fluid was freed from protein, concentrated, and treated with excess of alcohol. Acetylation of the precipitated material yielded an *anhydrotrisaccharide*,  $C_{18}H_{30}O_{15}$ ,  $[\alpha]_{5461} + 187^\circ$ , reducing power 8.5% of that of dextrose. By addition of excess of barium hydroxide to a 70% alcoholic solution of the digestion products a barium salt was obtained, which, when decomposed, yielded the *trisaccharide*,  $C_{18}H_{32}O_{16}$ ,  $[\alpha]_{5461} + 181^\circ$ , reducing power

31% of that of dextrose; the *osazone* of the trisaccharide, m. p. 186°, could be isolated directly from the digestion fluid. Hydrolysis of glycogen with salivary or pancreatic amylase takes a different course with the production of dextrose and *iso*-maltose. The muscle-glycogenase is inhibited markedly by the trisaccharide or its anhydro-derivative and slightly by sucrose and dextrose; it is accelerated markedly by protein, and slightly by sodium chloride, sodium or potassium phosphate, and carbamide.

C. R. HARRINGTON.

**Mitogenetic radiation in the digestion of protein.** (Third source of mitogenetic radiation.) A. M. KARPASS (Biochem. Z., 1929, 215, 337—343).—Both peptic and tryptic digests of albumin and fibrin *in vitro* and also material removed from the small intestine during protein digestion form sources of mitogenetic radiation (cf. A. 1929, 1330).

P. W. CLUTTERBUCK.

**Plant proteases. XV. Identity of animal and plant dipeptidase.** W. GRASSMANN and L. KLENK (Z. physiol. Chem., 1929, 186, 26—49; cf. Grassmann and Haag, A., 1927, 794).—The rate of hydrolysis of leucyl- and of glycyl-glycine by dipeptidases derived from various animal organs and from yeast was studied. The substrate concentration was varied. The actual rate of hydrolysis varied considerably, but was always greater in the case of leucylglycine, further the hydrolysis was not inhibited by alanine as was that of glycylglycine. The differences can be accounted for by the different affinities of the enzyme for the two substrates. It is concluded that no essential difference exists between the enzymes from the various sources.

J. H. BIRKINSHAW.

**Nuclein metabolism. XIX. Behaviour of a nucleosidase from ox bone-marrow towards a fission product of thymus-nucleic acid.** W. DEUTSCH and R. LASER. **XX. Increase of liver-nucleotidase action.** W. DEUTSCH. **XXI. Enzymic fission of thymus-nucleic acid with liver-nucleotidase for the production of purine- and pyrimidine-carbohydrate complexes.** S. J. THANNHAUSER and M. ANGERMANN (Z. physiol. Chem., 1929, 186, 1—10, 11—12, 13—25).—XIX. From bone-marrow a nucleosidase was prepared which, by following the sugar production, was shown to hydrolyse pyrimidine-nucleoside more rapidly than adenosine, in contrast to kidney-nucleosidase, for which the reverse holds. The optimum  $p_H$  was 6.5. Attempts to purify the enzyme met with little success, although acid precipitation of the proteins at the isoelectric point slightly increased the activity.

XX. The activity of liver-nucleotidase is increased by the addition of magnesium acetate-ammonia mixture to the substrate to precipitate the phosphoric acid. After three additions of enzyme 99% of the phosphoric acid is hydrolysed.

XXI. Liver-nucleotidase eliminates from thymus-nucleic acid not only phosphoric acid but also a considerable portion of the purine-carbohydrate complexes. Adenine, hypoxanthine, guanine, and xanthine were isolated, also a substance crystallising in needles, probably an adenine-carbohydrate complex. The pyrimidine-carbohydrate complex was

obtained in better yield than the purine complex. Hydrolysis of the thymine complex with 30% sulphuric acid led to partial oxidation. Lævulinic and oxalic acids were isolated. The greater part of the pyrimidine remained attached to the carbohydrate complex, the terminal group of which was oxidised to an acid. It gave a crystalline barium salt, decomp. 191°.

J. H. BIRKINSHAW.

**Fermentation of uric acid, produced by animal** R. FOSSE, A. BRUNEL, and P. DE GRAEVE (Compt. rend., 1930, 190, 79—82).—Uric acid is transformed quantitatively into allantoin by the liver of the horse. The livers of certain batrachians and fish, however, produce allantoinic acid by the action of allantoinase.

K. V. THIMANN.

**Enzymes and light.** L. PINCUSSEN. XV. Hydrolysis of lecithin by the lecithase and the phosphatase of takadiastase preparations. XVI. Optimum  $p_H$  for aldehydease of milk and influence of light on this enzyme. T. OYA (Biochem. Z., 1929, 215, 366—371, 398—401).—XV. The inorganic and organic phosphorus and the choline liberated from lecithin by takadiastase at  $p_H$  6.6 were determined. In one experiment, under the action of lecithase 72.4% of the choline was set free in 10 days. The separation of choline corresponds with that of the total inorganic+organic phosphorus and therefore the action of the lecithase and phosphatase run parallel. The phosphatase of a takadiastase solution at  $p_H$  6.6 is injured to a very much greater extent than the lecithase by irradiation with ultra-violet light.

XVI. The methylene-blue and the nitrate methods for the determination of the aldehydease of milk (Schardinger enzyme) give comparable results. The optimal  $p_H$  is 7.35. Considerable destruction of the enzyme occurs when it is irradiated in presence of air.

P. W. CLUTTERBUCK.

**Metabolic changes during irradiation.** VI. L. PINCUSSEN. Changes of liver autolysis in irradiated animals. T. IWATSU (Biochem. Z., 1929, 215, 372—380).—The total, residual, amino-, and carbamide-nitrogen of samples of liver taken from normal rabbits and rabbits which were un-irradiated but shorn, shorn and feebly irradiated, or shorn and strongly irradiated, were determined after 24 and 48 hrs. Autolysis was increased after feeble, and decreased after powerful, irradiation.

P. W. CLUTTERBUCK.

**Fermenting power of yeasts of the first subgroup of *Saccharomyces* (Meyen), Rees.** K. TRAUTWEIN and J. WASSERMANN (Biochem. Z., 1929, 215, 293—318).—The half fermentation times of fifteen different representatives of this group are tabulated, using sucrose, dextrose, and maltose. The values for sucrose are usually slightly higher than for dextrose (100:107), but the two sets of values for these sugars vary together according to the yeast. The half fermentation times for maltose are much higher than for sucrose and dextrose, except for three yeasts when they are the same.

P. W. CLUTTERBUCK.

**Acceleration of alcoholic fermentation of sucrose by vegetable charcoal and other inert**

**substances.** W. L. OWEN and W. P. DENSON (Zentr. Bakt. Par., 1929, II, 77, 481—523; Chem. Zentr., 1929, ii, 438).—Small quantities of vegetable charcoal exercise a catalytic accelerating influence on the fermentation; substances which form positively charged colloids are more active than those forming negatively charged colloids. Carbon, e.g., from pressed dried beet, independently favours the growth of the yeast.

A. A. ELDRIDGE.

**Fermentation of sucrose in the presence of sulphite.** F. POLAK (Biochem. Z., 1929, 216, 179—186).—Since crude sucrose ferments in the presence of sulphite much more rapidly than does pure sugar it follows that the former contains small amounts of substances which accelerate the fermentation or stimulate the activity of the yeast used. Nutrient inorganic salts have no accelerating effect on the progress of the fermentation. In order to obtain the best yields of aldehyde and of glycerol the quantity of sulphite added should be 60—70% of the amount of sucrose and the sulphite should be added gradually, beginning soon after fermentation commences.

W. MCCARTNEY.

**Action of sulphite in the second type of fermentation.** C. NEUBERG and H. COLLATZ (Biochem. Z., 1929, 216, 233—237).—Invert-sugar, prepared by mixing the pure components, is fermented by yeast in the presence of sulphite more quickly than is an equivalent amount of sucrose, but the amounts of acetaldehyde formed are the same in both cases. Crude sucrose is not invariably more rapidly fermented by yeast in presence of sulphite than is pure sucrose, although the presence of certain impurities may accelerate fermentation. The amount of aldehyde produced in the sulphite fermentation of sucrose is independent of the time during fermentation at which the sulphite is added. Hence, and since acetaldehyde can be isolated as an intermediate product in biochemical reactions in which are involved fixing agents which do not combine with hexoses or in which substances with which it cannot react are decomposed by sulphite, it follows that the hypotheses of Polak (cf. preceding abstract) must be rejected, especially as his results depend on an inaccurate method of analysis.

W. MCCARTNEY.

**Production of fat from carbohydrate and similar media by a species of *Penicillium*.** H. H. BARBER (Biochem. J., 1929, 23, 1158—1164).—The mould grew equally well in solutions of dextrose, sucrose, or xylose, but less freely on glycerol. In every case the fat formed contained palmitic, stearic, oleic, and  $\alpha$ - and  $\beta$ -linoleic acids, both free and as glycerides, together with some sterols.

S. S. ZILVA.

**Utilisation of micro-organisms for human food materials.** V. Composition of mycelium of *Aspergillus oryzae*. VI. Fats. VII. Nitrogenous bases. R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, 32, 169B—172B).—The mycelium contains 34.61% of protein, 8.1% of ash, 1.81% of fats, 1.83% of phosphorus, and small amounts of nitrogenous bases. The fatty acids are 98.1% unsaturated, and include 8% of unsaponifiable matter, which contains sterol. Hydrolysis with 70% sulphuric acid

yields 32-39% of reducing sugars. Figures are given for the subdivision of the fractions into their principal constituents. K. V. THIMANN.

**Relation between purine-nitrogen and protein-nitrogen in micro-organisms.** E. F. TERROINE and F. SZUCS (Compt. rend., 1930, 190, 76-78).—The ratio of purine- to protein-nitrogen has been determined for certain moulds, bacilli, and *Saccharomyces*. Its value is different for each organism, but only slightly affected by temperature. In *Aspergillus niger* the ratio falls more rapidly during nitrogen starvation than during total starvation, indicating a preferential utilisation of the nuclear substances rather than the protoplasm as food reserve. K. V. THIMANN.

**Composition of certain bacteria; carbon and nitrogen content.** E. W. HOPKINS, W. H. PETERSON, and E. B. FRED (J. Biol. Chem., 1929, 85, 21-27).—Root nodule bacteria have C 52.8-54.6, N 4.4-4.9, lipin (ether- and chloroform-soluble matter) 11.4-22.6%; butyl alcohol bacteria C 47.4, N 11.2, lipin 3.0%; lactic acid bacteria C 46.0-47.9, N 11.3-12.3, lipin 1.8%; all figures are calculated on the dry weight of the organisms. The first group therefore approximate to carbohydrate and the second and third groups to protein in composition.

C. R. HARRINGTON.

**Biochemical dismutation. Acetic fermentation.** E. MOLINARI (Biochem. Z., 1929, 216, 187-215).—By the action of fresh or dried acetic bacteria (*B. ascendens*, *B. pasteurianum*, *B. xylinum*) acetaldehyde is converted, even in the presence of a large excess of oxygen, into acetic acid and alcohol and after the conversion the bacteria are alive and capable of normal growth. The conversion takes place under a variety of very different conditions, in the presence or absence of calcium carbonate, is not affected by the presence of sodium fluoride, and is not completely inhibited by potassium cyanide. *iso*Valeraldehyde, propionaldehyde, benzaldehyde, furfuraldehyde, citronellal, cinnamaldehyde, and anisaldehyde undergo analogous conversions. W. MCCARTNEY.

**Bacterial decomposition of formic acid.** L. H. STICKLAND (Biochem. J., 1929, 23, 1187-1198).—Tryptic digestion of a suspension of *B. coli* cells causes a transitory increase in the activity of the succinic and lactic dehydrogenases and a permanent one in that of the formic dehydrogenase to five times its original value. Filtration of the digest through a Seitz filter and through a layer of kieselguhr gave similar results. This preparation does not oxidise formic acid by means of molecular oxygen nor, unlike the intact organism, will it decompose it into hydrogen and carbon dioxide anaerobically. In aerobic conditions *B. coli* oxidises formic acid completely, giving no free hydrogen. A state equivalent to the aerobic condition can be produced by adding various hydrogen acceptors other than oxygen such as nitrate or fumarate to the medium. The decomposition of formic acid by a suspension of *B. coli* into hydrogen and carbon dioxide depends, not merely on the number of viable cells, but also on the rate of their multiplication. *B. typhosus* reduces methylene-blue in the presence of formate, but cannot liberate molecular hydrogen from formate. S. S. ZILVA.

**Decomposition of dextrose and of lævulose by *Bacillus coli*.** F. LIEBEN and G. EHRLICH (Biochem. Z., 1929, 216, 4-10).—Dextrose is not converted into lævulose by animal tissues, by yeast, or by the bacteria of putrefying material. Lævulose is more rapidly decomposed by *B. coli* than is dextrose.

W. MCCARTNEY.

**Mechanism of the reduction of nitrates [by bacteria].** I. M. P. KORSKOVA and G. B. LOPATINA (Bull. Acad. Sci. U.S.S.R., 1929, 505-518).—Experiments with two pure bacterial cultures isolated from soil show that, unlike obligate aerobes, facultative anaerobes obtain their necessary energy at the expense of the fermentation of sodium citrate, and the reduction of nitrates is not a process necessary to their existence. In this fermentation, one of the cultures forms carbon dioxide, formic and acetic acids, and a small proportion of hydrogen. The reduction of nitrates proceeds partly by means of the free hydrogen, but principally in virtue of the oxidising-reducing process of the activated system formic acid + nitrate. With an insufficiency of formic acid, the system citric acid + nitrate is evidently activated, so that, with small quantities of citric acid, this undergoes complete oxidation to carbonic acid. The second facultative anaerobe, yielding the same products of fermentation as the first culture, is characterised by the same mechanism of reduction of nitrates. The systems formic acid + nitrate and citric acid + nitrate are activated energetically, but the system acetic acid + nitrate only extremely slightly, by this second culture. T. H. POPE.

**Mechanism of the reduction of nitrates [by bacteria].** II. M. P. KORSKOVA (Bull. Acad. Sci. U.S.S.R., 1929, 599-605; cf. preceding abstract).—*B. coli communis* represents a facultative anaerobe giving free hydrogen and only a small amount of formic acid on fermenting dextrose. Unless calcium carbonate is added, the acid formed retards this fermentation, especially in presence of nitrates. The latter undergo reduction to nitrites, which, when the solution contains calcium carbonate, are reduced still further. No evolution of free nitrogen is, however, observed and the product of this reduction is probably nitrous oxide. The carbon dioxide and hydrogen formed are the products of decomposition of the formic acid, so that *B. coli*, unlike the two bacterial cultures previously examined (*loc. cit.*), readily activates the decomposition of this acid. If the fermentation is effected in presence of peptone, succinic acid is formed. The products of these fermentations are qualitatively those required by Harden and Penfold's equation (A., 1912, ii, 970), but the amount of carbon dioxide is lower, and the amounts of alcohol and acetic acid are higher, than the calculated amounts. The introduction of a nitrate alters the relations between the quantities of the products of the fermentation, so that the reduction proceeds, not only by means of nascent hydrogen, but also in virtue of the action of one or more systems, organic substance + nitrate. The reduction of nitrates in presence of the various end-products of the *B. coli* fermentation, namely, lactic acid, acetic acid, and alcohol, proceeds at different rates, the system lactic acid-nitrate being

the most, and the system alcohol-nitrate the least, energetically activated. T. H. POPE.

**Production of organic acids by excised intestines.** W. F. VON OETTINGEN and T. SOLLMANN (J. Biol. Chem., 1929, 85, 245—250).—When excised rabbit's intestine is suspended in a warm aerated solution of dextrose, production of acid takes place. The acid-producing factor is destroyed by boiling, but is not affected by change of  $p_H$  from 3.0 to 7.9; the rate of acid production is greater with the ileum than with the relatively sterile small intestine, and the acid-production continues after removal of the intestine from the solution, whence it is concluded that the process is due to the intestinal bacteria.

C. R. HARRINGTON.

**Luminous bacteria.** S. E. HILL and C. S. SHOUP (J. Bact., 1929, 18, 95—99).—The optimal  $p_H$  is 8.0; barium carbonate is toxic, and magnesium carbonate favourable. The bacteria do not produce indole; they produce acid from glycerol and dextrose but are only slightly luminescent on dextrose.

CHEMICAL ABSTRACTS.

**Fermentation of glycuronic acid by certain bacteria.** A. J. QUICK and M. C. KAHN (J. Bact., 1929, 18, 133—137).—Members of the colon-typhoid-dysentery group can utilise glycuronic acid as a source of energy; a strain of *Staphylococcus albus* fermented it.

CHEMICAL ABSTRACTS.

**Influence of *Azotobacter chroococcum* on the physiological activities of cellulose destroyers.** J. R. SANBORN and W. B. HAMILTON (J. Bact., 1929, 18, 169—173).—*Azotobacter* produces a laevorotatory gummy carbohydrate which contains a trace of combined nitrogen and is not readily hydrolysed by boiling acid.

CHEMICAL ABSTRACTS.

**Lipins of tubercle bacilli. V. Acetone-soluble fat.** R. J. ANDERSON and E. CHARGAFF (J. Biol. Chem., 1929, 84, 703—717; see Anderson, A., 1929, 1493).—The acetone-soluble portion of the lipins was hydrolysed with alcoholic potassium hydroxide. The aqueous solution remaining after isolation of the fatty acids contained a preponderance of polyhydric alcohols other than glycerol. The unsaponifiable matter (12% of the fat) failed to give cholesterol reactions; it contained unsaturated compounds. The fatty acids were divided into a solid fraction consisting of palmitic, stearic, and cerotic acids; a liquid saturated fraction comprising phthioic and tuberculostearic acids; and a liquid unsaturated fraction, mainly linoleic acid. The original fat contained considerable amounts of free fatty acids.

C. R. HARRINGTON.

**Lipins of tubercle bacilli. VI. Tuberculostearic and phthioic acids.** R. J. ANDERSON and E. CHARGAFF. **VII. Soft wax.** **VIII. Unsaponifiable wax.** **IX. Hexacosic acid in unsaponifiable wax.** R. J. ANDERSON (J. Biol. Chem., 1929, 85, 77—88, 327—338, 339—349, 351—354).—VI. The crude liquid saturated fatty acids from the acetone-soluble fat of tubercle bacilli (A., 1929, 1493) were converted into the methyl esters and the latter were fractionated under diminished pressure. The fraction having b. p. 145—150°/0.0005 mm. was methyl tuberculostearate,  $C_{19}H_{38}O_2$ ,

and when hydrolysed yielded tuberculostearic acid, m. p. 14—15°; the fraction having b. p. 200°/0.001 mm., m. p. 10°, was methyl phthioate; it had  $[\alpha]_D^{25} + 8.79^\circ$  in ether, and, when hydrolysed, gave phthioic acid,  $C_{26}H_{52}O_2$ , m. p. 28°,  $[\alpha]_D^{25} + 7.40^\circ$  in ether. Biological activity is associated with phthioic but not with tuberculostearic acid.

**VII.** The soft wax (45.6 g.) obtained previously from the crude wax of tubercle bacilli (A., 1929, 1342) was hydrolysed and yielded 2.5 g. of syrupy material soluble in water and alcohol and composed in part at least of glycerol, 6.2 g. of a neutral sweet-smelling substance, 5.6 g. of unsaponifiable wax, and 31.7 g. of fatty acids. The substance is therefore of the nature of a glyceride rather than of a true wax. The fatty acids were divided into solid acids comprising a mixture of palmitic and stearic acids, and liquid acids consisting of a mixture of tuberculostearic and phthioic acids with a small amount of highly unsaturated acids.

**VIII.** The unsaponifiable wax (A., 1929, 1342) is an optically and biologically inactive substance, and is the only constituent of the lipins of tubercle bacilli which shows acid-fastness. The substance, m. p. 57—58°, has C 81.7, H 13.6% [potassium salt, m. p. 90° after sintering at 60—64°; silver salt m. p. 160° (decomp.) after sintering at 60°]. When heated with acetic anhydride it gave a compound, m. p. 50° after sintering at 40°, which yielded 7.12—7.66% of acetic acid on hydrolysis; treatment with acetic anhydride and pyridine yielded a compound, m. p. 43—44°, which afforded only 4% of acetic acid. When the wax was heated at 20 mm. it decomposed above 300°, yielding a distillate of an acid,  $C_{26}H_{52}O_2$ , m. p. 87—88°, and a neutral non-volatile residue. Heating with hydriodic acid caused liberation of volatile iodide which, calculated as isopropyl iodide, represented 4% of glycerol.

**IX.** The acid  $C_{26}H_{52}O_2$  (see above) has, when pure, m. p. 88—89°, and is identical with the hexacosic acid of Levene and Taylor (A., 1924, i, 827). The potassium salt darkens at 230°; the silver salt has m. p. 210° after sintering at 130—140° and darkening at 190—200°.

C. R. HARRINGTON.

**Carbon dioxide. V. Mechanism responsible for the preservative action of carbon dioxide on diphtheria toxin.** W. N. PLASTRIDGE and L. F. RETTGER (J. Bact., 1929, 18, 101—105).—The effect is due to control of  $p_H$  and exclusion of molecular oxygen.

CHEMICAL ABSTRACTS.

**Action of ions and work of cells.** F. BOAS (Biochem. Z., 1929, 215, 257—266).—The influence of sulphate, thiocyanate, phosphate, and iodide ions on the growth of mixed cultures is investigated using as medium neutral or faintly alkaline yeast-water containing 0.1M-sucrose. With 0.3M or higher concentrations of iodide or thiocyanate moulds did, but bacteria did not, grow, whereas with corresponding amounts of sulphate first bacteria and then moulds grew. The results with phosphate resemble those with sulphate. A concentration of 0.033M-sodium iodide caused a 60% increase of yeast-cell count, of 0.003M a 12% increase, whilst a concentration of  $8 \times 10^{-6}M$  caused a decrease of count. The results are



explained in terms of the physico-chemical properties of the ions. P. W. CLUTTERBUCK.

**Disinfectants and the mechanism of anti-septics.** COFMAN-NICORESTI (Bull. Biol. Pharm., 1929, 4, 7).—The effective action of emulsified disinfectants depends partly on their ability to break up colonies of bacteria. The resistance of bacterial colonies is reduced by addition of sodium or calcium chlorides, except where these salts break up the disinfectant emulsion. K. V. THIMANN.

**Different action of alkali salicylates and benzoates and of *p*-hydroxybenzoic esters on micro-organisms.** C. PI-SUNER BAYO (Anal. Fis. Quím. [tecn.], 1929, 2, 302—312).—Whilst comparative measurements of the concentrations toxic to brewer's yeast, *B. coli communis*, and *B. proteus vulgaris* show that sodium salicylate and benzoate are much less active than the free acids, the activity of propyl *p*-hydroxybenzoate ("Nipazol") is only slightly diminished by conversion into the sodium salt. Measurements of the surface tension of aqueous solutions show that there is no parallel between this property and bactericidal activity, contrary to Traube's rule. However, measurements of the partition coefficients of the substances between water and ether, and of the degree of absorption from aqueous solution by active charcoal, show that salicylic and benzoic acids, but not the sodium salts, are extracted from water by ether and adsorbed by active charcoal, whilst propyl *p*-hydroxybenzoate is readily removed in these ways from both neutral and alkaline solutions as the free phenol. R. K. CALLOW.

**Action of low-velocity electrons on micro-organisms.** D. A. WELLS (Nature, 1929, 124, 983—984).—*Staphylococcus aureus* may be killed by the action of low-velocity electrons, the lethal action being a function of the energy of the individual electrons, and the percentage killed being a function of the total energy of exposure. A. A. ELDRIDGE.

**Effect of ultra-violet rays on bacteriophage, and its physico-chemical nature.** K. MIZUNO (Japan. J. Med. Sci., VI, Bact. and Par., 1929, 1, 52—87).—Bacteriophage is destroyed by ultra-violet rays; it is non-volatile, difficult to dialyse, and is probably a sensitive, ionised colloid. It is not destroyed by X-rays. CHEMICAL ABSTRACTS.

**Calcium studies. VI. Effect of parathyroid extract on the diffusibility of calcium in human beings.** A. CANTAROW (Arch. Int. Med., 1929, 44, 834—842).—The administration of parathyroid extract to patients suffering from various conditions brought about changes both in diffusible and non-diffusible calcium, the diffusible calcium being taken as the calcium content of the cerebrospinal fluid. The changes in calcium distribution were usually such that the ratio of diffusible to non-diffusible calcium underwent a definite and prolonged decrease, but in certain cases this decrease was preceded by a preliminary rise. W. O. KERMAK.

**Acetyl derivatives of thyroxine.** J. N. ASHLEY and C. R. HARRINGTON (Biochem. J., 1929, 23, 1178—1181).—The "acetyl sulphate" of thyroxine per-

pared by Kendall and Osterberg (A., 1920, i, 180) is shown to be *diacetylthyroxine ethyl ester*,  $C_{21}H_{19}O_6NI_4$ , m. p. 216—217°. *dl*-Phenylalanine is similarly converted by acetic anhydride in alcoholic solution into the ester of its acetyl derivative. The compound obtained by Kendall and Osterberg by the second "method of purification" of the acetyl derivative is identical with *N*-acetylthyroxine,  $C_{17}H_{13}O_5NI_4$ , m. p. 210—215° (decomp.), obtained by the action of alcoholic sodium hydroxide on *N*-acetylthyroxine methyl ester,  $C_{18}H_{15}O_5NI_4$ , m. p. 208—209° (decomp.), prepared from thyroxine methyl ester by the action of acetyl chloride in anisole. S. S. ZILVA.

**Influence of the thymus on the respiratory metabolism of rats during work.** K. WYSSMANN (Biochem. Z., 1929, 216, 66—84).—Intramuscular injections of extracts of thymus gland have no effect on the respiratory metabolism of rats during periods of work even if the animals are suffering from hyperthyroidism caused by administration of thyroid preparations. The influence of the thymus on muscle fatigue is not expressed by changes in respiratory metabolism. W. MCCARTNEY.

**Influence of liver preparations on the metabolism of men during work.** C. MÜLLER (Biochem. Z., 1929, 216, 85—108).—The basal metabolism, the metabolism during work, and that during the period of restoration to the normal state immediately after work of four normal healthy men have been measured, the measurements being made before and again after administration of medicinal liver preparations. It was found that the administration had only very slight influence on the basal metabolism, but that it reduced the metabolism during work, and still more that during the period of restoration. Liver preparations contain a substance which affects the activity of muscle in healthy persons in such a way that the activity proceeds more economically. W. MCCARTNEY.

**Vegetative endocrine system as regulator of intermediate metabolism. I. Rôle of adrenaline in the regulation of the carbohydrates and fats of the blood.** D. ALPERN and L. TUTKEWITSCH (Biochem. Z., 1929, 215, 319—336).—In normal dogs adrenaline causes, besides hyperglycemia, a decrease of the total and neutral blood-fat content, the values returning to normal towards the end of the experiment. The amount of ketonic substances is always increased, but the increase is not parallel with the degree of decrease of fat. In starving dogs adrenaline causes an increase of total blood-fat and ketonic substances decrease. Administration of oleic acid to starving dogs causes the blood-sugar curve after adrenaline to rise. In phloridzin diabetes a lipæmia is obtained which is little altered with adrenaline. Ketonaemia is considerable and is very marked after preliminary administration of olive oil. After adrenaline, this is much decreased. In phloridzinised dogs, adrenaline causes either no, or only a faint hyperglycemia. The lactic acid values are little affected. Adrenaline injected into starving animals after thyroxine often causes an increase of blood-fat and ketonic substances increase considerably.

P. W. CLUTTERBUCK.

**Influence of adrenaline and insulin on distribution of glycogen in rabbits.** M. SAHYUN and J. M. LUCK (*J. Biol. Chem.*, 1929, **85**, 1—20).—Injection of 0.5 mg. of adrenaline per kg. into fasting rabbits caused a rapid depletion of glycogen from both liver and muscles during the first 1½ hrs.; after this the hepatic glycogen increased in amount until the 18th hour, when it fell rapidly again to the normal fasting level. The muscle-glycogen remained low for 42 hrs. after the injection of adrenaline. Administration of insulin following the injection of adrenaline prevented the loss of glycogen from the liver and caused the muscle-glycogen to increase. It is concluded that adrenaline stimulates the release of glycogen from the liver, but inhibits utilisation of sugar by the peripheral tissues, whilst insulin has the reverse effect in both cases. The confusion which has resulted from previous work is due to failure to take into account the fact that the hepatic and peripheral actions of these substances may predominate at different times after their administration.

C. R. HARRINGTON.

**Influence of insulin and adrenaline on glycogen formation in the liver.** C. F. CORI and G. T. CORI (*J. Biol. Chem.*, 1929, **85**, 275—280).—During continuous intravenous injection of excess of dextrose into nephrectomised rats, animals receiving insulin showed a blood-sugar content and liver-glycogen content about one half as great as the controls. Since, when the rate of dextrose infusion was adjusted to maintain equal levels of blood-sugar in the two groups, the deposition of glycogen in the liver also became equal, the latter is regarded as a function of the blood-sugar concentration. Injection of adrenaline lessened the glycogen deposition, although the blood-sugar was raised, owing to the rapid mobilisation of the liver-glycogen.

C. R. HARRINGTON.

**Effect of insulin on the dextrose absorption of normal red corpuscles.** F. RATHERY, R. KOURILSKY, and Y. LAURENT (*Compt. rend. Soc. Biol.*, 1929, **100**, 726—728; *Chem. Zentr.*, 1929, ii, 587).—No definite increase in absorption by the blood-corpuscles could be observed.

A. A. ELDRIDGE.

**Effect of insulin on the absorption of dextrose by blood corpuscles in diabetic dogs.** F. RATHERY, R. KOURILSKY, and S. GIBERT (*Compt. rend. Soc. Biol.*, 1929, **100**, 728—731; *Chem. Zentr.*, 1929, ii, 587—588).—No effect was observed.

A. A. ELDRIDGE.

**Glycogen in the nerve cells of the central nervous system of mammals. IV. Changes in glycogen distribution after injection of insulin. V. Post-mortal changes in glycogen distribution. VI. H. TANAKA** (*Sci-i-kwai Med. J.*, 1929, **48**, No. 3, 1—17, 18—26, 27—40).—IV. The diminution of glycogen content of certain cells and the lack of change in others after injection of insulin are recorded. Subsequent injection of dextrose produces a return to the normal picture except for the spinal cord.

V. The relative rates of disappearance of glycogen from various cells after death are recorded.

VI. Glycogen is found in all ganglion cells. The disappearance of the glycogen present in the central

nervous systems of rabbits and guinea-pigs during fasting is described. The glycogen is diminished (with these animals) in insulin hypoglycaemia; it exhibits the same reactions as liver-glycogen, and is attacked by the enzymes which digest carbohydrates but not by proteases. Ganglion cells show glycogen after immersion in 6% lævulose solution.

CHEMICAL ABSTRACTS.

**Comparative effects of synthalin and insulin on the depancreatized dog.** E. P. RALLI and A. M. TIBER (*J. Pharm. Exp. Ther.*, 1929, **37**, 451—461).—Insulin invariably causes a fall in the amino-acid-nitrogen of the blood, whereas "synthalin" usually causes a rise. Oral administration of synthalin does not appear to affect the combustion of carbohydrate and only in a partly depancreatized animal does it cause a lowering of blood-sugar, which, in this case, probably takes place by its action on the vagus producing an increased secretion of insulin. Blood-urea rises after administration of insulin to a partly depancreatized dog, whilst with synthalin no marked rise occurs, although, in general, the results for urea-nitrogen are not consistent.

P. G. MARSHALL.

**Blood-sugar content of normal rabbits and rabbits used for assay of insulin.** P. BOTSCHKAREV and N. GRIGORIEV (*Biochem. Z.*, 1929, **215**, 493—497).—The mean blood-sugar values for rabbits after starvation for 18—24 hrs. is 0.104%, and this remains unaffected by repeated injection of insulin over a period of 1—2 years. The mean value does not vary with the breed of rabbit, but is increased in the warm season of the year.

P. W. CLUTTERBUCK.

**Male hormone.** C. FUNK and B. HARROW (*Proc. Soc. Exp. Biol. Med.*, 1929, **26**, 325—326).—An (evaporated) alcoholic extract of (male) human urine, when injected into castrated cocks, caused an increase in the size of the comb.

CHEMICAL ABSTRACTS.

**Estri. II. Methods of purification.** G. F. MARRIAN (*Biochem. J.*, 1929, **23**, 1233—1241).—After treating the unsaponifiable ether-soluble fraction from urine of pregnancy with 70% and 50% alcohol, the hormone is found in each case in the soluble fraction with considerable loss of the total solid matter. Estri can be extracted quantitatively from neutral or acid aqueous solutions by ether with ease, but is much less readily extracted from alkaline aqueous solution. After passing carbon dioxide into an aqueous alkaline solution the hormone may be extracted quantitatively by ether. Estri may be extracted from an ethereal solution by aqueous potassium hydroxide almost quantitatively, removing only a small proportion of the solid matter. The high stability of estri to boiling aqueous alkalis and sodium ethoxide is confirmed. By the above means a concentrate with an activity of 1 mouse unit=0.000135 mg. (Marrarian and Parkes, *J. Physiol.*, 1929, **67**, 389) has been prepared.

S. S. ZILVA.

**Estrius-producing hormone.** C. FUNK (*Proc. Soc. Exp. Biol. Med.*, 1929, **26**, 568—569).—Estri, which is sparingly soluble even in hot water, occurs chiefly in the free condition in the ovary, placenta, or urine; it forms soluble sodium, potassium, ammonium, and barium salts.

CHEMICAL ABSTRACTS.

**Female sexual hormone.** H. WIELAND, W. STRAUB, and T. DORFMÜLLER (Z. physiol. Chem., 1929, 186, 97—103).—From the urine of pregnancy 7 mg. of a crystalline substance have been isolated (m. p. 165—210° after previous sintering). In the Salkowski reaction the chloroform layer remains colourless, whilst the sulphuric acid becomes yellow. With the Liebermann-Burchard test a reddish colour is developed. 0.0005 Mg. of this crystalline material brings about oestrus in the castrated mouse. A second method is also described for the purification of the hormone, which depends on the property of the alkali salts of the bile acids to bring into aqueous solution certain substances otherwise insoluble in water, but so far the method has not yielded a crystalline compound, although the material obtained had approximately the same activity as the crystalline substance obtained by the first method. W. O. KERMACK.

**Hormone of the anterior pituitary lobe.** B. ZONDEK and S. ASCHHEIM (Klin. Woch., 1928, 7, 831—839; Chem. Zentr., 1929, ii, 441—442).—For the preparation of the hormone urine of pregnancy is slightly acidified with acetic acid, filtered, and evaporated at 40° to half-volume. It is then filtered, extracted with ether, and the portion insoluble in ether is dialysed; the hormone dialyses more rapidly than many other constituents. The solution is evaporated to dryness at a low temperature and again extracted with ether. The hormone preparation so obtained is a yellowish-white, amorphous powder which dissolves in water to a clear solution. The solution is free from protein. The hormone is destroyed by treatment with mineral acids or fixed alkalis, or by boiling. It is insoluble in the usual lipin solvents, and is not identical with the female sexual hormone. The effect of injection of the hormone into male and female animals is described. A. A. ELDRIDGE.

**Liver oils yielding a strong colour reaction with antimony trichloride.** SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (Biochem. J., 1929, 23, 1153—1157).—Oil obtained by boiling the liver of the porbeagle (*Lamna cornubica*, Gmel.) gives a blue coloration several hundred times less strong than does the residual oil extracted with ether. This disparity is not marked in the case of cod's liver. Liver oils from fishes such as the halibut, salmon, red perch, or mackerel which cannot be obtained by direct heating of the liver, but only by extraction with solvent, give also a very strong colour reaction with antimony trichloride. Extracted liver oils promote growth in very small doses (0.04—0.1 mg. per day). Rats need more vitamin-A at the onset of puberty.

S. S. ZILVA.

**Vitamin-A and carotene.** II. Vitamin-A activity of red palm-oil carotene. III. Absence of vitamin-D from carotene. IV. Effect of various dietary modifications on the vitamin-A activity of carotenes. T. MOORE (Biochem. J., 1929, 23, 1267—1272).—Carotene (m. p. 162°) obtained from red palm oil was active for rats in daily doses of 0.01 mg. Carotene (m. p. 174°) obtained from carrots was inactive as a source of vitamin-D to rats in doses greatly in excess of the minimal dose for vitamin-A. Carotene (m. p. 174°) at the level of

0.01 mg. daily was active in daily doses of 0.01 mg. even when the rats' basal diet was fat-free. The activity of the pigment tends to weaken when medicinal paraffin is used as a solvent instead of arachis oil. S. S. ZILVA.

**Distribution of vitamin-A in some corn-milling products.** C. R. MEYER and R. A. HETTLER (J. Agric. Res., 1929, 39, 767—780).—From the rate of growth, and the recovery or non-recovery from ophthalmia of vitamin-A-depleted rats when fed with basal diets supplemented with whole yellow maize, etc., it is deduced that maize is rich in vitamin-A. Rapid growth followed the use of 1.5 g. supplements per animal per day, and the minimal amount needed to cure ophthalmia was 1 g. daily, or about 11% of the total food intake. Three of four milling products that constitute gluten feed, viz., steep water, reel slop, and grits, failed to effect a cure, but the gluten was remarkably potent, the minimal supplement needed being 0.25 g. daily. It follows, therefore, that vitamin-A is concentrated in the endosperm of yellow maize kernel, the greatest concentration being in the pigmented, nitrogenous outer layer of the endosperm. Crude maize oil in 1.5 g. daily doses cured ophthalmic rats, maize germs, the source of the crude maize oil, were ineffective at 2 g. daily, and the germ meal was totally lacking in vitamin-A. E. HOLMES.

**Effect of curing on vitamin-A and -D content of alfalfa (lucerne).** W. C. RUSSELL (J. Biol. Chem., 1929, 85, 289—297).—Alfalfa leaves dried by artificial heat so as to retain their green colour contained seven times as much vitamin-A as the sun-cured (partly bleached) leaves; on the other hand, vitamin-D was almost absent from the artificially cured alfalfa, but was increased in amount in the sun-dried material.

C. R. HARRINGTON.

**Guinea-pigs fed on irradiated oats with and without addition of vitamin-A and -C.** N. BEZSSONOFF (Bull. Soc. Chim. biol., 1929, 11, 1146—1163).—Vitamin-A concentrates can be prepared from the juice of the cabbage, carrot, or tomato, by precipitating with lead acetate, drying, extracting with ether or benzene, and mixing with arachis oil, all operations being carried out in red light or darkness, and in absence of air. On exposure to air for 30 days the vitamin content is considerably reduced. Guinea-pigs, which are shown to be more sensitive to avitaminosis-A than mice, require 0.75 g. of fresh cabbage per 100 g. body-weight as source of vitamin-A, the basal diet consisting of oats and yeast. 1 Mg. of the above concentrate, prepared from tomato, per 100 g. body-weight, gave identical results. Diets of irradiated oats, or of whole corn, produced symptoms of avitaminosis-A, which were averted by fresh cabbage or by the concentrate. The colour reactions of Drummond and Rosenheim (A., 1925, i, 1515) and of the author (A., 1925, i, 107) are more specific for vitamin-A than that of Carr and Price (A., 1926, 870), and are not given by lipochromes if the latter are present in concentration less than 12 mg. per litre.

K. V. THIMANN.

**Hypervitaminosis. I. Metabolism of the hypervitaminised rabbit.** H. SUGATA (Sei-i-Kwai Med. J., 1929, 48, No. 4, 1—44, No. 6, 1—37).—

Injection of excess of vitamin-A into a rabbit causes a gradual increase in blood-non-protein nitrogen, -uric acid, and -creatinine, and a fall in -urea. The blood-sugar rises and subsequently falls; liver- and muscle-glycogen decrease. Plasma-lecithin and -fatty acids increase more than does cholesterol, whilst in controls receiving injection of cod-liver oil, or of cholesterol and olive oil, the cholesterol and not the lecithin tends to increase. With moderate doses of the vitamin there is subcutaneous accumulation of fat and decrease in urinary excretion; the nitrogen balance is negative, the excretion of urea decreasing and that of ammonia increasing. Death results from destruction of cell activity due to overfunction.

#### CHEMICAL ABSTRACTS.

**Carbon : nitrogen ratio in the urine of rats deprived of one or both factors of the vitamin-B complex.** S. K. KON (J. Nutrition, 1929, 1, 467—473).—Deficiency in the thermostable component caused an increased C:N ratio. The effect is less marked in animals deprived of the whole vitamin-B complex, and is negligible with rats receiving autoclaved yeast. The thermostable, but not the thermolabile, factor appears to be associated with the metabolic processes of the body. CHEMICAL ABSTRACTS.

**Antiscorbutic fraction of lemon juice. VIII.** S. S. ZILVA (Biochem. J., 1929, 23, 1199—1205; cf. A., 1927, 702; 1928, 801).—There is no modification in the stability of the antiscorbutic activity of decitrated lemon juice previously heated for 1 hr. under anaërobic conditions at 55—58° or at 80—85° as there is when the juice is autoclaved. The addition of decitrated lemon juice in which the vitamin has been inactivated by aëration at the ordinary temperature to autoclaved juice does not compensate for the modification in stability, nor does the addition of the fraction obtained from decitrated lemon juice by precipitation with alcohol or with neutral lead acetate. Sources of the antiscorbutic factor such as lemon juice, cabbage juice, tomato juice, and swede juice contain a thermolabile peroxidase. Autoclaving decitrated lemon juice under anaërobic conditions diminishes somewhat its capacity for reducing phenol-indophenol, but increases its capacity for decolorising iodine. This increased capacity for decolorising iodine is not observed after the decitrated lemon juice has been heated anaërobically at 58° or 85°. The addition of autoclaved decitrated juice to unheated juice accelerates the destruction of the "reducing principle" and of the antiscorbutic activity in it on storage at  $p_H$  7. The addition of quinol has a similar effect. It is suggested that the modification in the antiscorbutic stability of decitrated lemon juice produced by autoclaving may possibly be due to the formation of a substance or substances conducing to the deterioration of the vitamin rather than to the inactivation of a thermolabile stabilising factor.

S. S. ZILVA.

**Vitamin-D content of fats of certain fish.** S. N. MATZKO (Biochem. Z., 1929, 215, 381—386).—The fat of the lamprey (*Caspiomyzon wagneri*) and of the internal organs of the flat fish (*Rutilus rutilus caspicus*) contain fairly large amounts, and of the perch-pike (*Lucioperca*, L.) a smaller amount, of

vitamin-D. 0.15 G. per day of the two former fats was sufficient to prevent rickets in rats.

P. W. CLUTTERBUCK.

**Fractionation of provitamin-D.** F. C. KOCH, E. M. KOCH, and I. K. RAGINS (J. Biol. Chem., 1929, 85, 141—158).—A commercial sample of cholesterol from spinal cord which contained small amounts of ergosterol was boiled with alcohol containing 10% of sodium hydroxide. The cholesterol which separated on cooling was fractionated by dissolving in ether, shaking the solution with water, filtering off the cholesterol which separated in the emulsion, and subjecting the cholesterol which remained in solution in the ether to successive crystallisations from acetone. These latter fractions showed no great difference in provitamin-D content from the original material. The residue obtained on evaporation of the alkaline-alcoholic solution had very little provitamin-D. The fraction separated from the emulsion, as also both sublimates and residues obtained on heating the purified fractions in an atmosphere of nitrogen, showed increased provitamin-D content. The optimum effect, i.e., a 25-fold increase in the provitamin-D content, was obtained by heating slightly above the m. p. for 1—3 hrs. in absence of oxygen. After bromination and reduction, treatment with permanganate, and acetylation and regeneration, the cholesterol still contained some provitamin-D, and this amount could still be raised by the heat treatment; the presence of a provitamin other than ergosterol must therefore be assumed. No increase in provitamin content was observed as the result of treating the cholesterol with dehydrating agents, metallic salts or oxides, or yellow phosphorus. The increased provitamin content which resulted from heating could not be correlated with changes in the iodine value, refractive index, or colour reactions of the cholesterol.

C. R. HARRINGTON.

**Vitasterol-D. III. An active crystalline substance from the product of irradiation of ergosterol.** A. JENDRASSIK and G. KEMÉNYFFI (Biochem. Z., 1929, 216, 238—240; cf. A., 1929, 104).—An alcoholic solution of ergosterol was irradiated and unchanged ergosterol was then removed by concentration and cooling. By further concentration another substance was removed from the solution, which was then evaporated to small volume, an oily product being obtained. When this was fractionated from alcohol a white, hygroscopic, crystalline substance, m. p. (corr.) 92°,  $[\alpha]_D -35.4^\circ$ , which did not absorb ultra-violet rays was obtained. In daily doses of 0.01 g it healed rickets in rats. The substance was easily soluble in alcohol and in chloroform. Since, however, it was found to contain 20% of ergosterol it was purified with digitonin and crystallised from ether. The recrystallised substance had m. p. 38°, and may be the antirachitic vitamin. The properties of the other products of the irradiation showed that they were not identical with the antirachitic substance.

W. MCCARTNEY.

**Vitamin-D. I. Photochemical reactions of ergosterol.** E. H. REERINK and V. VAN WIJK (Biochem. J., 1929, 23, 1294—1307).—Irradiation of ergosterol by light of wave-length greater than 275  $\mu$  results in the direct formation of a product, which

appears to be vitamin-*D*. This product after continued irradiation is gradually transformed into a more stable substance. As the rate of this transformation is slow it is possible to convert about 60% of the ergosterol into vitamin-*D* before the secondary reaction interferes seriously. Irradiation with light of wave-length 254  $\mu$  produces two reaction products in the early stages of exposure. One, which is most probably identical with vitamin-*D*, is quickly destroyed on prolonged irradiation; the other, into which the main portion of ergosterol is transformed, is much more stable to this irradiation. The absorption spectra of vitamin-*D* and of the "short-wave" product have been evaluated. By means of the absorption spectrum it is possible to estimate the amount of vitamin-*D* present in correctly irradiated solutions. Feeding tests on children and rats have shown the first reaction product produced by the "long-wave" irradiation, characterised by a distinct absorption spectrum and obtained in crystalline state, to have an antirachitic activity of a magnitude not hitherto reached.

S. S. ZILVA.

**Structure of surface films. XIII. Sterols and their derivatives.** O. ROSENHEIM and N. K. ADAM (Proc. Roy. Soc., 1929, A, 126, 25—34; B, 105, 421).—Experiments have been carried out in which the relation between the surface tensions and the areas of surface films of certain sterols and their derivatives have been determined. The area of the cholesterol molecule in unimolecular surface films is now found to be 40.8 sq. Å. and not 39.0 sq. Å. as previously reported (cf. A., 1928, 1172). Several other natural sterols give liquid films indistinguishable from that of cholesterol. Ergosterol gives a solid, rather unstable film of similar area.  $\psi$ -Cholesterol in which the CH-OH group is at C<sub>3</sub> gives a much larger and much more compressible film, in which probably the molecules are very much tilted. This change is presumably brought about by the change in the position of the water-attracting group in the molecule. A study of cholestenone and its oxime shows that a change in the nature of a water-attracting group in one corner of the cholesterol ring system may make a considerable change in the structure of the films; this change is most easily accounted for by a considerable alteration in the tilt of the molecules. Oxycholestenone, oxycholesterylene, and  $\beta$ -oxycholesteryl acetate give films the properties of which are extremely difficult to explain on the basis of the accepted formulæ.

W. O. KERMACK.

**Unimolecular films of irradiated ergosterol in relation to the production of vitamin-*D*.** O. ROSENHEIM and N. K. ADAM (Proc. Roy. Soc., 1929, B, 105, 422—428).—Observations have been carried out on the unimolecular films formed on a water surface by the substances A, B, and C obtained from ergosterol by ultra-violet irradiation (cf. Bourdillon and others, A., 1929, 727). The results when compared with those obtained with cholesterol derivatives, the constitutions of which are partly known (see preceding abstract), appear to indicate the presence in the irradiated products of a ketonic group. When the ultra-violet spectrum of  $\Delta^{4:6}$ -cholestadien-8-one is compared with the ultra-violet spectrum of

substance A (probably vitamin-*D*), a very close similarity exists in both in regard to position and shape of the absorption band at 280  $\mu$ , although neither  $\Delta^{4:6}$ -cholestadien-8-one nor its irradiation product possesses any antirachitic power.

W. O. KERMACK.

**Absorption spectra of cholesterol and ergosterol.** E. M. KOCH, F. C. KOCH, and H. B. LEMON (J. Biol. Chem., 1929, 85, 159—167; cf. this vol., 256).—After cholesterol has been purified by methods which remove all substances showing absorption in the ultra-violet region it can still be activated to some extent by ultra-violet irradiation; the increased provitamin content which develops when such purified cholesterol is heated anaerobically is accompanied by development of general absorption in the ultra-violet, but not of the absorption bands characteristic of ergosterol.

C. R. HARRINGTON.

**Serum-calcium and organ calcification under the action of irradiated ergosterol.** V. DEMOLE and K. FROMHERZ (Arch. exp. Path. Pharm., 1929, 146, 347—360).—When the blood-calcium of rats and rabbits is raised by doses of irradiated ergosterol, calcification of various organs readily occurs, but in the cat and more especially in the dog such calcification of the organs takes place much less readily or not at all. In the parathyroidectomised dog calcification occurs much more readily and extensively and is comparable with that which occurs in the normal rabbit. When single doses of irradiated ergosterol are administered to a dog, the rise in blood-calcium which occurs is approximately proportional to the quantity administered, and it is suggested that this observation may provide a basis of a method for the approximate assay of preparations of irradiated ergosterol.

W. O. KERMACK.

**Action of irradiated ergosterol in the rabbit.** M. I. SMITH and E. ELVORE (U.S. Publ. Health Rep., 1929, 44, 1245—1256).—Repeated large doses (2 mg. and upwards) of irradiated ergosterol produce hypercalcaemia and death in rabbits. There is a tendency for the inorganic phosphate of the serum to increase and when this occurs accompanied by hypercalcaemia, an abnormal calcium deposition occurs in certain tissues, e.g., aorta, kidney, and lung. Doses of less than 1 mg. are fairly well tolerated.

F. O. HOWITT.

**Course and prognosis of the malady produced by overdoses of vitamin-*D* solutions.** T. VON BRAND and F. HOLTZ (Z. physiol. Chem., 1929, 185, 217—233).—Daily overdoses of vitamin-*D* per os produce in adult rats a decrease in body-weight up to 40% of the original. Typical symptoms of hypervitaminosis are observed. The serum-calcium and -phosphate are increased from 9.8 to 16.9 and 8.3 to 13.1, respectively, after 37 days, although the ratio is practically unchanged. The values sink slowly to normal with cessation of the overdoses. Histological examination of various organs shows that vitamin-*D* in excess produces calcification in varying degree. The kidneys are the most sensitive and show heavy deposits after 4 days; after a longer period the deposits may persist when the overdoses cease. The

stomach, lungs, heart, and aorta show a moderate but completely reversible calcification.

J. H. BIRKINSHAW.

**Rôle of enzyme action in seed germination.** J. STEPHAN (Ber. Deut. bot. Ges., 1929, 47, 561—564).—Catalase activity during germination of seeds of hemp (*Cannabis sativa*) and correlation with germination period are investigated. The catalase activity is followed manometrically. Maximum catalase activity occurs at completion of germination. Treatment of seeds with orthophosphoric acid accelerates the increase in catalase action and shortens the time for completion of germination from 12 to 8 hrs. Seeds soaked in water or potassium chloride solution show no difference in catalase activity.

F. O. HOWITT.

**Proportions and localisation of carbohydrates in the seeds of *Helianthus annuus* and their variations during germination.** J. LEMARCHANDS (Compt. rend., 1929, 189, 1323—1325).—The dry, ripe seeds of the sunflower contain 0.2% of reducing sugars (dextrose, a small amount of maltose, but no lævulose), and 1.2% of non-reducing sugar (mainly sucrose). Dextrose is also present in the epidermis of the cotyledons, but the embryo is free from reducing sugars. During germination, the amount of reducing sugars increases; the total sugar increases rapidly at first and then diminishes owing to the rapid disappearance of non-reducing sugars.

H. BURTON.

**Variation in composition of the banana during ripening.** C. BOURDOUL (Bull. Soc. Chim. biol., 1929, 11, 1130—1142).—There is a loss of weight during ripening, mainly due to loss of water. Starch is transformed into sucrose rapidly at first, the starch content falling from 23% to 3.6% of the dry weight of the pulp in 7 days. The total sugar content reaches a maximum just before the brown coloration appears.

K. V. THIMANN.

**Influence of humidity on sugar concentration in the nectar of various plants.** O. W. PARK (J. Econ. Entomol., 1929, 22, 504—544).—See also A., 1929, 612.

**Changes in the pectic constituents of apples in relation to softening.** M. H. HALLER (J. Agric. Res., 1929, 39, 739—746).—Softening of Ben Davis, Winesap, and Jonathan apples as they approach maturity on the tree is, to a limited extent, associated with a decrease in the percentage of protopectin and a corresponding decrease in total pectic substances, whereas the pectin, present in very small amounts, remains constant. Softening in storage is apparently due to conversion of insoluble pectic substances, principally protopectin, into soluble form. The rates of conversion at temperatures of 0—15.6° are proportional to the rate of softening.

E. HOLMES.

**Carbohydrate metabolism in tobacco leaf. Detection of methylglyoxal as an intermediate product in the metabolism of green leaves.** M. KOBEL and M. SCHEUER (Biochem. Z., 1929, 216, 216—223).—Methylglyoxal has been isolated from the material obtained when extracts of fresh or air-dried tobacco leaf act on magnesium hexosediphosphate.

W. MCCARTNEY.

**Chlorophyll of wheat leaves.** A. DUSSEAU (Compt. rend., 1930, 190, 68—70).—The alcoholic extracts of the leaves of hard, semi-hard, and soft varieties of wheat were examined for intensity of coloration, intensity of fluorescence, rate of decolorization by light, and absorption spectrum. The identification and classification of varieties made possible by this method are recommended for use with cereals generally.

K. V. THIMANN.

**Colour reaction of Japanese acid clay with carotene.** K. KOBAYASHI, K. YAMAMOTO, and J. ABE (J. Soc. Chem. Ind. Japan, 1929, 32, 182—183b).—Japanese acid clays give a bluish-green colour with solutions of carotene in benzene, carbon tetrachloride, or light petroleum. The reaction is intensified after drying the clay, 2 hrs. at 150° giving a maximum effect. Anhydrous zinc chloride, aluminium chloride, or phosphoric acid produces the same reaction with carotene, and the results, both with these substances and with the acid clays, are of the same order as those obtained with cod-liver oil or vitamin-A preparations.

K. V. THIMANN.

**Phylloerythrin.** L. MARCHLEWSKI (Compt. rend., 1929, 189, 1032—1034, and Bull. Acad. Polonaise, 1929, A, 599—603).—Phylloerythrin, extracted from cow's faeces with chloroform, crystallises from that solvent in violet needles, the chloroform additive product being decomposed as described previously (A., 1928, 1468). The pure pigment thus obtained has the empirical formula  $C_{33}H_{34}O_3N_4$  and is similar to phylloporphyrin. The chloroform additive product has the formula  $(C_{33}H_{34}O_3N_4)_2 \cdot CHCl_3$ .

P. G. MARSHALL.

**Influence of alcohol treatment on the extraction of tannin from vegetables.** E. MICHEL-DURAND (Compt. rend., 1929, 189, 1306—1308).—Preliminary treatment of acorns with alcohol at 90° renders the tannin almost insoluble in acetone but very soluble in 40% aqueous acetone. The tannin is also relatively insoluble in acetone when the material is dried at 100—105°, indicating that the tannin complex is sensitive to heat. The results confirm the notion of free and combined tannins previously proposed (A., 1924, i, 477).

H. BURTON.

**Tremetol, the compound producing "trembles" (milk-sickness).** J. F. COUCH (J. Amer. Chem. Soc., 1929, 51, 3617—3619).—Details are given for the extraction of tremetol, probably  $C_{16}H_{22}O_3$ ,  $[\alpha]_D^{20}$ —33.82° in alcohol, from *Eupatorium urticifolium* and *Aplopappus heterophyllus*. The substance is a thick oil which decomposes on attempted distillation at 3 mm., it is readily oxidised in air, is insoluble in water, acid, or alkali, and absorbs 2 mols. of bromine in carbon tetrachloride solution at the ordinary temperature.

H. BURTON.

**Distribution of piceoside (picein of Tanret) in the vegetable kingdom.** M. BRIDEL and J. RABATÉ (Compt. rend., 1929, 189, 1304—1305).—Amelarioside (Bridel, Charaux, and Rabaté, A., 1928, 992) is identical with piceoside (*p*-hydroxyacetophenone  $\beta$ -glucoside) [the picein of Tanret (A., 1894, i, 564, 616)]. Jowett's salinigrin (J.C.S., 1900, 77, 707) is also identical with piceoside, since, on hydrolysis, it furnishes *p*-hydroxyacetophenone and not *m*-



hydroxybenzaldehyde as stated by Jowett. The names ameliaroside and salinigrin should, therefore, be deleted from the literature. Piceoside has now been isolated from one member of each of the following classes: *Coniferae*, *Rosaceae*, and *Salicaceae*.

H. BURTON.

**Rutoside in fresh flowers of *Forsythia pendula*, L.** J. GOLLAN (Bull. Soc. Chim. biol., 1929, 11, 1164—1169).—From 100 g. of fresh flowers 0.35 g. of a yellow, crystalline glucoside was obtained. Hydrolysis by rhamnodiastase proved its identity with rutoside, which contains 1 mol. each of quercitol, rhamnose, and dextrose.

K. V. THIMANN.

**Sugars. III. Galactose from sea-weed "Tengusa."** Y. UYEDA (J. Soc. Chem. Ind. Japan, 1929, 32, 175—176B).—A yield of 5% of galactose was obtained by hydrolysing the material with sulphuric acid.

K. V. THIMANN.

**Spanish seaweeds. Algin.** J. GIRAL (Anal. Fis. Quím. [tecn.], 1929, 2, 144—163).—An investigation has been made of the ash and of the mucilaginous constituent (algin) of *Fucus platycarpus*, Thuret. When dried in air, powdered, and finally dried at 100°, the fresh weed yields 13% of dry material containing 19% of ash constituted as follows: soluble in water 13.57% ( $\text{SO}_3$  3.82, halogen 3.03,  $\text{K}_2\text{O}$  1.49,  $\text{Na}_2\text{O}$  4.48,  $\text{CO}_2$  0.39%); insoluble in water, soluble in hydrochloric acid 3.43% ( $\text{Al}_2\text{O}_3$  0.66,  $\text{CaO}$  1.16,  $\text{MgO}$  0.25,  $\text{CO}_2$  1.36%, Fe,  $\text{SiO}_2$ , and  $\text{SO}_3$  traces); insoluble in hydrochloric acid 1.8% ( $\text{SiO}_2$ ). The dry weed contains 1.94% of nitrogen, equivalent to 12.12% of proteins. In order to extract the algin the powdered weed is macerated three times with water acidulated with hydrochloric acid and then repeatedly washed with water to remove soluble salts. The residue is lixiviated with 1% sodium carbonate solution, from which the algin is precipitated by acid and exhaustively washed with water. Algin contains 4.8% of ash ( $\text{SiO}_2$  0.59,  $\text{Al}_2\text{O}_3$  34.75,  $\text{CaO}$  44.04,  $\text{MgO}$  20.50%, traces of sulphate and iron, no chlorides or carbonates), 0.4% of nitrogen, and carbon and hydrogen in the proportions required by the formula  $\text{C}_{24}\text{H}_{40}\text{O}_{29}$  [ $?(C_6H_{10}O_7)_n$ ]. Oxidation of algin by nitric acid yields an insoluble substance A,  $\text{C}_{24}\text{H}_{40}\text{O}_{29}$ , probably algin less the inorganic constituents, and the solution yields a crystalline substance B,  $\text{C}_{17}\text{H}_{51}\text{O}_{46}$ , m. p. 112°, and inorganic material. Substance B is an acid, equivalent 66.2, the reactions of which indicate that it is a saturated hydroxy-acid. Algin is incompletely decomposed by boiling with acids or alkalis. As a result of examination of the effects of numerous reagents, it is concluded that algin is a mixed salt of aluminium, calcium, and magnesium with an acid closely analogous to pectic acid, containing partly methylated hexose and pentose or methyl-pentose components.

R. K. CALLOW.

**Plant cuticles. I (contd.). Modern plant cuticles. II. Fossil plant cuticles.** V. H. LEGG and R. V. WHEELER (J.C.S., 1929, 2444—2449, 2449—2458).—I. The cutin from *Agave rigida* on oxidation with dilute nitric acid gives suberic acid and a mixture of azelaic and sebacic acids; an acid  $\text{C}_{11}\text{H}_{20}\text{O}_3$  insoluble in water, soluble in cold alkali (silver salt); and an acid,  $\text{C}_{22}\text{H}_{42}\text{O}_3$ , m. p. 85—86°,

insoluble both in water and cold alkali (silver salt), also obtained, of m. p. 83°, by oxidation with a cold mixture of hydrogen peroxide and glacial acetic acid. Destructive distillation under high vacuum gives a large proportion of saturated hydrocarbons from which 20% of pentatriacontane was isolated. From the wax of the cuticle there were isolated the acids corresponding with montanyl alcohol ( $\text{C}_{28}\text{H}_{56}\text{O}$ ) and mellisyl alcohol ( $\text{C}_{30}\text{H}_{60}\text{O}$ ) by a potash-lime fusion of the two fractions of crude acetylated alcohols separated by fractional crystallisation from light petroleum.

II. The cuticles of "Papierkohle," unlike those of modern plants, contain no water-soluble material or cellulose, but extraction with organic solvents gives 4% of wax. Oxidation with dilute nitric acid gives sebacic acid and an acid,  $\text{C}_{15}\text{H}_{28}\text{O}_3$ , m. p. 81—82° (silver salt; ethyl ester, m. p. 57—59°), also obtained by oxidation with hydrogen peroxide and glacial acetic acid or with alkaline permanganate. Destructive vacuum distillation yields saturated and unsaturated hydrocarbons together with phenolic and acidic oils, aromatic hydrocarbons, etc. A pale yellow hydrocarbon was obtained by this means, m. p. 68—71° (C 85.3; H 14.1%). Saponification of the neutral compounds of the wax (chloroform- and ether-soluble) with 10% alcoholic potassium hydroxide yields saturated and unsaturated acids (the latter predominating). From the unsaturated acids are obtained oleic acid and an acid, m. p. 56—60°. The saturated acids appear to consist of a mixture of stearic and palmitic acids. The ether-insoluble portion of the chloroform extract of the wax yields, on saponification, a saturated fatty acid,  $\text{C}_{24}\text{H}_{48}\text{O}_3$ , m. p. 69—71° (silver salt). Resolution of the alcohol-soluble wax in a similar manner yields an acid,  $\text{C}_{18}\text{H}_{36}\text{O}_3$ , m. p. 89° (silver salt), and a small amount of hydrocarbons. The cuticle of bituminiferous coal is similar to "Papierkohle" in constitution.

P. G. MARSHALL.

**[Constituents of] *Illicium religiosum*, Siebold.** S. Y. CHEN (Amer. J. Pharm., 1929, 101, 550—574, 622—637, 687—716).—A botanical and chemical examination of *Illicium religiosum*, Sieb., from China is described. The volatile oils from two separate samples of the powdered fruit have, respectively,  $d^{20}_4$  0.9884,  $d^{20}_4$  0.9834;  $\alpha_D^{20}$  -4.52°,  $\alpha_D^{20}$  -5.2°,  $n^{20}_D$  1.4874, acid value 0.35, 0.42, saponification value 43.7, 28.83, congealing pts. below -8°. The yields of oil are 0.25% and 0.31%. 1.65% of fatty oil ( $d^{20}_4$  0.9268, acid value 17.5, saponification value 210, iodine value 102) was obtained from the first of the above samples and the fatty oil from the second contained melissic, daturic, stearic (?), palmitic (?), oleic, and linoleic acids, myricyl alcohol, sitosterol, a hydrocarbon, a volatile oil (in the unsaponifiable matter),  $d^{20}_4$  1.0547,  $n^{20}_D$  1.4692,  $\alpha_D^{20}$  -0.72°, congealing pt. below -10°, and containing isosafrole (?). The toxic principles, m. p. 65—70° and 60—65°, from the seeds and whole fruit respectively were found to be highly toxic to the rat. Shikimic acid (yield of crude, 17.5%) obtained from the fruit has been converted into the ammonium, sodium (m. p. 268° decomp.), calcium, copper, methylamine (m. p. 162°), pyridine (m. p. 184°), and aniline salts; its behaviour on halogenation, oxidation, and hydrogenation (dihydro-

shikimic acid, m. p.  $180^{\circ}$ ,  $[\alpha]_D -12.8^{\circ}$ ) and condensation with acetone (acetone-shikimic acid, m. p.  $186^{\circ}$ ) is discussed. It has a much smaller inhibitive effect on plant growth than has benzoic acid and the moulds growing on shikimic acid do not produce either alcohol or reducing substances. Physiological and phytochemical studies of the acid are described. (Cf. Eymann, A., 1891, 919.) E. H. SHARPLES.

**Hydrocyanic acid content of *Lotus*.** P. GUÉRIN (Compt. rend., 1929, 189, 1011—1013).—Hydrocyanic acid is widely distributed in the genus *Lotus* as a glucoside (twelve varieties have been examined). The leaves and stems are finely chopped and macerated with ten times their weight of water at  $20-22^{\circ}$  for 24 hrs. About one third of the liquid is distilled off and the hydrocyanic acid determined in the distillate by titration with 0.1N-silver nitrate. The content of this acid varies widely in plants of the same species grown at different altitudes. *L. edulis*, L., shows the highest content (0.918 g. per kg. fresh weight in early July), the content varying at different periods of the year. The lowest value recorded is for *L. corniculatus*, L. (0.02 g. per kg.).

P. G. MARSHALL.

#### Proteins of Indian foodstuffs. II. Proteins

of the Pigeon pea (*Cajanus Indicus*). P. S. SUNDARAM, R. V. NORRIS, and V. SUBRAHMANYAN (J. Indian Inst. Sci., 1929, 12A, 193—205).—The meal of *Cajanus Indicus bicolor* (arhar) contains moisture 8.73%, ash 3.57, ether extractives 2.05, crude protein 22.52, crude fibre 3.10, carbohydrate 60.03%. The extract obtained by means of salt solution contains an albumin which coagulates at  $46-55^{\circ}$ , and two globulins which coagulate at  $80-85^{\circ}$  and  $95-96^{\circ}$ , respectively. 40% saturation of the saline extract of the meal precipitates globulin I (concajanin, N 15.19%, S 1.01%). By increasing the ammonium sulphate content of the filtrate to 60% a precipitate of mixed globulins occurs and is removed. Further increase in the ammonium sulphate content to 90% precipitates globulin II (cajanin, N 16.19%, S 0.38%, present in the largest amount). The albumin, prepared from the acidified filtrate after removal of globulins by heating at  $55^{\circ}$  for  $\frac{1}{2}$  hr. and treatment of the precipitate as in the case of globulins, has isoelectric point at  $p_H$  4.2, that of both globulins being about 5.0. The albumin, cajanin, and concajanin contain cystine 2.32, 1.39, 1.98, tryptophan 2.05, 0.21, 1.48, and tyrosine —, 3.16, and 3.45%, respectively. All three proteins contain a high percentage of the essential acids lysine and arginine, although cajanin is deficient in tryptophan. The meal is therefore not a complete protein food by itself. The results for the *flavus* variety approximate to those for the *bicolor* variety. P. G. MARSHALL.

**Transport of nitrogenous substances in the cotton plant. II. Concentration gradients.** E. J. MASKELL and T. G. MASON (Ann. Bot., 1929, 43, 615—652).—Sea Island cotton plants devoid of bolls were used in the majority of the experiments. In the bark, although organic nitrogen is being transported downwards, there is a negative vertical gradient for non-protein-nitrogen, the greater part of which is asparagine. With protein-nitrogen the

gradient is absent, whilst for carbohydrate it is positive. In the wood the gradient for non-protein-nitrogen is reversed as it is in the leaf, in which there is also a positive gradient for protein-nitrogen, a phenomenon not shown either by the wood or the bark. The negative gradient for non-protein-nitrogen is greater in the inner layers of the bark than in the outer, and the mobile form of nitrogen for the downward transport in the bark appears to be residual nitrogen. The radial concentration gradient in the bark (inner minus outer) for non-protein-nitrogen is positive, but the asparagine-nitrogen only accounts for a minor portion of this fraction, whereas the amino-acid- plus residual nitrogen forms the major portion. The following types of distribution are shown: (1) the amino-acid- and residual nitrogen plus nitrate-nitrogen fractions have high values in the sieve tubes and low values in the cortex and ray tissues, (2) reducing sugars show an exactly reverse behaviour, (3) the asparagine content of the sieve tubes is nearly double that of the cortex, but is higher still in the ray tissues, (4) protein-nitrogen has a lower concentration in the rays than in the other tissues. The gradient of non-protein-nitrogen out of the leaf is almost entirely due to residual nitrogen, the drop being very marked between parenchyma and midrib, whereas asparagine-nitrogen shows only a small change in concentration. The nitrate-nitrogen gradient from petiole through midrib to parenchyma is in the opposite direction and is well marked. It is suggested that the gradient for non-protein-nitrogen in the sieve tubes of the bark is in reality positive, but is masked by a strong negative gradient in the companion cells. The evidence brought forward favours the theory that amino-acids or residual nitrogen are mainly concerned with transport, whilst asparagine is concerned with storage. (Cf. A., 1929, 854.) P. G. MARSHALL.

**Regularities in the glyceride structure of vegetable seed-fats.** G. COLLIN and T. P. HILDITCH (Biochem. J., 1929, 23, 1273—1289).—The composition of the total fatty acids of the fat, the fully saturated glycerides, and the fatty acids in the fully saturated glycerides has been determined in dika fat (kernel-fat from various species of *Irvingia*), nutmeg butter (*Myristica officinalis*) fat, *M. malabarica* fat, and laurel fat. The results are compared with those obtained from other seed-fats. The first two fats have shown a similar association ratio for the saturated and unsaturated acids, whilst *M. malabarica* was found to be somewhat exceptional in this respect. The figures obtained for laurel fat suggest the presence of tri-unsaturated glycerides in quantity.

S. S. ZILVA.

**Organic phosphorus compounds in plants and animals. I. Phosphatides and lecithides from the bean (*Vicia faba*). II. Diffusion of water-insoluble phosphatides and of the colouring matter of the cells from the carrot (*Beta vulgaris*, *Rapa f. rubra*). H. MAGISTRIS and P. SCHÄFER (Biochem. Z., 1929, 214, 401—439, 440—481).—I. The water-soluble dialysable phosphatides of the bean and the lecithides obtained from it by extraction with hot solvents (preferably alcohol) have been examined and it has been shown that products obtained by any**

other method than dialysis in cold water differ profoundly from those originally present in the source. The material obtained by such dialysis was insoluble in organic solvents but hygroscopic and easily soluble in water. It was separated into three fractions: (i) that precipitated by a mixture of methyl and ethyl alcohols and by acetone; (ii) that precipitated by calcium or barium chloride, (iii) the residual fraction. (Precipitation with salts of heavy metals is not recommended.) The products of acid hydrolysis of fraction (i) were: choline, aminoethyl alcohol, glycerophosphoric acid, an unsaturated fatty acid, palmitic acid, a carbohydrate, and (possibly) phytosterol; those of fraction (ii): palmitic acid (possibly also stearic acid), choline, glycerophosphoric acid, and a carbohydrate; and those of fraction (iii): palmitic, oleic, and linoleic acids, a base isomeric with betaine, choline, aminoethyl alcohol, glutaric and glycerophosphoric acids, a carbohydrate, and (possibly) arginine. The lecithides, on acid hydrolysis, yielded choline, glycerophosphoric acid, palmitic and oleic acids, and dextrose.

II. The influence of such external factors as change the permeability of the walls of the cells on the diffusion of water-insoluble phosphatides and of colouring matter from portions of carrot has been studied. Neither the phosphatides nor the dyes pass into water at the ordinary temperature, but at higher temperatures both diffuse readily until at 30° an irreversible change takes place in the cells. Below 30° the process is completely reversible. Irradiation also causes increase in the amounts of phosphatide and dye which diffuse into water. The presence of alkali or magnesium ions favours the diffusion of the phosphatides, but ions of the alkaline-earth metals inhibit it. The combined influence of salts and higher temperatures (not above 30°) greatly increases the permeability of the cell-walls. Alkalis and (to a greater extent) acids, within certain limits of concentration, favour diffusion. In the case of strong (but not weak) acids and bases the extent of diffusion increases as the concentration of substance is increased until a maximum is reached, and then the amount diffused begins to decrease. Progressive addition of salts to acid or alkaline solutions reduces diffusion of phosphatide eventually to zero. The effect of other agents on diffusion has been studied. Substances which increase the power of the cells to take up water favour the diffusion of the phosphatides and dyes; those which have a dehydrating effect retard the diffusion. The results can be explained on the supposition that the cells are enclosed in phosphatide-protein membranes.

W. McCARTNEY.

#### Phosphatides in potatoes, turnips, and carrots.

B. REWALD (Biochem. Z., 1929, 216, 11-14).—Potatoes, turnips, and carrots contain up to 0.5% of phosphatides which can be purified by precipitation from cooled acetone.

W. McCARTNEY.

Distribution of phosphatides in seeds and seedlings. B. REWALD (Biochem. Z., 1929, 216, 15-18).—The phosphatide content of young soya plants (5 weeks old) differs only slightly from that of the beans from which they are grown. Most of the phosphatide of the plants is found in the green

portions; the roots and cotyledons contain very little.

W. McCARTNEY.

Degradation of wood by simultaneous action of ethyl alcohol and hydrochloric acid. W. G. CAMPBELL (Biochem. J., 1929, 23, 1225-1232).—The action of the above reagents under various conditions on the wood of Sitka spruce has been studied. At least two reactions are involved, namely, the hydrolysis of carbohydrates influenced by the presence of alcohol, and the action of alcohol on lignin in the presence of hydrochloric acid. Absence of water from the system favours depletion of carbohydrates, the maximum effect on the lignin in wood being obtained by treating the oven-dry material with a concentrated solution of hydrogen chloride in absolute alcohol. The association of lignin and cellulose in wood is of a physical rather than a chemical nature. As the extracts obtained from the wood after treatment with acid alcohol solutions were derived from portions of all the main constituents, the precipitate of "alcohololysis lignin" obtained on neutralisation contains most probably constituents other than lignin.

S. S. ZILVA.

#### Biological decomposition of plant materials.

I. Nature and quantity of furfuraldehyde-yielding substances in straws. II. Rôle of furfuraldehyde-yielding substances in the decomposition of straws. A. G. NORMAN (Biochem. J., 1929, 23, 1353-1366, 1367-1384).—I. Oat straw contains approximately 22.8% of free hemicelluloses consisting of a hemicellulose A with about 11% of uronic anhydride, 79% of arabinose and xylose, and 10% of anhydrogalactose, and a hemicellulose B with about the same percentage of furfuraldehyde but containing 32% of uronic anhydride and 68% of arabinose. Rye straw contains about 33% of free hemicelluloses, the A fraction consisting of approximately 5% of uronic anhydride, 60% of anhydropentose, and 35% of anhydrohexose, and the B fraction containing approximately 29% of uronic anhydride, 60% of anhydropentose, and 11% of anhydrohexose. The substance yielding furfuraldehyde associated with the Cross and Bevan cellulose fraction in both oats and rye does not consist of oxidation products arising from the chlorination process, but is due to xylan free from uronic groups. This xylan is extremely resistant to extraction. Figures obtained for "pentosan" by the use of the Kröber factor on total furfuraldehyde yield are untrustworthy.

II. The most prominent feature of the decomposition of straw under optimum conditions by a mixed natural flora in the presence of sufficient available nitrogen, is the rapid loss of cellulose which accounts for the major part of the loss of organic matter. The hemicelluloses decompose very rapidly in the first few days and then remain at much the same level while the cellulose is still decreasing. The xylan associated with Cross and Bevan cellulose fraction is removed slowly, the rate being controlled by the loss of the cellulose with which it is intimately associated. A transitory intermediary substance which yields furfuraldehyde is produced. The loss of uronic acid from the straw is steady but small and is

not paralleled by the apparent loss of hemicellulose. Pectin is removed during the decomposition only if acid conditions set in. A compound determined as pectin is synthesised in the process of fermentation. Decomposition is favoured by the presence of cellulose and hemicelluloses and is retarded by the presence of the lignin fraction. Rye straw made practically, hemicellulose-free by extraction is decomposed. A simple method for the prediction of probability of decomposition of any plant material is given.

S. S. ZILVA.

**Presence and distribution of titanium in phanerogamic plants.** G. BERTRAND and (MME.) C. VORONCA-SPIRT (Bull. Soc. chim., 1929, [iv], 45, 1044—1052).—See A., 1929, 855.

**Occurrence of iodides, bromides, and iodide-oxidases in marine algæ.** H. KYLIN (Z. physiol. Chem., 1929, 186, 50—84).—The iodine content of a number of marine algæ was determined by means of starch solution and hydrogen peroxide after ashing the material. The highest iodine value was shown by *Trilliella intricata* (0.53% on the undried material). Iodine appears to be present in both organic and inorganic combination. Bromine occurs in many algæ, particularly in the *Rhodomelaceæ* in organic combination. Iodide-oxidases are present in many species. In the brown algæ they diffuse easily out of the living cell; the oxidases of the red algæ can be detected only after death of the cell. No evidence was obtained in *Laminaria* from the Swedish coast for the so-called "iodine volatilisation" noted by other observers.

J. H. BIRKINSHAW.

**Inorganic nitrogen compounds in the sap of plants.** I. E. BIKOV (Bull. inst. recherches biol. Univ. Perm, 1929, 6, No. 6, 277—290).—The nitrate content of maize decreases on transfer to water or a solution free from nitrate. The ammonia- and nitrate-nitrogen contents of the sap of maize grown in ammonium salt, nitrate, or nitrite solutions resemble those for plants grown in soil. Nitrite is transformed into other forms more, and nitrate less, rapidly than other mineral nitrogen compounds.

CHEMICAL ABSTRACTS.

**Nitrates and ammonium salts as sources of nitrogen for higher plants at constant  $p_H$ .** K. PIRSCHLE (Ber. Deut. bot. Ges., 1929, 47, 86—92).—Plants have been grown in running salt solution at various  $p_H$  ranges between 3 and 9, in one case nitrates, and in the other ammonium salts, being used as the sole source of nitrogen. The  $p_H$ -growth curves show in most cases two peaks, or growth optima, at  $p_H$  4—5 and 7—8. In all but two of numerous experiments growth was much more vigorous on nitrate than on ammonium salts, although in the region of the neutral point the effect was minimised. Similar results were obtained by pot growths of wheat and oats. Disagreement with the results of Prianischnikov (A, 1929, 728) is attributed to differences in the nutrient salt solutions and other factors.

K. V. THIMANN.

**Relative importance of sulphur and phosphorus in plant nutrition.** G. BERTRAND and L. SILBERSTEIN (Compt. rend., 1929, 189, 1045—

1049).—The sulphur : phosphorus ratio has been determined for 34 plants (or various parts) and is found to vary between 0.3 and 1.7. The results emphasise the importance of an adequate amount of sulphur in fertilisers.

H. BURTON.

**Antagonistic action of calcium and magnesium ions on seeded peas.** F. BOLELOUCKY (Zeměd. Archiv, 1928, 9, 493).—Peas absorb calcium during the whole vegetative period; the absorption is maximal during the formation of stalks and leaves, and decreases after the formation of the nodules, whilst that of magnesium, which is low during early development, then increases. Calcium and magnesium are replaceable, although not so physiologically. Peas withstand an excess of both elements, but not of one in absence of the other. Lack of magnesium lowers the yield to a greater extent than lack of calcium, but both are normally necessary to produce a good crop.

CHEMICAL ABSTRACTS.

**Equilibrium of potassium and nitrogen in peat, water, and alluvium.** W. R. RÜDIGER (Biochem. Z., 1929, 215, 387—397).—The potassium and nitrogen contents of peat, flowing water, and alluvium show an inverse relationship, the product giving a constant. The same hyperbolic relationship is shown to hold for a variety of plants.

P. W. CLUTTERBUCK.

**Regulation of the reaction of an external solution by plants.** D. A. SABININ and E. G. MININA (Bull. inst. recherches biol. Univ. Perm, 1928, 6, No. 4, 165—190).—Plants able to assimilate calcium phosphate do not reach equilibrium with the nutrient solution at more acid reactions. Such plants secrete more organic acids at the zone of  $p_H$  equilibrium than do non-assimilating plants.

CHEMICAL ABSTRACTS.

**Assimilation of phosphoric acid by barley in an aqueous solution.** O. TUEVA (Bull. inst. recherches biol. Univ. Perm, 1929, 6, No. 6, 261—275).—With high concentration of phosphate absorption continued to the end of the vegetative period, and migration of phosphate from vegetative to reproductive organs did not occur. Such migration occurred on restriction of the quantity of phosphate. An excess reduces the yield.

CHEMICAL ABSTRACTS.

**Destruction of oak wood by powder post and death watch beetles *Lyctus* sp. and *Xestobium* sp.** (Biochem. J., 1929, 23, 1290—1293).—*Lyctus* frass (borings collected from a number of samples of infected English oak sapwood) is of the same general composition as sound English oak sapwood of a similar particle size. *Xestobium* frass collected from a badly infected sample of English oak heartwood showed a higher alkali-solubility and lignin content and a lower cellulose and pentosan content than the healthy wood. Part of the latter components in the original wood must have been consumed during larval activity.

S. S. ZILVA.

**Chemical aspect of disease-resistance in the onion.** J. C. WALKER, K. P. LINK, and H. R. ANGELL (Proc. Nat. Acad. Sci., 1929, 15, 845—850).—See A., 1929, 613.

C. A. SILBERRAD.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

MARCH, 1930.

### General, Physical, and Inorganic Chemistry.

**New bands in the secondary spectrum of hydrogen. II.** D. B. DEODHAR (Phil. Mag., 1930, [vii], 9, 37—49).—A detailed examination of seven new band systems in the blue region of the secondary hydrogen spectrum is described. The frequencies of the null lines in each system have been determined from the  $Q(1)$ ,  $P(2)$ , and  $R(1)$  members and the values are in good agreement, those corresponding with the  $Q(1)$  members being 21323.17, 21444.45, 21580.70, 21716.22, 21885.13, 22063.62, and 22261.70. In each band the initial moment of inertia is greater than the final one and the moment of inertia decreases gradually with the increasing frequency. The bands are attributed to excited hydrogen molecules and it is suggested that they are related to band systems in the yellow region of the spectrum previously described (A., 1928, 1067).  
A. E. MITCHELL.

**Theory of relativity and the spectral lines of hydrogen.** T. RAMOS (Ann. Acad. Brasil. Sci., 1929, 1, 20—27).—Mathematical. The Balmer series of the hydrogen spectra is discussed from the point of view of the general theory of relativity.

H. F. GILLBE.

**Dissymmetry of emission of series lines.** J. STARK (Naturwiss., 1929, 17, 983).—Experiments on the line series of hydrogen and helium have shown in both cases that those lines which are shifted to the red by the electric field are emitted, along the axis of the field, with greater intensity against the field than in the direction of the field. The effect is reversed in the case of those lines which are shifted towards the violet.

G. E. WENTWORTH.

**Radiation from the hydrogen-oxygen flame.** W. E. GARNER and K. TAWADA (Trans. Faraday Soc., 1930, 26, 36—45).—Measurements of the infra-red radiation from "wet" and "dry" hydrogen-oxygen explosions do not confirm the conclusions reached indirectly by Wohl and Elbe (A., 1929, 1394) that the "dry" flame exhibits chemiluminescence which is suppressed on saturation with water. The radiation-composition curve for mixtures of dry hydrogen and oxygen shows a maximum at 55% H and a subsidiary peak at 20%. The radiation decreases with the pressure more rapidly than the pressure itself. The density of an inert gas determines its effect on the amount of radiation emitted; thus argon, oxygen, and nitrogen increase it, whilst it is diminished by hydrogen or helium. When 2 volumes of argon are added to 3 volumes of the stoichiometrical hydrogen-oxygen mixture, there is a threefold increase in the radiation

emitted. These effects are attributed to changes in the duration of the high temperature of the flame, and it is concluded that the phenomena are best explained by assuming that the radiation from this flame is thermal in character.  
J. W. SMITH.

**Lyman helium lines.** F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 662—666).—The calculation of the wave-lengths of spectral lines is now based on certain spectral laws. Many spectra are sufficiently accurately analysed to permit the calculation of short wave-lengths on the basis of their term systems, e.g., Al II and Hg II. The wave-lengths of the intensity maxima of the hydrogen and He II spectra are calculated with reference to the relativistic fine structure and intensity of the components. Using these as standards, the lines of the He I series discovered by Lyman are fixed. A spectrogram by Kruger on which the hydrogen series and both the helium spectra He I and He II were present with great sharpness was used.  
A. J. MEE.

**Fine structure and Zeeman effects in helium band lines.** R. S. MULLIKEN and G. S. MONK (Physical Rev., 1929, [ii], 34, 1530—1540).—Second and third order grating photographs of helium band lines  $\lambda$  6400, 5733, 4546, and others, having the  $2^3\Pi$  state as their final electron level show fine structure. The  $3^3\Pi \rightarrow 2^3\Sigma$  bands ( $\lambda$  4650, 4670) show no evidence of fine structure. The  $2^3\Pi$  levels show types of fine structure for the odd and even  $K$  values. Theoretical interpretation of observed fine structures is discussed. The Zeeman effect of the  $\lambda$  6400 band ( $3^3\Sigma \rightarrow 2^3\Pi$ ) was investigated at three field strengths. The Zeeman patterns replacing the original fine structures are in good agreement with predictions for a  $1^1\Sigma \rightarrow 1^1\Pi$  transition, indicating that the spin effect giving rise to the original fine structure is overpowered by the external field.  
N. M. BLIGH.

**Spectrum of helium.** D. BURGER (Arch. Néerland., 1929, [iii A], 12, 147—163; cf. A., 1926, 985; 1929, 732).—A repetition of work already published.  
C. A. SILBERRAD.

**Hydrogen-like spectra of lithium and beryllium in the extreme ultra-violet.** B. EDLÉN and A. ERICSON (Nature, 1930, 125, 233—234).—The strongest lines 135.02 and 113.93 Å. in the hydrogen-like spectra of Li III and 75.94 Å. of Be IV have been observed.  
L. S. THEOBALD.

**Condensed spark spectra in the extreme ultra-violet to 88 Å.** B. EDLÉN and A. ERICSON (Compt. rend., 1930, 190, 116—118; cf. A., 1929,

1350).—By a further improvement of the apparatus previously used, lines down to  $1'S_0-3'P_1$  of beryllium, 88.36 Å., have been measured, as also many additional lines in the spectra of O III, O IV, O V, and O VI, and lines belonging to Mg III, Al IV, and Si V. The ionisation potentials of O III, O IV, O V, and O VI are respectively 54.87, 76.99, 110.5 (uncertain), and 137.49 volts. C. A. SILBERRAD.

**Perturbations in band spectra. II.** J. E. ROSENTHAL and F. A. JENKINS (Proc. Nat. Acad. Sci., 1929, 15, 896–902; cf. A., 1929, 866).—Perturbations in the carbon monoxide  $1S \rightarrow 1P$  bands were investigated by measuring the band lines from a set of grating plates and plotting curves for deviations from the formulæ for regular lines of the band. An analysis of the rotation structure of the system had indicated abnormalities in the (0,0) and (1,0) bands, and some other anomalies. These irregularities are shown to be due probably to perturbations of the rotation terms of the  $1P$  state. Results indicate that the rotation terms of the  $1P$  state are crossed by terms of another electronic state in such a way that terms of equal  $j$  come into close coincidence. N. M. BLIGH.

**Zeeman effect in the MgH bands.** G. M. ALMY and F. H. CRAWFORD (Physical Rev., 1929, [ii], 34, 1517–1529; cf. Watson and Perkins, A., 1928, 2).—The Zeeman effect in the MgH  $2\Pi \rightarrow 2\Sigma$  bands at fields between 5000 and 28,000 gauss produced by a magnetism in hydrogen were investigated. Using Hill's results (cf. this vol., 265) the magnetic energy pattern is calculated and the line patterns in the  $\lambda$  5211 band are plotted. A description of the observable patterns in this band and a quantitative comparison with theory are tabulated, and show good agreement. Qualitative intensities are discussed. N. M. BLIGH.

**Emission spectrum of magnesium.** D. VITALE (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], 35, 155–157).—The spectrum of magnesium obtained by exploding a thin wire by the passage of an electric current has been mapped in the region 2733–2711 Å. Lines of both the arc and spark spectra are observed. The line at 4481 is obtained, but not the related line at 3104 Å. Reversal is shown in all cases where a tendency to this exists, with the exception of the triplet 5183, 5172, 5167 Å. R. K. CALLOW.

**Spectrum of aluminium [and of other elements] in the extreme ultra-violet.** B. EDLÉN and A. ERIKSSON (Compt. rend., 1930, 190, 173–174; cf. this vol., 263).—The wave-lengths and intensities of lines of the spectra of Na III, Mg IV, Al V (group,  $2s^2p^3\ ^2P-2sp^6\ ^2S$ ) and Fe II, Ne III, Na IV, Al VI ( $pp'$  groups,  $2s^2p^4\ ^3P-2sp^5\ ^3P$ ) are tabulated. The strongest line obtained in the aluminium (Al V) spark spectrum is due to the hitherto unknown doublet of the lines 278.720 and 281.402 Å. (cf. Millikan and Bowen, A., 1924, ii, 214). J. GRANT.

**Band spectra of aluminium hydride.** E. BENGTSSON and R. RYDBERG (Z. Physik, 1930, 59, 340–357).—The band spectra of aluminium hydride are investigated more completely. A new band system was found in the further ultra-violet at a wave-length of 2033 Å., which fits in very well with the scheme of electron levels in the molecule. It corre-

sponds with the switch  $1\Sigma'' \rightarrow 1\Sigma$ . A further investigation of the effect of hydrogen pressure on the intensity of the bands was carried out. As the pressure is increased the series gradually lengthens, and the final lines become diffuse. The dissociation values for the different states can be derived on the basis of the relationship between the terms of AlH on the one hand, and those of the aluminium atom on the other. From the rotation terms some conclusions can be reached relative to the decomposition of the molecule. The intensity distribution inside a band is obtained from the relationship  $I=i.e^{E \cdot RT}$ . It is probable that the intensity effect is due to a labile change of the molecule into the  $1\Pi$  state. A. J. MEE.

**Continuous spectra of flames containing the halogens.** H. C. UREY and J. R. BATES (Physical Rev., 1929, [iii], 34, 1541–1548; cf. Kondratév, A., 1928, 1075).—The Franck-Condon theory for the dissociation of molecules by light (cf. A., 1929, 235) indicates that two colliding atoms may recombine with emission of light if appreciable quantities of the free atoms are present. Spectrograms were taken in the visible and ultra-violet of flames of chlorine and hydrogen, and hydrogen-oxygen flames containing the halogens, and the short wave-length limit of the spectra was determined and found to be in agreement with the hypothesis that they are due to the recombination of the normal and excited halogen atoms. Calculations show that there are enough collisions of this type in the flames to account for the intensity of the light emitted. N. M. BLIGH.

**Classification of the spectral lines of chlorine, bromine, and iodine.** K. ASAGOE (Mem. Coll. Sci. Kyoto, 1929, 12, 275–326).—The spectral lines of these three halogens were classified into arc and spark types by observing (1) the effect of constriction of a part of a Geissler tube on the intensities of the lines, (2) the change of relative intensities resulting from introduction of a capacity in the circuit, and (3) the effect of insertion of self-inductance in the condensed heavy discharge circuit. The spark lines were sorted out into spark and super-spark by varying the intensity of a magnetic field applied to a Geissler tube and by (2) and (3) above. Arc lines were found only in the visible region, whereas spark lines were distributed all over the region investigated. W. E. DOWNEY.

**Wave-lengths of the blue argon spectrum with contributions to the term analysis.** A. H. ROSENTHAL (Ann. Physik, 1930, [v], 4, 49–81).—The intense blue glow excited in carefully purified argon using discharge tubes of various types has been studied in the region 2100–9000 Å., by means of a Rowland grating and prism spectrographs. The spectrum discloses a very large number of lines, many being recorded for the first time. Part of the spectrum can be classified in the doublet-quadruplet-multiplet system of A II with the limit  $3P$ , and 14 new terms of this system have been calculated. R. A. MORTON.

**Atomic resonance radiation in potassium vapour.** J. R. NIELSEN and N. WRIGHT (J. Opt. Soc. Amer., 1930, 20, 27–30).—Resonance radiation was excited in a tube illuminated by a specially constructed argon-filled arc lamp containing potassium



vapour, and was observed first at  $170^\circ$ , increasing in intensity to  $215^\circ$ , at which temperature the red potassium doublet was observed spectroscopically. A line in the violet was faintly indicated.

N. M. BLIGH.

**New band system of titanium oxide.** A. CHRISTY (*Astrophys. J.*, 1929, 70, 1—10).—Twenty-two bands between 5737 and 7988 Å. are now arranged in a new system, the lower level of which is the same as that of the blue-green system. Evidence has been obtained of the presence of  $Q$ -branches in these bands, indicating that the transition is a  $^3P-^3S$ . The moment of inertia of the molecule in the  $^3S$ -state is estimated to be  $54.8 \times 10^{-40}$  g.-cm.<sup>2</sup>, and the corresponding nuclear separation is  $1.66 \times 10^{-8}$  cm. The heat of dissociation for the lowest level, with linear extrapolation, is 6.74 volts. The two systems are resonance systems of the TiO molecule. At 3300° Abs., the temperature at which the titanium bands persist in stellar spectra,  $p_{Ti} \cdot p_O / p_{TiO} = 10^{-3}$  atm., where  $p$  is the partial pressure. The partial pressure of oxygen in stellar reversing layers is estimated to be about  $10^{-6}$  atm.

L. S. THEOBALD.

**Structure of the cobalt spectrum.** III. M. A. CATALÁN (*Anal. Fis. Quím.*, 1929, 27, 832—845; cf. A., 1928, 338).—The previous work has been extended, and 70 new lines are recorded. The calculated minimum ionisation potential, i.e., the potential necessary for the separation of an electron of the  $3d^7 4s^2$  configuration when the other  $4s$  electron of the atomic residue occupies the  $3d$  position, is 7.8 volts.

H. F. GILLBE.

**Spectrum of trebly-ionised krypton.** D. P. ACHARYA (*Nature*, 1930, 125, 204).—Strong lines having  $\nu$  42,475.1 (10) and 40,560.3 (9) have now been observed in the spectrum of krypton; they are the  $^4P_3-^4D_4$  and  $^4P_2-^4D_3$  lines.

L. S. THEOBALD.

**Separations in hyperfine structure.** S. GORDSMIT and R. F. BACHER (*Physical Rev.*, 1929, [ii], 34, 1501—1506).—Theoretical. The separations in hyperfine structure are due to the interaction energy between the nuclear moment and the total extranuclear moment. The quantum mechanics of the spinning electron in an  $s$  state is applied to a consideration of the hyperfine structure separations of those configurations which involve a deeply penetrating  $s$  electron. Results are applied to these configurations of Cd I, Tl I, Tl II, La I, and La II.

N. M. BLIGH.

**Spectrum of ionised xenon (Xe II).** C. J. HUMPHREYS and T. L. DE BRUN (*Science*, 1928, 68, 573).—The probable classification of combinations of the xenon spectrum from the data of Abbink and Dorgelo (A., 1928, 338) is given. The doublet separation is 9621 cm.<sup>-1</sup>

L. S. THEOBALD.

**Interpretation of hyperfine structure in spectral terms.** H. E. WHITE (*Physical Rev.*, 1929, [ii], 34, 1404—1410; cf. following abstract).—The hyperfine structures in cadmium, bismuth, and lanthanum are interpreted; term analysis indicates that for cadmium, the fine structures of  $\lambda$  5086, 4800, and 4678 are due to isotopes. Some of the fine structure terms in bismuth and lanthanum are inverted, and an explanation of term inversion, based on the penetration of an  $s$  valency electron, is advanced.

N. M. BLIGH.

**Hyperfine structure in singly-ionised praseodymium.** H. E. WHITE (*Physical Rev.*, 1929, [ii], 34, 1397—1403; cf. A., 1929, 1207).—Wave-lengths and frequency separations of the fine structure of 173 spectral lines of Pr II are given; about 100 have been resolved into six components, and each group reveals a decrease in intensity and interval towards either longer or shorter wave-lengths, and follows closely the Landé interval rule. The quantum theoretical interpretation of the fine structure is deduced from the assignment of angular momentum  $5/2(h/2\pi)$  to the atomic nucleus.

N. M. BLIGH.

**Electric furnace spectrum of hafnium.** A. S. KING (*Astrophys. J.*, 1929, 70, 105—113).—The furnace, arc, and spark spectra of hafnium between 2640 and 6500 Å. have been photographed. In the carbon-tube furnace a temperature of 2600° is required to show any effective number of lines, whilst 2900—3000° is required for the neutral spectrum. 338 lines are classified and compared with Meggers' data (A., 1929, 112). Lines belonging to the ionised atom are apparently absent from the furnace spectrum. Two new bands with heads at 3236 and 4101 Å. are added to those given by Meggers (*loc. cit.*) for the arc spectrum. The whole band system is attributed to the oxide since it is shown only in the arc in air and not by the vacuum-furnace spectrum.

L. S. THEOBALD.

**Spectrum of ionised mercury hydride.** T. HORI (*Nature*, 1930, 125, 131).—The system of mercury hydride bands appears when an arc discharge between mercury and tungsten electrodes takes place at a low voltage (60—70 volts) in an atmosphere of 2 mm. of hydrogen. The bands in the extreme ultra-violet recorded by Jezevski (A., 1929, 8) are to be associated with ionised mercury hydride; they belong to a  $^1\Sigma \rightarrow ^1\Sigma$  system. The molecular constants are recorded.

L. S. THEOBALD.

**Series in the spectrum of radium emanation.** E. RASMUSSEN (*Naturwiss.*, 1930, 18, 84—85).—The arc spectrum of radium emanation has been investigated in the presence of argon and helium. Two strong lines, presumably the resonance lines, were observed in the Schumann region, at frequencies 55,997 and 68,889 ( $\Delta\nu=12,892$ ), corresponding with 6.905 and 8.494 volts, respectively. The infra-red, visible, and ultra-violet spectra were also photographed and many new lines observed. All the strongest terms are arranged in series which approach the same limits.

J. W. SMITH.

**Zeeman effect in doublet band spectra.** E. L. HILL (*Physical Rev.*, 1929, [ii], 34, 1507—1516; cf. A., 1929, 1076).—Theoretical. The Zeeman effect in doublet bands is investigated by the application of perturbation quantum mechanics to Hund's case ( $b$ ) for diatomic molecules. The magnetic terms are treated as a small correction to the coupling energy between the electron spin and orbital magnetic moments: the terms leading to a Paschen-Back effect are then included. A physical interpretation is discussed in relation to experiment.

N. M. BLIGH.

**Employment for spectrography of the extreme ultra-violet of gratings at grazing incidence.** M. DE BROGLIE (*Compt. rend.*, 1930, 190, 93—95;

cf. Thibaud, A., 1929, 225).—It is suggested that a crystal surface might serve as a (molecular) diffraction grating at grazing incidence for rays of very short wave-lengths. Dempster has apparently effected the diffraction of protons by this means.

C. A. SILBERRAD.

**Spectral phenomena in spark discharges.** J. W. BEAMS (Physical Rev., 1930, [ii], 35, 24—33; cf. A., 1926, 1069).—The differences in the time of appearance of the spectrum lines in sparks was measured by two methods: (1) the Kerr cell method dependent on the rapid disappearance of the Kerr effect in some liquids after the electric field producing it is relaxed; (2) Henriot's method (cf. J. Phys. Radium, 1927, [vi], 8, 443) for the rapid rotation of a mirror which either reflects the dispersed light of the spark to a photographic plate or the undispersed light to the slit of a spectrograph, the position of the beginning of a line on the plate giving its time of appearance. The second method was most suitable for studying the appearance and duration of the metallic lines not present in the earliest stages of the spark discharge, and the Kerr method for the air lines in the initial stages of the spark.

N. M. BLIGH.

**Stark effect and polarisation.** R. WIERL (Naturwiss., 1930, 18, 86).—The recent observations of Stark (this vol., 263) are discussed in connexion with the views of the author (cf. A., 1929, 367, 963, 1354).

J. W. SMITH.

**Spectrum of the solar corona.** R. MECKE and R. WILDT (Z. Physik, 1930, 59, 501—507).—The origin of the corona spectrum may possibly be explained on the basis of the Raman effect. This point of view is here considered, but no positive answer is reached. It seems possible, however, to explain the absorption-less continuum of the inner corona on the basis of the Raman effect.

A. J. MEE.

**Thermal excitation of atoms in the reversing layer of the sun.** A. UNSÖLD (Astrophys. J., 1929, 69, 322—329).—By means of photometric measurements of the contours of a Fraunhofer line, the number of atoms in a particular state of excitation lying above 1 cm.<sup>2</sup> of the photosphere, multiplied by the oscillatory power of the line, has been determined. The data thus obtained from Ca<sup>+</sup> and Ba<sup>+</sup> show that for excitation potentials below 1.7 volts Boltzmann's relation holds. An upper limit for the transition probability of the forbidden Ca<sup>+</sup> lines 4<sup>2</sup>S—3<sup>2</sup>D is derived, and the lifetime of the metastable 3<sup>2</sup>D state must be greater than 10<sup>-2</sup> sec. L. S. THEOBALD.

**Stellar calcium lines in spectral types A and B.** O. STRUVE and C. D. HIGGS (Astrophys. J., 1929, 70, 131—134).—The contour of the K line of Ca<sup>++</sup> has been determined in four class A stars; in only one case does the contour agree with the requirements of Unsöld's formula. The total numbers of atoms in the reversing layer have also been determined for many stars; the values range from 4 × 10<sup>16</sup> for type A2 to 3 × 10<sup>15</sup> for type B5. L. S. THEOBALD.

**Composition of the sun's atmosphere.** H. N. RUSSELL (Astrophys. J., 1929, 70, 11—82).—A survey, and a discussion of existing evidence concerning the relative abundance of elements showing lines in the

solar spectrum. The energy of binding of an electron in different quantum states is discussed for neutral atoms of atomic numbers 1—39 and for singly-ionised atoms of atomic numbers 2—32. The energy of binding for an electron in a given state increases with the atomic number and the increase of energy is most rapid when electrons are being added to complete a shell and when *s* electrons are being added. The characteristics of the spectra of the elements present are discussed and the ionisation potentials and most persistent lines are tabulated. The excitation potential, *E*, for the strongest lines in the observable part of the spectrum is the main factor; almost all the elements for which this is small appear in the sun and there are few solar lines for which *E* > 5 volts, the only strong ones being those of hydrogen. Using the calibration of Rowland's scale previously developed (*ibid.*, 1928, 68, 1) and Unsöld's investigations (A., 1928, 456) the abundance of various elements in the sun's atmosphere is calculated. The numbers of atoms in the more important energy states for each element are determined and are found to decrease with increased excitation, but somewhat more slowly than is demanded by thermodynamical considerations. The level of ionisation in the solar atmosphere is such that atoms of 8.3 volts ionisation potential are 50% ionised.

Tables of the relative abundance of 56 elements and 6 compounds show that sodium, magnesium, silicon, potassium, calcium, and iron form 95% of the whole mass. The number of metallic atoms above 1 cm.<sup>2</sup> of the surface is 8 × 10<sup>20</sup>, and 80% of these are ionised. The mean at. wt. is 32 and their total mass 42 mg./cm.<sup>2</sup> The elements of even atomic number are ten times as abundant as those of odd atomic number. The hypothesis that the heaviest atoms sink below the photosphere is not confirmed. The metals from sodium to zinc, inclusive, are far more common than any others. Compounds are present only in small amounts, cyanogen being rarer than scandium, and the presence of band lines due to C<sub>2</sub>, CH, CN, NH, and BO constitutes the chief evidence for the existence of carbon, nitrogen, and boron in the sun. Most of the elements which are absent should not show observable lines unless their abundance is much greater than is probable. The possibility of discovering faint lines of some additional rare earths and heavy metals, as well as of boron and phosphorus, still exists. The abundance of the non-metals, especially of hydrogen, is difficult to estimate from the scanty data available, but the solar atmosphere appears to contain 60 parts of hydrogen (by volume), 2 of helium, 2 of oxygen, 1 part of metallic vapour, and 0.8 of free electrons. The estimated temperature of the reversing layer is 5600° and the pressure at its base is 0.005 atm.

L. S. THEOBALD.

**Spectrum of B.D.+11° 4673.** P. W. MERRILL (Astrophys. J., 1929, 69, 330—378).—The spectrum of this star exhibits bright lines of H, He, Fe II, Al II, Al III, N II including two forbidden lines, Si I (?), Si II, Si III, Ti II, Cr II, Mg II, C II (?), and Sc II (?). The iron spectrum includes some forbidden lines. The lines of this star vary both in position and intensity.

L. S. THEOBALD.

**New types of emission spectra.** L. VEGARD (Naturwiss., 1930, 18, 67—68).—Study of the luminescence of solidified gases has shown the existence of a new type of spectrum due to the combination of electron switches and atomic oscillations. It is a type of vibrational band spectrum uninfluenced by rotation. A number of spectra of this type have been investigated. The majority of series are not made up of single lines, but of two or more components, the splitting being more noticeable at the temperature of liquid helium than at that of liquid hydrogen. This multiplicity of lines does not depend on rotation energy, and the first explanation was based on a decomposition of the electron terms. Series with quite different electron terms and different principal vibration series show the same frequency difference between successive components. The separation is in some cases ten to fifteen times as large as that corresponding with the fundamental frequency of molecular rotation. It is shown that probably the force which binds the molecules in the crystal lattice and is closely bound up with the elastic forces of the crystal makes a molecule with oscillating atoms vibrate itself. As the distance between the molecules in the lattice is much greater than that between the atoms in a molecular element, the inner condition of the molecule will exert little effect on the molecular vibration. Hence the separation of lines in series derived from molecular oscillations will be nearly the same irrespective of the inner condition of the molecular elements.

A. J. MEE.

**Indefinite characteristic spectra.** E. SCHRÖDINGER (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 668—682).—Theoretical. The treatment of wave mechanics is applied to unidimensional point motion, and in particular an extended spectrum is investigated. All so-called discrete characteristic spectra are really "almost" discrete, the former being an ideal case.

A. J. MEE.

**K-Absorption edges in X-ray spectrum.** H. T. MEYER (Naturwiss., 1930, 18, 34).—With bromates, structure lines which are absent in bromides are shown at the bromine absorption edge. The energy difference between the principal absorption edge and the shortest wave-length structure line reaches the high value of 240 volts. Very similar results are obtained with arsenates and selenates. Zinc sulphide gave no structure of the K-absorption edge, nor did rubidium carbonate and strontium nitrate. Yttria showed a bright absorption line on the short-wave side of the K-absorption edge, but no dark line, as in the bromates, selenates, and arsenates. Zirconium nitrate and oxychloride both exhibited a bright and a dark line, the difference in wave-length between the principal edge and the dark line being the same for both compounds. Niobium compounds indicated a very weak dark line. Molybdenum trioxide gave no certain evidence of structure. R. A. MORTON.

**Form of the X-ray diffraction bands for regular crystals of colloidal size.** C. C. MURDOCK (Physical Rev., 1930, [ii], 35, 8—23).—Theoretical. The form of the diffraction bands of a fine uniform crystalline powder was computed for the (1,0,0), (1,1,0), and (1,1,1) planes for regular cubical and

octahedral crystals and found to be approximately that of the Gauss error curve, the shape and half-intensity breadth varying from band to band characteristically with the shape of the crystals. There is a correlation between the form of the band and the direction of the corresponding Bragg planes with respect to the external features of the crystal.

N. M. BLIGH.

**Scattering of X-rays by gases.** G. HERZOG (Helv. phys. Acta, 1929, 2, 169—216; Chem. Zentr., 1929, ii, 1379).—A new method for measuring the distribution of intensity is described, and the results of experiments with argon are recorded.

A. A. ELDRIDGE.

**Raman effect in the X-ray region.** A. CARRELLI (Nature, 1930, 125, 201—202).—Theoretical. In order to observe this effect it is necessary to use substances presenting semi-optical lines, and of low atomic number, and to use wave-lengths, directions of observations, and substances for which the ratio  $E_e/|E_\mu|$  is very high, where  $E_e$  is the kinetic energy of the electron emitted for the Compton effect in a particular direction of observation and for a given exciting frequency, and  $E_\mu$  is the energy of the K level if the jump is  $K \rightarrow 1s$ . L. S. THEOBALD.

**Photometric determination of relative intensities in the  $\beta$  group in the L-spectrum of tungsten.** W. H. LOVE (Med. J. Austral., 1929, 2, 246).—For homogeneous radiations of wave-lengths corresponding with those in the  $L\beta$  group of tungsten the relation between the photographic density of the line and the intensity of the radiation is linear when the time of exposure is constant and the density small. The relative intensities of the strongest four lines were evaluated.

CHEMICAL ABSTRACTS.

**Ionisation and dissociation processes in gases.** H. KALLMANN and B. ROSEN (Physikal. Z., 1929, 30, 772—773).—See this vol., 16.

**Ionisation potential of atomic configurations with two electrons.** E. A. HYLLEAAS (Naturwiss., 1929, 17, 982).—The earlier calculation of the ionisation potential of helium (cf. A., 1928, 698; 1929, 616) has been applied to the results recently obtained by Edlén for the ionisation potential of  $Li^+$  and  $Be^{++}$  (A., 1929, 1350). The theoretical values are compared with Edlén's experimental values.

G. E. WENTWORTH.

**Ionisation potential of atomic configurations with two electrons.** G. W. KELLNER (Naturwiss., 1930, 18, 86).—A claim for priority over Hylleraas (preceding abstract). The ionisation potentials of the configurations He,  $Li^+$ ,  $Be^{++}$ ,  $B^{+++}$ , and  $C^{++++}$  had previously been calculated by Kellner using a similar method (cf. A., 1927, 912).

J. W. SMITH.

**Detection of excitation potentials of various spectra in gaseous discharge.** E. LAU and O. REICHENHEIM (Naturwiss., 1930, 18, 86—87).—A method is described whereby the excitation potentials of different spectral lines can be determined by observation of the spectra in various regions of the positive column and the Faraday dark space of a gaseous discharge tube, with and without the addition of a gas of lower ionisation potential than the gas

under investigation. Illustrations of the application of this method are given. J. W. SMITH.

**Emission of electrons from conductors under intense fields.** P. W. BRIDGMAN (Physical Rev., 1929, [ii], **34**, 1411—1417; cf. A., 1928, 213, 682).—Theoretical. The current drawn from metals by intense fields produced by the Volta *P.D.* between two metals is discussed thermodynamically, using the classical concept of the electron, and modifications required by the wave mechanical picture are examined. Expressions are given for the change in heat of evaporation of electrons and in the photo-electric threshold efficiency produced by intense fields in terms of a slight change of Volta difference.

N. M. BLIGH.

**Effect of light on the electron emission from oxide-coated filaments.** K. NEWBURY (Physical Rev., 1929, [ii], **34**, 1418—1425; cf. Crew, A., 1927, 85).—The increase in electron emission from oxide-coated platinum filaments when light is focussed on them was studied as a function of applied potential, filament temperature, and wave-length of the incident light. The effect was zero at zero applied field and reached a saturation value at from 2 to 10 volts, depending on the thickness of the oxide coating. At an applied potential giving saturation the effect reached a maximum at a filament temperature of about 1000° and then decreased. The long wave-length limit of the effect was about 4000 Å.; there is a sharp increase in sensitivity for wave-lengths less than about 2500 Å. Results can be explained on the assumption that the normal photo-electric emission so modifies the distribution of the intrinsic surface field as to alter the effect of the externally applied field on the work function of the surface.

N. M. BLIGH.

**Investigations on secondary emission.** K. SIXTUS (Ann. Physik, 1929, [v], **3**, 1017—1054).—The emission of secondary electrons at the anode of technical tubes with different cathode materials has been studied. The differences in secondary emission arise from changes in the condition of the anode following volatilisation of the cathode material. The geometrical arrangement of electrodes affects the results. Striking irregularities in the course of the anode characteristic between 0 and 10 volts in tubes with oxide-equipotential cathodes probably arise from selective absorption and reflexion in the electrode surface. The measured contact *P.D.* between tungsten and thoriated tungsten is about 10% smaller than the difference in the work of escape for the two materials. The magnitude of the secondary emission is independent of the temperature of the emitting substance over a wide range. Whilst the primary emission of a tungsten wire is increased 10<sup>5</sup> times when it is thoriated, the secondary emission or the secondary yield is increased by not more than 20%. The high characteristic velocity of the secondary electrons accounts for smallness of the increase, a small reduction in the work of escape making no important difference. By assuming Maxwellian velocity distribution of secondary electrons (the data show approximate agreement), the mean velocity of the secondary electrons of metals is calculated. The

measurements concerning electrodes carrying a layer of oxide disclose no clear relationship between work of escape and the strength of the secondary emission.

R. A. MORTON.

**Electron velocities in a high-frequency discharge in hydrogen.** C. J. BRASEFIELD (Physical Rev., 1930, [ii], **35**, 92—97; cf. A., 1929, 1115).—The mean velocity of the electrons in a high-frequency discharge in hydrogen, obtained by applying undamped high-frequency voltages to the movable electrodes of a cylindrical tube, was determined from the ratio of the densities of certain singlet and triplet lines of the molecular spectrum of hydrogen. It was found that the electron velocity increases with rise of voltage at constant gas pressure and oscillation frequency, is greater the longer is the wave-length of oscillation at given voltage, and decreases as the pressure is increased. The mechanism of the discharge is discussed and an explanation of its behaviour is proposed.

N. M. BLIGH.

**Ionisation of alkali atoms by slow electrons.** H. FUNK (Ann. Physik, 1930, [v], **4**, 149—184).—The question of ionisation-sharing for ionisation brought about by collision of slow electrons is dealt with. An apparatus for the determination of the sharing is described. The substances investigated were sodium and potassium, which were obtained in the form of an atomic radiation. An electron beam of approximately uniform velocity was directed perpendicularly to the atomic radiation, and the primary electron current and the resulting ionic current were measured. From these quantities the sharing can be calculated. The sharing can be given on the one hand as a cross-section in cm.<sup>2</sup>/cm.<sup>3</sup>, by analogy with a Ramsauer cross-section, or as a percentage. The experiments show a maximum effect in the neighbourhood of twice the ionisation potential. The value obtained for sodium was 29 cm.<sup>2</sup>/cm.<sup>3</sup>, and for potassium 11 cm.<sup>2</sup>/cm.<sup>3</sup>. This is in agreement with the theory of Sir J. J. Thomson on ionisation by electron collision, and the theoretical values are 54% for sodium and 50% for potassium. There is thus also agreement as regards the relative size of the effect for the two metals, but the difference between the values is different.

A. J. MEE.

**Effect of light on the electron emission from cerium dioxide.** C. E. BERGER (Physical Rev., 1929, [ii], **34**, 1566—1574; cf. Crew, A., 1927, 85).—An increase in photo-emission with rise of temperature was found for calcium iodide, calcium oxide, thorium oxide, and cerium oxide on platinum, calcium oxide and cerium oxide on tungsten, and cerium oxide on nichrome. No effect was found for barium iodide on platinum and zirconium oxide on tungsten. For cerium dioxide on platinum at about 1000° the photo-emission varied linearly with the intensity of the ultra-violet light; wave-lengths above 3000 Å. were not effective. Air, hydrogen, or oxygen in small amounts caused a decrease in the photo-emission. The saturation photo-currents showed an increase with rise of temperature. The explanation of results as a variation of the true photo-electric effect or as due to some cause such as change of surface by bombardment is discussed.

N. M. BLIGH.

**Scattering of positive lithium ions in mercury vapour.** I. W. COX (Physical Rev., 1929, [ii], 34, 1426—1437).—An apparatus giving a high-speed vacuum system constantly flushed with mercury vapour is described. The number of positive lithium ions passing through a fixed distance was observed with different mercury vapour pressures. Kennard's method (cf. A., 1928, 453) giving curves showing the variation of the electrometer current with magnetic field current for a particular pressure, and a second method using two coaxial Faraday cylinders and added collimating slits in front of the absorption chamber, were used. The rate of absorption depended on the aperture of the apparatus, indicating that the absorption is largely due to small angle scattering of the ion at a collision with a mercury atom, and incompatible with elastic collision scattering.

N. M. BLIGH.

**Secondary electrons of high velocity from metals bombarded with cathode rays.** P. B. WAGNER (Physical Rev., 1930, [ii], 35, 98—106).—The work of Stehberger (A., 1928, 1069) and Lorenz (A., 1929, 14) is discussed critically, and to investigate further the secondary emission process, the magnetic spectra of high-speed secondary electrons emitted by gold, silver, and aluminium when bombarded by cathode rays of from 16 to 40 kilovolts were photographed and densitometer graphs obtained. From the high-velocity end the density is zero down to the energy  $eV_0$ , equal to that of a primary ray, then rises rapidly to a maximum at about  $0.94eV_0$  for gold or silver and  $0.85eV_0$  for aluminium, and then decreases. The density is continuous, but there is apparently a discontinuity in the first derivative in every spectrum at the high-velocity end, and occurring at a velocity equal to that of the primary cathode rays. The resemblance of spectra for thin and thick targets indicates that most of the secondary electrons come from very near the surface. N. M. BLIGH.

**Ions produced by discharges at liquid surfaces.** J. J. NOLAN and J. G. O'KEEFE (Proc. Roy. Irish Acad., 1929, A, 39, 21—30).—Chattock's method (Phil. Mag., 1899, 48, 401) can be applied to measure the mobilities of the ions concerned in the discharge from liquid surfaces. The mobilities observed show that these ions are of the same character as the ordinary small ions produced by discharge at a metal point or by the ionising radiations. The observation of Tyndall and Phillips (A., 1926, 877) that in air saturated with *n*-butyl or *n*-amyl alcohol at the ordinary temperature, the mobility of the positive ion is greater than that of the negative ion is confirmed.

R. A. MORTON.

**Crucial experiment on diffusion of electrons.** F. DACOS (Bull. Acad. roy. Belg., 1929, [v], 15, 452—460).—The calibration and arrangement of the apparatus are described. Electrons accelerated at 360 volts pass in a parallel pencil between two slits, then pass through a V-shaped slit and impinge on a photographic plate. The influence of a magnetic field on the results is discussed. W. R. ANGUS.

**Radiation of free electrons in a Coulomb field.** J. A. GAUNT (Z. Physik, 1930, 59, 508—513).—Mathematical. An error in Oppenheimer's recent

work on the subject is pointed out. When corrected this leads to a smaller deviation from Kramers' theory than was previously the case. A. J. MEE.

**Intensity of electron interference.** F. KIRCHNER (Naturwiss., 1930, 18, 84).—The order of magnitude of the influence of the electron shell on the nuclear scattering by gold atoms can be estimated if the electron shell be assumed to be, as a whole, like that of hydrogen. On this basis wave-mechanical calculations lead to a value of the scattering intensity expressed approximately by the wave function  $1/(\sin^2 \theta/2 + \alpha^2)^2$  instead of  $1/\sin^4 \theta/2$  ( $\alpha = \lambda/2\pi r$ ;  $\lambda = h/mv$ , the De Broglie electronic wave-length;  $r$  = the "mean radius" of the electron shell). If  $\alpha = 0.02$  and  $\lambda = 7 \times 10^{-10}$  cm. this equation agrees well with the results of Thomson (A., 1929, 1209) and corresponds with a "mean radius" of the electron shell of about  $0.5 \text{ \AA}$ . J. W. SMITH.

**Collision between two electrons.** N. F. MOTT (Proc. Roy. Soc., 1930, A, 126, 259—267).—Mathematical. The exclusion principle is applied to the problem of the collision between two particles possessing spin (e.g., electrons), and also between two particles without spin (e.g.,  $\alpha$ -particles). Assuming an inverse square law between the particles and neglecting the actual spin forces, a scattering law, differing considerably from that of the classical theory, is deduced from the symmetry properties of the wave functions. Some experimental evidence in favour of the theory is advanced.

L. L. BIRCUMSHAW.

**Effective cross-section of non-inert-gas molecules with respect to electrons below 1 volt.** C. RAMSAUER and R. KOLLATH (Ann. Physik, 1930, [v], 4, 91—108).—Methods already applied to the inert gases have been extended to hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, and methane. Cross-section/volt<sup>1/2</sup> curves for velocities down to 0.16 volt have been obtained. The curves for nitrogen and carbon monoxide are similar, whilst the methane curve resembles that of argon and of krypton, the resemblances extending over the range 0.16—36 volts. The similarity between hydrogen and helium does not extend into the region below 1 volt. Some of the curves indicate increasing cross-section as the electron velocity decreases from 1 to 0.16 volt; in others the reverse is the case, but the existence of a very sharp minimum in oxygen at 0.24 volt demonstrates the risk involved in extrapolation towards zero velocity. The influence of the gas on photo-electric emission is vanishingly small for nitrogen, hydrogen, carbon monoxide, and carbon dioxide, considerable for methane, and very strong for oxygen. R. A. MORTON.

**Report of the German Commission on atomic weights.** X. M. BODENSTEIN, O. HAHN, O. HÖNIGSCHMID, and R. J. MEYER (Ber., 1930, 63, [B], 1—24).—The report is drawn up on the same lines as its predecessors (cf. A., 1929, 232). No change is made in the table of practical atomic weights except that  $\text{Re} = 188.7$  is introduced. H. WREN.

**Arithmetical relation between at. wt. and atomic number.** G. FOURNIER (Compt. rend.,

1930, 190, 118—119; cf. A., 1929, 863).— $p_n$  is plotted against  $p_n + i_n$  as abscissa, where  $p_1, p_2, \dots$  are the odd prime numbers 1—59, and  $i_1, i_2, \dots$  the odd numbers 1—33;  $p_{17} + i_{17}$  thus = 92, the atomic number of uranium. On the same scale  $A/4$ , where  $A$  is the number of protons in successive elements, is plotted against  $N$ , the corresponding atomic number, each isotope being separately indicated. The two curves are nearly coincident.

C. A. SILBERRAD.

**Vibrational quantum analysis and isotope effect for the lead oxide band spectra.** S. BLOOMENTHAL (Physical Rev., 1930, [ii], 35, 34—45).—Measurements were made of the wave-lengths of the band heads from moderate-dispersion spectrograms of the lead arc in air, and from high-dispersion spectrograms taken with a lead arc and with a uranium-lead arc. Each strong line ( $\text{Pb}^{206}\text{O}$ ) in the band spectrum from the uranium-lead arc is represented by three lines ( $\text{Pb}^{208, 207, 206}\text{O}$ ) in the band spectrum from the lead arc with relative intensities in agreement with Aston. Corresponding band line separations of isotopic molecules are in good agreement with the isotope effect theory with  $\text{PbO}$  as the emitter. Vibrational quantum analysis gives an expression for a new band system  $D$  in the region 3209—3594 Å. The systems  $A, B$ , and  $C$  (very weak), all having a common lower state, are discussed. N. M. BLIGH.

**Fine structure analysis of the bands in the  $A$  and  $D$  systems of lead oxide.** A. CHRISTY and S. BLOOMENTHAL (Physical Rev., 1930, [ii], 35, 46—50; cf. preceding abstract).—Theoretical. The bands of the  $A$  and  $D$  systems are composed of single  $R$  and  $P$  branches only; the rotational constants of the molecule are determined by application of the combination principle. The nuclear separation of the common final state is found to be  $1.9207 \times 10^{-8}$ , that of the upper state of  $A$ ,  $2.0927 \times 10^{-8}$ , and of  $D$ ,  $2.0424 \times 10^{-8}$  cm. No  $Q$  branches have been found for the two systems, the electronic levels of which are singlets. The electron states involved are probably all  $^1\Sigma$  states.

N. M. BLIGH.

**Isotopy.** A. VAN DEN BROEK (Arch. Néerland., 1929, [iii A], 12, 143—146; cf. A., 1920, ii, 540; 1921, ii, 295).—An elaboration of the author's views on isotopy. Atoms with even atomic number and mass number divisible by 4 are regarded as normal, intermediate members of the series are abnormal ("polytopes") and interabnormal ("interpolytopes").

C. A. SILBERRAD.

**Application of adiabatic microcalorimeter to measurements of the heats of radiation of uranium, thorium, and radioactive minerals.** A. DORABIALSKA (Bull. Acad. Polonaise, 1929, A, 487—496).—See A., 1929, 1358.

**Status of the  $\gamma$ -ray change.** N. FEATHER (Physical Rev., 1929, [ii], 34, 1558—1565).—Theoretical. The work of Jacobsen (cf. A., 1928, 104) is considered in connexion with the view that the emission of  $\gamma$ -rays in radioactive disintegration is subsidiary to the ejection of the  $\alpha$ - or  $\beta$ -particle from the nucleus, and is shown to imply that the emission of a quantum of  $\gamma$ -radiation between the  $\beta$ -particle disintegration of radium- $C$  and the  $\alpha$ -par-

ticle disintegration of radium- $C'$  is essential. The difficulties attending this condition are discussed. An attempt is made to connect the complexity of the "normal"  $\alpha$ -radiation of thorium- $C$  and the emission of long-range  $\alpha$ -particles from radium- $C$  and thorium- $C$  with the occurrence of certain lines in the  $\gamma$ -ray spectra of these elements. N. M. BLIGH.

**Passage of "fast"  $\beta$ -particles through gases.** E. J. WILLIAMS and F. R. TERROUX (Proc. Roy. Soc., 1930, A, 126, 289—309).—The Wilson cloud method is applied to an investigation of phenomena representing loss of energy by fast  $\beta$ -particles in oxygen and in hydrogen. A radioactive source of high-speed  $\beta$ -particles, with energy varying from about 100 to 1500 kilovolts, is used, and the phenomena investigated include the primary ionisation, the frequency of production of branches, and the momentum relations in branch collisions. The results indicate that the classical theory gives only the order of magnitude of the observed effects. For both the primary ionisation and the frequency of branch production the observed values are much greater than the classical theoretical values, and vary with the velocity according to a different law. In both cases the ratio of the observed to the theoretical value decreases with decreasing velocity, and for "slow"  $\beta$ -particles the number of branches may be equal to or less than the classical number. If it is assumed that an electron has a magnetic moment equal to one Bohr magneton, then the classical calculations for the theoretical number of branches gives values of a different order of magnitude from those observed, and from the actual ratios of the observed and calculated numbers it is inferred that the maximum magnetic moment is considerably less than a Bohr magneton. Observations are described which show that the deflexion of fast  $\beta$ -particles due to the production of branches corresponds approximately with the ratio of the momentum of the branch to that of the  $\beta$ -particle.

L. L. BIRCUMSHAW.

**Radioactive disintegration of potassium.** O. HÖNIGSCHMID (Nature, 1930, 125, 91).—The methods and data of Frost and Frost (this vol., 130) are considered to be insufficiently trustworthy to permit conclusions concerning the formation of calcium isotopes from potassium to be reached.

L. S. THEOBALD.

**Scattering of  $\alpha$ -particles by light atoms.** A. C. BANERJI (Nature, 1930, 125, 167—168).—An expression for scattering of  $\alpha$ -particles giving good agreement with the results obtained by Rutherford and co-workers has been obtained by using the law  $F = Ze^2/r^2 - \mu/r^n$  when  $n=3$ . The assumption of the same law in Schrödinger's equation permits the calculation of the "Eigenwerte" of  $\alpha$ -particles in the nucleus; positive and negative values result and the former explain the  $\gamma$ -radiations of the six radioactive elements which so far have been accurately measured.

L. S. THEOBALD.

**Effect of solar radiation on radioactive phenomena and transmutation.** (MLLE.) S. MARACINEANU (Bull. Acad. Sci. Roumaine, 1929, 12, 5—9).—Lines characteristic of mercury have been found in the spectrum of lead which has been exposed to sun-



light. Solar radiation can cause the transmutation of 0.001% of lead into gold. C. W. GIBBY.

**Supposed transmutation of lead by sunlight.** C. FABRY and E. DUBREUIL (Compt. rend., 1930, 190, 91).—The experiments described by Maracineanu (cf. preceding abstract) as resulting in the formation of gold, mercury, and helium from lead by prolonged exposure to sunlight have been repeated with old roof lead. No trace of any such transmutation was found. C. A. SILBERRAD.

**Quantum mechanics of  $\alpha$ -radiation.** T. SEXL (Z. Physik, 1930, 59, 579—582).—Mathematical.

**Anode spots and their relations to the absorption and emission of gases by the electrodes of a Geissler discharge.** C. H. THOMAS and O. S. DUFFENDACK (Physical Rev., 1930, [ii], 35, 72—91).—An investigation was made of the anode spots into which the anode glow breaks up in a Geissler discharge containing hydrogen, nitrogen, carbon monoxide, and mixtures of hydrogen or mercury vapour with the rare gases, but not oxygen, argon, or neon. One electrode was allowed to serve as a cathode for a given time, during which it absorbed gas through positive ion bombardment; the polarity of the electrodes was then reversed. Spots formed on iron, nickel, aluminium, copper, brass, and mercury; a necessary condition for their formation was found to be the emission of gas from the anode surface. Conditions governing the size, number, and duration of the spots were determined. It is concluded that their formation and existence depend on the joint action between the gases released from, and the electron stream to, the anode, and that they are manifestations of a splitting up of the electronic current into discrete "rays" or current-beams. An explanation of their formation is advanced. It is shown that in a Geissler discharge between cold electrodes, the cathode absorbs and the anode emits gas at rates which are functions of the current density, gas pressure, kind of gas, and electrode temperature.

N. M. BUGH.

**Charging of small suspended particles in the corona discharge.** H. SCHWEITZER (Ann. Physik, 1930, [v], 4, 33—48).—The number of elementary charges carried by droplets of paraffin oil of radius  $2-5 \times 10^{-5}$  cm. in a corona discharge of  $1-2 \times 10^{-6}$  A. varies between 20 and 100 for the large majority of the particles. A small percentage of highly charged particles is observed, the number of elementary charges being 42 for droplets of radius  $2.44 \times 10^{-5}$  cm. and 694 when the radius is  $6.3 \times 10^{-5}$  cm. The normal values are in good agreement with the calculations of Arendt and Kallmann (Z. Physik, 1926, 35, 421), whilst the small proportion of highly charged particles possess values approaching the extrapolated maximum values arrived at by Deutsch (Z. tech. Physik, 1926, 17, 628) for cigarette smoke.

R. A. MORTON.

**Stern-Gerlach experiment with active nitrogen.** L. C. JACKSON (Nature, 1930, 125, 131).—The presence of the  $^2P_{\frac{1}{2}}$  state in active nitrogen is considered to be established by an analysis by the Stern-Gerlach method of a stream of nitrogen,

activated by means of a condensed electrical discharge. L. S. THEOBALD.

**Peculiar behaviour of nitrogen on ionisation by X-rays.** K. BRUMMER (Strahlenther., 1929, 32, 759—760; Chem. Zentr., 1929, ii, 1628).—Of the gases examined, only with nitrogen was the ionisation affected by the velocity of passage of the gas. With increasing velocity the ionisation rose to a maximum value, then diminished somewhat to constant value.

A. A. ELDRIDGE.

**Quantum mechanics of chemical reactions: predissociation and unimolecular decompositions.** O. K. RICE (Physical Rev., 1929, [ii], 34, 1451—1462; cf. A., 1929, 734, 1016).—Theoretical. The processes of activation, reaction of the activated products, and deactivation in a chemical change can be described quantum mechanically, and are illustrated by consideration of the predissociation of diatomic molecules activated by light. The wave function immediately after the excitation can be described as the wave function of a discrete state which interacts with a continuum. Wentzel's calculation of the rate of dissociation can be applied with some limitations which are discussed. Predissociation and unimolecular decompositions of complex molecules are compared, and the difficulties of theoretical treatment in the latter case are considered; although the perturbations giving rise to the decompositions are of the same nature, there will be many intermediate states before the final state of the molecule is reached, and the perturbations cannot be put into the same equation to give the rate of reaction. The decomposition of azomethane is considered.

N. M. BUGH.

**Theory of electrons and protons.** P. A. M. DIRAC (Proc. Roy. Soc., 1930, A, 126, 360—365).—The relativity quantum theory of an electron moving in a given electromagnetic field involves the difficulty that the wave equation has, besides the wanted solutions referring to positive kinetic energy, an equal number of solutions for negative kinetic energy of the electron, which appear to have no physical meaning. The fact that an electron with negative energy can be shown to move in an external field as though it carried a positive charge has led to the suggestion that a close connexion exists between the negative-energy electron and the proton. The view, however, that a negative-energy electron is a proton would lead to a number of paradoxes. Accordingly, a new theory is now advanced which postulates only one fundamental kind of particle instead of electron and proton. It is assumed that protons are simply holes in the distribution of negative-energy electrons, and that when an electron of positive energy drops into a hole and fills it up, an electron and a proton disappear together with emission of radiation. The problem of the scattering of radiation by an electron, free or bound, is considered in the light of the above ideas.

L. L. BIRCUMSHAW.

**Test of quantum mechanics of hydrogen by measurements of absorption in the Balmer series.** J. L. SNOEK, jun. (Arch. Néerland., 1929, [iii A], 12, 164—204).—A more detailed account of work previously published (cf. A., 1928, 1293).

Measurements of the absorption of  $H_\alpha$ ,  $H_\beta$ , and  $H_\gamma$  are recorded. The results obtained are in satisfactory agreement with the theoretical considerations advanced. C. A. SILBERRAD.

**Probability of the simultaneous action of two light quanta in one elementary process.** (FRL.) M. GÖPPERT (Naturwiss., 1929, 17, 932).—A probability calculation. H. F. GILLBE.

**Theory of intermittent action and infra-red band spectrum.** K. C. KAR and B. BISWAS (Z. Physik, 1930, 59, 570–572).—Mathematical. The theory of intermittent action previously put forward is here applied to the problem of the anharmonic oscillator and leads to the well-known formula for the infra-red band spectrum. A. J. MEE.

**X-Ray search for the origin of ferromagnetism.** J. C. STEARNS (Physical Rev., 1930, [ii], 35, 1–7).—With the object of ascertaining whether inner-orbit electrons are responsible for ferromagnetism, a sensitive null method employing two crystals and two ionisation chambers was used to detect any change in intensity of an X-ray beam reflected from a crystal of magnetite or silicon steel when magnetised. Although the sensitivity was several times that theoretically necessary, no change was observed. Results indicate that the spinning electron and not an orbital electron should be identified with the ultimate magnet. N. M. BLIGH.

**Gibbs-Ewald reciprocal lattice.** A. L. PATTERSON (Nature, 1930, 125, 238).—A simple analytical expression for defining this lattice is developed.

L. S. THEOBALD.

**Correct formulation of Pauli's exclusion principle.** J. FRENKEL (Nature, 1930, 125, 235–236).—Theoretical. The usual statement of this principle as applied to the two-electron or two-proton system is incorrect. L. S. THEOBALD.

**Influence of foreign gases on the absorption spectrum of nitric oxide.** M. LAMBREY (Compt. rend., 1930, 190, 261–263; cf. A., 1929, 1363).—The increase in absorption of nitric oxide due to the presence of non-absorbing foreign gases may be expressed by  $f(\pi/p) = k'(\pi/p)^{0.90}$ , where  $\pi$  and  $p$  are the respective pressures of the mixture and of the foreign gas, and  $k'$  has the values for hydrogen 0.69, nitrogen 0.87, argon 0.91, and carbon dioxide 0.87. This function was deduced for the (0,0) band of the  $\gamma$ -system from measurements of the pressure required to give the same optical density in pure nitric oxide under the same conditions as in the mixture. A similar study of the equilibrium  $2NO_2 \rightleftharpoons 2NO + O_2$  showed that the presence of nitrogen dioxide, an absorbing gas, increases the optical density of nitric oxide. J. GRANT.

**Existence of two limits of pre-dissociation in the nitrogen peroxide molecule and the heat of dissociation of oxygen.** V. HENRI (Nature, 1930, 125, 202).—In the absorption spectrum of nitrogen peroxide vapour the first limit of pre-dissociation occurs between 3800 and 3700 Å., whilst that of the second limit occurs between 2450 and 2200 Å. These limits correspond with the two limits of dissociation of the nitrogen peroxide molecule into nitric oxide

and a normal or an activated oxygen atom. The corresponding energies are  $NO_2 \rightarrow NO + O - 77,000$  g.-cal. (3700 Å.) and  $NO_2 \rightarrow NO + O^* - 116,000$  g.-cal. (2459 Å.), from which the calculated heat of dissociation of the oxygen molecule is  $-128,000$  g.-cal. and the heat of activation of an oxygen atom is  $-39,000$  g.-cal. L. S. THEOBALD.

**Colours of inorganic salts.** M. N. SAHA (Nature, 1930, 125, 163–164).—An hypothesis to explain the colours of inorganic salts is advanced and is illustrated by a consideration of the case of chromium. The absorption of light in the visible region is due to a change from  $\frac{1}{2}$  to  $-\frac{1}{2}$  in the  $r$ -vector of some of the  $\alpha$ -electrons. This type of transition is possible only in transitional groups, and although usually forbidden, becomes prominent in all molecular formations.

L. S. THEOBALD.

**Absorption by carboxyl groups in the short-wave ultra-violet.** H. LEY and B. ARENDS (Z. physikal. Chem., 1929, B, 4, 234–238).—The absorption bands in the short-wave ultra-violet have been determined for pure acetic acid and ethyl acetate, for solutions of these two, and also for solutions of sodium acetate. Acetic acid, both homogeneous and in solution, has a marked absorption band at 2040 Å., although the maximum for the pure acid appears to be shifted slightly towards the long-wave region. There is probably a second, more intensive band at still shorter wave-lengths. Ethyl acetate behaves similarly, the maximum being at about 2090 Å. No such band is observed in the case of sodium acetate solutions. It is possible that this difference may be associated with some difference in the carbonyl chromophore group due to electrolytic dissociation.

M. S. BURR.

**Absorption spectrum of histidine and histamine in the ultra-violet.** F. ELLINGER (Biochem. Z., 1929, 215, 279–285).—The ultra-violet absorption spectra of a 1-cm. layer of 1% solutions of histidine and histamine hydrochloride were measured by photographic and photo-electric methods. Histidine showed a steep increase of absorption commencing at 313  $\mu$  with a maximum at 275  $\mu$  succeeded by a minimum at 254  $\mu$  and then followed by a further steep increase. With histamine hydrochloride a linear increase of absorption was obtained starting at 366  $\mu$  and increasing continuously toward the shorter wave-length region.

P. W. CLUTTERBUCK.

**Absorption of light by nitrophenols. I. Weakly alkaline aqueous solutions.** J. EISENBRAND and H. VON HALBAN (Z. physikal. Chem., 1930, 146, 30–40).—Absorption spectra of mono- and di-nitrophenoxide and picrate ions have been examined over the range 250–550  $\mu$ . Alteration of the position of a nitro-group in the nucleus exercises a powerful influence on the value of the extinction coefficient, which may be changed ten-fold. Introduction of a second or a third nitro-group produces a change in the extinction coefficient of the same order of magnitude as above if the group introduced occupies a new position relative to the hydroxyl group; otherwise the effect is of a lower order of magnitude.

F. L. USHER.

**Absorption spectra of the azobenzene crystal.** J. W. OBREIMOW and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1324—1328).—The change of colour of crystals at low temperatures is a general phenomenon, probably due to the contraction of absorption bands. The spectrum of azobenzene at 20° Abs. is very regular. It has been measured by the use of a plane grating, and the lines are classified. At this temperature and below, azobenzene shows a line spectrum when the light vector is parallel with the *b*-axis of the crystal. Spectral photographs were taken at 14° and 4.22° Abs. It was not possible to measure all the lines with the apparatus used. There is a continuous background of diffuse bands as well as the lines; these diffuse bands become stronger towards the violet. At 4.22° Abs. the absorption lines are considerably sharper than at 14°, but the same lines appear at both temperatures, with nearly the same distribution of intensity. The absorption spectrum was also investigated for the component of the light perpendicular to the *b*-axis, but no structure could be found in this spectrum even at 4.22° Abs. There was a continuous absorption in the violet without discrete bands. In the spectrum of the vapour of azobenzene under atmospheric pressure, no lines or bands could be found.

A. J. MEE.

**Relation between ultra-violet absorption spectra and heats of combustion.** E. P. CARR (Nature, 1930, 125, 237).—The heat of combustion of a hydrocarbon in the liquid state containing *m* double linkings can be represented by the equation  $Q = (3n+1)52.1 - m(Nh\nu_2 - Nh\nu_1)$ , where  $\nu_1$  and  $\nu_2$  are the centres of the absorption bands. For acetylenic hydrocarbons 2*m* replaces *m* in the above formula where *m* now stands for the number of triple linkings present.

L. S. THEOBALD.

**Infra-red absorption spectra of benzene and its halogen derivatives.** J. F. DAUGHERTY (Physical Rev., 1929, [ii], 34, 1549—1557; cf. Ellis, A., 1924, ii, 219; 1926, 454; Dreisch, A., 1925, ii, 627).—With the view of discovering series relations or any shifting of the maxima due to halogen substitution, the infra-red absorption spectra of benzene and its monohalogen derivatives were measured from 1 to 7.5  $\mu$ , and several previously unobserved weak bands were found. Good agreement with existing data was found for other bands. In the region 1—1.9  $\mu$ , a maximum at 1.12 is associated with a smaller maximum at 1.14 (cf. Barnes, A., 1928, 1306); an intense maximum at 1.66 and smaller maxima at 1.72, 1.78, and 1.88  $\mu$  were found. The region at 3.3  $\mu$  showed maxima at 3.29, 3.32, and 3.44  $\mu$ ; the region 5—7.5  $\mu$  showed bands for benzene at 5.06, 5.56, 6.20, 6.74, and 7.16  $\mu$ . The spectra showed a general similarity, but no definite rule for shifting was found. Calculations of combination bands and harmonics are given.

N. M. BLIGH.

**Infra-red investigations of molecular structure. IV. Overtone of nitric oxide.** C. P. SNOW and E. K. RIDEAL (Proc. Roy. Soc., 1930, A, 126, 355—359).—The NO overtone ( $n''=1/2 \rightarrow n'=5/2$ ) has been detected with the gas at atmospheric pressure, and partly resolved at 0.5 atmosphere.

It consists, like the fundamental, of *R*, *P*, and *Q* branches, the existence of the *Q* branch (at  $3744 \pm 1.5$  cm.<sup>-1</sup>) being explained by the 2 $\Pi$  character of the molecule. The constants  $\omega_0$  and  $\omega_0 x$  are evaluated as 1895.2 and 12.2, respectively, in fair agreement with the electronic band spectral values of 1892 and 13.7. From these, the constants of the Mecke value are obtained. The ratio of the intensities of the fundamental and overtone is compared with the theoretical value.

L. L. BIRCUMSHAW.

**Infra-red spectra. XIV. Band attributed to amino-nitrogen.** G. B. BONINO (Atti Soc. Ligustica Sci. Lett., 1926, 5, 6 pp.; Chem. Zentr., 1929, ii, 1507).—All compounds with nitrogen directly united with hydrogen show a band at about 3  $\mu$ . With increasing mol. wt. the compounds in a particular series with the same number of amino-hydrogen atoms have almost equal maximal molecular absorption coefficients for 3  $\mu$ , whilst for the 3.4—3.5  $\mu$  bands the values may vary considerably.

A. A. ELDRIDGE.

**Short-duration phosphorescence in fused quartz.** H. W. WEBB and (Miss) H. A. MESSENGER (Physical Rev., 1929, [ii], 34, 1463—1465; cf. Gillam and Morton, A., 1929, 240).—Radiation from a water-cooled quartz-mercury arc was passed through a narrow slit and fell on a sample of fused quartz. The phosphorescence, measured by Zemansky's rotating device (cf. A., 1927, 491), was found to have a decay constant of approximately  $5 \times 10^3$  sec.<sup>-1</sup>; the wave-length of the exciting radiation was less than 2270 Å. The phosphorescence radiation is a continuous band from 3700 to 4750 Å. with a maximum at 4000 Å., and is unaffected by temperature changes from 20° to 240°; it was not observed in crystalline quartz.

N. M. BLIGH.

**Light absorption and dispersion in phosphorescent alkali halides containing a known number of heavy metal ions.** W. KOCH (Z. Physik, 1930, 59, 178—385).—The absorption and dispersion of phosphorescent potassium bromide containing lead and of potassium chloride containing thallium have been determined and the number of electrons causing dispersion calculated by means of the classical electron theory. The numbers calculated from the height and width of the absorption band are in good agreement with those calculated from the nature of the anomalous dispersion. Using potassium chloride crystals containing a varying and experimentally determined number of thallium ions (Koch, A., 1929, 1364), the short- and long-wave absorption bands were investigated and the number of dispersing electrons calculated. For the long waves about one electron was found for every 10 thallium ions present, and for the short waves about one for every 2 thallium ions, the relation being linear in each case. From this it is deduced that single thallium ions replace single potassium ions in the lattice, but that since doubling the ion content does not quite double the number of dispersing electrons, some of the thallium exists in colloidal form at the higher concentrations. Potassium chloride crystals containing lead were similarly investigated but no such definite relationship was found and it is inferred that the lead is mainly colloidal.

H. A. JAHN.

**Phosphorescence.** R. TOMASCHEK (Sitzungsber. Ges. Beförd. ges. Wiss., 1928, 63, 119—136; Chem. Zentr., 1929, ii, 1382).—Spatial differentiation between the excitation and emission processes at a centre of phosphorescence is postulated and the appearance of the sodium *D*-lines in after-glow is interpreted. The phenomena of phosphorescence, photo-electric conductivity, solid catalysis, and chemiluminescence are correlated.

A. A. ELDRIDGE.

**Photo-voltaic properties of phototropic mercury compounds.** S. V. R. RAO (J. Indian Inst. Sci., 1929, 12A, 225—232; cf. A., 1929, 627, 660).—Of eleven phototropic mercury compounds previously described, seven have been found to show a "dark potential" between the light- and dark-coloured modifications. In general the dark potential increases linearly with the duration of the time of previous exposure of the preparation to the light, this in turn being proportional to the quantity of the dark-coloured compound. The potential reaches a maximum value, at which it remains constant in less than an hour. The highest value recorded was about 140 millivolts for the compound  $\text{IHg}\cdot\text{CNS}$ . Exposure to light causes a photo-potential which increases to a maximum, at which it remains constant without fatigue. The original condition is rapidly regained on cutting off the light, the fall in potential amounting to 50% in 30 sec.

In many cases the photo-potential is proportional to the light intensity up to a value at which a saturation potential occurs. The maximum potential measured was 170 millivolts for the compound  $\text{HS}\cdot\text{Hg}\cdot\text{CNS}$ . With visible light the shortest wavelengths produce the highest potential, and dyeing the electrodes with erythrosin caused an increase in potential.

The dark potential of most of the compounds is almost independent of temperature in the range 30—50°, but in a few cases, notably that of the compound  $\text{HgBr}_2\cdot 2\text{HgS}$ , it has a negative temperature coefficient.

F. G. TRYHORN.

**Raman effect.** P. DAURE (Ann. Physique, 1929, [x], 12, 375—441; cf. A., 1929, 11, 240, 865, 866).—The Raman effect was investigated for a number of pure substances, mixtures, and solutions, and liquefied gases. Results are given and discussed for liquefied hydrogen chloride, ammonia, and carbon tetrachloride, the chlorides of arsenic, phosphorus, carbon, antimony, bismuth, silicon, titanium, and tin, and for a number of organic series. A constant difference, the characteristic frequency, was found between the exciting frequency and that of the negative secondary radiation. A liquid mixture gave a superposition of the spectra of the constituents; dissociation was marked by a broadening of the lines, and the view of a molecular origin for the Raman lines was supported. The spectra of the inorganic chlorides and the organic series showed, respectively, marked analogies, indicating a connexion with molecular constitution. Spectro-photometric measurements verified the theoretical law for the decrease, with respect to the characteristic frequency, of the ratio of the intensities of the corresponding positive and negative lines; showed that the Raman intensities for a given charac-

teristic frequency were proportional to the intensities of the diffuse lines of the same exciting frequency, and vary as the fourth power of the exciting frequency, and allowed a comparison of the intensities of some diffuse and Raman lines. A comparison of the positions and intensities of infra-red absorption bands and Raman lines showed a similarity and a greater intensity for high-frequency Raman lines of hydrogen compounds. No general results were obtained relating Raman spectra and molecular structure, but certain lines were found to be associated with certain molecular linkings for hydrogen, the carbon chain, and the CO group.

N. M. BLIGH.

**Constitution of water and the Raman effect.** W. GERLACH (Naturwiss., 1930, 18, 68).—Experiments on the magnetic and optical properties of salt solutions led to the conclusion that in certain solutions a change in the constitution of the water may take place. The Raman photographs of pure water and of 60% solutions of lithium and calcium chlorides were taken. Distilled water showed only a trace of fluorescence. The Raman spectrum gave the double band in the blue and a very wide, sometimes unresolved band in the violet. The salt solutions, prepared from pure salts and the same water as used above, showed only the long-wave component of the blue band with any great intensity. The short-wave part was missing. With the lithium chloride solution the violet band was small and quite weak, whilst the blue band was fairly intense. For calcium chloride, the violet band has a very sharp maximum. The explanation is the depolymerisation of water. The present work leaves open the possibility of the existence of a new Raman band for lithium chloride at  $\lambda$  4850 Å.

A. J. MEE.

**Raman effect for some organic substances.** J. SÖDERQVIST (Z. Physik, 1930, 59, 446—465).—The Raman spectra for benzene, toluene, ethylbenzene, ethyl chloride, ethyl bromide, allyl chloride, *n*-propyl chloride, and *n*-propyl bromide were examined. It was found that substances frequently gave similar Raman frequencies, especially if their structures were similar. Pringsheim and Rosen (cf. A., 1928, 1307) have proved that a Raman frequency of  $3050\text{ cm}^{-1}$ , corresponding with a wave-length of  $3.3\mu$ , is obtained with all organic substances containing the CH linking. This value is, however, a little different for aromatic and for aliphatic compounds, the former showing a value of  $3.27\mu$  and the latter one of  $3.37\mu$ . The aromatic substances investigated also showed a wave-length almost twice this, and this, as well as the  $10\mu$  and  $16\mu$  wave-lengths also investigated, were given by Kohlrausch and Dadiou as characteristic values for ring compounds (cf. A., 1929, 976). It was found that substances containing the methyl group gave a characteristic Raman frequency of wave-length  $3.40\mu$ . In cases where the methyl occurs in an aromatic compound, this wave-length is found in addition to those mentioned above. With the aromatic substances investigated a line was found at approximately  $8.5\mu$ . This may be characteristic of benzene and its derivatives. Aliphatic substances, especially the halides, often gave similar Raman lines. The two propyl halides gave values very

near each other, the greatest difference being  $0.2\mu$ . The wave-lengths of the bromide were always greater than those of the chloride, owing presumably to the greater mass of the bromine. A. J. MEE.

**Raman effect in liquid pyridine.** S. VENKATESWARAN (J. Physical Chem., 1930, **34**, 145—152).—The Raman effect in liquid pyridine has been investigated, using the light from a mercury arc as the incident source. The spectrum of the scattered light exhibits several modified lines, which have been measured, and a faint continuous spectrum. The corresponding infra-red wave-lengths for pyridine are  $16.58$ ,  $15.36$ ,  $11.32$ ,  $10.12$ ,  $9.735$ ,  $8.214$ ,  $6.343$ , and  $3.271\mu$ . The modified lines are differently polarised and the two most prominent lines corresponding with  $10.12\mu$  and  $9.735\mu$  are the most strongly polarised. A comparison of the Raman effect in benzene and pyridine indicates that the two substances possess a similar structure. L. S. THEOBALD.

**"Common third level" in the Raman effect.** R. C. MAJUMDAR and D. S. KOTHARI (Nature, 1930, **125**, 165).—Theoretical. Combination scattering of light (Raman effect) is dependent on the existence of a third common level  $E_n$  whereby a molecule may pass from  $E_i$  to  $E_n$  and may return from  $E_n$  to  $E_i$  or  $E_n$  to  $E_k$ . L. S. THEOBALD.

**Molecular scattering of light.** J. R. NIELSEN (Science, 1929, **69**, 15).—The wave-length shift reported by Cabannes and Daure (A., 1928, 812) may be due to the Compton effect, but no unmodified line was reported. An interpretation in terms of the Raman effect is also out of the question. Further investigation is desirable. L. S. THEOBALD.

**Raman effect with optically active substances.** S. BHAGAVANTAM and S. VENKATESWARAN (Nature, 1930, **125**, 237—238).—Differences in the relative intensities of some of the lines of the spectra of *d*- and *l*-pinene especially in the Raman line about  $74\mu$  have been observed. L. S. THEOBALD.

**Ionisation produced in the oxidation of nitric oxide.** L. A. M. HENRY (J. Physical Chem., 1929, **33**, 1941—1952).—In connexion with a study of the reaction  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$  an apparatus capable of measuring currents of  $10^{-15}$  to  $10^{-16}$  amp. is described. At temperatures up to  $100^\circ$  the introduction of the reacting mixture into the ionising chamber produced no permanent ionisation; only short-lived, temporary effects were observed when nitric oxide was introduced into and cut off from a stream of oxygen. At  $300^\circ$ , a permanent ionisation, proportional to the *P.D.* in the chamber and to the percentage of nitric oxide, was observed. Possible explanations are discussed, the most probable one being that ionisation results from the dissociation of nitrogen peroxide. L. S. THEOBALD.

**Molecular polarisation of symmetrical but non-rigid molecules.** G. JUNG and A. SCHLEDE (Z. physikal. Chem., 1929, **B**, **4**, 207—216).—Theoretical. The relationship between temperature and the molecular polarisation *P* which can be induced in a symmetrical but non-rigid molecule (*i.e.*, one capable of rotation of one part with respect to another), is of the form  $p_{(\text{non-rigid})} = \alpha' - b'T$ , whilst Debye's

equation for the natural polarisation of an unsymmetrical molecule is  $p_{(\text{rigid})} = \alpha + b/T$ . Thus by determining the way in which *P* depends on *T* it is possible to distinguish between the two types of molecule. M. S. BURR.

**Effect of temperature on the molecular polarisation of gases and vapours.** R. SÄNGER and O. STEIGER (Helv. phys. Acta, 1929, **2**, 136—144; Chem. Zentr., 1929, ii, 1135).—The dielectric constants of methyl, ethyl, and propyl ether vapour between  $300^\circ$  and  $400^\circ$  Abs. at constant density have been measured. The relation between dielectric constant and density accords with Debye's theory. The electric moment diminishes with increasing mol. wt.

A. A. ELDRIDGE.

**Variation of dielectric constant with frequency.** J. H. L. JOHNSTONE and J. W. WILLIAMS (Physical Rev., 1929, [ii], **34**, 1483—1490).—The dielectric constants of solutions of nitrobenzene and *p*-dichlorobenzene in mineral oil of high viscosity were measured at three concentrations, and the critical frequency at infinite dilution was found by extrapolation. The dielectric constant of nitrobenzene decreased with increasing frequency, and was constant for the non-polar *p*-dichlorobenzene, which showed no dispersion effect, in accordance with Debye's dipole theory. The diameter of the nitrobenzene molecule is calculated to the correct order of magnitude.

N. M. BLYTH.

**Dielectric constants of solutions of oximes and ketones in benzene.** Dipole moment of benzaldoxime *O*-methyl ether, acetophenone, and benzophenone. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1929, **B**, **4**, 217—222).—The method employed for the determination of dielectric constants is described. By the dissolution of oximes in benzene only a small increase in the dipole moment of benzene takes place, in spite of the large dipole moment of the simple oxime molecule. This behaviour is to be attributed to the association of the oxime molecules in solution. This association annuls the dipole moments. The dipole moment of the *O*-methyl ether of *anti*-benzaldoxime is  $0.86 \times 10^{-18}$  e.s.u. It is known that aliphatic ketones have practically the same dipole moment, but the results obtained show that the substitution of alkyl by phenyl groups leads to an increase in the dipole moment. The dipole moments of acetone, acetophenone, and benzophenone are  $2.72 \times 10^{-18}$ ,  $2.97 \times 10^{-18}$ , and  $3.13 \times 10^{-18}$  e.s.u., respectively.

M. S. BURR.

**Variation of the dielectric constants of some organic liquids with frequency in the range  $1$ — $10^3$  kilocycles.** R. W. LUNT and M. A. G. RAU (Proc. Roy. Soc., 1930, **A**, **126**, 213—230).—By measuring the capacities of condensers comprising two metal surfaces separated by air or by the liquid under examination, the dielectric constants of benzene, ethyl ether, methyl ether, chloroform, ethyl alcohol, acetone, aniline, and nitrobenzene, and the conductivities of the last four substances have been determined in the frequency range  $1$ — $10^3$  kilocycles. The results show that within the limits of experimental error ( $0.5\%$ ) there is no change in the dielectric

constant of benzene, ethyl ether, methyl ether, or chloroform over the range studied, whilst for the remaining liquids a slight increase takes place at frequencies higher than  $10^2$  kilocycles. Bryan's work on nitrobenzene (Physical Rev., 1922, **22**, 391) is confirmed. The conductivity of aniline diminishes slowly up to  $10^2$  kilocycles and then more rapidly, so that at  $10^3$  kilocycles it cannot be measured on the bridge available. It is considered possible that the degree of dehydration of aniline determines the conductivity.

L. L. BIRCUMSHAW.

**Dipole moment of s-trinitrobenzene.** A. PARTS (Z. physikal. Chem., 1929, **B**, **4**, 227—233).—The dielectric constants of solutions of s-trinitrobenzene in benzene, between  $10^\circ$  and  $50^\circ$ , have been determined by a method which is described. The total polarisation appears to be independent of concentration, at least up to a mol. fraction of trinitrobenzene of 0.0389, and is approximately 54 at  $25^\circ$ . From optical data the electron polarisation is 40. Hence the combined atomic and dipole polarisation are 14, giving a dipole moment of  $0.8 \times 10^{-18}$  e.s.u. on the assumption that the atomic polarisation is zero (cf. Williams, A., 1928, 1180).

M. S. BURR.

**Refraction of light by alkali hydrides.** H. BODE (Z. physikal. Chem., 1930, **B**, **6**, 251—255).—The molecular refractions of sodium and potassium hydrides have been determined and those of lithium, rubidium, and caesium calculated from them. The hydrogen anion itself has a high refraction. In the alkali hydrides hydrogen is analogous to the halogens. Both the mol. vols. and refractions of hydrogen and the halogens increase in the order  $F', H', Cl'$ .

F. L. USHER.

**Optical properties of mixed crystals.** T. F. W. BARTH (Amer. J. Sci., 1930, [v], **19**, 135—146).—Work on refractive indices of mixed crystals is summarised. Mixed crystals of thallous bromide and iodide were prepared and their refractive indices found. The refractive index was plotted against composition, and from the graph thus obtained it was evident that none of the theoretical formulæ hitherto proposed for the optical properties of mixed crystals fits this system. Mixed crystals of silver bromide and silver iodide, with sodium chloride structure, were also investigated, but here, too, deviations from the theoretical formulæ were found. Mixed crystals of  $BaO, 2SiO_2$  and  $2BaO, 3SiO_2$  show great deviations. Investigation of the majority of mixed crystals indicates, however, that most of them show proportionality between refraction and composition. It is not possible to tell which of the laws a system obeys. The cause of these deviations is that the refractive power of a mixture depends not only on its density, but also on the nature of the chemical linkings and the degree of deformation of the ions. If the formation of mixed crystals takes place without any deformation of the anions or change of chemical linkings, the refractive indices of the mixtures will vary approximately proportionally to the composition (except for triclinic and partly monoclinic crystals). The application of this to optical mineralogy is considered.

A. J. MEE.

**Optical rotation and chemical constitution.** W. KUHN (Ber., 1930, **63**, [B], 190—207; cf. A., 1929, 981).—The optical activity of a compound must be regarded as the sum of the activity contributions depending on individual bands which can be attributed to definite substituents. The magnitude of the contribution of a band depends on its position in the spectrum and the product of its strength and the so-called anisotropic factor. The circular dichroism of the band depends on the latter factor. The weak and medium strong bands immediately proximate to the visible portion are particularly important, since, for them, the anisotropic factor is unusually great and because they largely eliminate the activity contributions of the bands in the extreme ultraviolet. The bands of substituents placed particularly close to the active carbon atom have a very large anisotropic factor. This anisotropy ("induced anisotropy") is conferred on these bands by the disturbance ("vicinal action") which the surrounding substituents exert on the particular group (bands) (cf. Born, A., 1915, ii, 659; 1918, ii, 283). It is shown in a series of examples (simple carbinols, substituted alcohols, vinylcarbinols, derivatives of amyl alcohol) that simple rules apply to vicinal action and, in part, to induced anisotropy. An alkyl group containing halogen, carboxyl, hydroxyl, or a double linking remote from the optically active carbon atom behaves like a larger alkyl group in its vicinal effect.

H. WREN.

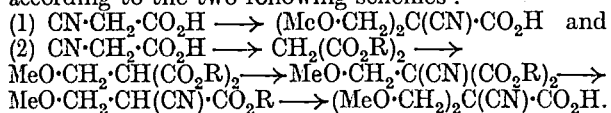
**Co-ordination. I. Ion hydrates.** F. J. GARRICK (Phil. Mag., 1930, [vii], **9**, 131—141).—It is assumed that the most stable hydrato-complex ions are those in which the electrostatic energy is a maximum. The electrostatic energies are calculated for a number of such ions and it is found that the co-ordination number is 6 for  $Na^+$ ,  $K^+$ ,  $Mg^{++}$ , and  $Ca^{++}$ , 8 for  $Cs^+$ ,  $Sr^{++}$ , and  $Ba^{++}$ , and 4 or 6 for  $Li^+$  and  $Be^{++}$ , whilst the co-ordination number 12 is never found. The electrostatic mechanism of the formation of such co-ordination complexes is in satisfactory agreement with observed results.

A. E. MITCHELL.

**Experimental test of the theory of geometrical stereochemistry.** A. P. SEMENOV (Ukrain. Chem. J., 1929, **4**, 309—321).—The literature dealing with the configuration of pentaerythritol is reviewed and the possible types of isomerides of a molecule  $CR_2R'R''$ , assuming the pyramidal configuration, are considered. Two geometrical isomerides may exist, one with the two identical radicals situated at the ends of a side of the quadrilateral formed by the four radicals (*cis*-isomeride) and the other with these radicals at the ends of a diagonal (*trans*-isomeride). In the latter case there is a plane of symmetry perpendicular to the line joining the two similar radicals. With the *cis*-isomeride, the molecule has no plane of symmetry and is thus not identical with its mirror-image, so that there should be optical isomerism. As regards which of these compounds may be assumed to have a pyramidal configuration of the molecule, this should be looked for in cases where Ebert and von Hartel (A., 1928, 462) observed a considerable electrostatic moment, that is, in molecules containing the groups  $CH_2-OR$ ,  $CO_2R$ ,  $CH_2-CO_2R$ , and  $OR$  combined with



the central atom. Hence, with citric acid there is, according to this hypothesis, justification for expecting optical isomerism. Attempts to prepare optically active citric acids by means of the quinine and brucine salts proved unsuccessful, but this may be because this acid is the *trans*-isomeride. Similar experiments with the monoamide of maleic acid also resulted only in optically inactive compounds. In the hope of obtaining dimethoxycyanoisobutyric acid in *cis*- and *trans*-forms, this acid is now being prepared according to the two following schemes:



T. H. POPE.

**Stereochemistry of compounds with quinquevalent nitrogen.** A. P. SEMENCOV (Ukrain. Chem. J., 1929, 4, 323—325).—The various hypotheses which have been advanced concerning the stereochemical configuration of compounds containing a quinquevalent nitrogen atom are discussed, the conclusion being reached that the necessary and sufficient condition for the optical isomerism of such compounds is that four radicals combined with the nitrogen atom shall be different. The fifth radical (anion of the acid) exerts no influence on the phenomenon of optical isomerism; thus, the absence of such radical, as in oxides of the form  $\text{NabcO}$ , or its identity with one of the first four radicals, as in  $\text{Nabc}(\text{OH})_2$ , does not interfere with the optical isomerism. Hence, the deciding factor is the structure of the cation quite independently of the anion, this structure being the same as that of methane derivatives and the nitrogen occupying a space-centred position. About the nucleus of the central nitrogen atom eight electrons are distributed at the angles of a cube, the directions of the attractive forces between the central atom and the radicals being perpendicular to four edges of the cube.

T. H. POPE.

**Distinction between ionic and atomic compounds.** E. RABINOWITSCH and E. THILO (Z. physikal. Chem., 1930, B, 6, 284—306).—Calculations of Grimm and Herzfeld (cf. A., 1924, ii, 102) on the existence and stability of various ionic compounds have been extended with the aid of new physical data which permit a wider application of the Born-Haber cycle. The ionic compounds predicted by theory are all known, excepting manganese monochloride and the mono- and di-halides of aluminium, scandium, titanium, yttrium, and lanthanum. The results show definitely that nitrogen and boron trichlorides, and the tetrachlorides of carbon, tin, and lead, among other volatile hydrides and halides, are not ionic compounds, and indicate that cadmium and cuprous iodides, and aurous, mercurous, and mercuric chlorides are typical atomic compounds in the solid state. The solid hydrogen halides are also non-ionic.

F. L. USHER.

**Dissociation work of oxygen.** G. HERZBERG (Z. physikal. Chem., 1929, B, 4, 223—226).—Theoretical. A re-examination of the experimental data from which the dissociation tension of the oxygen molecule has been calculated leads to the conclusion

that the value of 7 volts hitherto assigned to it is 1—2 volts too high. The corresponding values for carbon monoxide and nitric oxide, which are calculated from the oxygen value, now become approximately 10 and 6.5 volts instead of 11 and 7 volts, respectively.

M. S. BURR.

**Affinity.** T. DE DONDER (Bull. Acad. roy. Belg., 1929, [v], 15, 615—625).—Mathematical. Expressions are derived for the affinity in systems in which the mass is variable.

O. J. WALKER.

**Diamagnetism of ions.** P. WEISS (Compt. rend., 1930, 190, 95—98).—With reference to Reicheneder's assumption (cf. A., 1929, 1370) that the magnetic susceptibility of  $\text{H}^+$  ion is nil, thus neglecting the effect of that ion on the diamagnetism of water, it is proposed to deduce this effect from that of  $\text{H}^+$  ion on refraction. The changes in refraction and in diamagnetism consequent on the deformation of the ions resulting from the change from solution to crystallisation show that the refraction is almost exactly twice as sensitive to such change as the diamagnetism. This result is shown to be in conformity with theory. The loss of diamagnetism due to, i.e., the apparent paramagnetism of, the  $\text{H}^+$  ion is in this way determined as  $1.1 \times 10^{-6}$ . Susceptibilities of several substances calculated on this basis are shown to be in fair agreement with experimental results.

C. A. SILBERRAD.

**Diamagnetic anomaly in gases. V. Critical examination of methods. I.** A. GLASER (Ann. Physik, 1929, [v], 3, 1119—1136).—The diamagnetic anomaly (A., 1925, ii, 82, 642; 1929, 628, 982) is considered by Hammar (A., 1926, 1197) to arise from the adsorption of gases or water vapour at the surface of the material used in the susceptibility measurements, whilst Buchner (A., 1929, 249) ascribes the phenomenon to temperature differences within the apparatus. The actual course of the anomaly is qualitatively different from that consistent with the conjectural adsorption mechanism; it is independent of great differences in the surface condition, etching with hydrofluoric acid and plating with gold, silver, and platinum effecting no change. Exhaustive experiments on drying the gases demonstrate that the presence or adsorption of water vapour cannot account for the anomalous diamagnetism. The presence of traces of oxygen leads to untrustworthy results; in this connexion it is shown that the oxygen pressure corresponding with the reaction  $4\text{CuO} \longrightarrow 2\text{Cu}_2\text{O} + \text{O}_2$  is negligible only at temperatures distinctly below  $800^\circ$ , at  $1000^\circ$  it is about 100 mm. and at  $1100^\circ$  about 560 mm. Hence, in order to prepare gases free from traces of oxygen, the tube containing heated copper should show a considerable decrease in temperature between the inlet and outlet ends. The presence of oxygen accounts for certain failures to reproduce the author's results.

R. A. MORTON.

**Interpretation [energetic] of the molecular field and paramagnetism.** P. WEISS (J. Phys. Radium, 1930, [viii], 1, 1—10).—The necessary and sufficient condition for a paramagnetic substance to obey the relation  $\sigma = CH/(T - \theta)$  is that the energy  $U = -n\sigma^2/2 + f(T)$ . It is recommended (with

examples) that  $1/\chi T$  (instead of  $1/T$ ) be plotted against  $T$ . Theories of the molecular field are discussed, and it is concluded that where the Curie point is independent of concentration the carrier of magnetic moment must be a portion only of the ion.

C. A. SILBERRAD.

**Diamagnetic anomaly in gases. VI. Critical examination of methods.** II. A. GLASER (Ann. Physik, 1930, [v], 4, 82—90).—Reconsideration of experimental methods appears to dispose of the view that Buchner's temperature effect (A., 1929, 249) and the magnetic anomaly possess a common origin.

R. A. MORTON.

**Magnetic investigations on adsorbed gases.** J. AHARONI and F. SIMON (Z. physikal. Chem., 1929, B, 4, 175—189).—A null method for the measurement of magnetic susceptibility is described. No knowledge of field strength is required and the method is especially suitable for low temperatures. The standardisation curve has been tested by determinations of the magnetic susceptibility of iron ammonium alum at different temperatures, and of solutions of manganous sulphate at different concentrations at 0°. The magnetic susceptibilities of the following systems of adsorbed gases have been measured at different temperatures and gaseous concentrations: chabasite-oxygen; carbon-oxygen; palladium-hydrogen. Oxygen adsorbed by chabasite has a smaller magnetic susceptibility than free oxygen, and a break occurs in the susceptibility-concentration curve when the two components of the system are present in equimolecular proportions. This behaviour confirms the authors' view that the gas molecules are taken up, one by one, into separate cells in the adsorbent (cf. A., 1928, 580). The relationship between concentration and magnetic susceptibility shows a similar discontinuity in the case of the system carbon-oxygen. This may perhaps be ascribed to a transition from a unimolecular to a bimolecular layer. When hydrogen is adsorbed by palladium there is, with increasing concentration, a marked linear diminution of susceptibility which comes to an end at a concentration corresponding with  $\text{Pd}_2\text{H}$ . After this point very little more hydrogen is taken up and the magnetic susceptibility remains constant. The molecular transformation which the ammonium halides are considered to undergo between  $-30^\circ$  and  $-40^\circ$  has no effect on the magnetic susceptibility of the salts, and similar observations have been made with regard to the transition points of manganous oxide and manganese dioxide at  $116^\circ$  and  $92^\circ$ , respectively.

M. S. BURR.

**Determination of the variation with pressure of the force between two plates at different temperatures at low pressures, with a view to the determination of molecular mean free paths.** A. E. MARTIN (Phil. Mag., 1930, [vii], 9, 97—130).—At low pressures the force between two small plane parallel plates at different temperatures is found to be directly proportional to the temperature difference and inversely proportional to the square of the distance between them provided the distance is large compared with their linear dimensions. In both air and hydrogen at low pressures the force is found to be directly proportional to the pressure, but at higher

pressures there is a departure from the linear relationship. A maximum is observed in air at a pressure of 0.07 mm., whilst one is predicted in hydrogen at about 0.13 mm. The mean free paths of air and hydrogen molecules have been calculated from these deviations from the linear relationship.

A. E. MITCHELL.

**Parachor of chlorine dioxide.** G. H. CHEESMAN (J.C.S., 1930, 35—37).—The structure of chlorine dioxide has been deduced from its parachor. Two independent methods gave an average result of 1.642 for the density; the surface tension was found to be 33.1 dynes/cm. at  $0^\circ$ . The parachor is therefore 98.7 units. Determination of the Ramsay-Shields coefficient confirmed absence of association. Thus the structural parachor is 4.4 units. The possible electron distributions are discussed and three involving singlet linkings are found to have the correct sign. The structure preferred is one having a three-membered ring and a semi-polar singlet linking.

W. R. ANGUS.

**Calculation of absorption in X-ray powder photographs and the scattering power of tungsten.** A. CLAASSEN (Phil. Mag., 1930, [vii], 9, 57—65).—The total absorption factor for X-rays of glancing angle  $\theta$  for a heavy powder is shown to be  $A_\theta = \int_0^{2\theta} \sin \phi \sin (2\theta - \phi) / \{\sin \phi + \sin (2\theta - \phi)\} d\phi$ , where  $\phi$  is the angle of incidence. The expression is valid under conditions of X-ray powder photography in which the rod of heavy powder is rotated during exposure. The result is applied to the calculation of the scattering power of tungsten on the basis of the Thomas model of the atom. The results obtained are in good agreement with experimental values.

A. E. MITCHELL.

**X-Ray investigation of easily deformable crystals.** L. CHROBAK (Bull. Acad. Polonaise, 1929, A, 497—505).—The technique of obtaining undeformed specimens of easily deformed crystals for X-ray investigations is given. New apparatus for the work is also described including a simple precision chamber for Laue photographs.

A. J. MEE.

**Examination of two technical X-ray tubes for purity of spectra.** K. F. JAHR, F. A. SCHNEIDER, and A. WINKEL (Z. physikal. Chem., 1930, B, 6, 256—260).—Two tubes, with anticathodes of iron and molybdenum respectively, have been examined by means of Seemann's spectrograph (cf. A., 1918, ii, 383) and in each case a pure spectrum has been obtained. Both tubes had been in use for a considerable time, so that no detectable contamination through atomising of metal parts occurs when the tubes are carefully made and properly handled. The result is of importance in the analysis of X-ray structure diagrams for which it is necessary to use only pure spectra.

F. L. USHER.

**Reflexion of X-rays.** F. JENTZSCH and E. NÄHRING (Naturwiss., 1929, 17, 980).—A claim for priority against Schön with respect to some of the results published by him (A., 1929, 1355). Experiments by the authors on Schott glasses have shown that the sharpness of the boundary of total reflexion depends largely on the absorption coefficient.

G. E. WENTWORTH.

**X-Ray examination of crystal defects.** W. BERG (Naturwiss., 1930, 18, 115).—An image of the crystal face is obtained by reflecting a beam of X-rays from it. Crystals having no defects give an image of uniform darkness; defects are shown by light and dark striations. W. R. ANGUS.

**Optical method for demonstrating the results of X-ray analyses.** W. L. BRAGG (Z. Krist., 1929, 70, 475—492; Chem. Zentr., 1929, ii, 969).

**Determination of refractive indices for X-rays.** K. KELLERMANN (Ann. Physik, 1930, [v], 4, 185—214).—The substance is made into a plate with a slight curvature, so that a homogeneous small bundle of X-rays is obtained with different angles of refraction. The totally reflected X-rays give on a photographic plate a certain widening of the blackening. For the exposures the curved plates were rotated about an axis in their surface. By finding the change of widening, and knowing the angle of rotation, the angle of total reflexion can be calculated. The method was applied to crown glass and to silver. It can also be used for liquids which are held in a curved plate. Glycerol and concentrated calcium chloride solution were used. The accuracy of the method with the present arrangement is for solids  $\pm 4\%$ , and for liquids  $\pm 7\%$ . A. J. MEE.

**Crystal structures of the B sub-groups and their connexion with the periodic table and atomic structures.** W. HUME-ROTHERY (Phil. Mag., 1930, [vii], 9, 65—80).—It is held that in the B sub-groups there is a tendency for an element to crystallise so that each atom is surrounded by  $(8-N)$  neighbours, where  $N$  is the number of the group to which the element belongs. Opposing this tendency there is a tendency to form close-packed structures. For groups IV to VII the first tendency is explained on the basis of co-valency linkings, the atom taking  $(8-N)$  neighbours and sharing one electron with each. In group IV the tetrahedral arrangement requires no other forces to ensure the stability, but in groups V to VII the stability can be explained only by the assumption of additional molecular linkings. In groups III and II the presence of simple covalency linkings will not account for each atom having five or six neighbours, there being an insufficient number of electrons for the necessary sharing. The stability in these cases is explained by the existence of a metallic linking. The typical close-packed structures of group I-B elements are attributed wholly to the metallic linkings, since there are not sufficient available electrons for covalency linkings, each electron being shared by more than two atoms.

A. E. MITCHELL.

**Influence of the symmetry of the medium on the symmetry of crystalline form.** G. FRIEDEL and R. WEIL (Compt. rend., 1930, 190, 243—245; cf. Royer, A., 1929, 750).—Illustrations are provided of the correlation of the symmetry of crystalline forms with the symmetry of the medium. The former may exist in 32 forms, but the latter has only 2, namely, complete spherical symmetry which includes all the elements of symmetry of the crystal, and holoaxial spherical symmetry which is that of isotropic (active) amorphous media. The symmetries of the cubic,

quadratic, orthorhombic, and clinorhombic crystal systems are considered, and the apparently new types of merihedry involved are reconciled with existing ideas by considering them as due not to the symmetry of the crystal itself, but to that of one only of its properties, e.g., the external form it assumes under certain conditions. J. GRANT.

**Relation between "active centres" and the "attracting places" (Lockerstellen) of crystals.** I. N. STRANSKI (Z. Elektrochem., 1930, 36, 25—26).—Crystal growth is considered to be easier at the "active centres" of a crystal than at the attracting places, e.g., corners, where dissolution occurs more readily.

H. T. S. BRITTON.

**Orientation of single crystals obtained by recrystallisation.** G. SACHS and J. WEERTS (Z. Physik, 1930, 59, 497—500).—The orientation of aluminium crystals and of crystals of an alloy of aluminium with 5% Cu is investigated. Purity of materials greatly influences the orientation. The cause of this is uncertain, but it may be connected with the ease of preparation of single crystals. With pure materials single crystals are, as a rule, more difficult to prepare than with impure material. It appears that the formation of large crystals by recrystallisation does not in this case, as in other recrystallisation phenomena, depend on the preferential growth of a large number of nuclei. A. J. MEE.

**Crystal structures of magnesium, zinc, and cadmium ferrites.** E. POSNJAK (Amer. J. Sci., 1930, [v], 19, 67—70).—Magnesium, zinc, and cadmium ferrites have been prepared by heating equivalent proportions of the carbonates with finely-divided ferric oxide to 800°. Powder diffraction data have been obtained showing that the lengths of the edges of the unit cubes, containing 8 mols., are  $8.36 \pm 0.01$ ,  $8.41 \pm 0.01$ , and  $8.67 \pm 0.01$  Å. respectively ( $d$  obs. 4.481, 5.290, 5.764). C. W. GIBBY.

**Orientation of single crystals of tin.** K. TANAKA (Mem. Coll. Sci. Kyoto, 1929, 12, 275—379).—The dependence of the crystallographic orientation on the previous history of the crystal is much less than in the case of zinc (A., 1929, 15). The favourable crystallographic direction of growth is found to be roughly parallel to the basal plane of the tetragonal crystal. W. E. DOWNEY.

**Crystal structure of iron.** R. BACH (Helv. phys. Acta, 1929, 2, 95—114; Chem. Zentr., 1929, ii, 1131).— $\alpha$ -,  $\beta$ -, and  $\delta$ -iron have a cubic body-centred, and  $\gamma$ -iron a cubic face-centred lattice. A study of the relation between the lattice constant and the temperature indicates that  $\beta$ - and  $\delta$ -iron are identical, whilst  $\alpha$ - and  $\gamma$ -iron differ considerably.

A. A. ELDRIDGE.

**Crystal structure of barium tungstate.** I. I. NAVANO and J. PALACIOS (Anal. Fis. Quím., 1929, 72, 846—849).—X-Ray investigation demonstrates that barium tungstate belongs to the  $C_{2v}$  class, there being 4 molecules in the elementary parallelepiped.

H. F. GILLBE.

**Crystal structure of glaserite and potassium sulphate.** B. GOSSNER (Neues Jahrb. Min., 1927, 57, 89—116; Chem. Zentr., 1929, ii, 1505—1506).—

The unit cell ( $a$  5.65,  $c$  7.29 Å.) of glaserite, referred to hexagonal axes, contains 2 mols. of  $\text{NaK}_3(\text{SO}_4)_2$ ; the space-group is  $D_{3h}^2$ . The unit cell of potassium sulphate has  $a$  10.06,  $b$  5.85,  $c$  7.33 Å., and contains 4 mols. of  $\text{K}_2\text{SO}_4$ ; the space-group is  $V_1^2$ . A. A. ELDRIDGE.

**Structure of zunyite.** B. GOSSNER (Neues Jahrb. Min., 1926, 15, 319—332; Chem. Zentr., 1929, ii, 1506).—Zunyite, cubic, has  $a$  13.92 Å.; space-group  $T_d^2$ . The unit cell contains 6 mols. of  $3\text{SiO}_2 \cdot 3\text{AlO}(\text{F}, \text{Cl}) \cdot 4\text{HAlO}_2 \cdot \text{H}_3\text{AlO}_3$ .

A. A. ELDRIDGE.

**Tetrahedral-pyramidal configuration of methane derivatives.** F. M. JAEGER (Chem. Weekblad, 1930, 27, 50—52).—The space configuration of the atoms in molecules of the methane type is discussed with special reference to pentaerythritol, having regard to the X-ray spectrum, the optical and pyroelectric properties, and the structure of certain derivatives.

H. F. GILLBE.

**Crystal form of adrenalone hydrochloride.** W. FABER (Z. Krist., 1929, 70, 497—505; Chem. Zentr., 1929, ii, 1157).—Adrenalone hydrochloride,  $\text{C}_9\text{H}_{11}\text{O}_3\text{N} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , crystallises in rhombic plates,  $d$  1.394,  $n_d$  1.5166,  $n_g$  1.6255,  $n_r$  1.7605  $\pm$  0.0002, passing into a monoclinic form,  $d$  1.393,  $n_d$  1.5049,  $n_g$  1.6444  $\pm$  0.0003,  $n_r$  1.7424  $\pm$  0.001.

A. A. ELDRIDGE.

**X-Ray diagram of mercerised cellulose.** K. R. ANDRESS (Z. physikal. Chem., 1929, B, 4, 190—206).—In continuation of previous work on the X-ray diagram of native cellulose (A., 1929, 630), the X-ray diagram of mercerised cellulose has now been interpreted on the basis of a monoclinic unit cell having  $a$  8.1,  $b$  10.3,  $c$  9.1 Å.,  $\beta$  62°. The interference intensities are in agreement with a structure based on glucose residues in a cellobiose combination, the atomic arrangement within the hexoses being very nearly the same as for native cellulose. The difference between mercerised and native cellulose consists in a different orientation of the chief valency chains with respect to one another, and the mercerised lattice appears to represent the more stable configuration.

M. S. BURR.

**Structure of gelatin.** J. J. TRILLAT (Compt. rend., 1930, 190, 265—267).—The author's method (A., 1929, 763) has been used for the examination, by means of the copper K-lines, of a sample of gelatin of  $p_H$  6.2 (0.4% ash) in its normal state, dried on a thread, and stretched 200%. As in the case of cellulose (*loc. cit.*) chains of principal valency are formed by elementary groups of length 9.7 Å. joined end on end. A number of these form crystallites, the orientation of which differs for the dried or elongated specimens, and a group of crystallites forms a micelle. The amorphous phase of gelatin has low powers of polymerisation and cannot form long chains, whilst the pseudo-crystalline phase is strongly polymerised.

J. GRANT.

**Structure of norbergite.** W. H. TAYLOR and J. WEST (Z. Krist., 1929, 70, 461—474; Chem. Zentr., 1929, ii, 979).—Norbergite,  $\text{Mg}(\text{F}, \text{OH})_2 \cdot \text{Mg}_2\text{SiO}_4$ , has  $a$  4.70,  $b$  10.2,  $c$  8.72 Å.; the unit cell contains 4 mols., and the space-group is  $V_1^2$ . A. A. ELDRIDGE.

**Algodonite and whitneyite.** F. MACHATSCHKI (Neues Jahrb. Min., 1929, A, 59, 137—158; Chem. Zentr., 1929, ii, 1639).—The minerals are crystallo-

graphically inhomogeneous. The regular crystals, apparently metallic copper containing arsenic, have  $a$  3.647—3.651 Å. The hexagonal crystals contain less copper than corresponds with the formula  $\text{Cu}_3\text{As}$ , and have  $a$  2.599, 2.598;  $c$  4.215, 4.213 Å., with  $d$  8.71, 8.72.

A. A. ELDRIDGE.

Is it possible to determine the piezoelectric constant at high temperature by the static method? R. D. SCHULWAS-SOROKINA (Physical Rev., 1929, [ii], 34, 1448—1450; cf. Dawson, *ibid.*, 1927, [ii], 29, 541).—The relation between the piezoelectric effect in quartz and the temperature was investigated by Dawson's method. It is concluded that his results for quartz, and those of Valasek for Rochelle salt, are untrustworthy because of failure to take into account the effect of the electrical conductivity of the crystals.

N. M. BLIGH.

**Thermal and electrical properties of beryllium.** E. J. LEWIS (Physical Rev., 1929, [ii], 34, 1575—1587).—The specific heat of pure beryllium increased rapidly with rise of temperature from 0.0389 at  $-175.6^\circ$  to 0.593 at  $190^\circ$ . The thermal conductivity increased with rise of temperature from 0.232 at  $-176.2^\circ$  to 0.508 at  $190.4^\circ$ . The specific resistance varies according to the heat treatment; after establishing a steady condition by repeated treatments from liquid-air temperature to  $700^\circ$  the values obtained were 1.56, 6.76, 19.05, and 40.00 microhms at  $-191^\circ$ ,  $22^\circ$ ,  $305^\circ$ , and  $690^\circ$ , respectively. The temperature coefficient of resistance over the above range has been determined, the curve showing three distinct sections; the values obtained were: 0.000371 at  $-190^\circ$ , 0.00667 at  $20^\circ$ , 0.008 at  $310^\circ$ , 0.00858 at  $500^\circ$ , and 0.01196 at  $685^\circ$ . The thermoelectric power against lead appears to vary linearly with temperature, but the graph shows a break at  $-50^\circ$ , indicating a change in allotropic form. The metal does not obey the Wiedemann-Frantz law.

N. M. BLIGH.

**Electrical resistivities and temperature coefficients of lead, tin, zinc, and bismuth in the solid and liquid states.** W. B. PIETENPOL and H. A. MILEY (Physical Rev., 1929, [ii], 34, 1588—1600; cf. A., 1928, 9).—A method of measuring the resistance-temperature coefficients of metals of low  $m. p.$  in the solid and liquid states is described, oxide films being employed as containers for the molten metals. Resistivity-temperature curves, and resistance-temperature coefficients at  $20^\circ$  intervals are given for the range  $20$ — $460^\circ$ . The coefficients for zinc above the  $m. p.$  are positive; allotropic transformations are indicated at about  $180^\circ$  and  $340^\circ$ . Possible explanations of the high resistivity of non-annealed bismuth below  $160^\circ$  are discussed; in the range  $225$ — $275^\circ$  the negative coefficients are due to a molecular derangement.

N. M. BLIGH.

**Electrical conductivity of metallic layers formed by cathodic sputtering.** E. PERUCCA (Ann. Physik, 1930, [v], 4, 252—272).—The electrical properties of thin layers of gold and platinum formed by cathodic sputtering were investigated. The initial phase of the conduction as a function of the duration of projection was especially determined. The conductivity is purely metallic in character, and

the potential gradient is uniform along the length of the layer. The use of these layers as unpolarisable resistances of values up to  $10^{12} \Omega$  is mentioned. They have practically no temperature coefficient. An explanation of their electrical properties is given.

A. J. MEE.

**Ruthenium a superconductor.** J. C. MCLENAN (Nature, 1930, 125, 168).—Ruthenium becomes a superconductor at  $2.04^\circ \text{Abs}$ . The metal was of high purity and it retained its high resistance nearly to  $4^\circ \text{Abs}$ .

L. S. THEOBALD.

**Magnetic behaviour of nickel and iron films condensed in vacuum on various metal backings.** J. H. HOWEY (Physical Rev., 1929, [ii], 34, 1440—1447; cf. Edwards, A., 1927, 299; Miller, *ibid.*, 1928, 1314).—Using a high-sensitivity magnetometer and a special arrangement of the magnetising coil, the magnetic nature of evaporated iron and nickel films deposited at various temperatures on backings of aluminium, copper, platinum, and molybdenum was investigated to determine the effect of the two-dimensional strain due to differential thermal contraction imposed by the backing. Special precautions were taken to secure gas-free deposition, and magnetisation curves were obtained. Nickel films under tension were magnetically very hard, and under compression were soft. The magnetic intensity of iron films was practically unchanged by the stresses. All the films were harder than bulk metal, and for high-temperature deposition were more like annealed bulk metal.

N. M. BLIGH.

**[Magnetisation of] the mixed oxide of nickel and cobalt and the corresponding ferrite.** (MLLE.) S. VEIL (Compt. rend., 1930, 190, 181—183).—The calcined precipitates produced by sodium hydroxide from solutions containing varying proportions of nickelous and cobaltous sulphates are paramagnetic, and the magnetisation coefficient is a maximum for the mixed oxide  $\text{NiO} \cdot \text{CoO}$ . Mixtures of the corresponding ferrites, containing 68% of ferric sulphate, gave ferromagnetic calcined precipitates, the magnetisation-composition curve rising to sharp maxima for the pure ferrites ( $\text{Fe}_2\text{O}_3 \cdot \text{NiO}$  and  $\text{Fe}_2\text{O}_3 \cdot \text{CoO}$ ) and for the mixed ferrite  $(\text{Fe}_2\text{O}_3)_2 \cdot \text{NiO} \cdot \text{CoO}$ . J. GRANT.

**Mechanism of demagnetisation.** (FRAU) H. TROSIEN (Ann. Physik, 1930, [v], 4, 109—120).—Investigation of the relation between magnetisation and the decrease in a strong alternating field superposed on a definite direct-current field, carried out on steel and iron, has provided evidence for a law of corresponding states between the observed magnetisation and the amplitude of the alternating field for different direct-current fields.

R. A. MORTON.

**Hall effect in permalloy.** A. W. SMITH and R. W. SEARS (Physical Rev., 1929, [ii], 34, 1466—1473).—The Hall effect was studied in nickel-iron permalloys containing 84, 81, and 78% Ni, and was at first positive, becoming negative for larger magnetic fields; for those less than about 11,000 gauss an increase in iron concentration increases the Hall effect. The maximum of the Hall *E.M.F.*-magnetic field curve shifts towards greater magnetic fields, and the magnetic field at which a reversal in the direction of

the Hall *E.M.F.* takes place increases with rise of iron concentration. The interpretation of the Hall *E.M.F.* curves is discussed.

N. M. BLIGH.

**Anomalies in the physical properties of the amorphous state.** Amorphous sulphur and selenium. P. MONDAIN-MONVAL and P. GALET (Compt. rend., 1930, 190, 120—122; cf. Samsoen, A., 1928, 354).—Anomalies similar to those in glasses and other amorphous substances are shown to exist in amorphous sulphur and selenium, indicating a new allotropic modification of these elements. Abrupt changes occur in viscosity (in sulphur at  $-21^\circ$ , in selenium at  $45^\circ$ ), and in density and dilatation (sulphur  $-29^\circ$ , selenium  $30-33^\circ$ ). The change in selenium is accompanied by an absorption of heat at  $37^\circ$ . The temperatures of these changes are slightly below those of softening.

C. A. SILBERRAD.

**Polymorphism of sodium sulphate.** III. Dilatometer investigations. F. C. KRACKER and R. E. GIBSON (J. Physical Chem., 1930, 34, 188—206; cf. A., 1929, 1221).—Previous results have been confirmed and extended by the use of a dilatometer, designed to study changes in volume under pressure, for the lower inversions of sodium sulphate and by an ordinary dilatometer for the upper inversions. The more accurate transition temperatures now obtained are  $\text{Na}_2\text{SO}_4 \cdot \text{V} \rightleftharpoons \text{IV}$ ,  $160-180^\circ$ ;  $\text{IV} \rightleftharpoons \text{III}$ ,  $185^\circ$ ;  $\text{III} \rightarrow \text{I}$ ,  $241^\circ$ ; and the respective volume changes are 0.0005,  $-0.0034$ , and  $0.0070 \text{ cm}^3/\text{g}$ . At low pressures,  $\text{Na}_2\text{SO}_4 \cdot \text{II}$  has no region of stability, but if the change  $\text{I} \rightarrow \text{III}$  is inhibited, that of  $\text{I} \rightarrow \text{II}$  takes place reversibly at  $236^\circ$  with a decrease in volume of  $0.004 \text{ cm}^3/\text{g}$ . The changes occur slowly and are accompanied by marked hysteresis when the salt is dry, but in the presence of water or a trace of sulphuric acid inversion is prompt and rapid.

L. S. THEOBALD.

**Use of effect of pressure on electrical resistance of manganin as a method of measuring pressure.** A. MICHELS and M. H. LENSSEN (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1379—1385).—The treatment required by the manganin before it can be used for this purpose was investigated. It was found that after heat treatment the variation of the resistance of manganin with pressure for the lower temperatures was sufficiently reproducible to allow of its use for measuring pressure.

A. J. MEE.

**Change of electrical conductivity in strong magnetic fields.** W. MEISSNER and H. SCHEFFERS (Naturwiss., 1929, 18, 110—113).—A discussion of the results of Kapitza (A., 1929, 632) and of Auwers (cf. this vol., 17).

J. FARQUHARSON.

**Theory of electrical and thermal conductivity.** R. PEIERLS (Ann. Physik, 1930, [v], 4, 121—148).—Previous theories of electrical and thermal conductivity are considered, and the assumptions made by them are discussed, especially the theory of Bloch (cf. A., 1929, 247). A more strict law is given. For low temperatures there is proportionality between conductivity and  $T^{-4}$ , in agreement with the empirical law. The same method is used for the calculation of thermal conductivity. For low temperatures the thermal conductivity is proportional to  $T^{-2}$ , and for

high temperatures it is independent of temperature, in agreement with experimental observations.

A. J. MEE.

**Electrification and conductivity of liquid hydrocarbons.** L. BRÜNINGHAUS (J. Phys. Radium, 1930, [vii], 1, 11—36).—When petrol or similar oil is passed through an earthed metal tube and collected in an insulated metal vessel connected with an electro-scope a considerable negative charge is observed. When a thick film of oil is subjected to a field of about 110 volts there is at first slight conductivity, which gradually disappears; as the thickness of the film diminishes a "semi-conducting" stage is reached in which a large current may pass, the period of such passage increasing with diminution of thickness, until for thicknesses of the order of  $10\ \mu$  conductivity of metallic order is exhibited, with no visible action on the oil. This explains the use of lubricants to improve sliding contacts and in certain other cases (cf. Watson and Menon, B., 1929, 361). These results are explained as contact phenomena affected by the presence of water.

C. A. SILBERRAD.

**Magnetic susceptibility of oxygen as a function of temperature and density.** H. R. WOLTJER, C. W. COPPOOLSE, and E. C. WIERSMA (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1329—1333).—The formula of Onnes expressing the dependence of magnetic susceptibility ( $\chi$ ) of a paramagnetic substance on the temperature ( $T$ ),  $\chi(T+\Delta)=\text{const.}$ , where  $\Delta$  is a function of the density, is tested on gaseous oxygen. Deviations from Curie's law are noted, and these cannot be reconciled with Onnes' formula. The deviations become very marked below  $175^\circ$  Abs. Above this they are within the experimental error. There appears to be no systematic difference for the different densities as given by Onnes' formula. If the small deviations from Curie's law between  $291^\circ$  and  $175^\circ$  Abs. are neglected the formula  $\chi T = \text{const.}$  holds, the constant being dependent on density. This implies an atomic volume of oxygen dependent on density.

A. J. MEE.

**Anomalous specific heats of solid hydrogen at helium temperatures.** F. SIMON, K. MENDELSSOHN, and M. RUHEMANN (Naturwiss., 1930, 18, 34).—The molecular heat of hydrogen in the region  $11$ — $14^\circ$  Abs. agrees well with a Debye function of characteristic temperature  $\phi=91$ . If, however, a 50% mixture of ortho- and para-hydrogen is studied at still lower temperatures a marked divergence from the Debye curve becomes increasingly noticeable as the temperature falls. The figures in parentheses denote the number of times the Debye function is exceeded:  $10^\circ$  (1.05),  $8^\circ$  (1.4),  $6^\circ$  (2.7),  $5^\circ$  (4.4),  $4^\circ$  (9),  $3^\circ$  (25). At  $3^\circ$  the anomaly for a 50% mixture attains an absolute value of 0.4 g.-cal./degree. Pure parahydrogen agrees closely with the Debye function  $\phi=91$  down to the lowest temperatures, whilst a 75% (ortho-hydrogen) mixture exhibited a much greater anomaly than the 50% mixture. Hence it is likely that a splitting of the ortho-term is responsible for the anomaly.

R. A. MORTON.

**Specific heat of nickel.** (MEE.) E. LAPP (Ann. Physique, 1929, [x], 12, 442—521).—With the view of investigating reported anomalies in the specific heat

of ferromagnetic substances, the specific heat of pure nickel was measured with high precision between  $-175^\circ$  and  $460^\circ$ , using an electrical heating method. The specific heat curve shows a region of quantum degeneracy, a rise towards the Curie point, a discontinuity in the region  $353.5$ — $360^\circ$  greater than previously observed, and a paramagnetic region of slowly rising specific heat. The Curie point and the discontinuity are in agreement with the magnetic Curie point and the calculations based on the Weiss molecular field theory. The terms having a known effect on the specific heat (the quantum, expansion, and magnetic terms) were calculated, and the magnetic unknown term was deduced. The latter rises to a constant value at the Curie point, corresponding with the active force of one degree of freedom.

N. M. BLIGH.

**Temperature variation of the specific heats of hydrogen and nitrogen.** J. H. BRINKWORTH (Proc. Roy. Soc., 1930, A, 126, 204—212).—A new empirical formula is advanced, in which it is proposed to represent the rapidly varying part (quantised) of the specific heat of a gas,  $S_q$ , by a single frequency of the Planck-Einstein expression  $S_q = R x^2 e^x (e^x - 1)^{-2}$ , but with  $x = \beta v / (T - X)$ ,  $X$  being a temperature, instead of the usual  $x = \beta v / T$ . The total specific heat at constant volume of any diatomic gas at any temperature is therefore  $S_t = 3R/2 + S_q +$  (thermodynamic correction) + (term representing increase in specific heat at high temperatures). In the case of hydrogen, where the thermodynamic correction may be neglected, the formula gives excellent agreement with the author's experimental values below  $600^\circ$  (cf. A., 1925, ii, 373). An extension to the case of nitrogen shows that  $S_t$  attains the classical value, 4.96, at  $50^\circ$ , but below this temperature  $S_t$  decreases rapidly owing to the very high value of the thermodynamical correction. Values are deduced for the moments of inertia of hydrogen and nitrogen which are in good agreement with those deduced from band spectra data.

L. L. BIRCUMSHAW.

**Flow method for comparing the specific heats of gases.** I. Experimental method. P. M. S. BLACKETT, P. S. H. HENRY, and E. K. RIDEAL. II. Theory of the method. P. M. S. BLACKETT and P. S. H. HENRY (Proc. Roy. Soc., 1930, A, 126, 319—332, 333—354).—I. A description is given of a simple method for the direct comparison of the specific heats of gases at constant pressure. The method consists essentially in passing a slow stream ( $<30$  c.c. per minute) of gas through a narrow iron tube along which a temperature gradient has been established. The change of the temperature distribution along the tube depends on the properties of the gas and the rate of flow. A particular form of the method, which yields highly accurate results, consists in keeping the two ends of a narrow tube at the same temperature and heating the central portion by means of an electric current. Thermo-junctions are attached to the tube at two positions symmetrical about the centre of the tube, so that the junctions are initially at the same temperature. On passing a gas at a known slow speed through the tube a temperature difference between the two junctions is established, and this is shown to be



related to the flow speed by a cubic equation of the form  $\Theta = C_1\alpha + C_3\alpha^3$ , where  $C_1$  is a constant for the tube,  $C_3$  is a constant depending also on the conductivity and other properties of the gas, and  $\alpha = Q/2KA$ ,  $Q$  is the heat capacity of the gas passing per sec.,  $K$  the thermal conductivity of the tube material, and  $A$  its area of cross-section. The relative values of the specific heats for carbon dioxide, hydrogen, air, and helium determined by this method with different central temperature differences are tabulated. The mean values  $C_p(\text{CO}_2)/C_p(\text{air}) = 1.264$ ,  $C_p(\text{H}_2)/C_p(\text{air}) = 0.986$ , and  $C_p(\text{He})/C_p(\text{air}) = 0.717$  at  $20^\circ$  are in good agreement with the most trustworthy values hitherto obtained, and serve to establish the practicability of the method.

II. A theory is given of the heat transfer between a tube, along which there is a temperature distribution, and a gas flowing in it, and this theory is applied to the particular form of apparatus (a symmetrically heated tube) described above. The validity of the equation  $\Theta = C_1\alpha + C_3\alpha^3$  is proved, and the coefficients  $C_1$  and  $C_3$  are evaluated and found to be in excellent agreement with the experimental values given in Part I. It is shown that the rise in temperature of the centre of the tube should be proportional to the electrical energy dissipated in the tube, and also that the sensitivity (*i.e.*, the temperature change  $\Theta$  for a given flow) should be proportional to the central temperature. These conclusions are supported by the experimental results.

L. L. BIRCUMSHAW.

**Kinetic theory of heat conduction in crystals.** R. PEIERLS (Ann. Physik, 1929, [v], 3, 1055—1101).—The mechanism of heat conductivity in the crystal lattice has been studied. The condition for finite conductivity is identical with the condition for an  $H$ -theorem. The effect of temperature has been considered from the theoretical point of view.

R. A. MORTON.

**Ebullioscopic paradox.** A. BERTHOUD, E. BRINER, and A. SCHIDLOF (J. Chim. phys., 1929, 26, 505).—A reply to Verschaffelt (A., 1929, 1136).

C. A. SILBERRAD.

**Analytical expression of van 't Hoff's rule.** A. ALBERTO (Ann. Acad. Brasil. Sci., 1929, 1, 138—141).—A mathematical expression, of which that obtained by Carneiro is a special case, is derived for van 't Hoff's rule.

H. F. GILLBE.

**Critical point of water.** J. HAVLIČEK (Engineering, 1930, 129, 1—3).—A theoretical discussion of the gas equation with special reference to the observations of Callendar (A., 1928, 1179).

C. W. GIBBY.

**Equation of state of an ionised gas.** W. H. MCCREA (Proc. Camb. Phil. Soc., 1930, 26, 107—114).—Theoretical. The pressure is investigated in a gas of given temperature, in which the numbers of atoms per unit volume at the different stages of ionisation are supposed to be known. The validity of treating an atom or ion consisting of several particles with large relative motions as a single particle is examined in computing its contribution to the dynamical pressure. The dynamical correction for free charged particles is calculated, and found to be of the same order of magnitude as the additional electrostatic correction, but of opposite sign; it is evaluated independently

for iron when retaining only two  $K$  electrons as 3.1%, and appears to reduce the electrostatic correction by about one half. It is concluded that the deviations from perfect gas laws in stellar material may be too small to give observable effects.

N. M. BUGH.

**Vapour-pressure curve of liquid helium. II.** W. H. KEESOM, S. WEBER, and G. SCHMIDT (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1314—1323; cf. this vol., 145).—The results previously obtained are extended for lower pressures. The lowest pressure reached was 0.005 cm. The correction for thermomolecular pressure difference becomes important, especially in the helium thermometers which were used in which the pressure becomes very small. The size of the effect is known with sufficient accuracy to be used. The method of correcting is indicated. Two empirical formulæ are derived connecting the vapour pressure with the temperature, one for temperatures above  $2.19^\circ$  Abs., and the other for temperatures below this. The change of behaviour of helium at this temperature has still to be investigated.

A. J. MEE.

**Vapour pressure of toluene up to the critical temperature.** N. W. KRASE and J. B. GOODMAN (Ind. Eng. Chem., 1930, 22, 13).—Determinations of the vapour pressure of toluene have been made by a static method from  $0^\circ$  to  $320.6^\circ$  (the critical temperature). The critical pressure was found to be 41.6 atm.

H. INGLESON.

**Vapour density of sodium.** W. H. RODEBUSH (Nature, 1930, 125, 130).—A redetermination of the vapour pressure and vapour density of sodium agrees with an apparent mol. wt. of 25 for the saturated vapour at  $706^\circ$ . This yields a calculated value of 0.75 volt, approximately, for the heat of dissociation.

L. S. THEOBALD.

**Heat of dissociation of the molecule  $\text{O}_4$  and Sutherland's constant for oxygen.** S. BRESSLER and V. KONDRATJEV (Nature, 1930, 125, 164—165).—Theoretical. It is shown that the mutual energy of two molecules at the moment of collision is equal to Sutherland's constant. This receives support from the fact that the values of this constant obtained by various workers for oxygen are near to that obtained by Lewis for the molar heat of dissociation of  $\text{O}_4$  into  $2\text{O}_2$ .

L. S. THEOBALD.

**Compressibilities of gases at  $0^\circ$  and below 1 atm., and their divergence from Avogadro's law. IV. Carbon monoxide and nitrogen.** T. BATUECAS, C. SCHLATTER, and G. MAVERICK (J. Chim. phys., 1929, 26, 548—555; cf. A., 1925, ii, 497).—The method is that previously described. The mean of 48 determinations for carbon monoxide gives  $(1+\lambda) = 1.00048$  and coefficient of compressibility at  $0^\circ = 6.3 \times 10^{-6}$ . For nitrogen 45 determinations give as means  $(1+\lambda) = 1.00045$  and compressibility  $= 5.9 \times 10^{-6}$ . In both cases individual results show such divergence that the figures are regarded as only provisional.

C. A. SILBERRAD.

**Viscosity of vapours of organic compounds. I.** T. TITANI (Bull. Chem. Soc. Japan, 1929, 4, 277—287).—See A., 1929, 993.

**Pressure of gaseous mixtures. III.** C. C. TANNER and I. MASSON (Proc. Roy. Soc., 1930, A,

126, 248—288).—Previous measurements with helium and hydrogen (Gibby, Tanner, and Masson, A., 1929, 253) are now extended to mixtures of each of these gases with argon. Argon deviates from Boyle's law over the range 25—75° as far in the negative sense as hydrogen and helium do in the positive sense; at 100° it almost follows Boyle's law, and at higher temperatures its deviations become positive. Compressions were made on the three pure gases and 13 binary mixtures of them at temperatures from 25° to 175° and pressures from 30 to 125 atm. As a result of further improvements in the technique, the average deviation of the experimental values of  $p_v$  from smooth isotherms is now only about 0.02%. The equation  $p_v = a + bp + cp^2$  is applied to the isotherms of each gas and mixture, and tables are drawn up showing the effect of varying composition and temperatures on the values of  $a$ ,  $b$ ,  $c$ , and  $\Delta$ , where  $\Delta$  is the mean experimental deviation in  $p_v$  for each isotherm. By plotting  $b$  against gas composition it is found that, as with helium-hydrogen mixtures (*loc. cit.*), Lennard-Jones' partial pressure law (A., 1927, 727) also holds for argon-helium and argon-hydrogen mixtures, and the assumption that the intermolecular fields of force are spherically symmetrical about each molecule appears to be justified. The data for the influence of temperatures on the constants of the isotherms are applied to Lennard-Jones' equations for intermolecular action (*loc. cit.*). Taking the distance index for the attractive component as  $-5$ , the index for the repulsive component is found to be  $-10$  or  $-11$  for pure hydrogen and helium, and  $-9$ ,  $-10$ ,  $-11$ , or  $-14\frac{1}{2}$  for pure argon. The force constants are evaluated for each type of encounter according to the different models. Values are also calculated for the "cohesion energy" (a quantity equivalent to the latent heat of separation of a pair of molecules at 0° Abs.), and for the kinetic diameters at various temperatures. The results indicate that the radius of a given gaseous molecule in collision is a function, not only of the kinetic energy of the invading molecule, but also of the nature of this molecule; the argon atom is smaller when it stops another argon atom than when it stops a hydrogen molecule, and in stopping a helium atom is probably larger than when it stops a hydrogen molecule. The special result found with helium and hydrogen is therefore not typical. It is shown that it is not possible to predict the isotherms of mixtures from those of their pure components alone.

L. L. BIRCUMSHAW.

Viscosity, heat conductivity, and diffusion in gas mixtures. VII. Relationships with homogeneous gas reactions. M. TRAUTZ (Ann. Physik, 1929, [v], 3, 1102—1118).—Theoretical. Formal substitutions are made which involve implications which are not self-evident in the physical sense but are capable of experimental test. An expression which may be substituted for the ordinary molecular diameter is suggested; this is less influenced by the special characteristics of models.

R. A. MORTON.

Viscosity formula for binary mixtures, taking into consideration association effects. IV. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1929, 4, 288—297; cf. A., 1929, 500, 994).—The author's formula is

applied to the systems toluene-benzyl benzoate, benzene-benzyl benzoate, benzene-guaiacol, toluene-guaiacol, ethyl alcohol-ether, *n*-propyl alcohol-ether, chlorobenzene-phenol, and benzene-phenol. Very good agreement exists between the association values obtained experimentally and those calculated from the formula.

F. G. TRYHORN.

Viscosity isotherms of binary mixtures. IV. System benzaldehyde-sulphur monochloride. F. DE CARLI (Atti R. Accad. Lincei, 1929, [vi], 10, 250—253; cf. this vol., 26).—Viscosity curves for this system at 3°, 9°, 13.2°, and 20° are given. Below 20° mixtures of the two components show a maximum viscosity. The maximum deviation from the value calculated from the mixture rule corresponds with 60% of benzaldehyde, which indicates that the compound  $2\text{Ph}\cdot\text{CHO}, \text{S}_2\text{Cl}_2$  may be formed in solution.

O. J. WALKER.

Viscosity isotherms of binary mixtures. V. Nitrobenzene-stannic bromide. F. DE CARLI (Atti R. Accad. Lincei, 1929, [vi], 10, 372—375; cf. preceding abstract).—Although the thermal diagram for this system is of the simplest type, with a eutectic mixture containing about 53% of stannic bromide, the viscosity isotherms at 32° and 40° suggest the formation of a compound, probably  $2\text{PhNO}_2, \text{SnBr}_4$ , which is stable in the liquid state.

F. G. TRYHORN.

X-Ray analysis of system nickel-bismuth. G. HÄGG and G. FUNKE (Z. physikal. Chem., 1930, B, 6, 272—283; cf. Voss, A., 1908, ii, 194).—X-Ray and microscopical examination have revealed the existence of two intermediate phases. The  $\beta$ -phase, with 40—50 at.-% Bi, has the nickel arsenide structure, and is composed of an equal number of nickel and bismuth atoms, the excess nickel atoms being distributed in the interspaces. The  $\gamma$ -phase has approximately the composition  $\text{NiBi}_3$ . Its structure could not be determined on account of the complexity of the powder diagram and failure to obtain single crystals.

F. L. USHER.

Germanium. XXXII. Alloys of germanium. System lead-germanium. T. R. BRIGGS and W. S. BENEDICT (J. Physical Chem., 1930, 34, 173—177; cf. A., 1929, 996).—The equilibrium diagram for the system lead-germanium has been determined from thermal data obtained by methods previously described (*loc. cit.*). Germanium and lead are probably completely miscible as liquids, but form no solid solutions. Cooling the liquid alloys results in the complete separation of the germanium before the lead, and the usual type of eutectic is absent. Photomicrographs (not reproduced) show characteristic crystals of germanium embedded in a matrix of lead. Germanium falls between silicon and tin in its behaviour towards lead, miscibility increasing in the order silicon < germanium < tin; the systems lead-germanium and tin-silicon are similar.

L. S. THEOBALD.

Ternary silver alloys. I. The system silver, copper, zinc. S. UENO (Mem. Coll. Sci. Kyoto, 1929, 12, 347—374).—The system has been examined thermally and microscopically. No three-phase region was found, but the  $\beta$ -solid solution of the

copper-zinc system unites with the  $\beta$  of the silver-zinc system, and the  $\epsilon$  of the copper-zinc system with the  $\epsilon$  of the silver-zinc system. This results in two wide homogeneous fields and three heterogeneous fields within the triangular base of the diagram.

W. E. DOWNEY.

**Ternary system of Cu-Sn-Sb.** M. TASAKI (Mem. Coll. Sci. Kyoto, 1929, 12, 227—256).—Copper-tin alloys with 60—80% Cu and tin-antimony alloys with 40—60% Sb have been examined. In the ternary equilibrium the  $\gamma$  and  $\delta$  eutectoids of the Cu-Sn system form ternary mixed crystals with the  $\gamma$  and  $\delta$  eutectoids of the Cu-Sb system. The  $\epsilon$  eutectoid of Cu-Sn gives in the ternary system a compound  $\text{Cu}_{12}\text{Sb}_3\text{Sn}_7$ . The equilibrium diagram is used in discussing the white metal bearing alloys.

W. E. DOWNEY.

**Dependence of some optical properties on temperature in the softening interval of glasses.** G. TAMMANN and H. HARTMANN (Z. anorg. Chem., 1930, 185, 305—323).—Refractive indices of the following substances have been determined at different temperatures above and below the softening temperature: salicin, brucine, sucrose, colophony, and mastic. For the first three substances the refractive index changes linearly with temperature in both the viscous and the vitreous state, and the two straight lines meet at a temperature 2—3.5° higher than the temperature at which brittleness begins. For colophony and mastic, which are mixtures, there is no sharply-defined point of intersection. The refractivities are also given for salicin, brucine, and colophony. For salicin, the refractivity increases with temperature from 5° to 80° by 0.4%, the increase being slightly greater in the liquid state than in the solid. The difference is much more marked in the case of brucine, but still small. The results indicate that molecular changes do not take place on melting. The refractivity of colophony increases in the vitreous state with rising temperature, but falls in the liquid state. The angle of rotation of the plane of polarisation and the specific rotation of colophony decrease linearly with temperature in the liquid state. In the solid state they rise with falling temperature, but the measurements are very difficult to make. For the angle of rotation of salicin there appears to be a maximum and a minimum in the neighbourhood of the temperature at which brittleness sets in, but the results cannot be repeated exactly. Anhydrous dextrose has a maximum angle of rotation at the temperature at which brittleness begins, but with 4% of water the angle of rotation increases linearly as the temperature falls to this point and then increases still more rapidly. The time required for the disappearance of the double refraction produced by distortion under a load has been determined for colophony and salicin at different temperatures. The time increases with falling temperature along a hyperbolic curve of which the asymptote lies near the temperature at which brittleness commences.

M. S. BURR.

**B. p. of (ternary) water-alcohol mixtures.** P. BRUN (Compt. rend., 1930, 190, 122—124).—The b. p. of various ternary mixtures of water with ethyl and isoamyl alcohols have been determined with

special precautions to ensure uniformity of pressure and homogeneity of imperfectly miscible mixtures. The results are shown by a trilinear graph, on which is also indicated the limit of miscibility at the b. p. The critical b. p. is 88.7—88.8°.

C. A. SILBERRAD.

**Steam-distillation of lower volatile fatty acids from a saturated salt solution.** W. H. OLMSTED, W. M. WHITAKER, and C. W. DUDEN (J. Biol. Chem., 1929, 85, 109—114).—The rate of steam-distillation of the lower volatile fatty acids from aqueous solution is much increased by adding to every 100 c.c. of the solution 70 g. of magnesium sulphate and 2 c.c. of 50% sulphuric acid. Characteristic distillation rates are given.

C. R. HARRINGTON.

**Solubility determinations of U.S.P. chemicals.** W. SCHNELLBACH and J. ROSIN (J. Amer. Pharm. Assoc., 1929, 18, 1230—1235).—The data recorded refer to 25° and 100 parts of solvent. Sodium sulphate decahydrate in glycerol ( $d_4^{25}$  1.246) 7.52; sodium nitrite (96.86%) in alcohol ( $d_4^{25}$  0.808) 1.424; arsenic trioxide in water about 1.99, in glycerol about 15.88. The determination of sodium by the method of Barber and Kolthoff (A., 1928, 859) is discussed.

E. H. SHARPLES.

**Optical detection of the solubility of mercury in water.** K. F. BONHOEFFER and H. REICHHARDT (Naturwiss., 1929, 17, 933).—The solubility of mercury in water is demonstrated by the exhibition of ultra-violet absorption bands at approximately 2610, 2510, and 2270 Å. The solubility of the vapour is of the same order as that of an inert gas.

H. F. GILLBE.

**Solubility of sulphur in certain saturated hydrocarbons, in the benzene series, and in chloro-substituted benzenes.** I. S. TELETOV and N. D. PELICH (Ukrain. Chem. J., 1929, 4, 387—402).—The solubility of sulphur in saturated paraffin hydrocarbons increases with the specific gravity of these. In any one hydrocarbon it is very low at 20° and increases gradually up to 60°, and rapidly at higher temperatures. In hydrocarbons of the benzene series, the solubility of sulphur is diminished by the introduction of methyl groups but increased by that of chlorine atoms. The benzene hydrocarbons and probably their chloro-derivatives are said to form definite compounds, the character of which is under investigation.

T. H. POPE.

**Solubility of benzoquinhydrone in aqueous-alcohol mixtures.** M. I. ALFEROV and A. I. BRODSKI (Ukrain. Chem. J., 1929, 4, 403—404).—See A., 1929, 1302.

**Stability of the submicron. II. Dissolution and formation of crystals.** W. VON BEHREN and J. TRAUBE (Z. physikal. Chem., 1930, 146, 1—29; cf. A., 1929, 259).—A continuation of work previously published. Photographs are given showing the ultramicroscopic appearance of various stages observed during the dissolution and formation of crystals. The results are discussed theoretically and shown to support Smekal's theory of "lattice blocks."

F. L. USHER.

**Crystalline form in the formation of solid solutions. VI. Thermal and X-ray analyses of**

the anhydrous systems  $\text{CaCl}_2\text{--CoCl}_2$ ,  $\text{CaCl}_2\text{--FeCl}_2$ ,  $\text{CaCl}_2\text{--MnCl}_2$ , and  $\text{CaCl}_2\text{--CdCl}_2$ . A. FER-RARI and A. INGANNI (Atti R. Accad. Lincei, 1929, [vi], 10, 253—258; cf. A., 1929, 996).—Cobaltous and ferrous chlorides form eutectic mixtures with calcium chloride; the eutectic points at  $61.4^\circ$  and  $59.2^\circ$  correspond with 54.3 and 44.5 mol.-%  $\text{CaCl}_2$ , respectively. Manganese and cadmium chlorides form mixed crystals in all proportions with calcium chloride; these decompose into their components at about  $475^\circ$  and  $414^\circ$ , respectively. The behaviour of these systems indicates that calcium chloride is structurally different from the bivalent chlorides of cobalt, iron, manganese, and cadmium. O. J. WALKER.

**Fractional precipitation. IV. Influence of the formation of mixed crystals and adsorption compounds.** O. RUFF and E. ASCHER (Z. anorg. Chem., 1930, 185, 369—386).—Fractional precipitation of different pairs of salts, in which the crystal structure makes the formation of mixed crystals possible, has been studied with reference to the conditions necessary for equilibrium and the influence of the size and ratio of the solubility products. Immediately after formation the precipitate always contains more of the more soluble constituent than in the equilibrium state, which can often be reached only after stirring for several hours. The composition of the precipitate depends on the ratio of the concentrations of the constituents in solution. With continued stirring and rise in temperature the proportion of the more soluble constituent of the precipitate at first increases to a maximum and then decreases. When the solubility products are approximately equal, fractional precipitation is impossible, the precipitate always containing a large quantity of the more readily soluble component. This holds until the ratio of solubility products of approximately  $10^{-4}$  is reached, e.g., in the system  $\text{PbCrO}_4\text{--BaCrO}_4$ . The facility of separation increases from this point as the difference between the solubility products increases. M. S. BURR.

**Fractional precipitation. V. Inclusion of foreign matter in the crystal lattice.** O. RUFF (Z. anorg. Chem., 1930, 185, 387—402).—Inclusions in crystals during precipitation depend mainly on two factors: (1) the relation of the affinity between unlike to that between like molecules, (2) failure to attain equilibrium conditions. Electrokinetic phenomena are of minor importance. A small difference in affinity is associated with one or more of the following conditions: similar space relationships, a common ion, and similar solubility products. The following cases have been investigated experimentally: the inclusion of zinc sulphide by copper sulphide, manganese sulphide by zinc sulphide, and potassium permanganate by barium sulphate, and the separation of silver and copper iodides and also of calcium and magnesium oxalates. These phenomena can all be explained, and, at the same time, fractional separation of all these salt pairs can be obtained, by taking into consideration the above conditions. M. S. BURR.

**Nature of pyrosols.** A. MAGNUS and E. HEY-MANN (Naturwiss., 1929, 17, 931—932).—The partition equilibria of cadmium between bismuth and cadmium

chloride at  $600^\circ$  and  $700^\circ$  have been determined, and indicate that the cadmium is in the same molecular state in the two phases. Since the solution in bismuth is monatomic, the pyrosol (metallic fog) formed by cadmium in cadmium chloride is caused by atomic dispersion of the metal. H. F. GILLBE.

**Nature of "active carbon."** H. H. LOWRY (J. Physical Chem., 1930, 34, 63—73; cf. B., 1929, 929).—The adsorption of hydrogen, carbon dioxide, and air by charcoal prepared from an anthracite coal has been investigated. The activity of an adsorbent carbon is best defined by the amount of gas adsorbed per unit area and not per unit weight. The pore volume is considered to be a measure of the adsorbing surface. In this case the adsorptive capacity per unit pore volume decreases with a rise in the temperature (above  $1000^\circ$ ) to which the material is heated. The data indicate that activity defined as above is independent of the atmosphere in which the charcoal is prepared, but is dependent on the maximum temperature to which it is subjected. At temperatures between  $900^\circ$  and  $1300^\circ$  an increase in adsorptive capacity is probably accompanied by a proportional increase in extent of adsorbing surface. In agreement with previous results on the relation between adsorptive capacity and hydrogen content (*loc. cit.*), the activity of the charcoal is now found to increase with hydrogen content up to a value of the latter of 0.5%, after which it remains approximately constant. The view that the simultaneous decrease in activity and hydrogen content above  $1000^\circ$  may be due to a gradual crystallisation of the carbon is discussed. L. S. THEOBALD.

**Adsorption of air on glass as a function of temperature.** A. S. ADAMS (Physical Rev., 1929, [ii], 34, 1438—1439; cf. Frazer, A., 1929, 503, 1376).—With rise of temperature the thickness of the adsorbed layer decreases at a somewhat slower rate than for rock salt. An "ageing" effect is indicated. The adsorption may be due to some relatively rarer constituent of the atmosphere. N. M. BUGH.

**Adsorption by various silica gels from gaseous mixtures of air, alcohol, and ether.** II. L. VON PUTNOKY and G. VON SZELÉNYI (Z. Elektrochem., 1930, 36, 10—15).—Five different commercial silica gels and one produced by the hydrolysis of silicon tetrachloride were dried in a vacuum and activated by heating at  $200^\circ$ . Three series of adsorption experiments were made with alcohol and ether vapours at  $20^\circ$  under different vapour pressures in an apparatus described by Bachmann and Maier (A., 1928, 119). Curves are given to elucidate the sorption and desorption processes; these show the relationship between  $p/P$  ( $p$  vapour pressure above the gel,  $P$  the initial pressure) and  $x/m$  ( $x$  mass of vapour adsorbed, and  $m$  mass of adsorbent). H. T. S. BRITTON.

**Adsorption by active charcoal.** E. ENGEL (Z. ges. Schiess- u. Sprengstoffw., 1929, 24, 495—497).—See A., 1929, 998.

**Adsorption of a sodium chloride solution by sand.** T. NOMITSU, R. KAMIMOTO, and Y. TOYOHARA (Mem. Coll. Sci. Kyoto, 1929, 12, 265—274).—

The negative adsorption of five different specimens of sand for sodium chloride has been measured.

W. E. DOWNEY.

**Soap solutions. VII. Adsorption of soap on charcoal.** J. MIKUMO (J. Soc. Chem. Ind. Japan, 1929, 32, 178—180B).—The adsorption from alcoholic solution of potassium laurate, myristate, palmitate, stearate, and oleate by charcoal has been investigated. For soaps of the same series Freundlich's adsorption isotherm is valid up to the concentration limit at which the formation of aggregates commences, and Traube's rule also is applicable. For binary mixtures of soaps the component derived from the higher acid is present in excess in the adsorbed layer.

H. F. GILLBE.

**Solubility and adsorbability of benzoic acid and salicylic acid in presence of mixed organic solvents.** W. HERZ and M. LEVI (Kolloid-Z., 1930, 50, 21—22).—Measurements of the adsorption of benzoic acid and salicylic acid by carbon from solutions in mixtures of benzene and heptane, heptane and carbon tetrachloride, and benzene and carbon tetrachloride show that solubility varies antipathetically with adsorbability.

E. S. HEDGES.

**Adsorption processes in precipitates undergoing coagulation. I. Adsorption of lead, bismuth, and thallium on silver and mercurous halides.** L. IMRE (Z. physikal. Chem., 1930, 146, 41—62).—Silver and mercurous halides formed in presence of excess of the halogen ion have been used as adsorbents for lead, bismuth, or thallium, the amount adsorbed being determined by means of the  $\gamma$ -radiation from the radioactive indicators thorium-B, thorium-C, or thorium-C', respectively. The silver halides are more effective adsorbents than the corresponding mercurous compounds. The values of the exponent  $1/n$  in the Freundlich adsorption formula show a gradual drift both with increasing concentration of the solute and, for a given concentration, with time, the effect being most marked when the adsorbent sol is unstable. The observed drift is explicable on the assumption that, along with diminished adsorbing power resulting from the partial neutralisation of the surface charge, molecules of solute become imprisoned in the interstices of the coagulating particles and are thus less easily reached by the external liquid. Adsorption appears to be strictly reversible only in the initial stages and at the surface of particles not undergoing coagulation.

F. L. USHER.

**Behaviour of adsorbed electrolytes in direct- or alternating-current electrolysis.** S. L. BHATNIA (Kolloid-Z., 1930, 50, 55—58).—Oxalic acid which has been adsorbed by aluminium hydroxide or silicic acid is obtained therefrom when the adsorbent is placed in water and a direct current is passed. By this process, about 80% of copper sulphate and about 50% of nickel sulphate adsorbed by animal charcoal can be reclaimed. An alternating current obtained from the secondary of an induction coil is not effective in this respect.

E. S. HEDGES.

**Surface tension in a vacuum.** S. RAY (Kolloid-Z., 1930, 50, 19—21).—When a flask containing water in which a glass capillary stands is evacuated through a sulphuric acid wash-bottle, the height of

the water in the capillary falls. This behaviour is discussed in relation to the author's colloid-chemical theory of surface tension (A., 1928, 702). After the fall of the water column, the inside wall of the capillary was marked by parallel ridges of water, giving the effect of an etched thermometer tube—a phenomenon which is considered to be connected with the Liesegang phenomenon.

E. S. HEDGES.

**Surface tension and heat of vaporisation.** J. J. VAN LAAR (Z. anorg. Chem., 1930, 185, 425—427).—Polemical against Herz (A., 1929, 1001).

M. S. BURR.

**Surface solutions on mercury. Oleic acid.** F. EMIR (Compt. rend., 1930, 190, 176—178).—Surface solutions of oleic acid on mercury and on water are analogous in behaviour. The former have a surface tension corresponding with saturation of 60 dynes/cm. (approximately double that for water), whilst the thickness of the film is 24 Å. (23 Å. for water). There is therefore evidence that the molecular orientation is the same in both cases. Elaborate attempts to eliminate oxidation of the mercury surface were not completely successful.

J. GRANT.

**Surface tension of protein solutions.** L. DE CARO and M. LAPORTA (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], 35, 171).—Dilute solutions of serum- and egg-albumins show a minimum surface tension, whether determined by static or dynamic methods, at the isoelectric point. When the concentration of serum-albumin is greatly reduced a uni-molecular surface layer is formed, and the surface tension determined by static methods is again minimal at the isoelectric point. This minimum is the result of the increased power of the individual molecules to reduce surface tension when they are undissociated, in accordance with the conclusions of Bottazzi (A., 1929, 642).

R. K. CALLOW.

**Effect of addition of proteins on the surface tension of a solution containing surface-active acid or base.** R. SUGINO (J. Biochem. Japan, 1929, 11, 31—45).—In the  $p_H$  region where the added protein exists as an anion the surface tension of a solution of amylamine is affected owing to combination. The isoelectric point of protamine is at  $p_H$  11.

CHEMICAL ABSTRACTS.

**Double refraction in cellulose acetate and nitrate films.** J. G. McNALLY and S. E. SHEPPARD (J. Physical Chem., 1930, 34, 165—172).—An instrument suitable for determining the direction of orientation of micelles in transparent colloidal films is described. Uniaxial, biaxial, or isotropic films can be prepared from a given sample of cellulose acetate or nitrate by varying the tension on the film during drying. Films made by pouring a 2% solution of the ester on to a clean surface of mercury and allowing it to dry slowly were completely isotropic.

L. S. THEOBALD.

**Dynamics of amalgamation.** C. E. GUYE and (Mlle.) I. ARCHINARD (Arch. Sci. Phys. Nat., 1929, [v], 11, 312—344).—Measurements have been made of the rate of creep of mercury along wires of silver, copper-gilt, and brass-gilt, and of the rate of spread of mercury drops on copper-gilt plates. Experiments

with silver wire showed a lack of concordance attributable to surface oxidation, which was in some degree improved by making the measurements under petrol. In these latter experiments and in those with gilt wires, the progress of the amalgamation, except in the initial stages, may be satisfactorily represented by means of an equation proposed by Guye (*ibid.*, 1925, 7, 39) for the rate of ascent of the sap in plants. The rate of ascent of the mercury is accelerated by rise of temperature, which affects both viscosity and the capillary constant of the system. The process of amalgamation is considered to consist in the replacement of the interface air-gold by the interface air-amalgamated gold with the liberation of free energy. The creep of the mercury results from the excess of the energies of amalgamation and of wetting over the work which must be done against gravity and viscosity forces. The rate of spread of a drop of mercury on a gilt plate is proportional to the initial dimensions of the drop provided this is not very small. The process of spreading is analogous to, although not wholly comparable with, that of the ascent of mercury up a wire. After the drop has made contact with the gold it assumes a hemispherical shape and spreading takes place radially from the circumference.

F. G. TRYHORN.

**Membrane and osmosis. II.** F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1024—1031).—The behaviour of ternary liquid mixtures in contact with a membrane is considered.

H. F. GILLBE.

**Membrane and osmosis. IV.** F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1305—1313).—Mathematical.

A. J. MEE.

**Collodion membranes. IV. Permeability of the membranes to water.** E. MANEGOLD and R. HOFMANN (Kolloid-Z., 1930, 50, 22—29; cf. this vol., 154).—A new apparatus for the preparation of collodion membranes having reproducible properties is described. An account is given of the characterisation of the prepared membranes by their thickness, water content, and permeability to water, and of the determination of the size of the pores. The relation previously given, that the product of the permeability to water and the membrane thickness is constant, has been confirmed, and it is found that if this product is multiplied by the viscosity a new constant is obtained which is independent of the temperature and of the nature of the liquid. This constant is termed the specific permeability and is regarded as a constant and characteristic membrane value. The specific permeability may vary as the result of structural changes in the membrane, such as changes in the structure, size, and arrangement of the pores. The specific permeability decreases with the duration of the filtration and this effect has been traced to compression of the capillary structure, and to the substance in suspension stopping up the pores and forming a layer over the membrane surface. Over the range 10—20° no temperature influence on the capillary structure is observed.

E. S. HEDGES.

**Abnormal osmosis at non-swelling membranes. I.** K. SÖLLNER (Z. Elektrochem., 1930,

36, 36—47).—The magnitude of the *P.D.* between two solutions of electrolytes separated by a collodion membrane has been found to depend on the previous treatment of the collodion, whereby the size of the pores is affected. Such membranes contain fine pores of widely differing dimensions, thereby causing potentials to be set up which differ from place to place and from pore to pore and in consequence tend to establish closed current circuits within and around the membrane.

H. T. S. BRITTON.

**Application of the Donnan effect to nucleic acid compounds.** E. HAMMARSTEN (Acta Med. Scand., 1928, 68, 10 pp.; Chem. Zentr., 1929, ii, 756—757).—Solutions of thymonucleic acid containing hydrogen chloride and sodium chloride were treated with varying amounts of a solution of crystallised egg-albumin and dialysed; the *p<sub>H</sub>* and osmotic pressure are of the same order of magnitude in almost all cases. The means whereby carbon dioxide can produce in the cell nucleus a higher hydrogen-ion concentration than is generally supposed is discussed. The nucleic acid in the cell nucleus has a very small velocity of diffusion.

A. A. ELDRIDGE.

**Imbibition of some natural colloidal complexes. Cellular exchange.** L. EMERIQUE (Ann. Physiol. Physicochim. biol., 1928, 251—296; Chem. Zentr., 1929, ii, 435—436).—The degree of imbibition and change in weight occurring when hen's egg-white or the mucin of frog's eggs is immersed in solutions of sodium, potassium, or calcium chloride was followed. Addition of a non-electrolyte has an effect other than that anticipated according to the osmotic pressure. Imbibition experiments with pig's bladder in sodium chloride solutions in presence of bile acids show that the surface tension is not the only controlling factor.

A. A. ELDRIDGE.

**Partition of light between two dissolved absorbents.** K. WEBER (Z. Elektrochem., 1930, 36, 26—36).—The absorption constants for  $\lambda = 366 \mu$  of solutions of  $\alpha$ -esculin in aqueous alcohol (40% alcohol), quinine sulphate in *N*-sulphuric acid, sodium naphthionate in water, amyl nitrite in aqueous alcohol (40—90% alcohol), sodium nitrite in water, and potassium chromate, have been measured with Plotnikov's fluorometer; for these solutions Beer's law has been found to be obeyed. The variations in the amounts of fluorescence produced in the systems  $\alpha$ -esculin-amyl nitrite, quinine sulphate-amyl nitrite, sodium naphthionate-sodium nitrite, sodium naphthionate-potassium chromate were also investigated. In some cases fluorescence was entirely suppressed. An exponential formula is derived for the partition phenomena.

H. T. S. BRITTON.

**Absorption of cobalt salts in concentrated solutions.** P. VAILLANT (Compt. rend., 1930, 190, 170—172).—By adjusting the thickness (*l*) of the solution measured so that the quantity  $n\beta l$  had a maximum value, *n* being the concentration and  $\beta$  the molecular absorption coefficient for a given wavelength (5000—6000 Å.), it is found that the spectral curves obtained for solutions of cobalt chloride (2*N*), sulphate (0.5*N*), and nitrate (2*N*) in water, and for 0.2*N*-cobalt nitrate in concentrated zinc chloride and



sulphate solutions, are superposable. Change of anion, concentration, or solvent therefore modifies the absorption spectrum only by a Kundt displacement and a change in intensity, a conclusion which may be interpreted in terms of the theory of activity if it is assumed that the absorption of the  $\text{Co}^{++}$  ion increases when its activity decreases (cf. this vol., 10).

J. GRANT.

**Sedimentation of clay suspensions.** A. BOUTARIC and (MLLE.) M. ROY (Compt. rend., 1930, 190, 272—275).—The rate of sedimentation of kaolin may be followed from the rate of fall ( $dx/dt$ ) of the surface separating the upper limpid layer and the lower layer of the suspension, and is given by  $dx/dt = A/[1 + Bc/(l-x)]$ , where  $l$  is the initial height,  $x$  the height after the time  $t$ , and  $c$  the concentration. The initial rate of fall ( $v$ ) varies with  $c$  according to the function  $v = 1/(\alpha + c)$  whatever the diameter of the containing vessel, and decreases with time. Experiments with acid solutions rendered strictly comparable by control of the  $p_H$  values showed that small quantities of camphor, menthol, or isoamyl alcohol do not accelerate the rate of sedimentation, but if anything, slightly retard it. Dubrisay's results (A., 1929, 877) were confirmed.

J. GRANT.

**Absorption capacity of some substances for light of various wave-lengths as a function of the particle size.** G. P. VORONKOV and G. I. POKROVSKI (Kolloid-Z., 1930, 50, 17—19).—The change in light absorption with diminution in the size of the particles (cf. A., 1927, 1138) is discussed theoretically and measurements of the light absorption and size of particles in suspensions of mercuric sulphide and ultramarine in water have been made. With progressive decrease in the particle size Rayleigh's law of absorption is followed more closely, and a marked change in the colour of the suspension occurs when the effective radius of the particles becomes smaller than the wave-length of light. E. S. HEDGES.

**From atom to structure.** V. KOHLSCHÜTTER (Kolloid-Z., 1930, 50, 1—12).—A lecture on the structures produced by chemical growth, such as lead "trees," "hair" silver, silicate growths, etc., particularly in relation to the simulation of living structures. These forms of growth are conditioned mainly by topochemical processes, or the localisation of chemical change, and are in many cases characteristic of the substance. E. S. HEDGES.

**Comparison of silver and lead sols made by the Bredig method.** H. Q. WOODARD (J. Physical Chem., 1930, 34, 138—144).—Silver and lead sols prepared as described for lead (A., 1928, 948) are alike in rising to a maximum concentration during arcing after which silver sols are completely precipitated with further arcing; those of lead decrease with prolonged arcing. In the case of silver, sol formation is determined mainly by the anion present in the arcing solution. No sols could be obtained in solutions of silver or ammonium nitrates, and only transient and dilute sols in solutions of sodium nitrate or acetate, but concentrated and stable sols could be made in solutions of sodium carbonate or potassium hydroxide. Dilute and stable sols resulted in hydrochloric acid, sodium or ammonium chloride, and

sodium thiocyanate or sulphide. In the case of lead, the cation chiefly determines the sol formation.

L. S. THEOBALD.

**Molybdenum-blue.** J. DUCLAUX and R. TITFICA (Rev. gén. Colloid., 1929, 7, 289—294).—Molybdenum-blue has a variable chemical composition and its colloid-chemical properties depend on the method of preparation. It may be obtained by chemical or photochemical reduction of molybdic acid by a variety of methods. Molybdenum-blue is considered to be a strong acid, comparable in strength with mineral acids; the colloidal anion of which contains molybdenum in two states of oxidation and is capable of union with metallic ions to form salts. Molybdenum-blue is peculiar in its solubility in a large number of organic solvents, whilst it is insoluble in all liquids of low dielectric constant. When certain organic solvents are shaken with an aqueous solution of molybdenum-blue, the aqueous solution is almost immediately decolorised, the molybdenum compound passing into the organic liquid phase. This is the first example recorded of a colloid passing from one solvent into another; glycerol appears to be the best solvent. The solubility in butyl alcohol provides a rapid means of purifying molybdenum-blue by extraction of the aqueous solution. E. S. HEDGES.

**Influence of autoclave treatment on the form of hydroxides and on the nature of colloidal suspension.** T. KATSURAI (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1929, 12, 161—166).—When gelatinous ferric hydroxide is heated with a slight excess of alkali under a pressure of 5—10 atm., a finely powdered form similar to rouge is obtained. The hydroxides of magnesium, aluminium, chromium, and cobalt, prepared by adding a slight excess of either sodium hydroxide or ammonia to salts of these metals, suffered no change under this treatment. Sols of zinc potassium ferrocyanide and of copper ferrocyanide were completely coagulated when heated in an autoclave, and sols of Prussian-blue and of Turnbull's blue deposited rouge: this same deposit was obtained when solutions of potassium ferrocyanide or ferriocyanide were treated in this way. An arsenious sulphide sol was not coagulated, but sols of silver halides were coagulated when heated under a pressure of 10 atm. E. S. HEDGES.

**Hydrogels. IX. Lead dioxide hydrate.** A. SIMON (Z. anorg. Chem., 1930, 185, 280—299).—Hydrated lead dioxide has been prepared by four different methods: (1) Electrolysis of sodium lead tartrate giving  $\text{PbO}_2 \cdot 1.24\text{H}_2\text{O}$ . (2) Hydrolysis of sodium plumbate; three samples contained 0.32, 0.36, and 0.44  $\text{H}_2\text{O}$ , respectively. (3) Decomposition of sodium plumbate by liquid hydrogen cyanide; three samples contained 0.84, 0.88, and 0.82  $\text{H}_2\text{O}$ , respectively. (4) Heating sodium plumbate with water under pressure; all samples obtained in this way contained less than 0.3  $\text{H}_2\text{O}$  for  $1\text{PbO}_2$ . Isobaric decomposition curves have been obtained from the products of 1, 2, and 3 by a method previously described (cf. A., 1927, 730). At 76° all the samples reached approximately the same composition,  $\text{PbO}_2 \cdot 0.3\text{H}_2\text{O}$ . The general form of the curves is that of other colloidal metal oxide hydrates. The

relationship between the vapour pressure of the hydrate and its water content follows the same logarithmic law as observed for other oxide hydrates (A., 1927, 510), i.e.,  $\log_e p_0/p = kn$ ,  $k$  in this case having a value 1 below  $120^\circ$ . Above this temperature, however, the value falls rapidly, due to the fact that ageing proceeds at a greater rate and the osmotic system splits up into free water and lead dioxide, causing a rise in the vapour pressure,  $p$ . The heat of formation of the system lead dioxide-water, calculated from the pressure-concentration diagram, is 19,500 g.-cal., whilst the value for  $k=1$  is 20,500 g.-cal. When examined under a polarisation microscope, the colour varied from chocolate or yellowish-brown to black, but there was no crystalline structure or double refraction. Sols were easily prepared in water, alcohol, or ether. Brownian movement was observed in these by the ultramicroscope, the size of the particle varying with the method of preparation of the original oxide. The products obtained by the pressure method (4) did not form sols and were coarsely crystalline. X-Ray diagrams of the products of method 3 were obtained by the Debye method. All the lines obtained were identical with those of crystalline lead dioxide. In all the samples obtained ageing was rapid and consisted in the loss of water, as in the case of other oxides studied. The rate varied with the method of preparation and the final condition was the crystalline anhydrous dioxide. M. S. BURR.

**Formation of lyophobic organosols.** H. B. WEISER and G. L. MACK (J. Physical Chem., 1930, 34, 86—100).—The methods of formation of organosols stabilised by preferential adsorption of ions have been classified. Details are given of new and improved methods for the preparation of sols of mercuric sulphide in methyl alcohol, acetone, and *n*-propyl alcohol, of ferric oxide, copper ferrocyanide, zinc ferrocyanide, and Prussian-blue in methyl alcohol, and of ferric, manganic, and chromic oxides in *n*-propyl alcohol. L. S. THEOBALD.

**Refractive indices of hydrosols. II.** B. V. DUMANSKI and B. J. PUTSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1301—1307).—See A., 1929, 1142. The formula should read  $n = c_1(n_2 - n_1)/d_2 + n_1$ .

**Viscosity of emulsions. I.** J. O. SIBREE (Trans. Faraday Soc., 1930, 26, 26—36).—Using the concentric cylinder viscosimeter, measurements have been made of the viscosities of emulsions of paraffins in sodium oleate solution, bromoform being added to the paraffin in order to obtain an oil of the same density as the oleate solution. The viscosity of such solutions is not constant, but decreases with increasing velocity gradient, becoming nearly constant when the latter reaches a certain value. The viscosity of an emulsion does not depend directly on the viscosity of the disperse phase; thus with disperse phases for which the viscosities in the pure state are in the ratio 38 : 1, the emulsions have viscosities only in the ratio 1.4 : 1 in the constant region; at very low velocity gradients the viscosities appear to be identical. Difficulty was experienced in testing the validity of Hatschek's equation  $\eta_e/\eta_0 = 1/(1 - \sqrt[3]{\phi})$  (A., 1911, ii, 98) owing to the uncertainty of the effect of adsorbed

films on the size of the drops and hence on the apparent concentration of the disperse phase.

J. W. SMITH.

**Kinetics of formation of colloids.** K. JABŁCZYŃSKI and S. KOBRYNER (Rocz. Chem., 1929, 9, 704—722).—The rate of reduction of selenious acid to selenium by hydrazine is found by spectrophotometric measurements to be a linear function of the time; the reduction of gold chloride by white phosphorus follows a similar course; the temperature coefficients are respectively 1.96 and 2.05. The velocity-time curve for the reduction of an ammoniacal solution of silver hydroxide by hydrazine is of the autocatalytic type; the temperature coefficient is 1.85 between  $20^\circ$  and  $30^\circ$  and 1.68 between  $30^\circ$  and  $40^\circ$ . R. TRUSZKOWSKI.

**Constitution of colloidal solutions by pectography.** P. BARY and J. V. RUBIO (Rev. gén. Colloid., 1929, 7, 308—318).—Further experiments on the production of pectographs of metallic sulphides (cf. A., 1929, 136) by slow evaporation of aqueous colloidal solutions are described. In addition to the periodic formations previously noted, it has been observed that the pectograph is frequently broken by cracks which appear in a characteristic form. These cracks are either vertical or horizontal, or curved in an ellipsoidal form. The pattern is generally horizontal when obtained by the evaporation of dilute solutions and is vertical for solutions above a certain concentration. A relation has been found between the intensity of the Tyndall effect and the complexity of the pectograph. Sols showing little or no Tyndall effect give an almost uniform deposit and the complexity of the periodic deposits increases with the intensity of the Tyndall light and thus with the colloidal instability of the solution. It is deduced that the sols contain two forms of the same chemical substance, lyophilic and lyophobic respectively, one of which protects the suspension of the other. The term "autoprotection" is suggested for this phenomenon. On ageing, the lyophilic component is gradually transformed into the lyophobic and the pectograph becomes more complex.

E. S. HEDGES.

**Structure and stability of colloid particles.** S. LIEPATOV (Kolloid-Z., 1930, 50, 74—76).—Von Weimarn's views of the structure of colloid particles (A., 1921, ii, 324) are further developed. The adsorbed ion giving the charge to the particles is generally the ion of one of the atoms present in the particle. For example, silver iodide particles are negatively charged when formed in presence of excess of potassium iodide because the iodine ion is adsorbed, and are positively charged when formed using excess of silver nitrate because the silver ion is adsorbed. The stability of the particles is considered in this light.

E. S. HEDGES.

**Stabilising action of capillary-active substances on suspensions of hydrophobic and hydrophilic powders in water and non-aqueous dispersion media. I.** P. REHBINDER (Z. physikal. Chem., 1930, 146, 63—78).—The protection of various suspensions by adsorbed layers of capillary-active substances has been investigated. Hydrophilic sub-

stances can be thus stabilised in organic liquids, but not in water, whilst the converse is true of hydrophobic powders. These results can be explained by the author's theory of polarity differences (cf. A., 1927, 1136). The mean size of the particles decreases with increasing concentration of the stabiliser and tends to a minimum value corresponding with the limit of adsorption. The effectiveness of fatty acids in stabilising suspensions of graphite in benzene is in accordance with Traube's rule. Capillary-active substances bring about an increase in the volume of a sedimented powder. F. L. USHER.

**Stability of lyophobic organosols.** H. B. WEISER and G. L. MACK (J. Physical Chem., 1930, 34, 101—121).—The effect of water and organic liquids on the stability of sols of mercuric sulphide in methyl and propyl alcohols and of ferric oxide in propyl alcohol and the effect of organic liquids on mercuric hydrosol has been investigated by determining the precipitation concentration of lithium or calcium chloride necessary as well as the  $\zeta$ -potential. The precipitation concentration gives a more reliable measure of stability than the  $\zeta$ -potential. The influence of foreign non-electrolytes on the stability can be accounted for in a qualitative manner by a consideration of their influence on the dielectric constant of the medium, on the ionisation of the electrolytes present, and on the selective adsorption of ions by the colloidal particles. In general, the stability of the hydrosols or organosols towards electrolytes increases or decreases with a corresponding change in dielectric constant. L. S. THEOBALD.

**Effect of dilution and non-electrolytes on the charge of emulsion particles and the mixing of sols.** S. S. BHATNAGAR and D. C. BAHL (Kolloid-Z., 1930, 50, 48—55).—The cataphoretic migration velocity of the particles of mixed sols has been measured, using hydrosols of arsenious sulphide, cadmium sulphide, ferric oxide, and silver, and emulsions of oil in water; curves connecting the migration velocity with composition of the mixture are shown. In a mixture of sols of arsenious sulphide and of silver the migration velocity rises to a higher value than is obtained for either sol singly, indicating that coagulation occurs at a higher potential rather than by reducing the charge below a certain critical value. The supposition of Kruyt and Willigen (A., 1928, 18) that this behaviour is to be explained by the increase in the dielectric constant is not acceptable and it is suggested that larger complexes of particles of similar charge are produced as the result of the chemical affinity of silver atoms in the one sol and of sulphur in the other. When sols of opposite sign precipitate each other the coagulation is influenced by the relative concentrations of the sols, the particle size, and the rate of mixing. The composition of the precipitate is not constant and the remaining sol contains particles of both components. The migration velocity of particles of a sol increases on dilution. Addition of non-electrolytes (ethyl alcohol, acetone, and sucrose) lowers the velocity of cataphoresis and increases the viscosity; the product of these values also decreases, except in the case of alcohol, where a maximum is observed at 20%. This

behaviour is due to the lowering of the dielectric constant of the medium by the non-electrolyte.

E. S. HEDGES.

**Influence of light on the coagulation, electrical conductivity, and the absorption spectra of some colloids.** (MISS) S. ROY and N. R. DIXAR (J. Physical Chem., 1930, 34, 122—137; cf. A., 1922, ii, 604).—Sols of ferric, chromium, zirconium, and ceric hydroxides, vanadium pentoxide, Odén sulphur, and manganese dioxide become less stable towards electrolytes on exposure to light, whilst sols of Prussian-blue, cupric ferrocyanide, mastic, and gum dammar are stabilised. The specific conductances of sols of ferric, chromium, zirconium, and cerium hydroxides, manganese dioxide, arsenious sulphide, Prussian-blue, and cupric ferrocyanide increase on long exposure to light, but those of vanadium pentoxide, gum dammar, and mastic decrease. More marked absorption is shown in the spectra of exposed sols of ferric hydroxide, arsenious sulphide, and Prussian-blue and less absorption in those of gum dammar and mastic. In most cases, the effect produced by light is an accentuation of the time effect and coagulation by light is considered to be due to decomposition of the stabilising ion and loss of reactivity of the sol particles.

L. S. THEOBALD.

**Temperature coefficient of suspensions of the second order.** K. JABŁCZYŃSKI and A. EMIN (Rocz. Chem., 1929, 9, 694—697).—The temperature coefficient of the velocity of coagulation of suspensions of silver chloride or bromide is about 2, i.e., equal to that found for suspensions of the first order, such as ferric hydroxide. R. TRUSZKOWSKI.

**Problems of present-day colloid chemistry. II. Decrease of potential produced by electrolytes.** H. R. KRUYT (Chem. Weekblad, 1930, 27, 54—56).—In the light of published experimental data it appears that the mechanism of the influence of electrolytes on phenomena such as electroendosmosis and cataphoresis and on the stability of sols cannot yet be satisfactorily explained. H. F. GILLBE.

**Structure of jellies.** P. THOMAS (Rev. gén. Colloid., 1929, 7, 295—307).—The conditions of gelation are discussed, and views of the structure of jellies are reviewed. Experiments have been conducted on the crystallisation of *l*-arabinoxazone, which is soluble in hot water and readily crystallises on cooling to form clusters of needles which interpenetrate to give a firm mass. When crystallisation takes place in presence of small amounts of gum, microscopical examination of the units of structure showed them to be intertwining hairs instead of straight needles, and it was found that the flexibility of the hairs as well as their length could be varied by altering the proportion of gum in the mixture. The experiments demonstrate that there is a relation between the flexibility and length of the hairs, their ability to intertwine so as to form a coherent mass, and their power to retain water, and that these factors can be varied by the presence of impurities. Similar, though less striking, results were obtained with lactosazone, rhamnosazone, and xylosazone.

E. S. HEDGES.

**Identity of the colloidal particles in soap sols and jellies.** M. E. L. MCBAIN and J. W. MCBAIN (*Nature*, 1930, **125**, 125).—A defence of the conclusion that the rigid structure of the jelly is built up by progressive linkings of the particles pre-existent in the sols (*J.C.S.*, 1920, **117**, 1506) against recent criticisms. In reply to Krishnamurti (*A.*, 1929, 1379), it is recorded that samples of the same solution of sodium oleate have been prepared which show both in the sol and gel states an identical light-scattering power. L. S. THEOBALD.

**Precipitation of soaps, particularly stearolates, from aqueous solution.** A. S. C. LAWRENCE (*Kolloid-Z.*, 1930, **50**, 12—17).—The differences in the physical properties of soaps are greater than is generally supposed. In particular, stearolic acid is more crystalline than any of the other higher fatty acids, and its salts exhibit characteristic forms, the particles being observable in the ordinary microscope. Whilst the other acids crystallise from alcohol in thin microscopic flakes, stearolic acid forms large clusters of needles. In crystallising the soaps from aqueous solution, single crystals of considerable size can be obtained. On cooling a hot 2% aqueous solution of the potassium, sodium, or ammonium salt, thin crystalline leaflets are obtained; the sodium and ammonium soaps change to a more amorphous form when kept. The solutions also contain aggregates of colloidal particles, the sodium salt showing the greatest tendency to exist in the colloidal form. The aggregates are generally in the form of fibres and are generally curved. The fibrous form, which has also been observed in other soap solutions, is a consequence of the long-chain structure of the fatty acid molecule. Stearolic acid and its soaps differ from the higher saturated fatty acids and their salts in the triple linking, which causes the molecules to arrange themselves side by side, thus producing much larger and more crystalline particles. It is argued that since the highly disperse soap solutions exhibit anisotropy, the ultimate particles must have the same structure as the larger crystals of the substance. E. S. HEDGES.

**Soaps of fatty acids of the oleic series.** III. Sodium oleate. IV. Sodium zoomarate. M. HIROSE and T. SHIMOMURA (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 263—265B, 266—268B).—III. Both the surface tension and the drop number of sodium oleate solution decrease with rise of temperature. With increase in concentration the drop number rises, whilst the surface tension at first falls and subsequently rises. The lathering volume increases with rise of temperature and concentration, but its value is less than that for sodium gadoleate.

IV. The drop number-temperature curve of sodium zoomarate solutions resembles that of sodium gadoleate. The surface tension of sodium zoomarate solution decreases with rise of temperature; with rise of concentration it first decreases and then increases. For soap solutions of the oleic series the power of lowering the surface tension and the drop number decrease in the order  $C_{18}$ ,  $C_{20}$ ,  $C_{16}$ ,  $C_{22}$ . The influence of mol. wt. on the lathering properties of members of this series is discussed.

A. A. GOLDBERG.

**Morphology of chemical reactions in colloidal media.** II. F. M. SCHENJAKIN (*Kolloid-Z.*, 1930, **50**, 58—65).—See this vol., 33.

**Characteristic equation for binary gaseous mixtures.** G. VAN LERBERGHE and (ILLE.) G. SCHOOLS (*Bull. Acad. roy. Belg.*, 1929, [v], **15**, 583—589).—The equation  $p = p_1 + p_2 + C_1 C_2 \omega_{12}$ , where  $C$  refers to molar concentrations in the gas phase, and  $\omega$  to functions dependent solely on temperature, is suggested for the behaviour of gaseous mixtures. For mixtures of methane and nitrogen it is considerably more accurate in application than Dalton's law. It leads to simple expressions for the fugacities of the gaseous components in terms of the fugacities of the pure gases and the new coefficient  $\omega$  introduced into the characteristic equation. An analogous equation is proposed for ternary gaseous mixtures.

F. G. TRYHORN.

**Empirical calculation of the fugacities in gaseous mixtures.** II. Its relation to the tangents on certain thermodynamic diagrams. Approximate equations for some important thermodynamic properties of gas mixtures. L. J. GILLESPIE (*Physical Rev.*, 1929, [ii], **34**, 1605—1614; cf. *A.*, 1929, 1138).—Mainly mathematical. Using the results of previous work, methods are derived for calculating the limiting value of the tangents to curves of functions of the energy, entropy, heat content, and the  $t$ - $p$  and  $t$ - $v$  thermodynamic potentials; the limiting tangents are found to depend only on the cohesive pressure term of the equation of state, and a group of functions of the fugacity and equilibrium pressure. From these limiting values equations are derived for the change of energy, entropy, heat content,  $t$ - $p$  and  $t$ - $v$  thermodynamic potentials in the mixing of gases at constant temperature and pressure.

N. M. BLIGH.

**Methyl alcohol equilibrium.** B. F. DODGE (*Ind. Eng. Chem.*, 1930, **22**, 89—90).—The published data concerning the equilibrium  $2H_2 + CO = CH_3OH$  are discussed and the following reason is given to explain some of the discrepancies. The calculation of the free-energy change for the synthesis, although based on the third law, and therefore requiring a knowledge of absolute entropies, is far more dependent on exact data for the various heats of reaction than on the entropy data. Thus if the value for the heat of combustion of methyl alcohol is in error by 0.1%, the corresponding error in the dissociation constant at 298.1° Abs. is 33%.

H. INGLESON.

**Extended theory of acids and bases.** T. M. LOWRY (*Trans. Faraday Soc.*, 1930, **26**, 45—46).—A claim for priority over Brönsted (cf. *A.*, 1929, 273).

J. W. SMITH.

**Apparent dissociation constants of tryptophan and histidine.** C. L. A. SCHMIDT, W. K. APPLEMAN, and P. L. KIRK (*J. Biol. Chem.*, 1929, **85**, 137—140).—Tryptophan has  $K_a' 4.05 \times 10^{-10}$ ,  $K_b' 2.4 \times 10^{-12}$ , the isoelectric point lying at  $p_H 5.89$ ; histidine has  $K_a' 6.7 \times 10^{-10}$ ,  $K_b' 1.01 \times 10^{-8}$ ,  $K_i' 6.6 \times 10^{-13}$ , the isoelectric point being at  $p_H 7.7$ .

C. R. HARRINGTON.

**Dissociation constants of certain sulphone-phthalein indicators.** M. KILPATRICK and M.

KILPATRICK, jun. (J. Physical Chem., 1930, **34**, 211—213).—Errors in a paper by Sendroy and Hastings (A., 1929, 765) are pointed out.

L. S. THEOBALD.

**Nitrates and the equilibrium law.** K. JABE-CZYŃSKI and K. DEMBOWSKI (Rocz. Chem., 1929, **9**, 698—703).—An ebullioscopic study of solutions of the nitrates of caesium, rubidium, and potassium shows that the ionisation constant is the same in all cases, namely, 1.47. None of the ions present in the above systems is hydrated at 100°. In all cases association of nitrate ions with undissociated molecules takes place; this is most marked in the case of caesium, and diminishes in extent with rising temperature.

R. TRUSZKOWSKI.

**Hydrolysis of aluminium salts.** E. O. WILSON and R. C. KUAN (J. Amer. Leather Chem. Assoc., 1930, **25**, 15—31).—The  $p_H$  value of solutions of aluminium sulphate and potassium alum increases with the dilution. The former show a slight increase on keeping for a week, whilst the latter show a decrease. The  $p_H$  value of both solutions is increased by the addition of potassium sulphate and continues to increase on keeping. The  $p_H$  is diminished by the addition of sodium chloride, but there is no further alteration on keeping. The  $p_H$  value of a solution of aluminium sulphate is much higher than that of an equivalent solution of chromium sulphate.

D. WOODROFFE.

**Hydrolysis of solutions of chromic salts.** L. MEUNIER and M. LESBRE (Compt. rend., 1930, **190**, 183—185).—The Toussaint photo-electric colorimeter has been used to follow the changes in a 0.445% solution of chromic chloride,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , at 25°, by observing the variations in the transmission of the individual colours of the spectrum. The results confirm those obtained by determinations of the flocculation index (Meunier and Caste, A., 1921, ii, 512) and the electrical resistance, viz., that simultaneous formation of the compounds  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$  and  $[\text{CrOH}(\text{H}_2\text{O})_5]\text{Cl}_2$  occurs, which is complete after 300 hrs.

J. GRANT.

**Pseudo-component of hydrogen.** A. SMITS (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1118—1123).—The variations of the internal equilibrium with temperature are described: above 170° Abs. the equilibrium constant corresponds with about 25% of  $\alpha$ - and 75% of  $\beta$ -hydrogen.

H. F. GILLBE.

**Determination of transition point by the vapour-pressure method.** M. MATSUI, S. OGURI, S. KAMBARA, and K. KATO (J. Soc. Chem. Ind. Japan, 1929, **32**, 172—174B).—By the differential vapour-pressure method the transition temperature of sodium sulphate is found to be 32.60°, whilst by the absolute vapour-pressure method the value 32.57° is obtained.

H. F. GILLBE.

**Transition point of sodium sulphate [decahydrate] by the dynamical vapour-pressure method.** S. OGURI and M. NARA (J. Soc. Chem. Ind. Japan, 1929, **32**, 274—276B).—By a slight modification of Partington's method (J.C.S., 1911, **99**, 467) the value 32.4° was found graphically. Combination of the equations representing the vapour

pressures above and below the transition leads to 32.57°.

S. K. TWEEDY.

**Binary systems of certain nitrotoluenes with salicylic acids.** H. D. CROCKFORD and F. W. ZURBURG (J. Physical Chem., 1930, **34**, 214—216; cf. Bell and McEwen, A., 1922, i, 726).—F.-p. data for the systems formed by 2:4:6-trinitrotoluene, *p*-nitrotoluene, and 2:4-dinitrotoluene with salicylic acid are recorded. The eutectic temperatures are 76.3°, 49.4°, and 66.3° at 90, 94.9, and 89.9 mol.-% of the nitro-derivative, respectively.

L. S. THEOBALD.

**Points of fusion and of decomposition in the system  $\text{KClO}_3$ - $\text{NaClO}_3$ .** A. P. VITORIA (Anal. Fis. Quím., 1929, **27**, 787—797).—The m. p. of potassium chlorate and sodium chlorate are 356° and 256°, respectively, the corresponding decomposition temperatures being 364° and 350°. The m. p.-composition and decomposition temperature-composition curves exhibit a minimum, which for the former occurs at 25%  $\text{KClO}_3$  and 237°, and for the latter at 85%  $\text{KClO}_3$  and 305°.

H. F. GILLBE.

**Liquid ammonia and calcium nitrate.** N. KAMEYAMA (J. Soc. Chem. Ind. Japan, 1929, **32**, 242—243B).—The vapour pressure of liquid ammonia saturated with calcium nitrate has been determined at -40° to -10°. The depression caused by calcium nitrate is less than that effected by sodium nitrate. The heat of condensation of ammonia in the saturated solution is 6.32 kg.-cal. per mol. of  $\text{NH}_3$  at -20°, and the heat of dissolution of pure liquid ammonia 0.9 kg.-cal. Solid anhydrous calcium nitrate absorbs gaseous ammonia and the compound so formed dissolves in liquid ammonia with precipitation of a less soluble salt, possibly calcium nitrate.

C. IRWIN.

**Oxide hydrates. XVIII. System magnesium oxide-water. XIX. System magnesium oxide-carbon dioxide.** G. F. HÜTTIG and W. FRANKENSTEIN (Z. anorg. Chem., 1930, **185**, 403—412, 413—416; cf. Hüttig and Kassler, this vol., 162).—XVIII. The dehydration curves at constant pressure, and the Debye spectrograms of the mineral brucite and of twelve other samples of magnesium oxide, prepared by different methods and containing varying quantities of water, have been determined. A hydration experiment was also carried out on one sample after dehydration. The results indicated the presence of the compound  $\text{MgO} \cdot \text{H}_2\text{O}$  with a dissociation temperature a little above 300°. In three cases the results appeared to suggest the presence of the compound  $\text{MgO} \cdot 0.5\text{H}_2\text{O}$ , with approximately the same dissociation temperature as the monohydrate. Two different lattice structures were observed, one belonging to brucite and the other to calcined magnesium oxide, and some of the preparations combined both these structures. It seems probable that the only stable hydrate is the monohydrate, and that the so-called hemihydrate is simply a mixture of brucite and magnesium oxide. By different methods of preparation magnesium oxide of different degrees of activity, as measured by the readiness of combination with water, is formed, but there are no indications of these differences in the X-ray spectrograms. The

possibility of the existence of an amorphous magnesium oxide, giving no interference figures, is not excluded. Variations in the activity, or free energy content, of the monohydrate seem to be indicated by changes in the dissociation temperature, and in the breadth of the lines in the X-ray spectrogram when comparing brucite with the freshly-precipitated monohydrate.

**XIX.** The system magnesium oxide-carbon dioxide has been investigated in a way similar to that previously described for the system calcium oxide-carbon dioxide (Z. angew. Chem., 1928, 41, 1034). "Dense" magnesite of the Krauparth type and "crystalline" magnesite of the Veitel type formed the starting materials. The times required to reach the equilibrium pressures at different temperatures were extraordinarily long. Debye spectrograms have been obtained of the initial materials and of the products at different stages. Throughout, the system shows a close analogy with that of calcium oxide-carbon dioxide (*loc. cit.*). The results confirm the opinion that composition and previous history of the solid phase must be taken into account when attempting to determine decomposition values in such systems, and that their equilibrium pressures, in the thermodynamic sense, have scarcely ever been measured.

M. S. BURR.

**Concentrated solutions.** V. P. SCHISCHOKIN (Z. anorg. Chem., 1930, 185, 360—368; cf. A., 1929, 995).—The fusion diagrams of the following ternary systems have been investigated by the Alexeiev-Schröder optical method: phenylallylthiocarbamide-*o*-toluidine-*m*-toluidine; *p*-dibromobenzene-nitrobenzene-allylthiocarbamide; phenylallylthiocarbamide-acetanilide-aniline; *p*-dibromobenzene-benzene-aniline; phenylallylthiocarbamide-acetanilide-allylthiocarbamide. In the first three cases the ternary regions are limited by binary systems of which the fusion curve branches are all represented by the Schröder equation of the form  $S = ke^{-a/T}$  (*loc. cit.*). In such cases the isotherms in the crystalline fields of the components are all straight lines, and the eutectic is a simple mixture of the three components. In the last two cases, however, the branches of the binary systems do not satisfy such an equation and the isotherms are curves. By fusion together of the three components chemical combination takes place. It is probable that the Schröder equation can also be applied to more complicated systems.

M. S. BURR.

**Heterogeneous equilibria of metal halides with hydrogen and with hydrogen chloride.** K. JELLINEK and R. KOOP (Z. physikal. Chem., 1929, 145, 305—329; cf. A., 1928, 1191).—The equilibrium concentrations of hydrogen and hydrogen fluoride or chloride have been determined when each of the following metal halides is reduced by hydrogen at temperatures between 200° and 1100°: cobaltic and manganous fluorides, ferric, chromic, and cupric chlorides, the stage of reduction reached being the lower halide except in the case of manganese. From the results the dissociation pressure curves and heats of formation are calculated. The equilibrium between hydrogen chloride and the fluorides of cobalt, cadmium, zinc, manganese, and sodium has been

investigated in a similar manner, and the heats of reaction have been calculated. Vapour pressures of ferric, chromic, and zinc chlorides have been determined.

F. L. USHER.

**Thiol-disulphide system. I. Complexes of thiol acids with iron.** R. K. CANNAN and G. M. RICHARDSON (Biochem. J., 1929, 23, 1242—1262).—The rate of the spontaneous autoreduction and its relation to  $p_H$  (8—10.5) of the ferrithiol complex have been studied. The autoxidation of the ferrothiol complex is rapid at  $p_H$  8 and not demonstrable below  $p_H$  6 and is not amenable to direct measurements. The equilibrium potentials of the ferrithiol-ferrothiol reversible oxidation-reduction system have been determined and an electrode equation has been established which defines the electrode behaviour within a limited range of  $p_H$  and concentration of thiol acid. Suggestions have been made as to the nature of the complexes. The electrode behaviour of thiol compounds without added iron has also been considered.

S. S. ZILVA.

**Equilibrium in reduction of antimony trioxide by carbon monoxide.** M. WATANABE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 973—977).—The reaction  $Sb_2O_3 + 3CO \rightleftharpoons 2Sb + 3CO_2$  has been studied at 502° and 596°. The change in free energy given by  $\Delta F = -33,461 + 34.286T \log T - 0.011107T^2 + 0.000000937T^3 - 88.65T$  agrees with the experimental data.

R. A. MORTON.

**Isotherms of the system  $MgSO_4-Na_2SO_4-H_2O$  between 0° and 100°.** W. SCHRÖDER (Z. angew. Chem., 1929, 42, 1076—1077).—The isotherms have been determined and the results are compared with those of previous observers.

H. F. GILLBE.

**Reciprocal salt pair  $MgSO_4-2NaNO_3-H_2O$ .** VI. W. SCHRÖDER (Z. anorg. Chem., 1930, 185, 267—279; cf. A., 1929, 267).—On the basis of the results of previous investigations a space model showing the behaviour of the system  $MgSO_4-2NaNO_3-H_2O$  for a range of temperature 0—100° has been constructed. The axes are  $a$ ,  $b$ , and  $t$ , where  $t$  is the temperature,  $a$  the amount of  $Na_2$ , and  $b$  the amount of  $(NO_3)_2$ . The amount of  $Mg$  is then  $(100-a)$  and of  $SO_4$   $(100-b)$ . Plane diagrams have also been drawn indicating the changes in water content with temperature for the binary, ternary, and quaternary systems, respectively. By means of the space model and the diagrams all possible changes in the system, over the range of temperature considered, are quantitatively mapped out.

M. S. BURR.

**Reciprocal salt pair  $2NH_4NO_3+K_2SO_4=2KNO_3+(NH_4)_2SO_4$ , and its aqueous solutions.** E. JÄNECKE (Z. angew. Chem., 1929, 42, 1169—1172).—Solubilities in the system ammonium nitrate, potassium sulphate, potassium nitrate, ammonium sulphate, water, have been determined from the eutectic points to 50°. In the quaternary systems the solid phases are: (a) mixed crystals of potassium sulphate and ammonium sulphate, (b) mixed crystals of a known double salt,  $(NH_4)_2SO_4 \cdot 2NH_4NO_3$ , with the salt  $K_2SO_4 \cdot 2KNO_3$ , which cannot be prepared by itself, (c) mixed crystals of potassium nitrate with relatively small amounts of ammonium nitrate, (d)



mixed crystals of ammonium nitrate with relatively small amounts of potassium nitrate. There are two quadruple points at which the solid phases *a*, *b*, *c* and *a*, *b*, *d*, respectively, are in equilibrium with the solution.

J. A. V. BUTLER.

**Heat capacities of real gases and mixtures of real gases.** J. A. BEATTIE (Physical Rev., 1929, [ii], 34, 1615—1620).—From Beattie and Bridgeman's equation of state (cf. A., 1927, 819) simple approximate formulæ are derived for the heat capacities of a gas at constant volume ( $C_v$ ) and at constant pressure ( $C_p$ ). Values for the latter agree well with the experimental data for air, and fairly well for ammonia. Complete and approximate equations giving  $C_p$  and  $C_p$  for gas mixtures, in terms of pressure, volume, and temperature, are deduced from the generalised equation of state for gas mixtures (cf. A., 1929, 253), on the assumption that the energies of the gases at very low pressure are additive (cf. A., 1928, 1315; this vol., 292).

N. M. BLYTH.

**Heat of dissociation of the oxygen molecule and energy of activation of the oxygen atom.** V. HENRI (Compt. rend., 1930, 190, 179—181).—The absorption spectrum of gaseous nitrogen peroxide indicates dissociation into nitric oxide and either a normal or an active oxygen atom, the corresponding wave-lengths being 3700 and 2459 Å., and the heats of reaction —77,000 and 116,000 g.-cal., respectively. The value —136,000 g.-cal. (5.5 volts) may then be deduced for the heat of dissociation of the oxygen molecule and —39,000 g.-cal. (1.7 volts) for the energy of activation of the oxygen atom. The first stage of activation of the oxygen atom corresponds with passage from the normal state  $^3P_2$  to the metastable state  $^1D$ . The position of the latter term is discussed, with special reference to the green ray of the aurora borealis, which may be due to oxides of nitrogen dissociated by solar electrons into oxygen in the metastable  $^1S$  state, and subsequent passage of oxygen atoms to the metastable  $^1D$  state (cf. McLennan, A., 1928, 1165).

J. GRANT.

**Thermochemistry of hypochlorous acid.** B. NEUMANN and G. MÜLLER (Z. anorg. Chem., 1930, 185, 428).—A correction (cf. A., 1929, 1238). Recalculated on the basis of a corrected value for the heat of dilution of hypochlorous acid, the mean heat of neutralisation of hypochlorous acid becomes 10,033 g.-cal./mol. The heats of formation of HOCl, Aq from the six hydroxides employed are, in g.-cal., NaOH, 29,300; KOH, 29,250; LiOH, 29,410; Ca(OH)<sub>2</sub>, 29,210; Sr(OH)<sub>2</sub>, 29,350; Ba(OH)<sub>2</sub>, 29,230; mean 29,290. For the complete hydrolysis of gaseous chlorine to form HCl, Aq + HOCl, Aq the corresponding figures are: 230, 180, 340, 140, 280, and 170 g.-cal., mean 220 g.-cal.

M. S. BURR.

**Thermochemistry of iron, manganese, and nickel.** W. A. ROTH (Arch. Eisenhüttenw., 1929—1930, 3, 339—346; Stahl u. Eisen, 1929, 49, 1763—1765).—The following heats of formation have been redetermined (values in kg.-cal./mol.): MnO +93.5 (±0.7%); FeO +64.3 (±0.7%); NiO +58.9 (±1%); Mn<sub>2</sub>O<sub>4</sub> +345.0 (±0.3%); Fe<sub>2</sub>O<sub>4</sub> +266.9 (±0.2%); Fe<sub>2</sub>O<sub>3</sub> +198.5 (±0.4%); MnCO<sub>3</sub> +219.1 (±0.4%); FeCO<sub>3</sub>

+172.6 (±0.5%), Mn<sub>2</sub>C +23 (±10%); Fe<sub>2</sub>C —5.4 (±30%); Ni<sub>2</sub>C —9.2 (±10%); Fe(CO)<sub>5</sub> +57.3 (±3%). The heat of formation of manganous carbonate from the oxide and carbon dioxide is +28.3 (±2—3%) and that of ferrous carbonate from ferrous oxide and carbon dioxide +14.0 (±11%).

A. R. POWELL.

**Thermochemistry of the higher oxides of nickel.** F. GIORDANI and E. MATTHIAS (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, 35, 172—182).—Measurements have been made of the heat of dissolution in hydrochloric and sulphuric acids of preparations of nickelous hydroxide containing varying amounts of higher oxides. The heat of dissolution of nickelous hydroxide in 2.63*N*-hydrochloric acid at 26° is 20,652 g.-cal., and in 5.52*N*-sulphuric acid at 28° is 22,165 g.-cal. When the heats of dissolution in sulphuric acid of the superoxygenated preparations are plotted against the atomic ratio active oxygen/nickel (= *n*) three lines are obtained which are represented respectively by  $\Delta H = 22,263 + 70,405n$ ,  $65,483 - 120,960n$ , and  $9900 + 29,838n$ . From these results the existence of the oxides Ni<sub>3</sub>O<sub>4</sub> and Ni<sub>4</sub>O<sub>5</sub> is indicated. The results, however, are in moderate agreement with those required by the presence of the oxides Ni<sub>2</sub>O<sub>3</sub> and Ni<sub>3</sub>O<sub>4</sub>.

The results are used to calculate the heats of the probable reactions in the Edison cell, viz., Ni<sub>2</sub>O<sub>3</sub> + Fe + 3H<sub>2</sub>O = 2Ni(OH)<sub>2</sub> + Fe(OH)<sub>2</sub> + 65,215 g.-cal., and Ni<sub>3</sub>O<sub>4</sub> + Fe + 4H<sub>2</sub>O = 3Ni(OH)<sub>2</sub> + Fe(OH)<sub>2</sub> + 63,950 g.-cal. The first reaction leads to a value of 1.338 volts and the second to 1.311 volts for the potential of the Edison cell, both of which are rather lower than the measured value of 1.36 volts. F. G. TRYHORN.

**Thermochemical revisions. II.** W. A. ROTH and G. BECKER (Z. physikal. Chem., 1929, 145, 461—469; cf. A., 1929, 1389).—The following heats of formation have been determined: ZrO<sub>2</sub>, +264.0 ± 0.3 kg.-cal.; Cr<sub>2</sub>O<sub>3</sub>, +288.0 ± 1.0 kg.-cal. (both by combustion in the presence of paraffin in a bomb calorimeter); CrO<sub>3</sub>, +147.1 ± 0.6 kg.-cal. by reduction to Cr<sub>2</sub>O<sub>3</sub> and +140.0 in a few direct determinations. The heat of formation of zirconium dioxide is in good agreement with the relation between heat of formation and atomic number. The calculated heat of formation of zirconium carbide is +52.5 kg.-cal. per g.-atom. The following densities have been determined at 21°: ZrO<sub>2</sub>, 5.68 ± 0.02; Zr, 6.47<sub>3</sub>; Cr<sub>2</sub>O<sub>3</sub>, 5.20—5.21; CrO<sub>3</sub>, 2.80 ± 0.01.

J. A. V. BUTLER.

**Heat of combustion of camphor, azobenzene, and hydrazobenzene.** W. ŚWIĘTOSŁAWSKI and J. BOBIŃSKA (Rocz. Chem., 1929, 9, 723—730).—The heats of combustion of the above three substances are respectively 9260.7, 8483.8, and 8624.3 g.-cal./15/g.

R. TRUSZKOWSKI.

**Limiting heat of dissolution of hydrated manganous chloride.** J. PERREU (Compt. rend., 1930, 190, 52—54).—The limiting heat of dissolution of manganous chloride tetrahydrate is found to be —4.57 and —4.56, respectively, by the direct method and by a method which involves the heats of dilution (A., 1929, 1014). A concordant value is obtained by a modified form of the second method (A., 1929, 1238).

R. K. CALLOW.

**Thermodynamic data on lead sulphide and the standard potential of sulphur.** M. WATANABE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 978—983).—From Jellinek's equilibrium constants (A., 1925, ii, 401) for the reduction of lead sulphide by hydrogen, the values of  $\Delta H$  and  $\Delta F$  referred to liquid and solid lead have been calculated. The following data for the reaction  $\text{Pb(s)} + \text{S(rhombic)} = \text{PbS(s)}$  are recorded:  $\Delta H_{298} = -22,855$  g.-cal.,  $\Delta F_{298} = -22,224$  g.-cal.; entropy of lead sulphide  $S = 21.01$  entropy units; standard potential of sulphur  $E_{298}(S/S^-) = 0.48$  volt. R. A. MORTON.

**Thermodynamic data on some metallic sulphates.** F. ISHIKAWA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 965—972).—The following thermodynamic data, based on the standard free energy of formation of aqueous sulphuric acid, are recorded: mercurous sulphate,  $\Delta F_{298} = -147,829$  g.-cal.,  $S = 50.13$ ; lead sulphate,  $\Delta F_{298} = -192,607$  g.-cal.,  $\Delta H_{298} = -217,165$  g.-cal.,  $S = 38.83$ ; thallous sulphate,  $\Delta F_{298} = -196,741$  g.-cal.,  $\Delta H_{298} = -219,071$  g.-cal.,  $S = 59.93$ ; silver sulphate,  $\Delta F_{298} = -145,951$  g.-cal.,  $S = 54.56$ . R. A. MORTON.

**Rule for the mechanism of reactions.** P. ROBINSON (J. Physical Chem., 1930, 34, 207—210).—When several reactions are possible in an isothermal system, the one which occurs first is said to be that for which the reaction products have the largest entropy value. The application of the rule to the sulphur and water systems is examined and the rule is considered valid. L. S. THEOBALD.

**Stability of crystals and their heats of formation and dissolution.** A. ALBERTO (Ann. Acad. Brasil. Sci., 1929, 1, 17—19).—Endothermic crystals with a negative heat of dissolution become less stable as the size diminishes; for exothermic crystals with a negative heat of dissolution the reverse is true. For crystals with a positive heat of dissolution the relations are reversed. H. F. GILLBE.

**Dimensions of crystals formed in a viscous medium.** A. ALBERTO (Ann. Acad. Brasil. Sci., 1929, 1, 1—4).—Theoretical arguments suggest that increase in the viscosity of a crystallising solution should result in the production of smaller crystals when the heat of dissolution of the solid is negative and of larger crystals when the heat of dissolution is positive. H. F. GILLBE.

**Electrical conductivity and viscosity of aqueous solutions.** M. CHANOT and G. CLUZET (Compt. rend. Soc. Biol., 1929, 100, 1205—1207; Chem. Zentr., 1929, ii, 1384).—The electrical conductivities of solutions of potassium chloride, sodium chloride, hydroxide, and sulphate, hydrochloric and sulphuric acid, and cupric chloride are reduced by addition of sucrose, glycerol, agar, or gelatin. A. A. ELDRIDGE.

**Electrochemistry of non-aqueous solutions.** I. Influence of nature of solvent on equivalent conductivity of typical salts. II. Conception of "strong" binary salts and differences between strong and weak electrolytes. P. WALDEN (Suomen Kem., 1929, 2, 163—165).—A review. A. I. VOGEL.

**Temperature coefficients of the quinhydrone and calomel electrodes.** A. I. BRODSKI and S. M. BORUCHOVITSCH (Ukrain. Chem. J., 1929, 4, 379—386, and J. Chim. phys., 1929, 26, 542—547).—The *E.M.F.* of the cell, calomel electrode ( $\text{KCl } 0.1$ ) |  $\text{KNO}_3$  (satd.) | quinhydrone electrode is given by  $E = 0.2607 - 0.00105t$  at  $p_{\text{H}} 2.15$ ,  $E = 0.1547 - 0.00150t$  at  $p_{\text{H}} 4.155$  and  $E = 0.0413 - 0.00174t$  at  $p_{\text{H}} 6.145$ . The first of these is in good agreement with that obtained by Kolthoff and Tekelenburg (A., 1927, 329). The variation of the temperature coefficient with  $p_{\text{H}}$  is given by  $dE/dT = +0.00011 - 0.0001983t$ . Similar equations hold for the hydrogen electrode. Since the temperature coefficients of both the quinhydrone and hydrogen electrodes vary with the  $p_{\text{H}}$  of the solution it is not permissible to obtain the *E.M.F.* at  $18^\circ$  from tables of values of  $dE/dT$ . If  $p_{\text{H}0}$  represents the  $p_{\text{H}}$  of the standard electrode against which comparison is made, then  $p_{\text{H}} = p_{\text{H}0} - [(E - E_0) - (A - B)(t - 18)] / [0.0577 + 0.0001983(t - 18)]$ , where  $E$  is the *E.M.F.* of the cell at  $t^\circ$ ,  $E_0$  the potential of the electrode measured in relation to the standard at  $p_{\text{H}} = 0$  and  $t^\circ$ , and  $A$  and  $B$  are constants, the values of which and of  $E_0$  are given for a number of pairs of electrodes. T. H. POPE.

**Temperature measurements at working electrodes.** II. B. BRUŽS (Z. physikal. Chem., 1929, 145, 470—476; cf. this vol., 185).—The temperature changes in the separation of oxygen, hydrogen, and silver at bright platinum electrodes have been determined. For oxygen and silver the effect is independent of the time; for hydrogen it increases exponentially with time. The final values are in the ratio  $\text{O}_2 : \text{H}_2 : \text{Ag} = 7.3 : 4.9 : 0.6$ .

J. A. V. BUTLER.

**Electrocapillary properties of amalgams.** A. FRUMKIN and F. J. CIRVES (J. Physical Chem., 1930, 34, 74—85; cf. A., 1928, 1193).—Using the null solution method it has been shown that the addition of thallium or cadmium to mercury brings about a shift in the point of zero charge towards higher values of *P.D.* between solution and metal. The concentration of thallium ions at the zero point varies with the thallium content of the amalgams; this is not the case with cadmium. The data obtained with thallium amalgams agree with the determinations of electrocapillary maxima (*loc. cit.*), confirming in the case of amalgams the validity of the Lippmann-Helmholtz equation for metals.

L. S. THEOBALD.

**Methods for the determination of absolute potentials.** J. BILLITER (Amer. Electrochem. Soc., May, 1930. Advance copy. 10 pp.).—Methods which have been used in attempts to determine the absolute value of the zero electrode potential on the hydrogen scale are classified and critically examined. Modern methods give values between  $+0.4$  and  $+0.5$ , the most trustworthy being  $+0.475 \pm 0.005$  obtained by Bennewitz using the "scrape method" (A., 1926, 1212). The old value ( $-0.277$ ) obtained from the electrocapillary curve for mercury and the mercury dropping electrode is regarded as subject to several errors, of which that due to a film of hydrogen on the mercury surface is particularly

important. This view is supported by new experiments in which the surface of a polarised metal wire in an electrolyte solution is increased by stretching and allowed to decrease again on releasing the strain. Wires of various metals were charged to different potentials, either by cathodic or anodic treatment or more frequently by the action of reducing or oxidising agents, and the direction in which the potential changed on stretching or releasing was determined. Critical potentials were found above which the stretching of the wire caused a change of potential in one direction and below which the change was in the opposite direction, these effects being reversed on releasing the tension on the wire. These critical potentials are shown to correspond with the potentials for hydrogen (or oxygen) evolution and the phenomena observed are regarded as due to the stretching of gas films on the metal surface resulting in a reduction of the effective gas pressure.

H. J. T. ELLINGHAM.

**Potentiometric study of equilibria in solutions containing quinque- and sexa-valent molybdenum.** W. F. JAKÓB and W. TRZEBIATOWSKI (Rocz. Chem., 1929, 9, 676—693).—Ammonium paramolybdate solutions exhibit on titration with solutions of Klason's salt two potential minima. The colour of the solution at the first minimum is green, due to the formation of a compound

$[\text{Mo}^{\text{V}}(\text{Mo}^{\text{VI}}\text{O}_4)_6](\text{NH}_4)_3\text{H}_4.5\text{H}_2\text{O}$ ; it was not found possible to isolate the complex causing the reddish-brown coloration observed at the second minimum. The reactions taking place may probably be represented by the following equations:  $6\text{MoO}_4^{''} + 5\text{H}^+ + \text{MoO}(\text{OH})_3 \rightleftharpoons [\text{Mo}(\text{MoO}_4)_6]^{'''''} + 4\text{H}_2\text{O}$ , and  $3\text{MoO}_4^{''} + 2\text{H}^+ + 2\text{MoO}(\text{OH})_3 \rightleftharpoons [\text{Mo}_2\text{O}_2(\text{MoO}_4)_6(\text{OH})_4]^{'''''} + 2\text{H}_2\text{O}$ . The potential attains a constant value after the minima have been reached; this is due to the platinum electrode being covered with a layer of inactive molybdenum-blue.

R. TRUSZKOWSKI.

**Potential of solutions of carbohydrates.** (MLLE.) N. MAYER (J. Chim. phys., 1929, 26, 565—573).—See A., 1929, 1147.

**Behaviour of the quinhydrone electrode in liquid ammonia.** E. ZINTL and S. NEUMAYR (Ber., 1930, 63, [B], 237—243).—Constant and reproducible results are not obtained in the measurement of *E.M.F.* of concentration chains,  $\text{H}_2, \text{Pt}|\text{NH}_4\text{Cl}(c_1)$  in liquid ammonia  $|\text{NH}_4\text{Cl}(c_2)$  in liquid ammonia  $|\text{Pb}, \text{H}_2$ , in spite of variation in the mode of preparation of the electrodes. Satisfactory results are, however, obtained with the quinhydrone electrode if the concentration of the quinhydrone does not fall below  $5 \times 10^{-5}$ . In ammonium chloride not exceeding  $0.002N$ , variation in the quinhydrone concentration between  $5 \times 10^{-5}$  and  $10^{-3}$  is without appreciable effect, but in  $0.001N$ -solution the *E.M.F.* depends appreciably on the concentration of quinhydrone. The observed potential values can be satisfactorily explained by the Debye-Hückel theory (A., 1923, ii, 459) if complete dissociation of the ammonium chloride is assumed.

H. WREN.

**Studies on hydrogen overpotential by the dropping mercury cathode.** W. V. LLOYD (Trans.

Faraday Soc., 1930, 26, 12—15).—The hydrogen overpotential *w* varies logarithmically with the current *i*, provided that the rate of dropping is constant, and that the current is measured at corresponding periods during the formation of a drop and after the same interval from the beginning of an experiment. Deviations are observed with very low and very high currents; in the latter case concentration effects are pronounced in more dilute solutions. The current varies logarithmically with the time from the beginning of the experiment, so both *i* and  $dw/d \log i$  can be varied considerably by varying the rate of dropping. Related with this is the variation of  $dw/d \log i$  with different solutions. These phenomena may account for the discrepancies between the results of Herasymenko (A., 1928, 482) and those of Bowden and Rideal (*ibid.*, 1088). It is suggested that the mechanism of the dropping electrode is too complicated to render it suitable for the study of hydrogen overpotential.

No conclusion regarding the hydrogen overpotential in potassium hydroxide solution could be reached from experiments with the dropping mercury cathode, the latter behaving simply as a potassium electrode.

J. W. SMITH.

**Hydrogen overpotential in acid solution.** H. J. S. SAND (Trans. Faraday Soc., 1930, 26, 19—26).—The results of Bowden (*ibid.*, 1928, 24, 473) on the dependence of hydrogen overpotential on current density in acid solution are explained by postulating the intermediate formation of an ion  $\text{H}_2^+$ . The process is assumed to take place exclusively at the interface electrode-electrolyte, and the surface concentrations are related to the equilibrium concentrations in the body of the liquid by the Freundlich isotherm, the exponent for both hydrogen atoms and ions being 4. When the concentration of atomic hydrogen on the electrode surface is greater than in Bowden's experiments, overvoltage may be governed by the velocity of direct combination of hydrogen atoms, in which case it is independent of the hydrogen-ion concentration (cf. Bowden and Rideal, A., 1928, 1088; Sand, Grant, and Lloyd, A., 1927, 317; Lloyd, A., 1929, 1241). The double layer is supposed to be capable of existence in two forms. At lower overpotentials a random distribution of ions with respect to electrons in the layer is assumed, whereas at higher overpotentials the ions and electrons are believed to be combined in doublets. In the latter case the hydrogen ions are assumed not to be free for purposes of chemical combination. The double layer must be assumed to behave as a Helmholtz double layer, *i.e.*, to have a constant polarisation capacity and a dielectric constant of unity for the medium. Attention is directed to the significance of the polarisation capacities measured by Bowden and Rideal (*loc. cit.*) which are only one fifth as large as those deduced previously from indirect experiments. Since the polarisation capacity is almost entirely due to the building up of the double layer and the current required for charging the electrode with hydrogen ions is negligible in comparison, the result obtained by Bowden and Rideal, that the polarisation capacity is independent of the material of the electrode, follows immediately. J. W. SMITH.

**Overpotential of arsenic and the yields of arsine at an arsenic cathode in acid solutions.** W. V. LLOYD (Trans. Faraday Soc., 1930, 26, 15—18).—The overpotential of arsenic has been measured, using a plane polished surface of a piece of compact arsenic as cathode. A commutator method was used, similar to that previously described (Sand, Grant, and Lloyd, A., 1927, 317). Initial polarisation at low current densities yields a high overpotential which is not maintained at higher current densities. In the latter case a maximum overpotential is attained, as with antimony and bismuth, so long as no arsine is produced. The average commutator overpotential when there is no high degree of supersaturation and no arsine is being evolved is about 0.6 volt in acid solution, corresponding with the average polarisation during an interval of 0.0059 sec. after interruption of the current. Continued electrolysis leads to the production of an "active" form of arsenic, and arsine is evolved. This is accompanied by an appreciable decrease in the overpotential. When the cathode is in an "active" state the percentage of arsine produced at a fixed current density is approximately the same for sulphuric, hydrochloric, phosphoric, and tartaric acids, and does not vary considerably with the concentration. The largest percentage yield of arsine was obtained in 4*N*-hydrochloric acid solution by the method of Sand and Lloyd (A., 1927, 38) with anodic and cathodic current densities of 44 and 525 milliamp. per cm.<sup>2</sup>, respectively, when a yield of 60% was obtained. J. W. SMITH.

**Decomposition potential of solutions of metal bromides in fused zinc bromide.** W. ISBEKOV (Z. anorg. Chem., 1930, 185, 324—332).—The decomposition potentials of a number of metal bromides in fused zinc bromide have been determined and found to stand in the following order, beginning with that of highest potential: Al, Zn, Cd, Pb, Fe, Cu, Ag, Ni, Hg (mercurous), Bi. This is in the same order as the heats of formation of the bromides, with the probable exception of nickel, and, so far as the same metals are included, in the same order as the decomposition potentials of bromides in fused aluminium bromide (A., 1925, ii, 796). Moreover, any metal in this series will displace any subsequent member from a solution of the bromide in zinc bromide. Data have also been obtained for sodium and potassium bromides in zinc bromide, but the decomposition potentials observed in these solutions, and also in that of aluminium bromide, have all the same value and indicate that the ultimate product of electrolysis in these cases is zinc. The relationship of solvent to decomposition potential is discussed and it is considered that the relative positions of the metals will change when a solvent markedly different in chemical character is employed. M. S. BURR.

**Theory of passivity.** VII. Anodic behaviour of copper in electrolyte solutions containing sulphuric acid. VIII. Anodic behaviour of zinc in electrolyte solutions containing sulphuric acid. W. J. MÜLLER and L. HOLLECK. IX. Passivity of lead in sulphuric acid, and theory of forming of the lead anode. X. Variation of autopassivity with time. W. J. MÜLLER and K.

KONOPICKY. XI. Anodic behaviour and passivity of iron in sodium sulphate solutions. W. J. MÜLLER and W. MACHU (Monatsh., 1929, 52, 409—424, 425—441, 442—462, 463—473, 474—492; cf. A., 1929, 1241).—VII. The anodic passivation of copper in aqueous solutions of sulphuric acid and in mixed solutions of sulphuric acid and copper sulphate is in agreement with the equation  $t_p = B(i_0/F_0)^n$  for coating passivation (A., 1928, 713) and examination of the electrode shows a layer of copper sulphate pentahydrate to have been formed on it. At low acid concentrations, this ultimately changes into a basic salt, this transformation occurring the sooner the lower is the acid concentration. Both *B* and *n* fall continuously with rise in the acid concentration. The value of *B* runs approximately parallel with the solubility of copper sulphate in the acid solution, although it is not exactly proportional to it. In pure 10*N*-acid solution the temperature coefficient of *B* is 1.5. The form of the current strength-time curves also accords with the equations developed for rate of growth of surface layers (cf. A., 1929, 146).

VIII. In the anodic passivation of a protected zinc electrode in an aqueous solution of sulphuric acid, the metal first becomes coated with a transparent layer, which appears from the conductivity of the liquid in its pores and from microscopical investigation to be zinc sulphate heptahydrate. This is formed sooner in acid solutions saturated with zinc sulphate than in absence of sulphate. In pure acid solutions or saturated sulphate solutions less than 5*N* in respect of acid, the layer soon becomes opaque, probably as a result of transformation into basic salt. The lower the concentration of acid the sooner this change occurs. The relation between the initial current density and the time of passivation corresponds with that observed for copper, and the form of the current strength-time curves is in accordance with the laws of coating growth, except that the transition to basic salt may interfere with the growth in thickness.

IX. The  $i_0$  and  $t_p$  data for the anodic passivation of lead in a 25% aqueous solution of sulphuric acid conform to the above equation, the value of *n* being unity, apparently as a result of the small solubility of lead sulphate. The current strength-time curves also agree with the coating theory of passivation. As the effective applied voltage is increased, both *B* and the effective current density increase in a linear manner. At 2 volts, however, the effective density assumes a steady value, whilst *B* increases abruptly and rapidly. If the graph connecting *B* with the voltage is now extrapolated to zero *B*, a value of 1.95 volts above the reversible potential of lead is obtained. Corresponding with the change in *B* there is an abrupt increase in the conductivity of the liquid in the pores of the coating from a value corresponding with a saturated solution of lead sulphate to a value approximating to the conductivity of the acid solution. At an effective applied potential of 2 volts it thus appears that the potential of the metal changes discontinuously from the value corresponding with the dissolution of bivalent lead to that for the dissolution of quadrivalent lead, which then furnishes acid by hydrolysis. The results thus support Elbs' theory of the forming of accumulator plates.

X. Application of the coating theory of passivity to autopassivity leads to the equation  $t = M + N \log (e_m - \varepsilon) / (\varepsilon - e_s)$ , where  $e_m$  is the reversible potential of the metal in the pores,  $e_s$  the potential of the coating, and  $\varepsilon$  the measured potential of the electrode at a time  $t$  after immersion in the solution, and  $M$  and  $N$  are constants. The value of  $e_s$  will not be constant, however, until an appreciable coating has been formed, but when this point has been reached the above equation is in satisfactory agreement with experimental results for the autopassivation of aluminium and also with Tammann and Sotter's data for chromium-iron alloys (A., 1923, ii, 825).

XI. In the anodic passivation in aqueous sodium sulphate solutions of iron free from a surface film of oxide the time of passivation and the initial current density are connected by an equation of the above type. The values of  $B$  and  $n$  vary with the electrolyte concentration in much the same way as they do for sulphuric acid. The results show, in confirmation of those previously obtained (A., 1928, 713), that the actual passivation of the metal occurs in very much less time than would be required for the formation of an oxide film, and that Tronstad's theory of the passivation of iron in acid solutions (A., 1929, 1002) is untenable. The passivation time of nickel is considerably reduced by the presence of a film of oxide.

R. CUTHILL.

Passivity and over-voltage. A. SMITS (Z. Elektrochem., 1930, 36, 20–25).—The passivity theory of Müller (cf. A., 1929, 886) is criticised, chiefly with reference to the author's theory of autotropy.

H. T. S. BRITTON.

Application of chiolite to the electrolysis of alumina. I. The fusion diagram of the system alumina-cryolite-chiolite. L. WASILEWSKI and S. MANTEL (Przemysł Chem., 1930, 14, 25–31).—The m. p. of mixtures of alumina and chiolite rise steadily from 735° for 100% chiolite to a constant value of about 890° at 8–20%  $\text{Al}_2\text{O}_3$ ; this is due to loss of fluorides by volatilisation. Above 20%  $\text{Al}_2\text{O}_3$  the m. p. again rises, until at 50% fusion is not achieved at 1300°. No eutectic mixture is formed in this system. The fusion diagram of the system chiolite-cryolite shows a minimum m. p. of 687° at 95% of chiolite. The diagram for the ternary system chiolite-cryolite-alumina shows that the electrolysis of alumina, using chiolite as a flux, can be carried out below 900°, using a mixture containing 10–16%  $\text{Al}_2\text{O}_3$  and cryolite and chiolite in the proportions from 20 : 80 to 35 : 65, and below 850° with mixtures containing 11–16%  $\text{Al}_2\text{O}_3$ , and 32 parts of chiolite to 68 of cryolite. Electrolysis proceeds smoothly at 850–900° with a current of 6 volts, the efficiency being over 60%, and the aluminium produced falls to the bottom of the electrolyser, no visible vaporisation of metal taking place. Preliminary experiments show that chiolite is a more convenient flux than fluoride.

R. TRUSZKOWSKI.

Experimental basis of the international scale of temperature so far as concerns low temperatures. W. H. KEESOM (Arch. Néerland., 1929, [iii], 12, 115–139).—A critical examination of the bases of the international scale of temperature fixed

by the 7th General Conference of Weights and Measures held at Paris in 1927 has been made as far as concerns low temperatures, both as regards reproducibility and agreement with the ideal thermodynamic scale. It is concluded that reproducibility has not been achieved even to the extent ( $\pm 0.02^\circ$ ) to which the various platinum resistance thermometers on which the Conference based its results agree among themselves; for this thermometers of other kinds should also be used. As regards the thermodynamic scale the limit of agreement is  $\pm 0.04^\circ$ , depending chiefly on Henning's Avogadro scale (1913), whereas the Leyden platinum resistance and a helium thermometer show variations of only  $\pm 0.014^\circ$ , and the helium thermometer is reproducible with an error of only  $\pm 0.010^\circ$ . Leyden is therefore unable to accept the international scale in preference to its own, which corresponds with the thermodynamic scale within  $\pm 0.02^\circ$ .

C. A. SILBERRAD.

X-Ray oscillography. H. SEEMANN and K. F. SCHOTZKY (Naturwiss., 1930, 18, 85–86).—A correction and explanation of a previous communication (this vol., 138).

J. W. SMITH.

Ignition limits of the mixtures  $2\text{H}_2 + \text{O}_2$  and  $2\text{CO} + \text{O}_2$ . D. KOPP, A. KOVALSKY, A. SAGILUN, and N. SEMENOV (Z. physikal. Chem., 1930, B, 6, 307–329; cf. A., 1929, 147).—Pressure-temperature diagrams are given to show the regions of explosion and non-explosion for each of the reactions  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$  and  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ . The existence of upper and lower limiting pressures has been confirmed. The upper limit decreases, the lower increases with fall of temperature. The upper limit is defined by the total pressure of the mixture and not by the partial pressure of the explosive constituents. Neither the pressure of inert gas nor change in the dimensions of the reaction vessels affects the shape of the  $p$ - $t$  curve. Slight traces of nitrogen peroxide markedly lower the ignition temperature and the residual pressure in the reaction  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ , but larger quantities, e.g., 0.1%, have less effect than traces. The results are discussed from the point of view of the "chain" theory.

F. L. USHER.

Combustion limits of air-vapour mixtures at high pressures. E. BERL and H. BAUSCH (Z. physikal. Chem., 1929, 145, 451–460; cf. B., 1927, 546; 1929, 158).—Increasing pressure causes a widening of the range of combustion with mixtures of air with ethyl alcohol, *n*-hexane, cyclohexane, and cyclohexene. The lower combustion limit of hexane-air mixtures is extended by increase of pressure owing to the separation of hydrogen and the formation of peroxides. With cyclohexane the extension is smaller owing to the greater difficulty of separation of hydrogen. In mixtures of aromatic with aliphatic compounds, the influence of peroxide formation is reduced. Unsaturated hydrocarbons resinify in oxygen under the influence of pressure at low temperatures. They cannot be exploded in air.

J. A. V. BUTLER.

Kinetics of certain simultaneous processes. E. N. GAPON (Ukrain. Chem. J., 1929, 4, 333–339).—Orlov (Diss., Kinetics of chemical reactions and

catalysis, 1913) deduced kinetic equations of the general form  $dx/dt=k_1(A-mx)$ ,  $dx/dt=k_2(A-mx)^2$ , etc., and showed their derivation from the differential equations  $dx/dt=k(A-x)\pm k_1x$ ,  $dx/dt=k(A-x)^2\pm k_1\phi(x)$ , etc. As a result of numerous calculations Orlov concluded that, if the calculated velocity coefficients  $k_1$ ,  $k_2$ ,  $k_3$  do not satisfy the differential equations of the first, second, and third orders but gradually diminish, the differential equation of general type may be applied for calculating the constant. The above equations are applicable either to successive reactions, or when the principal reaction is complicated by a secondary reaction, or to catalytic reactions,  $m$  being greater than 1 in the case of negative catalysis.

It is now shown that Orlov's equations of general type are applicable to the case when one substance A reacts simultaneously in independent directions, giving the products  $M_1$ ,  $M_2$  . . .  $M_i$ , the number of which may be 1, 2, 3 . . .  $i$ . Three cases are considered, the product M being formed either by unimolecular, or by bimolecular, or partly by unimolecular and partly by bimolecular transformation of A. By means of the results of Lebedev and Mereshkovski (A., 1913, i, 1285) on the polymerisation of isoprene and diisopropenyl, it is shown that the kinetics of simultaneous reactions, in particular of polymerisation, proceed according to equations formally identical with those of catalytic reactions.

T. H. PORE.

**Rate of reaction in a changing environment.** G. SCATCHARD (J. Amer. Chem. Soc., 1930, 52, 52—61).—Theoretical. Approximate relationships are developed on the basis of Brönsted's theory to include the effect of changing environment on the velocity of ionic and non-ionic reactions in non-ideal solutions. The principles involved in evaluating the changes of activity coefficients with concentration are applied to the oxidation of ammonia by the persulphate ion in the presence of the silver ion (Yost, A., 1926, 819) and to the reaction between *p*-nitrobenzyl chloride and certain alcohols (Ashdown, this vol., 301).

J. G. A. GRIFFITHS.

**Temperature coefficient of reactions in solution.** F. O. RICE and H. C. UREY (J. Amer. Chem. Soc., 1930, 52, 95—101).—Theoretical. The reactive complex of Brönsted's theory of acid and basic catalysis is replaced by a series of fugitive molecules differing only in energy content. The distribution of these complexes and their probabilities of reaction do not change with the addition of salts of strong acids and therefore the temperature coefficient is independent of the concentration of salt (cf. Rice and Kilpatrick, A., 1923, ii, 548). In catalysis by weak acids there may be several simultaneous reactions, each with its own characteristic energy of activation. Salts of weak acids therefore affect the temperature coefficient (cf. Rice and Lemkin, A., 1923, ii, 678).

J. G. A. GRIFFITHS.

**Velocity of hydrolysis and alcoholysis of acetic anhydride in mixtures of water and ethyl or methyl alcohol.** J. F. M. CAUDRI (Rec. trav. chim., 1930, 49, 1—16; cf. A., 1929, 655).—The rate of the simultaneous hydrolysis and alcoholysis of acetic

anhydride by binary mixtures of water with methyl and ethyl alcohols has been determined at 25°. With increase in the amount of alcohol, the unimolecular velocity coefficient of hydrolysis decreases continuously, but that of alcoholysis first rises and then falls again, the maximum being attained with a solvent containing about 40% by volume of alcohol. The quotient of the former coefficient by the water concentration and also the quotient of the latter coefficient by the alcohol concentration decrease continuously with increase in the alcohol concentration, the alcoholysis being retarded more than the hydrolysis, but both appear to have finite values in pure alcoholic solutions. Methyl alcohol is about 3.5 times as reactive towards the anhydride as is ethyl alcohol.

R. CUTHILL.

**Kinetics of the interaction of esters with potassium alkyl oxides in alcohol-water mixtures. II. Reaction between potassium ethoxide and ethyl propionate in ethyl alcohol-water mixtures.** R. F. W. SELMAN (Trans. Faraday Soc., 1930, 26, 7—11).—The reaction between potassium ethoxide and ethyl propionate is similar to that between potassium ethoxide and ethyl acetate (cf. A., 1929, 1018) and can be represented by the equations  $\text{EtOK} + \text{H}_2\text{O} \rightleftharpoons \text{EtOH} + \text{KOH}$  and  $\text{CH}_3\text{CH}_2\text{CO}_2\text{Et} + \text{KOH} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{K} + \text{EtOH}$ . As in the former case a simple velocity equation is derived, assuming the reaction to be bimolecular and the concentration of water and alcohol to be commensurate with the concentration of ethoxide, the velocity coefficients being composite values involving the concentrations of water and of alcohol and the hydrolysis constant of the ethoxide. It is concluded that the evidence available is insufficient to warrant the inclusion of the possibilities of complex formation between reactants and solvents as part of the mechanism of these reactions. A series of alcohol-water complexes such as have been suggested at various times is inadequate to explain the mechanism of the reaction unless an infinite series of such complexes be postulated.

J. W. SMITH.

**Velocity of inversion of sucrose. I.** N. TAKE-TOMI (J. Soc. Chem. Ind. Japan, 1929, 32, 260—262B).—The inversion velocity, measured polarimetrically, is nearly directly proportional to the hydrogen-ion concentration in the presence of weak organic acids. The proportionality does not obtain in the presence of strong acids. Neutral salts (alkali chlorides, nitrates, and sulphates) are incapable of catalysing the inversion, but chlorides and nitrates accelerate, and sulphates retard, the rate of inversion produced by acids. The cation of the added salt is almost without effect. The anions probably act by influencing the catalytic activity of the hydrogen ions.

S. K. TWEEDY.

**Velocity of decomposition of diazo-compounds in water.** E. YAMAMOTO.—See this vol., 337.

**Velocity of decomposition of diazo-compounds in water. II.** E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 308—311B).—The rate of decomposition of phenyldiazonium chloride in water at 0° has been studied. The velocity coefficient becomes constant after 20 hrs. Inorganic acids, neutral salts,



and the concentration of the diazo-compound are without influence on the velocity. Nitrous acid does not affect the stability of the diazo-compound. Sodium carbonate increases the value of the velocity coefficient.

C. W. GIBBY.

**Relative rates of reduction of aromatic nitro-compounds [by stannous chloride].** J. R. SAMPEY (J. Amer. Chem. Soc., 1930, 52, 88—92).—Relative rates of reduction by aqueous-alcoholic acid stannous chloride (cf. A., 1928, 57) of 28 aromatic nitro-compounds to corresponding amines are recorded. The reaction is of the second order with respect to stannous chloride over a tenfold range of concentration and is retarded by water and decrease of acidity. The velocity of reduction of isomeric nitrotoluenes, nitrophenols, chloro-, bromo-, and iodo-nitrobenzenes decreases in the order  $\alpha$ -,  $m$ -,  $p$ -. For the nitrobenzoic acids, this order is reversed. Corresponding chloro-, bromo-, and iodo-nitrobenzenes are reduced at nearly equal rates. J. G. A. GRIFFITHS.

**Rate of reaction of alcohols with  $p$ -nitrobenzoyl chloride in anhydrous ether.** A. A. ASHDOWN (J. Amer. Chem. Soc., 1930, 52, 268—278).—The reactions between alcohols and  $p$ -nitrobenzoyl chloride, previously studied by Norris and Ashdown (A., 1925, i, 626) and Norris and Cortese (A., 1927, 1166), are of the third order. The mechanism requires 2 mols. of the alcohol and 1 mol. of the chloride. An equation for calculating the third order constants at infinite dilution has been developed.

H. BURTON.

**Kinetics of the reaction of hexaphenylethane with oxygen.** R. C. MITHOFF and G. E. K. BRANCH (J. Amer. Chem. Soc., 1930, 52, 255—268).—The rate of absorption of oxygen by solutions of hexaphenylethane in carbon tetrachloride has been studied at  $-21^\circ$  to  $5^\circ$ , using mixtures of oxygen and nitrogen. Varying partial pressures (0.2—0.93 atm.) of oxygen were employed, and the reaction mixture was shaken sufficiently vigorously to permit the transfer of oxygen from the gaseous to the liquid phase to occur at a rate faster than that of oxidation. The absorption of oxygen occurs in three phases: (i) rapidly, due to saturation of the solvent, (ii) less rapidly, representing oxidation of the hexaphenylethane, i.e., dissociation of the ethane into triphenylmethyl, and subsequent rapid oxidation of the free radical, and (iii) very slowly, apparently due to the presence of a small amount of an undissociated but active form of hexaphenylethane. This active form reacts at a slower rate than the free radical, the oxidation of which is a first order reaction.

The rate of oxidation of hexaphenylethane is proportional to the concentration of the ethane, and also to a function of the oxygen pressure, namely,  $K_0 - 1/(a + bP_{O_2})$ , where  $K_0$ ,  $a$ , and  $b$ , are constants. The heats of activation increase with rise of temperature, but are approximately constant to the change in the pressure of oxygen. Little or no energy appears to be needed to activate the oxygen.

Diphenylamine and anthracene have no appreciable effect on the velocity of the reaction, whereas phenol causes an increase in the rate of more than 50%.

H. BURTON.

**Hydrolysis and polymerisation of cyanamide in alkaline solutions.** G. H. BUCHANAN and G. BARSKY (J. Amer. Chem. Soc., 1930, 52, 195—206).—The rate of formation of carbamide and dicyanodiamide from cyanamide has been studied in buffer solutions at  $p_H$  6—13 and  $50^\circ$ . At a constant  $p_H$ , the polymerisation of cyanamide to dicyanodiamide proceeds as a second order reaction, and up to  $p_H$  about 10 dicyanodiamide is the only product formed; the velocity of formation is a maximum at  $p_H$  9.6. At  $p_H$  12.6—13.6, cyanamide is hydrolysed to carbamide. The reaction is of the first order, and the velocity coefficient is independent of the alkali concentration. Solutions of dicyanodiamide are stable up to  $p_H$  10; above this value decomposition occurs, the rate increasing with rise in  $p_H$ . H. BURTON.

**$\beta$ -Glucosidase. II. Hydrolysis of cellobiose.** R. WEIDENHAGEN (Z. Ver. deut. Zuckerind., 1930, 80, 11—24).—The  $\beta$ -glucosidase of emulsin hydrolyses cellobiose at about one eighth the rate of its action on salicin; the reaction is unimolecular. There is no direct relation between the concentration of the enzyme and the rate of hydrolysis. The optimum is at  $p_H$  5.0. With salicin as substrate the velocity coefficient increases in inverse ratio to decreasing substrate concentration, but with cellobiose this relation only holds even approximately over a narrow range at about 2—3% of substrate. For the dissociation constant of the salicin-enzyme complex the value  $K_{sal} = 0.033$  found is in good agreement with that found by previous workers, but the point of maximum reaction rate is ill defined on the activity- $p_s$  curve for cellobiose-emulsin, and neither of the two values deduced,  $K_c = 0.118$  or  $0.139$ , fits the data completely. It is suggested that the application of Langmuir's adsorption isotherm might lead to a better understanding of the discrepancies (see following abstract). The  $\beta$ -glucosidase of malted barley acts more strongly on cellobiose than on salicin, which would seem to point to the existence of two enzymes, a salicinase and a cellobiase. On account, however, of the uncertainty of the value of  $K_c$  and the low  $\beta$ -glucoside activity of malt an accurate comparison of the enzymes from the two sources is at present impossible, and the author considers that the identity of all enzymes splitting normal  $\beta$ -linkings is not to be doubted.

F. E. DAY.

**Application of the mass action law to the enzymic decomposition of sucrose.** R. WEIDENHAGEN and E. LANDT (Z. Ver. deut. Zuckerind., 1930, 80, 25—27).—It is shown that the velocity of this reaction can be represented equally well by formulæ of the same type derived respectively from the mass action law and from Langmuir's adsorption isotherm, based on the idea of heterogeneous catalysis. The latter is to be preferred as it is broader and allows of conceptions such as explanation of inhibition phenomena as being due to the exclusion of the substrate by foreign substances adsorbed on the enzyme.

F. E. DAY.

**Chemical kinetics in mixtures of solvents. VII. Reaction between pyridine and allyl bromide in ethyl benzoate.** G. E. MUCHIN and M. I. ZILBERFARB (Ukrain. Chem. J., 1929, 4, 327—

331; cf. A., 1927, 1149).—Determinations of the velocity of interaction of pyridine and allyl bromide in ethyl benzoate and its mixtures with benzene at 45° and 55° give continuous curves, free from singular points, for the relationship between the constant of the reaction and the composition of the mixed solvents. The observed velocity coefficients are less than those calculated additively and, although the general course of the curves is analogous to that found with mixed nitrobenzene-benzene solvents, the extents of the divergences from additivity and the displacement of the curve caused by change of temperature are less marked in the present case. T. H. POPE.

**First order solid-phase reaction.** B. LEWIS and H. J. SCHUMACHER (*Nature*, 1930, 125, 129).—The reaction between bromine and ozone (A., 1929, 1395) is regarded as one of the first order which takes place in the solid phase of the crystals. For a given amount of bromine oxide it appears to be of zero order, since any oxide which decomposes is at once reformed by ozone. L. S. THEOBALD.

**Oxidation of copper at higher temperatures.** W. FEITKNECHT (*Z. Elektrochem.*, 1930, 36, 16—17).—The formula advanced by Wilkins (A., 1929, 1019) to account for the author's data (A., 1929, 517) is shown to be unsatisfactory.

H. T. S. BRITTON.

**Catalysis by nitrous acid of the reaction between oxygen and hydrogen iodide and a method for the determination of oxygen.** G. ALSTERBERG (*Biochem. Z.*, 1929, 216, 278—300).—Nitrogen trioxide when present in amounts greater than 1 mg. per litre causes considerable error in the usual Winkler determination of oxygen dissolved in water. The catalytic effect of nitrogen trioxide on the reaction between hydrogen iodide and oxygen is investigated by titration of the iodine liberated. The reaction is not a true catalysis, since some of the trioxide is irreversibly oxidised to pentoxide. The amount of hydrogen iodide, so long as it is in excess, does not affect the result. Temperature, so long as oxygen is in excess, has little effect, but otherwise rise of temperature accelerates the reaction. With excess of oxygen the extent of reaction is determined by the amount of trioxide, whilst if oxygen is not in excess the reaction proceeds in proportion to the amount of oxygen. The amount of iodine separated at low concentrations of oxygen is greater than theoretical for the amount of oxygen, due to reduction of tri- to di-oxide, and at high concentrations of oxygen is less, due to oxidation of nitrogen tri- to pent-oxide. A method for the determination of oxygen is described. P. W. CLUTTERBUCK.

**Conversion of thiosulphuric acid into polythionic acids with the aid of catalysts.** II. A. KURTENACKER and I. A. IVANOV (*Z. anorg. Chem.*, 1930, 185, 337—359).—In order to follow the course of the reaction between mineral acids and thiosulphates, of which the end-point only had been previously investigated (A., 1928, 1195), sulphurous acid has been employed in place of, or in addition to, hydrochloric acid. In this way, provided the thiosulphate is not too dilute, no sulphur separates, and so it is not necessary to wait for its coagulation

before proceeding with the analysis. The limiting amount of arsenite necessary as catalyst is approximately the same as previously required when hydrochloric acid alone is present. The influence of acidity on the reaction has been investigated by adding different amounts of hydrochloric acid to the sulphurous acid. Even for a high concentration of hydrochloric acid, neither arsenious sulphide nor sulphur separates. The velocity of polythionate formation increases very markedly with the acidity. The influence of the sulphurous acid varies with the acidity. In absence of hydrochloric acid, or in presence of a very small quantity, sulphurous acid has a strong accelerating action, but it has the opposite effect in presence of an excess of hydrochloric acid. The accelerating action is attributed to the hydrogen ion of the sulphurous acid, and the inhibiting action to the formation of a complex ion  $[S_2O_3 \cdot SO_2]''$  (cf. Foerster and Vogel, A., 1926, 1016). The kind of polythionate formed depends on the acidity and follows the rule previously observed that, in strongly acid solutions, polythionates with higher sulphur content are formed. In sulphurous acid solution alone, tri- and tetra-thionate are obtained, and practically no pentathionate. At the beginning of the reaction in feebly acid solution, however, appreciable quantities of pentathionate are formed, but this disappears as the reaction proceeds, the time-concentration curve thus possessing a maximum. This maximum is also observed even in the strongly acid solutions where considerable quantities of pentathionate remain at the end of the reaction. Within much narrower limits of concentration of the different reagents similar results are obtained when the arsenite is replaced by antimony trichloride, but sulphur and antimony sulphide or oxysulphide readily separate. The observation that bismuth trichloride exercises a slight catalytic action on the decomposition of thiosulphate has been confirmed, because, throughout the reaction, there is a slightly greater production of polythionate and smaller separation of sulphur in presence than in absence of bismuth. The probable mechanism of the catalysis is discussed. M. S. BURR.

**Oxidation catalysis.** H. VON EULER, D. RUNEHJELM, and S. STEFFENBURG (*Arkiv Kemi, Min., Geol.*, 1929, 10, B, No. 7, 6 pp.).—Solutions of hæmin, mesohæmin, and deuterohæmin produce catalytic oxidation of reduced phenolphthalein in presence of small amounts of hydrogen peroxide. The reaction rapidly comes to a standstill, but the colour is intensified on addition of more hydrogen peroxide. Copper sulphate has a similar effect, a maximum intensity of coloration being obtained with a given ratio of copper to hydrogen peroxide. Blood also produces the colour reaction, whether previously heated to 100° or not. Hæmin, mesohæmin, and copper sulphate also cause the evolution of oxygen from solutions of hydrogen peroxide containing phenolphthalein. K. V. THIMANN.

**Active hydrogen.** II. Wall-catalysis. H. VON WARTENBERG and G. SCHULTZE. III. Lead hydride. G. SCHULTZE and E. MÜLLER (*Z. physikal. Chem.*, 1930, B, 6, 261—271).—II. Washing the glass

walls of the discharge tube with ortho- or metaphosphoric acid greatly retards the conversion of active into molecular hydrogen. The protective action of oxygen is due to formation of water.

III. A volatile hydride has been produced by the interaction of metallic lead and active hydrogen. The hydride decomposes at a red heat, giving a lead mirror. Attempts to condense it led to spontaneous decomposition, on account of which no chemical analysis was possible. It is considered that active hydrogen rather than the methyl radical is the intermediate product in Paneth's experiments on the decomposition of lead tetramethyl (cf. A., 1929, 788).

F. I. USHER.

**Mechanism of oxidation of mercury vapour.**  
I. Equilibrium formula. II. Condensation of oxygen in the molecular or the atomic state. III. Condensation of oxygen in the molecular and atomic states. Y. OKAYAMA (J. Soc. Chem. Ind. Japan, 1929, 32, 163—164B, 164—166B, 167—169B).—I. The mechanism of the oxidation of mercury vapour by oxygen in presence of a platinum catalyst has been studied. The equation  $a_2 n_2 f = v_2 f_2$ , where  $a_2$  is a factor for the condensation of the oxygen molecules on the platinum surface,  $n_2$  the number of molecules impinging on unit area of surface per sec.,  $f_2$  the fraction of the total surface which is covered by oxygen molecules,  $v_2$  the number of molecules which evaporate per sec. when  $f_2 = 1$  cm.<sup>2</sup>, and  $f$  is the fraction of surface uncovered, is a valid expression for the equilibrium even when reaction takes place.

II. The mechanism of the reaction when the oxygen condenses in the atomic or in the molecular state is described and the appropriate equations for the velocity are derived.

III. An equation is derived representing the velocity of the reaction when simultaneous condensation in the molecular and atomic states occurs.

H. F. GILLBE.

**Temperature distribution along a heated filament used as a catalyst.** E. S. LAMAR and W. E. DEMING (Phil. Mag., 1930, [vii], 9, 28—36).—An expression has been deduced which gives the temperature gradient at any point along a heated molybdenum filament used as a catalyst in the decomposition of ammonia. Temperatures at any points along the filament are determined by integrating this expression and the temperature distribution so obtained is found to correspond closely with that indicated by the measured resistance of the wire. From the temperature distribution is calculated the effective length of the filament as a catalyst at the maximum temperature. The mean heat of dissociation of ammonia over the range 954—1164° Abs. has been calculated from consideration of the heat losses from the filament. The value 12,067 g.-cal. per mol. so obtained is in fair agreement with the generally accepted value of 13,375 g.-cal. per mol.

A. E. MITCHELL.

**Catalytic and chemical characteristics of cubic and rhombohedral ferric oxide.** P. H. EMMETT and K. S. LOVE (J. Physical Chem., 1930, 34, 41—62; cf. Welo and Baudisch, A., 1925, ii,

1071).—The catalytic activity, the sorption of water vapour, the rate of reduction by hydrogen, and the effect of alumina on the magnetic permeability and the rate of reduction of the cubic and rhombohedral forms of ferric oxide have been investigated. The cubic form was prepared by heating ferrosferric oxide in air at 300°, whilst the rhombohedral form was obtained by precipitation with ammonia and drying in air at the same temperature. The catalytic activity of the two oxides with respect to the oxidation of benzidine or of guaiacum resin by hydrogen peroxide is approximately the same and is not a function of crystal structure as was concluded by Welo and Baudisch (*loc. cit.*). The catalytic activity of both forms is destroyed by heating at 550° for several hours. The catalytic combination of hydrogen and oxygen at 250° is the same for both oxides and is unaffected by heating at 550°. The catalytic decomposition of ozone between -75° and 25° is also the same for the two forms, but is less rapid with the samples which had been heated to 550°. Decomposition in an ozone (2%)-oxygen mixture is practically complete with the most active oxides even at -74°. The decomposition is apparently unimolecular, with a temperature coefficient corresponding with an energy of activation of approx. 2000 g.-cal. Experiments on the sorption of water at 25° and 210° from a stream of nitrogen containing 0.57% of water vapour show that for unit weight of oxide sorption on the cubic form is 10—60% less than that on the rhombohedral form, and that the sorption on samples heated at 550° is less than that on those dried at 300° and is unaffected by activation of the oxide with a mixture of hydrogen and oxygen. The loss of magnetic permeability on heating is quickest with cubic ferric oxide prepared from hydrated ferrosferric oxide precipitated by ammonia and slowest with cubic ferric oxide prepared from ferrosferric oxide precipitated by sodium hydroxide; a sample similar to the first but containing 1.5% of alumina is intermediate between the two. The rates of reduction of the cubic and rhombohedral forms are approximately the same, being slightly faster in the former case. Heating at 550° for 2 hrs. reduces the rates of reduction considerably. Coprecipitation of alumina with ferrosferric oxide has little effect on the rate of reduction of ferric to ferrosferric oxide, but appears markedly to retard further reduction to metal. The results are discussed and Welo and Baudisch's work (*loc. cit.*) is adversely criticised.

L. S. THEOBALD.

**Application of nickel to certain reactions of organic chemistry.** A. KORCZYŃSKI, A. REINHOLZ, and E. SCHMIDT (Rocz. Chem., 1929, 9, 731—740).—The catalytic action of nickel is similar to that of copper in reactions with aromatic hydrocarbons halogenated in the side-chain; thus with benzyl chloride a polymeride of dibenzyl is produced, whilst with benzylidene chloride diphenyltetrachloroethane and diphenyldichloroethylene are obtained. Nickelous cyanide can be substituted for cuprous cyanide in the reaction between aromatic halogen derivatives and potassium cyanide. The action of nickel on the bromination of benzene, nitrobenzene, and naphthal-

ene is analogous to that of iron. Nickel has no catalytic action on the bromination of *s*-tribromophenol. R. TRUSZKOWSKI.

**Catalytic oxidation of toluene by air.** M. I. KUSNETZOV and M. A. STEPANENKO (Ukrain. Chem. J., 1929, 4, [Tech.], 153—177).—Results are given of a large number of experiments on the oxidation of toluene in presence of heated basic zinc manganate, vanadium pentoxide on asbestos or pumice, molybdenum trioxide on asbestos, or bismuth vanadate on pumice. With molybdenum trioxide, which gave the best results, of 26.32 g. of toluene oxidised, 7.1 g. were oxidised to benzaldehyde, 0.12 g. to benzoic acid, 7.0 g. to carbon dioxide, and 12.1 g. to carbon monoxide. The carbon monoxide is formed together with benzene by decomposition of benzaldehyde and the carbon dioxide partly by direct oxidation of toluene and partly, along with benzene, by decomposition of benzoic acid. The products obtained were 8.1 g. of benzaldehyde, 0.16 g. of benzoic acid, and 10.3 g. (calculated) of benzene. Of the total quantity of toluene evaporated (89.7 g.), 55.84 g. remained unchanged, and 7.54 g. (8.3%) represented losses and experimental errors. In a further series of experiments in which tin vanadate formed the catalyst and a large excess of air was employed, considerably higher proportions of benzoic acid were obtained.

T. H. POPE.

**Chemical action in the glow discharge. II. Further investigation on the synthesis of ammonia.** A. K. BREWER and J. W. WESTHAVER (J. Physical Chem., 1930, 34, 153—164; cf. A., 1929, 891).—The relative reactivity of various portions of the discharge in synthesising ammonia, together with the effect of added gases on the rate of synthesis, have been determined. Maximum synthesis occurs in the negative glow, whilst the positive column, including the anode glow, produces a uniform but smaller synthesis throughout its length, the respective rates being 33 to 1; no formation of ammonia occurred in the Crookes or Faraday dark spaces. The effects of the addition of excess of nitrogen or hydrogen, and of helium and argon, have been investigated. The rate of reaction is independent of pressure in these cases so long as the composition of the gas mixture remains constant. The maximum rate of synthesis for hydrogen-nitrogen mixtures occurs in a 2:1 rather than in the expected 3:1 mixture. Helium added in quantity up to 70% of the total amount of gas present has no effect on the rate of formation of ammonia, but even small amounts of argon decrease the rate considerably. The data indicate that the synthesis is initiated principally by  $N_2^+$  ions, whilst the production of atoms, excited molecules, and  $H_2^+$  ions represents lost energy. The formation of  $N_2^+$  ions is followed by union with hydrogen to form ammonia and the three possible mechanisms for this last step are discussed. L. S. THEOBALD.

**Electrolysis of water at high pressure.** G. FAUSER.—See B., 1930, 107.

**Polarographic studies with the dropping mercury cathode. VIII. Maxima of current due to electro-reduction of oxygen in solutions of strong electrolytes.** E. VARASOVA (Coll. Czech.

Chem. Comm., 1930, 2, 8—30).—A theoretical interpretation of the maxima in current-voltage curves produced in the presence of oxygen with the dropping mercury cathode is given and the influence of various experimental factors studied. In solutions saturated with air at the ordinary temperature, the current maximum is greatest when the specific conductance of the solution is  $2.5 \times 10^{-4}$  ohm; with varying oxygen content the conductance of the solution for the highest maximum is proportional to the oxygen content and is independent of the rate of dropping of the mercury and of the applied external resistance. The magnitude of the maximum is proportional to the oxygen concentration for the same dropping mercury cathode. The shape of the curve is influenced by the rate of dropping. The general character of the current-voltage curves is independent of the valency of the cation; bivalent ions have a larger suppressive effect on the maxima than the univalent ions, whilst cyanide ions, and to a smaller degree hydroxyl ions, produce an abnormal suppression.

A. I. VOGEL.

**Mechanism of electrolytic rectification.** M. E. MACGREGOR (Nature, 1930, 125, 128).—The hypotheses of Burgess and Hambuechen and of Günther-Schulze are only partly correct and, as the result of experiments with a special electrolyte which shows electrolytic reversibility with anodes of aluminium and cathodes of a special passive steel, a combination of the two is now advanced as the true explanation of the mechanism of electrolytic rectification.

L. S. THEOBALD.

**Theory of the electro-deposition of chromium from aqueous chromic acid solutions. IV.** E. MÜLLER and O. ESSIN (Z. Elektrochem., 1930, 36, 2—9).—From electrolytic experiments carried out on chromic acid solutions with potentials up to those necessary to cause the evolution of hydrogen, it is concluded that the smallest cathodic polarisation of a perfectly bright electrode is sufficient to bring about the formation of a porous, invisible diaphragm covering the surface of the cathode. This diaphragm is composed of basic chromium chromate, such that the basic part faces the cathode, and the acid radical part the anode. It hinders the passage of chromic acid up to the electrode. By increasing the cathodic polarisation hydrogen ions become able to pass through the pores on account of the enhanced electrostatic attraction, but unless the associated anion is able to follow rapidly, in which case acid is formed within the diaphragm, the diaphragm will remain intact. Hence a greater cathode potential is necessary, it being very great with anions of very large diameter, e.g.,  $HCrO_4^-$ ,  $ClO_4^-$ , and  $H_2PO_4^-$ . This explains why a solution of pure chromic acid failed to be reduced. On addition of sodium salts, the anions of which were of small diameter, e.g.,  $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $ClO_3^-$ , and  $HSO_4^-$ , the cathode potential becomes smaller than the hydrogen potential and the diaphragm dissolves, and an appreciable reduction of chromic acid ensues. The behaviour at platinised platinum and carbon cathodes was also investigated. Electrodes with rough surfaces caused greater reduction of chromic acid, apparently through the discontinuous nature of the diaphragm, there being a tendency for

chromic acid to gain access to the electrode surface through holes formed at peaks in the surface. As long as such conditions prevail that both hydrogen ions and hydrochromate ions can diffuse quickly through to the electrode, then reduction to the trivalent state occurs and no diaphragm forms.

H. T. S. BRITTON.

**Electrolysis of metallic oxides dissolved in boric anhydride and in fused borates. Preparation of amorphous boron, borides, and some metals.** L. ANDRIEUX (Ann. Chim., 1929, [x], 12, 423—507).—The electrolysis in a carbon resistance furnace of sodium pyroborate at 900° with a carbon cathode and a water-cooled iron anode, of potassium and lithium pyroborates, of calcium, strontium, and barium pyroborates at 1000°, of mixtures of boric anhydride and magnesia either alone or mixed with the fluorides of magnesium, sodium, potassium, lithium, or calcium, of manganese pyroborate, and a mixture of cerium oxide and boric anhydride, is described and the relative yields of boron and borides are determined. Boron of highest purity was obtained from electrolysis of magnesia, boric anhydride, and metallic fluoride mixtures. Electrolysis of calcium, strontium, and barium pyroborates to which the corresponding fluorides had been added, with carbon electrodes, gave the corresponding borides in a state of purity. *Cerium boride*,  $\text{CeB}_6$ , was obtained from the mixture  $\text{CeO}_2 + 2\text{B}_2\text{O}_3 + \text{CeF}_3$ ; the *borides*,  $\text{XB}_6$ , where  $\text{X} = \text{La}, \text{Nd}, \text{Gd}, \text{Y}, \text{Er}, \text{or } \text{Yb}$ , from the oxides of the metal and lithium or magnesium pyroborate and fluoride; *thorium boride*,  $\text{ThB}_6$ , from thoria, sodium pyroborate, and sodium fluoride; *zirconium boride*,  $\text{Zr}_3\text{B}_4$ , from zirconia and the magnesium, calcium, or lithium pyroborate and fluoride; *titanium boride*,  $\text{TiB}_2$ , from titania and magnesium, calcium, or sodium pyroborate and fluoride; *vanadium boride*,  $\text{VB}_2$ , from vanadium pentoxide and magnesium, calcium, or lithium pyroborate and fluoride; *chromium boride*,  $\text{Cr}_3\text{B}_2$ , from chromium sesquioxide and magnesium or calcium pyroborate and fluoride; *uranium boride*,  $\text{UB}_4$ , from  $\text{U}_3\text{O}_8$  and magnesium, calcium, or lithium pyroborate and fluoride; *manganese boride*,  $\text{MnB}$ , from manganous oxide and boric anhydride mixed with manganese fluoride, or with the oxide and fluoride of manganese, lithium, or sodium. Electrolysis of zinc oxide in a bath of sodium pyroborate preferably mixed with sodium, potassium, lithium, calcium, barium, or zinc fluoride, with carbon electrodes gave zinc (best yield with  $\text{ZnO} + 2\text{B}_2\text{O}_3 + \text{Na}_2\text{O} + \text{BaF}_2$ ), whilst tungsten and molybdenum were obtained from the trioxides of the metals and the pyroborates and fluorides of sodium, calcium, or magnesium. The maximum yield of tungsten was obtained from a bath with the composition  $\frac{1}{2}\text{WO}_3 + 2\text{B}_2\text{O}_3 + \text{Na}_2\text{O} + \text{NaF} + \text{ZnO}$ , and of molybdenum,  $\frac{1}{2}\text{MoO}_3 + 2\text{B}_2\text{O}_3 + \text{Na}_2\text{O} + \text{NaF} + \text{ZnO}$ .

A. I. VOGEL.

**Quantum yield in the photochemical decomposition of azoimide.** A. O. BECKMAN and R. G. DICKINSON (J. Amer. Chem. Soc., 1930, 52, 124—132; cf. A., 1928, 970).—Over the pressure range 2—131 mm. and in homogeneous light ( $\lambda = 1990 \text{ \AA}$ ),  $3.0 \pm 0.5$  mols. of azoimide are decomposed per quantum of light absorbed. In the full radiation

of an aluminium spark, the reaction velocity was directly proportional to pressure for the range 0.06—0.5 mm. It is suggested that the primary reaction process is one of dissociation.

J. G. A. GRIFFITHS.

**Photochemical dissociation of triatomic molecules. Hydrogen cyanide.** D. S. VILLARS (J. Amer. Chem. Soc., 1930, 52, 61—67).—The energies required to dissociate hydrogen cyanide in different modes are calculated, the least (4.3 volts) being for dissociation into hydrogen and cyanogen. The brown colour acquired by hydrogen cyanide is believed to be due to the polymerisation of cyanogen formed in this way. Absorption of light by the gas was not detected between 6593 and 2094  $\text{\AA}$ . even at 760 mm. and 1000°. Light from the silver arc ( $>1800 \text{ \AA}$ .) did not excite fluorescence.

J. G. A. GRIFFITHS.

**Photolysis of solutions of hydrogen sulphide in hexane and water.** E. WARBURG [with RUMP] (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1929, 29, 624—625).—Photolytes may be divided into two classes according to whether reaction between the photolyte and its solvent occurs or not. Hydrogen sulphide in water belongs to the former class, but in hexane it belongs to the second class. The photoequivalence law may be applied satisfactorily only in the second instance.

F. G. TRYHORN.

**Photochemistry of silver halides.** W. LESZYN-SKI (Z. wiss. Phot., 1930, 27, 304).—The quantities of silver found in unexposed emulsions by the method of Schmidt and Pretschner (B., 1928, 625) are greater in amount than the photolytic silver determined by Eggert and Noddack (cf. B., 1922, 232) after exposure. This need not imply inaccuracy in the latter work, but only a difference in chemical properties between the two forms of silver.

L. V. CHILTON.

**Absorption of infra-red radiations and the activation in chemical reactions of molecules.** N. R. DHAR and A. K. BHATTACHARYA (Trans. Faraday Soc., 1930, 26, 1—6).—All radiations between 7000 and 4400  $\text{\AA}$ . have been shown to be absorbed by an aqueous solution of neocyanine and by a mixture of chromic acid and citric acid. Extinction coefficient measurements are much more satisfactory than photographic methods in such cases. Radiation of wave-length greater than 6570  $\text{\AA}$ . is absorbed completely by a very dilute solution of neocyanine, whilst there is a minimum at about 5200  $\text{\AA}$ . This agrees approximately with the velocity of reaction in the different regions. Appreciable absorption of all radiations from 7000 to 4400  $\text{\AA}$ . has also been observed with other reacting mixtures, this being accompanied by acceleration of the reactions. These wave-lengths being much shorter than those which should accelerate the change according to the radiation theory, it is suggested that the latter should be regarded as threshold limits, radiation of wave-length longer than these being ineffective. The relation between intensity of illumination and velocity of reaction is complicated, depending on both the amount of adsorption and on the acceleration of the reaction in the presence of light. The relationship between intensity and velocity of a single reaction can be changed in several cases by changing the

velocity of the dark reaction and the intensity and quality of the incident radiation. The quantum yield of a reaction may vary considerably with experimental conditions. Since chemical reactions involving halogens can be accelerated by radiations of wave-length  $7304 \text{ \AA}$ ., it is considered that the theory that halogens are initially converted into atoms on illumination is doubtful. J. W. SMITH.

**Photochemical decomposition of nitrosyl chloride.** G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1930, 52, 102—108).—In homogeneous light of various wave-lengths between 6350 and 3650  $\text{\AA}$ ., 2 mols. of nitrosyl chloride are decomposed into nitric oxide and chlorine by each light quantum absorbed (cf. Bowen and Sharp, A., 1925, ii, 695). It is suggested that the reaction proceeds by the excitation of a molecule followed by decomposition on collision with a normal molecule of nitrosyl chloride. Nitrogen has no influence on the quantum efficiency.

The absorption of light commences at 6350  $\text{\AA}$ . and increases towards the ultra-violet. Maxima occur at 5990, 4690, 3300, and beyond 2500  $\text{\AA}$ . This spectrum has band structure down to 3300  $\text{\AA}$ . Fine structure was detected in the bands as far as 4100  $\text{\AA}$ .

J. G. A. GRIFFITHS.

**Combined photographic action of light and  $\alpha$ -rays or mesothorium rays.** H. ISHIDŌ (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 992—998).—The combined effect of light and  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays from ionium and mesothorium has been studied. For a certain definite exposure to the radioactive emission, the increase in darkening of the photographic plate decreases as the previous exposure to ordinary light is increased; if the plate is exposed first to radioactive radiation and then to ordinary light the increase in density decreases with increasing exposure to ordinary light. An effect similar to the Herschel effect is shown.

R. A. MORTON.

**Displacement of metals and their oxides from solutions of their salts by hydrogen at high temperatures and pressures. Action of hydrogen on metallic nitrates.** V. IPATIEV and B. MUROMTSEV (Ber., 1930, 63, [B], 160—166; cf. A., 1923, ii, 639).—Replacement of metals by hydrogen occurs more readily from nitrates than from solutions of other salts, probably owing to the ready reducibility of the anion. Formation of nitrite in very small amount commences at about 200°. At about 300°, the anion is almost completely reduced to nitrogen, production of ammonia occurring to a very small extent. The solutions are enclosed in quartz or glass tubes and heated in the bomb under an initial pressure of 50—80 atm. of hydrogen, rising to 200—250 atm. during the experiments. Above a certain pressure, the qualitative results are independent of the actual pressure of the gas and the concentration of the solution has little influence. Nickel nitrate in gold tubes at 200° gives the compound  $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{NO} \cdot 2\text{H}_2\text{O}$ , mixed with nickelous oxide if the temperature rises to 270°; in quartz tubes between 200° and 240° the basic salt,  $\text{Ni}(\text{NO}_3)_2 \cdot 5\text{NiO}$ , is deposited, whereas at 245° the compound  $\text{Ni}(\text{NO}_3)_2 \cdot 3\text{NiO}$  is produced. Between 330° and 360°,

nickelous oxide is produced, accompanied by nickel if the experiment is prolonged. Cobalt nitrate yields the sesquioxide at all temperatures between 200° and 360° in quartz or gold tubes; a basic nitrate could not be obtained. In quartz tubes at 250—300°, manganese nitrate yields trimanganic tetroxide of varying appearance, whereas in gold tubes at 190—240° the hydrate  $\text{Mn}_3\text{O}_4 \cdot \text{H}_2\text{O}$  is produced, the anhydrous substance being formed at 250°. Uranyl nitrate in gold tubes at about 300° gives the acid  $\text{H}_2\text{UO}_4$ , accompanied by uranium trioxide when the temperature is raised or the experiment is prolonged; further rise of temperature causes the appearances of the oxide  $\text{U}_3\text{O}_8$ , whilst, finally, at 360° and greatly prolonged time the oxide  $\text{UO}_2$  is produced. At about 200°, cadmium nitrate in gold tubes yields cadmium hydroxide monohydrate, which, at 250—350°, becomes admixed with cadmium oxide. At 350° and above, the metallic oxide becomes mixed with the metal when the experiment is prolonged. Zinc nitrate in gold tubes at 250—350° yields zinc hydroxide; at 350° and higher, zinc oxide is precipitated, accompanied by zinc when the experiment is prolonged. Zinc hydroxide does not yield zinc below 380—390°. Crystalline calcium hydroxide is obtained from calcium nitrate at 300° and higher temperatures. H. WREN.

**Displacement of metals from solutions of their salts by hydrogen at high temperatures and pressures. Displacement of arsenic from its salts by hydrogen.** V. IPATIEV, G. RAZUBAIEV, and V. MALINOVSKI (Ber., 1930, 63, [B], 166—174; cf. A., 1926, 487).—In the author's high-pressure apparatus, arsenic is only slightly oxidised by water, not more than 7% of arsenious acid being obtained at 350°; the formation of arsine could not be detected. In presence of alkali hydroxide the oxidation is more vigorous, arsenious acid, accompanied by arsenic acid in small amount, being formed in quantity. Increase in concentration of the alkali hydroxide facilitates oxidation up to a point beyond which further increase results in marked diminution of the amount of arsenic oxidised. Reaction commences at 200°; the rate increases rapidly up to 350° and then decreases sharply. Quantitative oxidation of arsenic cannot be effected by rise of temperature or prolongation of the experiment. The hypothesis that the reaction is balanced,  $2\text{As} + 3\text{H}_2\text{O} \rightleftharpoons \text{As}_2\text{O}_3 + 3\text{H}_2$ , is supported by the following evidence. If the hydrogen is removed periodically, the oxidation of arsenic becomes nearly quantitative; if, on the other hand, the apparatus is filled initially with hydrogen at 30 atm. the quantity of arsenic oxidised is diminished to 15%, whereas under similar conditions, but without initial hydrogen pressure, 58% is oxidised. Displacement of arsenic from sodium arsenate solution by hydrogen commences at 300° and increases rapidly with rising temperature (15% at 300°/25 atm., 77% at 350°/25 atm.). The arsenic separates in large, well-defined crystals. The initial pressure of the hydrogen has a very marked influence on the production of arsenic. At 350°, and after 24 hrs., the separation of the element in notable amount occurs at 15 atm. Under lower pressures, arsenic acid is



reduced to arsenious acid. The increase in pressure has no effect at pressures higher than 40 atm.

H. WREN.

**Lithium chlorate.** L. BERG (J. Russ. Phys. Chem. Soc., 1929, **61**, 1801—1805).—See A., 1929, 1145.

**Sodium hydride.** I. Preparation and density. II. Heat of formation. H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1930, **185**, 239—253, 254—266).—I. Pure sodium hydride has been prepared as fine white needles by bringing together hydrogen and sodium vapour at 400—450° in an apparatus which is described. An exact method for the analysis of sodium hydride is given. By the floating method, using mixtures of benzene and carbon tetrachloride,  $d^{25}$  is  $1.396 \pm 0.005$ , in good agreement with the results of Proskurnin and Kasarnovski (A., 1928, 697);  $d$  (X-ray), however, is only 1.29.

II. The mean value of the heat of formation of 1 g.-mol. of sodium hydride from solid sodium and gaseous hydrogen is 12.8 kg.-cal. This is the difference between the heat of dissolution of sodium ( $44.38 \pm 0.21$  kg.-cal.) and that of sodium hydride ( $31.57 \pm 0.15$  kg.-cal.) in water as measured in a calorimeter especially designed to obviate errors due to the violence of reaction.

M. S. BURR.

**Reduction of alkali nitrates by hydrous ferrous oxide.** S. H. CARSLY (J. Physical Chem., 1930, **34**, 178—187).—Hydrous ferrous oxide reduces sodium nitrate quantitatively to ammonia and is itself oxidised to ferrosiferrous oxide. In neutral and dilute solutions previously boiled ferrous oxide reduces nitrate more slowly than does the freshly-precipitated oxide owing to agglomeration and dehydration. In dilute alkaline solution ferrous oxide tends to precipitate in a denser and more agglomerated form than in a neutral solution. Boiling with concentrated alkali favours peptisation and hence the speed at which reduction takes place. These results do not agree with Baudisch's conclusions (A., 1924, i, 1141), which are adversely criticised.

L. S. THEOBALD.

**Complex alkali copper carbonates.** A. COCOSINSCHI (Bull. Acad. Sci. Roumaine, 1929, **12**, 19—21).—The following complex salts were prepared by the use of sodium or potassium hydrogen carbonate:  $\text{CuCO}_3, \text{Na}_2\text{CO}_3, \text{H}_2\text{O}$  and  $3\text{H}_2\text{O}$ ;  $\text{CuCO}_3, 2\text{Na}_2\text{CO}_3, 2\text{H}_2\text{O}$ ;  $\text{CuCO}_3, 3\text{Na}_2\text{CO}_3, 2\text{H}_2\text{O}$ ;  $2\text{CuCO}_3, \text{Na}_2\text{CO}_3, 3\text{H}_2\text{O}$ ;  $2\text{CuCO}_3, 3\text{Na}_2\text{CO}_3, 5\text{H}_2\text{O}$ ;  $\text{CuCO}_3, \text{K}_2\text{CO}_3$ ;  $\text{CuCO}_3, 2\text{K}_2\text{CO}_3, \text{H}_2\text{O}$ ;  $2\text{CuCO}_3, \text{K}_2\text{CO}_3, 2\text{H}_2\text{O}$ ;  $2\text{CuCO}_3, 2\text{K}_2\text{CO}_3, \text{H}_2\text{O}$ ;  $2\text{CuCO}_3, 3\text{K}_2\text{CO}_3, 3\text{H}_2\text{O}$ .

By precipitation with equimolecular proportions of sodium or potassium carbonate and hydrogen carbonate the following substances were obtained:

$\text{CuCO}_3, \text{Cu}(\text{OH})_2, \text{Na}_2\text{CO}_3$ ;  $\text{CuCO}_3, 2\text{Cu}(\text{OH})_2, \text{Na}_2\text{CO}_3$ ;  $\text{CuCO}_3, 2\text{Cu}(\text{OH})_2, 2\text{Na}_2\text{CO}_3$ ;  $\text{CuCO}_3, \text{Cu}(\text{OH})_2, 2\text{Na}_2\text{CO}_3$ ;  $2\text{CuCO}_3, \text{Cu}(\text{OH})_2, \text{Na}_2\text{CO}_3$ ;  $3\text{CuCO}_3, \text{Cu}(\text{OH})_2, 2\text{Na}_2\text{CO}_3$ ;  $\text{CuCO}_3, \text{Cu}(\text{OH})_2, \text{K}_2\text{CO}_3$ ;  $\text{CuCO}_3, \text{Cu}(\text{OH})_2, 2\text{K}_2\text{CO}_3, 2\text{H}_2\text{O}$ ;  $2\text{CuCO}_3, \text{Cu}(\text{OH})_2, \text{K}_2\text{CO}_3, \text{H}_2\text{O}$ , and  $3\text{CuCO}_3, \text{Cu}(\text{OH})_2, \text{K}_2\text{CO}_3, \text{H}_2\text{O}$ .

A. I. VOGEL.

**Preparation of phosphorescent substances.** II. Sulphides of calcium, strontium, and

barium. N. F. SHIROV (Ukrain. Chem. J., 1929, **4**, 361—378).—Further details (cf. A., 1929, 1025) of the preparation of phosphorescent materials are given, the subjects considered including improvements in the technique, especially in the heating, the influence of secondary solvents, new fluxes and their combination, investigation of new activators both separately and in combination, determination of the best combinations of all three components to give maximum permanence, stability, friability in relation to the brightness and variation of the colour of the luminescence. When the heating is effected at 900—1000°, the minimum time of heating is 1 hr. for BaS, 1.5 hrs. for CaBaS, 2 hrs. for CaSrS and CaS+BaS, 2.5 hrs. for SrBaS, and 3 hrs. for SrS. Preparations from calcium sulphide alone or mixed with strontium sulphide are soft, those from barium sulphide of medium hardness, and those from strontium sulphide and its mixtures with barium sulphide hard. Magnesium oxide confers softness when added to the extent of 10%, which may be increased to 25% with strontium and barium preparations. Calcium sulphide preparations require no addition of magnesium oxide, which effects slight displacement of the colour of the luminescence towards the violet region of the spectrum. Incorporation of 25% of calcium tungstate with the sulphides lowers the m. p. of the mixtures especially with barium sulphide, increases the hardness of the product, and causes a change in colour towards the violet. Zinc oxide gives no luminophores when added to the extent of 40%, but exhibits triboluminescence. Maximum intensity of luminescence is obtained by using the mixture  $\text{Na}_2\text{B}_4\text{O}_7 + \text{K}_2\text{B}_6\text{O}_{10} + \text{Li}_3\text{PO}_4 + \text{CaF}_2$  as flux, good results being obtained also with  $\text{K}_2\text{B}_6\text{O}_{10} + \text{K}_2\text{SO}_4$  and  $\text{Li}_3\text{PO}_4 + \text{Li}_2\text{CO}_3$ . Good luminophores are obtained by using sodium tungstate and, especially, lithium tungstate or sodium pyrophosphate. With calcium sulphide, gold gives greenish dark blue, palladium or caesium greenish-blue, osmium or thallium greenish-yellow luminescence; with strontium sulphide gold gives greenish-yellow, vanadium yellow, erbium yellowish-green, caesium yellowish; with barium sulphide, indium gives yellowish luminescence.

T. H. POPE.

**Action of ammonia on  $\text{HgBr}_2, 2\text{NH}_3$ .** Formation of  $\text{NH}_2\text{HgBr}$  and  $\text{NHg}_2\text{Br}$ . M. FRANÇOIS (Compt. rend., 1930, **190**, 125—126; cf. Gaudechon, A., 1909, ii, 670).—A small amount of ammonia solution ( $d$  0.922) converts the compound  $\text{HgBr}_2, 2\text{NH}_3$  into white mercuriammonium bromide,  $\text{HgBr}_2, 2\text{NH}_3 \rightleftharpoons \text{NH}_2\text{HgBr} + \text{NH}_4\text{Br}$ ; a larger quantity carries the reaction further, with production of yellow dimereuriammonium bromide,  $2\text{HgBr}_2, 2\text{NH}_3 \rightleftharpoons \text{NHg}_2\text{Br} + 3\text{NH}_4\text{Br}$ . Both reactions are reversible. The former continues until the ammonia solution contains 18.92 g. per litre of ammonium bromide, the latter stops when 1.56 g. per litre of ammonium bromide is present. The same equilibrium points are reached when the reactions are carried out in the reverse direction.

C. A. SILBERRAD.

**Ultramarine problem in the light of recent research.** J. HOFFMANN (Chem. Ztg., 1929, **53**, 953—955, 974—975).—A brief review of recent work

on the constitution of ultramarine, with especial reference to that of Jaeger during 1928—1929.

A. R. POWELL.

**Behaviour of amorphous carbon and sulphur compared with that of diamond and of graphite. Ciusa's carbon sulphide.** J. P. WIBAULT and E. J. VAN DER KAM (Rec. trav. chim., 1930, **49**, 121—141).—See A., 1929, 896.

**Germanium, indium, niobium, titanium, and hydrogen.** H. HAGEN and A. SIEVERTS (Z. anorg. Chem., 1930, **185**, 225—238).—The behaviour of hydrogen towards various metals at different temperatures and pressures has been investigated in an apparatus previously described (A., 1926, 810). Contrary to the results of other investigators, hydrogen appears to be practically insoluble in germanium and indium, since no greater absorption than 1 c.c. of gas in 100—200 g. of metal was observed. Both isotherms and isobars of the system niobium-hydrogen are similar in form to those for vanadium and tantalum hydrides. Exact repetition of the experiments was impossible, owing to increasing inactivity of the niobium as the result of an ageing effect. No formation of gaseous titanium hydride was observed. This is contrary to the results of Renz (A., 1906, ii, 173) and Billy (Ann. Chim. Phys., 1921, [x], 9, 1), but in agreement with Paneth's rule.

M. S. BURR.

**Oxides. V. Preparation, properties, density, and molecular volume of a crystalline lead dioxide.** A. SIMON (Z. anorg. Chem., 1930, **185**, 300—304).—Crystalline lead dioxide has been prepared by heating sodium plumbate, with or without water of crystallisation, for three days in an autoclave at 250°, in presence of water (cf. this vol., 289). Violet-black crystals, reddish-brown by transmitted light, and strongly doubly refracting, were formed in interlocking masses. When fractured the crystals displayed blue and red interference colours and dichroism of red with green or blue. X-Ray examination indicates that lead dioxide has a rutile structure. Crystalline lead dioxide is much more stable, both to heat and solvent action, than the amorphous compound. A commercial preparation for analytical purposes had  $d$  8.919, a product consisting of fine crystals admixed with amorphous material, prepared by the autoclave method, had  $d$  9.011, and a coarsely crystalline product,  $d$  9.604, whilst  $d$  (X-ray) is 9.5. Calculation of the mol. volume indicates that oxygen must be greatly compressed. The mol. volume of the heaviest sample (24.906) is very little larger than that of lead oxide (24.2).

M. S. BURR.

**Origin [and extraction] of protoactinium.** J. E. WILDISH (J. Amer. Chem. Soc., 1930, **52**, 163—177).—The extraction of protoactinium with tantalum from uranium minerals is described; 90% of the tantalum used was recovered. Difficulties due to barium and moderate quantities of silica were surmounted. Uranium and protoactinium were determined in five minerals. The number of atoms of protoactinium per 100 atoms of uranium was 5.16 in Colorado carnotite, 2.79 and 1.47 in two Bohemian pitchblendes, 3.67 in Belgian Congo soddite, 2.50 in Ceylon thorianite. The results support the view that

the actinium series arises from a source other than uranium II.

J. G. A. GRIFFITHS.

**Reduction by hydrazine of sexavalent molybdenum derivatives.** W. F. JAKÓB and W. KOZŁOWSKI (Rocz. Chem., 1929, **9**, 667—675).—Hydrazine in strongly acid boiling solution reduces sexavalent to quinquevalent molybdenum compounds, being itself oxidised quantitatively to nitrogen. In feebly acid solutions anion complexes containing both quinque- and sexa-valent molybdenum are produced, such as Rammelsberg's salt,  $\text{NH}_4[\text{Mo}_5\text{O}(\text{OH})_7\text{MoO}_4]$ , from ammonium paramolybdate. Solutions of the latter salt containing hydrochloric acid to 2*N* yield on reduction molybdenum-blue, whilst strongly acid solutions, containing 150 c.c. of concentrated acid to 100 g. of molybdate, yield Klason's salt,  $(\text{NH}_4)_2[\text{MoOCl}_5]$ .

R. TRUSZKOWSKI.

**Non-electrolytic compound of polonium.** M. GUILLOT (Compt. rend., 1930, **190**, 127—128).—When sodium dithiocarbamate is added to an acid aqueous solution of a heavy metal (e.g., bismuth, cobalt, copper, or nickel) containing polonium, all the polonium is found in the precipitate, which is wholly soluble in chloroform and can be recrystallised therefrom. In dithiocarbamates of copper or nickel the polonium is entirely in the surface layer of the crystals, in those of cobalt or bismuth it is more evenly distributed. The affinity of the polonium compound for the cobaltic, and to a smaller degree the bismuth, dithiocarbamate is markedly greater than for the nickel or copper compound. It is inferred that the polonium is present as dithiocarbamate, with valency 3 and co-ordination number 6, as  $\text{Po}(\text{S-CS-NR}_2)_3$ .

C. A. SILBERRAD.

**Fluosulphonic acid.** E. WILKE-DÖRFURT, G. BALZ, and A. WEINHARDT (Z. anorg. Chem., 1930, **185**, 417—424).—In continuation of previous work (cf. A., 1927, 120, 238) on the similarities between the complex salts of fluoboric, perchloric, permanganic, and fluosulphonic acids, the preparation and properties of a number of fluosulphonates and of some new permanganates and perchlorates are described. These are: *silver tetrapyridineperchlorate*,  $[\text{Ag}(\text{C}_5\text{H}_5\text{N})_4]\text{ClO}_4$ ; *nickelous, zinc, cadmium, cobaltous, ferrous, and manganous hexamminefluosulphonate*,  $[\text{M}(\text{NH}_3)_6](\text{SO}_3\text{F})_2$ ; *nickelous hexamminepermanganate*,  $[\text{Ni}(\text{NH}_3)_6](\text{MnO}_4)_2$ ; *cobaltic and chromic hexammine dinitrate fluosulphonate*,  $[\text{M}(\text{NH}_3)_6](\text{NO}_3)_2\text{SO}_3\text{F}$ ; *chromic hexammine-perchlorate and -permanganate*,  $[\text{Cr}(\text{NH}_3)_6]\text{X}_3$ ; *chromic hexacarbamidofluosulphonate*,  $[\text{Cr}(\text{CON}_2\text{H}_4)_6](\text{SO}_3\text{F})_3$ .

M. S. BURR.

**Preparation of manganese dioxide.** I, II. Y. KATO and T. MATSUHASHI (J. Soc. Chem. Ind. Japan, 1929, **32**, 313—314B, 315—316B).—I. Manganese dioxide may be prepared from any lower oxide by direct oxidation with oxygen, using sodium hydroxide as catalyst. At 400—500° a product containing 50—95%  $\text{MnO}_2$  may be obtained.

II. The composition of the air-dried product corresponds with the formula  $\text{MnO}_2 \cdot \text{H}_2\text{O}$ . It has high values of electrical resistance, oxidation potential, and adsorbing power for gases.

C. W. GIBBY.

**Pyrophoric iron. I. Preparation and properties. II. Adsorption of carbon dioxide and ammonia. Use in the ammonia synthesis.**

T. G. FINZEL (J. Amer. Chem. Soc., 1930, 52, 142—149, 150—156).—I. Pyrophoric iron, containing 1—2% of impurity, was prepared by reducing with hydrogen at 500° pure ferric oxide of different degrees of dispersion produced by interaction of ammonia and ferric nitrate. Limiting concentrations of oxygen in which this iron was pyrophoric were determined. Reaction occurred in air dried with phosphoric oxide and at -78°. The time of heating at 600° required to inactivate pyrophoric iron is longer for larger grains (estimated by von Weimarn's precipitation law) and is less according as the medium is helium, nitrogen, or hydrogen. Inactivated iron has larger grains than pyrophoric iron, but both are  $\alpha$ -iron.

II. The volume of carbon dioxide and ammonia adsorbed per g. of metal was increased in proportion to the grain size of the pyrophoric iron. Fine-grained pyrophoric iron did not catalyse the synthesis of ammonia and adsorbed less gas than coarser, non-pyrophoric iron. Sintering was prevented and catalytic activity was obtained in the fine-grained iron by preparation from a mixture of ferric and aluminium nitrates. It is suggested that the coarser grains of iron, which are catalytically active, had cores of iron oxide which prevented sintering.

J. G. A. GRIFFITHS.

**Iron oxide in borate beads.** W. D. BANCROFT and G. E. CUNNINGHAM (J. Physical Chem., 1930, 34, 1—40).—The blue colour of iron compounds is due to an unstable, blue modification of ferric oxide, which is stabilised chiefly by ferrous oxide. In alkali borate ferrous oxide is colourless, ferric oxide is yellow, whilst a certain mixture of ferrous and ferric oxides is blue. Reduction of iron oxide to metal by hydrogen occurs readily when the alkali concentration in the fused mass is low. A higher concentration of alkali prevents the formation of metal but does not favour complete reduction of ferric to ferrous oxide. A ratio  $\text{FeO} : \text{Fe}_2\text{O}_3$  equal to 3 : 1 in borate glasses gives a glass free from green and with a ratio 4 : 1 the blue colour becomes more pronounced. Reduction of ferric oxide is easier in a potassium borate bead than in one of sodium borate. The application of these results to fired clays and to iron-bearing minerals is fully discussed.

L. S. THEOBALD.

**Characterisation of iron carbonyls and their derivatives.** W. HIEBER (Naturwiss., 1930, 18, 33—34).—The carbonyl groups in iron pentacarbonyl can be replaced by pyridine or ethylenediamine, and well-defined carbonyls containing amines can be isolated in which the  $\text{Fe} : \text{CO}$  ratio is 1 : 3,  $2\frac{1}{2}$ , and 2. With ammonia and ethylenediamine interacting with iron pentacarbonyl (in the presence of pyridine) the molecules  $\text{Fe}(\text{CO})_3(\text{NH}_3)_2$  and  $\text{Fe}_2(\text{CO})_5\text{en}_2$  are formed, whilst pyridine alone leads to  $\text{Fe}_2(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_3$ , a substance very sensitive to oxygen. The polymeride  $[\text{Fe}(\text{CO})_4]_6$  appears to decompose according to the simplified equation  $2\text{Fe}(\text{CO})_4 = \text{Fe}(\text{CO})_3 + \text{Fe}(\text{CO})_5$ . The compounds  $\text{Fe}(\text{CO})_3(\text{C}_5\text{H}_5\text{N})$  and  $\text{Fe}(\text{CO})_3\text{MeOH}$  are readily formed. The tricarbonyl compounds are extremely red, soluble in organic solvents, and exceed-

ingly sensitive to oxygen. Acids result in reactions of the type  $2\text{Fe}(\text{CO})_3\text{MeOH} + 2\text{H}^+ \rightarrow \text{Fe}(\text{CO})_4$  (polymeride)  $+ \text{Fe}^{++} + 2\text{CO} + \text{H}_2 + 2\text{MeOH}$ . The significance of the results is discussed. R. A. MORTON.

**Oxidation of cobalt salts in alkaline medium.**

R. BERNARD and P. JOB (Compt. rend., 1930, 190, 186—187).—Spectrophotometric measurements indicate that the oxidation of solutions of cobaltous sulphate in concentrated sodium hydrogen carbonate solution by bromine water or by hydrogen peroxide cannot be expressed by the simple equation  $2\text{CoO} + \text{O} = \text{Co}_2\text{O}_3$ . In both cases there is probably the intermediate reaction  $\text{CoO} + \text{O} \rightarrow \text{CoO}_2$ . J. GRANT.

**Reaction of nickel carbide,  $\text{Ni}_3\text{C}$ , prepared at a moderate temperature.** H. A. BAHR and T. BAHR (Ber., 1930, 63, [B], 99—102).

—Nickel carbide, prepared as described previously (A., 1928, 1336), is strongly pyrophoric, but loses this property when heated in nitrogen at 250°, whereby its reactivity is also diminished. It has  $d^{18}$  7.97. Below 380—400° it is stable, but decomposes more or less rapidly above this temperature with deposition of elementary carbon. With molecular hydrogen at 250°/atm. pressure it gives mainly methane, but slight polymerising power is evidenced by the formation of ethane in small proportion. This tendency is emphasised when hydrogen at 200°/20 atm. is used. Superheated steam at 300° reacts principally according to the equation  $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$ ; some methane is formed, but its homologues do not appear to be produced. With ammonia at 420° the products are hydrogen and nitrogen with a little methane and ethane; ammonium cyanide is possibly produced. Hydrogen sulphide reacts readily at 240° without apparent formation of methane. Hydrogen chloride gives oily products at 290—300°. Hydrochloric acid yields a clear solution with nickel carbide; the ratio of gaseous to liquid hydrocarbons is 2 : 1. Simple compounds constitute 95% of the gas. Nitric acid appears to afford nitroderivatives of the hydrocarbons primarily produced. With dilute sulphuric acid a part of the carbide carbon separates in the elementary form from the solution.

H. WREN.

**Colorimetric methods.** N. SCHOORL (Chem. Weekblad, 1930, 27, 52—54).—Colorimetric methods of analysis are discussed under the headings of true colorimetry, nephelometry, titrimetric methods, and methods wherein the solution under examination is compared with a graded series of standard solutions. The importance of establishing the validity of Beer's law in the solution under consideration is emphasised in the first and third groups, whilst the velocity of the reaction, the stability of reactants and reaction products, the influence of other substances and of an excess of reagent, and the manner in which the reagent is added have all to be taken into account when considering any particular colorimetric process.

H. F. GILLBE.

**Borax and mercuric oxide as standard substances for all methods of volumetric analysis.** N. A. LAZARKEVITSCH (Ukrain. Chem. J., 1929, 4, 405—428).—Mercuric oxide may be employed as the standard substance for all the fundamental methods

of volumetric analysis if no high degree of accuracy is required; where accurate results are desired it cannot be used, especially in iodine and permanganate titrations. Borax, however, may be used as a standard for determining the titre of acids to be employed in measuring the strengths of thiocyanate, thiosulphate, and permanganate solutions, the results thus obtained agreeing well with those given by other methods (cf. Glücksmann, *Z. Oesterr. Apoth. Ver. Bel.*, 1899, **37**, 970; Rosenthaler and Abelman, *A.*, 1913, ii, 786; Tananaev, *A.*, 1925, ii, 441).

T. H. POPE.

**Aid to gravimetric analysis.** E. LEHMANN (*Chem.-Ztg.*, 1930, **54**, 62).—After preliminary washing, a filter-paper bearing a precipitate may be folded and washed from the outside.

S. I. LEVY.

**Carbon dioxide content of distilled water.** W. HOESCH (*Chem.-Ztg.*, 1929, **53**, 956).—Distilled water stored, with free access of air, in the lower part of a building always contains much more carbon dioxide in solution than that stored on an upper floor. This fact is of importance in conducting delicate acidimetric analyses of solutions containing weak acids.

A. R. POWELL.

**Conditions for evaporation of mineral waters from the point of view of chemical analysis.** P. BRETEAU (*J. Pharm. Chim.*, 1930, [viii], **11**, 5—7).—Evaporation of mineral waters for analysis after acidification with hydrochloric acid in platinum vessels leads to contamination of the solution with platonic chloride (since many waters contain traces of nitric acid) and also renders uncertain the detection of other metals, *e.g.*, iron, copper, zinc, etc., when these are present in traces. Hence waters should be made alkaline preparatory to evaporation.

R. J. W. LE FÈVRE.

**Determination of water in micas.** K. WISKONT and I. ALIMARIN (*Z. anal. Chem.*, 1929, **79**, 271—286).—The usual methods for the determination of water in silicates give untrustworthy results in the case of the micas, and an improved method, based on a combination of those of Penfield and Kuzirian, has been devised. The mica (0.3 g.) is weighed into a platinum boat, a few crystals of potassium chlorate are added, and the whole is covered with a layer of pure sodium tungstate. The expulsion and determination of the water are then carried out by Penfield's method, the glass tube employed containing a plug of spongy platinum and another of granulated lead oxide wrapped in platinum gauze, which serves to retain volatile constituents such as fluorine. Attention is directed to the importance of distinguishing between the "hygroscopic water" and "inclusion water" in minerals, and further study of the dehydration curves of minerals is recommended.

H. F. HARWOOD.

**Method of calculating analyses.** III. E. LIESCHE (*Z. angew. Chem.*, 1929, **42**, 1109—1100).—Equations and factors for calculating from the results of indirect analysis the composition of binary mixtures of ammonium and alkali halides are given together with the method of constructing a nomogram for reading directly the composition of a mixture of ammonium chloride and bromide from the number of

*c.e.* of 0.1*N*-silver nitrate solution required in the titration of a known weight of the mixture.

A. R. POWELL.

**Chlorometric, bromometric, and iodometric determination of available chlorine in hypochlorite solutions and bleaching powder.** I. H. DITZ and R. MAY (*Z. anal. Chem.*, 1930, **79**, 333—345).—The various chlorometric and iodometric methods are discussed. A comparison of these showed that the Penot-Lunge method (direct titration with arsenite) gave results which were 0.21% lower than those obtained by the iodometric method of Rupp, this being due to the greater sensitivity of the end-point in the latter case. Rodt's modification of the Penot-Lunge method renders the end-point more sensitive, but the results are still slightly lower than those afforded by the iodometric method. Kolthoff's process (titration of an acidified arsenite solution with the hypochlorite) gave varying results, which were about 0.81% too high.

H. F. HARWOOD.

**Determination of halogen by Gasparini's method.** III. K. HELLER [with K. WILLINGSHOFER and B. SADRAWETZ] (*Z. anal. Chem.*, 1929, **79**, 256—270; cf. *A.*, 1929, 528, 1158).—The reduction of perchlorates by electrolysis in concentrated sulphuric acid solution, using platinum electrodes, is ascribed to the formation of hyposulphurous acid as intermediary, this substance then catalysing the reduction of the perchlorate. The addition of nitric acid produces the same result, and the reduction is also accelerated by the presence of platinum or its salts. The chlorine in chlorides, chlorates, perchlorates, and many organic chloro-compounds can be determined by Gasparini's method if a mixture of 4 vols. of concentrated sulphuric acid and 1 vol. of concentrated nitric acid is used as electrode liquid; the electrolysis requires 4—6 hrs. In the analysis of chlorates, 1 g. of sodium sulphite must be added to the absorption bulbs containing the acidified silver nitrate before commencing the analysis. Substances which readily sublime cannot be analysed by this method, and it also fails with certain chloro-derivatives of phthalic acid, benzoylbenzoic acid, and anthraquinone.

H. F. HARWOOD.

**Iodometric micro-determination of bromides and iodides.** R. HOFMANN (*Pharm. Zentr.*, 1930, **71**, 18—21).—Some modifications in the standard apparatus and method of working are described. A mixture of lead peroxide and acetic acid is used in place of chromic acid to oxidise the bromide, and carbon dioxide in place of air to carry the liberated halogen over. The maximum error is 10%, but the determination is very rapid.

S. I. LEVY.

**Argentometric studies.** III. Determination of bromides and iodides in the presence of a large excess of chlorides. O. TOMČEK and A. JÁNSKY (*Coll. Czech. Chem. Comm.*, 1930, **2**, 1—7).—The boiling acid solution is treated with 0.05*N*-potassium permanganate solution until bromine ceases to pass into the distillate, which is collected in sodium sulphite solution. This treatment with potassium permanganate is repeated with the first distillate and the bromide and iodide in the second distillate are determined argentometrically by potentiometric titra-

tion. The iodate in the two residues is reduced with sodium sulphite in the presence of a very small concentration of bromide ions and the iodide determined potentiometrically. The application of this method to mineral waters and salts is described.

A. I. VOGEL.

**Iodine trichloride as a reagent for sulphide minerals, especially pyrites.** E. WILKE-DÖRFURT and E. A. WOLFF (*Z. anorg. Chem.*, 1930, 185, 333—336).—Birk's method (A., 1928, 976) for attacking with iodine trichloride minerals which are difficult of dissolution, has been tested on a pyrites which has also been analysed by two other methods using aqua regia and an ethereal solution of bromine, respectively. For accuracy, the iodine trichloride method is as satisfactory as other methods for bringing sulphides into solution, and it can be employed successfully where all oxidation media hitherto in use react incompletely, or can bring into solution, with the greatest difficulty only, the sulphur separated during the decomposition of the sulphide.

M. S. BURR.

**Determination of nitrogen in gaseous mixtures.** S. N. BLUMSTEIN (*Z. anal. Chem.*, 1930, 79, 324—333).—Lidoff's original method for the direct determination of nitrogen in gaseous mixtures (A., 1902, ii, 353) necessitates the employment of a very complex apparatus, and a simpler procedure has now been devised. Two gas burettes connected by a special three-way tap are used; the gas is freed from carbon dioxide and oxygen, dried with sulphuric acid, and passed over heated magnesium contained in a hard glass tube. When absorption of nitrogen is complete the contents of the tube are transferred to a flask, treated with alkali, and the ammonia formed is distilled into standard acid. An analysis can be carried out in 4 hrs., and 99.2% of the nitrogen present can be determined, as compared with 97% by Lidoff's method. Full working details of the method are given.

H. F. HARWOOD.

**Determination of carbon monoxide in a gas containing 0.25–0.3%.** M. NICLOUX (*Compt. rend. Soc. Biol.*, 1929, 100, 861–864; *Chem. Zentr.*, 1929, ii, 1182).—The gas is brought into contact with reduced blood in complete absence of oxygen, the determination of carbon monoxide in the blood being made eudiometrically.

A. A. ELDRIDGE.

**Detection of the principal anions by separate tests.** P. AGOSTINI (*Annali Chim. Appl.*, 1929, 19, 520–524).—The tests given are made, as far as possible, on the original solid or on its alkaline solution, interaction between oxidising and reducing anions being thus hindered.

T. H. POPE.

**Quantitative spectral analysis. I. Determination of potassium, magnesium, and copper in flame spectrum.** H. LUNDEGÅRDH (*Arkiv Kemi, Min., Geol.*, 1929, 10, A, No. 1, 26 pp.).—An apparatus for the quantitative analysis of dissolved compounds by means of absorption spectra is described. A constant stream of the solution is dispersed in minute drops by compressed air with a nozzle spraying apparatus (cf. Gouy, *Ann. Chim.*, 1879, 18, 5), and brought into a constant acetylene flame. Photographs of the flame spectrum allow the

inclusion of the ultra-violet region, and with 60 sec. exposure eliminate errors due to small variations in the flame and spraying apparatus. The spectral lines of the plate were projected on a thermo-element and the degree of intensity was read accurately from a galvanometer deflexion. Standard solutions for comparison are necessary. The region of suitable measurements depends on the time of exposure and other factors; under the conditions described it was for potassium and magnesium  $300^{-1}$  to  $20^{-1}$ , calcium and copper  $2000^{-1}$  to  $50^{-1}$ , lithium  $20,000^{-1}$ , and sodium  $10,000^{-1}$  mol. The practical and theoretical minimum sensitivities for potassium, magnesium, and copper are 0.36, 0.20, 0.10, and 0.004, 0.002, 0.001 mg., respectively. Experiments are described and results tabulated for these three metals, on the factors, including the presence of impurities, influencing the total error of the analysis. The minimum total error was of the order 2%. N. M. BLIGH.

**Determination of sodium hydroxide in presence of sodium carbonate.** W. POETHKE and P. MANICKE (*Z. anal. Chem.*, 1929, 79, 241–255).—The accuracy of Winkler's method has been investigated, using mixtures of 0.1N-sodium hydroxide and carbonate in varying proportions. The figures obtained for the sodium hydroxide present are invariably slightly too low, but the error is negligible if the precipitation with barium chloride takes place in the cold, and the solution is dilute. The amount of barium chloride employed must be such that the final concentration of barium in the solution after precipitation is 0.1N. The following procedure is recommended. The solution is diluted with water free from carbon dioxide, and the total alkali determined in an aliquot portion by titration with hydrochloric acid and methyl-orange. Another portion is added to an excess of cold N-barium chloride (previously diluted to 25 c.c.), and after shaking, the liquid is titrated with hydrochloric acid in presence of 1 drop of 1% phenolphthalein for every 25 c.c. of solution. An attempt to substitute strontium chloride for barium chloride in the method gave unsatisfactory results.

H. F. HARWOOD.

**Employment of sodium thiosulphate in analytical chemistry.** E. DONATH (*Chem.-Ztg.*, 1930, 54, 78–79).—Sodium thiosulphate may be advantageously substituted for the customary mixture of sodium carbonate and sulphur employed for opening up sulphide minerals by fusion, as the precipitation of large quantities of sulphur in the subsequent treatment of the resulting solution is thereby obviated. It may also be employed in place of hydrogen sulphide to precipitate copper and certain other metals from their solutions, and is particularly useful in separating copper from cadmium and zinc. The use of sodium thiosulphate for the determination of aluminium in presence of iron does not, however, offer any advantages over the usual indirect method.

H. F. HARWOOD.

**Volumetric determination of potassium with sodium hydrogen tartrate.** V. E. TOVARNITZKI and K. I. SLEZAK (*Zhur. Sakh. Prom.*, 1928, 2, 462–473).—After elimination of ammonium, rubidium, caesium, and sulphate the neutral solution containing

20—50 mg. of potassium is evaporated to dryness with excess of ammonia solution, the residue is ignited, 15—30 drops of 10% calcium chloride solution and 0.5—1 c.c. of ammonia solution are added, and the mixture is again evaporated and ignited. The residue is dissolved in hot, boiled distilled water, the solution is filtered, and the residue washed with 100—120 c.c. of water. The solution, after neutralisation with barium hydroxide or acetic acid, is evaporated to dryness on the water-bath, 10—12 c.c. of standard sodium hydrogen tartrate solution are added, the mixture is kept over-night, filtered through a dry filter, and 5 c.c. of the filtrate are titrated with 0.15*N*-barium hydroxide, using phenolphthalein. The standard sodium hydrogen tartrate solution is prepared by dissolving tartaric acid (55 g.) and sodium hydroxide (14 g.) in distilled water (800 c.c.), boiling to remove carbon dioxide, and making up to 1 litre; 5—7 drops of toluene and 6 g. of potassium hydrogen tartrate are then added. CHEMICAL ABSTRACTS.

**Determination of lead peroxide.** A. V. PAMFILOV and E. G. IVANČEVA.—See B., 1930, 142.

**Determination of non-sulphide lead.** H. K. HANSEN.—See B., 1930, 148.

**Ceric sulphate as a volumetric oxidising agent.** X. **Determination of thallium.** XI. **Oxidation of organic acids.** H. H. WILLARD and P. YOUNG (J. Amer. Chem. Soc., 1930, 52, 36—42, 132—142).—X. A rapid and accurate volumetric determination of thallium is based on the quantitative oxidation by ceric sulphate of thallous to thallic salts in hydrochloric acid solution. In determining the end-point electrometrically, the solution should be about 2*N* with respect to hydrochloric acid and at 55°. The visual end-point (A., 1928, 725) is best observed when solutions are of less acidity and at 80—90°. Small quantities of nitric acid, tervalent arsenic and antimony interfere. Many ions, including ferric and chromic (at low temperatures and high acid concentration; cf. A., 1929, 287), are without effect.

XI. The suitability of ceric sulphate for determining organic acids by oxidation in hot sulphuric acid solution has been investigated. After maintaining the solution at 95° for 1 hr., the excess of ceric sulphate was determined by electrometric titration with ferrous sulphate (A., 1928, 725). Formic, acetic, succinic, fumaric, and maleic acids are not oxidised. Tartaric, malonic, malic, glycollic, and citric acids are determined by the respective factors 7.2, 6.66, 9.25, 3.95, 15.85 (g.-equiv. of oxygen per g.-mol. of acid) over an approximately fourfold variation of experimental conditions. Benzoic, phthalic, and salicylic acids give variable results. J. G. A. GRIFFITHS.

**Determination and separation from other metals of rare metals.** XVI. **Separation of thallium from ter- and quadri-valent metals.** L. MOSER and W. REIF. XVII. **Precipitation of tungsten with tannin and antipyrine, and its separation from ter- and quadri-valent metals, from tin, and from silicic acid.** L. MOSER and W. BLAUSTEIN (Monatsh., 1929, 52, 343—350, 351—364).—XVI. The tannic acid method (A., 1928, 148)

cannot be used for the quantitative separation of thallium from aluminium, iron, and chromium, owing to extensive adsorption of the thallous ion by the tannic acid complex, which is little affected by varying the hydrogen-ion concentration. The ammonium nitrite-methyl alcohol method (*loc. cit.*) can be employed for the separation of thallium-aluminium, -iron, or -chromium mixtures in all proportions. Reprecipitation is generally unnecessary; thallium in the filtrate is determined as chromate by precipitation in boiling ammoniacal solution (cf. A., 1927, 436). The method is recommended on account of its accuracy for the determination of aluminium and chromium, and the metals should preferably be present originally as the sulphates. For determination of small quantities of thallium in the presence of the foregoing metals precipitation as thallous chromate from slightly alkaline solution in the presence of sulphosalicylic acid (A., 1927, 436) is especially advantageous.

The ammonium nitrite is preferably added to the slightly acid thorium solution in the cold, the mixture slowly warmed, and the methyl alcohol added after a part of the precipitate has formed; this method is applicable to the separation of zirconium and titanium. The nitrite method cannot be used to remove cerium. Precipitation of cerium as cerous oxalate can be employed, but the separation is not quantitatively exact. The nitrite method cannot be used to separate molybdenum and tungsten from thallium, but this may be effected by precipitation of thallium as chromate from hot ammoniacal solution. This method cannot be applied to the separation of vanadium and thallium. By taking advantage of the formation of a stable vanadium-tartaric acid complex (Barbieri, A., 1915, i, 380), a quantitative separation may be effected as follows: the precipitate of thallous metavanadate is dissolved in the smallest possible quantity of a concentrated tartaric acid solution at 40°, or below, and ammonia is added in excess to the red solution until the colour is changed to blue or discharged (according to the quantity of vanadium); thallium is determined by precipitation with potassium chromate at the ordinary temperature.

XVII. Tungsten may be determined by use of tannic acid and antipyrine as follows: a dilute, slightly alkaline solution of ammonium tungstate, containing an approximately known amount of tungsten, is treated with sulphuric acid and ammonium sulphate. The boiling liquid is precipitated with tannic acid; after being kept some time on the steam-bath, the mixture is cooled to 15°, a 10% solution of antipyrine is added with continuous stirring, and the precipitate is washed with a solution containing sulphuric acid, ammonium sulphate, and antipyrine, and ignited to tungsten trioxide.

Quantitative separation of tungsten from iron, aluminium, or chromium may be achieved by the foregoing method; reprecipitation is necessary with iron and chromium. Accurate results are obtained by a single precipitation of tungsten from manganese, zinc, nickel, or cobalt. By adding tartaric acid to a mixture containing tungsten and tin, a soluble tungsten-tartaric acid complex is obtained; tin can then be removed as sulphide. The soluble tungsten



complex is not precipitated with tannic acid and antipyrine, and after removal of hydrogen sulphide by heating, the tartaric acid is removed by oxidation with hydrogen peroxide in the presence of iron (cf. Meigen and Schnerb, A., 1924, ii, 506); the tungsten is now present as tungsten trioxide which does not react with tannic acid, but by addition of ammonium sulphate and tannic acid solution, saturation with ammonia, and boiling, followed by cooling, acidification with sulphuric acid, and reheating, the tungsten-tannic acid complex is completely precipitated, and the determination is completed by addition of antipyrine after cooling.

Separation of tungsten from silicic acid depends on the non-precipitation of colloidal silicic acid with tannic acid and antipyrine; if, however, before adding tannic acid, a solution containing tungstate and silicate is treated for a short time with mineral acid, or is kept for a long time, some silicic acid is adsorbed by the tungsten-tannic acid complex. If more than 0.1 g. of tungsten trioxide is to be determined, a single precipitation with tannic acid and antipyrine effects quantitative separation; with less than 0.05 g., the precipitate contains traces of silicic acid. The precipitate may either be treated with concentrated sulphuric acid and hydrofluoric acid after ignition, or may be collected, redissolved in hot ammonia, filtered, and reprecipitated with tannic acid and antipyrine after acidification with sulphuric acid and addition of ammonium sulphate. C. W. SHOPPEE.

**Volumetric determination of copper.** A. T. KÜCHLIN (Rec. trav. chim., 1930, 49, 151—152).—Copper may be determined volumetrically by adding to the solution a known excess of a standard stannous chloride solution in an atmosphere of carbon dioxide and shaking for at least 20 sec. in order to reduce the copper completely to the cuprous state, and then titrating the excess of stannous salt with iodine.

R. CUTHILL.

**Potentiometric determination of cerium sulphate.** K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1929, 18, 517—523).—See A., 1929, 1032.

**Drop method of detecting ferri- and ferrocyanide ions.** A. SCHAPOVALENKO (Ukrain. Chem. J., 1929, 4, 303—307).—In the detection of these ions in low concentrations, it is best to make a spot of the ferrous or ferric salt on the filter-paper and then add a drop of the solution to be tested; the colour is heightened by further addition of a drop of *N*- or 2*N*-hydrochloric acid. In this way ferricyanide is detectable in a concentration of 1 in 10,000 and ferrocyanide in one of 1 in 1000, the actual quantities of the two ions employed in these cases being 0.00007 and 0.00026 mg., respectively. When both ions are present, use may be made of a soluble lead salt, since the ferrocyanide ion is then fixed as an insoluble salt at the centre of the spot, whilst the ferricyanide ion filters through to the edge of the spot and may there be tested for. Addition of a lead salt also renders possible the detection of these ions in presence of sulphide, iodide, and thiocyanate ions. T. H. POPE.

**Determination of manganese, iron, and aluminium in presence of phosphoric acid.** I. S. TELETOV and N. N. ANDRONIKOVA (Ukrain.

Chem. J., 1929, 4, 341—347).—When the method previously described (A., 1929, 1260) is applied to solutions containing phosphoric acid, this passes entirely into solution on precipitation of the iron and manganese with sodium hydroxide and hydrogen peroxide. Moreover, the precipitate is very easily filtered and washed. Treatment of the alkaline filtrate with barium nitrate results in the total precipitation of the phosphoric acid as barium phosphate, the determination of the aluminium in the filtrate from this being carried out as usual. This procedure gives accurate results except when manganese is present in unduly large proportion.

T. H. POPE.

**Sensitive reagent for molybdate ion.** E. MONTIGNIE (Bull. Soc. chim., 1930, [iv], 47, 128).— $2.5 \times 10^{-6}$  part of molybdate ion may be detected by the formation of a red coloration with a reagent consisting of 3 parts of phenylhydrazine, 3 of sulphuric acid, and 65 of water. The test is specific.

C. W. GIBBY.

**Spectrophotographic detection of bismuth in the ashes of animal organisms.** G. PICCARDI (Atti R. Accad. Lincei, 1929, [vi], 10, 258—260).—The presence of bismuth is determined by photographing the ultra-violet portion of the spark spectrum formed between two vertical gold electrodes, the lower of which is sealed into a small glass cup containing the solution of the ashes in one drop of concentrated hydrochloric acid solution. The characteristic bismuth lines are obtained with solutions containing as little as  $10^{-6}\%$  of bismuth. O. J. WALKER.

**Determination of osmium by strychnine sulphate.** S. C. OGBURN, jun., and L. F. MILLER (J. Amer. Chem. Soc., 1930, 52, 42—48).—Solutions of salts of the platinum metals give precipitates with saturated strychnine sulphate. In the absence of all other platinum metals, the osmium in sodium chlorosmate is determined accurately by precipitation of the strychnine compound  $(C_{21}H_{22}O_2N_2)_3Os$  (factor 0.1758). It is suggested that in this compound osmium has the co-ordination number 6. A quantitative separation of osmium from ruthenium is effected, since the strychnine compounds of both metals are soluble in boiling 50% aqueous ethyl alcohol, but that of osmium alone is reprecipitated immediately on cooling the liquid.

J. G. A. GRIFFITHS.

**Apparatus for the determination of corrected *m. p.*** C. JUNGE (Chem.-Ztg., 1929, 53, 996).—The apparatus consists of a jacketed heating tube containing a small quantity of heating liquid into which are immersed the thermometer and specimen. The bottom of the jacket is connected externally with the top by means of a narrow circulating tube which can be heated at its lowest part by a small flame. The jacket is filled with sulphuric acid, which, on application of the flame, is caused to circulate, thus ensuring regular even heating of the specimen and keeping the stem of the thermometer at the same temperature as the bulb. A. R. POWELL.

**Ebullioscopic apparatus for study of mixtures of liquids.** W. ŚWIĘTOSŁAWSKI (Rocz. Chem., 1929, 9, 608—614).—See this vol., 56.

**Ebullioscopic and tonometric determinations.** W. SWIENTOSLAWSKI (Bull. Acad. Polonaise, 1929, A, 434—486).—See A., 1929, 786.

**Arrangement for obtaining a steady flow of gas at constant low pressure.** F. G. SLACK (Rev. Sci. Instr., 1930, 1, 33—35).—The pressure of hydrogen generated electrolytically is transmitted to a mercury manometer which makes and breaks the generating circuit by means of a relay. C. W. GIBBY.

**Capillary manometer system for preparing mixtures of gases with a very high ratio between components.** E. Q. ADAMS and E. R. H. CHARPENTIER (Rev. Sci. Instr., 1930, 1, 9—12).—The rate of flow of each gas is measured by the pressure produced in a calibrated manometer when it flows through a capillary tube. C. W. GIBBY.

**Growth of single crystals of low-m. p. metals in vacuum.** J. H. DILLON (Rev. Sci. Instr., 1930, 1, 36—38).—The metal is out-gassed at a temperature 60° above the m. p. for 24 hrs. in a pyrex tube, and filtered through a capillary into a limb which is then sealed off and lowered slowly into a furnace kept about 60° above the m. p. C. W. GIBBY.

**Platinum contamination of palladium in palladium point determinations.** C. L. UTTERBACK (Rev. Sci. Instr., 1930, 1, 39—44).—Spectral and chemical analyses show that palladium heated in contact with platinum becomes contaminated with the latter, with increasing velocity at temperatures above 1100°. Samples of palladium held by platinum supports close together melt at a higher temperature than if the supports are further apart. C. W. GIBBY.

**Methods and apparatus used in the cryogenic laboratory. XXIII. Horizontal cryostat for the measurement of magnetic susceptibilities at low temperatures.** E. C. WIERSMA and H. R. WOLTJER (Proc. K. Akad. Wetensch. Amsterdam., 1929, 32, 1046—1053).—An apparatus employing Weiss' method for the determination of magnetic susceptibility, and a vapour cryostat for use therewith, are described. H. F. GILLBE.

**Simple cryostat.** E. ZINTL and S. NEUMAYR (Ber., 1930, 63, [B], 234—236).—An apparatus is figured and described which differs from that of Shinozaki and Hara (A., 1926, 1118) essentially only in the thermoregulator. H. WREN.

**Freezing mixture.** F. NOACK.—See B., 1930, 124.

**Refractometer.** E. E. JELLEY (J. Sci. Instr., 1930, 7, 14—19).—The principle employed is that of grazing incidence, the plate of material under examination being immersed in a liquid of high refractive index, such as 1-bromonaphthalene or carbon tetrachloride. The refractive indices of thin films of aqueous solutions, celluloid, etc. can also be determined by enclosing the film between two glass plates of high refractive index prior to immersion. The apparatus is cheap and easily constructed and yields results which are accurate to 0.0002—0.0003. H. F. HARWOOD.

**Scale for determining the refractive indices of liquids under the microscope.** G. LINCK and E.

KÖHLER (Chem. Erde, 1930, 4, 458).—A set of eleven powdered glasses ranging in  $n$  from 1.5400 to 1.8052, also fluorite  $n$  1.4339, is supplied for checking the values of the liquids used for the determination of the refractive indices of minerals by the immersion method under the microscope. L. J. SPENCER.

**Trustworthiness of refractometric tables.** A. KARVONEN (Suomen Kem., 1929, 2, 115—117).—The tables for calculating refractive indices from refractometer readings are not always free from error. R. CUTHILL.

**Fallacious determination of the specific heats of gases by the explosion method.** O. C. DE C. ELLIS (Nature, 1930, 125, 165—166).—Determinations of the specific heats of gases by measurements of the maximum pressure developed on explosion are fallacious, since, as is shown by a consideration of the mechanism of such explosions, the constitution of the gas at the moment of maximum pressure is unknown, and the gas cannot be homogeneous, nor can combustion cease before sensible cooling occurs. L. S. THEOBALD.

**Small gas-muffle oven.** II. F. W. HORST (Chem. Fabr., 1929, 513).—Several minor modifications of the muffles previously described (A., 1929, 1033) are described. A. R. POWELL.

**Rapid evaporation.** I, II. H. N. NAUMANN (Biochem. Z., 1929, 216, 136—153, 154—164).—I. The efficiencies of laboratory apparatus and methods for evaporation and distillation of liquids and solutions have been investigated and performances have been compared with calculated values. The distillation, under reduced pressure, of large volumes of liquid can be conveniently and efficiently carried out with the help of a modified form of Liebig condenser having a copper condensation tube.

II. Small volumes of liquid such as those used in micro-analysis may be accurately concentrated to a required volume in a vacuum desiccator containing a heater which warms the liquid from above. A special form of evaporating dish having a small graduated cylindrical attachment at its base is used. W. MCCARTNEY.

**Reproducibility and constancy of the Weston element accepted as international standard.** A. K. KOLOSOV (J. Appl. Chem., Russia, 1929, 2, 369—388).—The preliminary purification of mercury by electrolysis is described. Crushed crystals of mercurous sulphate gave a higher *E.M.F.* than the original crystals. Elements prepared with electrolytes to which sulphuric acid of a concentration 0.1N or greater is added are characterised by a decrease in *E.M.F.* with time. The *E.M.F.* increases when mercurous sulphate is oxidised in a current of air, but, contrary to the effect of hydrolysis, it remains constant over a long period. The behaviour of the standard elements constructed is described.

#### CHEMICAL ABSTRACTS.

**New types of glass filtering apparatus.** P. H. PRAUSNITZ (Chem.-Ztg., 1929, 53, 935—936, 955—956).—Various new types of glass Buchner funnels, Soxhlet tubes, and extraction apparatus in which fused-in filter discs of sintered glass are employed, are illustrated and briefly described. A. R. POWELL.

**Apparatus for hot filtration of saturated solutions.** S. H. BERTRAM and W. A. VAN MEURS (Chem. Weekblad, 1930, 27, 7—8).—A simple apparatus for filtering saturated solutions in volatile solvents, in which the filter is heated by means of the vapour of the solvent, is described. S. I. LEVY.

**Universal distillation apparatus.** R. KATTWINKEL (Chem. Fabr., 1930, 18—20).—Various forms of apparatus for different purposes, in which the condenser is vertically above the distillation flask, are described. Vapours ascend by a side-tube entering the condenser above the lowest point, the latter being extended to one side to form measuring containers, extraction thimbles, reaction vessels, etc. Several applications are described. S. I. LEVY.

**High-frequency field.** I. H. RHEINBOLDT and A. HESSEL (Ber., 1930, 63, [B], 84—87).—An apparatus suitable for the examination of substances in a high-frequency field is based on that described by Esau (Elektrotechn. Z., 1926, 321). Only compounds which have a certain electrical conductivity suffer change. Finely-divided metals and active

charcoal become incandescent. Pure water, in contrast to tap-water, is almost unchanged, but addition of small amounts of electrolyte causes the liquid to boil more or less rapidly. Moist glass is heated to melting, whereas dry glass is unaffected. Hydrated salts are dehydrated. Moist potassium permanganate, in contrast to the dry salt, becomes decomposed. Organic solvents remain unaffected when absolutely anhydrous. Gases are unchanged at normal pressure, but glow under about 30 mm. pressure. Carbon monoxide and oxygen afford carbon dioxide. Hydrated sulphates of copper, nickel, manganese, and ferrous iron are decomposed in air with production of the metal or its oxide. Mercuric oxide is decomposed thermally. Petroleum and aromatic hydrocarbons in presence of air give tars. Primary alcohols are oxidised to aldehydes in presence of air or oxygen. Iodine combines rapidly with oxygen and sulphur dioxide with chlorine. Ethylenic compounds react with hydrogen.

H. WREN.

**Ultra-violet solar radiation and the solarisation of window materials.** W. W. COBLENTZ and R. STAIR.—See B., 1930, 103.

## Geochemistry.

**Ozone in northern and southern hemispheres.** F. G. FOWLE (J. Terrest. Mag. Atm. Elec., 1928, 3, 151—157).—Solar and magnetic observations on Table Mt. are correlated with variations in the ozone content of the atmosphere. CHEMICAL ABSTRACTS.

**Iodine content of sea-water.** J. F. REITH (Rec. trav. chim., 1930, 49, 142—150).—The iodine content of sea-water may be satisfactorily determined by Winkler's method (A., 1916, ii, 109), and the alcohol extraction method (cf. von Fellenberg, Biochem. Z., 1923, 139, 404) is also applicable if the final titration of the iodic acid is carried out in presence of acetic acid, to prevent interference by bromides (cf. A., 1929, 667). Sea-water from various localities has been examined, the results varying only from 43 to 69  $\gamma$  of iodine per litre, from which it is inferred that the discrepancies in the figures obtained by previous workers are due to analytical errors. No evidence of the presence of organically combined iodine was found, and the iodine content of deep sea-water proved not to differ very much from that of surface water. R. CUTHILL.

**Buszite.** E. STEINWACHS (Zentr. Min. Geol., 1929, A, 202—205; Chem. Zentr., 1929, ii, 1146).—A crystal of buszite from Khan, S.W. Africa, is ditrigonal-bipyramidal,  $a:c = 1:1.1792$ ,  $H$   $5\frac{1}{2}$ ,  $n$  1.72. Silica, neodymium, praseodymium, erbium, and some europium are present. A. A. ELDRIDGE.

**South Australian algal limestones in process of formation.** D. MAWSON (Quart. J. Geol. Soc., 1929, 85, 613—623).—Three types of recent limestones from the low-lying land on the south-eastern coast of South Australia are described: (1) Discs ("biscuits") covering the surface of swampy ground, which dries up during the summer. They are en-

crusted with bluish-green algæ, which evidently caused the precipitation of the calcium carbonate. (2) A reef-formation on the shore of a lake shows algal growths of *Lithothamnion*. Analysis gave MgO 4.73%. (3) Dolomitic lake-marl in the bed of shallow lakes, which dry up during the summer. Analysis shows CaO 28.60, MgO 12.46,  $SiO_2$  5.84, etc. L. J. SPENCER.

**Tourmaline group.** F. MACHATSCHKI (Chem. Erde, 1930, 4, 455—457).—A criticism of the formula of tourmaline proposed by Kunitz (A., 1929, 905). L. J. SPENCER.

**Experimental weathering of feldspar.** O. TAMM (Chem. Erde, 1930, 4, 420—430).—Feldspar when ground in cold water in a rotating vessel for a long period reduces to particles of 2 to 0.2  $\mu$  in size. The water has an alkaline reaction and the fine powder contains about 2% of water. L. J. SPENCER.

**Dolomitisation of Middle Devonian [limestone] in the Eifel.** P. MÜLLERS (Chem. Erde, 1930, 4, 431—454).—Many analyses are given of the dolomite-rock in the Gerolstein basin. They show in the majority of cases 80—96% of dolomite ( $CaCO_3$ ,  $MgCO_3$ ), but in a few streaks only 1—2%. The rock is a coral-reef formation and the dolomitisation took place contemporaneously by the action of the sea-water. The undolomitised streaks represent lagoon deposits. L. J. SPENCER.

**Dehydration and rehydration of kaolin.** P. SCHACHTSCHABEL (Chem. Erde, 1930, 4, 395—419).—Kaolin after being heated at 400—800°, when most of the water is lost, is capable of taking up water again. This is effected very slowly at 110°, but under pressure at 175—205° all the water is restored after 100 hrs. The rehydrated kaolin differs from the

original material by being partly soluble in hydrochloric acid, in its dehydration curve, refractive index, and X-ray pattern, but these differences become less marked after prolonged heating of the material in water at 200°.

L. J. SPENCER.

**Rocks of Gomera, Canary Islands.** W. MÜLLER (Chem. Erde, 1930, 4, 369—394).—The Tertiary or post-Tertiary volcanic rocks of the island of Gomera are underlain by a series of extensively weathered rocks which were believed by Gagel (1925) to represent a much older "Grundgebirge." A detailed examination with several analyses of these rocks shows that they are only the weathered equivalents of the ordinary types of volcanic rocks, which include basalts, trachytes, and trachytic phonolites. Analyses are also given of the portions of the weathered rocks soluble in hydrochloric acid.

L. J. SPENCER.

**Geology of Maine. IV. Geology of the Catahdin area. I. A new rhyolite from the State of Maine.** E. S. C. SMITH (Amer. J. Sci., 1930, [v], 19, 6—8).—An analysis of the rhyolite is given.

C. W. GIBBY.

**Samarskite from Petaca, New Mexico.** F. L. HESS and R. C. WELLS (Amer. J. Sci., 1930, [v], 19, 17—26).—Analyses of the samarskite are given. It consists of two parts, of formulae approximately  $Y_2O_3 \cdot Nb_2O_5$  and  $2Y_2O_3 \cdot 3Nb_2O_5$ . The ages, calculated from the following data, are found to be  $1.5 \times 10^8$  and  $3 \times 10^8$  years, respectively: U 4.85, Th 0.97, Pb 0.1%, and U 10.66, Th 1.39, Pb 0.40%.

C. W. GIBBY.

**Minerals of Transylvania.** D. GRUȘCĂ (Bull. Acad. Sci. Roumaine, 1929, 12, 10—17).—Crystallographic descriptions of barytes crystals from Transylvania are given.

C. W. GIBBY.

**Sapphirin from Alpe Brasciadega, Val Codera, Italy.** H. P. CORNELIUS and E. DITTLER (Neues Jahrb. Min., 1929, 59, 27—64; Chem. Zentr., 1929, ii, 1640—1641).—The sapphirin, isolated by means

of sulphuric and hydrofluoric acids, contained  $SiO_2$  15.19,  $TiO_2$  0.25,  $Al_2O_3$  61.69, Fe 4.31, MnO 0.12, CaO 0.49, MgO 16.23,  $H_2O + 1.60$ ,  $H_2O - 0.19\%$ , corresponding with the formula  $Mg(Fe, Mn, Ca, H_2)_{11}Al_2Si_5O_{57}$ .

A. A. ELDRIDGE.

**Bohemian clay.** G. LINCK and E. KÖHLER (Chem. Erde, 1930, 4, 459—460).—A clay from the Tertiary lignite beds was analysed in bulk and also the portion soluble in hydrochloric acid after ignition at 600°, and the dehydration curve is plotted. It contains 47.58% of kaolin with 18.94% of amorphous material, 40% of quartz, and some mica, pyrite, and organic matter.

L. J. SPENCER.

**Japanese acid clay. IV. Determination of water.** K. KOBAYASHI, K. YAMAMOTO, and K. BITO (J. Soc. Chem. Ind. Japan, 1929, 32, 297—298B).—The water contents of Japanese acid clays, fuller's earth, silica, alumina and aluminium silicate gels, and kaolin have been determined by means of the thermobalance. The heating curves of silica and aluminium silicate gels resemble those of acid clays, but differ from that of kaolin.

C. W. GIBBY.

**Genesis of Japanese acid clay.** K. KOBAYASHI and K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 174—175B).—Japanese acidic clay is found exclusively along an intrusion of liparite through pliocene strata; its formation is attributed to the interaction of sodium felspar and sodium silicate under the influence of gases such as carbon dioxide, sulphur dioxide, hydrogen sulphide, and steam. The presence of ferric, calcium, and magnesium oxides is probably due to accidental contamination and also to adsorption by the clay.

H. F. GILLBE.

**Brown soils of Crimea and Caucasus.** L. I. PRASSOLOV (Chem. Erde, 1930, 4, 461—474).—A review of Russian papers.

L. J. SPENCER.

**Chemical composition of peat.** S. A. WAKSMAN (Amer. J. Sci., 1930, [v], 19, 32—54).—A discussion.

C. W. GIBBY.

## Organic Chemistry.

**Action of benzoyl peroxide on saturated hydrocarbons.** J. BÖSEKEN and A. GASTER (Rec. trav. chim., 1930, 49, 102—108).—When benzoyl peroxide is boiled with purified petroleum (b. p. 95—100°), carbon dioxide (1 mol.) is evolved and benzene, benzoic acid, heptylbenzene, and probably a *tert*-heptyl alcohol (isolated after hydrolysis) are formed; small amounts of unidentified acid products are also produced. Reaction appears to occur in the manner formulated by Gelissen and Hermans (A., 1925, i, 545). Using *n*-octane, decomposition begins at about 100°, and carbon dioxide, benzene, and benzoic acid are initial products of the reaction. Hydrolysis of the neutral products formed during the reaction gives benzoic acid, a mixture (?) of *sec*-octyl alcohols, and resinous products.

H. BURTON.

**Polymerisation. XII. Polymeric forms of isobutylene.** S. V. LEBEDEV and G. G. KOBLIANSKY

(Ber., 1930, 63, [B], 103—112).—*iso*Butylene, when heated in a hard glass tube at 200° for 14 days, yields 6—8% of polymerised products, from which only triisobutylene could be isolated. The action of sulphuric acid on *isobutylene* affords predominately triisobutylene with a very small amount of diisobutylene and a less volatile residue which could not be separated into its components by fractional distillation. Butlerov's triisobutylene is, however, separable into two portions, (a) b. p. 179—181° (corr.), 56°/10 mm.,  $d_4^{25}$  0.7590,  $n_D^{25}$  1.43138, and (b) b. p. 195—196° (corr.), 75—77°/12 mm.,  $d_4^{25}$  0.7763,  $n_D^{25}$  1.44062. *iso*Butylene readily undergoes polymerisation in presence of Florida earth activated by previous ignition at about 300° (cf. Lebedev and Filonenko, A., 1925, i, 225). Reaction is very marked at -80°. If the gas is passed over the unheated catalyst, the temperature of the latter rises immediately to 110—135° and then slowly falls.

At 200° reaction is very slow, whereas at 290° the isobutylene is partly decomposed with deposition of carbon on the catalyst. Prolongation of the period of contact of hydrocarbon and earth leads to an increase in the proportion of more highly polymerised forms. The following polymerides are isolated by fractional distillation of the crude products: diisobutylene,  $(C_4H_8)_2$ , b. p. 101—102°/762 mm.,  $d_4^{20}$  0.7195,  $n_D^{20}$  1.41123, the identity of which with Butlerov's product is established by physical constants and by the similarity in the course of hydrogenation of the two products; the substance slowly passes into tetraisobutylene when preserved at the atmospheric temperature in contact with Florida earth; triisobutylene, b. p. 178.5—179.5° (corr.),  $d_4^{20}$  0.7600,  $n_D^{20}$  1.43060, apparently identical with the trimeride of lower b. p. (see above), which does not further polymerise in presence of Florida earth and is hydrogenated only slowly; tetraisobutylene,  $(C_4H_8)_4$ , b. p. 106°/7 mm.,  $d_4^{20}$  0.7944,  $n_D^{20}$  1.44817; pentaisobutylene, b. p. 148°/7 mm.,  $d_4^{20}$  0.8176,  $n_D^{20}$  1.46006, which appears to be formed also from di- and tri-isobutylene in presence of Florida earth; the tetra- and penta-compounds do not polymerise further and can be hydrogenated only with extreme slowness; hexaisobutylene, b. p. 158—161°/2.5 mm.,  $d_4^{20}$  0.8340,  $n_D^{20}$  1.46841; heptaisobutylene, b. p. 183—186°/2 mm.,  $d_4^{20}$  0.8455,  $n_D^{20}$  1.47393. The residue remaining after the separation of the heptameride is colourless and very viscous; there appears little prospect of isolating higher polymerides, since the temperature required for distillation under very greatly reduced pressure is sufficiently high to cause depolymerisation. The following changes appear to be established:

$$C_4H_8 + C_4H_8 \longrightarrow (C_4H_8)_2; (C_4H_8)_2 + C_4H_8 \longrightarrow (C_4H_8)_3; 2(C_4H_8)_2 \longrightarrow (C_4H_8)_4; (C_4H_8)_2 + (C_4H_8)_3 \longrightarrow (C_4H_8)_5.$$

H. WREN.

**Illipene, and higher alcohols in commercial illipé butter.** M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 365—367B).—The unsaponifiable matter of illipé butter was treated with 95% alcohol, and the insoluble portion was crystallised from ethyl acetate. So obtained, illipene has m. p. 64°, iodine value 352.0, probable formula  $C_{64}H_{106}$  or  $C_{65}H_{108}$ ; it decomposes on attempted distillation at 4.5 mm., and appears to be rather susceptible to atmospheric oxidation. It yields an ether-insoluble bromide and by hydrogenation furnishes a white, viscous semi-solid, m. p. about 100°, iodine value 56.

The solution of the portion of the unsaponifiable matter dissolved by alcohol yielded when concentrated a higher alcohol, *bassisterol*,  $C_{27}H_{46}O$ , m. p. 210—211°, iodine value 71.5,  $[\alpha]_D^{25} + 26.4^\circ$  in ether. Bassisterol does not give a precipitate with digitonin, but affords a pink colour with acetic anhydride and sulphuric acid; the hydroxyl group appears to be difficult to acetylate. C. W. SHOPPEE.

**cis-trans-Ethylenic isomerism. Addition of two atoms of hydrogen to the acetylenic linking.** M. BOURGUEL (Bull. Soc. chim., 1929, [iv], 45, 1067—1091).—The hydrogenation of tolane, six acetylenic acids, one diacid, one alcohol, one glycol, and one aldehyde in presence of colloidal palladium stabilised by starch (A., 1928, 28) uniformly gives the

cis-ethylenic derivative. The contradictory results obtained by other methods are attributed to the instability of the nascent molecule which is then sensitive to the influence of reagents that normally have little isomerising influence. Support for this view is afforded by the increased rate of formation of the internal oxide of  $\beta\epsilon$ -dimethyl- $\Delta^7$ -hexene- $\beta\epsilon$ -diol in the hydrogenation of  $\beta\epsilon$ -dimethyl- $\Delta^7$ -hexinene- $\beta\epsilon$ -diol in acid medium as compared with the direct dehydration of the hexenediol in acid medium (A., 1928, 989) and the rapid increase in the rate of polymerisation of phenylpropinene under hydrogenation at 20°.

Thus hydrogenation of phenylpropionic acid in ethyl acetate yields primarily Liebermann's *alloisocinnamic acid*, m. p. 55—56°, together with its more stable transformation products, Erlenmeyer's *isocinnamic acid*, m. p. 37—38°, and *allocinnamic acid*, m. p. 67—68°, but no *trans*-isomeride. Acetylenedicarboxylic acid similarly yields maleic acid and tolane, *isostilbene*, b. p. 140.5—141°/13 mm.,  $d^{13}$  1.023,  $n_D^{13}$  1.620, containing less than 2% of stilbene (formed by isomerisation during distillation). Phenylpropionic alcohol yields *cis-cinnamyl alcohol*, b. p. 125.5°/13.5 mm.,  $d^{20}$  1.044,  $n_D^{20}$  1.582 (*phenylurethane*, m. p. 89.5°), the known alcohol of higher b. p. and density being therefore the *trans*-isomeride. Hydrogenation of methyl  $\Delta^a$ -propinenyl ketone yields a mixture, b. p. 110—130°, of saturated, olefinic, and acetylenic ketones. Methyl phenylethynyl ketone gives a similar mixture containing phenyl styryl ketone and a saturated, b. p. 119—121°/16 mm., and acetylenic ketone, b. p. 126—127°/16 mm.  $\Delta^a$ -Pentinenic acid affords *cis- $\Delta^a$ -pentinic acid*, b. p. 88—88.5°/15 mm.,  $n_D^{15}$  1.448,  $d^{15}$  0.988, isomeric with the acid obtained by Auwers (A., 1923, i, 746) which is regarded as the *trans*-isomeride. Similarly,  $\Delta^a$ -hexinenic acid yields *cis- $\Delta^a$ -hexenonic acid*, b. p. 100.5—101.5°/15 mm., 201—202°/760 mm.,  $d^{21}$  0.962,  $n_D^{21}$  1.4495, and  $\Delta^a$ -octinenic acid, *cis- $\Delta^a$ -octenonic acid*, b. p. 127°/15 mm.,  $d^{10}$  0.944,  $n_D^{15}$  1.456, converted by insolation in presence of iodine into the *trans-isomeride*, m. p. 5—6°, b. p. 143°/15 mm.,  $d^{17}$  0.944,  $n_D^{17}$  1.461.  $\Delta^a$ -Noninenic acid yields *cis- $\Delta^a$ -nonenonic acid*, b. p. 140°/15 mm.,  $d^{15}$  0.9315,  $n_D^{15}$  1.458, similarly converted into the *trans-isomeride*, b. p. 154.5°/15 mm., m. p. 1—2°,  $d^{18}$  0.936,  $n_D^{15}$  1.4635. The structures of the *cis*- and *trans*-isomerides of this series of acids are based on the relation between the physical constants and those of crotonic and isocrotonic acids.

[With J. YVON.]—Tetrollic acid on hydrogenation similarly yields *isocrotonic acid*, m. p. 14—15°, b. p. 169°,  $d^{15}$  1.028,  $n_D^{15}$  1.446, and no crotonic acid. Phenylpropionaldehyde when hydrogenated under these conditions is hydrogenated in the aldehydic group, yielding three unsaturated compounds. The diethylacetal, obtained by Moureu and Delange's method (A., 1904, i, 650), undergoes hydrolysis, yielding a mixture containing  $\beta$ -phenylpropaldehyde, but no cinnamaldehyde. Hydrogenation in dimethylcyclohexane, which has no solvent power for water, yields an acetal, b. p. 130—132°/16 mm.,  $d^{15}$  0.966,  $n_D^{15}$  1.492, probably the *diethylacetal* of *cis-cinnamaldehyde*, hydrolysed to *cis-cinnamaldehyde*, b. p. 111—113°/16 mm.,  $d^{20}$  1.032,  $n_D^{20}$  1.565, probably con-

taining some saturated aldehyde, but not the known cinnamactal, which is regarded as having the *trans*-structure (from the relation of cinnamic acid to cinnamaldehyde).

[With RAMBAUD.]—Hydrogenation of  $\beta\epsilon$ -dimethyl- $\Delta^7$ -hexinene- $\beta\epsilon$ -diol in presence of palladium and starch at  $p_H$  7.1 or in 0.01*N*-sodium carbonate yields mainly the *cis*-glycol, the proportion of *trans*-isomeride being increased in heterogeneous or acid medium; in the latter case the dehydration of the *cis*-glycol already noted also occurs and tends to mask the formation of the *trans*-isomeride which yields no internal oxide. R. BRIGHTMAN.

**Preparation of alkyl chlorides from the corresponding alcohols.** R. H. CLARK and H. R. L. STREIGHT (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 77—89).—Alkyl chlorides have been prepared from methyl and ethyl, the isomeric propyl, butyl, and amyl alcohols, *n*-hexyl, *n*-heptyl, *n*-octyl, "capryl," *n*-nonyl, cetyl, allyl, and cinnamyl alcohols, ethylene, propylene, and trimethylene glycols, benzyl alcohol, phenylmethylcarbinol, and triphenylcarbinol. Four methods have been compared, viz., the action of (a) hydrochloric acid in presence of zinc chloride (Norris and Taylor, A., 1924, i, 602), (b) phosphorus trichloride and zinc chloride (Dehn and Davis, A., 1907, i, 885), (c) phosphorus pentachloride and zinc chloride, and (d) thionyl chloride in pyridine or benzene. Method (a) is recommended for the preparation of large amounts of aliphatic chlorides and benzyl chloride. Tertiary alcohols give high yields of chloride with hydrochloric acid alone in the cold. Method (b) gives yields of 60—80% of primary and secondary and 92—98% of tertiary chlorides. It is inferior to (a) only for lower aliphatic chlorides, and is useful for the other chlorides. Method (c) gives generally increased yields as compared with the use of phosphorus pentachloride alone. The yields are 70—80% with aliphatic alcohols, with the exception of *n*-hexyl to *n*-nonyl alcohols, with which it is lower; cetyl, cinnamyl, and aromatic alcohols form tars. Method (d) is suitable for the preparation of small amounts of pure products. With the lower aliphatic alcohols the use of pyridine is necessary, with the others no solvent, or benzene, is used. The yields are high (80—99%) except with diethylcarbinol (42—44%) and *n*-nonyl alcohol (62%). The relative costs of the methods are in the order (a) < (b) < (c) < (d), except when the alcohol is expensive, when (d) is cheapest.

The following new or revised data are given for the chlorides: *n*-hexyl,  $d_4^{20}$  0.8759,  $n_D^{20}$  1.42364; *n*-heptyl,  $d_4^{20}$  0.8741,  $n_D^{20}$  1.42844; *n*-octyl,  $d_4^{20}$  0.8745,  $n_D^{20}$  1.43424; *n*-nonyl, b. p. 98—100°/23 mm.,  $d_4^{20}$  0.8679,  $n_D^{20}$  1.43692; cetyl,  $d_4^{20}$  0.8384; methyl-*n*-hexyl,  $d_4^{20}$  0.8649,  $n_D^{20}$  1.42954. R. K. CALLOW.

**Tests for isopropyl alcohol.** H. LEFFMANN and C. C. PINES (Bull. Wagner Inst. Sci., 1929, 4, 47—50).—Various methods for the detection of isopropyl alcohol in the presence of other alcohols are reviewed. Rae's method (Pharm. J., 1926, 116, 630) slightly modified (10 c.c. of the sample oxidised with 20 c.c. of 1% potassium dichromate solution and 1 c.c. of sulphuric acid, ammonia and a little ammonium chloride added to the first 3 c.c. of the distillate which

is superimposed on a 1% solution of sodium nitroprusside in glycerol, a ring forming at the contact zone if acetone, formed by the oxidation of isopropyl alcohol, is present) gives a positive reaction with 10% of isopropyl alcohol in 50% alcohol, and negative results with similar concentrations of *n*-propyl, *n*-, *iso*-, and *tert*-butyl alcohols, and only a faint ring with *sec*-butyl alcohol. Dale and Simmonds' method (mixture of 1 c.c. of the sample, 1 c.c. of a saturated disodium hydrogen phosphate solution, and 3 c.c. of a saturated solution of potassium permanganate is warmed, left until the permanganate is destroyed, and then 3 c.c. of a 1% sodium hydroxide solution and 1 c.c. of 1% furfuraldehyde solution are added and the mixture is filtered; addition of 1 c.c. of concentrated hydrochloric acid to the filtrate gives a red colour if isopropyl alcohol was originally present) gave positive results with both the samples tested. Herstein's test (Pract. Drug., 1922, 38) seems to depend on the presence of some impurity, since not all samples of isopropyl alcohol give this test. J. W. BAKER.

**Theory of geometrical stereochemistry.** A. P. SEMENCOV.—See this vol., 276.

**Benzyl-alcoholic potassium hydroxide and its applications. Determination of halogen.** S. SABETAY and J. BRÉGER (Bull. Soc. chim., 1930, [iv], 47, 114—118).—Halogen in the following substances has been accurately determined with benzyl-alcoholic potassium hydroxide: glycerol mono- and di-chlorohydrins, methylene iodide, iodoform, chloral hydrate, chloro- and trichloro-acetic acid, ethyl  $\alpha$ -bromo- $\alpha$ -ethylbutyrate, iodoacetamide,  $\alpha$ -bromopropionamide, mono- and di-chloroquinolins, 4-chlorocyclohexanone-semicarbazone,  $\alpha$ -bromocamphorsulphonyl chloride, dibromo- and dichloro-styrene. The following method is used: 0.1—0.3 g. of substance is heated for 30—60 min. with 40 c.c. of benzyl alcohol and 10 g. of potassium hydroxide in a pyrex flask, with a long tube attached; 50 c.c. of water are added after cooling a little, followed by 30 c.c. of ethyl alcohol and 30 c.c. of nitric acid with a known excess of 0.5*N*-alcoholic silver nitrate solution. The excess of silver nitrate is determined by Volhard's method.

R. BRIGHTMAN.

**Ferric ethoxide.** R. SUTRA (Bull. Soc. chim., 1930, [iv], 47, 68—71).—A reply to Thiessen and Koerner (A., 1929, 675). Ferric ethoxide has not been obtained pure, but always contains sodium chloride or magnesium halides, as its instability renders crystallisation impossible. Thus ferric chloride and magnesium ethoxybromide, obtained from magnesium ethyl bromide and alcohol in benzene, in an atmosphere of nitrogen yield a solution of ferric ethoxide, which slowly crystallises after concentration. Addition of alcohol or benzene gives a precipitate containing, e.g., 34.6% of magnesium chlorobromide, 2.2% of ferric ethoxide, and 63.2% of ether. Ferric ethoxide does not give Tischtschenko's reaction with acetaldehyde, polymerisation and aldolisation taking place.

R. BRIGHTMAN.

**Reactions of magnesium compounds with ethylene oxide. I. Reaction between trimethylene oxide and magnesium ethyl bromide.** L. BERMEJO and V. G. ARANDO (Anal. Fis. Quim., 1929,



27, 798—800).—Treatment of trimethylene oxide with magnesium ethyl bromide in ethereal solution yields a substance which is hydrolysed to *n*-butyl alcohol and trimethylene bromohydrin, both in about 30% yield. If the mixture is not heated at any stage the yield may be raised to 38%. H. F. GILLBE.

Kanyl alcohol, a new alcohol in the liver oil of "Tarabakani," *Paralithodes Camtschatica* (Tilesius). M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 362—364B).—The portion of the unsaponifiable matter of the liver oil soluble in methyl alcohol at 0° was acetylated and distilled; the fractions of higher b. p. were brominated and the portion of the product soluble in light petroleum was debrominated and hydrolysed, thereby yielding *kanyl alcohol*, (?)  $C_{10}H_{18}O_2$ , b. p. 140—150°/5 mm.,  $d_4^{20}$  0.9553,  $n_D^{20}$  1.4740. When hydrogenated, it gives the compound  $C_{10}H_{20}O_2$ ,  $d_4^{20}$  0.9314,  $n_D^{20}$  1.4555. C. W. SHOPPEE.

Refractive index of solutions of certain  $\gamma$ -glycols of the acetylenic and saturated series. W. KRESTINSKI and N. PERSSIANZEW (Ber., 1930, 63, [B], 180—190).—The refractive indices for the  $\alpha$ ,  $\delta$ ,  $\beta$ , and  $\gamma$  lines of  $\beta\epsilon$ -dimethyl- $\Delta^7$ -hexinene- $\beta\epsilon$ -diol, m. p. 95°,  $\beta\epsilon$ -dimethylhexane- $\beta\epsilon$ -diol, m. p. 90°,  $\gamma\zeta$ -diethyl- $\Delta^8$ -octinene- $\gamma\zeta$ -diol, m. p. 74°,  $\gamma\zeta$ -diethyl-octane- $\gamma\zeta$ -diol, m. p. 70°,  $\beta\epsilon$ -dimethyl- $\Delta^6$ -decinene- $\delta\eta$ -diol, b. p. 159—160°/15 mm.,  $d_4^{20}$  0.9188,  $n_D^{20}$  1.45874,  $\gamma\zeta$ -dimethyl- $\Delta^8$ -octinene- $\gamma\zeta$ -diol, m. p. 55°, and  $\beta\beta\delta$ -trimethylpentane- $\alpha\gamma$ -diol have been determined in part with the homogeneous material and in part with their solutions in water, amyl alcohol, cyclohexanone, ethyl acetate, and aniline. The mol. refraction of acetylenic  $\gamma$ -glycols in solution is greater than the calculated value when the increment for the triple linking is taken into account; the mean value of the exaltation is 0.4—0.5. The values for the mol. refraction of the corresponding saturated glycols are smaller than the calculated data. With different solvents, somewhat distinct deviations are observed from case to case, but, generally, the effect of the solvent is not very pronounced. In the case of  $\beta\epsilon$ -dimethyl- $\Delta^6$ -decinene- $\delta\eta$ -diol, for example, the values obtained in amyl alcohol or cyclohexanone solution differ little from those observed with the homogeneous material. H. WREN.

Cyclic acetals. I. Formation of cyclic acetals from  $\Delta^{\beta\epsilon}$ -octadiene- $\delta\epsilon$ -diol. C. P. BURT and F. HOWLAND (J. Amer. Chem. Soc., 1930, 52, 217—219).—The following ethers of  $\Delta^{\beta\epsilon}$ -octadiene- $\delta\epsilon$ -diol are prepared from the diol and the requisite aldehyde or ketone at about 70°, using a small amount of 40% sulphuric acid as the catalyst (the figures in parentheses are the percentage yields): *ethylidene*, b. p. 88—89°/20 mm. (90), also obtained in 83% yield using paraldehyde; *propylidene*, b. p. 99—100.5°/21 mm. (90); *butylidene*, b. p. 104—105°/15 mm. (92); *heptylidene*, b. p. 129—131°/4 mm. (85), and *isopropylidene*, b. p. 72—75°/8 mm. (71). The length of the aldehyde carbon chain appears to have no appreciable effect on ether formation. Ethers could not be isolated from the diol and chloral, benzaldehyde, cinnamaldehyde, or crotonaldehyde. H. BURTON.

Polymerisation and ring formation. III. Glycol esters of carbonic acid. W. H. CAROTHERS

and F. J. VAN NATTA (J. Amer. Chem. Soc., 1930, 52, 314—326).—In agreement with the theory of condensation polymerides previously proposed (A., 1929, 1165), ethylene, b. p. 238°, m. p. 39°, and *trimethylene carbonates*, b. p. 135°/4 mm., m. p. 47—48°, can be obtained in the monomeric form. The latter ester is, however, converted by heating with a small amount of potassium carbonate at 130° into an additive polymeride (cf. *loc. cit.*), which on distillation in a vacuum regenerates the monomeric ester. When heated at 210°, the polymeride decomposes, yielding some allyl alcohol. Attempts to polymerise ethylene carbonate were unsuccessful. The polymethylene carbonates with a structural unit of 7 or more atoms are all polymeric. *Tetramethylene carbonate* ( $M=1300$ —1400), m. p. 55—59°, when heated at 300—325°/0.9 mm., gives about 1% of a dimeric *tetramethylene carbonate*, m. p. 175—176°. *Pentamethylene*, m. p. 44—46°, *hexamethylene*, m. p. 55—60°, *decamethylene*, m. p. 55°, and *diethylene carbonates*, syrupy, are described. *p-Xylylene carbonate* exists in two polymeric forms, m. p. 137—138° and 177—185°, soluble and insoluble in ethylene chloride, respectively. The above carbonates are all prepared from ethyl carbonate and the requisite glycol at 120—170°, in presence of a small amount of sodium; approximately equimolecular quantities are used.

When 2 mols. of ethyl carbonate are heated with 1 mol. of hexamethylene glycol, some *OO-dicarb-ethoxyhexane- $\alpha\zeta$ -diol*, b. p. 130—140°/0.8 mm.,  $d_4^{20}$  1.065,  $n_D^{20}$  1.4310, is obtained together with polymerised material. The *di-p-nitrobenzoates* of tetra- and penta-methylene glycols have m. p. 175° and 104—105°, respectively. H. BURTON.

Reactions of sulphurous esters. R. LEVAILLANT (Compt. rend., 1930, 190, 54—57).— *$\alpha\gamma$ -Dichloropropyl sulphite*, b. p. 149°/1.5 mm.,  $d_4^{20}$  1.531,  $n_D^{20}$  1.509, is obtained by treatment of  $\alpha\gamma$ -dichloropropyl alcohol with thionyl chloride. In presence of a little iodine the action of chlorine on the solution yields  $\alpha\gamma$ -dichloropropyl chlorosulphonate (Blanchard, A., 1929, 171) and  $\alpha\beta\gamma$ -trichloropropane.  $\beta$ -Chloroethyl sulphate is obtained in good yield by heating the corresponding chlorosulphonate and sulphite together at 160—180° for 3 hrs.; sulphur dioxide and ethylene dichloride are eliminated. The action of sulphuryl chloride on ethyl sulphite (1 mol.) at a low temperature yields ethyl chlorosulphonate, but when a mixture of sulphuryl chloride and ethyl sulphite (2 mols.) is heated at 150—160° for 2 hrs. ethyl sulphate is obtained in good yield. The interaction of benzoyl chloride and ethyl sulphite at 140—220° yields ethyl benzoate, and the interaction of acetyl chloride and propyl sulphite in presence of a little zinc chloride yields propyl acetate; alkyl chloride and sulphur dioxide are eliminated in each case. Acetic anhydride and ethyl sulphite yield similarly ethyl acetate. The interaction of phthalic anhydride and ethyl sulphite to give ethyl phthalate takes place at 150° only in presence of a little zinc chloride. A convenient method of preparing ethyl sulphate is by heating ethyl chlorosulphonate with ethyl carbonate at 135—160° for 4—5 hrs. or at 110° in presence of zinc chloride. R. K. CALLOW.

**Organic compounds of sulphur. XVI.** Thermal transformation of thiocarbonic esters into thiolcarbonic esters. A. SCHÖNBERG and L. VON VARGHA (Ber., 1930, 63, [B], 178—180; cf. A., 1929, 1451).—Phenyl thiocarbonate,  $\text{CS}(\text{OPh})_2$ , m. p.  $106^\circ$ , is isomerised when heated in absence of air at  $280^\circ$  into phenyl phenylthioformate, m. p.  $57^\circ$ . Similarly,  $\beta$ -naphthylthiocarbonate, m. p.  $212^\circ$ , at  $300^\circ$  affords  $\beta$ -naphthyl  $\beta$ -naphthylthioformate, m. p.  $136^\circ$ , hydrolysed by alkali hydroxide to  $\beta$ -naphthol and  $\beta$ -thionaphthol (identified by oxidation to di- $\beta$ -naphthyl disulphide). H. WREN.

**Dialkyl sulphurdicarbothionates.** G. S. WHITBY and H. GREENBURG (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 21—24).—By a reaction analogous to the conversion of thiuram disulphides into monosulphides (von Braun and Stechele, A., 1903, i, 618), dialkyl disulphurdicarbothionates (xanthogen disulphides) are converted into monosulphurdicarbothionates:  $(\text{RO}\cdot\text{CS})_2\text{S}_2 + \text{KCN} = (\text{RO}\cdot\text{CS})_2\text{S} + \text{KCNS}$ . The disulphides are prepared by the action of iodine (chlorine is unsuitable) on the alkali xanthate in aqueous solution, and treatment with potassium cyanide is carried out in aqueous-alcoholic solution at  $0$ – $10^\circ$ . The following are described: Disulphurdicarbothionates (xanthogen disulphides): dimethyl,  $(\text{OMe}\cdot\text{CS})_2\text{S}_2$ , m. p.  $22$ – $22.5^\circ$ ; di-*n*-propyl, b. p.  $150$ – $155^\circ/0.5$  mm.; diisopropyl, m. p.  $58.5^\circ$ ; di-*n*-butyl,  $d^{22}$  1.158, boils with decomposition below  $0.5$  mm.; diisobutyl, b. p.  $161$ – $164^\circ/0.5$  mm.,  $d^{22}$  1.1173; sulphurdicarbothionates (xanthogen monosulphides): dimethyl, m. p.  $55^\circ$ ; diethyl, m. p.  $52^\circ$ ; di-*n*-propyl, b. p.  $135$ – $136^\circ/0.5$  mm.; diisopropyl, m. p.  $54^\circ$ ; di-*n*-butyl,  $d^{22}$  1.121; diisobutyl,  $d^{22}$  1.126; diisooamyl, an oil.

Diethyl sulphurdicarboxylate,  $(\text{OEt}\cdot\text{CO})_2\text{S}$ ,  $d^{23}$  1.158 (Holmberg, A., 1905, i, 323), is obtained in the same way from the monosulphide, and also by the interaction of potassium ethyl thiolcarbonate with ethyl chloroformate.

Simple aryl and alkyl disulphides, e.g., phenyl disulphide, do not react with potassium cyanide, but benzyl tetrasulphide is converted almost quantitatively into benzyl disulphide. R. K. CALLOW.

**Synthesis of lengthened sulphur chain compounds.** P. C. RAY and S. K. MITRA (J. Indian Chem. Soc., 1929, 6, 865—869).—During the preparation of dithiopropylene glycol from trimethylene dibromide and alcoholic potassium hydrogen sulphide (cf. Autenrieth and Wolff, A., 1899, i, 579), some  $\gamma\gamma'$ -dithioldipropyl disulphide, b. p.  $180^\circ/40$  mm., is also produced. Acetylation of dithiopropylene glycol with acetic anhydride and a small amount of pyridine gives the diacetyl derivative, b. p.  $178^\circ/50$  mm., which is hydrolysed by 15% potassium hydroxide solution at  $28$ – $30^\circ$  to the monoacetyl derivative, b. p.  $115$ – $116^\circ/40$  mm. This is converted by iodine in ethereal solution into  $\gamma\gamma'$ -diacetyldithioldipropyl disulphide, which is then hydrolysed to the above disulphide. The diacetyl derivative, m. p.  $60^\circ$ , of dithioethylene glycol is converted similarly by way of the monoacetyl derivative, b. p.  $95$ – $97^\circ/40$  mm., into  $\beta\beta'$ -diacetyldithioldiethyl disulphide. This diacetate decomposed on attempted hydrolysis. H. BURTON.

**Action of bases on complex compounds derived from organic thio-compounds and platinum chloride.** P. C. RAY and P. C. MUKHERJEE (J. Indian Chem. Soc., 1929, 6, 885—891).—Treatment of an aqueous solution of platinum chloride with an excess of methyl sulphide affords the compound  $\text{PtCl}_2\cdot 2\text{Me}_2\text{S}$ , converted by prolonged boiling with water into the complexes  $\text{PtCl}_2\cdot 2\text{Me}_2\text{S}$  and  $\text{PtCl}_4\cdot 2\text{Me}_2\text{S}$ . The last-named compound is practically a non-electrolyte. When treated with ethylamine it furnishes the substance  $\text{PtCl}_2\cdot 4\text{NH}_2\text{Et}\cdot 2\text{H}_2\text{O}$ , m. p.  $211^\circ$  (decomp.); piperidine gives the compound  $\text{PtCl}_2\cdot 2\text{C}_5\text{H}_{11}\text{N}\cdot 2\text{H}_2\text{O}$ , whilst pyridine affords the complex  $\text{PtCl}_4\cdot 2\text{C}_5\text{H}_5\text{N}$  (cf. A., 1926, 1023). Diethylamine converts the compound  $\text{PtCl}_4\cdot 2\text{Et}_2\text{S}$  (loc. cit.; A., 1927, 444) into the substances  $\text{PtCl}_2\cdot \text{Et}_2\text{S}\cdot \text{NH}_2\text{Et}$  and  $\text{Pt}_2\text{Cl}_4\cdot 2\text{Et}_2\text{S}\cdot \text{NH}_2\text{Et}$ , whilst with trimethylamine the complex  $\text{PtCl}_2\cdot \text{Et}_2\text{S}\cdot \text{NMe}_3$  results. The substance  $\text{PtCl}_2\cdot 2(\text{CH}_2\text{Ph})_2\text{S}$  (A., 1928, 751) yields with propylamine and diethylamine, the compounds  $\text{PtCl}_2\cdot 4\text{NH}_2\text{Pr}\cdot 2\text{H}_2\text{O}$ , m. p.  $198^\circ$  (decomp.), and  $\text{PtCl}_2\cdot (\text{CH}_2\text{Ph})_2\text{S}\cdot \text{NH}_2\text{Et}$ , respectively; with methylamine, the complex  $[\text{MeNH}_2 \dots \text{PtCl}_2]$  results. The majority of the above complexes are postulated as compounds of the Werner type. H. BURTON.

**Hydroxymethanetrissulphonic acid.** P. FANTL and J. FISCH (J. pr. Chem., 1930, [ii], 124, 159—162).—Potassium and barium hydroxymethanetrissulphonates, prepared by Pechmann and Manck's method (A., 1896, i, 14), are salts of methanetrissulphonic acid, m. p.  $150^\circ$  (silver salt) (Bagnall, J.C.S., 1899, 75, 278).

A. I. VOGEL.

**Catalysis in organic chemistry. I. Reactions of ethers with acid chlorides, acids, and anhydrides.** H. W. UNDERWOOD, jun., and R. L. WAKEMAN. II. Mechanism of the reactions. H. W. UNDERWOOD, jun., and G. C. TOONE (J. Amer. Chem. Soc., 1930, 52, 387—391, 391—394).—I. When a mixture of anhydrous ether (1 mol. + 10—15%), zinc chloride (about 0.25 mol.), and an acid chloride (1 mol.) is boiled for 2—3 hrs. ethyl esters are often obtained. The chlorides of the following acids all yield ethyl esters, the percentage yield being given in parentheses: acetic (40); chloroacetic (35); propionic (15); *n*-butyric (21); isovaleric (20); benzoic (60); phenylacetic (79); oxalic (4); diphenic (77). Ester formation occurs also with 3:5-dinitrobenzoyl and phthalyl chlorides; in the last case some phthalic anhydride is also produced. Benzene- and *p*-toluenesulphonyl chlorides do not react with ether under the above conditions. With acetyl, propionyl, and benzoyl chlorides and isopropyl, *n*-butyl, and isoamyl ethers varying amounts of the corresponding alkyl esters are produced. Diphenyl ether and anisole do not undergo fission with acetyl or benzoyl chlorides; nuclear acylation takes place.

When the following acids or anhydrides are treated with an ethereal solution of hydrogen bromide, first at the ordinary temperature (10—12 days), and then at the b. p. (3 hrs.), ethyl esters are again obtained (the first figures represent the percentage yields of ester from the acids, those in parentheses the yields from the anhydrides): acetic, 8 (13); chloroacetic, 30; propionic, 34 (23); *n*-butyric, 41 (38); isovaleric,

42 (41); oxalic, 8; malonic, 6; succinic, 16 (13); benzoic, 28 (49); phenylacetic, 56;  $\beta$ -phenylpropionic, 80; *p*-toluic, 23; mandelic, 24; anisic, 5; *p*-chlorobenzoic, 10; *o*-, *m*-, and *p*-nitrobenzoic, 5, 42, and 10, respectively; 3:5-dinitrobenzoic, 27; *p*-aminobenzoic, 1; phthalic 9 (13); diphenic, 16 (25). No esters were obtained from stearic, picric, *p*-toluenesulphonic, and 2:4:6-trinitrobenzoic acids by the same procedure.

II. When 1 mol. of ethyl, isopropyl, *n*-butyl, or isomyl ether is heated with 0.5 mol. of zinc chloride at the b. p. small amounts of the corresponding alcohol and unsaturated hydrocarbon are produced. In presence of an acid chloride, the alcohol affords the alkyl ester and the liberated hydrogen chloride converts some of the alcohol into alkyl chloride. A 77–79% yield of ethyl acetate can be obtained from ether and acetyl chloride, using only a relatively small amount of zinc chloride; the zinc chloride can be used repeatedly. When 1 mol. of the ether is treated with dry hydrogen bromide (about 0.25 mol.) fission into the alcohol and alkyl bromide occurs. Acetic anhydride is converted into acetyl bromide and acetic acid by treatment with hydrogen bromide. Anisole and diphenyl ether are not affected by treating with zinc chloride.

H. BURTON.

Catalysis in organic chemistry. III. Decomposition of esters by anhydrous zinc chloride. H. W. UNDERWOOD, jun., and O. L. BARIL (J. Amer. Chem. Soc., 1930, 52, 395–397).—When 1 mol. of methyl benzoate is heated with zinc chloride (0.5 mol.) at the b. p. some decomposition into benzene and benzoic acid occurs; ethyl benzoate affords ethylene in addition. Similarly, ethyl phthalate gives phthalic anhydride and ethylene; ethyl salicylate affords phenol, *o*-ethylphenol, and ethylene; methyl salicylate furnishes *o*-cresol; isomyl acetate, *n*-butyrate, and benzoate yield varying amounts of the corresponding acids, isopropylethylene, and polymerised isopropylethylene; ethyl cinnamate gives styrene, distyrene, metastyrene, and ethylene; ethyl oxalate furnishes ethyl chloride, saturated hydrocarbons, and a zinc salt (ethyl succinate behaves similarly), and ethyl malonate affords ethyl acetate, ethylene, and *n*-pentane. Ethyl formate, acetate, propionate, and *n*-butyrate are unaffected by heating with zinc chloride.

H. BURTON.

Effect of heat on crotonic acid. E. L. SKAU and B. SAXTON (J. Amer. Chem. Soc., 1930, 52, 335–341).—The mixtures obtained when crotonic acid is heated at 125–175° are not binary as stated by Morrell and Hanson (J.C.S., 1904, 85, 1520), but contain at least three acids, namely, crotonic, isocrotonic, and probably  $\beta$ -crotonoxybutyric,  $\text{CHMe}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The last-named acid has not been obtained pure, and its amount is decreased by heating at higher temperatures. The system does not exhibit the phenomenon of false equilibrium as stated by Morrell and Hanson (*loc. cit.*).

H. BURTON.

Conjugated systems. II. Bromination of  $\beta$ -vinylacrylic acid. I. E. MUSKAT, B. C. BECKER, and J. S. LOWENSTEIN (J. Amer. Chem. Soc., 1930, 52, 326–332).—Treatment of vinylacrylic acid, m. p. 72°

(improved method of preparation given), with 1 mol. of bromine in chloroform affords  $\gamma\delta$ -dibromo- $\Delta^a$ -pentenoic acid, b. p. 156°/3 mm., which on keeping crystallises partly to a solid, m. p. 47° (cf. Farmer and Healy, A., 1927, 646). Thermal decomposition of the above dibromo-acid (in a vacuum) affords hydrogen bromide and the lactone,  $\text{CH}_2\cdot\overset{\text{O}}{\text{C}}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}$ , m. p. 143°, resolidifying at 162°, hydrolysed by alkali to acetoacrylic acid. Treatment of the dibromopentenoic acid with 2 mols. of sodium hydroxide solution at 0° affords the sodium salt of  $\gamma$ -bromovinylacrylic acid, m. p. about 106°. Addition of bromine to the last-named acid gives  $\gamma\delta$ -tribromo- $\Delta^a$ -pentenoic acid, b. p. about 172°/10 mm., which on ozonisation affords  $\alpha\beta$ -tribromopropaldehyde.

H. BURTON.

Synthetic glycerides. II. Refractive indices of glycerides of known constitution. H. P. AVERILL, J. N. ROCHE, and C. G. KING (J. Amer. Chem. Soc., 1930, 52, 365–367).—An apparatus for the use of an immersion refractometer in a constant-temperature bath is described. The values of  $n$  at 70° and 75° for five pairs of isomeric mixed triglycerides show that of each pair the symmetrical isomeride has the higher value; equivalent mixtures show intermediate values. The values of  $n^{70}$  quoted are:  $\alpha$ - and  $\beta$ -stearodilaurin, 1.43986 and 1.44031;  $\alpha$ - and  $\beta$ -stearodipalmitin, 1.44289 and 1.44325;  $\alpha$ - and  $\beta$ -laurodimyristin, 1.43798 and 1.43901;  $\alpha$ - and  $\beta$ -laurodipalmitin, 1.44016 and 1.44044;  $\alpha$ - and  $\beta$ -acetodipalmitin, 1.43709 and 1.43749, respectively.

H. BURTON.

Electrolysis of palmitic acid and preparation of pentadecene. S. LANDA and M. LANDOVA (Coll. Czech. Chem. Comm., 1930, 2, 31–35).—Electrolysis of potassium palmitate by Petersen's method (A., 1900, ii, 522) and under reflux furnished two main fractions, b. p. 141–143°/15 mm., and 170–180°/15 mm. The former, after conversion into  $\alpha\beta$ -dibromopentadecane, b. p. 204–205°/17 mm.,  $d_4^{20}$  1.2235,  $n_D^{20}$  1.48971 (corresponding diacetate, m. p. 52–53°), and treatment with zinc-copper alloy in the presence of alcohol, yielded pentadecene, b. p. 144–145°/15 mm.,  $d_4^{20}$  0.7809,  $n_D^{20}$  1.44434, heat of combustion at constant volume 2356.8 kg.-cal., oxidised by potassium permanganate to myristic acid, m. p. 50°. The viscosity of pentadecene over the range 0–50° has been determined. The fraction of higher b. p. gave pentadecanol, isolated as the phenylurethane, m. p. 72°.

A. I. VOGEL.

Sulphonated oils. VI. Reaction mechanism between aqueous solution of sulphuric acid esters of hydroxy-fatty acids and salts. VII. Preparation and properties of pure alkali hydrogen salts of the sulphuric acid ester of ricinoleic acid. K. NISHIZAWA, K. WINOKUTI, and T. KIKUTTI (J. Soc. Chem. Ind. Japan, 1929, 32, 277B, 278B).—VI. Addition of inorganic salts to the aqueous solution of the sulphonation product of ricinoleic acid causes precipitation of the acid salt according to the equation  $(\text{SO}_3\text{H}\cdot\text{O})_n\cdot\text{R}\cdot\text{CO}_2\text{H} + n\text{XA} \rightleftharpoons (\text{SO}_3\text{X}\cdot\text{O})_n\cdot\text{R}\cdot\text{CO}_2\text{H} + n\text{HA}$ , where X and A are metallic and acidic radicals, respectively.

VII. The *hydrogen salts*,  $\text{CH}_3\cdot(\text{CH}_2)_5\cdot\text{CH}(\text{O}\cdot\text{SO}_3\text{X})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$  ( $\text{X}=\text{K}, \text{Na}, \text{and } \text{NH}_4$ ), have been prepared in the pure state. They are less stable towards precipitation by calcium and magnesium salts than is the normal salt.

A. A. GOLDBERG.

**Formation of petroleum of the naphthene type. Transformation of fatty acids into hydrocarbons under high pressure.** A. D. PETROV (Ber., 1930, 63, [B], 75—84).—When linolenic or myristic acid is heated with water in presence of aluminium oxide at 400° and a maximum pressure of 170 atm. and 250 atm., respectively, a product is obtained of which the fractions of lower b. p. contain a very considerable and similar content of naphthenes. The saturated acid is considered to lose carbon dioxide, giving a saturated hydrocarbon which undergoes cracking with production of unsaturated derivatives or to yield unsaturated acids which undergo cyclisation. Formation of ketones is observed to a minor extent. Support is thus rendered to the hypothesis of the formation of naphthenic petroleum from fatty acids of animal or vegetable origin.

Treatment of lactic acid with water and calcium hydroxide at 360°/130 atm. (maxima) yields an oil identical with those obtained by hydrolysis of cellulose with aqueous alkalis under pressure, and differing from the "synthol" of Fischer mainly in its smaller alcohol content. Treatment of the oil with sulphuric acid affords hydrocarbons identical with the corresponding "synthin" fractions, thus indicating a possible second source of naphthene hydrocarbons.

H. WREN.

**Action of peracetic acid on the acetylenic linking.** J. BÖESEKEN and G. SLOOFF (Rec. trav. chim., 1930, 49, 95—99).—Treatment of stearic acid (containing about 5% of stearic acid) with an acetic acid solution of peracetic acid gives, after 8 days, nonoic, azelaic, and small amounts of keto-stearic acids; more than 30% of the original acid is unaccounted for.  $\Delta^6$ -Undecenoic acid affords a mixture of products containing suberic and formic acids; oxidation occurs less readily than with oleic acid.  $\Delta^6$ -Undecenoic acid is oxidised even less readily than its isomeride (sebacic acid is isolated after 50 days), indicating that hydrogen attached to the acetylenic linking has a retarding action on the oxidation. When oxidation of the acetylenic linking does occur, the course of the reaction is more complicated than with the double linking.

H. BURTON.

**Isolation of erucic acid.** W. KIMURA (J. Soc. Chem. Ind. Japan, 1929, 32, 262—263b).—The various methods for isolating erucic acid from the liquid unsaturated acids contained in rape oil are compared.

A. A. GOLDBERG.

**Constitution of arylamides of lævulic acid. Transformation of 2-hydroxy-1-phenyl-2-methyl-5-pyrrolidone into lævulanilide.** R. LUKES and V. PRELOČ (Coll. Czech. Chem. Comm., 1929, i, 617—623; cf. A., 1929, 824).—Of the three theoretically possible constitutions for lævulanilide only the structure  $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$  is in accordance with experimental evidence.

Lævulanilide and *p*-toluidine in hot toluene afford lævulanilide *p*-tolylimide, m. p. 153°, decomposed by boiling water into *p*-toluidine and lævulanilide. Similarly, aniline and lævul-*p*-toluidide, m. p. 108—109°, are derived from lævul-*p*-toluidide anil, m. p. 142—143°. Hydrogenation of the last-named compound followed by hydrolysis of the product affords 1-phenyl-2-methyl-5-pyrrolidone, m. p. 51—52°, whereas the *p*-tolylimide of lævulanilide affords *p*-toluidine and 1-*p*-tolyl-2-methyl-5-pyrrolidone, m. p. 82.5°. Lævulanilidephenylhydrazone, m. p. 107°, prepared from lævulanilide or 2-hydroxy-1-phenyl-2-methyl-5-pyrrolidone, is converted by benzaldehyde in boiling alcohol into lævulaldehyde.

A. I. VOGEL.

**Action of peracetic acid on *o*-diketostearic acid, benzil, 1:2-naphthaquinone, and *o*-benzoquinone.** J. BÖESEKEN and G. SLOOFF (Rec. trav. chim., 1930, 49, 91—94).—*o*-Diketostearic acid is oxidised by peracetic acid in acetic acid solution to nonoic (90% of theory) and azelaic acids (95% of theory). Whilst diacetyl is oxidised readily, benzil is only slowly converted into benzoic acid. 1:2-Naphthaquinone is oxidised readily to 2-carboxy-*allocinnamic acid*, m. p. 198—203° (anhydride, m. p. 152°), whilst *o*-benzoquinone yields probably *cis-cis-muconic acid*, m. p. 195°.

H. BURTON.

**Formation of *cis-cis*-muconic acid from *o*-benzoquinone with peracetic acid.** J. BÖESEKEN and G. SLOOFF (Proc. K. Akad. Wetensch. Amsterdam., 1929, 32, 1043—1045).—See preceding abstract.

H. F. GILLBE.

**Catalytic decomposition of tartronic acid.** A. TALVITIE (Suomen Kem., 1929, 2, 166—168).—The quantity of formic acid produced in the electrolytic oxidation of alkaline tartronate solutions shows that a fission of the molecule occurs in addition to oxidation.

A. I. VOGEL.

**Preparation and determination of sodium citrate.** M. CATULLO.—See B., 1930, 119.

**Preparation of  $\gamma$ -*D*-mannonolactone.** W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1930, 52, 403—405).— $\gamma$ -*D*-Mannonolactone is obtained in good yield by oxidising mannose, or the mannose-containing hydrolysate of ivory-nut meal, by Hudson and Isbell's method (A., 1929, 1043).

H. BURTON.

**Irreversible oxidation of organic compounds.**

IV. **Oxidation of aldehydes.** J. B. CONANT, J. G. ASTON, and C. O. TONGBERG (J. Amer. Chem. Soc., 1930, 52, 407—419).—The rates of oxidation of acetaldehyde, propionaldehyde, *n*- and *iso*-butaldehyde (all unimolecular), and dextrose (bimolecular) have been determined at 80° in presence of *N*-sulphuric acid and varying amounts of ceric sulphate, by the method previously described (A., 1927, 116). Except for dextrose, the rate alters only slightly with change in concentration of the ceric sulphate. The rate decreases considerably when oxidation is carried out at 60°. Oxidation of various aliphatic aldehydes (second order reaction), and dextrose, lævulose, and  $\alpha$ - and  $\beta$ -naphthols (all first order reaction) with potassium ferricyanide (cf. *loc. cit.*; A., 1928, 1357), molybdicyanide, and tungsticyanide shows that the

rate is a function of the alkalinity of the solution, and that, it increases with rise of  $pH$ . The reactions studied can be formulated in terms of "apparent oxidation potentials" (cf. *loc. cit.*).

Oxidation of phenyl isopropyl ketone with alkaline potassium ferricyanide at 85–90° affords some phenyl  $\beta$ -aminoisopropyl ketone (Gabriel, A., 1911, i, 212). Similarly, methyl isopropyl ketone furnishes some methyl  $\beta$ -aminoisopropyl ketone (*benzenesulphonyl* derivative, m. p. 93.5–94°) H. BURTON.

**Romijn's formaldehyde titration.** R. SIGNER (Helv. Chim. Acta, 1930, 13, 43–46).—In the determination of formaldehyde by Romijn's method (A., 1897, ii, 166), the concentrations of both formaldehyde and sodium hypiodite (*i.e.*, iodine) are important. With relatively concentrated solutions of both reactants, better results are obtained than with dilute solutions containing the same amounts. With a small amount of formaldehyde and a very large excess of iodine, dilution does not cause such differences in the results. In the first of the above cases, transformation of the hypiodite into iodide and iodate occurs more readily than the oxidation of the aldehyde.

H. BURTON.

**Aldehydes containing the ether-oxygen group.** S. SABETAY (Bull. Soc. chim., 1929, [iv], 45, 1161–1169).—The following aldehydes containing an ether-oxygen linking have been obtained from the corresponding acetals by hydrolysis with dilute sulphuric acid. The latter were obtained by condensation of chloroacetal with the corresponding alcohol or phenol in presence of potassium hydroxide and copper powder:  $\gamma$ -phenylpropoxyacetaldehyde, b. p. 130–131°/6 mm. (semicarbazone, m. p. 120°; ethylacetal, b. p. 146–149°/7 mm.,  $d^{20}_D$  0.9785,  $n^{20}_D$  1.4798); *n*-octoxyacetaldehyde, b. p. 93–94°/6 mm. (semicarbazone; ethylacetal, b. p. 121.5–122°/5 mm.,  $d^{15}_D$  0.8823,  $n^{15}_D$  1.4286); *o*-methoxyphenoxyacetaldehyde, b. p. 120–121°/6 mm. (semicarbazone, m. p. 153°; acetal, b. p. 167–168°/19 mm.,  $d^{20}_D$  1.059,  $n^{20}_D$  1.4937); *p*-methoxyphenoxyacetaldehyde, b. p. 143–144°/14 mm.,  $d^{20}_D$  1.176,  $n^{20}_D$  1.5383 (semicarbazone, m. p. 168–169°; acetal, b. p. 166–168°/15 mm.,  $d^{20}_D$  1.058,  $n^{20}_D$  1.4954); eugenyl- (? isoeugenyl)-oxyacetaldehyde (semicarbazone, m. p. 189–189.5°; acetal, b. p. 175–176°/6 mm.,  $d^{20}_D$  1.036,  $n^{20}_D$  1.5116); 1:2:3:4-tetrahydro-6-naphthoxyacetaldehyde, b. p. 150–151°/7 mm. (semicarbazone, m. p. 168.5°; acetal, b. p. 172–174°/6 mm.,  $d^{20}_D$  1.043,  $n^{20}_D$  1.5114); and *p*-tert-butylphenoxyacetaldehyde, b. p. 122–123°/5 mm.,  $d^{20}_D$  1.024,  $n^{20}_D$  1.5142 (semicarbazone, m. p. 190–191°; acetal, b. p. 151–152°/5 mm.,  $d^{15}_D$  0.974,  $n^{15}_D$  1.4866). The acetals of the following aldehydes were obtained by condensation of the alcohol with sodium ethoxide and removal of the ethyl alcohol under reduced pressure (5 mm.): citronelloxyacetaldehyde, b. p. 128–130°/12 mm. (acetal, b. p. 147–149°/8 mm.,  $d^{19}_D$  0.8911,  $n^{19}_D$  1.4438); rhodinoxyacetaldehyde, b. p. 112–116°/5 mm. (acetal, 143–147°/8 mm.); neryloxyacetaldehyde (acetal), geranoxyacetaldehyde (acetal), *n*-dodecoxyacetaldehyde, b. p. 155–156°/9 mm., m. p. 16–17°,  $d^{21}_D$  1.44 (acetal, b. p. 176°/8 mm.,  $n^{20}_D$  1.4335,  $d^{20}_D$  0.8697); and cyclohexoxyacetaldehyde (acetal, b. p. 107–108°/6.5 mm.,  $d^{20}_D$  0.94;  $n^{20}_D$  1.4382). The acetal of linaloxyacet-

aldehyde, b. p. 128–130°/5 mm.,  $n^{20}_D$  1.4456, is decomposed completely on hydrolysis. Introduction of the ether-oxygen linking, *e.g.*, into myristaldehyde, giving laurinoxyacetaldehyde, definitely increases the strength and persistency of the odour. In compounds of the type  $R \cdot O \cdot CH_2 \cdot CHO$  this effect is more pronounced when R is alkyl or aralkyl than when R is aryl or a hydroaromatic group. *n*-Octoxyacetaldehyde possesses a very strong and persistent odour and similarly in geranoxy- and rhodinoxy-acetaldehydes the odour of roses is persistent and slightly piquant.

R. BRIGHTMAN.

**Action of ammonia on bromoacetaldehyde and preparation of pyrazine.** A. E. TSCHITSCHIBABIN and M. N. SCHTSCHUKINA (J. Russ. Phys. Chem. Soc., 1929, 61, 1645–1650).—See A., 1929, 686.

**Formation of glyoxalosazones by the interaction of dichloroacetaldehyde and arylhydrazines.** F. D. CHATTAWAY and L. H. FARINHOLT (J.C.S., 1930, 94–98).—When dichloroacetaldehyde (or its alcoholate) is treated with an arylhydrazine in acetic acid solution, the initially formed arylhydrazone loses hydrogen chloride, yielding a crimson solution. The colour is due to the intermediate production of an unstable azo-derivative of chloroethylene, and since this arises from a reversible reaction,  $NHAr \cdot N : CH \cdot CHCl_2 \rightleftharpoons NAr \cdot N : CH : CHCl + HCl$ , the colour disappears on heating and a glyoxalosazone is obtained:  $NHAr \cdot N : CH \cdot CHCl_2 \xrightarrow{NHAr \cdot NH} (NHAr \cdot N : CH)_2$ . Thus, dichloroacetaldehyde alcoholate and phenylhydrazine yield glyoxaldiphenyl-osazone, m. p. 169–171°. Using the requisite arylhydrazine the following are prepared: glyoxal-di-*p*-chlorophenylosazone, m. p. 227° [decomp.; diacetyl derivative, m. p. about 330° (decomp.)]; -di-2:4-dichlorophenylosazone, m. p. 253–254° [decomp.; diacetyl derivative, m. p. 291–292° (decomp.)]; -di-2:4:6-trichlorophenylosazone, m. p. 189° [diacetyl derivative, m. p. about 370° (decomp.)]; -di-*p*-bromophenylosazone, m. p. 215° [decomp.; diacetyl derivative, m. p. about 340° (decomp.)]; -di-2:4-dibromophenylosazone, m. p. 243° (decomp.) after darkening at 237° [diacetyl derivative, m. p. 300° (decomp.)], and -di-2:4:6-tribromophenylosazone, m. p. 226–228° [decomp.; diacetyl derivative, m. p. about 365° (decomp.)].

When glyoxal-diphenyl-, -*p*-chlorophenyl-, or -2:4-dichlorophenyl-osazone is chlorinated in acetic acid solution, dichloroglyoxaldi-2:4-dichlorophenylosazone, m. p. 248–251° (decomp.) after darkening at about 240°, is produced in each case. Dichloroglyoxaldi-2:4:6-trichlorophenylosazone, m. p. 229–231° (decomp.), is obtained by chlorination of the di-2:4:6-trichlorophenylosazone. Bromination of the above osazones causes replacement of both nuclear and glyoxal hydrogen atoms. Dibromoglyoxal-di-2:4-dibromophenylosazone, m. p. 205° (decomp.), -di-2:4:6-tribromophenylosazone, m. p. 230° (decomp.), -di-2:4-dichlorophenylosazone, m. p. 270–273° (decomp.), and -di-2:4:6-trichlorophenylosazone, m. p. 246° (decomp.), and dichloroglyoxaldi-2:4:6-tribromophenylosazone, m. p. 257° (decomp.), are described.

H. BURTON.

**Interaction of butyl chloral hydrate and 2:4-dihalogenated phenylhydrazines.** F. D. CHATTAWAY and H. IRVING (J.C.S., 1930, 87—94).—Butyl chloral hydrate and 2:4-dichlorophenylhydrazine hydrochloride react in aqueous sodium acetate at 75°, yielding an unstable, crimson product, which eliminates hydrogen chloride very readily, forming  $\alpha\beta$ -dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone (I), m. p. 112°. The colour of the initial product is probably due to the reversible loss of hydrogen chloride from butyl chloral-2:4-dichlorophenylhydrazone, giving  $\beta\gamma$ -dichloro- $\alpha$ -2:4-dichlorobenzeneazo- $\Delta^2$ -butene. Reduction of I with tin and hydrochloric and acetic acids affords 2:4-dichloroaniline, and treatment with bromine in cold acetic acid furnishes  $\alpha\beta$ -dichloro- $\alpha\beta$ -dibromobutaldehyde-2:4-dichlorophenylhydrazone, m. p. 126—127° (decomp.). Treatment of I with chlorine in acetic acid suspension affords  $\alpha\beta\beta\omega$ -pentachlorobutaldehyde-2:4:6-trichlorophenylhydrazone, m. p. 84—85° (N-acetyl derivative, m. p. 108—109°), which on reduction yields 2:4:6-trichloroaniline. Carefully regulated addition of chlorine to the N-acetyl derivative, m. p. 122.5°, of I furnishes  $\alpha\alpha\beta\beta$ -tetrachlorobutaldehyde-N-acetyl-2:4-dichlorophenylhydrazone, m. p. 97—98°.

Butyl chloral hydrate and 2:4-dichlorophenylhydrazine hydrochloride react in boiling alcohol or acetic acid affording  $\beta$ -chloro- $\alpha$ -ketobutaldehyde-2:4-dichlorophenylhydrazone (II), m. p. 129° (N-benzoyl derivative, m. p. 166.5°). Treatment of this with methyl-alcoholic 2:4-dichlorophenylhydrazine hydrochloride gives  $\alpha$ -keto- $\beta$ -methoxybutaldehyde-2:4-dichlorophenyllosazone, m. p. 196° (decomp.) [the corresponding  $\beta$ -ethoxy-compound, m. p. 162° (decomp.), is produced when alcohol is used], which is also formed, together with II, when butyl chloral hydrate and 2:4-dichlorophenylhydrazine hydrochloride react in boiling methyl alcohol.

Similar series of reaction with 2-chloro-4-bromo- and 2:4-dibromo-phenylhydrazines give rise to the following new compounds:  $\alpha\beta$ -dichlorocrotonaldehyde-2-chloro-4-bromophenylhydrazone, m. p. 118° (N-acetyl derivative, m. p. 134°), and -2:4-dibromophenylhydrazone, m. p. 119.5° (N-acetyl derivative, m. p. 141°);  $\alpha\beta$ -dichloro- $\alpha\beta$ -dibromobutaldehyde-2:4-dibromophenylhydrazone, m. p. 132—133° (decomp.);  $\beta$ -chloro- $\alpha$ -ketobutaldehyde-2-chloro-4-bromophenylhydrazone, m. p. 135°, and -2:4-dibromophenylhydrazone, m. p. 143.5° (N-benzoyl derivative, m. p. 183.5°);  $\alpha$ -keto- $\beta$ -methoxy-, m. p. 194° (decomp.), and  $\alpha$ -keto- $\beta$ -ethoxy-butaldehyde-2:4-dibromophenyllosazone, m. p. 177° (decomp.). H. BURTON.

**Compounds of the citronellic and rhodinol series.** J. DŒUVRE (Bull. Soc. chim., 1929, [iv], 45, 1098—1107).—A recapitulation of work already published (this vol., 59). On oxidation with potassium permanganate and chromic oxide, pure, natural d-citronellal yields 78% of acetone.

R. BRIGHTMAN.

**Bromomalonic dialdehyde.** J. GRARD (Compt. rend., 1930, 190, 187—189).—In aqueous solution bromomalonic dialdehyde behaves as a true acid,  $pH_2$ . The copper, zinc, and nickel salts are described. Application of Meyer's method (A., 1911, i, 301)

shows that the keto-enolic equilibrium in alcoholic solution is established only after 48 hrs. and corresponds with 24% of the enol at the ordinary temperature; a rise of temperature raises the concentration of the enol. When heated with alkalis it affords formic acid, methyl alcohol, and the alkali bromide. Sodium ethoxide and bromine yield the sodium salt, which is converted by dilute acids into the compound  $OH\cdot CH_2C(OEt)\cdot CHO$ , m. p. 135°. Bromomalonic dialdehyde gives with Grignard's reagent, in poor yield, the compound  $CHO\cdot CHBr\cdot CHMe\cdot OH$ ,  $d_4^{20}$  1.5258,  $n_D^{20}$  1.5105. Urethane condenses with the dialdehyde to give a compound, m. p. 169—171°.

C. C. N. VASS.

**Iodometric determination of organic compounds.** W. H. HATCHER and W. H. MUELLER (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 35—44).—The determination of acetone, formaldehyde, acetaldehyde, and pyruvic acid in dilute aqueous solutions by the action of iodine and sodium hydroxide solutions followed by determination of the residual iodine after acidification has been studied with reference to the effects of alkalinity and of the order of mixing of the reagents, viz., (a) substance, sodium hydroxide, iodine, (b) substance, iodine, sodium hydroxide, or (c) iodine, sodium hydroxide, substance.

A maximum of 94.5% of acetone was determinable with order (a) when the excess of alkali was increased to nine times the theoretical amount. About 45% reaction occurred with order (b) and 17% with order (c). Increased dilution or time of reaction increased the amount of acetone converted, but complete conversion was not attained. Increasing the time of keeping of acetone and sodium hydroxide before addition of iodine had no effect.

Formaldehyde (Romijn, A., 1897, ii, 166; Borgstrom and Horsch, A., 1923, ii, 590) is determined practically quantitatively with orders (a) or (b), and 40% excess of alkali. Order (c) gives very incomplete reaction.

The reaction of acetaldehyde (Wieland, A., 1924, i, 606) is only about 60% complete with order (a) and less with (b) and (c), even with seven times the theoretical amount of alkali.

The reaction of pyruvic acid is 94.5% complete with order (a), less with (b) and (c), with six times the theoretical amount of alkali (cf. Wieland, *loc. cit.*). Increasing the dilution or time of reaction has little effect.

In general, it is concluded that a large excess of hydroxyl ion must be present, and the effect of this is particularly marked where iodination is the principal reaction. R. K. CALLOW.

**Allyl and propenyl ketones.** L. COPPENS (Bull. Soc. chim. Belg., 1929, 38, 310—316).—By Blaise's method (A., 1904, i, 290) the following unsaturated ketones are prepared, a mixture of the allyl and propenyl ketones being obtained directly by the action of zinc and allyl or propenyl iodide on the nitrile, and their ultra-violet absorption spectra are plotted (with CASTILLE): ethyl allyl ketone, b. p. 124—124.2°,  $d_4^{20}$  0.84976,  $n_D^{20}$  1.42443 (absorption spectrum, maximum  $\lambda$  2824,  $\epsilon$  58.3; minimum  $\lambda$  2529,



$\epsilon$  23.3); ethyl propenyl ketone, b. p. 140.4—140.6°,  $d_4^{20}$  0.85587,  $n_D^{20}$  1.43911 (maximum,  $\lambda$  3247,  $\epsilon$  28; minimum  $\lambda$  2598,  $\epsilon$  4.6); cyclopropyl allyl ketone, b. p. 157—157.4°/761 mm.,  $d_4^{20}$  0.91721,  $n_D^{20}$  1.45846 (maximum  $\lambda$  2824,  $\epsilon$  58; minimum  $\lambda$  2620,  $\epsilon$  2.7); and cyclopropyl propenyl ketone, b. p. 173—173.5°/761 mm.,  $d_4^{20}$  0.93476,  $n_D^{20}$  1.47616 (maximum,  $\lambda$  3129,  $\epsilon$  28; minimum  $\lambda$  2703,  $\epsilon$  7). J. W. BAKER.

**Semicarbazones of isobutylidene- and isoamylidene-acetones.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 1126—1132).—When treated with the theoretical amount of semicarbazide in aqueous alcohol isobutylideneacetone affords no precipitate even on dilution; with 2 mols. of semicarbazide, the semicarbazidosemicarbazone, m. p. 188—189°, is obtained. If the isobutylideneacetone is previously boiled for a few minutes with 20% sulphuric acid, a semicarbazone, m. p. 126°, is obtained together with the isomeric compound, m. p. 164—165°, described by Kishner (A., 1913, i, 1165). The latter compound is also obtained by hydrolysis of the residues, b. p. 130—150°/15 mm., obtained in the preparation of 3-methyl-5-isopropylpyrazoline (this vol., 94) and is the semicarbazone of  $\beta$ -methyl- $\Delta^6$ -hexen- $\epsilon$ -one, b. p. 152—153°/745 mm.,  $d_4^{21}$  0.8643,  $n_D^{21}$  1.4417, and not of isobutylideneacetone, as Kishner supposed. With sodium hypobromite  $\beta$ -methyl- $\Delta^6$ -hexen- $\epsilon$ -one yields bromoform and an acid which with 20% sulphuric acid yields a tar and not isohexolactone. Attempts to synthesise this ketone by the action of magnesium methyl iodide on acetylacetone yielded almost exclusively  $\beta$ -dimethylhexane- $\beta$ -diol, b. p. 92—93°, with only traces of  $\beta$ -methyl- $\Delta^6$ -hexen- $\epsilon$ -one and a little  $\beta$ -methylhexan- $\beta$ -ol- $\epsilon$ -one (semicarbazone, m. p. 135°). With phenylmethylhydrazine acetylacetone yields in place of the expected monophenylhydrazone (cf. Diels and Johlin, A., 1911, i, 254) N-methylanilino-2:5-dimethylpyrrole, b. p. 145—146°/17 mm. The indefinite b. p. of isobutylideneacetone and the sticky deposits obtained by the action of semicarbazide are regarded as indicating the existence of this ketone and its semicarbazones in stereoisomeric forms. isoAmylideneacetone when similarly boiled with 20% sulphuric acid before treatment with semicarbazide yields the two semicarbazones, m. p. 100° and 113—114°, described by Léser (A., 1898, i, 512), the latter when kept at 90—100° for 24 hrs. having m. p. 118—120°. With 2 mols. of semicarbazide in aqueous alcohol, isoamylideneacetone yields the semicarbazidosemicarbazone, m. p. 205° (decomp. 185° when slowly heated; cf. Tiemann, A., 1900, i, 275).

R. BRIGHTMAN.

**Identification of stereoisomeric ethylenic ketones.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 1112—1124).—Largely a recapitulation of published results (A., 1928, 509). The property of unsaturated ketones containing an  $\alpha\beta$ -ethylenic linking of yielding pyrazolines with hydrazine (A., 1929, 1183), whereas other unsaturated ketones yield hydrazones or azines, is applied to the determination of the structure of the methyl  $\alpha$ -ethyl- $\Delta^a$ -propenyl ketones and methyl  $\alpha$ -n-propyl- $\Delta^a$ -butenyl ketones. The methyl  $\alpha$ -ethyl- $\Delta^a$ -propenyl ketones both yield 3:5-dimethyl-4-ethyl-

pyrazoline, b. p. 72—73°/10 mm., and hence must be stereoisomeric  $\alpha\beta$ -unsaturated ketones. This similarity of constitution is supported by the similarity of the absorption curves, both curves showing maxima at 3240 and 3000 Å., due to the carbonyl group and the conjugated double linking, respectively. Similarly, the methyl  $\alpha$ -n-propyl- $\Delta^a$ -butenyl ketones yield the same 3-methyl-5-ethyl-4-n-propylpyrazoline, b. p. 100°/11 mm.,  $d_4^{21}$  0.9055,  $n_D^{21}$  1.4692, and accordingly the ketones are  $\alpha\beta$ -unsaturated stereoisomerides. Hydroxyketones of the type  $(R\cdot CH_2)_2C(OH)\cdot CO\cdot Me$  thus yield stereoisomeric  $\alpha\beta$ -unsaturated ketones on dehydration.

Oxidation of the ketones with alkali hypochlorite or hypiodite did not yield substituted acrylic acids,  $CHR\cdot C(CH_2R)\cdot CO_2H$  (cf. Colonge, A., 1927, 449), but a lachrymatory oil, stable to sodium hydroxide, and traces of chloroform. Ozonisation similarly afforded little evidence regarding the constitution of these ketones. Methyl  $\alpha$ -ethyl- $\Delta^a$ -propenyl ketone yields much acetic acid, a small quantity of an oil, probably pentane- $\beta\gamma$ -dione, giving a dioxime, m. p. 170—171° (cf. Fileti and Ponzio, A., 1897, i, 317), but no propionic acid, and methyl  $\alpha$ -n-propyl- $\Delta^a$ -butenyl ketone yields a trace of hexane- $\beta\gamma$ -dione (dioxime, m. p. 165—166°; cf. Fileti and Ponzio, A., 1895, i, 499), a little acetic and propionic acids, but no butyric acid.

R. BRIGHTMAN.

**Dehydration of  $\alpha$ -hydroxyketones.** R. LOCQUIN and R. HEILMANN (Bull. Soc. chim., 1929, [iv], 45, 1107—1112).—Dehydration of  $\gamma$ -ethylpentan- $\gamma$ -ol- $\delta$ -one with sulphuric acid containing the theoretical amount of sulphuric anhydride for the dehydration, at 0° yields 65% of an oil,  $C_7H_{14}O_2$ , b. p. 150—155°, from which two ketones, b. p. 150°/747 mm.,  $d_4^{21}$  0.8718,  $n_D^{21}$  1.4593 (semicarbazone, m. p. 201°), and b. p. 153—154°/747 mm.,  $d_4^{21}$  0.8789,  $n_D^{21}$  1.4554 (semicarbazone, m. p. 161°), are separated by means of their semicarbazones. Similarly,  $\delta$ -propylhexan- $\delta$ -ol- $\epsilon$ -one yields 80—85% of an oil,  $C_9H_{16}O$ , b. p. 68—74°/10 mm., composed of a mixture of two ketones, b. p. 71°/11 mm.,  $d_4^{21.5}$  0.8620,  $n_D^{21.5}$  1.4563 (semicarbazone, m. p. 142°), and b. p. 74°/11 mm.,  $d_4^{21}$  0.8668,  $n_D^{21}$  1.4573 (semicarbazone, m. p. 110°, and then 120—121° after resolidifying).

R. BRIGHTMAN.

**Colorimetric determination of rhamnose.** R. McCANCE (Biochem. J., 1929, 23, 1172—1174).—The sugar is determined as methylfurfuraldehyde obtained by heating rhamnose with hydrochloric acid and extracting the compound with benzene.

S. S. ZILVA.

**Fucose (l-galactomethylose) and epifucose (l-talomethylose) series.** E. VOTOČEK and V. KUČERENKO (Coll. Czech. Chem. Comm., 1930, 2, 47—53).—Treatment of fuconolactone with aqueous pyridine for 3 hrs. at 145° gave epifuconic acid, separated from the attendant fuconic acid by precipitation of the aqueous solution of the barium salts with alcohol, converted into epifuconophenylhydrazide, m. p. 178°,  $[\alpha]_D^{20} +17.6^\circ$  in water, which yielded epifuconolactone, m. p. 126—127°,  $[\alpha]_D^{20} +36.7^\circ$  in water, with aqueous baryta at 100°. Reduction of the latter with sodium amalgam gave epifucose,  $[\alpha]_D^{20} -36.9^\circ$  in water (phenylmethylhydrazide, m. p.

137°; *p*-bromophenylosazone, m. p. 203—203.5°; further reduction in acid solution yielded *epifucitol*, m. p. 104°,  $[\alpha]_D -2.3^\circ$  in water (benzylidene derivative, m. p. 183°,  $[\alpha]_D +39.7^\circ$  in chloroform). The rotatory powers are in agreement with the views of Hudson.

A. I. VOGEL.

**Rhodoese (*d*-galactomethylose) and *epi*-rhodoese (*d*-talomethylose) series.** E. VOTOČEK and F. VALENTIN (Coll. Czech. Chem. Comm., 1930, 2, 36—46).—The rotatory powers of some rhodoese and *epi*rhodoese derivatives have been determined and are in agreement with Hudson's rules. Tadokoro and Nakamura's methylfucoside,  $[\alpha]_D -122^\circ$ , is optically impure, the pure *d*-compound having  $[\alpha]_D +189.9^\circ$  (Hudson predicted 189°). The mutarotation of rhodoese,  $[\alpha]_D^{18-19} +127.0^\circ$  to  $+76.0^\circ$  in water, follows a unimolecular law. *Methylrhodoese*,  $[\alpha]_D +189.9^\circ$  in water (*phenylbenzylhydrazone*,  $[\alpha]_D -14.9^\circ$  in methyl alcohol), is prepared by the action of methylalcoholic hydrogen chloride on rhodoese at 100° for 50 hrs. in a closed vessel. *Rhodoesephenylbenzylhydrazone* has m. p. 178—179°,  $[\alpha]_D -14.9^\circ$  in methyl alcohol; rhodionophenylhydrazide, from rhodionolactone, m. p. 106°, has m. p. 205°,  $[\alpha]_D +12^\circ$  in water. *epi*Rhodionolactone, m. p. 128°,  $[\alpha]_D -28.6^\circ$  in water (corresponding phenylhydrazide, m. p. 170°,  $[\alpha]_D -17.7^\circ$  in water), was prepared by oxidising rhodoese with bromine water, and fractionally crystallising the barium salts; rhodeotetrolactone,  $[\alpha]_D +44.2^\circ$  in water, was similarly prepared. Rhodeotetrose,  $[\alpha]_D +32.4^\circ$  in water, was obtained by the Wohl degradation of rhodoese. Reduction of *epi*-rhodionolactone with sodium amalgam gave *epi*-rhodoese (*phenylmethylhydrazone*, m. p. 136°), converted by a further quantity of sodium amalgam in acid solution into *epirhoditol*, m. p. 104°,  $[\alpha]_D +2^\circ$  in water, purified through the benzylideneacetal derivative, m. p. 184°,  $[\alpha]_D -40.9^\circ$  in chloroform.

A. I. VOGEL.

**Sugar carbonates. IV. Dicarbonates of dextrose, lævulose, mannose, galactose, and arabinose.** W. N. HAWORTH and C. R. PORTER (J.C.S., 1930, 151—157).—Dicarbonates are prepared from the sugars mentioned in the title by treatment with carbonyl chloride in cold pyridine solution; amorphous by-products are usually formed. The esters are hydrolysed rapidly by dilute alkali in the cold, but less readily by dilute acids. *Dextrose dicarbonate*, m. p. 224° (decomp.) after sintering at 200°,  $[\alpha]_D -29^\circ$  in acetone containing 25% of water, *galactose dicarbonate*, m. p. 212° (decomp.) after slight sintering at 190°,  $[\alpha]_D^{21-23} -86.5^\circ$  in acetone containing 25% of water, *lævulose dicarbonate*, m. p. 173—174° (decomp.),  $[\alpha]_D^{16-18} -143^\circ$  in 50% aqueous acetone, and *arabinose dicarbonate*, m. p. 200—202° (decomp.),  $[\alpha]_D^{23-25} +61.3^\circ$  in acetone containing 33% of water, do not exhibit mutarotation in aqueous acetone, even after the addition of a trace of hydrochloric acid. *Mannose dicarbonate*, m. p. 122—123° (decomp.) after slight sintering at 118°,  $[\alpha]_D^{21-23} +26^\circ$  in acetone, when heated with alcoholic aniline yields an *anilide*,  $C_{14}H_{13}O_3N$ , m. p. 174—175°,  $[\alpha]_D^{23-25} -70^\circ$  after 5 min.,  $-32^\circ$  after 18 hrs. (in alcohol). The amorphous by-product formed during the preparation of lævulose

dicarbonate decomposes between 150° and 180° without melting, and has  $[\alpha]_D^{16-18} -58^\circ$  in acetone. The mol. wt. is intermediate between the values for 3 and 4 condensed dicarbonate molecules. Fractions differing in their solubilities were obtained by fractional precipitation of an acetone solution with ether.

Constitutional formulæ, based on the similarity in properties to the diisopropylidene derivatives, are given for the five dicarbonates. H. BURTON.

**Conversion of simple sugars into derivatives of 4-pyrone and preparation of further unsaturated anhydro-sugars. III.** K. MAURER (Ber., 1930, 63, [B], 25—34; cf. A., 1927, 751; 1929, 428).—2-Hydroxyglucal tetra-acetate [formerly designated tetra-acetylglucoseen (*loc. cit.*)] is converted by chlorine in anhydrous ether into the unstable dichloride, m. p. (indef.) 46—70°,  $[\alpha]_D^{20} +48.57^\circ$  to  $+43.98^\circ$  (not equilibrium value) in chloroform in 3 hrs., which, with silver carbonate and aqueous ether, affords 2:3:4:6-tetra-acetylglucosone hydrate,  $C_{14}H_{20}O_{11}$ , m. p. 112°,  $[\alpha]_D^{20} +14.69$  to  $+53.66^\circ$  in aqueous alcohol. If crystallisation of the dichloride cannot be induced, conversion into the hydrate is effected by aqueous ether. Hydrolysis of the last-named compound by 0.1*N*-sodium hydroxide and treatment of the product with phenylhydrazine acetate affords glucosazone, m. p. 213°. 2:3:4:6-Tetra-acetylglucosone hydrate is converted by acetic anhydride and pyridine into *diacetylkojic acid*,  $C_{10}H_{10}O_6$ , m. p. 102°, transformed by methyl-alcoholic ammonia successively into *acetylkojic acid*, m. p. 136°, and *kojic acid* [5-hydroxy-2-hydroxymethyl-4-pyrone], m. p. 152° (*dibenzoyl* compound, m. p. 136°).

Treatment of acetobromolactose with diethylamine in chloroform affords 2-hydroxylactal hepta-acetate, m. p. 166—167°,  $[\alpha]_D^{21} -17.07^\circ$  in chloroform; *hydroxycellobial hepta-acetate*, m. p. 125°,  $[\alpha]_D^{20} -21.47^\circ$  in chloroform, is similarly prepared. Neither anhydride affords an osazone with phenylhydrazine.

H. WREN.

**Mechanism of carbohydrate oxidation. XI.** Action of potassium hydroxide on maltose. W. L. EVANS and M. P. BENNY (J. Amer. Chem. Soc., 1930, 52, 294—307).—The action of aqueous potassium hydroxide on maltose has been studied at 25° and 50° by the methods previously described for other sugars (A., 1926, 149, 1228; 1928, 397, 741, 1222). Maltose yields larger amounts of formic acid than does dextrose under the same conditions, but affords smaller amounts of pyruvaldehyde, mannose, lactic and acetic acids. The explanation advanced to account for these differences is that maltose is converted into both 1:2- and 2:3-dienols, with subsequent oxidative degradation of the former into formic acid, dextrose, and erythrose, and the latter into glycollaldehyde, dextrose, and erythrose. The lactic acid and pyruvaldehyde are then formed from the dextrose, the total amount being approximately half of the amount from dextrose alone. Mannose-phenylhydrazone is formed slowly from maltose by treatment with 0.05—0.42*N*-potassium hydroxide and phenylhydrazine at 25°. It is produced either from dextrose or 4-glucosidomannose. H. BURTON.

**Walden inversion in glucoside fission.** W. SCHNEIDER and M. BECKER (Naturwiss., 1930, 18, 133).—Scission of sinigrin by aqueous silver nitrate in the presence of silver carbonate to remove the free nitric acid formed in accordance with the equation  $C_3H_5N:C(O\cdot SO_3K)\cdot S\cdot C_6H_{11}O_5 + 2AgNO_3 + H_2O = C_3H_5N:C(O\cdot SO_3Ag)\cdot SAg + C_6H_{12}O_6 + HNO_3 + KNO_3$  yields a sugar solution which has a higher dextro-rotation (mutarotation ultimately the equilibrium value) than that required for the total liberated  $\beta$ -dextrose, showing that the product of hydrolysis is  $\alpha$ -dextrose. Conversely, enzymic hydrolysis of the same glucoside gives a small levorotation, converted by addition of a few drops of ammonia into a dextro-rotation of ten times this value (corresponding with 55% hydrolysis). Since sinigrin is a  $\beta$ -glucoside the silver nitrate scission must involve a Walden inversion about the terminal carbon atom of dextrose.

J. W. BAKER.

**Natural glucosides. I. Constitution of phloridzin.** F. R. JOHNSON and A. ROBERTSON (J.C.S., 1930, 21—26).—Methylation of phloridzin by prolonged treatment with methyl iodide and potassium carbonate in dry acetone or with ethereal methyl-alcoholic diazomethane affords *trimethylphloridzin* (monohydrate, m. p. 63—65° after softening at 60°). This is hydrolysed by aqueous methyl-alcoholic sulphuric acid to 6-hydroxy-2:4-dimethoxyphenyl  $\beta$ -p-methoxyphenylethyl ketone, m. p. 110° (acetate, m. p. 62—63°), which on treatment with acetic anhydride and sodium acetate at 180° yields 5:7:4'-trimethoxy-3-benzyl-2-methyl-1:4-benzopyrone, m. p. 165—166°. Phloridzin is, therefore, 4:6-dihydroxy-2-glucosidoxyphenyl  $\beta$ -p-hydroxyphenylethyl ketone. Dehydration of  $\beta$ -p-methoxyphenylpropionamide with thionyl chloride gives  $\beta$ -p-methoxyphenylpropionitrile, b. p. 172—173°/17 mm., which condenses with phloroglucinol dimethyl ether in presence of zinc chloride and ethereal hydrogen chloride, yielding a mixture of ketimine hydrochlorides, hydrolysed to the above ketone and the isomeric 4-hydroxy-2:6-dimethoxyphenyl  $\beta$ -p-methoxyphenylethyl ketone, m. p. 142°.

H. BURTON.

**Formation of bases from carbonyl compounds. V. N-Alkylation of secondary amines; diastereoisomeric amino-alcohols.** A. SKITA and F. KEIL [with H. HAVEMANN and K. P. LAVROVSKI] (Ber., 1930, 63, [B], 34—50; cf. A., 1928, 1228; 1929, 441, 808, 1436).—Ethylisoamylamine is converted by formaldehyde and hydrogen in presence of colloidal platinum into methylethylisoamylamine, b. p. 133—137° (picrate, m. p. 101—102°). When similarly treated with acetaldehyde, propaldehyde, and isobutaldehyde, the secondary amine affords diethylisoamylamine, b. p. 153—157° (picrate, m. p. 74—75°), ethyl-n-propylisoamylamine, b. p. 167—168°/atm. press., 52—53°/14 mm. (picrate, m. p. 82°), and ethyl-isobutylisoamylamine, b. p. 56—57°/40 mm. (picrate, m. p. 60.5—61°), respectively, with compounds of higher b. p. Since ethylisoamylamine and isovaleraldehyde yield the secondary amine,  $C_{12}H_{27}N$ , b. p. 74—76°/13 mm. (picrate, m. p. 96.5—97.5°; methiodide,  $C_{14}H_{33}NI$ , m. p. 148.5—149.5°), the production of tertiary amine appears to cease in this

instance with isobutaldehyde. With the simpler dimethylamine, aldehydes of higher mol. wt. can, however, be used, thus leading to the following compounds: dimethyl- $\gamma\gamma$ -dimethyloctylamine, b. p. 94—95° (hydrogen oxalate, m. p. 159°), from citral; dimethylisoamylamine, b. p. 110—116° (picrate, m. p. 135°), from isovaleraldehyde; dimethylbenzylamine, b. p. 66—67°/15 mm. (very hygroscopic hydrochloride; picrolonate, m. p. 151°), from benzaldehyde; dimethyl- $\alpha$ -phenylethylamine, b. p. 73.5°/14 mm. (picrate, m. p. 138°), from acetophenone. cycloHexylethylamine and acetaldehyde afford cyclohexyldiethylamine, b. p. 193—195°/760 mm. (picrolonate, m. p. 147°).

Acetylacetone when reduced in presence of dimethylamine affords  $\delta$ -dimethylaminopentan- $\beta$ -ol, b. p. 63—65°/16 mm. (picrolonate, m. p. 120—121°), in good yield, but it is preferable to hydrogenate the ketone in presence of methylamine to  $\delta$ -methylaminopentan- $\beta$ -ol, b. p. 80—82°/17 mm. (picrolonate, m. p. 170°), and to hydrogenate the last-named compound in presence of formaldehyde. A limit to the production of tertiary compounds exists, since  $\gamma$ -ethylamino- $\alpha$ -phenylbutan- $\alpha$ -ol, b. p. 156—160°/12 mm. (picrate, m. p. 158°), from benzoylacetone and ethylamine, is transformed by reduction in presence of acetaldehyde into  $\gamma$ -diethylamino- $\alpha$ -phenylbutan- $\alpha$ -ol, b. p. 163—165°/14 mm. (benzoate, b. p. 230—234°/20 mm.), whereas  $\gamma$ -isoamylamino- $\alpha$ -phenylbutan- $\alpha$ -ol, b. p. 182°/16 mm. (picrolonate, m. p. 201°), from benzoylacetone and isoamylamine, is unchanged by hydrogenation in presence of isovaleraldehyde.

Hydrogenation of a mixture of acetylbenzoyl and ethylamine leads to  $\beta$ -ethylamino- $\alpha$ -phenylpropan- $\alpha$ -ol, b. p. 138°/18 mm., m. p. 47—48° (hydrochloride, m. p. 196—197°; benzoyl derivative,  $C_{18}H_{21}O_2N$ , b. p. 205—207°/16 mm.), converted by reduction in presence of formaldehyde into  $\beta$ -methylethylamino- $\alpha$ -phenylpropan- $\alpha$ -ol, b. p. 135—136°/15 mm. (hydrochloride, m. p. 171—172°). The following compounds are prepared from acetylbenzoyl and the requisite base:  $\beta$ - $\beta'$ -hydroxyethylamino- $\alpha$ -phenylpropan- $\alpha$ -ol, m. p. 109° (hydrochloride, m. p. 166°);  $\beta$ -isoamylamino- $\alpha$ -phenylpropan- $\alpha$ -ol, b. p. 162°/13 mm., m. p. 75—77° (hydrochloride, m. p. 210—212°);  $\beta$ -heptylamino- $\alpha$ -phenylpropan- $\alpha$ -ol hydrochloride, m. p. 223—225°. The products in every case consist of only one of the two possible forms.

Catalytic reduction of benzoylacetone in presence of dimethylamine yields the two diastereoisomeric  $\gamma$ -dimethylamino- $\alpha$ -phenylbutan- $\alpha$ -ols, the main product being the crystalline base, m. p. 74° (picrate, m. p. 126°); the non-crystalline modification, b. p. 144°/10 mm., yields a picrate, m. p. 139—140°. The solid variety is obtained by reduction of  $\gamma$ -methylamino- $\alpha$ -phenylbutan- $\alpha$ -ol (picrate, m. p. 193°) in presence of formaldehyde, whereas the diastereoisomeric monomethyl compound (picrate, m. p. 119°) gives the liquid modification.

Catalytic reduction of acetylacetone in presence of ethylamine yields  $\delta$ -ethylaminopentan- $\beta$ -ol, b. p. 70—72°/10 mm., separable into two picrolonates, m. p. 260° and 159°, respectively, the base from the last-named salt having b. p. 74°/11 mm. The existence of pure aliphatic, diastereoisomeric amino-alcohols is thus established.  $\delta$ -Diethylaminopentan- $\beta$ -ol, b. p. 78°/10

mm. (*picrolonate*, m. p. 137°; *benzoate*, b. p. 195—200°/16 mm.), is obtained from  $\delta$ -ethylaminopentan- $\beta$ -ol and acetaldehyde, from acetylacetone, ethylamine, and acetaldehyde in a single operation, or from acetylacetone and diethylamine. H. WREN.

**Additive compounds of halides of bivalent metals with organic bases.** VII. G. SCAGLIARINI and G. TARTARINI (Atti R. Accad. Lincei, 1929, [vi], 10, 267—270).—By mixing cold saturated solutions of hexamethylenetetramine and the metallic halide, both in 95% alcohol, the following crystalline compounds are obtained:  $2\text{MgCl}_2 \cdot 16\text{H}_2\text{O} \cdot 5\text{C}_6\text{H}_{12}\text{N}_4$ ;  $2\text{MgI}_2 \cdot 16\text{H}_2\text{O} \cdot 5\text{C}_6\text{H}_{12}\text{N}_4$ ;  $2\text{MgBr}_2 \cdot 16\text{H}_2\text{O} \cdot 5\text{C}_6\text{H}_{12}\text{N}_4$ ;  $2\text{CaCl}_2 \cdot 8\text{H}_2\text{O} \cdot 5\text{C}_6\text{H}_{12}\text{N}_4$ . T. H. POPE.

**Acetylcholine chloride.** L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1930, 52, 307—310).—Acetylation of  $\beta$ -dimethylaminoethyl alcohol with acetyl chloride in ether gives  $\beta$ -dimethylaminoethyl acetate, b. p. 86—88°/80 mm. (*hydrochloride*, m. p. 129—130°), which with methyl iodide affords *acetylcholine iodide*, m. p. 160—162°. This is converted by treatment with silver chloride in warm alcohol into the hygroscopic acetylcholine chloride, m. p. 151° (*chloraurate*, m. p. 168—169° (lit. 154—155°); *chloroplatinate*, m. p. 227° (decomp.; lit. 223—224° and 256—257°)]. H. BURTON.

**Guanidoethyl alcohol.** E. FROMM, P. FANTL, and J. FISCH (J. pr. Chem., 1930, [ii], 124, 163—167).—Interaction of  $\beta$ -aminoethyl benzoate hydrobromide (I) (*allylthiocarbamide*, m. p. 92°; *phenylthiocarbamide*, m. p. 108°) and cyanamide in the presence of alcohol for 5 hrs. at 115° gives  $\beta$ -*guanidoethyl benzoate* (*picrate*, m. p. 186°), in which the presence of an open chain is beyond question; this yields the *tribenzoyl* derivative of *guanidoethyl alcohol*, m. p. 156° (also prepared from I, *S*-ethyl- $\psi$ -thiocarbamide hydrobromide, and alcoholic potassium hydroxide, on benzylation of the product). Fromm and Honold's *guanidoethyl alcohol* (A., 1922, i, 531) therefore has an open chain and not a ring structure as Fromm and others (A., 1925, i, 595) supposed. Fromm and Frieder's 2-amino-2-methylamino-oxazolidine (A., 1925, i, 596) is accordingly methylguanidoethyl alcohol. *Guanidoethyl alcohol picrate* has m. p. 147°. A. I. VOGEL.

[Action of nitrosyl bromide on amino-acids.] G. ZEMPLÉN and Z. CSÜRÖS (Ber., 1930, 63, [B], 98).—In their previous communication (A., 1929, 1283), the authors have overlooked the work of Karrer (A., 1927, 55). H. WREN.

**Conversion of  $\beta$ -ketonic esters into  $\beta$ -amino-esters.** J. DÉCOMBE (Compt. rend., 1930, 190, 268—270).—The oximes and azines of  $\beta$ -ketonic esters are not reduced by hydrogen in the presence of platinum-black or of colloidal palladium, or by aluminium amalgam. The acetyl- and benzoylhydrazones are reduced by aluminium amalgam (three times the theoretical quantity) to the corresponding  $\beta$ -amino-esters, the latter being obtained in yields of 50—100%.

*Ethyl acetoacetate acetylhydrazone*, m. p. 90° (from acetylhydrazine and the ester in alcohol), is reduced to ethyl  $\beta$ -aminobutyrate, b. p. 82°/20 mm. (*chloroplatinate*; normal *oxalate*, m. p. 88—90°; *phenyl-*

*carbamide*, m. p. 110°). *Ethyl  $\beta$ -ketovalerate acetylhydrazone* has m. p. 93°. The acetylhydrazones of the higher ketonic esters are not obtained pure; the only crystalline compound,  $\text{C}_6\text{H}_{10}\text{ON}_2$ , m. p. 206°, isolated from ethyl  $\beta$ -ketoheptanoate and acetylhydrazine is possibly propylpyrazolone (cf. Curtius, A., 1895, i, 33), but *ethyl  $\beta$ -aminohexanoate*, b. p. 102—104°/25 mm. (*chloroplatinate*; normal *oxalate*; *phenylcarbamide*, m. p. 76°), is readily obtained by reduction of the crude reaction product.

The benzoylhydrazones are similarly not isolated (cf. Struve, A., 1895, i, 35), but the crude products are directly reduced. The resulting amino-esters are less pure than when obtained from the acetylhydrazones and are best purified through the *oxalate*.

*Ethyl  $\beta$ -amino-octanoate* has b. p. 132—133°/25 mm. (*chloroplatinate*; normal *oxalate*; *phenylcarbamide*, m. p. 114°). R. CHILD.

**Preparation of glycerol esters of amino-acids.** L. HASKELBERG (Compt. rend., 1930, 190, 270—272; cf. A., 1929, 1048, 1269).—The reaction of glycerol and pyruvic acid leads to (i) the crystalline product "pyruvin," m. p. 83·5° (*phenylhydrazine* derivative, m. p. 156°) ( $\alpha$ -lactone of Brigl, Schütze, and Hartung, this vol., 193); (ii) an oil, b. p. 118—119°/10 mm. (*oxime*, m. p. 119·5°, and its *tribenzoyl* derivative, m. p. 110°; *phenylhydrazone*, m. p. 114°), described as glycide pyruvic ester, and (iii) a residue insoluble in water and in ether.

*isoPropylideneglyceryl  $\alpha$ -bromopropionate*, b. p. 138°/10 mm., is converted into the  $\alpha$ -*oximinopropionate*, m. p. 43°, which on careful hydrolysis yields *glyceryl  $\alpha$ -oximinopropionate*, m. p. 118—118·5° (not identical with the above-mentioned *oxime*; *tribenzoyl* derivative, m. p. 79°). The latter on reduction gives the  $\alpha$ -monoglyceride of *dl*-alanine, isolated as the *picrate*, m. p. 265° (decomp.). R. CHILD.

**Kolbe's synthesis with cyanoacetic acid.** F. FICHTER and A. SCHNIDER (Helv. Chim. Acta, 1930, 13, 103—107; cf. Moore, A., 1871, 701).—When solutions of potassium cyanoacetate containing some of the free acid are electrolysed, a small amount of ethylene dicyanide, m. p. 54·5°, is formed; the amount increases with rise in the current density. The main reaction occurring is, however, the oxidation of cyanoacetic acid to hydrogen cyanide, carbon dioxide, and formaldehyde:  $\text{CN} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H} + \text{O} = \text{HCN} + \text{CO}_2 + \text{CH}_2\text{O}$ . This occurs by way of the intermediate percyanoacetic acid, which decomposes at the anode into the three products.

Barium peroxide and cyanoacetyl chloride in ether give some cyanoacetyl peroxide, which is converted by water into percyanoacetic acid. The acid is also formed from cyanoacetyl chloride and hydrogen peroxide in ether at the ordinary temperature. Percyanoacetic acid decomposes when warmed into hydrogen cyanide, carbon dioxide, and formaldehyde. H. BURTON.

**Pellitorine, the pungent principle of *Anacyclus pyrethrum*.** J. M. GULLAND and G. U. HOPTON (J.C.S., 1930, 6—11).—The residue from the alcoholic extract of the powdered root of *Anacyclus pyrethrum* (pellitory root) is extracted with ether, and the acid-free solution evaporated. Distillation of the syrup

obtained gives an oil, b. p. 150—275°/0.3 mm., which when fractionated yields *pellitorine*,  $C_{14}H_{25}ON$ , b. p. 162—165°/0.3 mm., m. p. 72° (corr.) (0.04% yield) (cf. Buchheim, A., 1876, i, 195, who calls the active principle pyrethrin; Dunstan and Garnett, J.C.S., 1895, 67, 100; Schneegans, A., 1897, i, 485). Hydrolysis of *pellitorine* with 2*N*-hydrochloric acid at 150° gives *isobutylamine* (*p*-toluenesulphonyl derivative, m. p. 75—76°), neutral nitrogenous material, and an oily, unsaturated acid (amide, m. p. 35°). Catalytic reduction of *pellitorine*, using palladised charcoal and methyl alcohol, affords *tetrahydropellitorine*, m. p. 35° (corr.), which is identical with *n*-decoisobutylamide. *Pellitorine* is, therefore, the *isobutylamide* of a *n*-nonadienecarboxylic acid. It is not identical with *piperovatine* (Dunstan and Garnett, J.C.S., 1895, 67, 94), but is closely related to *spilanthol* (*n*-decoisobutylamide) (Asahina and Asano, A., 1920, i, 654; 1922, i, 505). *Pellitorine* is one fifth as pungent as *piperine*.  
H. BURTON.

**Synthesis of dioxypyrimidone** [ $\alpha$ -acetyl- $\beta$ -dimethyloxamyl- $\beta$ -phenyl- $\alpha$ -methylhydrazine]. R. DELABY and R. CHARONNAT (Compt. rend., 1930, 190, 59—61).—The constitution assigned to “dioxypyrimidone,” obtained by oxidation of *pyrimidone* (Charonnat and Delaby, this vol., 223) has been confirmed by synthesis. Dimethyloxamic acid yields with thionyl chloride the *acid chloride*, b. p. 86.5—89.5°/14 mm., which reacts with  $\alpha$ -acetyl- $\beta$ -phenyl- $\alpha$ -methylhydrazine to give  $\alpha$ -acetyl- $\beta$ -dimethyloxamyl- $\beta$ -phenyl- $\alpha$ -methylhydrazine, identical with “dioxypyrimidone.” The mechanism of the oxidation of *pyrimidone* is discussed. Formation of a diamine oxide and subsequent migration of oxygen to carbon is preferred to direct rupture of the 3 : 4-double linking by addition of hydrogen peroxide and oxidation, but this cannot be supported by the isolation of any intermediate compound.  
R. K. CALLOW.

**isoCarbamides and isoureides. II. Condensation of isocarbamides with diketones and ketonic esters.** S. BASTERFIELD and E. C. POWELL (Canad. J. Res., 1929, 1, 285—291).—Ethylisocarbamide and acetylacetone interact when mixed without a solvent to give *ethylisoureidoacetylacetone*,  $NH_2C(OEt) \cdot NH \cdot CMe \cdot CH \cdot CO \cdot Me$ , m. p. 49—50°, which is unstable, and yields at the ordinary temperature 2-ethoxy-4 : 6-dimethylpyrimidine, m. p. 162° (decomp.), which gives a 5-bromo-derivative, m. p. 196°. The condensation of ethylisocarbamide with impure ethyl oxalacetate under similar conditions yields a gum, but with fractions of redistilled ester two substances,  $C_8H_{12}O_4N_2$ , m. p. 154° and 149°, have been obtained. The product from ethylisocarbamide and ethyl acetylpyruvate has not been obtained crystalline. Ethylisocarbamide and ethyl acetonedicarboxylate yield *ethyl 2-ethoxyuracil-4-acetate*, m. p. 112.5°, which forms the 4 : 5-dibromide, m. p. 175°, and is hydrolysed by alkali to the *acid*, which loses carbon dioxide above 150° to yield 2-ethoxy-3-methyluracil.  
R. K. CALLOW.

**Guanyllthiocarbamides. I.** K. H. SLOTTA, R. TSCHESCHE, and H. DRESSLER (Ber., 1930, 63, [B], 208—222).—Treatment of methylthiocarbimide with a boiling alcoholic solution of sodium ethoxide and

guanidine thiocyanate followed by passage of carbon dioxide through the solution yields *N*<sup>1</sup>-methyl-*N*<sup>2</sup>-guanyllthiocarbamide carbonate, m. p. 103—104°, in 77% yield. Boiling water transforms the salt into the free base,  $NHMe \cdot CS \cdot NH \cdot C(NH) \cdot NH_2$ , m. p. 159°. The following compounds are analogously prepared: *N*<sup>1</sup>-ethyl-*N*<sup>2</sup>-guanyllthiocarbamide (carbonate, m. p. 94°; chloride, m. p. 158°; nitrate, decomp. 204°); *N*<sup>1</sup>-*n*-propyl-*N*<sup>2</sup>-guanyllthiocarbamide (carbonate; chloride, m. p. 133°); *N*<sup>1</sup>-isobutyl-*N*<sup>2</sup>-guanyllthiocarbamide (carbonate, decomp. 91°; non-crystalline chloride; sulphate, m. p. 120°; nitrate, m. p. 179°; picrate, m. p. 203°); *N*<sup>1</sup>-allyl-*N*<sup>2</sup>-guanyllthiocarbamide (carbonate, m. p. 95°; non-crystalline chloride; sulphate, m. p. 143°; nitrate, m. p. 187°; picrate, decomp. 213°) in the preparation of which *N*<sup>1</sup>-allyl-*N*<sup>2</sup>-allylthiocarbamylguanyllthiocarbamide,  $NH_2C(NH \cdot CS \cdot NH \cdot CH_2 \cdot CH \cdot CH_2)_2$ , softening at 240°, is obtained as by-product when an excess of allylthiocarbimide is employed; *N*<sup>1</sup>-isoamyl-*N*<sup>2</sup>-guanyllthiocarbamide (carbonate, m. p. 82°; nitrate, m. p. 176° after softening at 170°; picrate, m. p. 205°; sulphate, m. p. 96° after softening at 92°), also obtained by treatment of guanidine thiocyanate with aqueous potassium hydroxide, removal of water, and addition of *isoamylthiocarbimide* in acetone to the residue (*N*<sup>1</sup>-isoamyl-*N*<sup>2</sup>-isoamylthiocarbamylguanyllthiocarbamide hydrochloride, m. p. 95—100°, is obtained as by-product); *N*<sup>1</sup>- $\beta$ -phenylethyl-*N*<sup>2</sup>-guanyllthiocarbamide picrate, decomp. 215° after darkening at 200°. The preparation of arylguanyllthiocarbamides from guanidine thiocyanate, arylthiocarbimide, and alcoholic sodium ethoxide is less satisfactory, owing to the readiness of the reaction of the thiocarbimide with the solvent to form arylthiourethanes. Unsatisfactory results are also obtained when the guanidine is liberated from its salts by potassium hydroxide, since ammonia is readily liberated and combines with the carbimide more readily than does guanidine, so that the product contains arylthiocarbamide in considerable amount. The best results are obtained by use of the pasty mixture formed by the action of sodium on acetone which has been shaken with potassium carbonate and distilled over phosphoric oxide. Addition of guanidine thiocyanate gives a dark red solution in which the arylguanyllthiocarbamide is almost instantaneously produced after addition of arylcarbimide. The following compounds are thus obtained: *N*<sup>1</sup>-phenyl-*N*<sup>2</sup>-guanyllthiocarbamide, m. p. 178° (hydrochloride, decomp. 178°; sulphate, decomp. 282° after darkening at 210°; picrate, decomp. 250° after darkening at 232°); *N*<sup>1</sup>-*p*-anisyl-*N*<sup>2</sup>-guanyllthiocarbamide hydrochloride, m. p. 181°; *N*<sup>1</sup>-*p*-ethoxyphenyl-*N*<sup>2</sup>-guanyllthiocarbamide, m. p. 148° (hydrochloride, m. p. 188° after softening at 182°; salicylate, decomp. 139°; formate, m. p. 164°); *p*-phenylene-*N*<sup>1</sup>*N*<sup>1</sup>-di-*N*<sup>2</sup>-guanyllthiocarbamide hydrochloride,  $C_6H_4[NH \cdot CS \cdot NH \cdot C(NH) \cdot NH_2]_2 \cdot HCl$ , decomp. 212°; *N*<sup>1</sup>-3 : 4 : 5-trimethoxyphenyl-*N*<sup>2</sup>-guanyllthiocarbamide picrate, decomp. 270°; *N*<sup>1</sup>-*p*-carbethoxyphenyl-*N*<sup>2</sup>-guanyllthiocarbamide, m. p. 178° (picrate, decomp. 250°); *N*<sup>1</sup>-*m*-hydroxymethylphenyl-*N*<sup>2</sup>-guanyllthiocarbamide picrate, decomp. 240°; *N*<sup>1</sup>-*p*-acetoxyphenyl-*N*<sup>2</sup>-guanyllthiocarbamide, m. p. 305°; *N*<sup>1</sup>-*p*-hydroxyphenyl-*N*<sup>2</sup>-guanyllthiocarbamide hydrochloride, m. p. 199°;

*N*<sup>1</sup>-3-bromo-*p*-ethoxyphenyl-*N*<sup>2</sup>-guanythiocarbamide hydrochloride, decomp. 178°; *N*<sup>1</sup>-*p*-carbo-β-diethyl-aminoethoxyphenyl-*N*<sup>2</sup>-guanythiocarbamide hydrochloride, m. p. 213°; *N*<sup>1</sup>-*p*-dimethylaminophenyl-*N*<sup>2</sup>-guanythiocarbamide, m. p. 196° (hydrochloride; sulphate, decomp. 200°); *N*<sup>1</sup>-phenyl-*N*<sup>2</sup>-phenylguanythiocarbamide, NHPh·CS·NH·C(NH)·NHPh, decomp. 188°, from the sodium salt of phenylcyanthiocarbamide and aniline hydrochloride in boiling alcohol.

Phenylcarbimide and guanidine thiocyanate are converted by the sodium-absolute acetone method into *N*<sup>1</sup>*N*<sup>2</sup>-diphenylcarbamyguanidine, NH·C(NH·CO·NHPh)<sub>2</sub>, m. p. 176°, in 76% yield, whereas *p*-anisylcarbimide yields *p*-anisylcarbamide, m. p. 172°, in presence of technical acetone. *N*<sup>1</sup>*N*<sup>2</sup>-Di-*p*-ethoxyphenylcarbamyguanidine has m. p. 196°

H. WREN.

**Molecular compounds of ethyl diazoacetate with inorganic salts and oxides.** K. LOREY (J. pr. Chem., 1930, [ii], 124, 185—190).—The following compounds were prepared by interaction of ethyl diazoacetate with the appropriate inorganic substance in the correct proportions: CHN<sub>2</sub>·CO<sub>2</sub>Et, 1 and 2CaCl<sub>2</sub>; CHN<sub>2</sub>·CO<sub>2</sub>Et, 2, 3, and 6CaSO<sub>4</sub>; CHN<sub>2</sub>·CO<sub>2</sub>Et, 6CaO; CHN<sub>2</sub>·CO<sub>2</sub>Et, 6CaCO<sub>3</sub>; CHN<sub>2</sub>·CO<sub>2</sub>Et, MgO. Calcium sulphate hemihydrate and ethyl diazoacetate yield the compound 3CHN<sub>2</sub>·CO<sub>2</sub>Et, 2CaSO<sub>4</sub>. The ester is catalytically decomposed in ethereal solution by anhydrous copper sulphate to ethyl fumarate. A. I. VOGEL.

**Diethylarsine.** E. GRISCHKIEWITCH-TROCHIMOVSKI and A. SPORZYŃSKI (Rocz. Chem., 1929, 9, 741—746).—Diethylarsine, b. p. 96.5—97°, *d*<sub>4</sub><sup>20</sup> 1.1338, *n*<sub>D</sub> 1.4709, is prepared by the reduction by means of zinc and hydrochloric acid of diethylarsine chloride in alcoholic solution. Diethylarsine forms with mercuric chloride a compound, AsEt<sub>2</sub>Cl, 2HgCl<sub>2</sub>, which is not identical with that obtained from "Gosio-gas"; the formula has been wrongly given by Wigren (A., 1924, i, 888). R. TRUSZKOWSKI.

**Reaction between alkali alkyls and quaternary arsonium compounds.** M. E. P. FRIEDRICH and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 376—384).—Triethylarsine is oxidised by atmospheric oxygen to diethylarsinic acid, m. p. 136—137° (lit. 134°). Similarly, diethyl-*n*-butylarsine, b. p. 78°/28 mm., *d*<sub>4</sub><sup>20</sup> 1.0306, *n*<sub>D</sub><sup>20</sup> 1.4745, gives ethyl-*n*-butylarsinic acid, m. p. 93—96°, also obtained from dichloro-*n*-butylarsine and ethyl bromide by Quick and Adams' method (A., 1922, i, 600). Lithium *n*-butyl and tetraethylarsonium bromide, m. p. 298—300°, react in light petroleum, forming triethylarsine and a mixture of hydrocarbons containing a small amount of ethylene; ethylene is polymerised by lithium alkyls, affording non-gaseous products. Lithium ethyl and triethyl-*n*-butylarsonium bromide, m. p. 227°, give diethyl-*n*-butylarsine and hydrocarbons. Similar results are obtained with triethylarsine dibromide and the lithium alkyls. Tetramethylarsonium iodide, sublimes at 320—328°, and sodium triphenylmethyl react in dry ether, affording a coloured solid, which is unaffected by treatment with carbon dioxide and decomposed by pyridine to triphenylmethane. No

evidence of the formation of a stable penta-alkyl arsenic compound has been obtained.

H. BURTON.

**Reaction between polyhydric alcohols or phenols and arsenic compounds, in particular arsinoacetic acid.** II. B. ENGLUND (J. pr. Chem., 1930, [ii], 124, 191—208).—Measurements of the solubility of arsinoacetic acid and of arsenic trioxide in 99% acetic acid in the presence of various glycols have been made, and the constant *L* has been evaluated in each case (cf. A., 1929, 52, 945). The glycols studied were ethylene glycol, propane-αβ- and -αγ-diols, meso- and *r*-butane-αβ- and -βγ-diols, β-methylpropane-αβ-diol, butane-αγ-diol, hexane-βε-diol, decane-ακ-diol, and pinacol. α-Glycols have a greater influence on the solubility than other glycols; the effect is increased by the introduction of alkyl groups, but this depends on the number and nature of the substituents; stereoisomerides exert different effects. The bearing of these results on the relative ease of formation and on the configuration of rings is discussed. The method has also been applied to phenol, 2:4- and 2:6-dinitrophenols, pyrocatechol, 3- and 4-nitropyrocatechols, and to δ-keto-β-methylpentane-βγ-diol. Abnormal results were obtained for the 3- and 4-nitropyrocatechols, these being attributed to the presence of the tautomeric *aci*-form; the results for δ-keto-β-methylpentane-βγ-diol are not in agreement with those obtained by the boric acid and acetone method of Böeseken. A modification of the method involving the dissolution of arsenic trioxide in water is described and is applied to a number of hydroxy-compounds. The results are in qualitative accord with those obtained by the original method.

The action of arsenious oxide on pentaerythritol and pinacol gives the compounds C<sub>5</sub>H<sub>9</sub>O<sub>4</sub>As, m. p. 102—103°, and C<sub>12</sub>H<sub>25</sub>O<sub>4</sub>As, m. p. 110°; erythritol yields a substance containing 37.5% As.

A. I. VOGEL.

**Effect of prolonged ebullition on magnesium organo-halides.** H. GILMAN and (MISS) E. L. ST. JOHN (Bull. Soc. chim., 1929, [iv], 45, 1091—1095).—The rate of decomposition of magnesium organo-halides in boiling solvents has been determined with the colour reaction previously described (A., 1925, ii, 1011; 1928, 160; 1929, 303). Magnesium *n*-butyl bromide is decomposed by 135 hrs.' boiling in ether, 66 hrs.' in ether-benzene, 60 hrs.' in ether-toluene. Similarly, magnesium benzyl chloride is decomposed in 134 hrs. in boiling ether and in 82 hrs. in ether-benzene, and magnesium phenyl bromide by 84 hrs. in ether-benzene and 40 hrs. in boiling ether-toluene. Since after 9 hrs.' boiling in ether-benzene magnesium phenyl bromide gives practically the same yield (70.1%) of benzoic acid as is obtained without refluxing, the decomposition is not due to heat alone and is attributed to the action of diffused oxygen. Accordingly, reactions which necessitate prolonged boiling at high temperatures should be effected in an inert atmosphere.

R. BRIGHTMAN.

**Action of ultra-violet light on magnesium iso-butyl bromide and tert-butyl chloride.** H. GILMAN and L. L. BECK (Bull. Soc. chim., 1929, [iv], 45, 1095—1098).—No appreciable isomerisation of the



organic radical occurs when ethereal solutions of magnesium isobutyl bromide and magnesium *tert.*-butyl chloride are exposed for 63 hrs. to ultra-violet light. With magnesium isobutyl bromide 47% of isovaleric acid is subsequently obtainable by the usual method; magnesium *tert.*-butyl chloride similarly gives 58% of trimethylacetic acid containing up to 5% of isovaleric acid (cf. A., 1928, 255; 1929, 433).

R. BRIGHTMAN.

**cycloPropene and some of its derivatives.** N. J. DEMJANOV and M. N. DOJARENKO (Bull. Acad. Sci. U.S.S.R., 1929, 653—665; cf. A., 1923, i, 1188).—The total yield of hydrocarbons and that of allene obtained on heating the quaternary base (*loc. cit.*) increase as the temperature is raised, but the yield of cyclopropene diminishes. When heated with water in a sealed tube, dibromocyclopropane remains virtually unchanged at 100—105°, but at 150—155° about 77.5% and at 160—165° almost the whole of the bromo-compound reacts, yielding acraldehyde and a mixture of products of its condensation with loss of water. Similar results are obtained if the reaction takes place in presence of silver carbonate or lead oxide, no formation of the glycol corresponding with cyclopropene occurring. When treated with a concentrated absolute alcoholic solution of iodine, cyclopropene yields *di-iodocyclopropane*,  $C_3H_4I_2$ , m. p. below  $-5^\circ$ ,  $d_4^{25}$  2.725,  $n_D^{25}$  1.6765. Among the products formed by the action of potassium permanganate on cyclopropene at a low temperature (snow), only formic acid was identified. When heated at 245—255° in presence of aluminium oxide, cyclopropene undergoes polymerisation to some extent.

T. H. POPE.

**Cracking of cyclic hydrocarbons with hydrogen at high pressures.** V. N. IPATIEV, N. ORLOV, and N. LICHATSCHEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1339—1343, and Ber., 1930, 63, [B], 156—160).—The behaviour of the hydrides of aromatic hydrocarbons under conditions of pressure hydrogenation was investigated, with the view of elucidating the mechanism of the cracking of petroleum and primary coal tars in which the compounds selected occur. *Dicyclohexyl*, *dicyclohexylmethane*,  $\alpha\beta$ -*dicyclohexylethane*, and  $\alpha\epsilon$ -*dicyclohexylpentane* were hydrogenated at 440—450° and 75 atm. in the presence of iron and alumina as catalysts. Besides these *dicyclohexylparaffins*, *decahydronaphthalene*,  $\alpha\delta$ -*diphenylbutane*,  $\gamma$ -*diphenylpropane*, 1:3:5-triphenylbenzene, pentamethyldihydroxytetrahydroxanthene, and a primary tar were also investigated under similar conditions. The *dicycloparaffins* and *diphenylparaffins* gave only mono-substituted *cyclohexanes* and benzene homologues. *Decahydronaphthalene* gave a mixture of naphthenes, 1:3:5-diphenylbenzene was unaffected, whilst pentamethyldihydroxytetrahydroxanthene gave both naphthenes and aromatic hydrocarbons. The primary tar, which was anhydrous and contained 40% of phenols, yielded a considerable quantity of benzene hydrocarbons, which were, in part, due to the reduction of phenols, since water was also obtained.

M. ZVEGINTZOV.

**Thermal decomposition of perhydro-fluorene and -acenaphthene in presence of hydro-**

**gen under pressure.** N. A. ORLOV and M. A. BELOPOLSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1267—1277).—The behaviour of the perhydro-derivatives of the condensed nuclei hydrocarbons in the presence of hydrogen under pressure was investigated, since they occur in the products of coal distillation, and their reactions with hydrogen should throw light on the mechanism of that process. Fluorene was hydrogenated at 210—230°/60—75 atm. in the presence of nickel, silver, manganese, copper, and cobalt oxides as catalysts, and the perhydrofluorene, b. p. 254—258°,  $d_4^{25}$  0.9203, isolated from the liquid product by fractionation. It was hydrogenated at 380°/70—75 atm. with alumina and other oxides as catalysts, yielding a liquid product containing a mixture of mono- and di-cyclic naphthenes, among which perhydrindene and *cyclopentadiene* were isolated. When fluorene was distilled with anhydrous aluminium chloride, diphenyl and its hydrides were obtained.

Hydrogenation of acenaphthene under the same conditions gave perhydroacenaphthene, b. p. 232—239°,  $d_4^{25}$  0.9329,  $n_D^{25}$  1.5200, which, on further hydrogenation at 450°, yielded a mixture of benzene homologues, indene and its homologues, diphenylfulvene, and other cyclic hydrocarbons. The isolation of indene in these reactions is considered to explain the mechanism of its formation during the carbonisation of coal to yield a primary tar.

M. ZVEGINTZOV.

**Polarities and orienting influence of substituents in the benzene ring.** W. M. LATIMER and C. W. PORTER (J. Amer. Chem. Soc., 1930, 52, 206—211).—The residual charge on an atom attached to a benzene ring is calculated from a consideration of the electronic configuration of the group in which the atom occurs. It is assumed that the electrons are quantised with respect to the field between the atoms (except for hydrogen), the effects being distributed between the atoms in the ratio of the positive charges on the nuclei. The residual charge, calculated for 30 groups, varies from  $-0.4$  ( $\cdot\text{OR}$ ) to  $+2.1$  ( $\text{NO}_2$ ). A positive residual charge generally indicates a *m*-orienting substituent, but the division is not sharp. Groups with values of 0.1—0.6 usually give mixtures of *o*-, *m*-, and *p*-derivatives.

An electronic configuration for benzene is postulated, in which alternate carbon atoms possess, or share, six and eight electrons, respectively. Three pairs of electrons are assumed to be quantised with respect to the field of the molecule as a whole. H. BURTON.

**1:3:4:5-Tetranitrobenzene.** A. F. HOLLEMAN (Rec. trav. chim., 1930, 49, 112—120).—When picramide is suspended in cold nitric acid ( $d$  1.4) and then treated repeatedly with nitrous fumes, 1:3:4:5-tetranitrobenzene, m. p. 129—130°, is formed, probably through the intermediate 2:4:6-trinitrobenzene-diazonium nitrite. Some picric acid and hexanitrodiphenylamine are also produced; the latter is probably formed by interaction of the diazonium hydroxide with picramide. The tetranitrobenzene is purified by dissolution in benzene, washing the solution with sulphuric acid until pale yellow, and subsequently washing with cold water, drying, and evaporating; the tetranitrobenzene crystallises with 1 mol. of

benzene, which is lost at 60°. 1:3:4:5-Tetranitrobenzene is decomposed rapidly with boiling water, and slowly with cold water, to picric and nitrous acids: decomposition also occurs with any solvent containing oxygen. The ease of conversion of the tetranitrobenzene into picramide by dilute aqueous ammonia (97% yield) is used for the determination of the tetranitrobenzene in mixtures containing picric acid. 1:3:4:5-Tetranitrobenzene is a more powerful explosive than picric acid.

Details are given for the preparation of picramide from *p*-nitroaniline and acetanilide (cf. Witt, A., 1908, i, 874).  
H. BURTON.

**Nitration of aromatic thiocyanates.** F. CHALLENGER, C. HIGGINBOTTOM, and A. HUNTINGTON (J.C.S., 1930, 26—34).—Phenyl and substituted phenyl thiocyanates are prepared, generally by Korczyński's method (A., 1923, i, 159). The mixture of *o*- and *p*-nitro-derivatives obtained in 94% yield when phenyl thiocyanate is nitrated with nitric (*d* 1.41) and sulphuric acids at 0—5° contains 20% of the *o*-, and 80% of the *p*-derivative (cf. A., 1924, i, 953). *o*-Chlorophenyl thiocyanate, b. p. 160—160.5°/42—47 mm., is converted by nitric acid (*d* 1.5), first at —6° and then at the ordinary temperature, mainly into 2-chloro-4-nitrophenyl thiocyanate, m. p. 85°; a small amount of the 5-nitro-isomeride, m. p. 107°, is also produced. *o*-Bromophenyl thiocyanate, b. p. 161—165°/10—12 mm., m. p. about 24°, yields, similarly, 2-bromo-4-, m. p. 93° (main), and 2-bromo-5-nitrophenyl thiocyanate, m. p. 126° (trace). *m*-Chlorophenyl thiocyanate, b. p. 135°/12.5 mm., affords 3-chloro-4-, m. p. 59° (main), and 3-chloro-6-nitrophenyl thiocyanate, m. p. 104—105° (trace). These results show the strong *para*-directing influence of the thiocyano-group. *p*-Aminophenyl thiocyanate is converted by the usual method into *p*-iodophenyl thiocyanate, m. p. 53°, which is unaffected by nitric acid (*d* 1.41) at —10° or 15°, or by the acid of *d* 1.5 in acetic anhydride solution. With nitric and sulphuric acids at —14 to 5°, *p*-nitrophenyl thiocyanate is produced. Treatment of the iodo-compound with chlorine in cold chloroform affords a dichloride, m. p. 111°, which on thermal decomposition regenerates the original iodo-derivative. Attempts to decompose this dichloride under various conditions so as to induce nuclear chlorination failed (cf. Werner, J.C.S., 1907, 91, 240, 529); *p*-iodophenyl thiocyanate was regenerated in most cases. When decomposed by sunlight, the dichloride gives 4:4'-di-iododiphenyl disulphide.

H. BURTON.

**Action of selenium bromide on aromatic hydrocarbons.** J. LOEVENICH and K. SIPMANN (J. pr. Chem., 1930, [ii], 124, 127—132).—Interaction of benzene, aluminium bromide, and selenium bromide gives bromobenzene and a 22—27% yield of diphenyl selenide; in dilute carbon disulphide solution diphenyl diselenide, m. p. 62° (2% yield), is also obtained. Aluminium bromide and selenium bromide react with toluene to give chiefly *o*-bromotoluene and a small quantity of *oo'*-ditolyl selenide, b. p. 174—180°/13 mm.; mesitylene yields bromomesitylene and dimesityl, naphthalene affords 1-bromonaphthalene and 1:1'-dinaphthyl, whilst no well-defined products could be

isolated with anthracene. The bearing of these results on the constitution of selenium bromide is discussed.

A. I. VOGEL.

**Catalytic oxidation of toluene by air.** M. I. KUZNETZOV and M. A. STEPANENKO.—See this vol., 304.

**Thermal decomposition of coal-tar constituents.** V. Reaction products of the thermal decomposition of toluene. VI. Reaction mechanism of the thermal decomposition of toluene. Y. KOSAKA (J. Soc. Chem. Ind. Japan, 1929, 32, 298—299B, 299—300B).—V. Pyrolysis of toluene at 700° and 800°, employing various contact materials, and at 900° without a tube-filling, indicates that the decomposition is independent of the filling material (silica or coke), and the main reaction products consist of benzene, diphenyl, diphenylbenzene, and their homologues, minute quantities (1—2%) of naphthalene, anthracene, and phenanthrene, together with ethylene, methane, hydrogen, and free carbon. The amount of toluene undecomposed at 700° is 86—88%, at 800° 54—57%, and at 900° 3%. The formation of benzene increases from 3.5% at 700° to 26% at 900°. The yield of diphenyl and its homologues reaches a maximum (8%) at 800°, whilst the production of diphenylbenzene and its homologues rises from 1% at 700° to 11% at 900°. The amounts of methane, hydrogen, and free carbon produced increase with rising temperature, 27% of carbon being formed at 900°.

VI. Twelve reactions are proposed to express completely the exact nature of the pyrolysis of toluene, and their distribution at 700°, 800°, and 900° is traced by calculation.  
C. W. SHOPPEE.

**Separation of xylenes.** I. Fusion curves of the systems *o*-xylene-*m*-xylene and *o*-xylene-*p*-xylene. II. A. NAKATSUCHI (J. Soc. Chem. Ind. Japan, 1929, 32, 333—335B, 335—336B).—I. *p*-Xylene, m. p. 13.19°, *m*-xylene, m. p. —49.0°, and *o*-xylene, m. p. —25.74°, were employed. The points found for the systems lie on a smooth two-branch curve in each case. The heats of fusion of the xylenes have been calculated thermodynamically and are: *o*-, 3100, *m*-, 2800, and *p*-xylene, 4100 g.-cal.

II. Fractional distillation of a mixture of xylenes tends to concentrate *m*-xylene in the highest fraction, whereas the distribution of *p*-xylene is not appreciably affected. Selective sulphonation is more effective, since the chief component of the unsulphonated material is *p*-xylene; dissolution of the unsulphonated material in concentrated sulphuric acid at 95° affords crystalline *p*-xylenesulphonic acid, which by hydrolysis with 50% sulphuric acid furnishes pure *p*-xylene. The relation between the composition of hydrocarbon mixtures liberated by hydrolysis of sulphonic acids and the hydrolysis temperature is given in tabular form, and it is concluded that Patterson's process (A., 1925, i, 124) for the separation of *m*-xylene has no value for large-scale operations. It is found that in the Friedel-Crafts reaction *p*-xylene combines less readily than either isomeride with unsaturated hydrocarbons, e.g., isobutylene, and it is stated that 94% of the total *p*-xylene may be separated in this manner.

C. W. SHOPPEE.

**Highly-polymerised compounds. XXXIII. Relationships between viscosity and mol. wt. among polystyrenes.** H. STAUDINGER and W. HEUER (Ber., 1930, 63, [B], 222—234; cf. this vol., 78).—Examination of the viscosity of polystyrenes of differing concentration shows that the expression  $\eta_{sp}/C$  is not constant, but increases with increasing concentration. Only in very dilute solution is the deviation from  $K=\eta_{sp}/C$  relatively slight; at higher concentration the specific viscosity increases much more rapidly than the concentration. Association cannot entirely account for these observations, since the relative viscosity of hemicolloids in molar solution at 60° is only slightly less than at 20°. The deviation from the Einstein expression is attributed to the non-spherical form of the polystyrene molecule. On the assumption that the latter has a cylindrical form and is free to rotate around its centre, the modified expression,  $\eta_{sp}/C=K_m M$  is deduced. Preliminary determinations of the constant  $K_m$  for purified fractions of hemicolloidal polystyrenes in 0.25M-solution in benzene give the value  $K \times 10^3 = 0.20$ , the individual variations being slight. Application of the method to the determination of the mol. wt. of more highly-polymerised products gives values of the order 100,000. The constant  $K_m$  is valid only in one and the same polymeric-homologous series and for a single solvent. H. WREN.

**Compounds between metallic chlorides and polyenes.** H. VON EULER and H. WILLSTAEDT (Arkiv Kemi, Min., Geol., 1929, 10, B, No. 9, 6 pp.).—It was shown by Karrer, Euler, and Euler (this vol., 379) that the Carr and Price reaction is given by substances of the carotenoid group. The compounds between these substances and metallic chlorides were therefore studied. By mixing chloroform solutions of stilbene and antimony trichloride, colourless crystals,  $C_{14}H_{12}, 2SbCl_3$ , m. p. 106—107°, were obtained. With isostilbene, the same product seems to be obtained. With ferric chloride, yellow crystals,  $C_{14}H_{12}, 2FeCl_3$ , decomp. 326°, are obtained. In the same way, diphenylbutadiene gives a colourless substance,  $C_{16}H_{14}, 2FeCl_3$ . Dimethylfulvene produces with antimony trichloride a resinous substance, and in dilute solutions a deep violet colour, but the product could not be isolated without decomposition. Carotene gives rise to a blue product of approximate formula  $C_{40}H_{56}, 2SbCl_3$ . The cause of the colour reaction is believed to lie in the formation of readily dissociated compounds of the carotenoid and the metallic chloride. K. V. THIMANN.

**Substitution of bromine by chlorine in organic halogen compounds.** P. PFEIFFER and B. EISTERT (J. pr. Chem., 1930, [ii], 124, 168—184).—The influence of substituent groups on the replacement of bromine by chlorine in compounds of the stilbene type has been investigated by the interaction of the stilbene dibromides with tin tetrachloride in anhydrous thiophen-free benzene solution.  $\alpha$ -Stilbene dibromide, m. p. 237° (decomp.), gives *stilbene chlorobromide*, m. p. 225° (decomp.), after 5 min. at the ordinary temperature, and stilbene dichloride on boiling for 30 min. 4-Nitrostilbene dibromide, m. p. 205—206° (decomp.), yields only 4-nitro- $\alpha$ -bromo- $\alpha'$ -chlorostilbene,

$NO_2 \cdot C_6H_4 \cdot CHBr \cdot CHClPh$ , m. p. 180—181°, on prolonged boiling, whilst 4:4'-dinitrostilbene dibromide, m. p. 288° (decomp.) (4:4'-dinitrostilbene has m. p. 286°), is unaffected. 2:4-Dinitrostilbene dibromide, ( $\alpha$ -form, m. p. 185°,  $\beta$ -variety, m. p. 145—146°), yields a mixture of  $\alpha$ - and  $\beta$ -2:4-dinitrostilbene chlorobromides (m. p. 161° and 145—146°, respectively). 4-Methoxystilbene dibromide, m. p. 183—184° (decomp.), converted at 170—180° into 4-methoxy- $\mu'$ -bromostilbene, m. p. 53—54°, yielded the corresponding dichloride, m. p. 150—151° (slight decomp.); this change is more facile in the conversion of 4:4'-dimethoxystilbene dibromide, m. p. 172° (decomp.), into the corresponding dichloride, m. p. 184° (decomp.). 4-Nitro-4'-methoxystilbene dibromide, m. p. 166° (decomp.), converted at 150—170° into the monobromostilbene, m. p. 93°, yielded a substance, m. p. 200°. Under similar conditions, benzyl bromide gave diphenylmethane, *p*-nitrobenzyl bromide was unaffected, diphenylmethyl bromide, m. p. 42—43°, yielded triphenylmethane, and triphenylmethyl bromide afforded an additive compound,  $CPh_3Br, SnCl_4$ .

A. I. VOGEL.

**Molecular compounds and colour reactions of conjugated unsaturated hydrocarbons. II.** R. KUHN and T. WAGNER-JAUREGG (Helv. Chim. Acta, 1930, 13, 9—13; cf. A., 1928, 281).—The colorations obtained when the previously described unsaturated hydrocarbons (*loc. cit.*) are treated with benzoquinone, chloroanil, maleic, phthalic, and tetrachlorophthalic anhydrides, and oxalyl, fumaryl, phthalyl, thionyl, and sulphuryl chlorides are given. Diphenyl is used for comparison. The coloration increases in intensity with rise in the number of double linkings in the hydrocarbon molecule. Methylbixin gives deep reddish-brown and greenish-blue colours with fumaryl and thionyl chlorides, respectively. The f.p. diagram of  $\alpha\delta$ -diphenylbutadiene and methyl fumarate shows that no compound formation occurs. Picryl chloride and  $\alpha\delta$ -diphenylbutadiene give a compound containing 2 mols. of the former and 1 mol. of the latter substance. H. BURTON.

**Plant colouring matters. XVII. Carotenoids in faeces of sheep and cow.** P. KARRER and A. HELFENSTEIN (Helv. Chim. Acta, 1930, 13, 86—87).—The coloured compound isolated by Fischer (A., 1916, i, 574) from sheep's faeces has been investigated. It is essentially a xanthophyll,  $C_{49}H_{56}O_2, MeOH$ , m. p. 190—191°,  $[\alpha]_D^{20} + 90^\circ$  in chloroform. The same substance is also isolated from fresh cow's faeces. Lutein from egg-yolk has  $[\alpha]_D^{20} + 7.17^\circ$  in chloroform. H. BURTON.

**Plant colouring matters. XVIII. Constitution of carotenoids.** P. KARRER, A. HELFENSTEIN, and H. WEHRLI (Helv. Chim. Acta, 1930, 13, 87—88).—Succinic acid is obtained in small amount when lycopene is oxidised with potassium permanganate; it is formed by further oxidation of lävulic acid, which must be a primary oxidation product, if the previously assigned formula (A., 1929, 569) is correct. It is possible that the group  $CMe_2 \cdot CH \cdot [CH_2]_2 \cdot CMe \cdot CH \cdot$ , which is present in lycopene, becomes cyclised in carotene (cf. this vol., 76). Xanthophyll contains two hydroxyl groups (Zerevitinov), and is probably a di-

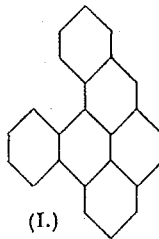
hydroxycarotene. Zeaxanthin (A., 1929, 1077) also contains two hydroxyl groups. H. BURTON.

**Action of peracetic acid on naphthalene.** J. BÖRSEKEN and G. SLOOFF (Rec. trav. chim., 1930, 49, 100—101).—Naphthalene is slowly oxidised by peracetic acid in acetic acid solution, yielding 2-carboxy-*allocinnamic acid*. H. BURTON.

**New class of coloured hydrocarbons.** N. MAXIM (Bull. Soc. chim., 1929, [iv], 45, 1137—1148).—The dehydration of 9 : 10-diethylacenaphthene-9 : 10-glycol to the coloured hydrocarbon, 9 : 10-diethylideneacenaphthene (A., 1928, 1137), is now shown to be characteristic of ditertiary acenaphthene glycols when treated with hydrochloric acid in glacial acetic acid. Only traces of the  $\alpha$ -pinacolins, resulting by loss of 1 mol. of water, obtained by Zincke and Tropp in the phenanthrene series (A., 1908, i, 786) are formed, but no  $\beta$ -pinacolin. The formation of a  $\beta$ -pinacolin in the dehydration of 9 : 10-diphenylacenaphthene-9 : 10-glycol (Beschke, A., 1909, i, 917) is due to pinacolin transformation of the  $\alpha$ -pinacolin first formed. Oxidation of these hydrocarbons with acetic and chromic acids yields a mixture of acenaphthenequinone and naphthalic anhydride. The ditertiary acenaphthene glycols are obtained by the action of Grignard reagents on acenaphthenequinone, magnesium methyl iodide alone yielding two stereoisomeric compounds. *cis*-9 : 10-Dimethylacenaphthene-9 : 10-glycol has m. p. 158°; the *trans*-isomeride, m. p. 184°. On dehydration, both isomerides yield 9 : 10-dimethylenacenaphthene, orange-yellow, together with a little  $\alpha$ -pinacolin,  $C_{10}H_6 \begin{smallmatrix} \text{CMe} \\ \diagup \diagdown \\ \text{CMe} \end{smallmatrix} O$ , in the case of the *cis*-isomeride. 9 : 10-Dipropylacenaphthene-9 : 10-glycol has m. p. 173°; 9 : 10-dipropylideneacenaphthene, m. p. 101°, orange; 9 : 10-diisobutylacenaphthene-9 : 10-glycol, m. p. 132° (yield 50%); 9 : 10-diisobutylideneacenaphthene, b. p. 215°/15 mm., reddish-orange; 9 : 10-diisoamylacenaphthene-9 : 10-glycol, m. p. 155° (yield 30%); 9 : 10-dibenzylacenaphthene-9 : 10-glycol, m. p. 174° (yield 80%), and 9 : 10-dibenzylideneacenaphthene, yellowish-orange, m. p. 142°. 9 : 10-Diisoamylideneacenaphthene was only obtained crude as an orange liquid. R. BRIGHTMAN.

**Polynuclear aromatic hydrocarbons and their derivatives. VI. Syntheses of 1 : 2 : 3 : 4-dibenzpyrene and its derivatives.** E. CLAR (Ber., 1930, 63, [B], 112—120; cf. A., 1929, 435, 689, 922; this vol., 203).—*o*-1-Naphthoylbenzoic acid is converted by benzene in presence of 1 mol. of aluminium chloride at the atmospheric temperature into phenyl-1-naphthylphthalide, m. p. 225.5—227° (cf. McMullen, A., 1922, i, 1025); *p*-tolyl-1-naphthylphthalide, m. p. 235—236°, and *m*-xyl-1-naphthylphthalide, m. p. 205—207.5°, are similarly prepared. *o*-Benzoylbenzoyl chloride and 2- and 1-methylnaphthalene under like conditions but in presence of carbon disulphide and benzene, respectively, afford phenyl-2-methylnaphthylphthalide, m. p. 207—208°, and phenyl-4-methyl-1-naphthylphthalide, m. p. 203—204°. If 2 mols. of aluminium chloride are used and the mixture is heated, the green colour of the additive compounds characteristic of all these phthalides becomes changed to reddish-brown, blue, or violet and acids are

produced of which *o*-benzanthran-10-ylbenzoic acid, m. p. 267—268° (sodium salt), is described in detail. If phenyl-1-naphthylphthalide is acted on by aluminium chloride in absence of solvent at 130—165° it yields 1 : 2 : 3 : 4-dibenzpyrene (I), m. p. 226—227° (picrate, m. p. 231°). The substance is more conveniently prepared by the distillation of *o*-benzanthran-10-ylbenzoic acid with zinc dust; as by-product, a colourless hydrocarbon,  $C_{24}H_{16}$ , which cannot be dehydrogenated catalytically, is produced. Support of the structure assigned to the dibenzpyrene is obtained by the following synthesis. 1 : 2-Benzanthraquinone is converted by magnesium phenyl bromide in ether-benzene into 9 : 10-dihydroxy-9 : 10-diphenyl-9 : 10-dihydro-1 : 2-benzanthracene, m. p. 246—248° (decomp.), transformed by aluminium chloride and benzene at the atmospheric temperature into 5-phenyl-1 : 2 : 3 : 4-dibenzpyrene, m. p. 242—243°, frequently accompanied by its dihydro-derivative from which it cannot be separated readily. More advantageously, the diol is reduced by glacial acetic acid and potassium iodide to 9 : 10-diphenyl-1 : 2-benzanthracene, m. p. 192°, which with aluminium chloride in boiling benzene yields 5-phenyl-1 : 2 : 3 : 4-dibenzdihdropyrene, m. p. 257—258°, dehydrogenated by platinised charcoal at 300° to 5-phenyl-1 : 2 : 3 : 4-dibenzpyrene. The absorption curves of 1 : 2 : 3 : 4-dibenzpyrene and its phenyl derivatives are very closely similar. H. WREN.

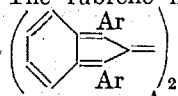


**Rubrenes.** A. WILLEMART (Ann. Chim., 1929, [x], 12, 345—422).—Diphenylheptinenylcarbinol, b. p. 184—185°/2 mm.,  $d_{20}^{20}$  1.0228,  $n_D^{20}$  1.5599, obtained in 43% yield by the successive action of  $\Delta^2$ -heptinene and benzophenone on magnesium ethyl bromide, is converted by phosphorus tri- or penta-chloride into a compound,  $C_{26}H_{21}Cl$  (I), b. p. 172—175°/2 mm. (not the corresponding chloro-compound), and isomerised by warm alcoholic sulphuric acid to  $\beta\beta$ -diphenylvinyl *n*-amyl ketone, b. p. 173°/1 mm., m. p. 7—8° (dibromide; semicarbazone, m. p. 129—130°; oxime, m. p. 83—84°), oxidised by potassium permanganate in acetone to benzophenone and hexoic acid. Dimethylphenylethynylcarbinol, m. p. 55—56°, similarly prepared from phenylacetylene, magnesium ethyl bromide, and acetone, gave an impure substance,  $C_{11}H_{11}Cl$  (II), b. p. 76—79°/1.2 mm., with phosphorus trichloride. No rubrene was obtained by heating I or II. Diphenyl- $\beta$ -*p*-tolylethynylcarbinol (III), m. p. 68—69°, prepared in 62% yield from *p*-tolylacetylene, magnesium ethyl bromide, and benzophenone, gives  $\alpha\alpha$ -diphenyl- $\gamma$ -*p*-tolyl- $\Delta^8$ -propenyl chloride (IV), m. p. 130—131°, in 88% yield, with phosphorus trichloride in light petroleum, which on heating at 15 mm., best in the presence of a little quinoline, afforded dimethylrubrene,  $C_{44}H_{32}$ , m. p. 315° (cf. Moureu and others, A., 1928, 996). *p*-Tolyl  $\beta\beta$ -diphenylvinyl ketone, m. p. 74—75°, is produced by heating III with alcoholic sulphuric acid or IV with alcohol. Interaction of magnesium phenylacetylenyl bromide and phenyl  $\alpha$ -naphthyl ketone or of magnesium  $\alpha$ -naphthyl bromide and phenyl  $\beta$ -phenylethynyl ketone gives

*phenyl- $\alpha$ -naphthyl- $\beta$ -phenylethynylcarbinol* (V), m. p. 137—138°, converted by phosphorus trichloride in ether into the corresponding *chloride* (VI), m. p. 130—131° (decomp.), and yielding no rubrene on heating.

*Phenyl  $\beta$ -phenyl- $\beta$ -1-naphthylvinyl ketone*, m. p. 107—108°, is obtained by boiling V with alcoholic sulphuric acid or VI with alcohol.

1:1-Dinaphthyl- $\beta$ -phenylethynylcarbinol (+Et<sub>2</sub>O), m. p. 70—71° (decomp.), prepared from magnesium phenylacetylenyl bromide and 1:1-dinaphthyl ketone in 90% yield, gave the corresponding *chloride*, m. p. 122—123° (decomp.), with phosphorus trichloride, converted into a coloured resin on heating. *Phenyl  $\beta$ -di-1-naphthylvinyl ketone* has m. p. 170—171°. *Dibenzorubrene*, C<sub>50</sub>H<sub>32</sub>, m. p. 80° (cf. A., 1928, 996), was prepared from *diphenyl- $\beta$ -naphthylethynylcarbinol*, m. p. 99—100° (obtained from magnesium ethyl bromide,  $\beta$ -naphthylacetylene, and benzophenone in 50% yield), through the *chloride*, m. p. 116—117° (decomp.), and heating the latter to 200° in the presence of quinoline. Dimethyl- and dibenzorubrene form *peroxides*, C<sub>44</sub>H<sub>32</sub>·O<sub>2</sub>·C<sub>6</sub>H<sub>6</sub> and C<sub>50</sub>H<sub>32</sub>·O<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>, respectively, when exposed to sunlight in benzene solution. The new rubrenes resemble closely those described previously in absorption spectrum. The mechanism of the formation of rubrenes by elimination of hydrogen chloride from the chloro-compounds CR'''C:CR'R''Cl is discussed; the three methods of Moureu and others (A., 1927, 355) are considered to be improbable and two alternative mechanisms suggested. The rubrene hydrocarbons

have the general formula .

A. I. VOGEL.

**Luminescence phenomena of the satellites of rubrene.** Two phosphorescent hydrocarbons; the so-called "brown" and the yellow substance. C. MOUREU, C. DUFRASSE, and P. LOTTE (Compt. rend., 1930, 190, 148—149; cf. A., 1929, 922, 1166).—The luminescence phenomena of these two substances, both of which have the probable formula C<sub>42</sub>H<sub>30</sub>, are closely analogous, and it is suggested that the substances are identical, and that differences in properties (e.g., in colour) are due to impurities, probably mineral in nature, which in the case of the brown substance are partly or completely destroyed by light. Both substances luminesce if exposed to light and warmed, but in the case of the yellow substance, irradiation activates only the solid substance and not its solutions.

J. GRANT.

**Chlorination of anilides. VI. Rates of N-chlorination of acetanilides and acetobenzylamides and effects of substituents on side-chain reactivity.** G. WILLIAMS (J.C.S., 1930, 37—46).—It is shown that, in accordance with the electronic theory, side-chain reactions may be classified into two main groups according as they are accelerated by the nitro- and retarded by the methyl group and *vice versa*; out of 36 such reactions only 5 cannot be allocated with certainty to either group. The velocities of chlorination in 40% acetic acid at 18° are tabulated for acetanilide, acetobenzylamide, and their *o*-, *m*-, and *p*-nitro-, -chloro-, and -methyl derivatives

(excepting aceto-*o*- and -*m*-methylbenzylamides), and also for aceto- $\beta$ -phenylethylamide and acetamide. The velocities of *N*-chlorination are given and compared with those of *C*-chlorination where the latter are not too slow to be determined, and it is shown that the former fall into these two groups. The experiments include new rates of *C*-chlorination for *m*-chloroacetanilide (*k<sub>c</sub>*=3140) and aceto-*m*-toluidide (*k<sub>c</sub>*=50,000), and a description of aceto-*p*-chlorobenzylamide, m. p. 109·5°, and aceto-*m*-chlorobenzylamide, m. p. 38°.

H. A. PIGGOTT.

**Conversion of N-chloroacetanilide into p-chloroacetanilide by hydrogen and chlorine ions.** J. W. BELTON (J.C.S., 1930, 116—124).—The velocity of conversion of *N*- into *p*-chloroacetanilide in relation to the concentrations of hydrogen and chlorine ions, on both of which it is dependent (Orton and Jones, Brit. Assoc. Rep., 1910, 85), was measured at 25°. The reaction was followed volumetrically: chlorination of the *p*-chloroacetanilide (Soper, A., 1927, 837) and hydrolysis of the *N*-chloroacetanilide known to occur as side reactions were considered negligible. In hydrochloric acid-sodium chloride solutions the rate bears no relation to the activities of the reactants, and reaction mechanisms involving intermediate formation of a charged complex (cf. Brønsted, A., 1922, ii, 699; 1925, ii, 681) do not agree with experimental data. In mixtures of hydrochloric and perchloric acids the rate is proportional to the product of the molecular proportions of hydrogen and chlorine ions.

H. A. PIGGOTT.

**Additive compounds of organic bases with salts of heavy metals.** J. V. DUBSKÝ and A. RABAS (Publ. Fac. Sci. Univ. Masaryk, 1929, No. 112, 1—12).—The following double compounds have been prepared: ZnCl<sub>2</sub>·2C<sub>5</sub>H<sub>5</sub>N, m. p. 210°; ZnCl<sub>2</sub>·2NH<sub>2</sub>Ph, decomp. 266°; ZnCl<sub>2</sub>·2*o*-toluidine, m. p. 234°; ZnCl<sub>2</sub>·2*p*-toluidine, m. p. 267°; ZnCl<sub>2</sub>·3glycine, decomp. 235°. These results are in disagreement with those of Lachowicz and Bandrowski (A., 1888, 1281).

R. TRUSZKOWSKI.

**Electrolytic reduction of nitriles.** I. K. OGURA (Mem. Coll. Sci. Kyōtō, 1929, A, 12, 339—342).—Optimum yields of the corresponding amines are obtained when benzonitrile, *p*-toluonitrile, and phenylacetoneitrile are reduced electrolytically in aqueous alcoholic solution containing ammonium sulphate and a small amount of ammonia, with a lead cathode. The yields are 49·5, 57, and 13%, respectively. With more alkaline or acid cathode solutions, hydrolysis of the nitrile occurs to varying extents, especially with phenylacetoneitrile.

H. BURTON.

**dl- $\beta$ -Phenylisopropylamine and related compounds.** D. H. HEY (J.C.S., 1930, 18—21).—Benzyl methyl ketoxime, described for the first time as a crystalline solid, m. p. 70°, is readily reduced in aqueous acetic acid to dl-*p*-phenylisopropylamine, b. p. 205°; the *acetyl* derivative, freshly crystallised from aqueous alcohol, has m. p. 64°, rising on vacuum drying to 93°; *picrate*, m. p. 143°; *hydrochloride*, m. p. 145—147°. The action of phosphoric oxide on the *acetyl* compound gave 1:3-dimethyl-3:4-dihydroisoquinoline, isolated as the *picrate*, m. p. 136°. Com-

plexes of oximinopropiophenone with *iron* (blue, soluble in benzene), *cobalt*,  $(C_9H_8O_2N)_3Co$ , and *copper*,  $C_9H_8O_2N \cdot CuOH$  are described. H. A. PRIGGOTT.

**Diphenylamine derivatives.** K. DZIEWOŃSKI and M. RUSSOCKI (Bull. Acad. Polonaise, 1929, **A**, 506—527).—The conclusions of Merz and Weith (A., 1873, 74) concerning the proportion of mono- and di-sulphonic acids formed by the action of concentrated sulphuric acid on diphenylamine are confirmed. With chlorosulphonic acid in nitrobenzene solution below 90°, however, the initial product is the unstable, crystalline, diphenylammonium chlorosulphonate which at higher temperatures readily decomposes, giving nuclear substitution products in accordance with the scheme  $Ph_2NH_2 \cdot SO_3Cl \rightarrow NPh_2 \cdot SO_3H \rightarrow NPh \cdot C_6H_4 \cdot SO_3H$ , the proportion of mono- and di-sulphonic acids produced depending on the molecular proportion of chlorosulphonic acid used. Thus with 0.5, 1.0, 1.5, and 2.0 mols. of chlorosulphonic acid for each mol. of diphenylamine the proportions of mono- and di-sulphonic acids and of unchanged diphenylamine are, respectively, 25, 5, 70; 38, 22, 40; 34, 50, 16; and 0, 99—100, 0 mols.%. Hence with 0.5 mol. of the reagent diphenylamine-4-sulphonic acid (*aniline* salt, m.p. 206.5°) is readily separated from the reaction mixture as its *magnesium* salt. Nitration of sodium diphenylamine-4-sulphonate with 1 mol. of nitric acid (*d* 1.48) in acetic acid gives the 4-nitro-derivative (*magnesium* salt) converted by hydrolysis with concentrated hydrochloric acid in a sealed tube at 190° into 4-nitrodiphenylamine (Goldberg, A., 1907, i, 1027), and further nitrated to *sodium* 2:4-dinitrodiphenylamine-4'-sulphonate. Excess of nitric acid converts sodium diphenylamine-4-sulphonate into the 2:4:6-trinitro-derivative identical with a specimen obtained by the condensation of 2:4:6-trinitrochlorobenzene and sulphanilic acid (Turpin, J.C.S., 1891, 59, 717) and hydrolysed by concentrated hydrochloric acid at 180—200° to 2:4:6-trinitrodiphenylamine. The action of bromine (2 mols.) on a suspension of sodium diphenylamine-4-sulphonate in carbon tetrachloride at 45—50° converts it into its 4-bromo-derivative, whilst with 6 mols. of bromine at 60—70° the product is *sodium* 2:4:2'-tribromodiphenylamine-4-sulphonate (*magnesium* salt), converted by excess of hydrobromic acid at 60° into 2:4:2'-tetrabromodiphenylamine and by dilute hydrochloric acid at 190° into 2:4:2'-tribromodiphenylamine, m.p. 94°, whilst the action of nitric acid (*d* 1.48) in acetic acid at 165—190° yields 2:4:2'-tribromo-6'-nitrodiphenylamine, m.p. 215°, together with the corresponding 4':6'-dinitro-derivative, m.p. 179°, and *sodium* 2:4:2'-tribromo-6'-nitrodiphenylamine-4-sulphonate. Diphenylamine-4:4'-disulphonic acid (*magnesium*, +2.5H<sub>2</sub>O, and *aniline*, m.p. 239°, salts) is best obtained by the action of an excess of chlorosulphonic acid on diphenylamine in nitrobenzene at 110—115°. By reactions similar into those described in the case of the monosulphonic acid, its sodium salt is converted into the 2-nitro- and 2:2'-dinitro-diphenylaminedisulphonic acids (converted into 2:2'-dinitrodiphenylamine), 2:4:2'-trinitrodiphenylaminedisulphonic acid, and 2:4:2':4'-tetranitrodiphenylamine, small quantities of the 2:4:6:2':4'-pentanitro- and 2:4:6:2':4':6'-

hexanitro-derivatives being formed as by-products of the nitrations. Similarly, bromination of barium diphenylamine-4:4'-disulphonate converts it into the 2:2'-dibromo-, +0.5H<sub>2</sub>O, together with some 2-bromo-derivatives, and, ultimately, into 2:4:2':4'-tetrabromodiphenylamine. J. W. BAKER.

**Catalytic reduction of nitrosoamines.** C. PAAL and W. N. YAO (Ber., 1930, **63**, [B], 57—66).—Reduction of diphenylnitrosoamine in alcoholic solution in presence of palladised calcium carbonate or barium sulphate gives, almost quantitatively, nitrogen and diphenylamine; *as*-diphenylhydrazine or ammonia is not produced. Reaction proceeds according to the

following scheme:  $2NPh_2 \cdot NO \xrightarrow{+2H} 2H_2O + NPh_2 \cdot N \cdot N \cdot NPh_2 \xrightarrow{+2H} NPh_2 \cdot NH \cdot NH \cdot NPh_2 \rightarrow 2NPh_2 + N_2$ . The intermediate condensation of unchanged nitrosoamine with *as*-diphenylhydrazine is improbable, since these substances react only slowly in alcoholic solution and do not form the tetrazene. The last-named compound is reduced catalytically or by zinc dust and hydrochloric acid to nitrogen and diphenylamine without formation of *as*-diphenylhydrazine or ammonia. Conversion of diphenylnitrosoamine into diphenylamine and nitrogen occurs more rapidly in alkaline solution, whereas in presence of acetic acid hydrogenation is slow and incomplete, giving diphenylamine and a little *as*-diphenylhydrazine. Phenylethylnitrosoamine is quantitatively converted into ethylaniline and nitrogen only in alcoholic-alkaline solution; in alcoholic solution *as*-phenylethylhydrazine and ammonia are also formed to some extent. In presence of acetic acid the change is similar to that in neutral alcohol except that ammonia is not formed.

Nitrosopiperidine in alcoholic solution undergoes slow catalytic reduction to nitrogen, piperidine, and piperylhdyrazine; ammonia is also produced in acetic acid solution. Similarly, in alcoholic solution di-*n*-propylnitrosoamine affords nitrogen, di-*n*-propylamine, and di-*n*-propylhydrazine.

*p*-Nitrosodimethylaniline is smoothly hydrogenated to *p*-aminodimethylaniline. H. WREN.

**1-Methylnaphthalene derivatives.** K. DZIEWOŃSKI and T. WASZKOWSKI (Bull. Acad. Polonaise, 1929, **A**, 604—610).—Sulphonation of 1-methylnaphthalene with concentrated sulphuric acid at 150—170° gives 1-methylnaphthalene-7-sulphonic acid (*sodium* and *aniline*, m.p. 248—250°, salts; *chloride*, m.p. 120—122°; *amide*, m.p. 188—189°), isolated as its crystalline *barium* salt, and converted by fusion with moist potassium hydroxide at 180° into 7-hydroxy-1-methylnaphthalene (*benzoyl* derivative, m.p. 107—108°; *azo*-compound with benzenediazonium chloride, m.p. 137°; *azo*-compound with *p*-nitrobenzenediazonium chloride, m.p. 258—260°). This is converted by heating with a solution of ammonium sulphite and concentrated ammonia in a sealed tube at 150—170° into 7-amino-1-methylnaphthalene, b.p. 170—180°/8 mm., m.p. 46—47° [*acetyl* derivative, m.p. 146°], that of m.p. 158—160° described by Veselý and others (A., 1929, 1288) probably not being obtained from the pure base]. The configuration of these derivatives is based on the fact that the new amino-



derivative is different from the other six isomerides, all of which are known. J. W. BAKER.

**Diphenyl and its derivatives.** V. L. MAS-CARELLI and D. GATTI (Atti R. Accad. Lincei, 1929, [vi], 10, 441—446).—See this vol., 205.

**Azobisazoxybenzene and its oxidation product.** D. MCINTOSH, H. E. BIGELOW, and W. H. MCNEVIN (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 119—123).—*Azobisazoxybenzene*, m. p. 214·7° (corr.), is formed, accompanied by *p*-nitroazobenzene, when *p*-nitroazoxybenzene is boiled for 6 hrs. with excess of sodium arsenite solution. It is unattacked by bromine, and probably has the structure  $[\text{Ph}\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot]_2$ . Prolonged boiling with benzene and peracetic acid yields azoxybisazoxybenzene,  $\text{Ph}\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NO}\cdot\text{Ph}$ , m. p. 242°. Doubt is cast on the work of Passerini (A., 1921, i, 624), who records m. p. 223° for a compound for which this structure is claimed, prepared from *p*-acetamidoazobenzene, m. p. 157° (lit. and present authors, 146°).

R. K. CALLOW.

**Electrolytic reduction of 2-nitro-4'-hydroxyazobenzene.** H. IROMI (Mem. Coll. Sci. Kyōtō, 1929, A, 12, 343—346).—2-Amino-4'-hydroxyazobenzene is obtained in 75% yield when 2-nitro-4'-hydroxyazobenzene is reduced electrolytically at 50—60°, using a lead cathode, and a cathode solution of alcohol containing 10% sulphuric acid and a small amount of stannous chloride. During many of the reductions tried, using a lead or copper cathode, and acid or alkaline cathode solutions, 2-*p*-hydroxyphenylbenzotriazole (Elbs and Keiper, A., 1903, i, 662) was formed.

H. BURTON.

**Velocity of decomposition of diazo-compounds in water.** I. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 279—282B).—A method of titrating diazo-compounds is described in which the potassium  $\alpha$ -naphthol-5-sulphonate is mixed in solution with rather less than the equivalent quantity of the diazo-compound, an experimentally determined quantity of alkali then being added. The titration is finished by addition of the diazo-compound until an end-point is reached. By working thus the dye is precipitated before the diazo-compound can be affected by the alkali and phenol. The velocity coefficient for the decomposition of diazobenzene chloride at 0° was determined. (See also this vol., 300.)

S. K. TWEEDY.

**Condensation products of phenols and aldehydes.** XIV. **Intermediate products containing nitrogen.** I. T. SHONO (J. Soc. Chem. Ind. Japan, 1929, 32, 212—214B).—When an aqueous solution of hexamethylenetetramine-triphenol is shaken with ether, the phenol is quantitatively extracted, leaving an aqueous solution of hexamethylenetetramine. A mixture of phenol (200 g.), formaldehyde (168 c.c.), and ammonia (29%; 147 c.c.), kept at 37° for 24 hrs., acidified, and extracted with ether, yielded a nitrogenous compound, m. p. 137—138°. At 50° this reaction yields 2:2'-dihydroxydibenzylamine.

A. A. GOLDBERG.

**Dimorphism of 2:4-dinitroanisole.** J. VAN ALPHEN (Ber., 1930, 63, [B], 94—95).—2:4-Dinitroanisole is dimorphous. The labile form, m. p. 86·9°,

has the greater rate of crystallisation and, hitherto, has been almost exclusively described. The stable variety, m. p. 94·55°, can be obtained only from technical preparations or from very old specimens. Once prepared, it infects the whole working space, so that the labile form can be again isolated only under particular conditions. H. WREN.

**Manufacture of alkylisopropylphenols and their hydrogenation products [thymol, menthol].** CHEM. FABR. AUF ACTIEN VORM. E. SCHERING.—See B., 1930, 136.

**Electrometric studies on  $\beta$ -naphtholsulphonic acids.** I. **Preparation of  $\beta$ -naphthol-6-sulphonic acid.** K. H. ENGEL and A. W. HUTCHISON (J. Amer. Chem. Soc., 1930, 52, 211—217).— $\beta$ -Naphthol-6-sulphonic acid, m. p. 167° (corr.) [monohydrate, m. p. 129° (corr.); dihydrate, m. p. 118° (corr.)], is obtained pure by repeatedly saturating an aqueous solution of the crude acid with hydrogen chloride. The acid is then kept over potassium hydroxide until free from chloride. Electrometric titration of potassium  $\beta$ -naphthol-1- and -6-sulphonates gives values of  $1\cdot1\times10^{-11}$  and  $1\times10^{-9}$ , respectively, for the dissociation constants of the hydroxyl groups. The first dissociation constant of  $\beta$ -naphthol-6-sulphonic acid is  $3\cdot3\times10^{-2}$ ; the break occurring in the curve for this acid makes possible its determination in presence of the 1-acid or neutral salts. H. BURTON.

**2'-Nitro-2- and -4-aminodiphenyl sulphides and 4'-nitro-2- and 4-aminodiphenyl sulphides.** H. H. HODGSON and W. ROSENBERG (J.C.S., 1930, 180—181).—The following derivatives of diphenyl sulphide were prepared by reaction of the appropriate "diaminodiphenyl sulphides" (apparently diaminodiphenyl disulphides) with sodium in alcohol followed by *o*- or *p*-chloronitrobenzene in slight excess: 2'-nitro-2-amino-, m. p. 81·5°; 2'-nitro-4-amino-, m. p. 102°; 4'-nitro-2-amino-, m. p. 93°; 4'-nitro-4-amino-, m. p. 143° (cf. Kehrman and Bauer, A., 1897, i, 27). Constitutions were confirmed by reduction to the known diaminodiphenyl sulphides.

H. A. PIGGOTT.

**Thermochemical studies of cycloparaffins and their derivatives.** Experimental data for 5- and 6-membered cyclic diacetates, XVII, and dibenzoates, XIX. P. E. VERKADE, J. COOPS, (FRAU) A. VERKADE-SANDBERGEN, and C. J. MAAN (Annalen, 1930, 477, 279—297).—XVII. The molecular heats of combustion (kg.-cal. at 15° at constant volume,  $Q_v$ , and, in parentheses, at constant pressure,  $Q_p$ ) of the acetates (prepared by acetylation of the corresponding alcohol with acetic anhydride and a few drops of concentrated sulphuric acid) of the various *cis*- and *trans*-diols previously investigated (A., 1929, 142) have been determined. The configuration of both the acetates and benzoates (below) was confirmed in several cases by hydrolysis to the original diol. The following data are given: *cis*-cyclopentane-1:2-diol diacetate, b. p. 80—80·5°/2 mm., setting point —5·0°, 1113·9 (1114·7); *trans*-cyclopentane-1:2-diol diacetate, b. p. 85·5—86·5°/3·5 mm., setting pt. —3·9°, 1113·1 (1114·0); *cis*-, m. p. 50·8—51·6°, 1514·9 (1515·7), and *trans*-1:2-dihydroxyhydrindene diacetate, b. p. 160·0—160·2°/10 mm., 1518·4 (1519·3); *cis*-, m. p. 78·6—79·4°, 1667·9

(1669-1), and *trans*-1:2-dihydroxy-1:2:3:4-tetrahydronaphthalene diacetate, m. p. 84—84.5°, 1664.4 (1667.5); *cis*-, b. p. 113.8—114°/12 mm., 1260.9 (1262.1), and *trans*-cyclohexane-1:2-diol diacetate, b. p. 113—113.2°/11.5 mm., 1262.5 (1263.7) (Brunel, A., 1905, i, 869, erroneously assigned the *cis*-configuration); *cis*-1-phenylcyclohexane-1:2-diol diacetate, m. p. 136.4—137.8°, 1982.5 (1984.3). Berner's method for the determination of the heat of combustion of supercooled diethyl antitartrate (Archiv Math. Naturvidenskab, 1926, 39, 116, 129) is shown to be invalid, since the value calculated for supercooled *cis*-1:2-dihydroxyhydrindene diacetate from a determination of the heat of combustion of a mixture of 32% *trans*- and 68% *cis*-isomerides is nearly 100 kg.-cal. below that obtained with the pure solid *cis*-diacetate.

XIX. Similar data for the corresponding dibenzoates (prepared by the action of benzoyl chloride and pyridine on the appropriate diol) are recorded: *cis*-, m. p. 46.5—47.5°, 2240.9 (2242.3), and *trans*-cyclopentane-1:2-diol dibenzoate, m. p. 62.2—63.2°, 2239.0 (2240.5); *trans*-1-methylcyclopentane-1:2-diol dibenzoate, m. p. 60.2—61.2°, 2394.5 (2396.2) (*cis*-isomeride could not be obtained crystalline); *cis*-, m. p. 109.5—110.5°, 2643.8 (2645.3), and *trans*-1:2-dihydroxyhydrindene dibenzoate, m. p. 77.5—78.5°, 2645.8 (2647.3); *cis*-, m. p. 123—124°, 2797.7 (2799.4), and *trans*-1:2-dihydroxy-1:2:3:4-tetrahydronaphthalene dibenzoate, m. p. 137.2—137.8°, 2796.2 (2797.9); *cis*-, m. p. 128.8—129.8°, 2796.1 (2797.8) (erroneously described as *trans*- by Leroux, A., 1910, ii, 828, who gave m. p. 127°), and *trans*-2:3-dihydroxy-1:2:3:4-tetrahydronaphthalene dibenzoate, m. p. 91.6—92.0°, 2798.3 (2800.1); *cis*-, m. p. 62.6—63.6° (71.5° on remelting), 2390.7 (2392.5) (Brunel, *loc. cit.* erroneously described this as the *trans*-isomeride), and *trans*-cyclohexane-1:2-diol dibenzoate, m. p. 93.0—93.5°, 2386.9 (2388.7) (Brunel, *loc. cit.*, erroneously described as *cis*-isomeride); *trans*-1-methylcyclohexane-1:2-diol dibenzoate, m. p. 101.8—102.6°, 2543.2 (2545.2) (*cis*-isomeride could not be obtained crystalline).

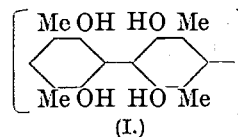
J. W. BAKER.

**Replacement of a nitro-group in 4:5-dinitromethylenedioxybenzene and 4:5-dinitroveratrole by other groups.** A. H. PARIJS (Rec. trav. chim., 1930, 49, 45—56).—The following derivatives of 4-nitromethylenedioxybenzene are prepared from 4:5-dinitromethylenedioxybenzene and the requisite amine in alcoholic solution at 100°: 5-amino-, m. p. 197° (lit. 195—199°); 5-methylamino-, m. p. 171°; 5-ethylamino-, m. p. 133°; 5-n-propylamino-, m. p. 115°; 5-n-butylamino-, m. p. 137°; 5-n-amylamino-, m. p. 95°; 5-n-heptylamino-, m. p. 79°, and 5-dimethylamino-, m. p. 98°. 6:6'-Dinitro-3:4:3':4'-di(methylenedioxy)diphenyl sulphide, m. p. 234°, yellow and orange modifications, and disulphide, m. p. 267° (decomp.) after darkening at 260°, are formed from the above dinitro-derivative and alcoholic sodium sulphide and disulphide, respectively. The following derivatives of 4-nitroveratrole are prepared from 4:5-dinitroveratrole and the requisite amine: 5-methylamino-, m. p. 146°; 5-ethylamino-, m. p. 174—175°; 5-n-propylamino-, m. p. 141—142°; 5-n-butylamino-, m. p. 114°; 5-n-amylamino-, m. p. 90.5°; 5-n-heptyl-

amino-, m. p. 84°, and 5-dimethylamino-, m. p. 130—131°. 4:5-Dinitroveratrole is converted by methylalcoholic sodium methoxide into 4-nitro-1:2:5-trimethoxybenzene; with aqueous methylalcoholic sodium sulphide, 6:6'-dinitro-3:4:3':4'-tetramethoxydiphenyl sulphide, m. p. 220—220.5°, is produced. The 6-nitroveratryl-4:5-thiotriazoveratrole of Jones and Robinson (J.C.S., 1917, 111, 910, 925) is identical with the above sulphide. 6:6'-Dinitro-3:4:3':4'-tetramethoxydiphenyl disulphide has m. p. 212° (decomp.).

H. BURTON.

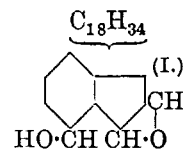
**Oxidation of *m*-xylorcinol [4:6-dihydroxy-*m*-xylene].** T. L. DAVIES and J. F. WALKER (J. Amer. Chem. Soc., 1930, 52, 358—365).—4:6-Dihydroxy-*m*-xylene, m. p. 124.5—125.2° (obtained by the usual method from 4-amino-6-hydroxy-*m*-xylene, using copper sulphate as a catalyst), is oxidised by ferric chloride solution to a mixture of 2:6:2':6'-tetrahydroxy-3:5:3':5'-tetramethyldiphenyl, m. p. 242—243° (tetra-acetate, m. p. 158—159°), and the ether (I), chars gradually above 250°; I is formed by



further oxidation of the diphenyl derivative, which O is obtained in optimum yield when the oxidation is carried out in presence of ether. Bromination of 4:6-dihydroxy-*m*-xylene in chloroform affords a bromo-derivative, m. p. 119—119.5°, which is oxidised by ferric bromide solution to a mixture of a compound, C<sub>20</sub>H<sub>16</sub>O<sub>4</sub>Br<sub>2</sub> (?), chars gradually between 265° and 278°, and an amorphous substance, m. p. 128—135°. Bromination of the above tetrahydroxytetramethyldiphenyl in boiling chloroform affords a compound, C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>Br<sub>2</sub>, m. p. 274—277° (decomp.). An excess of bromine water converts 4:6-dihydroxy-*m*-xylene into small amounts of three substances, m. p. 71—72°, 173°, and 194°, respectively.

H. BURTON.

**Constitution of cholesterol. X. Action of persulphuric acid.** E. MONTIGNIE (Bull. Soc. chim., 1930, [iv], 47, 93—95).—With persulphuric acid in light petroleum cholesterol yields an oxide, m. p. 141°, which does not combine with bromine in chloroform and yields an acetate, m. p. 98° (cf. Westphalen, A., 1915, i, 884). The constitution (I) is suggested. With xanthydrol in acetic acid at 100°, cholesterol yields xanthyl-cholesterol, m. p. 141.5—142°, [α]<sub>D</sub><sup>20</sup> —53° (bromide, m. p. 103°).



R. BRIGHTMAN.

**Dehydroergosterol and ergosterol.** A. WINDAUS, W. BERGMANN, and H. BUTTE (Annalen, 1930, 477, 268—278).—Reduction of dehydroergosterol (Windaus and Linsert, A., 1928, 1372) with sodium and alcohol converts it into dihydrodehydroergosterol (ergosterol-F), m. p. 150—151°, [α]<sub>D</sub><sup>20</sup> —20° (acetyl derivative, m. p. 152—153°, [α]<sub>D</sub><sup>20</sup> —23.5°; phenylurethane, m. p. 167°, [α]<sub>D</sub><sup>20</sup> —18.4°, depressing the m. p. of the phenylurethane, m. p. 178°, [α]<sub>D</sub><sup>20</sup> —16°, of dihydroergosterol), which has characteristic bands in the spectrum at 252 and 235 μμ, and is reduced by platinum and hydrogen in acetic acid to allo-α-ergosterol acetate. Reduction of dehydroergosterol (or its peroxide) with sodium and boiling propyl

alcohol, however, yields *dihydroergosterol-II*, m. p. 158—159°,  $[\alpha]_D^{25} -6.6^\circ$  (acetyl derivative, m. p. 157°,  $[\alpha]_D^{25} -7.27^\circ$ ; *phenylurethane*, m. p. 177—178°) (band at 240  $\mu$ ), isomeric with dihydroergosterol and also reduced at *allo- $\alpha$ -ergostanol*. Reduction of dehydroergosterol peroxide with zinc dust and boiling alcoholic potassium hydroxide yields an *ergostatrienediol*,  $C_{27}H_{42}O_2$ , m. p. 220—221°,  $[\alpha]_D^{25} +48.3^\circ$  (monoacetyl derivative, m. p. 216°,  $[\alpha]_D^{25} +48.05^\circ$ ) (band at 240  $\mu$ ), reduced catalytically to *allo- $\alpha$ -ergostanol*, but converted by sodium and alcohol into an *ergostenediol*, probably identical with that obtained by Windaus, Bergmann, and Lüttringhaus (A., 1929, 1065) from ergosterol peroxide. When ergosterol is heated with alcoholic sodium ethoxide in a sealed tube at 175° it is converted into two isomeric alcohols,  $C_{27}H_{44}O$  (two double linkings), dihydroergosterol II (above), separated by its insoluble digitonin compound from *epidihydroergosterol*, m. p. 208°,  $[\alpha]_D^{25} -20.4^\circ$ , the *acetate*, m. p. 148—149°, of which is reduced by hydrogen and a platinum catalyst to the *acetate*, m. p. 144°,  $[\alpha]_D^{25} +20.5^\circ$ , of *epiergostanol* characterised by Reindel and Detzel (A., 1929, 61). Similar treatment of the ketone of dihydroergosterol with sodium ethoxide gives mainly dihydroergosterol and only a small amount of *epidihydroergosterol*. J. W. BAKER.

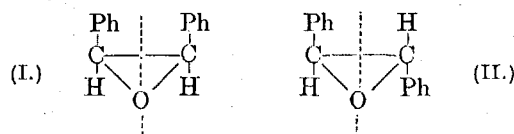
**Three homologues of ephedrine.** E. FOURNEAU and C. E. BARRELET (Bull. Soc. chim., 1930, [iv], 47, 72—86).—See this vol., 85.

**Grignard compounds of certain polyhalogenated benzene derivatives and their condensation products with aromatic aldehydes and ketones.** M. A. MIHĂILESCU and S. P. CARAGEA (Bull. Acad. Sci. Roumaine, 1929, 12, 7—18).—Decomposition of the Grignard reagents prepared from *p*-chloriodo- and *p*-chlorobromo-benzene, respectively, with water yielded, in both cases, chlorobenzene and traces of 4:4'-dichlorodiphenyl; *p*-dibromobenzene gave bromobenzene and a small quantity of 4:4'-dibromodiphenyl. The following compounds were obtained by condensation of magnesium *p*-chlorophenyl iodide and the under-mentioned aldehydes and ketones: 4-chlorobenzhydrol, m. p. 62°, from benzaldehyde; 4-chloro-4'-methoxybenzhydrol, m. p. 60°, from anisaldehyde; 4-chloro-4'-dimethylaminobenzhydrol, m. p. 103—104°, from *p*-dimethylaminobenzaldehyde; *p*-chlorotriphenylcarbinol, m. p. 85°, from benzophenone; *p*-chlorophenylbenzoin, m. p. 84°, or *s*-4:4'-dichlorotetraphenyl glycol, m. p. 169°, depending on the experimental conditions, from benzil. Using magnesium *p*-bromophenyl bromide, the following substances were prepared: *p*-bromobenzhydrol, m. p. 65°, 4-bromo-4'-dimethylaminobenzhydrol, m. p. 107°, 4-bromo-4'-methoxybenzhydrol, m. p. 75°, *p*-bromotriphenylcarbinol, *p*-bromophenylbenzoin, m. p. 88°, and 4:4'-dibromotetraphenyl glycol, m. p. 178°.

A. I. VOGEL.

**Optically active diphenylethylene oxide.** J. READ and I. G. M. CAMPBELL (Nature, 1930, 125, 16—17).—*s*-Diphenylethylene oxide has been prepared from *d*-diphenyl- and *l*-isodiphenyl-hydroxyethyl amine; the optically active and externally compensated forms of the *iso*-base yielded an identical optically inactive diphenylethylene oxide (I), whilst

the former gave a strongly laevorotatory oxide (II); hence the configurations allocated to the bases by Erlenmeyer must be reversed.



The specific rotatory power of the *l*-oxide (for sodium light in absolute alcohol) exceeds  $-300^\circ$ , whilst that for *l*-isohydrobenzoin is only  $-92^\circ$ , whence the optical effect of the three-membered ring is apparent.

A. A. ELDRIDGE.

**Configuration of *l*-phenylalanine, *l*-tyrosine, and *l*-dihydroxyphenylalanine.** P. KARRER and W. KEHL (Helv. Chim. Acta, 1930, 13, 50—63).—The rotatory powers of a series of *N*-acyl derivatives of *l*-leucine (and its methyl ester) are similar in sign and magnitude to the corresponding series from *l*-hexahydroxyphenylalanine (and its methyl ester), indicating that the amino-acids have the same stereochemical configuration. The results also show that *l*-phenylalanine, *l*-tyrosine, and *l*-dihydroxyphenylalanine have the same configuration as *d*-alanine and the other acids in group 1 of Karrer, Escher, and Widmer's classification (A., 1926, 505).

The *N*-benzoyl derivative, m. p. 102°,  $[\alpha] -21.14^\circ$  (all rotatory powers are at 20° for the *D* line in alcoholic solution), of *l*-leucine methyl ester is hydrolysed by aqueous-alcoholic sodium hydroxide to *N*-benzoyl-*l*-leucine,  $[\alpha] -10.82^\circ$ , purified through the quinidine salt, m. p. 148°. The following *N*-acyl derivatives of *l*-leucine are also described: *p*-nitrobenzoyl, m. p. 219—220°,  $[\alpha] -8.87^\circ$  (methyl ester, m. p. 103.5°,  $[\alpha] -16.92^\circ$ ); benzenesulphonyl, m. p. 119°,  $[\alpha] -4.36^\circ$  (methyl ester, m. p. 64°,  $[\alpha] -20.75^\circ$ ); toluenesulphonyl, m. p. 113.5°,  $[\alpha] -4.05^\circ$  (methyl ester, m. p. 55°,  $[\alpha] -15.95^\circ$ ), and  $\beta$ -naphthalenesulphonyl, m. p. 117.5—118°,  $[\alpha] +1.72^\circ$  (methyl ester, m. p. 91.5—92°,  $[\alpha] -31.09^\circ$ ).

*l*-Hexahydroxyphenylalanine,  $[\alpha] -11.37^\circ$  (hydrochloride,  $[\alpha] +13.4^\circ$ ), is conveniently prepared by the catalytic reduction (platinum) of *l*-tyrosine in presence of dilute hydrochloric acid (cf. Waser and Brauchli, A., 1924, i, 1068). The following *N*-acyl derivatives of *l*-hexahydroxyphenylalanine are described: benzoyl, m. p. 124.5—125°,  $[\alpha] -12.68^\circ$  (cf. *loc. cit.*) (methyl ester, m. p. 104.5—105°,  $[\alpha] -26.66^\circ$ , prepared by esterification with ethereal-alcoholic diazomethane); *p*-nitrobenzoyl, m. p. 158.5—159°,  $[\alpha] -5.04^\circ$  (the methyl ester, m. p. 72°,  $[\alpha] -21.2^\circ$ , is accompanied by a small amount of by-product); benzenesulphonyl, m. p. 147.5°,  $[\alpha] -2.33^\circ$  (methyl ester, m. p. 61—61.5° after sintering at 56°,  $[\alpha] -21.92^\circ$ ); toluenesulphonyl, m. p. 160.5°,  $[\alpha] +1.14^\circ$  (the methyl ester, m. p. 114°,  $[\alpha] -17.13^\circ$ , is accompanied by a by-product, m. p. 59°), and  $\beta$ -naphthalenesulphonyl, m. p. 185°,  $[\alpha] +11.24^\circ$  (methyl ester, m. p. 99° after sintering at 95°,  $[\alpha] -22.77^\circ$ ).

H. BURTON.

**$\beta$ -Phenylisobutyl alcohol and derivatives.** G. DARZENS and A. LÉVY (Compt. rend., 1929, 189, 1287—1289).—Phenylacetone nitrile is methylated by Bodroux and Taboury's method (A., 1910, i, 257) to

$\alpha$ -phenylisobutyronitrile, b. p. 115–116°/14 mm., which is hydrolysed by 90% sulphuric acid, first in the cold and then at 70°, to  $\alpha$ -phenylisobutyramide, m. p. 160–161°. This is converted by isoamyl alcohol and sulphuric acid at 150° into isoamyl  $\alpha$ -phenylisobutyrate, b. p. 155°/10 mm., which is reduced by sodium and isoamyl alcohol to  $\beta$ -phenylisobutyl alcohol, b. p. 115–116°/10 mm.,  $d_4^{20}$  1.013 (benzoate, m. p. 37.5°; acetate, b. p. 127°/13 mm.; corresponding bromide, b. p. 103°/12 mm.; ethyl ether, b. p. 72°/12 mm.).

H. BURTON.

**Fatty acid derivatives. II. Solid derivative of phenylstearic acid.** T. MAZUME and K. KINO (J. Soc. Chem. Ind. Japan, 1929, 32, 338–339B).—Phenylstearic acid, obtained by hydrolysing the methyl ester, b. p. 228°/4 mm., reacts with *p*-aminoazobenzene to give phenylstearyl-*p*-aminoazobenzene, m. p. 82–82.5°. An analogous azo-derivative from  $\beta$ -naphthylamine could not be isolated.

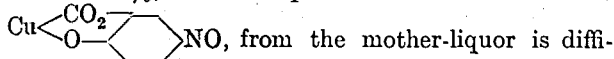
C. W. SHOPPEE.

**Autocatalysis in oxidation. I. Auto-oxidation of abietic acid.** G. DUPONT and J. LÉVY (Bull. Soc. chim., 1930, [iv], 47, 60–68).—See this vol., 86.

**Carbithioic acids. I. *p*-Tolylcarbithioic [dithio-*p*-toluic] acid and derivatives.** R. W. BOST and W. J. MATTOX (J. Amer. Chem. Soc., 1930, 52, 332–335).—Magnesium *p*-tolyl bromide and carbon disulphide react at 0° forming dithio-*p*-toluic acid, which solidifies at 27° (cf. Sakurada, A., 1927, 134) [zinc, m. p. 180°, and lead, m. p. 200° (decomp.), salts methyl, b. p. 130°/3 mm., ethyl, b. p. 132°/3 mm.,  $d_4^{20}$  1.1173 (cf. loc. cit.), *n*-butyl, b. p. 169°/5 mm.,  $d_4^{20}$  1.070, and *p*-nitrobenzyl esters, m. p. 70.5° (all prepared from the sodium salt and the corresponding alkyl halide or sulphate); amide, m. p. 155°; *p*-toluidide, m. p. 170.5°]. The acid decomposes on attempted distillation, does not furnish an acid chloride, and when treated with nitric acid in ethereal solution is oxidised to *p*-toluic acid.

H. BURTON.

**Nitrosation of salicylic acid by copper nitrite.** V. G. GULINOV (Ukrain. Chem. J., 1929, 4, [Tech.], 215–225).—The yield of nitroso-compound obtained when sodium salicylate is treated with copper nitrite reaches 95%, but the separation of the nitroso-salt,



This separation occurs more readily at 22–23° than at 7–8° or at 14–15°, a 93.2% yield being obtained from the reacting solution after 80 hrs., with a lower proportion of sodium sulphite in the precipitate. An experiment on a larger scale with commercial salicylic acid (560 g.) gave a yield of 86.2%.

T. H. POPE.

**Preparation of aminosulphosalicylic acid from nitrososalicylic acid.** V. G. GULINOV (Ukrain. Chem. J., 1929, 4, [Tech.], 227–239).—Reduction of copper nitrososalicylate by means of sulphite results in the formation of 3-amino-6-hydroxy-2:4-disulphobenzoic acid. The best results are obtained by using normal sodium sulphite as reducing agent. When either a mixture of sodium and ammonium sulphites, or ammonium sulphite alone, or sodium hydrogen sulphite is employed, the yield is low, the product is diffi-

cult to separate, and it is impossible to remove copper salts which largely remain in solution with the amino-compound. The acid obtained always contains admixed 3:6-dihydroxy-4-sulphobenzoic acid.

T. H. POPE.

**Stereoisomerism of disulphoxides and related substances. V. Dioxides of 3:5-dimethylthiolbenzoic acid.** E. V. BELL and G. M. BENNETT (J.C.S., 1930, 1–6).—3:5-Dimethylthiolbenzoic acid dioxide exists in two forms,  $\alpha$ - or *meso*-, and  $\beta$ -, which is potentially active and has been resolved by means of brucine. 3:5-Dimethylthiolbenzoic acid, m. p. 153° [sodium salt, m. p. 283° (decomp.)], was synthesised as follows: carboxybenzene-3:5-disulphonyl chloride (preparation by improved method described) was reduced by zinc and hydrochloric acid in acetic acid to 3:5-dithiolbenzoic acid, not isolated as such, but oxidised in solution to 3:5-disulphidobenzoic acid, m. p. 195–200° (decomp.), which was then reduced with dextrose in alkaline solution and treated with methyl sulphate. On oxidation with hydrogen peroxide it gave  $\alpha$ - and  $\beta$ -dimethylthiolbenzoic acid dioxides, m. p. 251° (decomp.) and 209° (decomp.), separated by crystallisation from alcohol. The brucine salts, when freed from chloroform of crystallisation, melted at 170–175° (decomp.) and 130°, respectively. The former was unchanged on recrystallisation from chloroform, consequently the  $\alpha$ -dioxide is the *meso*-form; the brucine salt of the  $\beta$ -dioxide after seven recrystallisations from chloroform had  $[\alpha]_D -59.7^\circ$  and m. p. 184°, but was not optically pure. The 1-3:5-dimethylthiolbenzoic acid dioxide isolated from this had  $[\alpha]_D -99.65^\circ$  in water, m. p. 200–202° (after recrystallisation). d-3:5-Dimethylthiolbenzoic acid dioxide was isolated from the mother-liquors in an optically impure form, m. p. 190–205°,  $[\alpha]_D +22.7^\circ$  in water.

s-Diphenylthioethane-mm'-dicarboxylic acid, m. p. 265°, obtained by reduction of *m*-dithiobenzoic acid with dextrose in alkaline solution and condensing the product with ethylene dibromide, did not give a pure product on oxidation with hydrogen peroxide. Its methyl ester, m. p. 73°, however, gave a mixture of  $\alpha$ - and  $\beta$ -dioxides, m. p. 195° (decomp.) and 126–129° (decomp.), respectively. Both yielded the parent sulphide on reduction, but on hydrolysis suffered disruption. Consequently resolution could not be effected.

H. A. PRIGGOTT.

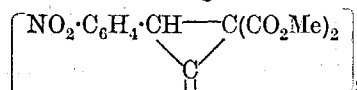
**Bromination of 2:4-dimethoxycinnamic acid.** M. REIMER and E. TOBIN (J. Amer. Chem. Soc., 1930, 52, 341–347).—Treatment of 2:4-dimethoxycinnamic acid with bromine in presence of chloroform affords 5: $\alpha$  $\beta$ -tribromo-2:4-dimethoxy- $\beta$ -phenylpropionic acid (I), m. p. 228–229° (decomp.) [the methyl (II), m. p. 142° (decomp.), and ethyl esters (III), m. p. 158° (decomp.)], can be obtained only by esterification with ethereal diazomethane and diazoethane, respectively; addition of bromine could not be accomplished without nuclear bromination. Attempted esterification of I with methyl-alcoholic hydrogen chloride gives the methyl ester, m. p. 149°, of  $\alpha$ :5-dibromo- $\beta$ :2:4-trimethoxy- $\beta$ -phenylpropionic acid, m. p. 171° (decomp.) (the ethyl ester, m. p. 109°, is prepared from the acid and diazoethane or by

dissolution of III in methyl alcohol), also formed together with the methyl ester by dissolution of I in methyl alcohol. The ethyl ester, m. p. 105–107°, of  $\alpha$ :5-dibromo-2:4-dimethoxy- $\beta$ -ethoxy- $\beta$ -phenylpropionic acid, m. p. 161–162° (decomp.) (methyl ester, m. p. 138° after softening at 134°, is also prepared from the acid and diazomethane or from II and ethyl alcohol), is obtained similarly. Treatment of I with methyl-alcoholic potassium hydroxide solution, affords  $\omega$ :5-dibromo-2:4-dimethoxystyrene, m. p. 67–68°, readily decomposed by light. The dibromide, m. p. 146° (slight decomp.), of this styrene is converted by dissolution in methyl alcohol into  $\alpha$ :5-tribromo- $\beta$ :2:4-trimethoxy- $\beta$ -phenylethane, m. p. 138–139° (the corresponding  $\beta$ -ethoxy-derivative, m. p. 117–120°, is prepared similarly). Addition of bromine to methyl 2:4-dimethoxycinnamate affords II, but attempted addition to ethyl 2:4-dimethoxycinnamate, m. p. 68–69°, results in the formation of 5-bromo-2:4-dimethoxybenzaldehyde, m. p. 134–138° (semicarbazone, decomp. about 275°). Distillation of the ethyl ester, m. p. 68–69°, gives an isomeric ethyl 2:4-dimethoxycinnamate, b. p. 219°/22 mm., m. p. 61°, which when treated with bromine affords III.

H. BURTON.

**cycloPropane series. XII. Nitrocyclopropanes.** E. P. KOHLER and S. F. DARLING (J. Amer. Chem. Soc., 1930, 52, 424–432).—Methyl *m*- and *p*-nitrobenzylidenemalonates, m. p. 98–99° and 133–134°, respectively, are converted by short treatment with sodium methoxide and subsequent acidification with acetic acid into methyl  $\beta$ -*m*- and *p*-nitrophenyl- $\beta$ -methoxyethane- $\alpha\alpha$ -dicarboxylates, m. p. 66° and 116°, respectively. These are brominated in chloroform solution to the corresponding  $\alpha$ -bromo-derivatives, m. p. 78–80° and 133°, respectively. Methyl  $\alpha$ -cyano-*m*-nitrocinnamate has m. p. 135–137°. Addition of nitromethane to the above nitrobenzylidenemalonates and bromination of the products formed in chloroform affords  $\alpha$ -bromo-esters, whilst bromination in presence of sodium methoxide gives  $\gamma$ -bromo-esters. The following are described: ethyl  $\alpha$ -bromo- $\gamma$ -nitro- $\beta$ -*m*-nitrophenylpropane- $\alpha\alpha$ -dicarboxylate, m. p. 85.5° (methyl ester, m. p. 123°); ethyl  $\alpha$ -bromo- $\gamma$ -nitro- $\beta$ -*p*-nitrophenylpropane- $\alpha\alpha$ -dicarboxylate, m. p. 88°; methyl  $\alpha$ - and  $\gamma$ -bromo- $\gamma$ -nitro- $\beta$ -phenylpropane- $\alpha\alpha$ -dicarboxylates, m. p. 107–109° and 81.5–83°, respectively, and methyl  $\gamma$ -bromo- $\gamma$ -nitro- $\beta$ -*m*-nitrophenylpropane- $\alpha\alpha$ -dicarboxylate, m. p. 147–148°. Treatment of the last-named ester with methyl-alcoholic potassium acetate affords methyl 3-nitro-2-*m*-nitrophenylcyclopropane-1:1-dicarboxylate, m. p. 122–123.5°. This is converted by treatment with methyl sodiomalonate into methyl  $\beta$ -*m*-nitrobenzylidenepropane- $\alpha\alpha\gamma\gamma$ -tetracarboxylate (I), m. p. 92–94° (ozonolysis product *m*-nitrobenzaldehyde), and by boiling methyl-alcoholic potassium acetate into methyl  $\beta$ -methoxy- $\gamma$ -*m*-nitrophenyl- $\Delta^{\beta}$ -propene- $\alpha\alpha$ -dicarboxylate (II), m. p. 104–105°, which is hydrolysed by methyl-alcoholic hydrochloric acid to methyl *m*-nitrophenacylmalonate, m. p. 64–66° [copper derivative, m. p. 195–200° (decomp.)]. Treatment of this ketonic ester with semicarbazide gives a compound, C<sub>26</sub>H<sub>11</sub>O<sub>6</sub>N<sub>4</sub>, m. p. 177–179°.

When the above cyclopropane ester is treated with methyl-alcoholic sodium methoxide, a red sodium salt is first produced. When this is added to methyl-alcoholic hydrogen chloride at 0°, nitrous acid is evolved, and II and a compound (III), C<sub>26</sub>H<sub>22</sub>O<sub>12</sub>N<sub>2</sub>, m. p. 115–116°, are produced. Treatment of this compound with sodium methoxide or methyl sodiomalonate furnishes II or I, respectively. With bromine in boiling chloroform it yields a bromo-derivative, m. p. 154–155°, and with sulphuric acid at the ordinary temperature yields two substances, C<sub>22</sub>H<sub>18</sub>O<sub>8</sub>N<sub>2</sub>, m. p. 140° after softening at 135°, and C<sub>24</sub>H<sub>20</sub>O<sub>11</sub>N<sub>2</sub>·H<sub>2</sub>O, m. p. 122° (with loss of water), m. p. (anhydrous) 157°. The compound III is readily oxidised with cold potassium permanganate solution but it is relatively inert to acidic reagents. The following constitution is assigned to III:



H. BURTON.

**Synthesis of dimethoxyphthalimidineacetic acid.** W. M. RODIONOV and A. M. FEDOROVA (J. Amer. Chem. Soc., 1930, 52, 368–371).—Opianic and malonic acids react in presence of 10% alcoholic ammonia at 100°, yielding a mixture of meconine-acetic acid, m. p. 165–167°, and  $\beta$ -amino- $\beta$ :3:4-dimethoxy-2-carboxyphenylpropionic acid, m. p. 132–134° with loss of water. Dehydration of this amino-acid at 140–150° gives 3:4-dimethoxyphthalimidine-acetic acid (I), m. p. 174–175° [methyl ester, m. p. 141–143°; nitroso-derivative, m. p. 167° (decomp.)]. Methyl opianate and malonic acid condense similarly, forming I, whilst opianic acid and ethyl malonate afford ethyl meconinemalonate, m. p. 74–75°.

H. BURTON.

**Action of sodium ethoxide on ethyl cyclohexane-2:3-dione-1:4-dicarboxylate.** L. S. DEDUSENKO (Acta Univ. Asiae Med., 1928, [vi], No. 1, 3–16).—With excess of alcohol, ethyl cyclohexane-2:3-dione-1:4-dicarboxylate is converted by sodium ethoxide into ethyl cyclopentan-2-ol-1:2:3-tricarboxylate, the reverse change taking place in the absence of alcohol under the influence of sodium and sodium ethoxide. In the condensation of adipic with oxalic ester, only ethyl oxaladipate, in addition to cyclohexane-2:3-dione-1:4-dicarboxylate, cyclopentenetricarboxylate, and cyclopentan-2-ol-1:2:3-tricarboxylate, was identified. Probably the last-named compound is a primary transformation product of the oxaladipate, which may eliminate water to form the cyclopentenetricarboxylate, or alcohol to form ethyl cyclohexane-2:3-dione-1:4-dicarboxylate. The hypothesis that the conversions  $\text{CO} \cdot \text{CO} + \text{EtOH} \rightleftharpoons >\text{C}(\text{OH}) \cdot \text{CO}_2\text{Et}$  constitute a reversible process is supported.

CHEMICAL ABSTRACTS.

**Oxidation of benzaldehyde.** W. P. JORISSEN and P. A. A. VAN DER BEEK (Rec. trav. chim., 1930, 49, 138–141).—The various theories of autoxidation of benzaldehyde are reviewed. When benzaldehyde is kept in sealed tubes in the dark (a small quantity

of air being present), the product gives a peroxide reaction (liberation of iodine from potassium iodide). This cannot be due to the formation of benzoyl hydrogen peroxide, which would have reacted with the benzaldehyde (cf. A., 1926, 519; 1928, 413). Exposure of the stored material to sunlight for a short time causes the disappearance of the peroxide reaction. The autoxidation process is not yet satisfactorily explained.

H. BURTON.

**Action of bromine on the *p*-tolylhydrazones of benzaldehyde and of the nitrobenzaldehydes.** F. D. CHATTAWAY and A. B. ADAMSON (J.C.S., 1930, 157—163).—Bromination of the *p*-tolylhydrazones of benzaldehyde and of the nitrobenzaldehydes occurs first in the *o*-position with respect to the nitrogen atom of the *p*-tolyl nucleus and the  $\omega$ -position simultaneously, further action of bromine substituting the remaining *o*-position in the *p*-tolyl nucleus. The  $\omega$ -bromohydrazones produced are converted by acetic anhydride and sodium acetate into  $\beta$ -acetylhydrazides of the corresponding acids, and by ammonia into hydrazidines of the general formula

$\text{NHR}'\cdot\text{N}'\text{C}(\text{NH}_2)\text{R}$ , highly coloured weak bases yielding colourless hydrochlorides. In the case of *o*-nitrobenzaldehyde these  $\omega$ -bromo-compounds on crystallisation from alcohol yield the violently explosive ketoendoaryliminodihydrobenzisodiazole oxides (the so-called isodiazole compounds; cf. A., 1926, 169), which on long boiling with the same solvent are reduced to the corresponding isodiazoles (A., 1927, 353).

By the action of 2 mols. of bromine in acetic acid on *m*-nitrobenzaldehyde-*p*-tolylhydrazone,  $\omega$ -bromo-*m*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone, m. p. 145.5°, is obtained ( $\beta$ -acetyl derivative not obtained crystalline); further bromination gave  $\omega$ -bromo-*m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, m. p. 154.5° ( $\beta$ -acetyl compound, m. p. 170°), also obtained by brominating *m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone. Similarly prepared are:  $\omega$ -bromo-*p*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone, m. p. 176° ( $\beta$ -acetyl compound, m. p. 173°),  $\omega$ -bromo-*p*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, m. p. 161° ( $\beta$ -acetyl compound, m. p. 183°);  $\omega$ -bromobenzaldehyde-3-bromo-*p*-tolylhydrazone, m. p. 74°, and  $\omega$ -bromobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, m. p. 106° ( $\beta$ -acetyl compound, m. p. 190°). In every case the acetyl compounds of the dibromohydrazones gave on hydrolysis the corresponding benzoic acid, 3-bromo-*p*-tolylhydrazine, and acetic acid, whilst those of the tribromohydrazones gave the corresponding benzoic acid, and  $\alpha$ -acetyl-3 : 5-dibromo-*p*-tolylhydrazine. 3-Bromo-*p*-tolyl-*m*-nitrobenzhydrazidine, red, has m. p. 136°, [hydrochloride, m. p. 230° (decomp.)]; 3 : 5-dibromo-*p*-tolyl-*m*-nitrobenzhydrazidine, m. p. 151°; 3-bromo-*p*-tolyl-*p*-nitrobenzhydrazidine, deep purple, m. p. 155°; 3 : 5-dibromo-*p*-tolyl-*p*-nitrobenzhydrazidine, orange-yellow, m. p. 145°.

$\omega$ -Bromo-*o*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone, m. p. 105°, yields, when crystallised from alcohol, the highly explosive 3-keto-1 : 2-endo-3'-bromo-*p*-tolylimino-2 : 3-dihydrobenzisodiazole 1-oxide, explosion point 139°, which, when boiled for 2 hrs. with alcohol, gives 3-keto-1 : 2-endo-3'-bromo-*p*-tolylimino-2 : 3-dihydrobenzisodiazole, m. p. 166°. *o*-Nitrobenzaldehyde-

*p*-tolylhydrazone yields with excess of bromine in the cold 3 : 5-dibromo-*p*-toluidine perbromide, m. p. 134° (decomp.).  $\omega$ -Bromo-*o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, obtained by brominating *o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, has m. p. 123° (decomp.). The benzisodiazole oxide, obtained by crystallisation from alcohol, had explosion point 167°, and the benzisodiazole, m. p. 190° (decomp.). *o*-Nitrobenzaldehyde-*p*-tolylhydrazone with bromine in acetic acid in presence of sodium acetate yields 3-keto-1 : 2-endo-*p*-tolylimino-2 : 3-dihydrobenzisodiazole 1-oxide, explodes at 143°; even with excess of bromine the product remains halogen-free.

H. A. PIGGOTT.

**Structure and tautomerism of *o*-nitrobenzaldehyde.** Interference of nitro-groups with the Zerevitinov method for the determination of active hydrogen. H. GILMAN and R. E. FOTHERGILL (Bull. Soc. chim., 1929, [iv], 45, 1132—1136).—With nitrobenzene and *o*-nitrotoluene in *n*-butyl ether, magnesium methyl iodide yields from 1.13 to 1.57 equivalents of hydrogen. In pyridine the reaction is slower and the results were less accurate, but nitrobenzene gave 1.49 equivalents of hydrogen in 10 min. *n*-Butyl ether and pyridine thus give higher results (cf. A., 1928, 64, 536) than ether as solvent. The gas evolved contains unsaturated compounds, and even with 1 : 2 : 4 : 6-tetrachloro-3 : 5-dinitrobenzene and tribromonitromethane in *n*-butyl ether or with trichloronitromethane in isoamyl ether, which contain no hydrogen, gas is liberated on treatment with magnesium methyl iodide, 1 : 2 : 4 : 6-tetrachloro-3 : 5-dinitrobenzene affording 1.96—2.24 equivalents, containing very little methyl chloride. Accordingly, the quantitative liberation of methane by Zerevitinov's method cannot be adduced as evidence for Tanasescu's cyclic hydroxy-formula for *o*-nitrobenzaldehyde (A., 1926, 726).

R. BRIGHTMAN.

**Isomerisation of hydroxyaldehydes. II. Transformation of bromodicyclohexylacetaldehyde and dicyclohexylglycolaldehyde.** S. DANILOV and E. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1929, 61, 1661—1682).—See A., 1929, 1448.

**Replacement of the aldehyde group in piperonal and its derivatives.** A. H. PARIJS (Rec. trav. chim., 1930, 49, 17—32).—Nitration of piperonal in acetic acid suspension gives 4-nitromethylenedioxybenzene and 6-nitropiperonal (azine, decomp. about 257°; phenylhydrazone, m. p. 218.5° with blackening and evolution of gas; *p*-nitrophenylhydrazone, decomp. 245—248°; semicarbazone, decomp. 272.5—278°; semioxamazone, m. p. 325° with blackening and evolution of gas). The acetic acid appears to exert some protective influence on the aldehyde group, since the yield of the former nitro-compound is only 15—18% (cf. Salway, J.C.S., 1909, 95, 1163). Chlorination of piperonal, using a slight modification of the method of Robinson and others (J.C.S., 1917, 111, 948), affords a small amount of 4 : 5-dichloromethylenedioxybenzene in addition to 6-chloropiperonal [diacetate, m. p. 133°; azine, m. p. 303° (decomp.) after darkening at 300°; phenylhydrazone, m. p. 117—118°; *p*-nitrophenylhydrazone, m. p. 281—282° (decomp.); semicarbazone, m. p. 280° (violent decomp.) after



darkening at 278°; *semioxamazone*, m. p. 299° (decomp.) after darkening at 291°. 5-Chloro-4-nitromethylenedioxybenzene (from 6-chloropiperonal by nitration) is reduced by stannous chloride and alcoholic hydrochloric acid to the corresponding amino-derivative, m. p. 99° [*hydrochloride*, m. p. 254—255° (decomp.) after becoming yellow at 189° and blackening at 247°]. Treatment of the chloro-nitro-derivative with alcoholic methylamine at 135° gives 4-nitro-5-methylaminomethylenedioxybenzene, also obtained by similar treatment of 4:5-dinitromethylenedioxybenzene. Similar treatment of the chloro-derivative with alcoholic ammonia affords only a small amount of the 5-amino-derivative, but the 5-ethylamino-, 5-*n*-propylamino-, and 5-dimethylamino-compounds are readily produced with the appropriate amine. Treatment of 5-chloro-4-nitromethylenedioxybenzene with alcoholic sodium sulphide or disulphide gives 6:6'-dinitro-3:4:3':4'-di(methylenedioxy)diphenyl disulphide, m. p. 267° (decomp.) after darkening at 260°.

Bromination of piperonal in acetic acid furnishes 6-bromopiperonal [*azine*, m. p. 252° (decomp.) after darkening at 249°; *p*-nitrophenylhydrazone, m. p. 253° (decomp.); *semicarbazone*, m. p. 230° (decomp.); *semioxamazone*, m. p. 278—279° (decomp.)], and some 4:5-dibromomethylenedioxybenzene. 5-Bromo-4-nitromethylenedioxybenzene is converted by alcoholic sodium disulphide into the above disulphide (also obtained by similar treatment of 4:5-dinitromethylenedioxybenzene); reaction is much slower than with the corresponding chloro-compound. 5-Bromo-3:4-dinitromethylenedioxybenzene (prepared by nitration of 6-bromopiperonal) is converted by alcoholic methylamine at 100° into 5-bromo-3-nitro-4-methylaminomethylenedioxybenzene, m. p. 167° (decomp.).

H. BURTON.

**Opening of the methylenedioxy-ring.** A. H. PARLIS (Rec. trav. chim., 1930, 49, 33—44).—Attempted nitration of 6-nitropiperonylidene diacetate, m. p. 142°, with a mixture of 100% nitric acid and acetic anhydride at -5° affords 6-nitroprotocatechualdehyde, m. p. 203° (decomp.) [*azine*, darkens at 241° and becomes black at 278°; *semicarbazone*, m. p. 254° (decomp.); *phenylhydrazone*, m. p. 203° (decomp.); *p*-nitrophenylhydrazone, m. p. 290° (decomp.)], fission of the methylenedioxy-ring having occurred. Similarly, 6-bromopiperonylidene diacetate, m. p. 128°, yields 6-bromoprotocatechualdehyde, m. p. 220° [*azine*, m. p. 251° (decomp.); *semicarbazone*, m. p. 239° (decomp.); *p*-nitrophenylhydrazone, m. p. 243° (decomp.)].

4:5-Dinitromethylenedioxybenzene is converted by methylalcoholic sodium methoxide solution into 4:5-dinitroguaiacol, m. p. 177° (lit. 172°) (corresponding 2-ethoxy-derivative, m. p. 113°), methylated to 4:5-dinitroveratrole. Under similar conditions piperonal undergoes the Cannizzaro reaction, whilst 4:5-dibromomethylenedioxybenzene is unaffected.

Other methods (lit.) of opening the methylenedioxy-ring are reviewed.

H. BURTON.

**Derivatives of cyclohexanone including several new indicators.** B. SAMDAHL (J. Pharm. Chim., 1930, [viii], 11, 8—19).—The following compounds

were prepared by treatment of 1 mol. of the required cyclohexanone with 2 mols. of the appropriate aldehyde dissolved in hot acetic acid through which a current of hydrogen chloride was passing: *di*-5-bromovanillylidene-cyclohexanone, m. p. 222—224° (decomp.); *di*-5-bromovanillylidene-*m*- and -*p*-methylcyclohexanones, m. p. 171° [+EtOH, m. p. 120° (decomp.)] and 189°, respectively; *di*-5-nitrovanillylidene-cyclohexanone, m. p. 241—242° (decomp.); *di*-4-hydroxy-3-ethoxybenzylidenecyclohexanone, m. p. 158° (corresponding derivatives of *m*- and *p*-methylcyclohexanones have m. p. 153° and 148—149°, respectively); *di*-3:4-dihydroxybenzylidenecyclohexanone, m. p. 242—245° (decomp.), and *di*-3:4-dihydroxybenzylidene-*m*- and -*p*-methylcyclohexanones, m. p. 242—245° (decomp.) and 221—223° (decomp.), respectively.

Several of these compounds may be of use as indicators. Their colour changes from yellow to orange between  $p_H$  6.8 and 7.0, passing through red to violet at about  $p_H$  11.7. R. J. W. LE FÈVRE.

**Constitution of so-called tetrahydropyrene compounds.** R. CORNUBERT (Compt. rend., 1930, 190, 308—309).—Reduction of benzylidene-2:2-dimethylcyclohexanone with hydrogen and a nickel catalyst gives 6-benzyl-2:2-dimethylcyclohexanone, b. p. 179°/29 mm.,  $d_{20}^{25}$  1.005,  $n_D^{25}$  1.5251 (*oxime*, m. p. 145°; *semicarbazone*, m. p. 201—202° in 41% yield), whilst similar reduction of benzylidene-2-methylcyclohexanone affords 6-benzyl-2-methylcyclohexanone (*oxime*, m. p. 115°; *semicarbazone*, m. p. 163—164° in 58% yield). Benzylation of 2:6-dimethylcyclohexanone gives 6-benzyl-2:6-dimethylcyclohexanone, b. p. 174°/22 mm.,  $d_{20}^{25}$  1.014,  $n_D^{25}$  1.5297 (*oxime*, m. p. 155—156°; gives only a trace of semicarbazone with great difficulty), together with a small quantity of the 2:6-dibenzyl derivative, m. p. 78°, as a by-product. Of the above cyclohexanones only the 2:6-dimethyl and 6-benzyl-2-methyl derivatives give so-called tetrahydropyrene condensation products with 2 mols. of benzaldehyde in the presence of hydrochloric acid. This condensation probably involves the hydrogen atoms in the  $\alpha$ -positions to the carbonyl group.

J. W. BAKER.

**Benzylpinacolones and their reduction products.** I. G. A. HILL and W. F. BRUCE (J. Amer. Chem. Soc., 1930, 52, 347—351).—Treatment of the sodium derivative of methyl *tert*.-butyl ketone (prepared by the action of sodamide in dry ether) with benzyl chloride gives a mixture of  $\beta$ -phenylethyl *tert*.-butyl ketone, b. p. 132°/10 mm.,  $d_{20}^{25}$  0.9483,  $n_D^{25}$  1.4999 (cf. A., 1923, i, 789), and dibenzylmethyl *tert*.-butyl ketone, m. p. 49° (crystallographic data given). Tri-benzylmethyl *tert*.-butyl ketone, b. p. 268.9° (corr.)/8 mm., m. p. 161.5° (corr.) (crystallographic data given), is obtained similarly, using toluene as the solvent. Reduction of the above ketones with sodium and alcohol affords  $\beta$ -phenylethyl-*tert*.-butylcarbinol, b. p. 145.5° (corr.)/15.5 mm.,  $d_{20}^{25}$  0.9578,  $n_D^{25}$  1.5097 (cf. *loc. cit.*) [*phenylcarbimide* derivative, m. p. 88.1° (corr.)], dibenzylmethyl-*tert*.-butylcarbinol, b. p. 206—208°/15 mm.,  $d_{20}^{25}$  1.005 (*phenylcarbimide* derivative, m. p. 148°), and tribenzylmethyl-*tert*.-butylcarbinol, m. p. 156.5° (crystallographic data given),

respectively. Reduction of  $\beta$ -phenylethyl *tert*-butyl ketone with red phosphorus and 57% hydriodic acid at 180–190°, with subsequent treatment of the mixture with zinc and dilute sulphuric acid, furnishes  $\alpha$ -phenyl- $\delta\delta$ -dimethylpentane, b. p. 115°/9 mm.,  $d_{20}^{20}$  0.9443,  $n_D^{20}$  1.5281.

H. BURTON.

**Electrolytic reduction of ketones. I.  $\alpha\beta$ -Unsaturated ketones.** G. SHIMA (Mem. Coll. Sci. Kyōtō, 1929, A, 12, 327–337).—Electrolytic reduction of styryl methyl ketone to  $\beta$ -phenylethyl methyl ketone is best carried out at 30–35°, using a lead or platinum anode, a mercury cathode, an aqueous-alcoholic solution of sodium hydrogen carbonate as the cathode solution, 5% sodium hydroxide as the anode solution, and a current density of 6–8 amp./100 cm.<sup>2</sup> The yield is about 90%. With aqueous-alcoholic sodium hydroxide as the cathode solution, benzylacetone, dibenzylidiacetone, m. p. 161°,  $\alpha\zeta$ -diphenyl- $\gamma\delta$ -dimethyl- $\Delta^{\alpha\epsilon}$ -hexadiene- $\gamma\delta$ -diol, b. p. 194–195°/3 mm.,  $d_{20}^{20}$  1.0842, and resinous material are obtained. With cathode materials other than mercury, the formation of dimeric products is favoured.

Reduction of phenyl styryl ketone in ethereal-alcoholic solution containing sodium hydrogen carbonate at 20–25°, gives a 70–75% yield of phenyl  $\beta$ -phenylethyl ketone; at 35–40°,  $\alpha\delta$ -dibenzoyl- $\beta\gamma$ -diphenylbutane and  $\alpha\gamma\delta\zeta$ -tetraphenyl- $\Delta^{\alpha\epsilon}$ -hexadiene- $\gamma\delta$ -ol, m. p. 194–195°, are also produced. The last-named substance, contrary to the statement of Harries and Hübner (A., 1897, i, 549), is also produced when phenyl styryl ketone is reduced with sodium amalgam and acidified alcohol. If the electrolytic reduction is carried out in absence of the ether, resinous products are formed in large amount.

H. BURTON.

**Action of alcoholic hydrochloric acid on unsaturated ketones.** B. COFFEY and H. RYAN (Proc. Roy. Irish Acad., 1929, 39, B, 107–113).—Styryl ethyl ketones are converted by the action of cold alcoholic hydrogen chloride, or alcoholic stannic chloride, into dimerides to which, in accordance with the structures assigned by Staudinger and Breusch (A., 1929, 434) to the dimerides of  $\alpha$ -methylstyrene derivatives, the constitution  $\begin{matrix} \text{CHR}\cdot\text{CH}\cdot\text{COEt} \\ \text{CHR}\cdot\text{CH}\cdot\text{COEt} \end{matrix}$  is assigned. Thus styryl ethyl ketone gives the substance  $\text{C}_{22}\text{H}_{24}\text{O}_2$  (I) ( $\text{R}=\text{Ph}$ ), m. p. 195–196°, which does not form a phenylhydrazone or a semicarbazone, will not condense further with piperonal or methyl ethyl ketone, is stable to potassium permanganate in acetone, is not reduced either by sodium amalgam in alkaline solution or by phosphorus and hydrogen iodide in acetic acid, but reacts with bromine in acetic acid to give the substance  $\text{C}_{22}\text{H}_{21}\text{O}_2\text{Br}_3$ , m. p. 171–172°. With hydroxylamine hydrochloride in aqueous-alcoholic sodium carbonate solution, I is converted into a substance, m. p. 242–243°, which by treatment with phosphoric oxide in boiling benzene gives another substance, m. p. 249°. Similar condensation of *p*-methoxystyryl and 3:4-methylenedioxystyryl ethyl ketones gives the substances  $\text{C}_{24}\text{H}_{26}\text{O}_4$  ( $\text{R}=\text{MeO}\cdot\text{C}_6\text{H}_4$ ), m. p. 199–200°, and  $\text{C}_{24}\text{H}_{24}\text{O}_6$  ( $\text{R}=\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3$ ), m. p. 202°, respectively.

J. W. BAKER.

**Mechanism and application of the Fries reaction.** E. H. COX (J. Amer. Chem. Soc., 1930, 52, 352–358).—When *m*-tolyl butyrate is treated with aluminium chloride in presence of diphenyl ether and carbon disulphide, the carbon disulphide removed after a short time by distillation, and the residue then heated at from 100° to 175°, 4-butyryl-diphenyl ether, m. p. 50°, and 6-butyryl-*m*-cresol, m. p. 88°, are obtained. Similarly, *o*-tolyl acetate furnishes 4-acetyldiphenyl ether and 5-acetyl-*o*-cresol; *p*-tolyl acetate yields 4-acetyldiphenyl ether and 3-acetyl-*p*-cresol, and *o*-tolyl benzoate gives 4-benzoyldiphenyl ether and 5-benzoyl-*o*-cresol. The results support Skraup and Poller's conclusion (A., 1925, i, 143) that an acid chloride is an intermediate product in the Fries reaction.

Treatment of methyl 2-acyloxybenzoates with aluminium chloride in presence of carbon disulphide, and subsequent short heating of the solvent-free residue, affords methyl 5-acylsalicylates. These are hydrolysed to the free acids, of which the following are described: 5-propionyl-, m. p. 177–179° (methyl ester, m. p. 64–65°); 5-butyryl-, m. p. 152–153° (methyl ester, m. p. 73°); 5-isohexoyl-, m. p. 132–133.5° (methyl ester, b. p. 195–198°/15 mm.), and 5-hexoyl-salicylic acids, m. p. 117° (methyl ester, m. p. 50–51°). Reduction of these acyl derivatives by Clemmensen's method gives 5-propyl-, m. p. 99–100°; 5-butyl-, m. p. 84–86°; 5-isohexyl-, m. p. 104–105°, and 5-hexyl-salicylic acids, m. p. 83–84°, respectively. These acids are more toxic than salicylic acid, but possess higher phenol coefficients.

H. BURTON.

**Derivatives of *p*-methoxy- $\alpha$ -methylstyryl methyl ketone.** H. RYAN, P. M'GEOWN, and J. KEANE (Proc. Roy. Irish Acad., 1929, 39, B, 132–141).—By the action of various aromatic aldehydes (1 mol.) on *p*-methoxy- $\alpha$ -methylstyryl methyl ketone (Iwamoto, A., 1927, 566) in the presence of aqueous-alcoholic potassium hydroxide, various cyclopentenone derivatives of the type  $\text{CO} < \begin{matrix} \text{CH}=\text{CR} \\ \text{CMe}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \end{matrix}$  (I) have been prepared. Thus with the appropriate aldehyde are obtained 4-phenyl-3-anisyl-2-methyl- ( $\text{R}=\text{Ph}$ ), m. p. 57–59°; 3:4-dianisyl-2-methyl- ( $\text{R}=\text{C}_6\text{H}_4\cdot\text{OMe}$ ), m. p. 88.5–90° (which could not be converted into a crystalline isomeride by the action of alcoholic hydrogen chloride), and 3-anisyl-4-piperonyl-2-methyl- ( $\text{R}=\text{C}_6\text{H}_3\text{O}_2\text{CH}_2$ ), m. p. 113–114°, - $\Delta^4$ -cyclopentenones. When *p*-methoxy- $\alpha$ -methylstyryl methyl ketone is condensed with 2 mols. of the aldehyde in the presence of alcoholic hydrogen chloride or when a further mol. of the aldehyde reacts with the above condensation products, the following are obtained: 4-phenyl-3-anisyl-5-benzylidene-2-methyl-, m. p. 150–151°; 3:4-dianisyl-5-anisylidene-2-methyl-, m. p. 158–160°, and 3-anisyl-4-piperonyl-5-piperonylidene-2-methyl-, m. p. 172–174°, - $\Delta^3$ -cyclopentenones.

J. W. BAKER.

**Condensation of aldehydes with ethyl benzyl-acetoacetate.** H. RYAN, W. B. CORNELIA, and P. HURLEY (Proc. Roy. Irish Acad., 1929, 39, B, 142–145).—Anisaldehyde condenses with ethyl benzyl-acetoacetate in cold aqueous-alcoholic sodium

hydroxide to give, initially,  $\alpha$ -*p*-methoxycinnamoyl- $\beta$ -phenylpropionic acid,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{H}$ , m. p. 147° (decomp.), which is converted on keeping in the reaction mixture into *p*-methoxystyryl  $\beta$ -phenylethyl ketone, m. p. 89° (phenylhydrazine, m. p. 119–120°). Similar condensation with piperonal gives 3:4-methylenedioxystyryl  $\beta$ -phenylethyl ketone, m. p. 137°, the intermediate derivative, m. p. 150° (decomp.), not being investigated. J. W. BAKER.

**Reaction of aniline and benzoin.** C. N. CAMERON (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 53–60).—So-called benzoinanil (desylaniline), m. p. 99°, is obtained either by interaction of desyl chloride with aniline (Bischler and Fireman, A., 1893, i, 519), or by the condensation of benzoin and aniline (Voigt, A., 1886, 887), preferably in boiling dilute alcoholic acetic acid. Bromination yields successively *p*-bromodesylaniline, m. p. 171° (lit. 168°), and *tri*-bromodesylaniline, m. p. 157°, identical with the products obtained synthetically. Benzil-*p*-bromoanil has m. p. 97°. Methylation of desylaniline with methyl iodide alone (silver oxide causes oxidation) gives the *N*-methyl derivative, m. p. 100°, also obtained from desyl chloride and methylaniline. The *N*-acetyl derivative is obtained in poor yield by acetylation or by condensation of benzoin with acetanilide or sodioacetanilide. These reactions establish that desylaniline is not an anil.

Phenyl anilinodiphenylmethyl ketone ( $\alpha$ -phenyl-desylaniline), m. p. 182°, obtained by interaction of aniline and  $\alpha$ -phenyldesyl chloride, is, on the other hand, distinct from phenylbenzoinanil, m. p. 168°. The latter is not obtainable by condensation of phenylbenzoin with aniline, but is obtained in poor yield by the action of magnesium phenyl bromide on benzilanil. In this case the replacement of the mobile hydrogen has made the transformation of anil to anilide impossible. Phenyl  $\alpha$ -anilino- $\alpha$ -phenylethyl ketone ( $\alpha$ -methyl-desylaniline), m. p. 105–106°, is obtained from methylbenzoin by interaction of the chloro-compound (not isolated) with aniline. Methylbenzoinanil could not be prepared. R. K. CALLOW.

**Mixed benzoin.** I. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1930, 52, 220–224).—Aldehydes forming simple benzoin possess both a reactive carbonyl group and a mobile hydrogen atom (cf. Staudinger, A., 1913, i, 1354) and are termed type 1; the rate of formation of the benzoin is a qualitative measure of either carbonyl reactivity or hydrogen mobility. Aldehydes not forming simple benzoin have either a reactive carbonyl group or a mobile hydrogen atom; these are designated type 2. By the regulated addition of an aldehyde of type 1 (benzoin formation normally rapid) to an aqueous-alcoholic solution of an aldehyde of type I (slow benzoin formation) or type 2, containing potassium cyanide it is possible to synthesise mixed benzoin. The following are described: *furfuroyl-p*-dimethylaminophenylcarbinol, m. p. 168°; *o*-chlorobenzoyl-*p*-dimethylaminophenyl-, m. p. 166°; *m*-bromobenzoyl-*p*-dimethylaminophenyl-, m. p. 145°; benzoyl-3:4-methylenedioxyphenyl-, m. p. 120°; 3:4-methylene-dioxybenzoylphenyl-, m. p. 112°; benzoyl-*m*-bromo-

phenyl- (?), m. p. 129–130°; 3:4-methylenedioxybenzoyl-*m*-bromophenyl- (?), m. p. 106°, and 3:4-methylenedioxybenzoyl-*o*-chlorophenyl-carbinol (?), m. p. 115°. H. BURTON.

**Dioximes.** LVII. G. PONZIO and M. TORRES (Gazzetta, 1929, 59, 718–723).—The conditions of formation of several dioximes from oximinoketones,  $\text{R}\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{R}'$ , are investigated with special reference to the yields of the two forms at different hydrogen-ion concentrations. The  $\alpha$ - and  $\beta$ -forms are separated as the copper and nickel salts, respectively. Oximinoacetophenone yields dioximes in acid solution only. Phenyl oximinocetyl ketone yields no dioxime in neutral solution, mixtures in acid solution, and only the  $\beta$ -form in alkaline solution. Oximinobenzyl methyl ketone yields only the  $\beta$ -form in acid, neutral, or alkaline solution. Oximino-benzoylacetone yields mixtures in acid solution, the  $\beta$ -form only in neutral solution, and no dioxime in alkaline solution. The proportions of  $\alpha$ - and  $\beta$ -forms, when both are obtained, vary with the hydrogen-ion concentration. In no case is the  $\alpha$ -form obtained exclusively. The variation in behaviour is assigned to the influence of hydrogen-ion concentration on the configuration of either the existent or entrant oximino-group. The different behaviour of the oximino-groups of isomeric oximinoketones to certain reagents has previously been noted (Gazzetta, 1901, 31, 133). The behaviour is similar, however, on methylation.  $\beta$ -Phenylmethylglyoxime methyl ether,  $\text{C}_6\text{H}_5(\text{N}\cdot\text{OMe})\cdot\text{CMe}_2\cdot\text{N}\cdot\text{OH}$ , m. p. 162°, is prepared by treating oximinobenzyl methyl ketone with methyl sulphate and alkali, and heating the oily product with hydroxylamine hydrochloride. It is converted into the dimethyl ether (Avogadro and Tavola, A., 1925, i, 1040) when methylated. An improved method of preparing  $\alpha$ -phenylmethylglyoxime (Avogadro, A., 1924, i, 1202) is described, in which the  $\beta$ -compound is removed by crystallisation and precipitation of the nickel salt from the mixture obtained from hydroxylamine and phenyl oximinocetyl ketone.

R. K. CALLOW.

**Benzilic acid rearrangement.** T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, 52, 252–254).—When benzil is treated with an equimolecular quantity of solid potassium hydroxide in dry ether at the ordinary temperature for 4 days, potassium benzilate is obtained; water is not necessary for the reaction. An additive compound is first formed, which undergoes molecular rearrangement in the solid phase. Similar results are obtained using furil. H. BURTON.

**Inner complex salts of  $\alpha$ -benziloxime.** P. PFEIFFER and H. BUCHHOLZ (J. pr. Chem., 1930, [ii], 124, 133–143).—*cis*-Hydroxyaquo-diethylene-diaminecobaltic bromide,  $[\text{en}_2\text{Co}(\text{OH}_2)(\text{OH})]\text{Br}_2$ , condenses with  $\alpha$ -benzilmonoxime in alcoholic solution to the orange-coloured complex bromide,  $[\text{en}_2\text{Co}(\text{C}_{14}\text{H}_{10}\text{O}_2\text{N})]\text{Br}_2 + 3\text{H}_2\text{O}$  (iodide +  $x\text{H}_2\text{O}$ ; thiocyanate; perchlorate +  $\text{H}_2\text{O}$ ; dichromate; hexanitrocobaltate +  $8\text{H}_2\text{O}$ ). This salt is formulated as  $[\text{en}_2\text{Co} \begin{smallmatrix} \text{NO}\cdot\text{CPh} \\ \diagdown \\ \text{O}=\text{CPh} \end{smallmatrix}] \text{Br}_2$ , the oxime residue occupying two co-ordination positions. Analogous constitutions

are assigned to the cobalt salt of nitroso- $\beta$ -naphthol, the nickel salt of dimethylglyoxime, and to Tschugaev's dioxime cobaltic salts.  $\alpha$ -Benzilmonoxime and sodium cobaltinitrite in warm alcoholic solution give the compound  $[\text{Co}(\text{C}_{14}\text{H}_{10}\text{O}_2\text{N})_3]$ .

A. I. VOGEL.

**Diacylstyrenes.** II. C. F. H. ALLEN and J. R. HUBBARD (J. Amer. Chem. Soc., 1930, 52, 384—386).—Benzil condenses with 2-acetylthiophen, 2-acetylfuran,  $\beta$ -naphthyl methyl ketone, 4-acetyldiphenyl, *p*-ethylacetophenone, and 3:4-dichloroacetophenone under the conditions previously described (A., 1927, 971), yielding 2-thiophenyl  $\beta$ -benzoylstyryl ketone, m. p. 152°, 2-furyl  $\beta$ -benzoylstyryl ketone, m. p. 168°,  $\alpha$ -benzoyl- $\beta$ -naphthoylstyrene, m. p. 152°,  $\alpha$ -benzoyl- $\beta$ -*p*-phenylbenzoylstyrene, m. p. 132°,  $\alpha$ -benzoyl- $\beta$ -*p*-ethylbenzoylstyrene, m. p. 117°, and  $\alpha$ -benzoyl- $\beta$ -3:4-dichlorobenzoylstyrene, m. p. 199°, respectively.  $\alpha$ -Naphthyl methyl ketone and 2:4-dihydroxyacetophenone do not condense with benzil, nor does acetophenone condense with 2:2'-dimethoxybenzil. Groups in the *o*-position of either component appear to prevent condensation (cf. *loc. cit.*).

H. BURTON.

**Influence of substituents on the benzoin reaction.** H. H. HODGSON and W. ROSENBERG (J.C.S., 1930, 14—18).—The effect of substituents on the benzoin reaction is considered from the point of view both of the intermediate mandelonitrile and of the hypothetical intermediate benzoin cyanohydrin (cf. Lapworth, J.C.S., 1903, 83, 1004). On the first consideration it is shown that the electronic influences on the activity of the labile hydrogen atom of the mandelonitrile and the carbonyl group of the benzaldehyde are in opposite direction, with the net result of inhibition to a greater or smaller degree of the formation of benzoin. The following are described: 2:2'-dichlorobenzoin, m. p. 56—57°; 2:2'-dichlorobenzil, m. p. 128°; 3:3'-dimethoxybenzoin, m. p. 41—42°; 2:2'-dichloro-3:3'-dimethoxybenzoin, m. p. 133—134° (*p*-nitrophenylhydrazones, m. p. 129°); 2:2'-dichloro-3:3'-dimethoxybenzil, m. p. 200°; 2:2'-dichloro-3:3'-dimethoxybenzylidic acid, m. p. 182—185°; 2-chloro-3-methoxybenzoic acid, m. p. 161.5°.

H. A. PIGGOTT.

**Action of phenylhydrazine on substituted anilinoquinones.** M. COVELLO (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], 35, 86—89).—By the interaction of an alcoholic solution of phenylhydrazine with concentrated solutions of tetra-substituted *p*-benzoquinones, or the powdered solids, phenylhydrazides [monophenylhydrazones] of the following have been prepared: 3:5-ditoluidino-2:6-diphthalimidobenzoquinone, decomp. about 275°; 3:5-dianisidino-2:6-diphthalimidobenzoquinone, decomp. about 290°; 3:5-ditoluidino-2:6-disuccinimidobenzoquinone, m. p. 202—203°; 3:5-dianisidino-2:6-disuccinimidobenzoquinone, m. p. 256—259°. The usual red colorations are given with nitric or sulphuric acid.

R. K. CALLOW.

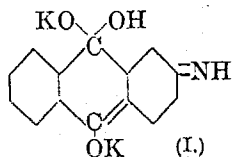
**Action of hydroxylamine on substituted anilinoquinones.** M. COVELLO (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], 35, 90—95).—By the interaction of hydroxylamine hydrochloride (2 mols.)

with tetra-substituted *p*-benzoquinones in boiling alcoholic solution dioximes of the following have been prepared: 3:5-ditoluidino-2:6-diphthalimido-, m. p. 232—235°; 3:5-dianisidino-2:6-diphthalimido-, m. p. 247—248°; 3:5-ditoluidino-2:6-disuccinimido-, m. p. 208—210°; and 3:5-dianisidino-2:6-disuccinimido-benzoquinone, m. p. 155—156°. Characteristic colorations are given with Liebermann's reagent. Treatment of the quinones with hydroxylamine in alkaline solution merely brings about reduction to the quinols.

R. K. CALLOW.

**Action of alkali on 2-aminoanthraquinone at 150°.** T. MAKI (J. Soc. Chem. Ind. Japan, 1929, 32, 303—305B).—The product obtained by heating 2-aminoanthraquinone with potassium hydroxide (75%) at 150° for 2 hrs., after treatment with water and aëration has the following composition. (i) Soluble in water 5%, mainly benzoic acid; (ii) soluble in ammonia, 22.5%, chiefly alizarin; (iii) soluble in potassium hydroxide, 17.5%, 2-amino-1-hydroxyanthraquinone (acetyl derivative, m. p. 247°, uncorr. 242°, cf. lit.); (iv) soluble in hot nitrobenzene, unchanged 2-aminoanthraquinone, 42%; (v) insoluble in hot nitrobenzene, 13%, pure indanthrone. The maximum yield of indanthrone (19%, or allowing for recovered 2-aminoanthraquinone, 27%) is obtained after heating for 4 hrs.

When 2-aminoanthraquinone is added to molten alkali at 150°, a dark violet colour appears; if a specimen of the mass be removed immediately and treated with water, 2-aminoanthraquinone is regenerated without formation of detectable quantities of alkali-soluble products; with increasing time the latter appear in increasing quantity. It is suggested that the violet colour is to be associated with the compound (I), which is probably the active intermediate in the formation of indanthrone and 2-amino-1-hydroxyanthraquinone.



C. W. SHOPPEE.

**Formation-curve of 2-aminoanthraquinone in the presence of sodium dichromate.** T. MAKI (J. Soc. Chem. Ind. Japan, 1929, 32, 344—347B).—Conditions for the production of 2-aminoanthraquinone from sodium anthraquinone-2-sulphonate and aqueous ammonia at 200° in the presence of sodium dichromate (cf. G.P. 256515) have been systematically investigated. If the reaction period is prolonged above 20 hrs., a blackish-brown by-product is produced, with consequent decrease in the yield of 2-aminoanthraquinone. The optimum period at 200° is about 15 hrs. The highest yield of 2-aminoanthraquinone is obtained using 0.50 mol. of dichromate (theory requires 0.33 mol.). The yield of 2-aminoanthraquinone increases with increasing concentration of ammonia up to 16%, but not with higher concentration. The highest yield obtained, at 200° in 15 hrs., using excess of 16.13% ammonia, is 63% of theory.

C. W. SHOPPEE.

**Anthraquinoneazo-compounds.** I. Some anthraquinoneazo- $\beta$ -naphthols. T. MAKI (J. Soc. Chem. Ind. Japan, 1929, 32, 347—352B).—2-Aminoanthraquinone is diazotised in cold concentrated

sulphuric acid, the diazo-compound filtered and coupled with an alkaline solution of  $\beta$ -naphthol. Anthraquinone-2-azo- $\beta$ -naphthol (I) is readily soluble in acetylene tetrachloride, and crystallises therefrom in scarlet needles, m. p. 267.8° (corr.). It is slowly sulphonated by concentrated sulphuric acid in the cold, more rapidly on heating; the azo-group is reduced by sodium hyposulphite, whilst molten potash furnishes some indanthrone. 1-Aminoanthraquinone similarly affords *anthraquinone-1-azo- $\beta$ -naphthol* (II), m. p. 305.8° (corr.), and 1:5-diaminoanthraquinone yields *anthraquinone-1:5-bisazo- $\beta$ -naphthol* (III), m. p. 389° (corr.; decomp.); II and III are readily sulphonated. All three dyes colour acetate silk when used in colloidal suspension or emulsion. Their water-soluble sulphonic acids behave as acid dyes, whilst that from III exhibits, to some degree, a substantive nature and dyes cotton rose.

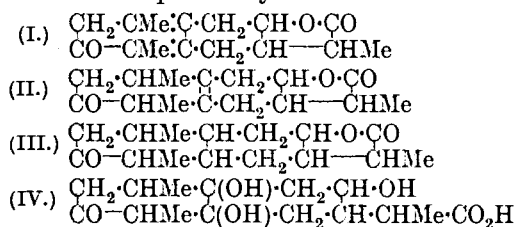
The absorption curves and extinction coefficients of I, II, and III, in acetylene tetrachloride and sulphuric acid (concentrated) solution have been determined; in the first-named solvent, the absorption maxima ( $\text{\AA}$ .) and maximal extinction coefficients are: I, 5100, 0.348; II, 5180, 0.335; III, 5490, 0.465. In concentrated sulphuric acid, 1—2 hrs. after preparation of the solution the corresponding figures are: I, 6480, 0.330; II, 5880, 0.255; III, 5960, 0.615. As sulphonation gradually occurs, the absorption maxima change with time, finally having the values, 6140, 5640, and 5700, respectively. C. W. SHOPPEE.

**Velocity of decomposition of indanthrone by molten alkali.** T. MAKI (J. Soc. Chem. Ind. Japan, 1929, 32, 300—303B).—Contrary to the general assumption that indanthrone is not decomposed by alkali below 300° (cf. Scholl, A., 1904, i, 109, 110; "Das Anthracen u. die Anthrachinone," Leipzig, 1929), it is found that extensive decomposition occurs at a much lower temperature. From the alkali-soluble decomposition products, benzoic acid and a water- and ether-insoluble brown, amorphous powder containing about 10% N were isolated. Finely-powdered indanthrone (1 mol.) was treated with potassium hydroxide (36 mols.) and water (37 mols.) in a nickel vessel with continuous stirring (a) for 1 hr. at temperatures from 150° to 290°, and (b) at 250° for varying periods. (a) Decomposition occurs to the extent of 8% at 150°, 16% at 180°, 25% at 200°, 61% at 250°, and 85% at 290°. (b) Decomposition takes place rapidly, 36% and 48% of indanthrone being destroyed in 15 and 30 min., respectively. The time-decomposition curve appears to correspond closely with a reaction of the third order (mean velocity coefficient  $K=0.047 \text{ min.}^{-1}$ ), but from the decomposition products isolated, the main phase of the reaction must be of the fifth order at least. It is concluded that the usual temperature (about 250°) employed for the production of indanthrone is dangerously high. C. W. SHOPPEE.

**2:4-Dichloro-1-aminoanthraquinone.** I. GUBELMANN, H. J. WIELAND, and O. STALLMANN.—See B., 1930, 94.

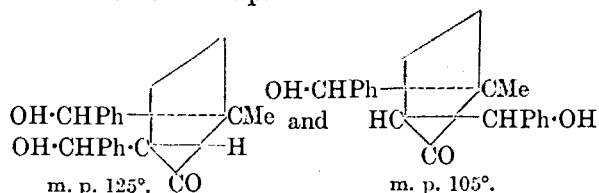
**Santonin. XIV. Dihydrosantonin.** E. WEDEKIND, T. GOOST, and I. JÄCKH (Ber., 1930, 63, [B],

50—56; cf. A., 1915, i, 705).—Reduction of santonin according to the method of Wedekind and Beniers (A., 1913, i, 476) yields a mixture of tetrahydrosantonin and an oil from which, after treatment with hydroxylamine, dihydrosantoninoxime, m. p. 230°,  $[\alpha]_D^{25} +118^\circ$  in methyl alcohol, is obtained (cf. Cusmano, A., 1913, i, 864). Decomposition of the oxime with cold hydrochloric acid in presence of formaldehyde yields dihydrosantonin (II), m. p. 105°,  $[\alpha]_D^{25} +75.3^\circ$  in ethyl alcohol (cf. Cusmano, *loc. cit.*). The dihydro-compound absorbs 2 atoms of hydrogen per mol. in methyl alcohol in presence of palladised charcoal, giving tetrahydrosantonin (III). Dihydrosantonin is readily converted by ozone into a mixture of acids which could not be separated into its components. Potassium permanganate in acetone transforms it into a *dihydroxydihydrosantoninic acid* (IV), m. p. 198°,  $[\alpha]_D^{25} +448^\circ$  in ethyl alcohol, which, when distilled in a vacuum, loses carbon dioxide and yields a mixture of compounds. The relationships of santonin (I) to its derivatives are expressed by the formulæ:



H. WREN.

**Constitution of cyclanones.** I. R. CORNUBERT and C. H. R. BORREL (Bull. Soc. chim., 1929, [iv], 45, 1148—1161).—In presence of hydrogen chloride at  $-15^\circ$ , benzaldehyde and *l*-menthone,  $[\alpha]_D^{25} -28.67^\circ$ , give 65% of benzylidenementhone hydrochloride, m. p. 140° (cf. Martine, A., 1904, i, 903), but no "tetrahydropyrone" compound. Thujone after 24 hrs. gives benzylidenethujone, b. p. 190—210°/17 mm., and a "tetrahydropyrone" compound, m. p. 115—115.5°, converted in benzene solution or by fusion into an isomeric compound, m. p. 147—147.5°, from which the original compound, m. p. 115°, could not be regenerated. 1-Methylcyclopentanone similarly gives an oil, b. p. 153—154°/12 mm., forming a *semicarbazone*, m. p. 180—181° (decomp.) (*benzylidene-1-methylcyclopentanone* has m. p. 57°, b. p. 187—188°/23 mm.; *semicarbazone*, m. p. 205°), and a *tetrahydropyrone compound*, m. p. 105—105.5°, b. p. 230—240°/13 mm., which by evaporation of its solution in benzene is converted into an *isomeride*, m. p. 125°. The latter is obtained direct when hydrogen bromide is used for the condensation, and could not be converted into the isomeride of lower m. p. The structures



are suggested, but the possibility of isomerism in the pyrone ring is admitted.

1:5-Dimethyl- $\Delta^1$ -cyclohexen-3-one, b. p. 94°/17 mm.,

134°/80 mm., 1:5:5-trimethyl- $\Delta^1$ -cyclohexen-3-one (isoacetophorone), b. p. 95°/16 mm., 137°/90 mm. (benzylidene derivative, m. p. 78.5—79°), and 1-methyl-5-isopropyl- $\Delta^1$ -cyclohexen-3-one, b. p. 121°/16 mm. (benzylidene derivative, m. p. 91—92°), when condensed with benzaldehyde in presence of hydrogen chloride or sodium ethoxide give the corresponding benzylidene derivatives, but no pyrone derivative, although traces of viscous oils of high b. p. are formed in each case. 2-Benzyl-6-methylcyclohexanone, b. p. 167°/20 mm., obtained (yield 90%) by catalytic hydrogenation of benzylidene-2-methylcyclohexanone in presence of platinum or nickel reacts with benzaldehyde to give a theoretical yield of a substance,  $C_{28}H_{28}O_2$ , m. p. 196°. 2:6-Dibenzylcyclohexanone, m. p. 121—122°, similarly obtained by hydrogenation in presence of nickel, does not condense with benzaldehyde. When obtained by hydrogenation in presence of platinum, an oil, b. p. 235—240°/17 mm., is also obtained, and in one experiment the product  $C_{20}H_{22}O$  had m. p. 103° (? an isomeric dibenzylcyclohexanone).

These and earlier results (A., 1926, 953; 1927, 152, 666, 1075; 1929, 557, 560) show that six out of eight ketones examined of the type  $\cdot CHR \cdot CO \cdot CH_2 \cdot$  and sixteen out of seventeen of the type  $\cdot CHR \cdot CO \cdot CHR \cdot$  yield "tetrahydropyrone" compounds. The formation of such compounds may therefore frequently be used to detect the presence of these chains, but the non-formation of "tetrahydropyrone" derivative is not proof of the absence of the structures  $\cdot CHR \cdot CO \cdot CH_2 \cdot$  and  $\cdot CHR \cdot CO \cdot CHR \cdot$ .

R. BRIGHTMAN.

**Formation of *cis*-, *cis-trans*-derivatives in the terpene group.** K. SŁAWIŃSKI and S. HOFSAJN (Rocz. Chem., 1929, 9, 747—753).—Terpineol acetate *cis*-dibromide and sodium acetate give sobrerol and pinol. This result confirms Wagner's theory (A., 1899, i, 766) that Wurtz's method for the introduction of hydroxyl groups leads to the formation of *cis*-derivatives, whilst direct introduction by permanganate oxidation gives the *cis-trans*-isomerides.

R. TRUSZKOWSKI.

**Action of Japanese acid clay on terpenes. I. Isomerisation of *d*- $\alpha$ -pinene.** T. KAWATA (J. Fac. Eng. Tokyo, 1929, 18, 117—124, and J. Soc. Chem. Ind. Japan, 1929, 32, 372—373B).—When *d*- $\alpha$ -pinene,  $d_4^{20}$  0.8585,  $n_D^{20}$  1.4657, from American turpentine, is treated with 40% by weight of dry Japanese acid clay for 2 hrs., *d*-camphene (converted into isoborneol and its phenylurethane), *d*-limonene (tetrabromide and nitrosochloride), a small quantity of terpinene (?), and dipentene are produced.

A. I. VOGEL.

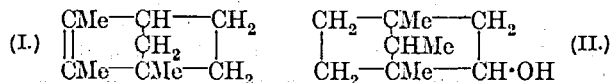
**Action of hydrazine hydrate on ketones in acidic solvents.** K. A. TAPPALE [with M. GUTNER] (Ber., 1930, 63, [B], 243—248; cf. Schapiro, A., 1929, 1302).—Camphorazine, m. p. 185°,  $[\alpha]_D^{25}$  -93.1° in benzene,  $[\alpha]_D^{25}$  +79.2° in chloroform, is obtained in more than 90% yield from 2 mols. of camphor and 1 mol. of hydrazine hydrate in alcohol containing much less than the equivalent proportion of hydrochloric acid. Increase in the concentration of the acid to the equivalent amount diminishes the yield to 50%. The azine is readily hydrogenated to *s*-dibornylhydrazine. In hot glacial acetic acid, camphor and hydrazine

hydrate afford camphoracetylhydrazone, m. p. 210°,  $[\alpha]_D^{25}$  -35.5° in chloroform, catalytically reduced to bornylacetylhydrazine, m. p. 95°,  $[\alpha]_D^{25}$  -53.1° in chloroform. The last-named substance is stable towards boiling water and alkalis, but is transformed by hydrochloric acid into bornylhydrazine hydrochloride, m. p. about 225° (decomp.). The hydrochloride is converted by potassium cyanate into bornylsemicarbazide, m. p. 191° (decomp.), and by benzoyl chloride and anhydrous sodium carbonate in benzene into dibenzoylbornylhydrazine, m. p. 199—200°. Benzaldehydebornylhydrazine hydrochloride has m. p. 116—117°. Fenchone in alcoholic hydrochloric acid solution gives a ketazine, m. p. 106°. Even with an excess of hydrazine hydrate in glacial acetic acid acetophenone affords exclusively the ketazine, m. p. 121—121.5°, whereas benzophenone gives the ketazine, m. p. 162—163°, and the acetyl derivative of benzophenonehydrazone. H. WREN.

**Lanthanum, cerous, neodymium, and samarium camphorates.** L. CONIGLIO (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], 35, 40—43).—The following camphorates, of the general formula  $M_2[C_8H_{14}(CO_2)_3]_3 \cdot 20H_2O$ , have been prepared from solutions of the acetates and camphoric acid. The solubilities in water at 25° are given in parentheses: lanthanum (0.21%); cerous (0.29%) (cf. Morgan and Cahen, A., 1907, i, 1021); neodymium (0.24%); samarium (0.26%). All the salts lose water of crystallisation at moderate temperatures, but dehydration is complete only at 110°. R. K. CALLOW.

**Phenyl-substituted camphor and its derivatives.** S. NAMETKIN, A. KITSCHIKIN, and D. KURSANOV (J. pr. Chem., 1930, [ii], 124, 144—158).—See this vol., 216.

**Catalytic dehydrogenation of fenchyl alcohol by aluminium phosphate; a new series of terpene and camphor compounds.** N. J. TOIVONEN and E. TIKKANEN (Suomen Kem., 1929, 2, 169—176).—Dehydration of fenchyl alcohol at 190° with aluminium phosphate gives mesantene [ $\alpha$ -methylsantene] (I), undergoing a Wagner rearrangement on hydration by the Bertram-Walbaum method to mesantenol (II) (acetate). This is oxidised by alkaline



potassium permanganate to mesantenic acid, m. p. 240° (decomp.) (anhydride, m. p. 93—94°), probably 1:2:3-trimethylcyclopentane-1:3-dicarboxylic acid, presumably by way of mesantenone, isomeric with camphor. The acid could not be resolved with cinchonidine. A. I. VOGEL.

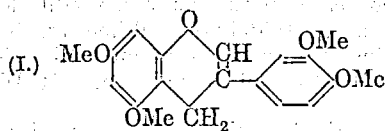
**3':4'-Dimethoxybenzyl-3:5-dimethoxycoumaranone.** J. J. DRUMM, S. M. MAQUIRE, and H. RYAN (Proc. Roy. Irish Acad., 1929, 39, B, 121—123).—In the reduction of veratrylidene-3:5-dimethoxycoumaranone (Drumm and others, *ibid.*, 1924, 36, B, 152) to the dihydro-compound the carbonyl group remains unaffected, since the dihydro-compound (3':4':3:5-tetramethoxybenzoylcoumaranone) reacts with magnesium phenyl bromide in



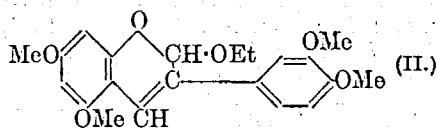
benzene at 40—50° to give the corresponding *phenylcarbinol*, m. p. 82.2—82.8°, converted by bromine in glacial acetic acid into a *monobromo-derivative*, m. p. 115°.

J. W. BAKER.

**Constitution of isocatechin tetramethyl ether.** J. J. DRUMM, R. J. P. CAROLAN, and H. RYAN (Proc. Roy. Irish Acad., 1929, **39**, B, 114—120).—On the basis of the results of Freudenberg (A., 1926, 73) and of the different properties of the chloride of catechin tetramethyl ether (Drumm, A., 1923, i, 1221) from those of the pyrylium chloride synthesised by Robinson (A., 1924, i, 306) the structure assigned to dehydrocatechin tetramethyl ether by the second author is corrected to I, with corresponding alterations in the structure of the pyrylium salt. Thus the action of



phosphorus pentachloride on catechin tetramethyl ether involves a wandering of the veratryl group. The following results are considered to be in agreement with this view. The substance previously called ethylcatechin tetramethyl ether (Drumm, *loc. cit.*) is renamed *B-catechin tetramethyl ethyl ether*,  $[\alpha]_D^{25} +119^\circ$  (all rotations in tetrachloroethane), the corresponding *B-catechin pentamethyl ether*, m. p. 80—81°,  $[\alpha]_D^{25} +42^\circ$ , being obtained similarly by the action of boiling methyl alcohol on the chloride of catechin tetramethyl ether. Cold acetic acid converts the last-named substance into the *acetate*, m. p. 154—155°,  $[\alpha]_D^{25} +171^\circ$ , of *B-catechin tetramethyl ether*, hydrolysed by boiling alcoholic hydrogen chloride to *B-catechin tetramethyl ether*, m. p. 121—122°. Methyl alcohol converts the pyrylium monobromide (Drumm, *loc. cit.*) into the methoxy-colour base, m. p. 116—117°, to which the structure II (alternative positions of ethoxy-group



and the double linking) is now assigned. The base is converted by reduction with hydrogen and platinum-black into deoxycatechin tetramethyl ether (Drumm and others, Proc. Roy. Irish Acad., 1924, **36**, B, 152).

J. W. BAKER.

**Preparation and oxidation of flavinogenides.** H. RYAN and G. CREUSS-CALLAGHAN (Proc. Roy. Irish Acad., 1929, **39**, B, 124—131).—Various arylidene-flavanones have been prepared by the action of the appropriate aldehyde on the flavanone in alcoholic hydrogen chloride, the experimental conditions varying slightly from case to case. Thus are obtained: *3-benzylidene-*, m. p. 103—104° (oxidised by potassium permanganate to a substance, m. p. 163—164°); *3-anisylidene-*, m. p. 148—149°; *3-piperonylidene-*, m. p. 155—156°; and *3-vanillylidene-*, m. p. 92—94°, *flavanone*: *3-anisylidene-*, m. p. 136—137°, and *3-piperonylidene-*, m. p. 145—147°, *-4'-methoxyflavanone*; and *3-piperonylidene-*, m. p. 183—185°,

and *3-benzylidene-*, m. p. 161—163°, *-3':4'-methylenedioxyflavanone*.

J. W. BAKER.

**1:3-Dithiolan.** D. T. GIBSON (J.C.S., 1930, 12—14).—Addition of ethylene dimercaptan (prepared by boiling the product of reaction of ethylene dibromide, water, sodium thiosulphate, and alcohol with hydrochloric acid) to formaldehyde solution containing a trace of hydrochloric acid led to 1:3-dithiolan, b. p. 175°/760 mm., 61°/11 mm.,  $d_4^{25} 1.259$ ,  $n_D^{25} 1.5975$  (*mercurichloride*, m. p. 119°; *disulphone*, m. p. 224°), accompanied by a voluminous *polymeride*, m. p. 105—110°. 1:3-Dithiolan was more conveniently prepared by treating sodium ethylene thiosulphate with hydrochloric acid and twice the calculated amount of formaldehyde; with hydrogen peroxide in acetic acid solution it formed a *monoxide*, b. p. 115—120°/1 mm., decomposed by warm hydrochloric acid into dithiolan and a *dioxide*, m. p. 134°. With methyl iodide dithiolan monoxide gives a *methiodide*, m. p. 96°; and with platinum chloride solution the compound  $(C_3H_5S_2)_2PtCl_3 \cdot H_2O$ , m. p. 146—150° (decomp.).

Long shaking of trimethylene bromide, sodium thiosulphate, and alcohol, followed by steam-distillation, afforded 1:3-dithian, m. p. 54°, the existence of which, like 1:3-dithiolan, although previously inferred, has not been recorded.

R. J. W. LE FÈVRE.

**Cyclic quaternary ammonium salts from halogenated aliphatic tertiary amines.** E. R. LITTMANN and C. S. MARVEL (J. Amer. Chem. Soc., 1930, **52**, 287—294).—Dimethyl- $\omega$ -bromoalkylamines,  $Br[CH_2]_nNMe_2$ , where  $n=4-7$ , have been prepared by the action of hydrogen bromide on the corresponding  $\omega$ -phenoxy-derivatives and their ease of conversion into the cyclic bromides,  $[CH_2]_n > NMe_2Br$ , has been studied. *Ethyl  $\epsilon$ -phenoxyhexoate*, b. p. 157—159°/3 mm.,  $d_4^{25} 1.031$ ,  $n_D^{25} 1.4928$  (the free acid is prepared from ethyl  $\delta$ -phenoxybutylmalonate), is reduced by sodium and alcohol to  $\zeta$ -phenoxyhexyl alcohol, b. p. 152—154°/3 mm., m. p. 31°. The *bromide*, b. p. 155—156°/3 mm.,  $d_4^{25} 1.248$ ,  $n_D^{25} 1.5361$ , from this reacts with dimethylamine, forming *dimethyl- $\zeta$ -phenoxyhexylamine*, b. p. 132—134°/3 mm.,  $d_4^{25} 0.942$ ,  $n_D^{25} 1.4988$  (*chloroplatinate*, m. p. 126°). *Ethyl  $\zeta$ -phenoxyheptoate*, b. p. 161—163°/3 mm.,  $d_4^{25} 1.015$ ,  $n_D^{25} 1.4932$ , is reduced similarly to  $\eta$ -phenoxyheptyl alcohol, b. p. 157—158°/3 mm., m. p. 34°, the *bromide*, b. p. 154—157°/3 mm.,  $d_4^{25} 1.199$ ,  $n_D^{25} 1.5240$ , of which reacts with dimethylamine, forming *dimethyl- $\eta$ -phenoxyheptylamine*, b. p. 158—160°/6 mm.,  $d_4^{25} 0.939$ ,  $n_D^{25} 1.4980$  (*chloroplatinate*, m. p. 162°). Dimethyl- $\delta$ -phenoxybutylamine (*chloroplatinate*, m. p. 104°) and dimethyl- $\epsilon$ -phenoxyamylamine (*chloroplatinate*, m. p. 112°) are also described. *Ethyl  $\delta$ -phenoxyvalerate* has b. p. 151°/6 mm.,  $d_4^{25} 1.041$ ,  $n_D^{25} 1.4982$ .

Hydrolysis of the above phenoxy-derivatives with 48% hydrobromic acid affords the bromoamine hydrobromides; the free bases are obtained by decomposition with cold 28% sodium hydroxide solution. Dimethyl- $\delta$ -bromobutylamine could not be isolated owing to the ease with which it undergoes transformation into *NN-dimethylpyrrolidinium bromide*, not melted at 325° (76% yield). Evaporation of the freshly-prepared ethereal solution of dimethyl-

$\alpha$ -bromoamylamine (*chloroaurate*, m. p. 57°) affords 63% of NN-dimethylpiperidinium bromide, m. p. 324° [the corresponding chloride chloroplatinate has m. p. 243° (lit. 209—210°)]. Dimethyl- $\zeta$ -bromoheptylamine, b. p. 78—80°/6 mm. (*chloroaurate*, m. p. 111°), on keeping gives 56% of NN-dimethylhexamethyleneiminium bromide, m. p. 289°, whilst dimethyl- $\eta$ -bromoheptylamine, b. p. 85—87°/7 mm.,  $d_4^{20}$  1.029,  $n_D^{20}$  1.4695 (*chloroaurate*, m. p. 126°), yields similarly 37% of NN-dimethylheptamethyleneiminium bromide, m. p. 268°.

H. BURTON.

**Nitration of 2'- and 4'-nitro-1-phenylpiperidines.** R. J. W. LE FÈVRE (J.C.S., 1930, 147—151).—Whereas 2'-nitro-1-phenylpiperidine cannot be further nitrated by the ordinary reagents, 4'-nitro-1-phenylpiperidine quantitatively yields 2':4'-dinitro-1-phenylpiperidine with nitric acid (*d* 1.4) at 0°. Similar, but less pronounced, differences are noticed in the nitration of 1:4-di-(2'- and 4'-nitrophenyl)piperazines, m. p. 193—194° and 263—264°, respectively (both prepared directly from piperazine and the appropriate chloronitrobenzene). The following derivatives of 2'-nitrophenylpiperidine are also described: *ferrichloride*, m. p. 147—148°; *mercurichloride*, m. p. 170—175°; *perchlorate*, m. p. 240—243° (decomp.). The *ferrichloride* and *mercurichloride* of 4'-nitro-1-phenylpiperidine have m. p. 130—135° and 70—80°, respectively.

R. J. W. LE FÈVRE.

**Local anæsthetics in the pyrrole series.** I. F. F. BLICKE and E. S. BLAKE (J. Amer. Chem. Soc., 1930, 52, 235—240).—Methyl, *n*- and *iso*-propyl, *n*- and *iso*-butyl, *iso*amyl, and ethyl pyrrole-2-carboxylates (*tribromo-derivative*, m. p. 195—196°) are prepared by the silver salt-alkyl iodide method. These esters possess marked local anæsthetic action on the tongue. Phenyl pyrrole-2-carboxylate, m. p. 44—45°, is prepared from the acid chloride and sodium phenoxide in ether.

Phenyl  $\beta$ -piperidinoethyl ketone (Mannich and Lammering, A., 1923, i, 43) [hydrochloride, m. p. 187—188° (lit. 192—193°)] is obtained from piperidine and  $\omega$ -bromopropiophenone, m. p. 59—60° (prepared from  $\beta$ -bromopropionyl chloride and benzene) in ether. The ketone is reduced catalytically (platinum oxide) to the corresponding carbinol, m. p. 64—65° (lit. 68—69°). Phenacyl bromide and piperidine afford N-phenacylpiperidine (I) (*hydrochloride*, m. p. 210—211°), reduced catalytically to the corresponding carbinol (II), m. p. 69—70° (*benzoate hydrochloride*, m. p. 193—194°). 2-Acetylpyrrole, piperidine hydrochloride, and paraformaldehyde react in alcohol, yielding 2-pyrrolyl  $\beta$ -piperidinoethyl ketone (III) (cf. Mannich and Lammering, *loc. cit.*). Anæsthetic action is shown by I, II, and III.

Further details for the preparation of pyrrole (cf. B., 1928, 82) are given.

H. BURTON.

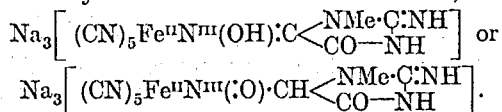
**Aromatic alkylvinylamines.** H. STACH and W. KÖNIG (Ber., 1930, 63, [B], 88—93).—Methyl- $\beta$ -hydroxyethylaniline is heated at 130—135° with hydrobromic acid saturated at 0°, whereby methyl- $\beta$ -bromoethylaniline, b. p. 122°/1 mm. (*picrate*, m. p. 125°), is prepared in 73.2% yield. With trimethylamine in alcohol at the ordinary temperature it slowly affords trimethyl- $\beta$ -methylanilinoethylammonium

bromide quantitatively (cf. von Braun, A., 1918, i, 107). 2-Methyl-1- $\beta$ -hydroxyethylindole when heated with ethylene chlorohydrin and ignited potassium carbonate yields 2-methyl-1- $\beta$ -hydroxyethylindoline, b. p. 123°/2 mm. [corresponding *methiodide*, m. p. 160° (decomp.)], converted by hydrobromic acid into 2-methyl-1- $\beta$ -bromoethyl-2:3-dihydroindole, b. p. 130°/2 mm., which readily undergoes change when preserved. Trimethylamine in alcohol converts the bromo-compound into trimethyl- $\beta$ -2-methylindolinoethylammonium bromide, from which the corresponding, very hygroscopic *hydroxide* and its *perchlorate*, m. p. 186°, are derived. Not too rapid distillation of the *hydroxide* in a vacuum affords 2-methyl-1-vinyl-2:3-dihydroindole, b. p. 100—103°/6 mm. The base readily polymerises under the influence of heat or acids. When heated with alkalis, it readily loses the vinyl group as acetaldehyde. When treated with alcoholic iodine in presence of mercury salts, the vinyl base absorbs 5.5 atoms of the halogen. H. WREN.

**Synthesis of isoquinoline derivatives.** E. SPÄTH, F. BERGER, and W. KUNTARA (Ber., 1930, 63, [B], 134—141).—The general procedure consists in the conversion of an amine of the type of  $\beta$ -phenylethylamine into its acyl derivative by heating with a 10—20% excess of the appropriate acid at 170° and removal of the product in a high vacuum. The product is treated with three times its weight of phosphoric oxide in 20—50 times its weight of gently boiling tetrahydronaphthalene for 15 min., and ebullition continued for a like period after addition of a further equal quantity of the dehydrating agent. The free base is isolated by distillation and purified through the *picrate*. It is dehydrogenated by spongy palladium at 190°. The following compounds are thus prepared: 3:4-dihydroisoquinoline (*picrate*, m. p. 175—176°); and thence isoquinoline from form- $\beta$ -phenylethylamide; 1-methyl-3:4-dihydroisoquinoline, b. p. 130°/10 mm.\* (*picrate*, m. p. 188—190°; cf. Pictet and Kay, A., 1909, i, 513), and 1-methylisoquinoline (*picrate*, m. p. 225—226°); 1-ethyl-3:4-dihydroisoquinoline (*picrate*, m. p. 190—192°) and 1-ethylisoquinoline [*picrate*, m. p. 209—210° (decomp.)], from propion- $\beta$ -phenylethylamide, m. p. 50—51°; 1-n-propyl-3:4-dihydroisoquinoline (*picrate*, m. p. 173—174°) and 1-n-propylisoquinoline (*picrate*, m. p. 200—201°) from n-butyl- $\beta$ -phenylethylamide, m. p. 49—50°; 1-n-butyl-3:4-dihydroisoquinoline, b. p. 170—180°/10 mm.\* (*picrate*, m. p. 153—154°), and 1-n-butylisoquinoline (*picrate*, m. p. 185—186°) from n-valer- $\beta$ -phenylethylamide, m. p. 44—46°; 1-phenyl-3:4-dihydroisoquinoline, b. p. 190—200°/12 mm. (*picrate*, m. p. 173—175°), and 1-phenylisoquinoline, m. p. 95—96° (*picrate*, m. p. 165—166°), from benz- $\beta$ -phenylethylamide; 1-benzyl-3:4-dihydroisoquinoline, b. p. 220°/12 mm.\* (*picrate*, m. p. 173—175°), and 1-benzylisoquinoline, b. p. 140—150°/1 mm.\* (*picrate*, m. p. 182°), from phenylacet- $\beta$ -phenylethylamide; 4-methyl-3:4-dihydroisoquinoline (*picrate*, m. p. 132—133°) and 4-methylisoquinoline (*picrate*, m. p. 202—203°) from form- $\beta$ -phenylpropylamide, b. p. 140—160°/0.35 mm.\*; 1:4-dimethyl-3:4-dihydroisoquinoline (*picrate*, m. p. 167—168°) and 1:4-dimethylisoquinoline, b. p. 140—160°/12 mm.\* (*picrate*,

m. p. 221—222°, from *acet-β-phenylpropylamide*, b. p. 160—180°/0.4 mm.; 5-methyl-3:4-dihydroisoquinoline [*picrate*, m. p. 182—183° (decomp.)] and 5-methylisoquinoline (*picrate*, m. p. 235—236°) from *form-β-o-tolylethylamide*, b. p. 160—180°/0.25 mm.\*; 1:5-dimethyl-3:4-dihydroisoquinoline (*picrate*, m. p. 182—184° after softening) and 1:5-dimethylisoquinoline, m. p. 97—98° [*picrate*, m. p. 230—231° (decomp.)], from *acet-β-o-tolylethylamide*. The temperatures marked \* are measured in the bath. H. WREN.

**Colour reaction between sodium nitroprusside and creatinine.** G. SCAGLIARINI and P. PRATESI (Atti R. Accad. Lincei, 1929, [vi], 10, 261—266).—The red compound formed in this reaction in alkaline solution may have either of the two formulæ,



T. H. POPE.

**Substituted phenylethylbarbituric acids.** E. W. BOUSQUET and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 224—229).—Nitration of 5-phenyl-5-ethylbarbituric acid with nitric (*d* 1.5) and sulphuric acids at −10° to 3° affords 5-*p*-nitrophenyl-5-ethylbarbituric acid, m. p. 276—277°, reduced catalytically (platinum oxide) to the corresponding 5-*p*-aminophenyl derivative, m. p. 205—206°. Bromination of 5-*p*-acetamidophenyl-5-ethylbarbituric acid, m. p. 147—148°, affords a 5-bromo-*p*-acetamidophenyl derivative, m. p. 291—292° (the bromoamino-compound has m. p. 253—255°), whilst nitration furnishes 5-nitro-*p*-acetamidophenyl-5-ethylbarbituric acid, m. p. 295—296° (nitroamino-derivative, m. p. above 320°). 5-*p*-Chlorophenyl-5-ethylbarbituric acid, decomp. 243—245°, has about the same hypnotic power as the original compound but is slightly more toxic. The other derivatives have no hypnotic action.

Nitration of methyl ethyl phenylethylmalonate with nitric and sulphuric acids at −10° to 0° gives the *p*-nitrophenyl derivative, b. p. 180—185°/4 mm. (oxidised to *p*-nitrobenzoic acid). This is reduced catalytically (platinum oxide) to methyl ethyl *p*-aminophenylethylmalonate, b. p. 182—185°/4 mm. (acetyl derivative, b. p. 192—197°/3 mm.), convertible by the usual method into methyl ethyl *p*-hydroxyphenylethylmalonate, b. p. 180—185°/4 mm. (methyl ether, b. p. 152—156°/4 mm.). Condensation of these esters with carbamide could not be effected. H. BURTON.

**Constitution of "dioxypyramidone."** R. CHARONNAT and R. DELABY (Compt. rend., 1929, 189, 1285—1286).—The compound,  $\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}_3$ , b. p. 194—201°/2 mm., m. p. 105.5°, previously described (this vol., 223) as dioxypyramidone, is unaffected by the usual reducing agents, acetic anhydride, and iodine, indicating that it is not a pyramidone. On complete hydrolysis with concentrated sodium hydroxide solution at 100°, dimethylamine, β-phenyl-α-methylhydrazine, sodium acetate, and sodium oxalate are obtained, whilst partial hydrolysis affords α-acetyl-β-phenyl-α-methylhydrazine and sodium *NN*-dimethylloxamate. The above compound is, therefore, α-acetyl-β-*NN*-dimethylloxamyl-β-phenyl-α-methylhydrazine,  $\text{NMeAc}\cdot\text{NPh}\cdot\text{CO}\cdot\text{CO}\cdot\text{NMe}_2$ . H. BURTON.

**Local anæsthetics derived from piperazine.** E. FOURNEAU and C. E. BARRELET (Bull. Soc. chim., 1929, [iv], 45, 1172—1189).—Monosubstituted derivatives of piperazine are obtained in 50—70% of the theoretical yield by refluxing ethylene oxides with excess of piperazine hydrate (cf. Moore and others, A., 1929, 331). Mixed disubstituted derivatives are obtained in the theoretical yield by treating a monosubstituted piperazine (1 mol.) with 1 mol. of a halogen compound in benzene. The *s*-disubstituted aminoalcohol derivatives of piperazine are obtained quantitatively from molecular quantities of piperazine and ethylene oxide. They give no additive products with carbon disulphide and when of high mol. wt. have a strong anæsthetic action. Attempts to obtain compounds of the stavaine or aminostavaine type failed, benzoylation of the aminoalcohol taking place on the free piperazyl imino-group. If the latter position was first blocked with a carbethoxyl group, subsequent benzoylation gave products similar to those obtained by Moore (*loc. cit.*) and on hydrolysis the benzoyl group is also removed. The following are described: 1-β-hydroxy-β-methyl-*n*-butylpiperazine, m. p. 77—78°, b. p. 133°/20 mm. (yield, 60%, from methylethylethylene oxide) [*hydrochloride*; *dihydrochloride*, m. p. 136° (decomp.); *picrate*, m. p. 230° (decomp.)]; *N*-benzoate, a neutral oil, b. p. 247°/17 mm. (*monohydrochloride*, m. p. 190°, anæsthetic powers), giving with ethyl chloroacetate ethyl 1-β-hydroxy-β-methyl-*n*-butylpiperazine-4-acetate, b. p. 183°/17 mm. (*hydrochloride*, m. p. 119°; *picrate*, 178°); *m*-nitrobenzoate *dihydrochloride*, m. p. 172° (*picrate*, m. p. 175°), *m*-aminobenzoate *trihydrochloride*, m. p. 173—174° (anæsthetic powers) [*picrate*, m. p. 169° (decomp.)], and with carbon disulphide the *dithiocarbamate*,  $\text{OH}\cdot\text{CMeEt}\cdot\text{CH}_2\cdot\text{N}\begin{array}{l} \text{CH}_2 \\ \text{CH}_2 \end{array}\text{N}\cdot\text{CS}\cdot\text{SH}$ , m. p. 137° [sodium salt, m. p. 225—226° (decomp.)]; 1:4-bis-β-hydroxy-β-methyl-*n*-butylpiperazine, m. p. 33°, b. p. 183—186°/19 mm. [*hydrochloride*; *dihydrochloride*, m. p. 218° (decomp.); *picrate*, m. p. 221° (decomp.)]; *dibenzoate*, m. p. 86—87° (*dihydrochloride*, m. p. 199°, weak anæsthetic powers; *picrate*, m. p. 195°)]; γ-butoxy-β-hydroxy-*n*-propylpiperazine, b. p. 185—188°/30 mm. (*dihydrochloride*, m. p. 108—109°; *picrate*, m. p. 204°; *dithiocarbamate*, m. p. 113°); β-hydroxy-γ-phenyl-*n*-propylpiperazine (piperazyl-phenylmethylcarbinol), b. p. 203—208°/18 mm., m. p. 63—64° (*dihydrochloride*, m. p. 147—148°; *picrate*, m. p. 209°; *dithiocarbamate*, m. p. 91°); 1:4-bis-β-hydroxy-γ-phenyl-*n*-propylpiperazine, m. p. 136° [*monohydrochloride*, m. p. 167° (0.5% solution  $p_H$  6.1—6.2 has complete anæsthetic action by intradermic injection into the arm); *dihydrochloride*, m. p. 229° (toxic for mice in doses of 0.01 g. per 20 g.-wt. by subcutaneous injection); *picrate*, m. p. 228—230° (decomp.)], obtained in the preparation of piperazyl-phenylmethylcarbinol, together with an isomeric base, m. p. 110°, resulting from the alternative rupture of the ethylene oxide ring; 1-β-hydroxy-γ-phenoxy-*n*-propylpiperazine, m. p. 58—59°, b. p. 220—225°/16 mm. [*monohydrochloride*; *dihydrochloride*, m. p. 156°; *picrate*, m. p. 210° (decomp.)]; *dithiocarbonate*, m. p. 124°; and 1:4-bis-β-hydroxy-γ-phenoxy-*n*-propylpiperazine, m. p. 135° [*hydrochloride*, m. p. 231° (decomp.)] after

darkening at 220° (anaesthetic powers); *picrate*, m. p. 223° (decomp.). Piperazine hydrate and 2-chloroquinoline in alcohol at 140° yield *N*-2-quinolylpiperazine, solid [*monohydrochloride*; *dihydrochloride*, m. p. 229—231° (decomp.); *picrate*, m. p. 243—245° (decomp.)]. 2-Chloroquinoline and *N*-β-hydroxy-β-methyl-*n*-butylpiperazine in benzene at 130° similarly yield 1-(2'-quinolyl)-4-β-hydroxy-β-methyl-*n*-butylpiperazine [*dihydrochloride*, m. p. 247° (decomp.) (slight anaesthetic action); *picrate*, sinters at 140°, m. p. 168—169°]. *N*-β-Hydroxy-β-methyl-*n*-butylpiperazine and ethylchloroformate yield the *N*'-carbethoxy-derivative, b. p. 184°/16 mm. [*hydrochloride*, m. p. 171° (decomp.)]. The *m*-nitrobenzoate [*hydrochloride*, sinters at 133°, m. p. 145° (decomp.) (strong anaesthetic action)] of this substance affords on hydrolysis with sodium hydroxide, *m*-nitrobenzoic acid and a viscous brown mass giving a hydrochloride, sinters at 143°, m. p. 161° (decomp.), and on reduction a brown solid from which the carbethoxyl group has been eliminated. The *o*- and *p*-nitrobenzoates behave similarly, the *o*-nitrobenzoate being the least stable. None of the anaesthetics obtained showed any advantage over those already known.

R. BRIGHTMAN.

**Pyrimidines.** CX. Condensation of Claisen's ethyl ethoxymethylenemalonate with  $\psi$ -ethylthiocarbamide. T. B. JOHNSON and Y. F. CHU (Rec. trav. chim., 1930, 49, 86—90; cf. Wheeler, Johnson, and Johns, A., 1907, i, 559).—Condensation of ethyl ethoxymethylenemalonate with  $\psi$ -ethylthiocarbamide in presence of excess (3.25 mols.) of potassium hydroxide solution, gives the potassium salt, m. p. 285—288° (decomp.), of ethyl 6-hydroxy-2-ethylthiopyrimidine-5-carboxylate. In presence of 1 mol. of potassium hydroxide solution the additive compound, m. p. 190—195° (decomp.), of 1 mol. of the above potassium salt and 1 mol. of the corresponding  $\psi$ -ethylcarbamide salt is produced. Both of the above salts yield the corresponding hydroxypyrimidine, m. p. 131° (ethyl 2-ethylthiol-6-keto-1:6-dihydro-pyrimidine-5-carboxylate), on acidification.

H. BURTON.

**2-Thiol-4(5)-β-aminoethylglyoxaline (2-thiol-histamine).** F. L. PYMAN (J.C.S., 1930, 98—100).—Hydrolysis of α-dibenzamido-β-ketobutane, m. p. 158—159° (corr.) (lit. 151°), with alcoholic hydrochloric acid at 150° gave α-diamino-β-ketobutane dihydrochloride, m. p. 221° (decomp.; corr.) [corresponding *picrate*, m. p. 212° (decomp.; corr.)], which, by interaction with aqueous sodium thiocyanate, formed 2-thiol-4(5)-β-aminoethylglyoxaline hydrochloride, m. p. 248—249° (corr.) [corresponding *picrate*, m. p. 225° (decomp.; corr.)]. This compound underwent oxidation when boiled with aqueous ferric chloride with formation of histamine; physiological tests showed it to possess no significant histamine-like action.

R. J. W. LE FÈVRE.

**Skraup's reaction applied to phenylenediamines.** Preparation of phenanthrolines and related dipyridyls. C. R. SMITH (J. Amer. Chem. Soc., 1930, 52, 397—403).—Details are given for the preparation of *m*- and *p*-phenanthrolines from *m*- and *p*-phenylenediamines, by the Skraup reaction, in 40—60% yield. Oxidation of *p*-phenanthroline with

alkaline potassium permanganate affords 3:3'-dipyridyl-2:2'-dicarboxylic acid, which on thermal decomposition in glycerol suspension yields 3:3'-dipyridyl, b. p. 300—301° (corr.). Similarly, *m*-phenanthroline furnishes 2:3'-dipyridyl-3:2'-dicarboxylic acid, which when heated at 190—200° gives two 2:3'-dipyridylmonocarboxylic acids (the acid formed in smaller amount has m. p. 152—154°, and is new). Both monocarboxylic acids are decomposed at about 290° to 2:3'-dipyridyl, b. p. 298°. The Skraup reaction with *o*-phenylenediamine furnishes a small amount of a compound, C<sub>12</sub>H<sub>8</sub>ON<sub>2</sub>, m. p. 253° (corr.), oxidised by alkaline potassium permanganate to a dicarboxylic acid, m. p. 167°. This undergoes thermal decomposition to a substance, m. p. 113°. *o*-Phenanthroline (+H<sub>2</sub>O), m. p. 91°, m. p. (anhydrous) 97°, is obtained with some difficulty by the Skraup reaction with 8-aminoquinoline. It is converted by oxidation and subsequent thermal decomposition into 2:2'-dipyridyl, m. p. 68°.

H. BURTON.

**Picoline of Scholtz and acetyl derivatives of indolizine and 2-methylindolizine.** A. E. TSCHITSCHIBABIN and F. N. STEPANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1635—1644).—See A., 1929, 704.

**Anserine.** F. L. PYMAN (J.C.S., 1930, 183—184).—The author points out that in consequence of previous work by himself and collaborators the dimethylglyoxaline isolated by Linneweh, Keil, and Hoppe-Seyler (A., 1929, 944) by distillation of anserine with soda-lime must be the 1:5-compound; consequently their methylhistidine (hydrolysis product of anserine) is *dl*-β-(1-methylglyoxalyl-5)-α-amino-propionic acid, CO<sub>2</sub>H·CH(NH<sub>2</sub>)·CH<sub>2</sub>·C<CH—N<sup>+</sup>Me, and the relative positions of the side-chains and the *N*-methyl groups are the same in anserine and pilocarpine.

R. J. W. LE FÈVRE.

**Components of the Chinese drug "Ma Huang."** VII. **1-Norephedrine.** S. KANAO (Ber., 1930, 63, [B], 95—98).—The concentrated aqueous extract of the drug is rendered alkaline and extracted with benzene. The neutralised solution of the bases deposits *l*-ephedrine hydrochloride, m. p. 216—217°. The mother-liquor, after addition of potassium hydroxide, yields *d*-isoephedrine, m. p. 118°. The remaining bases are neutralised with alcoholic oxalic acid, thereby giving crystals mainly of *l*-methyl-ephedrine oxalate, m. p. 187°. The mixture of bases still remaining is distilled under diminished pressure. The distillate affords *l*-methylephedrine, m. p. 87°, and the remainder is converted by absolute ethyl-alcoholic sulphuric acid into a mixture of sulphates. The bases derived from the last-named mixture are heated with aqueous *l*-tartaric acid, thereby giving successively *d*-norisoephedrine hydrogen *l*-tartrate, m. p. 202°, and *l*-norephedrine hydrogen *l*-tartrate, (also +1EtOH), m. p. about 160° after softening at 130°, [α]<sub>D</sub><sup>20</sup> −34.64° in water [corresponding hydrochloride, m. p. 171—172°, [α]<sub>D</sub><sup>20</sup> −33.74° in water; chloroplatinate, m. p. 221° (decomp.); chloroaurate, m. p. 188°]. The identity of the natural and synthetic product (A., 1929, 807) is further established by the conversion of the *N*-*p*-nitrobenzoyl derivative,

m. p. 175—176°, into *d*-norisocphedrine *p*-nitrobenzoate.

H. WREN.

**Papaverine.** Attempted Rügheimer synthesis. I. ALLEN, jun., and J. S. BUCK (J. Amer. Chem. Soc., 1930, 52, 310—314).—Reduction of veratril with tin and alcoholic hydrochloric acid containing copper sulphate, or treatment of veratrole with homoveratryl chloride in presence of aluminium chloride and carbon disulphide, affords *deoxyveratrolin*, m. p. 107°. The *oxime*, m. p. 128°, of this is reduced by sodium amalgam and alcoholic acetic acid to 3 : 4 : 3' : 4'-*tetramethoxystilbylamine* [ $\alpha\beta$ -di-(3 : 4-dimethoxyphenyl)-ethylamine], m. p. 107° (hydrochloride, m. p. 195°; hydrobromide, m. p. 241°; acetyl derivative, m. p. 160—162°), which reacts with bromodimethylacetal to form the corresponding *N*- $\beta\beta$ -dimethoxyethyl derivative (not obtained pure). Attempted conversion of this last-named compound into papaverine by treatment with sulphuric acid and arsenic oxide results in complete destruction of the base.

The *oxime*, m. p. 158°, of *deoxypiperoin*, m. p. 114° (obtained by reduction of piperoin), is reduced as above to 3 : 4 : 3' : 4'-*dimethylenedioxyethylamine* [ $\alpha\beta$ -di-(3 : 4-methylenedioxyphenyl)ethylamine], m. p. 111° (hydrochloride, m. p. 245°; acetyl derivative, m. p. 141°). The *N*- $\beta\beta$ -dimethoxyethyl derivative of this base is decomposed by treatment with arsenic oxide and cold 75% sulphuric acid.

H. BURTON.

**Constitution of conessine.** E. SPÄTH and O. FROMATKA (Ber., 1930, 63, [B], 126—133).—Determination of the methyl alcohol evolved shows that the main decomposition of conessine dimethyl hydroxide does not follow the course  $C_{24}H_{40}N_2Me_2(OH)_2 = C_{22}H_{33}N + NMe_3 + MeOH + H_2O$  (cf. Kanga, Ayyar, and Simonsen, A., 1926, 1047), but proceeds according to the equation  $C_{24}H_{40}N_2Me_2(OH)_2 = C_{23}H_{35}N + NMe_3 + 2H_2O$ . Confirmation of the consequently modified formula,  $C_{23}H_{35}N$ , for *apoconessine* is found in the observation that it contains two methyl groups attached to nitrogen. Further, conessine contains one double linking, since it is hydrogenated in presence of palladised charcoal to *dihydroconessine*, m. p. 105—105.5° (hydrochloride). On the authors' hypothesis, therefore, *apoconessine* contains three double linkings, as is proved by its conversion into *hexahydroapoconessine*, m. p. 69—70° [a by-product yielding a picrate, m. p. 255—256° (decomp.), is also obtained]. Analysis of *apoconessine* hydrochloride [corresponding picrate, m. p. 234° (decomp.)], confirms the composition  $C_{23}H_{35}N \cdot HCl$ . Attempts to apply the Hofmann degradation to the quaternary base from *apoconessine* and methyl iodide do not yield a nitrogen-free product. The methiodide is therefore converted into the corresponding *methochloride*, which is transformed by sodium amalgam into trimethylamine and a hydrocarbon,  $C_{21}H_{30}$ , m. p. 74—76°,  $[\alpha]_D^{25} - 183.7^\circ$  in pyridine. Hydrogenation of the last-named substance in presence of palladised charcoal yields the compound  $C_{21}H_{36}$ , m. p. 56—58°,  $d^{20}_4 0.9547$ ,  $n^{20}_D 1.50664$ ,  $[\alpha]_D^{25} + 14.5^\circ$  in benzene. The non-production of a more highly hydrogenated compound under conditions which cause the hydrogenation of unpurified mesitylene appears to imply the absence of a benzene nucleus from conessine. On the assumption that the number of hydrogen

atoms as previously determined in the alkaloid is correct, conessine appears to be a combination of four hydrogenated, carbocyclic rings to which a ring with one nitrogen atom is attached. In the ring complex or in a side-chain thereof, a difficultly reducible double linking is placed.

H. WREN.

**Harmala alkaloids :** harmaline, harmine, and harman. E. SPÄTH and E. LEDERER (Ber., 1930, 63, [B], 120—125).—3- $\beta$ -Aminoethylindole is converted by acetic anhydride at the ordinary temperature into its acetyl derivative, which, when treated with phosphoric oxide in boiling xylene, affords dihydroharman, m. p. 182°, in 56% yield (cf. Manske, Perkin, and Robinson, A., 1927, 265). Dehydrogenation of the compound to harman, m. p. 237°, is effected with spongy palladium at 200° (yield 89%). 3-Methoxyphenylhydrazine and  $\gamma$ -amino-*n*-butaldehydediethylacetal in presence of anhydrous zinc chloride at 130—150° appear to yield a mixture of 4- and 6-methoxy-3- $\beta$ -aminoethylindoles, from which, by treatment with acetic anhydride followed by ether, 6-methoxy-3- $\beta$ -acetamidoethylindole, m. p. 136°, is isolated in 30% yield. The compound is transformed by phosphoric oxide in boiling xylene into harmaline, m. p. 250—251°, from which harmine, m. p. 264—265°, is obtained by the action of spongy palladium at 200°.

H. WREN.

**Sinomenine and disinomenine.** XII. Sinomenine hydrate. K. GOTO and H. SUZUKI (Bull. Chem. Soc. Japan, 1929, 4, 271—277).—Treatment of sinomenine at 100° with dilute hydrochloric acid, followed by sodium carbonate, gives *sinomenine hydrate*, m. p. 139°,  $[\alpha]_D^{25} + 40.8^\circ$  in chloroform [methiodide, m. p. 264° (decomp.); disemicarbazone, m. p. 191° (decomp.); dioxime, m. p. 231° (decomp.)], reduced by sodium amalgam to  $\alpha$ -demethoxysinomenine hydrate, m. p. 128° (40% yield), and by palladium and hydrogen to  $\alpha$ -[oxime, m. p. 170° (decomp.); semicarbazone, m. p. 191° (decomp.); phenylhydrazone, m. p. 140°; methiodide, m. p. 274—276° (decomp.)] and  $\beta$ -demethoxysinomenine hydrates [methiodide, m. p. 280° (decomp.); semicarbazone, m. p. 206° (decomp.)], m. p. 129°,  $[\alpha]_D^{25} + 64.8^\circ$  in chloroform, and m. p. 104°,  $[\alpha]_D^{25} + 95.2^\circ$  in chloroform, respectively. *Bisdemethylsinomenilidene*, m. p. above 312°, is produced in 40% yield from sinomenine hydrate and aqueous ammonia (*d* 0.9).

A. I. VOGEL.

**isoQuinidine.** A. KONOPNICKI and J. SUSZKO (Rocz. Chem., 1929, 9, 640—660).—See this vol., 97.

**Microchemical reactions for hydrastine.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 57—58).—The alkaloid as precipitated is usually an oil or amorphous solid, which can be caused to crystallise by grinding with sodium hydrogen carbonate; borax gives a crystalline precipitate. The bromine and ferrocyanide reactions are mentioned. S. I. LEVY.

**Microchemical reactions for berberine.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 77—79).—Precipitation by addition of salts is exceedingly sensitive, and will indicate 0.5 mg., at a dilution of 1 : 2000. The reactions with iodine, bromine, and potassium bismuth iodide are also characteristic.

S. I. LEVY.

**Synthesis of arsenic  $\alpha$ -chlorostyryl dichloride.** V. IPATIEV, G. RAZUBAIEV, and A. SISOV (Ber., 1929, 63, [B], 174—178; cf. Turner, A., 1925, i, 843).—Arsenic  $\alpha$ -chlorostyryl dichloride, m. p. 40.6—41.2°, is obtained crystalline by cooling the product of the action of phenylacetylene on arsenic trichloride at 110°. It cannot be distilled without decomposition. It appears stable to water at the ordinary temperature, but is converted by alkali hydroxide or carbonate or by aqueous ammonia into arsenic  $\alpha$ -chlorostyryl oxide, m. p. 115—117°, and by hydrogen peroxide into the arsenic acid,  $C_8H_8O_3ClAs$ , m. p. 179—180°.

H. WREN.

**Preparation of 4- and 6-hydroxy-3-nitrophenylarsinic acids.** I. E. BALABAN (J.C.S., 1930, 183).—Reduction of 1-chloro-2:4-dinitrobenzene by West's method produces 4- and 6-chloro-3-nitroanilines in 23% and 45% yields, respectively, from which (by the Bart-Schmidt reaction) 4-chloro-3-nitrophenylarsinic acid (yield 32.4%) and 6-chloro-3-nitrophenylarsinic acid (yield 32.9%) may be obtained. Boiling with 25% aqueous sodium hydroxide converts these acids into the related hydroxynitrophenylarsinic acids.

R. J. W. LE FÈVRE.

**Condensation products of aminoarsanilic [3:4-diaminophenylarsinic] and arsanilic [*p*-aminophenylarsinic] acids.** P. L. CRAMER [with W. L. LEWIS] (J. Amer. Chem. Soc., 1930, 52, 229—234).—3:4-Diaminophenylarsinic acid condenses with glyoxal sodium hydrogen sulphite, forming 2:3-disodium 2:3-disulpho-1:2:3:4-tetrahydroquinoxaline-6-arsinic acid, hydrolysed by hydrochloric acid to quinoxaline-6-arsinic acid, not melted at 250°. Condensation of the diamino-acid with maltosone in boiling methyl alcohol gives 3-glucosidoerythrityl-quinoxaline-6-arsinic acid, purple, not melted at 250°, whilst with lactosone in methyl-alcoholic ethylene glycol the corresponding 3-galactosidoerythrityl derivative is obtained; these derivatives are readily hydrolysed by water.

**Condensation products**, all of which char below 100°, of *p*-aminophenylarsinic acid and the following sugars are obtained in presence of methyl alcohol: dextrose, mannose, galactose, arabinose, and xylose. Aqueous solutions of these compounds undergo rapid hydrolysis which can be followed polarimetrically. *p*-Aminophenylarsinic acid and ethylene oxide react in presence of sodium hydroxide solution, forming 4- $\beta$ -hydroxyethylaminophenylarsinic acid, m. p. 168°; with phenacyl bromide, 4-diphenacylamidophenylarsinic acid, m. p. 162.5°, results. The following new compounds are prepared by the usual methods: 3-amino-4-benzenesulphonamido-, m. p. 205—207° (decomp.); 3-amino-4-*p*-toluenesulphonamido-, m. p. 160—165° (decomp.); 3-amino-4-*p*-bromobenzenesulphonamido-, m. p. 180—185° (decomp.); 3-amino-4-picramido-, chars at 165°; 4-picramido-, not melted at 260°, and 4-*p*-bromobenzenesulphonamido-phenylarsinic acids, m. p. 210—212° (decomp.).

H. BURTON.

**Diarylarsinic acids, halogenodiarylarsines, and the constitution of 10-chloro-5:10-dihydrophenarsazine.** C. P. A. KAPPELMEIER (Rec. trav. chim., 1930, 49, 57—85).—The hydrochloride, m. p.

134°, of diphenylarsinic acid (Grignard and Rivat, A., 1919, i, 460) is formulated as diphenylarsinic acid chloride (dihydroxydiphenylarsonium chloride),  $[AsPh_2(OH)_2]Cl$ . When this is heated above its m. p. only a small amount of hydrogen chloride is evolved; decomposition occurs mainly thus:  $[AsPh_2(OH)_2]Cl \rightarrow PhCl + PhAsO + H_2O$ . When crystallised from acetone the above chloride passes into bisdiphenylarsinic acid chloride,  $\{AsPh_2(OH)O[AsPh_2(OH)_2]\}Cl$ , m. p. 114.5° (the second hydrochloride of Grignard and Rivat, *loc. cit.*). The former chloride is undoubtedly the intermediate in the reduction of diphenylarsinic acid to chlorodiphenylarsine by the well-known sulphur dioxide-hydrochloric acid method. The chloride,  $\{AsPh_2O_2[AsPh_2(OH)_2]\}Cl$ , m. p. 121°, is obtained when chlorodiphenylarsine dibromide is decomposed by moist air. The diphenylarsinic acid nitrate,  $AsPh_2O \cdot NO_3$ , of Michaelis (A., 1902, i, 515) is dihydroxydiphenylarsonium nitrate, m. p. 122—123° (corresponding sulphate, m. p. 119—120°), which on crystallisation from acetone passes into the nitrate,  $C_{24}H_{20}O_4 \cdot NAs_2$ , m. p. 113° after previous softening. Dihydroxyphenylbenzylarsonium and hydroxytriphenylarsonium chlorides have m. p. 115° and 175—176° after softening at 174°, respectively. The salts of phenarsazinic acid (Wieland and Rheinheimer, A., 1921, i, 371; Burton and Gibson, A., 1925, i, 84) are formulated thus:  $[NH(C_6H_4)_2As(OH)_2]X$ . Chlorodiphenylarsine dichloride, m. p. about 189° (lit. 174°), on crystallisation from acetone affords dihydroxydiphenylarsonium chloride, which with thionyl chloride in chloroform regenerates the trichloro-derivative. Whereas chloro- and bromo-diphenylarsines form polyhalides, 10-chloro-5:10-dihydrophenarsazine is converted by bromine in chloroform into tetrabromodiphenylamine (cf. Elson, Gibson, and Johnson, A., 1929, 834). Methylation of phenarsazinic acid is not possible, but treatment with thionyl chloride in chloroform suspension affords the compound  $NH(C_6H_4)_2AsCl_3$ .

10-Chloro-5:10-dihydrophenarsazine is considered to react like the hydrochloride of a weak base; the formula  $[N \leftarrow C_6H_4 \rightarrow As \cdot H]Cl$  is assigned to it (cf. Burton and Gibson, A., 1926, 418; Gibson and Johnson, A., 1929, 945), to explain the colour and the various reactions.

H. BURTON.

**Organo-aromatic derivatives of boron.** E. PACE (Atti R. Accad. Lincei, 1929, [vi], 10, 193—196).—Monophenylboron chloride (cf. Michaelis and Becker, A., 1880, 395; 1882, 731), prepared by passing benzene and boron trichloride vapours over platinised asbestos or palladium-black at 500—600°, yields phenylborine (or "boronaniline"),  $BH_2Ph$ , b. p. 193°, when heated with dry, gaseous hydrogen iodide in presence of iodine. Boronbenzene,  $BPh \cdot BPh$ , m. p. 155° (decomp.), formed when phenylborine is heated in a current of hydrogen in a reflux apparatus, is unstable in the air, giving rise to a pasty mass of boronxybenzene (?).

T. H. POPE.

**Organic germanium derivatives. II. Triphenylgermanium derivatives and their reactions.** C. A. KRAUS and C. B. WOOSTER (J.



Amer. Chem. Soc., 1930, **52**, 372—376; cf. A., 1927, 268).—Treatment of triphenylgermanium bromide with ammonia in presence of a solvent affords ammonium bromide and triphenylgermanium oxide; the oxide arises by hydrolysis of the initially formed triphenylgermaniumamine,  $\text{GePh}_3\text{NH}_2$ . The product formed from the bromide and liquid ammonia also contained oxide and unchanged material. When the bromide is treated with an excess of potassium amide in liquid ammonia, the salt,  $\text{GePh}_3\text{NHK}$ , is obtained. This is decomposed by ammonium bromide to the amine. The free amine loses ammonia readily at the ordinary temperature affording a mixture of the corresponding imine and nitride,  $(\text{GePh}_3)_2\text{N}$ , m. p. 163—164° (cf. *loc. cit.*). The nitride is best obtained when the amine is heated at 200°/vac.

Sodium reacts with triphenylgermanium oxide in liquid ammonia forming sodium triphenylgermanide and sodium triphenylgermanoxide (cf. *loc. cit.*).

H. BURTON.

#### Synthesis of aromatic mercurio-organic salts.

A. N. NESMEJANOV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1393—1405).—The preparation of organo-metallic derivatives of mercury by the action of copper powder on the double diazonium and mercuric chloride salts according to Gattermann's method is described. The yields obtained are 60—80% in the case of benzene and naphthalene homologues, 15—45% for halogen-substituted nuclei, and very low for nuclei containing nitro- or carboxyl groups. The double diazonium salts with mercuric chloride were prepared by three methods: (1) diazotisation of the amine, followed by addition of the diazonium salt to an equivalent amount of mercuric chloride, when the double salt was precipitated; (2) diazotisation of the amine by adding it to a mixture of sodium nitrite and mercuric chloride in hydrochloric acid solution, and (3) diazotisation of the amine by amyl nitrite, and addition to a solution of mercuric chloride under certain conditions. These methods were found to yield different products.

Mercury phenyl iodide, m. p. 269°, was obtained by Gattermann's method from the double salt, m. p. 63—64° (decomp.), of mercuric iodide and benzene-diazonium iodide. Mercury phenyl chloride, m. p. 258°, from the double salt (decomp. on heating). Mercury *p*-tolyl chloride, m. p. 238—239°, from the double salt, m. p. 107°, and the *o*-tolyl chloride, m. p. 143°, from the double salt (decomp. on heating). Mercury  $\alpha$ -naphthyl chloride, m. p. 191°, from the pale yellow double salt, m. p. 120—121°, and the  $\beta$ -naphthyl chloride, m. p. 270°, from the yellow double salt, m. p. 120—125°. Mercury *p*-hydroxyphenyl chloride, m. p. 226—227°, from the double salt, m. p. 156°. Mercury *o*-anisyl chloride, m. p. 180—181°, from the double salt, m. p. 121.5°. Mercury *p*-phenetyl chloride, m. p. 249—250°, from the double salt, m. p. 109°. Methyl mercury *o*-chlorobenzoate, m. p. 184.5°, from the double salt, m. p. 121°. Mercury *p*-chlorophenyl chloride, m. p. 228°, from the double salt, m. p. 124.5°; the *p*-bromo-compound, m. p. 249.5°, from the double salt, decomp. explosively at 119°, and the *p*-iodo-compound, m. p. 272.5°, from the double salt, m. p. 120—121.5°. Mercury 2:5-dichlorophenyl chloride, m. p. 208°, from the pale yellow double salt, m. p. 147°. The double salt, m. p.

146°, of 2:4:6-tribromophenyldiazonium chloride and mercuric chloride, and the double salt of *p*-diazoniumbenzoic acid and mercuric chloride did not give organo-metallic compounds of mercury by Gattermann's method, whilst the yellow double salt of *p*-nitrophenyldiazonium chloride and mercuric chloride gave only a very small quantity of mercury *p*-nitrophenyl chloride, m. p. 267—269°.

M. ZVEGINTZOV.

**Synthesis of symmetrical aromatic mercurio-organic salts.** N. A. NESMEJANOV and E. I. KAN (J. Russ. Phys. Chem. Soc., 1929, **61**, 1407—1410; cf. preceding abstract).—The halide salts of aromatic organo-metallic mercuric derivatives can be transformed into symmetrical di-derivatives of mercury by a number of reducing agents, including copper powder. By using excess in the Gattermann method of decomposing the double diazonium and mercuric chloride salts, the symmetrical di-derivatives are obtained instead of the organo-metallic halides, half the mercury being precipitated as metal. Mercury diphenyl, m. p. 125°; di- $\alpha$ -naphthyl, m. p. 249°; di-*p*-tolyl, m. p. 243—244°; di-*p*-bromophenyl, m. p. 243—244°; di-*p*-iodophenyl, m. p. 270—272°; di-2:5-dichlorophenyl, m. p. 237°; di-*o*-anisyl, m. p. 108°, and di-*p*-nitrophenyl, decomp. at 320°, were synthesised by this method.

M. ZVEGINTZOV.

**Antimony aryl compounds.** W. RIDDELL and S. BASTERFIELD (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 45—52).—The following stibinic acids have been prepared from the corresponding amines, generally by the method described by Dunning and Reid (A., 1927, 65; 1928, 80) for *p*-acetamidophenylstibinic acid: *p*-carboxymethylphenyl-, *p*-carbethoxyphenyl-, *p*-carbethoxyaminophenyl-, acetophenone-4-,  $\alpha$ -naphthyl-, 4-aminophenyl-4'- (by half-diazotisation of benzidine), 4-carbethoxyaminodiphenyl-4'-, 4-amino-diphenylmethane-4'-, 2-nitro-4-methoxyphenyl-, 2-acet-amido-5-methoxyphenyl-, 2-acetamido-4-methoxyphenyl-, 1:4-phenylenedi-, and 4:4'-diphenylmethanedi-stibinic acid. With the exception of acetophenone-4-stibinic acid (deep red) they form buff powders. Anisole-3:4-distibinic acid could not be prepared. Benzidine yielded 4-hydroxydiphenylstibinic acid, and not the distibinic acid, by the method of Dunning and Reid (A., 1928, 80).

Azo-dyes have been prepared by coupling diazotised *p*-aminophenylstibinic acid with phenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, and naphthionic acid. 4-Hydroxybenzene-azo-4'-methoxyphenyl-2'-stibinic acid was obtained from the acetamido-compound by hydrolysis, diazotisation, and coupling with phenol. A product other than the expected dye was obtained by stibinating, by the action of antimony trichloride, the diazonium chloride from *pp'*-diphenylbisazo- $\alpha$ -naphthylamine. 1-Naphthaleneazo- $\alpha$ -naphthylamine yielded  $\alpha$ -naphthylstibinic acid under similar treatment, but *p*-aminoazobenzene yielded azobenzene-*p*-stibinic acid.

4:4'-Diaminostibinobenzene was obtained by reduction of 4-nitrophenylstibinic acid with sodium hyposulphite, and 1-stibionaphthalene similarly from  $\alpha$ -naphthylstibinic acid. 4:4'-Carboxymethylstibinobenzene was only obtained impure. Stibino-compounds are readily oxidised, and unstable in acid or

alkaline solutions. No pure azostibino-compound could be obtained by diazotisation of 4:4'-diaminostibinobenzene and coupling with phenol.

R. K. CALLOW.

**New type of simple organic derivatives of tin.** K. A. KOTSCHESKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1385—1391).—The preparation and properties of organic derivatives of tin, of the hitherto unknown type  $\text{Ar}\cdot\text{SnX}_3$ , where Ar is an aromatic radical, and X a halogen atom, was investigated. The reactions used to obtain the analogous series of monoalkyl compounds are inapplicable, but by heating 1 mol. of tetraphenylstannane with 3 mols. of stannic chloride in a sealed tube at 210—220°, a good yield of *phenyltrichlorostannane*, b. p. 142—143°/25 mm., was obtained, as a heavy, colourless liquid, which fumed strongly in air. It dissolved in cold water without decomposition, but was partly hydrolysed on boiling. With ammonia solution, a white precipitate of amorphous phenylstannonic acid,  $\text{SnPh}\cdot\text{O}_2\text{H}$ , was obtained. The action of concentrated hydrobromic or hydriodic acid on a concentrated aqueous solution of the phenyltrichlorostannane gave the corresponding *tribromo-*, b. p. 182—183°/29 mm., and *tri-iodo-*compounds, respectively. Boiling with concentrated hydrochloric acid decomposed it into stannic chloride and benzene. In its preparation, some diphenyldichlorostannane, m. p. 42°, was obtained as a by-product.

M. ZVEGINTZOV.

**Removal of halogen from some homologous halogenoacyl derivatives of glycylglycine and their fission by N-sodium hydroxide at 37°.** E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1930, 11, 170—182).—The rate of removal of halogen from a number of homologous  $\alpha$ -substituted fatty acids in combination with glycylglycine (and in one case leucine) by N-sodium hydroxide at 37° was compared. The following have not previously been described: *bromoacetyl-dl-leucine*, m. p. 131°, decomp. 156°; *bromoacetylglycylglycine*, m. p. 174—175° (decomp.); *dl- $\alpha$ -bromo-n-butyrylglycylglycine*, m. p. 146—147° (decomp.);  *$\alpha$ -bromoisobutyrylglycylglycine*, m. p. 145° (decomp.). (All m. p. are uncorr.) Bromine is more readily removed than chlorine from the substituted acetic acid. The character of the amino-acid influences the rate of removal of the halogen, but less strongly than the nature of the fatty acid. The rate of hydrolysis of the  $\cdot\text{CO}\cdot\text{NH}\cdot$  linkings was also studied. Glycyl chains are very readily hydrolysed.

J. H. BIRKINSHAW.

**Influence of constitution of homologous dipeptides of dl-phenylalanine and the corresponding halogenoacyl compounds on their power of hydrolysis by alkali hydroxide, erepsin, and trypsin-kinase.** E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1930, 11, 224—250).—The action of N-sodium hydroxide, erepsin, and trypsin-kinase on a series of dipeptides containing *dl*-phenylalanine and the corresponding acyl compounds was examined. These included *potassium trihydrogen benzylmalonate*, m. p. 168—169° (loses carbon dioxide); *bromoacetyl-dl-phenylalanine*, m. p. 117—118°; *dl-alanyl-dl-phenylalanine*, m. p. 260° (decomp.);  *$\alpha$ -bromo-n-butyryl-dl-phenylalanine*, m. p.

122—123°; *dl- $\alpha$ -amino-n-butyryl-dl-phenylalanine*, m. p. 237°;  *$\alpha$ -bromoisobutyryl-dl-phenylalanine*, m. p. 114—115°;  *$\alpha$ -aminoisobutyryl-dl-phenylalanine*, m. p. 278°; *dl- $\alpha$ -bromo-n-valeryl-dl-phenylalanine*, m. p. 106·5°; *dl- $\alpha$ -aminovaleryl-dl-phenylalanine*, m. p. 210—211°; *dl- $\alpha$ -bromoisovaleryl-dl-phenylalanine*, m. p. 125°; *dl-valyl-dl-phenylalanine*, m. p. 239—240°; *dl- $\alpha$ -bromohexoyl-dl-phenylalanine*, m. p. 84—85°; *dl-aminohexoyl-dl-phenylalanine*, m. p. 210—211°; *dl- $\alpha$ -bromopropionyl-d-phenylalanine*,  $[\alpha]_D^{25}$  —3·85° (All temperatures uncorr.) The velocity of amination on conversion of the halogenoacyl compounds into the amino-compounds was high when the halogen was in the  $\alpha$ -position of a straight chain and greater with the short chains. Bromo-*n*-butyryl-*dl*-phenylalanine is an exception. In hydrolysis of the  $\cdot\text{CO}\cdot\text{NH}\cdot$  linking with sodium hydroxide, increase in the length of the chain attached to the amino-carbon atom implies increased resistance to alkaline hydrolysis. Branching of the carbon chain and especially a tertiary carbon atom seem to lend stability to the molecule. The halogenoacyl compounds show similar behaviour to the dipeptides. The action of erepsin on the halogenoacyl compounds showed no regularities; with trypsin-kinase the amount of hydrolysis decreased as the length of the carbon chain increased. The  $p_H$  optimum lay between 9 and 8·4.

J. H. BIRKINSHAW.

**Mol. wt. of casein.** I. T. SVEDBERG, L. M. CARPENTER, and D. C. CARPENTER (J. Amer. Chem. Soc., 1930, 52, 241—252).—Application of the centrifugal sedimentation velocity method to the determination of the mol. wt. of casein (Hammarsten) in phosphate buffer solutions at  $p_H$  6·8 shows that this substance is a mixture of proteins of different mol. wt. Extraction of the casein with 70% alcohol containing 0·1% of N-hydrochloric acid affords 33% of soluble material, which has a mol. wt. of about 375,000, as determined by the methods of sedimentation velocity and sedimentation equilibrium (cf. this vol., 233), and appears to be a definite chemical entity. The particle of the soluble casein is not spherical; the deviation from the spherical shape is of the same order as that found for serum-albumin and -globulin, phycocyan, and haemoglobin.

H. BURTON.

**Mol. wt. of amandin and excelsin.** T. SVEDBERG and B. SJÖGREN (J. Amer. Chem. Soc., 1930, 52, 279—287).—The specific volumes of amandin at  $p_H$  5·7, and of excelsin at  $p_H$  5·5, are identical with those of the proteins previously studied (A., 1929, 1092; this vol., 233). The positions of the absorption maximum (279  $\mu\mu$ ) and minimum (253  $\mu\mu$ ) for excelsin are the same at  $p_H$  5·5 and 12·2, but the extinction coefficient is higher at the latter  $p_H$ . Excelsin has a stronger light absorption than amandin, which shows the same maximum and minimum at  $p_H$  5·7. Determinations of the mol. wt. by the methods of sedimentation equilibrium and sedimentation velocity give values of  $208,000 \pm 5000$  for amandin (stable from  $p_H$  4·3 to about 10), and  $212,000 \pm 5000$  for excelsin (stable from  $p_H$  5·5 to about 10). At  $p_H$  12·2 amandin is disaggregated into molecules of one sixth of the original mol. wt.; excelsin behaves similarly at  $p_H$  11·9. The mol. wt., molecular radii (3·94—3·96  $\mu\mu$ ), sedimentation con-

stants, and molar friction constants of amandin and excelsin are identical, within the limits of experimental error, with the corresponding constants for edestin (*loc. cit.*). H. BURTON.

**Acid hydrolysis of proteins.** J. ENSELMÉ (*Compt. rend.*, 1930, 190, 136—138).—The methods of Van Slyke and Sørensen give different results for the amino-nitrogen of the same hydrolysates. The difference is minimal in the early stages, increasing to a maximum, and then decreasing as complete hydrolysis is attained. Various proteins and glycine anhydride have been used with 20 parts of hydrochloric acid (1.46—29.3%). A maximum difference of about 5% is observed in the values obtained by the two methods. The period of increase in the deviation of values obtained by these two methods probably corresponds with the production of polypeptides, and the decrease with the production of amino-acids from the polypeptides.

P. G. MARSHALL.

**Determination of oxygen in organic substances by hydrogenation.** H. TER MEULEN, H. J. RAVENSWAAY, and J. R. G. DE VEER (*Chem. Weekblad*, 1930, 27, 18).—A nickel boat filled with reduced nickel is employed in place of the nickel-asbestos mixture generally used; drying is much facilitated.

S. I. LEVY.

**Determination of sulphur in organic material by hydrogenation.** H. TER MEULEN, H. F. OPWYRDA, and H. J. RAVENSWAAY (*Chem. Weekblad*, 1930, 27, 19—20).—Pure asbestos may be used in place of platinised asbestos if the tube be heated to redness in a furnace.

S. I. LEVY.

**Interference of nitro-groups in the Zerevitinov method for the determination of active hydrogen.** H. GILMAN, R. E. FOTHERGILL, and E. B. TOWNE (*J. Amer. Chem. Soc.*, 1930, 52, 405—407; cf. A., 1928, 64, 536).—When tetranitromethane and pentabromonitrobenzene are treated with magnesium methyl iodide in *n*-butyl or isoamyl ether at 70°, evolution of gas occurs. Pentabromobenzene gives practically no gas under the same conditions, showing that gas formation is due to the nitro-group.

H. BURTON.

**Detection of acetic acid.** D. KRÜGER and E. TSCHIRCH (*Chem.-Ztg.*, 1930, 54, 42—44).—A review of tests for the detection of acetic acid indicates that the only trustworthy process which is specific is the microchemical reaction depending on the formation of sodium uranyl acetate.

H. F. HARWOOD.

**Use of vanadium salts for the differentiation of neutral and acid tartrates and citrates.** L. ROSSI (*Quim. e Ind.*, 1929, 6, 113—114; *Chem. Zentr.*, 1929, ii, 1187).—Acid tartrates or citrates, when added to an ammonium metavanadate solution, give respectively an intense orange-red or yellow coloration. Neutral tartrates and citrates do not give the reaction; addition of small quantities of an acid of moderate strength (*e.g.*, boric or benzoic) causes the coloration to appear. A. A. ELDRIDGE.

**Determination of halogens in cyclic compounds. Bromo-derivatives of *m*-xylenol.** L. PALFRAY and (MLLE.) D. SONTAG (*Bull. Soc. chim.*, 1930, [iv], 47, 118—127).—In the determination of bromine by Baubigny and Chavanne's method (A., 1903, ii, 510; 1904, ii, 203) it is essential to add the silver nitrate before the nitric acid. Replacement of the alkaline sodium sulphite by an alkaline solution of sodium arsenite yields accurate results for bromine in derivatives of cyclohexanediol and of *m*-xylenol, but low results are obtained with chloro-derivatives. Use of butyl alcohol in place of ethyl alcohol in Stepanov's method (A., 1907, ii, 50) gives quicker results than amyl alcohol (*cf.* Favrel and Bucher, A., 1928, 82), but the results are similar; with the 1:3- and 1:4-dichlorocyclohexanes accurate results are obtained for the *trans*-compounds, but the *cis*-isomerides yield low results. Glycerol cannot be used.

R. BRIGHTMAN.

**Oxidative degradation of physiologically important substances by Hehner's method.** F. LIEBEN and E. MOLNAR (*Monatsh.*, 1929, 53 and 54, 1—13).—Application of Hehner's method for the determination of glycerol to various substances gives results varying with the type of compound oxidised. Thus, carbohydrates and glucosamine are completely oxidised, but salts of hexosediphosphoric acid are only partly so (56—76; numbers in parentheses indicate the percentage of the theoretical Hehner value) (*cf.* Fürth and Marian, A., 1926, 428). Compounds of the chitin type are oxidised to the extent of about 66%. The values for phenolic derivatives are much higher than for the corresponding benzene derivatives. Pyrrole and indole are oxidised more readily than quinoline. In these cases oxidation proceeds further with a longer time of heating. With amino-acids generally, a considerable resistance to oxidation is observed; for the aliphatic series the highest value is given by aspartic acid (92.5 after 8 hrs.), whilst for the ring-acids, tyrosine and tryptophan show the highest values (85 and 88.2, respectively, after 2 hrs.). Comparison of the deamination (Kjeldahl) values with the Hehner values shows a close similarity in some cases. Higher Kjeldahl values are given by alanine, glutamic acid, and valine, whilst histidine and proline show higher Hehner values. These differences are ascribed to the relative ease of oxidation of the intermediate nitrogen-free acids. Determinations of the Hehner values of fatty acids show a progressive increase from acetic (<1) to *n*-valeric (67) and then a decrease. Oxalic and malonic acids give almost theoretical values, whilst succinic acid (1.2) is practically unattacked. An analogous series of figures is found for fatty acids using Beckmann's oxidation mixture (*cf.* Kollmann, A., 1928, 660), but the values are lower. During the oxidation of caseinogen more acetic acid is isolated than is derivable from its alanine content; other amino-acids (*e.g.*, leucine) present are, therefore, oxidised partly to acetic acid.

H. BURTON.

## Biochemistry.

**Carbon monoxide content of the blood of steel-mill operatives.** C. J. FARMER and P. J. CRITTENDEN (J. Ind. Hygiene, 1929, 11, 329—335).—The degree of saturation with carbon monoxide of the blood of steel-mill operatives was found to increase during working hours to an average maximum of 6—7%. In the morning after absence from the mill for 16 hrs. the carbon monoxide content of their bloods had not become zero, but averaged 2% saturation.

W. O. KERMACK.

**Crystallographic study of pure carbon monoxide-haemoglobin.** A. K. BOOR (J. Gen. Physiol., 1930, 13, 307—316).—The recorded crystallographic data of the oxy- and carboxy-haemoglobins of various animals are derived from impure specimens of the protein. Oxyhaemoglobin was prepared by the method of Marshall and Welker (A., 1913, ii, 568) and carboxyhaemoglobin by saturation of purified oxyhaemoglobin with pure carbon monoxide. Photomicrographs of the crystals of carboxyhaemoglobin and oxyhaemoglobin of the ox, sheep, pig, dog, rat, horse, and guinea-pig and of the carboxyhaemoglobin of the chicken and turkey are reproduced.

C. C. N. VASS.

**Intermediate compounds in the oxygenation of haemoglobin.** J. B. CONANT and R. V. MCGREW (J. Biol. Chem., 1930, 85, 421—434).—Analyses of mixtures of crystalline oxyhaemoglobin with its saturated solution in a phosphate buffer at  $p_H$  6.6, after varying degrees of deoxygenation by exposure to a vacuum, indicated that the solid phase was always exclusively oxyhaemoglobin, whilst the solution contained nothing but completely reduced and completely oxygenated haemoglobin; the hypothesis of the occurrence of intermediates in the oxygenation of haemoglobin is therefore rejected. C. R. HARRINGTON.

**Decomposition of blood pigment.** K. BINGOLD (Klin. Woch., 1929, 8, 866—873; Chem. Zentr., 1929, ii, 1020).—The decomposition of blood pigment proceeds in two phases; in one it is protected from oxidative decomposition by catalase, and in the other the iron acts as a catalyst in the oxidation. The mechanism of these phases is discussed.

A. A. ELDRIDGE.

**Oxidation-reduction potentials and the possible respiratory significance of the pigment of the nudibranch *Chromodoris zebra*.** P. W. PREISLER (J. Gen. Physiol., 1930, 13, 349—359).—A method for purifying the bluish-purple pigment in the blood and tissues of *Chromodoris zebra*, Heilpin, is given; in acid solution its colour is orange-red, in moderately alkaline buffered solutions bluish-purple. Reversible oxidation-reduction changes occur with both the orange-red and the bluish-purple forms, either being reduced to a yellow form by reducing agents. The pigment is soluble in aqueous alcoholic solutions. The oxidation-reduction potential curve agrees well with the standard electrode equation (cf. Conant, A., 1922, ii, 547) with a valency change from oxidant to reductant of 1.

C. C. N. VASS.

**Mitogenetic radiation from the blood and tissues of invertebrates.** A. POTOZKY, S. SALKIND,

and J. ZOGLINA (Biochem. Z., 1930, 217, 178—184).—Haemolymph of crabs and of molluscs acts as a source of mitogenetic radiation with which some oxidative process is associated. The hepatopancreas of the animals is also a source of the radiation.

W. MCCARTNEY.

**Preservation of ox blood.** K. HERING (Arch. Pharm., 1930, 268, 36—38).—Fresh blood which has been carefully freed from foreign matter and defibrinated may be kept for 12 days if 3% of a caffeine-sodium benzoate mixture is added. J. W. BAKER.

**Fixing action of certain dehydrated chemical reagents.** P. B. SEN (J. Roy. Micros. Soc., 1929, 49, 336—340).—The action of various fixatives on films of dried red blood-corpuscles has been examined. The degree of fixation of the cells after treatment with the reagent being determined by finding to what extent lysis took place when the cells were then treated with distilled water. The reagents tested may be classified into three groups: (1) those, such as acetone and chloroform, which when quite dry cause no fixation, but bring about fixation when they contain small quantities of water; (2) those, such as pyridine or acetone saturated with formaldehyde, which cause imperfect fixation when quite dry, but bring about good fixation when they contain small quantities of water; (3) those, such as ethyl or methyl alcohol, which effect good fixation when perfectly dry and are not materially improved by small quantities of water. It is suggested that the degree of fixation is related to the permeability of the cell membrane to the reagent and confirmatory experiments are described.

W. O. KERMACK.

**Numbers of molecules and ions in a single cell.** A. T. CAMERON (Trans. Roy. Soc. Canada, 1929, [iii], 23, V, 151—154).—The number of molecules or ions of any particular kind in a single red blood-corpuscle is calculated by means of the following formula: number of molecules (or ions) =  $5.9 \times 10^{11} \times W/M$ , where  $M$  is mol. (ionic) wt. and  $W$  the amount present in 100 g. of cells. Nearly 99% of the molecules are water and only hydrogen ion (220,000) is present in amount less than one million. P. G. MARSHALL.

**Erythrocyte membrane as a colloid system and its changes.** O. LEPESCHINSKAJA [with V. P. SMIRNOVA] (Fol. Hæm., 1928, 36, 41—93; Chem. Zentr., 1929, ii, 1016).—The (frog's) erythrocyte membrane behaves as a colloidal protein and probably becomes resolved in the plasma into fibrin. Deformation brought about by acids and alkalis suggests that the poikilocytosis of pernicious anæmia may be caused by changes in the  $p_H$  of the blood.

A. A. ELDRIDGE.

**Distribution of uric acid between plasma and erythrocytes.** A. W. KOSSIAKOVA (Biochem. Z., 1930, 217, 212—215).—In human blood there is always a greater percentage of uric acid in the plasma than in the erythrocytes. When the blood is kept (for 24—48 hrs.) the uric acid content of the plasma does not alter much, but that of the erythrocytes decreases. A stable solution of litmus and methylene-blue is recommended as a standard colour for use in

Benedict's method for the determination of uric acid. W. MCCARTNEY.

**Distribution of quinine between erythrocytes and blood-plasma.** L. BINET and R. FABRE (J. Pharm. Chim., 1930, [viii], 11, 55—58).—Examination of the blood of a 14-kg. dog at varying intervals of time after the injection of 0.8 g. of quinine hydrochloride showed that the erythrocytes contained more quinine than did the plasma and that it is only slowly eliminated from the former. J. H. BIRKINSHAW.

**Origin of plasma-proteins.** I. Action of various tissues on serum-proteins. II. Relation of hyperalbuminæmic and hyperglobulinæmic condition to the action of liver and muscle on serum-proteins. III. Nitrogen and sulphur content of liver and muscle in hyperalbuminæmia and hyperglobulinæmia. T. SENSU (J. Biochem. Japan, 1929, 11, 47—54, 55—63, 65—68).—I. Cell-free extracts from liver, bone-marrow, spleen, kidney, and muscle have no hydrolytic effect on blood-proteins. The extracted tissue pulp generally acts either on the albumin or globulin of the serum. Extracted liver or kidney pulp hydrolyses only serum-albumin, whilst extracted bone-marrow, spleen, or muscle pulp acts only on serum-globulin. Lung pulp has practically no action on the blood-proteins.

II. The proteolytic activity of liver is increased by hyperalbuminæmia, and that of muscle by hyperglobulinæmia.

III. In hyperalbuminæmia the S:N ratio of the liver-proteins decreased, whilst increase of plasma-globulin is accompanied by an increased S:N ratio of the muscle-proteins. CHEMICAL ABSTRACTS.

**Distribution of serum- and plasma-proteins in fish.** S. LEPKOVSKY (J. Biol. Chem., 1930, 85, 667—673).—Figures are given for the nitrogen content and distribution of proteins in the blood-serum and -plasma of various species of fish.

C. R. HARRINGTON.

**Electro-dialysis of serum.** II. Efficacy of blood-protein membranes. III. Efficacy of membranes of other proteins. G. ETTISCH and W. EWIG (Biochem. Z., 1929, 216, 401—429, 430—448).—II. Electro-dialysis of serum using a blood-protein-collodion membrane as anodic and parchment as cathodic membrane (cf. A., 1928, 785) is further investigated. Gradations of electro-dialysis are obtained according to whether whole blood, serum, hæmoglobin, serum-albumin, or -globulin is brought on to the collodion membrane, and in each case the membrane is prepared in two ways, either by the usual method of impregnation or by shaking the membrane with the protein. The course of electro-dialysis is essentially different using the same membrane but preparing it by the two methods, and is usually longer with the impregnated membrane. The course of electro-dialysis is very similar with a membrane impregnated with whole blood to that with hæmoglobin. It is the same also for a whole-serum as for a serum-albumin membrane. A layer of protein appeared on the cathodic membrane when the  $p_H$  of the inner chamber had fallen to 4. An increase of tension (500—1000 volts) often caused an acceleration of electro-dialysis.

B B

III. Further variation of the course of electro-dialysis is obtained by using for the anodic membrane a variety of substances not originating from blood, e.g., egg-albumin, gelatin, gliadin, nucleic acid, etc. The same differences are obtained between membranes obtained by impregnation and by shaking with protein. The course of electro-dialysis using an egg-albumin membrane strongly resembled that with serum-albumin.

P. W. CLUTTERBUCK.

**Refractometric investigation of serum-protein.**

I. Determination of total protein content from the refractive index. II. Robertson's method for the determination of protein. D. VON DESSEÖ (Biochem. Z., 1930, 217, 185—196, 197—211).—I. The changes in the refractive index and in the specific gravity of serum which correspond with regular changes in the total protein content have been determined and hence this content can be deduced either from the refractive index (provided allowance is made for the influence of water and of non-protein constituents) or from the specific gravity (if the effect of non-protein matter is taken into account).

II. When protein is coagulated in or salted out from serum the former carries with it bound water and the optical properties of the supernatant liquid are consequently altered. Robertson (A., 1915, ii, 851) did not take this into account and hence the use of his figures frequently gives incorrect results.

W. MCCARTNEY.

**Determination of protein in blood-serum.** F. GRENDL (Pharm. Weekblad, 1930, 67, 1—20).—The average increase in refractive index for 1% of pure serum-albumin or -globulin from horse, ox, and man, is  $0.00190 \pm 5\%$ . In Robertson's determination, the factor 0.00150 must be employed for human or ox globulin, and 0.00130 for horse globulin; the factor for albumin for the three sera is 0.00205. The values obtained by refractometric methods are approximate only. The viscosity method of Naegeli and Rohrer is also unsatisfactory, since the viscosity does not depend only on the total quantity of proteins and the relative proportions of albumin and globulin. The globulin contents of normal horse or ox serum are respectively 5.8 and 5.3%, the albumin contents 3.1 and 3.4%; for normal human serum the figures are globulin 2—2.5 and albumin 5.5—7.0%, being lower for children.

S. I. LEVY.

**Micro-determination of urea in blood and other body fluids.** V. PIOVANO (Rass. Clin. Terap. Sci. Aff., 1928, 27, 458—466; Chem. Zentr., 1929, ii, 1189).—The method depends on the determination of the carbon dioxide produced by the action of urease.

A. A. ELDRIDGE.

**Micro-Kjeldahl method.** W. J. YOUNG (Austral. J. Exp. Biol., 1929, 6, 315—316).—A rapid method especially convenient for the determination of non-protein-nitrogen in blood is described.

T. R. SESIADRI.

**Influence of poisons which inhibit oxidation on the formation of ammonia in the blood of mammals and birds.** I. ENOCH (Biochem. Z., 1929, 216, 457—461).—In dog's blood the ammonia content does not increase either in presence of oxygen or after poisoning with carbon monoxide or sodium

cyanide during the first 4 hrs., and after 24 hrs. the same small increase was obtained in all cases. In the blood of geese the ammonia content increases slowly in the unpoisoned animal and more quickly in the poisoned, but in both cases comes to the same final value. The increase in goose blood is much greater than with dog's blood. Addition of small amounts of quinine to goose blood also causes a small increase of the ammonia content. P. W. CLUTTERBUCK.

**Physico-chemical state of cholesteryl esters and lecithin in blood-serum and -plasma.** M. MACHEBŒUF (Rev. gén. Colloid., 1929, 7, 351—357, 393—405).—See A., 1929, 1326.

**Determination of cholesterol in small amounts of blood.** D. C. Y. SHEN (Chinese J. Physiol., 1929, 3, 405—408).—Blood (1 c.c.) is dried on a fat-free filter-paper and extracted with hot chloroform for about 1 hr. The cold extract is made up to 10 c.c. with chloroform, acetic anhydride (2 c.c.) and sulphuric acid (0.2 c.c.) are added, and the mixture, after keeping at a temperature below 25° for 8—24 hrs., when a permanent brown colour develops, is compared colorimetrically with a standard solution of cholesterol in chloroform, treated in the same way.

W. O. KERMACK.

**Methylglyoxal as the product of glycolysis by blood-corpuscles.** E. WIDMANN (Biochem. Z., 1929, 216, 479—492).—Co-enzyme is necessary for the conversion of hexose into hexosediphosphate and of methylglyoxal into lactic acid, but is unnecessary for the dismutation of hexosediphosphate to methylglyoxal. When, therefore, magnesium hexosediphosphate is treated with the co-enzyme-free blood-corpuscles of horse, sheep, or rabbit (either as macerate or as acetone-dried preparation) the formation of methylglyoxal is readily detected and amounts to 75% of the sugar utilised. P. W. CLUTTERBUCK.

**Blood-sugar. So-called protein-sugar in blood.** P. RONA and W. FABISCH (Biochem. Z., 1930, 217, 1—33).—Determinations, by the method of Hagedorn and Jensen and by that employing *B. coli*, of the dextrose content of normal human blood give concordant results, showing that in both cases only dextrose is determined. Dextrose is not formed during the hydrolysis of blood-plasma.

W. MCCARTNEY.

**Reducing substances of pigeons' blood.** J. M. GULLAND and R. A. PETERS (Biochem. J., 1930, 24, 91—103).—Although the total reducing value of pigeons' blood by the Hagedorn and Jensen method is approximately 200 mg. per 100 c.c. only 135 mg.  $\pm$  15 mg. of this can be dextrose. The residual reducing values obtained after glycolysis and during insulin convulsions are due to the presence of other reducing substances. Filtrates prepared from the blood by different methods contain different proportions of ergothioneine, uric acid, and glutathione (aliphatic thiol compounds). These substances when determined by a "cold" Hagedorn and Jensen method and referred to dextrose (100) yield the following corresponding values. Uric acid 53, glutathione 17 (hot 45), and ergothioneine 56. Zinc filtrates (Hagedorn and Jensen method) are the most trustworthy for determining reducing substances in avian blood, but

they contain in addition to dextrose, ergothioneine and some other unknown substances reducing the ferricyanide reagent. Approximately 60% of the residual value is not accounted for by ergothioneine. The zinc filtrates do not contain aliphatic  $\cdot S\cdot S\cdot$  and  $\cdot SH$  compounds. There are no significant variations from the normal in birds suffering from vitamin-B deficiency. S. S. ZILVA.

**Simple calculation of sugar content as determined by the method of Hagedorn and Jensen.** S. E. DE JONGH (Biochem. Z., 1929, 216, 400).—The amount of sugar in mg. as determined by the use of the Hagedorn-Jensen technique may be calculated from the formula  $0.358A - B/C$ , where *A* is the mean titration of the blank, *B* the titration of the unknown solution, and *C* the mean titration of 2 c.c. of the potassium iodate solution, all in c.c. of thiosulphate solution. P. W. CLUTTERBUCK.

**Influence of food on blood-sugar regulation.** II. (1) Potato feeding. (2) Influence of calcium chloride solution and Carlsbad water on the sugar tolerance. III. Investigation with Carlsbad water and animals nourished on green food or potatoes. E. GEIGER and H. KROFF (Arch. exp. Path. Pharm., 1930, 147, 272—280, 281—287).—II. Rabbits fed on a potato diet poor in calcium develop a high fasting blood-sugar level with reduced sugar tolerance. A similar effect results from continued administration of calcium chloride solution if an oat diet is employed, but not with a diet of greens. The high sugar tolerance of rabbits fed on oats is not altered by the administration of Carlsbad water.

III. Administration of Carlsbad water to rabbits on potatoes or greens increases the sugar tolerance and lowers the fasting blood-sugar level. Similar results were obtained with Carlsbad water which had been neutralised with acid, as well as with synthetic solutions containing calcium, sodium, potassium, and magnesium in the same proportions as in the natural water. W. O. KERMACK.

**Action of sodium nitrite on blood-sugar.** E. HERZFELD and R. KRUGER (Klin. Woch., 1929, 8, 1174—1175; Chem. Zentr., 1929, ii, 1312).—Injection of sodium nitrite into animals, or normal or diabetic man, leads to a fall, and then a rise, in the blood-sugar. A. A. ELDRIDGE.

**Action of physical factors on the catalase of blood.** A. I. ALEXEEV (Biochem. Z., 1929, 216, 301—312).—In man, the intensity of the action of blood-catalase varies considerably during the day, being much greater in the morning. The changes do not run parallel with periods of digestion etc., but are explained in terms of change of physical (e.g., climatic) factors. The catalase activity of the blood decreases on raising and increases on lowering the temperature and is strongly increased under the action of wind. A parallelism is obtained between the catalase activity and the amount of haemoglobin of the blood. P. W. CLUTTERBUCK.

**Blood of cattle and sheep in Australia.** J. H. NORRIS and W. E. CHAMBERLIN (Austral. J. Exp. Biol., 1929, 6, 285—300).—In order to provide standards of



comparison, determinations have been made of sugar, calcium, urea, non-protein-nitrogen, uric acid, creatinine, inorganic phosphate, and in some cases moisture content. The results for uric acid, which are much higher than the maximum found elsewhere, are similar to the high results obtained in the case of human blood in Australia.

T. R. SESHADRI.

**Determination of diffusible and non-diffusible serum-calcium.** D. M. GREENBERG and L. GUNTHER (J. Biol. Chem., 1930, 85, 491—508).—Of the serum from 12 c.c. of blood, 2 c.c. are used for determination of total calcium, 0.5 c.c. for determination of proteins, and the remainder is subjected to ultrafiltration in a special apparatus, the diffusible calcium being determined in the filtrate. After formation of the clot no further change takes place in the calcium of the serum in contact with the clot within 24 hrs. Changes of  $p_H$  from 7 to 8, brought about by varying the tension of carbon dioxide, had no effect on the partition between diffusible and non-diffusible calcium. The ratio of chloride in the ultrafiltrate to chloride in the serum is the same as that obtained by membrane distribution (cf. Loeb and Nichols, A., 1927, 584). Since the distribution of non-diffusible and diffusible calcium at constant  $p_H$  and protein concentration conforms to the Langmuir adsorption isotherm (J. Amer. Chem. Soc., 1918, 40, 384) the limiting amount of calcium which can be bound by the serum-proteins, whatever the concentration of ionic calcium, is not much greater than that normally present.

C. R. HARRINGTON.

**Distribution of chlorine in blood. Relation to the acid-base equilibrium.** A. LANDAU, G. GLASS, and S. KAMINER (Compt. rend. Soc. Biol., 1929, 101, 594—596; Chem. Zentr., 1929, ii, 1703).—The normal chlorine contents of blood, plasma, and corpuscles, respectively, are: 2.70—3.02, 3.41—3.62, and 1.70—1.95 g. per litre. The relation corpuscle-chlorine/plasma-chlorine normally varies only between 0.47 and 0.55, but is affected by pathological conditions.

A. A. ELDRIDGE.

**Vanadium in the blood of the *Ascidia*.** M. AZÉMA and H. PIED (Compt. rend., 1930, 190, 220—222).—The precipitates from the blood of three species of the *Ascididae* and two *Botryllidae* obtained after treatment with boiling alcohol were examined in the arc spectrum. Vanadium occurred in all species, but only in traces in the second group; in addition silicon, aluminium, sodium, magnesium, and calcium were observed in the precipitates or in the filtrates, whilst titanium and traces of silver were found in the precipitates from both species of the *Botryllidae*. Phosphorus was observed in all the precipitates with the exception of that derived from *Phallusia mamillata*.

C. C. N. VASS.

**Distribution of zinc in the blood of man and the higher animals.** A. I. BURSTEIN (Biochem. Z., 1929, 216, 449—456).—The concentration of zinc in the corpuscles is greater than that in the plasma of the blood of man, ox, sheep, dog, rabbit, and guinea-pig, the ratio of the concentrations varying from 1.88 to 2.68. Tables show the concentration of zinc in mg. per 100 c.c. and also the above ratios.

P. W. CLUTTERBUCK.

**Action of chloroform on mammalian plasma and serum.** P. BORDET (Compt. rend. Soc. Biol., 1929, 100, 751—753; Chem. Zentr., 1929, ii, 1554—1555).—Reactivation to coagulability of inactive rabbit's serum by treatment with chloroform takes place only with sera of high serozyme content. Chloroform in serum both causes (in presence of lime) the formation of thrombin and arrests its decomposition.

A. A. ELDRIDGE.

**Normal antithrombin and its relation to the production of thrombin by cytozyme or chloroform.** P. BORDET (Compt. rend. Soc. Biol., 1929, 100, 753—755; Chem. Zentr., 1929, ii, 1554).—Serum activated by chloroform can be inactivated by addition of aged inactive serum, and it cannot then be activated by chloroform. Antithrombin is decomposed at 65° and is precipitated from solution with chloroform. Thrombin originating from the action of cytozyme on serum is also decomposed by antithrombin.

A. A. ELDRIDGE.

**Antigenic properties of colloidal metals.** L. A. SILBER and W. FRIESE (Zhur. exp. Biol. Med., 1929, 11, 128—135).—Long-continued intravenous injection of colloidal iron or gold into rabbits induces in the serum the ability to react with the colloidal metals at great dilution.

CHEMICAL ABSTRACTS.

**Antigenic properties of arsenic.** V. TSCHERNOKHIVOSTOV and L. KATZ (Zhur. exp. Biol. Med., 1929, 11, 136—141).—Colloidal arsenious sulphide can act as a real antigen.

CHEMICAL ABSTRACTS.

**Hæmolytic action of saponin.** K. HARA (J. Biochem. Japan, 1929, 11, 69—78).—The action is least at  $p_H$  7.0.

CHEMICAL ABSTRACTS.

**Hæmolytic component of phenylhydrazine hydrochloride.** E. V. ALLEN and I. H. PAGE (Arch. exp. Path. Pharm., 1930, 147, 211—218).—Administration of hydrazine sulphate or of semicarbazide to a dog does not cause a reduction in the number of its red blood-cells. Diphenylhydrazine and azobenzene produce marked hæmolysis, whilst nitrobenzene, aniline, and acetanilide exhibit a similar effect. It is concluded that the phenyl group plays the essential rôle in hæmolysis by phenylhydrazine.

W. O. KERMACK.

**Dextrose and normohæmolysins.** I. DJURICIC (Compt. rend. Soc. Biol., 1929, 100, 1224—1225; Chem. Zentr., 1929, ii, 1704).—Dextrose has no influence on hæmolysis by hæmolysin; hence the mechanism is not that in hypertonia and is not accompanied by colloidal changes of the proteins of the surface layer.

A. A. ELDRIDGE.

**Hæmolysis. I. Pancreas-lipase. H. Purification of an amboceptor of hæmolysis. III. Combination of a purified amboceptor with erythrocytes.** H. VON EULER and E. BRUNIS (Arkiv Kemi, Min., Geol., 1929, 10, B, No. 4, 6 pp., No. 8, 6 pp.; A, No. 5, 6 pp.).—A series of researches designed to throw light on the analogy between the action of complement on erythrocytes in the presence of amboceptor, and the action of lipase on substrate in the presence of albumin. 1. The hæmolytic action of lipase prepared from pig's pancreas by the method of Willstätter and Waldschmidt-Leitz

(A., 1923, i, 403) was unchanged by previously heating the enzyme at 70° for 10 min. The hæmolysis was, however, inhibited by the addition of serum from the dog or guinea-pig, whilst the hæmolysis produced by the unheated enzyme was not affected. The factor producing the hæmolysis which is inhibited by serum is therefore thermolabile. Comparable results were obtained using erythrocytes which had been sensitised by digestion with amboceptor for an hour at 37°.

II. Dogs were immunised by the injection of goat's red blood-corpuscles and from the serum a concentrated preparation of amboceptor was obtained by first precipitating the globulin with 30% saturated ammonium sulphate and then increasing the saturation to 46%, when the amboceptor was completely precipitated. The precipitate was dissolved in water, dialysed free from salt, and the amboceptor precipitated with colloidal ferric hydroxide and taken up with 0.3*M*-disodium hydrogen phosphate. The phosphate was precipitated with magnesium acetate and ammonia, and the amboceptor adsorbed from acid solution by clay suspension and again set free by sodium phosphate. A concentration of 25 times the original was obtained.

III. Purified amboceptor was prepared from the immune serum of the dog as above; but finally precipitated repeatedly with one third saturated ammonium sulphate instead of the adsorption by clay, giving a concentration 30—33 times the original. The degree of absorption of this preparation by erythrocytes was identical with that of an immune serum of the same amboceptor concentration. It is calculated that 0.02 sq. m. of erythrocyte-surface combines with 500 amboceptor-units.

K. V. THIMANN.

**Human brain.** M. VERESS (Magyar orvosi Arch., 1929, [ii], 29, 74—83; Chem. Zentr., 1929, ii, 1019).—Iron detected in normal human brain does not originate from hæmoglobin of red blood-corpuscles.

A. A. ELDRIDGE.

**Glutathione content of the stomach.** H. C. CHANG and S. M. LING (Chinese J. Physiol., 1929, 3, 341—352).—At rest the sulphhydryl contents of the mucous membrane from the pylorus and fundus regions of the dog's stomach, determined by Tunnicliffe's method, are not significantly different. No change occurs as the result of activity either after a meal or after injection of histamine.

W. O. KERMAK.

**Preparation of glutathione from yeast and liver.** N. W. PIRIE (Biochem. J., 1930, 24, 51—54; cf. Hopkins, A., 1929, 1491).—The tissue is treated with a mixture of sulphuric acid, alcohol, and ether, and to the filtrate, after being made 0.5*N* with sulphuric acid, cuprous oxide is added. The cuprous compound is then decomposed with hydrogen sulphide and glutathione is crystallised from the concentrated solution.

S. S. ZILVA.

**Glutathione content of denervated skeletal muscle.** M. OKUDA (J. Biochem. Japan, 1929, 11, 183—190).—Diminution in weight of denervated muscle follows an increase in its glutathione content; increased metabolism may be indicated.

CHEMICAL ABSTRACTS.

**Enzyme activity of mummified muscle.** E. SEHRT (Klin. Woch., 1929, 8, 1177—1178; Chem. Zentr., 1929, ii, 1419).—Muscle of a 3000-year-old mummy showed strong precipitin, glycolytic enzyme, and respiratory enzyme reactions.

A. A. ELDRIDGE.

**Creatine and phosphoric acid content of various portions of the heart.** H. VOLLMER (Z. ges. exp. Med., 1929, 65, 522—534; Chem. Zentr., 1929, ii, 1020).—The ventricle of the calf's or lamb's heart often contains twice as much inorganic phosphoric acid as the auricle or aorta; in young animals the quantities are equal or in the ratio 1:0.8. The ratio of the creatine contents is about the same, 75% being combined with phosphoric acid. In man the ratio of creatine values is 1:0.28.

A. A. ELDRIDGE.

**Solubility of glycogen.** M. KERLY (Biochem. J., 1930, 24, 67—76).—Glycogen from mussels prepared without boiling with alkali takes from 3 to 4 days to reach saturation in water. A similar sample boiled for 2½ hrs. with 60% potassium hydroxide gives a slightly higher value within a few hours. The solubility in water of mussel-glycogen not boiled with potassium hydroxide at 0° is 16%, at 20° 17.7%, and at 37° at least 40%; that from skeletal muscle of frogs 14.9% at 20°, and from rabbit liver 21% at 20°. Curves are given showing the decreasing solubility of glycogen with increasing concentration of alcohol in the presence of potassium acetate, potassium trichloroacetate, potassium chloride, potassium hydroxide, and trichloroacetic acid. When glycogen prepared from mussels is precipitated with alcohol after two precipitations the nitrogen content of the preparation increases, the phosphorus content remaining nearly constant. A micro-modification of Pfüger's method of determining glycogen based on its solubility in aqueous alcohol is described.

S. S. ZILVA.

**Fats of Japanese birds.** VIII, IX. R. KOYAMA (J. Soc. Chem. Ind. Japan, 1929, 32, 210—212b).—The properties of the fats obtained from various Japanese birds are described.

A. A. GOLDBERG.

**Fats of Japanese birds.** X. R. KOYAMA (J. Soc. Chem. Ind. Japan, 1929, 32, 255—256b).—The characteristics of the fats of *Merula eumomus*, Temminck, *M. pallida*, Gmelin, *M. chrysolaus*, Temminck, and *M. celænops celænops*, Stejneger, are recorded.

C. C. N. VASS.

**Unsaturated fatty acids of human liver.** I—III. P. MÜLLER (Arch. exp. Path. Pharm., 1930, 147, 219—234, 235—239, 240—244).—I. Samples of crude oil from human livers had iodine values varying from 77.5 to 148.5. The higher the percentage of fat in liver the lower was the average iodine value. Attempts to separate the saturated and unsaturated fatty acids through their lead salts were unsuccessful because of the oxidation of the unsaturated acids during the process. When the methyl esters of the crude fatty acids were distilled at 0.2—0.5 mm. considerable losses occurred in the unsaturated acids and separation was incomplete, but by brominating certain of the fractions oleic acid and arachidonic acid were detected.

II. By a modification of the method a second un-

saturated acid,  $C_{16}H_{26}O_2$ , containing three double linkings was also detected and isolated as the *hexabromide*,  $C_{16}H_{26}O_2Br_6$ , m. p.  $122^\circ$ .

III. The percentage of highly unsaturated fatty acids in the liver-fat was determined by converting them into their bromine additive products and weighing the solid bromo-derivatives. When the percentage of fat in the liver increased the percentage of highly saturated fatty acids decreased, but to such a degree that the percentage of these acids calculated on the original liver is approximately constant.

W. O. KERMACK.

**Skin.** III. Sugar content of the skin under physiological and pathological conditions. E. URBACH and G. SIEHER (Arch. Derm. Syph., 1929, 157, 160—182; Chem. Zentr., 1929, ii, 907).—Values of the sugar content of the skin and blood, respectively, are: man 47, 98; rabbit 117, 109; guinea-pig 119, 117; rat 80, 83; dog 60, 92; mouse 53, 108 mg. per 100 g. (c.c.). After administration of sugar the skin-sugar increases like the blood-sugar and returns to normal values. The skin-sugar is diminished by insulin. The effect of pathological conditions of the skin is described.

A. A. ELDRIDGE.

**Spectrographic analysis of the ash of organs.** P. DUTOIT and C. ZBINDEN (Compt. rend., 1930, 190, 172—173).—Though the range of the spectra studied does not include all the mineral elements, e.g., boron, the same metals have been observed as were found in the blood (A., 1929, 952). Silver accumulates in the uterus, ovaries, and thyroid, in small quantities in the other organs; with traces in the heart, spleen, and kidney. Aluminium is found in all the organs, especially in the lungs, kidney, heart, and suprarenal glands. Cobalt and nickel are found in all organs except the liver, but to a greater concentration in the pancreas. Chromium occurs in traces in all the organs, somewhat more concentrated in the thyroid and spleen. Copper is abundant in the lungs, liver, and heart, and least in the kidney and spleen. Lead is relatively abundant in all organs, especially in the pancreas, liver, and thyroid, and least in the spleen, uterus, and ovaries. Tin occurs in all organs, chiefly in the brain, spleen, and thyroid. Zinc predominates in the genital organs and the thyroid, but is absent from the heart. Titanium accumulates in the lungs; only traces occur in the other organs.

C. C. N. VASS.

**Determination of total chlorides in tissue.** W. R. MANKIN (Med. J. Austral., 1929, 2, 358—366).—The material (0.2—1.0 g.) is digested with 0.01*N*-silver nitrate solution (5—10 c.c.) and concentrated nitric acid (5 c.c.) in a boiling water-bath until the volume is 3 c.c., the cooled solution being diluted and titrated with 0.01*N*-ammonium thiocyanate. Egg-white and -yolk contained, respectively, 1.39—2.02 and 1.23—1.74 mg. of chlorine per g. There is considerable variation, but for the same egg the white usually contains more chlorine than the yolk.

CHEMICAL ABSTRACTS.

**Iodine as a biogenic element.** XIX. Iodine content of the normal animal organism. XX. Influence of oral administration of small amounts of inorganic iodine on the iodine content of the

animal organism. E. MAURER and H. DUCRUE (Biochem. Z., 1930, 217, 227—230, 231—235).—XIX. The iodine content of various organs of female rabbits has been determined. Great variations were found in the proportion of iodine in the thyroid glands and differences were also found in the iodine contents of the two halves of the glands. Of the other parts investigated the ovaries had the highest iodine content. The iodine content of the various parts of the organism does not depend on that of the thyroid gland.

XX. Small doses of potassium iodide were administered to female rabbits and after 24 hrs. the iodine content of various organs was determined. In all parts various increases were found and only in those concerned with iodine excretion was the increase great. After 96 hrs. the iodine content in almost all parts had fallen to the normal level.

W. MCCARTNEY.

**Microscopical examination of wool fibres.** R. BURGESS and C. RIMINGTON (J. Roy. Micros. Soc., 1929, 49, 341—348).—When wool fibres are treated with Pauly's reagent staining takes place only where the epithelial scales of the fibres have sustained damage. The test has been found of great practical value in the technical examination of wool fibres. By the application of the Totani reaction evidence has been obtained that both tyrosine and histidine in the fibre unite with the Pauly reagent to produce the brownish-red colour.

W. O. KERMACK.

**The sulphur linking in wool.** C. RIMINGTON (Biochem. J., 1930, 24, 205—207).—Free -S-S- or -SH groups are not present in undamaged wool and can be induced only by the action of alkalis or of ultra-violet radiation.

S. S. ZILVA.

**Secretion and composition of milk in non-physiological activity of the male mamma.** A. TRAUTMANN and P. LUY (Deut. tierärztl. Woch., 1929, 37, 305—307; Chem. Zentr., 1929, ii, 1176).—The milk of a he-goat had *d* 1.028—1.035, and contained: dry substance 14.9, ash 0.85, fat 4.5%. The effect of hormonal preparations was investigated.

A. A. ELDRIDGE.

**Factors affecting yield and quality of milk.** II. Variations in successive lactations. J. GLEN and A. C. M'CANDLISH (J. Agric. Sci., 1930, 20, 45—52; cf. Kay and M'Candlish, A., 1929, 487).—Milk and butter-fat production of cows rises to a maximum at the fifth lactation period corresponding with 7 years of age, after which yields fluctuate but show a downward tendency. The milk-fat percentage is highest in the first lactation, drops markedly in the second, remains steady with a downward tendency for several lactations, and then decreases.

E. HOLMES.

**Fate of caseinogen in milk retention.** C. PORCHER and E. MUFFET (Compt. rend. Soc. Biol., 1929, 100, 1049; Chem. Zentr., 1929, ii, 1025).—The leucocytary enzymes appear to decompose caseinogen readily, removing phosphorus and leaving a heat-coagulable protein.

A. A. ELDRIDGE.

**Mode of combination of calcium in milk and its significance in clotting by rennin.** M. RÜDIGER and K. WÜRSTER (Biochem. Z., 1929, 216, 367—

399).—The clotting power of rennin is favourably influenced by addition of calcium chloride to milk up to a concentration of 1.42%, but above this is inhibited. By addition of calcium chloride to milk and whey the acid content is increased to a maximum and then remains constant. The shift of  $p_H$  is not sufficient to account for the acceleration of clotting by calcium chloride, which is due chiefly to change in the phosphate relationships. From comparison between an inorganic phosphate system and milk it is shown that calcium and phosphate ions in the normal concentrations of milk cannot exist as stable ions, but are retained in solution colloiddally by caseinogen. The buffering properties of milk are chiefly due to the system calcium phosphate-caseinogen-citric acid.

P. W. CLUTTERBUCK.

**Effect of the pancreas secretion on the alkali reserve of the blood and on the hydrogen-ion concentration of the gland.** E. HAMMARSTEN and E. JORPES (*Acta med. Scand.*, 1928, 68, 10 pp.; *Chem. Zentr.*, 1929, ii, 1022).—After injection of secretin into cats the  $p_H$  of the pancreas was increased, whilst the alkali reserve of the blood remained unchanged.

A. A. ELDRIDGE.

**Rôle of ions and electrolytes in the process of physiological stimulation.** O. V. NICOLAIEV (*Zhur. exp. Biol. Med.*, 1929, 11, 114—126).—By increasing the calcium chloride or sodium hydrogen carbonate content of the perfusing solution, salivary secretion by an isolated salivary gland (dog) is increased; increase of the amount of sodium or potassium chloride, or addition of hydrogen or magnesium chloride, diminishes the salivary flow. Hence ions play an essential rôle in the physiological responsiveness of tissue.

CHEMICAL ABSTRACTS.

**Fractionation of Australian snake venoms. I. Venom of death adder (*Acanthophis antarcticus*).** C. H. KELLAWAY, M. FREEMAN, and F. E. WILLIAMS (*Austral. J. Exp. Biol.*, 1929, 6, 245—260).—Heating the proteose fraction of the venom caused a diminution of activity. Quantitative fractionation of the venom by extraction with 45% ethyl alcohol is unattended by any loss of total activity of the venom. When injected subcutaneously in mice or guinea-pigs the insoluble fraction has but little of the toxicity of the whole venom, whereas it possesses all the coagulant activity. The soluble fraction contains the "neurotoxic" principle, which has a curare-like action. The hæmolytic activity is evenly distributed in both fractions, whereas more of the substance which stimulates plain muscle is present in the soluble fraction. Both fractions are equally toxic by intravenous injection in mice and guinea-pigs.

T. R. SESHADRI.

**Production of bile pigments *in vitro*.** A. VON CZIKE (*Deut. Arch. klin. Med.*, 1929, 164, 236—242; *Chem. Zentr.*, 1929, ii, 1318).—Bilirubin was produced in citrate or hirudin plasma kept at 37° for 24 hrs. Its appearance is not due to liberation of adsorbed bilirubin, but is apparently due to enzyme action.

A. A. ELDRIDGE.

**Detection of bile pigments in urine.** J. GLASS (*Med. Welt*, 1929, 3, 824—825; *Chem. Zentr.*, 1929, ii, 1189).—Sodium nitrite and concentrated hydrochloric acid are employed separately.

A. A. ELDRIDGE.

**Determination of gaseous tension in urine and other liquids containing carbonate.** F. MAINZER and C. T. SHEN (*Pflüger's Archiv*, 1929, 222, 1—11; *Chem. Zentr.*, 1929, ii, 919).—A method for the determination of the gaseous tension of small quantities of urine is described. The oxygen pressure in human urine is 23—101 (average 54) mm., and the carbon dioxide pressure 43—102 (average 81) mm.

A. A. ELDRIDGE.

**Colorimetric detection of acetone in urine.** C. STICH (*Pharm. Zentr.*, 1929, 70, 681).—A modification of the standard nitroprusside test for the detection of acetone in urine is described.

E. A. LUNT.

**Detection of acetone and acetoacetic acid in urine.** P. HORKHEIMER (*Münch. med. Woch.*, 1929, 76, 1128—1129; *Chem. Zentr.*, 1929, ii, 1052).—Lange's nitroprusside reaction indicates the presence of acetoacetic acid in diabetic urine; with 0.007% a violet ring is obtained in 2 min.

A. A. ELDRIDGE.

**Detection of ketonic substances in urine.** J. BAZOWSKI and H. SZANCER (*Pharm. Zentr.*, 1930, 71, 4—5).—The methods of detection are discussed. It is sufficient to employ first Lange's ring test; if this gives a negative result, Lieben's iodoform test should be applied. It is not necessary to distinguish between acetone and acetoacetic acid.

S. I. LEVY.

**Determination of sugar in urine.** K. BODENDORF and A. KOWNATZKI (*Apoth.-Ztg.*, 1929, 44, 636—637; *Chem. Zentr.*, 1929, ii, 920).—The urine is treated with Fehling's solution in excess, and the excess is determined colorimetrically.

A. A. ELDRIDGE.

**Lipin excretion. VII. Partition of faecal lipins in bile fistula dogs.** W. M. SPERRY (*J. Biol. Chem.*, 1930, 85, 455—463).—As in normal dogs, the faecal lipins of dogs with a bile fistula on a fat-free diet are confined almost entirely to the solid fractions of the faeces. The lipins of both bacterial and non-bacterial fractions were of similar composition, and therefore presumably of similar origin; the distribution of total lipins as between bacterial and non-bacterial portions was variable. When fat was administered to such dogs the unabsorbed portion appeared in the non-bacterial solid fraction of the faeces.

C. R. HARRINGTON.

**Viscosity of pathological blood-sera.** E. H. FISHBERG (*J. Biol. Chem.*, 1930, 85, 465—475).—The viscosity of blood-serum varies relatively little with dilution, or with changes in  $p_H$ ; it is increased by saturation with carbon dioxide in presence of the red blood-corpuscles, and is diminished by addition of cholesterol or of carbamide; bile acids cause an increase in viscosity. That these phenomena are due to a special state of the serum-proteins is indicated by the fact that the viscosity of exudates runs parallel to their tendency to form gels. The results afford an explanation of the diminished viscosity of the blood-serum in uræmia and the increased viscosity in cyanosis and in obstructive jaundice.

C. R. HARRINGTON.

**Reciprocal action of chloride and alkali on the body in acute diseases.** C. ACHARD and M. ENACHESCO (*Compt. rend.*, 1930, 190, 91—93).—In

a normal subject administration of chloride (10—15 g.) produces a large chloride excretion and an alkaline urine with excretion of carbonate. In cases of pneumonia a similar administration produces only a slight rise in urinary  $p_H$  and carbonate excretion along with slight hastening of the usual chloride crisis. In angina and acute rheumatism it produces only a slight chloride excretion without alkaline urine. In catarrhal jaundice half the salt is excreted, showing a less stubborn chloride retention, whilst the acid-base equilibrium is temporarily modified and the alkali reserve is scarcely affected. Administration of sodium hydrogen carbonate in cases of pneumonia, angina, or pleurisy is followed by a rapid increase in the alkalinity of the blood and urine without any effect on chloride excretion. In acute disease with chloride retention the body appears to have an affinity for chloride which must be satisfied before excretion can occur.

P. G. MARSHALL.

**Allergens. III. Pollen of *Alopecurus* (fox-tail grass).** L. F. LOEB (Klin. Woch., 1929, 8, 926—927; Chem. Zentr., 1929, ii, 1023).—The substance giving a skin reaction in hay-fever is contained in the precipitate obtained on addition of alcohol to the aqueous extract. Either it is a protein or is combined with protein, or it is active only in presence of a protein.

A. A. ELDRIDGE.

**Influence of inorganic elements on blood regeneration in nutritional anæmia.** V. C. MYERS and H. H. BEARD (J. Amer. Med. Assoc., 1929, 93, 1210—1212).—When iron (0.5 mg. daily) is administered to rats rendered anæmic by an exclusive milk diet, traces (0.01—0.5 g. (?) of manganese, nickel, copper, germanium, and arsenic all promote hæmoglobin regeneration.

CHEMICAL ABSTRACTS.

**Iron and blood regeneration. Effect of ultra-violet rays on blood regeneration and iron metabolism.** S. OSATO and S. TANAKA (Z. ges. exp. Med., 1929, 65, 692—704; Chem. Zentr., 1929, ii, 1022).—Animals with experimental anæmia experienced rapid blood regeneration when irradiated with ultra-violet rays. Reserve iron was mobilised from the liver and (when present) spleen and used in the production of blood pigment. There was a simultaneous retention of iron.

A. A. ELDRIDGE.

**Calcium metabolism in arthritis.** E. F. F. COPP (Arch. Int. Med., 1930, 45, 136—146).—A patient suffering from hypertrophic osteo-arthritis on a normal diet was found to have a positive calcium balance (retention). This was converted into a negative balance by use of a diet low in calcium. Phosphoric acid greatly retarded loss of calcium from the system, much more than hydrochloric acid or sodium salicylate. The latter salt and acids increased, and sodium hydrogen carbonate lowered, the calcium excreted in the urine. A case of atrophic osteo-arthritis showed a negative calcium balance. This was converted into a positive balance by a high-calcium diet. The greatest positive balance was shown during administration of phosphoric acid.

J. H. BIRKINSHAW.

**Inhibition of lactic acid formation in cancer and muscle.** S. T. HARRISON and E. MELLANBY

(Biochem. J., 1930, 24, 141—157).—The aerobic and anaerobic glycolysis of cancer tissue is inhibited by pancreatic extract; amylase-containing extracts from malt diastase, takadiastase, and salivary gland also inhibit glycolysis. Cancer tissue does not form lactic acid from hexosediphosphate or hexosemonophosphate. In the soluble muscle-enzyme system the production of lactic acid from hexosediphosphate but not from hexosemonophosphate is inhibited by pancreatic extract.

S. S. ZILVA.

**Effect of transplanted tumours on basal metabolism.** Y. YOSHIDA (Japan. J. Gastroenterol., 1929, 1, 93—116).—The growth of a fowl sarcoma is accompanied by an increase in blood-lactic acid and a decrease in -sugar and (with fluctuation) -lipoids; the ratio of albumin to globulin decreases, whilst the amino-nitrogen and fibrinogen increase.

CHEMICAL ABSTRACTS.

**Lactic acid production in tumours.** A. I. VIRTANEN (Suomen Kem., 1929, 2, 19—22).—The optimum reaction for lactic acid production by tumour tissue is about  $p_H$  7.0, the activity falling to about 50% of the maximum at  $p_H$  6.0. The reaction optimum in the case of lactic acid-producing bacteria is  $p_H$  6.2, and in blood  $p_H$  7.5—8.0.

W. O. KERMAK.

**Composition of melanotic pigment.** F. SCHAAF (Klin. Woch., 1929, 8, 1066—1068; Chem. Zentr., 1929, ii, 1551).—It is improbable that sulphur is an integral constituent of melanin.

A. A. ELDRIDGE.

**Physico-chemical theory of caries.** D. ENTIN (Z. Stomatol., 1929, 27, 239—274; Chem. Zentr., 1929, ii, 1706).—Caries is regarded as latent avitaminosis-D. The salivary phosphorus, calcium, potassium, reducing substances,  $d, f, p$ , conductivity, and viscosity were determined. Dental enamel and dentin behave as semi-permeable membranes towards solutions of salts and dyes.

A. A. ELDRIDGE.

**Bile-protein in diabetes.** I. GAVRILA and A. MOGA (Compt. rend. Soc. Biol., 1929, 101, 404—406; Chem. Zentr., 1929, ii, 1024).—In diabetes the bile-protein is increased.

A. A. ELDRIDGE.

**Presence of pancreatic enzymes in the bile.** H. L. PORPER (Wien. klin. Woch., 1929, 42, 800—803; Chem. Zentr., 1929, ii, 1168).—In certain pathological conditions the bile, which usually contains no diastatic enzyme, showed high diastatic values.

A. A. ELDRIDGE.

**Behaviour of the animal organism in pancreatic diabetes towards various carbohydrates.**

**II. Sodium hexosediphosphate.** W. ILJIN (Z. ges. exp. Med., 1929, 65, 399—410; Chem. Zentr., 1929, ii, 1025).—In cats after extirpation of the pancreas sodium hexosediphosphate which was injected subcutaneously suffered fission; the carbohydrate was utilised and the phosphoric acid excreted in the urine. Diminution of urinary and blood-sugar resulted.

A. A. ELDRIDGE.

**Blood-amylase in bacterial infections.** M. E. MAGARAM (Zhur. exp. Biol. Med., 1929, 11, 142—146).—Fasting does not affect the blood-amylase of the rabbit. Amylase activity increases immediately prior to parturition. Injection of diphtheria (and

sometimes dysentery) toxin, and diphtheria cultures considerably increases the blood-amylase.

#### CHEMICAL ABSTRACTS.

**Gaseous exchange in fever caused by naphthylamine-yellow or by  $\beta$ -tetrahydronaphthylamine.** J. DUDLEY and V. KOSKOVSKI (Compt. rend. Soc. Biol., 1929, 100, 1234—1236, 1238—1240; Chem. Zentr., 1929, ii, 1710).

**Physiological characteristics of fever. I. Water balance. II. Distribution of chlorides.** M. SUPONITZKA (Zhur. exp. Biol. Med., 1929, 11, 41—53, 54—62).—During the first hours of fever water migrates from the blood to the tissues, the swelling capacity of which is increased. The blood-chlorine at first rises considerably, then migration into the tissues occurs. Chlorine becomes concentrated in the affected organs.

#### CHEMICAL ABSTRACTS.

**Exophthalmic goitre. Protein content of the cerebrospinal fluid.** W. O. THOMPSON and B. ALEXANDER (Arch. Int. Med., 1930, 45, 122—124).—In 15 cases of exophthalmic goitre the concentration of protein in the fluid was within the lower limits of normal. After subtotal thyroidectomy there was a definite increase in protein concentration accompanying a gain in body-weight and a reduction in basal metabolism.

J. H. BIRKINSHAW.

**Hæmochromatosis: copper content of the liver.** E. H. FUNK and H. ST. CLAIR (Arch. Int. Med., 1930, 45, 37—45).—Analysis of the organs of a man, 44 years of age, who died of hæmochromatosis showed that the liver contained 140 mg. of copper per kg., or 331.8 mg. for the entire organ. The spleen contained less than 1 mg. The iron of the liver was at least 6.2 g. per kg. or 14.7 g. for the entire organ.

J. H. BIRKINSHAW.

**Blood-sugar in diseases of the heart.** M. CHASANOV (Klin. Woch., 1929, 8, 934—936; Chem. Zentr., 1929, ii, 903).

**Electrolyte content of blood-serum in heart and vascular diseases.** J. TEFLOW and A. KOSCHEVNIKOVA (Klin. Woch., 1929, 8, 1222—1223; Chem. Zentr., 1929, ii, 1023).—In circulatory diseases the ratio of potassium to sodium in the blood-serum is nearly always normal. In decompensation of cardiac activity the calcium, chlorine, and inorganic phosphorus fall, whilst the potassium content remains unchanged. In sclerosis of the arteries of the heart the potassium: sodium ratio is generally increased.

A. A. ELDRIDGE.

**Sugar metabolism and water economy. I.** H. TATERKA and F. OESTREICHER (Klin. Woch., 1929, 8, 1401—1402; Chem. Zentr., 1929, ii, 1421).—In cardiac oedema there is a low fasting blood-sugar value, postponed but more marked effect of insulin, and slower rise and fall of blood-sugar (with lower maximal values) after administration of dextrose than in normal cases.

A. A. ELDRIDGE.

**Behaviour of cholesteryl ester in the blood-serum in hepatic disease.** H. WENDT (Klin. Woch., 1929, 8, 1215—1218; Chem. Zentr., 1929, ii, 1023).—Human bile contains an enzyme which hydrolyses cholesteryl ester; dog's bile does not contain

the enzyme, and therefore both cholesterol and its ester are present.

A. A. ELDRIDGE.

**Relation between changes in the alkali reserve and relative chlorine and sodium content of the blood in experimental immobilisation of intestine and in histamine shock.** F. D. ALSINA (Compt. rend. Soc. Biol., 1929, 100, 1098—1101; Chem. Zentr., 1929, ii, 1022).—The changes in the alkali reserve are accompanied by a relative increase in blood-sodium and decrease in blood-chlorine.

A. A. ELDRIDGE.

**Nature of the toxic product arising from closure of the intestine.** A. BLANCHETIÈRE and L. BINET (Compt. rend. Soc. Biol., 1929, 101, 14—17; Chem. Zentr., 1929, ii, 1023).—On occlusion of the intestine there is present a single-chain substance of proteose character, probably arising from the decarboxylation of leucine; it is possibly isoamylamine.

A. A. ELDRIDGE.

**Urea content of blood and cerebrospinal fluid.** L. RICHON, M. VIGNEUL, and J. GIRARD (Compt. rend. Soc. Biol., 1929, 100, 747—748; Chem. Zentr., 1929, ii, 1023).—The blood and cerebrospinal fluid of a child with acute nephritis contained per litre, respectively, 3.59 and 1.229 g. of urea.

A. A. ELDRIDGE.

**Metabolism in pneumonia. I. Excretion and determination of organic acid.** I. GREENWALD (J. Biol. Chem., 1930, 85, 447—454).—The method of Van Slyke and Palmer (A., 1920, i, 459; ii, 131) for the determination of organic acids is improved by preliminary treatment of the urine with Lloyd's reagent, which eliminates the necessity for a correction for creatine and creatinine. The modified method gives much lower results than the original one, but added organic acids can be quantitatively recovered. The fact that the excretion of organic acid is increased in pneumonia is confirmed.

C. R. HARRINGTON.

**Spleen. IV. Formation of colourless form of hæmoglobin after splenectomy.** G. B. RAY and L. A. ISAAC (J. Biol. Chem., 1930, 85, 549—558).—In the blood after splenectomy a discrepancy exists between the total pigment as determined by the method of Stadie and the hæmoglobin determined either spectrophotometrically or by oxygen capacity. Since the discrepancy cannot be explained by the presence of any known derivative of hæmoglobin, it is suggested that the blood contains a non-functional colourless form of hæmoglobin designated "leuco-hæmoglobin."

C. R. HARRINGTON.

**Variations in mineral composition of bone in normal and rachitic rats and in rats cured of rickets.** J. ALQUIER, (Mlle.) L. ASSELIN, (Mlle.) M. KOGANE, and (Mlle.) G. S. DE SACY (Compt. rend., 1930, 190, 334—336).—The total ash, calcium, and phosphorus content of bones of 100 rats, 85 of which had been rendered rachitic, has been determined at different periods of growth. In the normal rat, although the phosphorus content remains constant, the total ash and calcium present increase with increase in body-weight, that is, with increasing age. In rachitic rats, if growth has not become active (total body-weight not above 90 g.), the total ash, calcium,



and phosphorus remain normal, but in rats where the body-weight has increased to 100—110 g. the deficiency of calcium and phosphorus becomes marked. Rats which have been cured of rickets by addition of irradiated dried milk, irradiated ergosterol, or cod-liver oil to the diet exhibit a marked increase in mineral matter, the calcium content exceeding the normal value, but if the cure is effected by irradiation of the original diet growth is slow, the calcium content remains normal, but there is a marked deficiency in total ash and phosphorus. J. W. BAKER.

**Experimental scurvy.** V. Calcium and phosphorus metabolism of guinea-pigs fed on a diet free from vitamin-C. T. NAGAYAMA and T. MUNEHISA (J. Biochem. Japan, 1929, 11, 191—201).—The urinary elimination of calcium and phosphorus by scorbutic guinea-pigs, although depending on the amount of food ingested, generally increases at first, and subsequently tends to decrease. As the urinary calcium decreases much fecal calcium is present. Serum-calcium and -phosphorus are normal.

#### CHEMICAL ABSTRACTS.

**Glutathione, cytochrome, and hydrogen-ion concentration in developing hen embryos.** H. YAOI (Japan. J. Exp. Med., 1928, 7, 135—143).—The glutathione content of hen embryos is maximal at the 12—14th day; the cytochrome content is negligible from the 4th to the 11th day, but then increases, approaching the adult level at hatching. The  $p_H$  is at first low, but becomes constant (7.4) at the 14—15th day. CHEMICAL ABSTRACTS.

**Iodine content of pigs, and passage of iodine from the mother to the foetus and new-born pigling.** H. COURTH (Landw. Jahrb., 1929, 69, 565—598; Chem. Abstr., 1929, ii, 1550).—The pig's thyroid gland contains 4—7 mg. of iodine. Iodine was not detected in the ovaries. The small quantity of iodine present in the fetal thyroid gland towards the end of gestation is not attributed to embryonic activity of the gland. The sow delivers the greater part of her iodine reserve particularly in the colostrum. A. A. ELDRIDGE.

**Nomogram deriving basal metabolism from height-weight co-ordinates.** C. BRUEN (J. Biol. Chem., 1930, 85, 607—609).—A simplified chart for the graphic solution of the equation of Du Bois and Du Bois (Arch. Int. Med., 1916, 17, 863) is given. C. R. HARRINGTON.

**Effect of humidity of the air on metabolism. Hypotony in warm and moist atmosphere.** J. LEFÈVRE and A. AUGUET (Compt. rend., 1930, 190, 326—328).—By means of a specially constructed chamber (*ibid.*, 1929, 188, 515), the effect of varying conditions of humidity on metabolic processes has been investigated with sheep at 19—20°. When the humidity does not exceed 80—85% the subject can readily give off its latent heat (up to 26—38 g.-cal.) by evaporation, but when the humidity exceeds 90%, evaporation becomes very small and the latent heat accordingly reduced. This effect is produced, not by a rise in the body temperature, but by a decrease of approximately 20% in the metabolic processes. J. W. BAKER.

**Influence of nutritive condition on the dextrose tolerance test.** V. J. HARDING and F. H. VAN NOSTRAND (Trans. Roy. Soc. Canada, 1929, [iii], 23, V, 293—301).—Du Vigneaud and Karr's results on the effect of a single meal of fat after starvation on the dextrose tolerance of rabbits is not confirmed, the tolerance being increased. This divergence is explained by the fact that emaciated rabbits have a much lower tolerance than well-nourished animals, and it is therefore necessary to use only standardised animals in good condition for such experiments. P. G. MARSHALL.

**Influence of proteins and their normal decomposition products on sugar content of blood.** E. LUNDGAARD (Biochem. Z., 1930, 217, 125—146).—Subcutaneous administration of glycine or of glutamic acid to rabbits causes hyperglycaemia only if the dose reaches 3 g. per kg. Oral administration of 5 g. per kg. does not cause hyperglycaemia. In dogs, oral administration of glycine, alanine, or meat does not affect the blood-sugar level and in men who have consumed large quantities of meat there is no change in the blood-sugar content. Only when excessive doses are given can proteins or amino-acids cause hyperglycaemia when orally administered. W. MCCARTNEY.

**Hyperglycaemia resulting from administration of amino-acids.** E. LUNDGAARD (Biochem. Z., 1930, 217, 147—161).—Determinations of the sugar, ammonia, and amino-acid contents of the blood of rabbits to which glycine, ammonium lactate, or glutamic acid was subcutaneously or orally administered show that the hyperglycaemia produced by amino-acids has no connexion with that produced by ammonia, but is due to the action of the acids as such. Hyperglycaemia due to administration of ammonium salts first appears when the ammonia content of the blood reaches 0.65—0.80 mg. per 100 c.c. In rabbits hyperglycaemia due to amino-acid administration first appears when the amino-nitrogen content of the blood exceeds 50 mg. per 100 c.c. in the case of glycine and in the case of glutamic acid when it exceeds 25 mg. per 100 c.c. Hyperglycaemia due to amino-acids is a toxic phenomenon without general physiological importance. W. MCCARTNEY.

**Metabolism of amino-acids. III. Glycogen formation after oral administration of amino-acids to white rats.** R. H. WILSON and H. B. LEWIS (J. Biol. Chem., 1930, 85, 559—569).—Definite gluconeogenesis was observed in white rats as the result of feeding with caseinogen, gelatin, or glycine, in each case supplemented with butter. Marked gluconeogenesis resulted from the administration of *D*- or *DL*-alanine to fasting rats by stomach tube; less effect was observed with glutamic acid, and little or no effect with glycine and leucine. These differences may be partly due to differences in the rates of absorption and in the specific dynamic effects of the amino-acids concerned. C. R. HARRINGTON.

**Animal calorimetry. XXXIX. Specific dynamic action in the normal and phloridzinised dog.** W. H. CHAMBERS and G. LUSK (J. Biol. Chem., 1930, 85, 611—626).—Glutamic acid has no specific dynamic effect in normal or phloridzinised dogs (cf.

Rapport and Beard, A., 1929, 213). The specific dynamic effect of glycine is dependent on the amount administered and independent of the weight of the animal; moreover, its effect, as also that of meat, is exercised equally in the normal and phloridzinised dog. The oxidation of dextrose can therefore play no part in the development of the effect. The energy required for the transformation of amino-acids into dextrose in diabetes is probably derived from fat, which itself exercises a small specific dynamic effect in normal, but not in phloridzinised dogs.

C. R. HARRINGTON.

**Muscle contraction without production of lactic acid.** E. LUNDSGAARD (Biochem. Z., 1930, 217, 162—177).—In rabbits and frogs poisoned with sodium iodoacetate the post-mortal production of lactic acid in striped muscle is totally inhibited and this inhibition may take place without damage to the contractive power of the muscle. When muscles in this condition are caused to contract the phosphagen present is rapidly and totally converted into hexosephosphate. It is concluded that phosphagen may be the energy-producing substance in muscle contraction and that the production of lactic acid causes progressive re-synthesis of the decomposed phosphagen.

W. MCCARTNEY.

**Formation of lactic acid in desiccated amphibian muscles.** E. C. SMITH and T. MORAN (Proc. Roy. Soc., 1930, B, 106, 122—131).—The effects produced by drying and by freezing the sartorius muscles of the frog are the same. The amount of lactic acid formation reaches a maximum somewhat below  $-2^{\circ}$ , or when 79% of the water is removed, and coincides approximately with the point of instantaneous death. It is improbable that any separation of sodium hydrogen carbonate or sodium phosphate occurs at this temperature and concentration, and the changes cannot therefore be connected with salt-precipitation.

K. V. THIMANN.

**Carbohydrate metabolism. I. A dextrose-lactic acid cycle involving muscle and liver.** H. E. HIMWICH, Y. D. KOSKOFF, and L. H. NAHUM (J. Biol. Chem., 1930, 85, 571—584).—In anaesthetised or decerebrate dogs the lactic acid content of the blood of the femoral vein was distinctly greater than that of the femoral arterial blood during exercise of the lower limbs; at the same time the hepatic arterial blood contained much more lactic acid than the hepatic venous blood. During exercise of the upper extremities an absorption of lactic acid occurred in the leg muscles, causing a reversal of its distribution as between the femoral arterial and venous blood. Evisceration caused a gradual increase in the lactic acid content of the arterial blood. The distribution of dextrose between the arterial and venous blood of the limbs and liver was in the reverse direction from that of the lactic acid. It appears therefore that a cycle exists in which lactic acid formed by the muscles is converted into carbohydrate by the liver and again distributed by this organ to the muscles in the form of dextrose.

C. R. HARRINGTON.

**Duration of life of particular parts of frog's heart in liquids of various ionic compositions.** N. A. POPOW and A. A. KUDRJAWZEW (Arch. exp.

Path. Pharm., 1930, 147, 331—338).—The life of separate parts of a frog's heart beating in salt solution is reduced by the removal of calcium. In normal Ringer solution, the bulbus usually continues to beat for the longest time, whilst in calcium-free Ringer solution the venous sinus usually survives longest.

W. O. KERMACK.

**Relation between carbohydrate and fat metabolism. I.** S. G. GENES and Z. DINERSTEIN (Zhur. exp. Biol. Med., 1929, 11, 5—11).—In dogs on a diet loaded with sugar or neutral fat a definite relationship between the intermediate metabolic products of fat and carbohydrate exists, and is well marked in the peripheral blood. Loading with fat or sugar respectively causes an increase or a decrease in ketonic substances and a decrease or an increase in lactic acid.

CHEMICAL ABSTRACTS.

**Nature and biological availability of almond carbohydrates.** A. F. MORGAN, C. M. STRAUCH, and F. BLUME (J. Biol. Chem., 1930, 85, 385—404).—Almonds of different crops varied in composition particularly in respect of their carbohydrate content. Defatted almond meal contained about 30% of carbohydrates, 47.8% of which is characterised as "available" (i.e., hydrolysable by acid); this fraction was composed for the most part of sucrose, pentoses, and pentosans, together with small amounts of starch and other polysaccharides, and reducing sugars. Rats fed on a diet composed of 70% of almond meal and 30% of almond oil excreted two to three times the weight of faeces excreted by normal animals; the almond diet had a pronounced laxative effect. When rats were fasted for 24 hrs. and fed with the almond diet for 24 hrs. their total glycogen content and blood-sugar were lower than those of rats after a 24 hrs. fast followed by 24 hrs. on a normal diet. The latter result indicates the possible dietetic use of the almond meal in diabetes and other diseases.

C. R. HARRINGTON.

**Relative nutritive values of carbohydrate and related substances.** H. ARIYAMA and K. TAKAHASHI (Biochem. Z., 1929, 216, 269—277).—The determination of the relative nutritive values of 28 different carbohydrates and related substances (e.g., pentoses, hexoses, di- and poly-saccharides, dextrin, dihydroxyacetone, glycerol, mannitol, glyceric, gluconic, and mucic acids was investigated, the substances being fed to white rats along with a basic diet of flesh powder, butter, and salts, and the resulting increases in weight being regarded as a measure of the relative nutritive values. The assimilation limits for these substances per 100 g. body-weight are tabulated and compared with those obtained by Mendel and Jones (J. Biol. Chem., 1920, 43, 491).

P. W. CLUTTERBUCK.

**Comparison of the nutritive properties of soya-bean "milk" and cow's milk.** E. TSO (Chinese J. Physiol., 1929, 3, 353—362).—Feeding experiments on albino rats show that soya-bean "milk" has a vitamin-A content approximately equal to that of cow's milk and that it is richer in vitamin-B. The deficiency of soya-bean "milk" in minerals can readily be supplied by the addition of suitable salts, whilst the protein is adequate if sufficient quantities are given. W. O. KERMACK.

**Nitrogen metabolism in sheep on high-protein diets.** J. STEWART (J. Agric. Sci., 1930, 20, 1—17).—Bi-weekly nitrogen balances, determined for five sheep fed with high-protein diets (containing linseed cake), showed in three cases nitrogen equilibrium during the first part of the tests and a negative balance towards the end of the 3- or 4-month period. This suggests some important but undetermined factor in the metabolism of excessive protein diet.

E. HOLMES.

**Influence of age of animal on nucleic acid and coagulable nitrogen content of tissues of sheep.** T. B. ROBERTSON and M. C. DAWBARN (Austral. J. Exp. Biol., 1929, 6, 261—275).—Improvements in the original method of determining nucleic acid and coagulable nitrogen in tissues of animals are described (cf. A., 1929, 715). In every organ the nucleocytoplasmic ratio falls considerably with age and the fall is not the same in different organs. The total amount of nucleic acid in the adult cerebrum is 50% less than in that of the new born; the total amount in the skin is also diminished with growth, whereas in the other organs it is greater in the adult. The curve relating the percentage increases of total nucleic acid and protein content with growth is sigmoid and indicates that the synthesis of nucleic acid is catalysed relatively to that of the protein. The anomalous nature of skeletal muscle is attributed to the presence of an extranuclear nucleic acid (inosic acid).

T. R. SESHADRI.

**Influence of cereals on retention of calcium and phosphorus in children and adults.** H. B. BURTON (J. Biol. Chem., 1930, 85, 405—419).—The calcium and phosphorus retention of children and adults on diets of which wheat or oats formed the cereal constituent was determined. Better retention was obtained with the wheat than with the oats; in the second case a larger amount of mineral matter was lost with the relatively bulky faeces. A minor difference observed was the lower retention of calcium and phosphorus by girls than by boys under similar conditions.

C. R. HARRINGTON.

**Influence of a low- and high-calcium diet on development and chemical composition of the skeleton in swine.** R. E. EVANS (J. Agric. Sci., 1930, 20, 117—125; cf. this vol., 107).—Skeletons of young pigs fed on a ration composed mainly of cereal grain with the addition of cod-liver oil showed distinct lack of calcification, the percentage of ash being 12% lower than in bones of normal animals. Calcification of bones proceeds up to maturity, but a difference of 360 g. of tricalcium phosphate was found between the mature bones of normal and calcium-deficient sows. The ratio of lime to phosphate is almost the same in the different bones of the same individual, as well as in the normal and rachitic bones of swine. The main characteristic of the bones in low-calcium rickets is a low ash content, but the composition of the ash is normal.

E. HOLMES.

**Stimulation of the respiratory centre by salts of lower fatty acids.** TIEMANN (Arch. exp. Path. Pharm., 1930, 148, 102—110).—Intravenous injection of the sodium salts of *n*-butyric,  $\beta$ -hydroxybutyric, or valeric acid stimulates the breathing of dogs,

whether in light narcosis or under morphine or chloral hydrate. The effect is therefore not dependent on the acidity of the injected substance. Salts of propionic, isobutyric, and acetoacetic acid are without effect.

K. V. THIMANN.

**Behaviour of glucose ureide in the animal body with special reference to blood-sugar.** K. WATANABE (J. Biochem. Japan, 1929, 11, 79—102).—Intraperitoneal injection of glucose ureide into rabbits causes the greater increase of bound blood-sugar, whilst that of dextrose and urea together influences chiefly the free sugar. Injection of the mixture increases the blood-urea to a greater extent than does that of the compound. In fasting or hypoglycaemic (insulin) animals injection of glucose ureide raises to normal values the bound, but not the free, blood-sugar.

CHEMICAL ABSTRACTS.

**Toxic action of methyl alcohol.** G. MARINESCO, S. Z. DRAGANESCO, and D. GRIGORESCO (Semana Méd., 1929, 36, 745—748).—The action is described and compared with that of ethyl alcohol. After fatal acute intoxication the following quantities of ethyl and methyl alcohol, respectively, were found: brain, 0.84, 1.25; 0.405, 0.47; 0.524; heart, 0.84, 0.924, 1.136; 0.39, 0.413; liver, 0.195, 0.24, 0.44; 0.24, 0.33, 0.36, 0.53; eye-ball, 0.18, 0.276, 0.242; 0.42, 0.64, 0.90; testicle, —; 0.868%.

CHEMICAL ABSTRACTS.

**Presence of thiocyanates in the human organism. Post-mortem transformation of veronal, dial, and gardenal into cyanogen compounds. Significance in toxicology.** E. KOHN-ABREST, (MLLE.) H. VILLARD, and L. CAPUS (Compt. rend., 1930, 190, 281—284).—The unexpected presence of thiocyanates in the viscera in certain cases in which there was no reason to suspect cyanide poisoning is ascribed to the administration of hypnotics of the barbituric series; the partial conversion of these into thiocyanates under the influence of putrefaction is experimentally demonstrated.

R. CHILD.

**Effect of acetylcholine on the blood-sugar.** M. LABBÉ, F. NEPVEUX, and L. JUSTIN-BESANÇON (Compt. rend. Soc. Biol., 1929, 100, 795—796; Chem. Zentr., 1929, ii, 1023).—Subcutaneous administration of acetylcholine causes a fall in blood-sugar.

A. A. ELDRIDGE.

**Effect of acetylcholine on the pancreatic secretion.** M. VILLARET, L. JUSTIN-BESANÇON, and R. EVEN (Compt. rend. Soc. Biol., 1929, 101, 7—8; Chem. Zentr., 1929, ii, 1023).—The pancreatic secretion following the administration of acetylcholine contains lipase, amylase, and trypsin.

A. A. ELDRIDGE.

**Effect of synthalin on gaseous exchange.** F. KLEIN and R. WEISS (Endokrinol., 1928, 1, 321—322; Chem. Zentr., 1929, ii, 1174).—Small doses of synthalin do not affect the respiratory quotient of rabbits. Larger doses reduce the oxygen requirement and the quotient rises.

A. A. ELDRIDGE.

**Arrest of the internal secretion of the pancreas during decamethylenediguanidine hypoglycaemia.** E. ZUNZ and J. LA BARRE (Compt. rend. Soc. Biol., 1929, 101, 141—143; Chem. Zentr., 1929,

i, 1022).—Synthalin hypoglycæmia is accompanied by a diminution of the secretion of insulin.

A. A. ELDRIDGE.

[Pharmacology of] *Allium sativum*. F. A. LEHMANN (Arch. exp. Path. Pharm., 1930, 147, 245—264).—Certain of the pharmacological actions of the pressed juice from the tubers of *A. sativum*, e.g., toxic action on *Paramecium caudatum* and formation of methæmoglobin, are dependent on the presence of a sulphur-containing oil which can be separated by extraction with ether or by steam-distillation. The fractions of the oil of high b. p. are especially active. The activity of the oil decreases when mixed with blood *in vitro*.

W. O. KERMACK.

Effect of yohimbine on blood-sugar. S. HANSON (Compt. rend. Soc. Biol., 1929, 101, 601—603, 603—605, 605—607; Chem. Zentr., 1929, ii, 1704).—Yohimbine causes a slight rise in blood-sugar; in small doses it suppresses adrenaline hyperglycæmia, although with larger doses the rise is observed. The increase by yohimbine of the hypoglycæmic action of insulin is discussed.

A. A. ELDRIDGE.

Effect of ergotamine on the threshold of sugar excretion. G. EDA (J. Biochem. Japan, 1929, 11, 13—29).—Ergotamine (0.3—0.5 mg.) does not affect, or only slightly lowers, the dextrose threshold in mild diabetes. Protein with fat exclusively diminishes the assimilative capacity and raises the threshold value in dogs, when ergotamine lowers the threshold. Ergotamine represses alimentary hyperglycæmia without affecting the threshold of excretion.

CHEMICAL ABSTRACTS.

Pilocarpine hyperglycæmia. I. A. ORRÙ (Boll. Soc. Ital. Biol. sper., 1928, 3, 135—137; Chem. Zentr., 1929, ii, 1422).—The hyperglycæmia caused by subcutaneous injection of pilocarpine (5—25 mg. per kg.) into rabbits is, up to a certain limit, proportional to the dose and to the duration of action, and is followed by hyperglycæmia.

A. A. ELDRIDGE.

Effect of atropine on respiratory metabolism. F. KERTI (Klin. Woch., 1929, 8, 1408; Chem. Zentr., 1929, ii, 1424).—Of 20 cases of disturbance of the endocrine system, 14 showed an increased fasting oxygen requirement after subcutaneous injection of atropine; in 4 cases the value was diminished, and in 2 cases unaltered.

A. A. ELDRIDGE.

Physiological rôle of the tertiary amino-group in the pyrrolidine-piperidine nucleus. Importance of isomerism. R. HAZARD and M. POLONOVSKI (Compt. rend., 1930, 190, 214—216).—Compared with their corresponding tertiary bases, the *N*-oxides of tropine and  $\psi$ -tropine produce a reduced cardiovascular effect. Whilst nortropine behaves as a weakened tropine, nor- $\psi$ -tropine exerts an effect equally as strong as that of  $\psi$ -tropine and appears to possess a true cardiovascular reaction.

C. C. N. VASS.

Pharmacological testing of brucine derivatives. W. THOMS (Arch. Pharm., 1930, 268, 57—58).—Comparative physiological tests have been made with brucine and its various quaternary derivatives (see this vol., 229). With white mice brucine has a quicker and more violent action than the

derivatives, whilst with frogs, symptoms of tetanus and paralysis occur more quickly with the derivatives, but the effect of brucine is of longer duration.

J. W. BAKER.

Action of caffeine on the protein fraction of blood. J. SZELÓCZKY and I. SÁRKÁNY (Biochem. Z., 1930, 217, 218—226).—Caffeine-sodium benzoate alone or with water was intramuscularly administered to rabbits and after various intervals the protein fraction of their blood was examined. It was found that while the effect of the drug lasted the albumin-globulin quotient of the fraction first decreased and then increased and that in the case of caffeine alone the first phase was shorter than the second, whilst in that of caffeine and water this phase was the longer.

W. MCCARTNEY.

Determination of salvarsan, its fate in blood, and passage into cerebrospinal fluid. T. HIRAMATSU (Sei-i-kwai Med. J., 1929, 48, 133—154).—The blackening of osmic acid by arsenic is proportional to the amount present. To 0.1 c.c. of blood are added 0.1 c.c. of distilled water and 3 drops of 20% thio-salicylic acid solution; the mixture is filtered and 3 drops of 1% osmic acid solution are added to the filtrate, the colour being compared with those of standards. The sensitivity is 0.0025 mg. Osmic acid may be added directly to serum or cerebrospinal fluid, the sensitivity being 0.001 mg. After large doses, salvarsan remained in the blood of rabbits for more than 24 hrs.; when more than 0.06 g. per kg. was used, cerebrospinal fluid gave a slight reaction after 5 hrs.

CHEMICAL ABSTRACTS.

Toxicity of arsenobenzene compounds. S. KIEBASINSKI (Przemysł Chem., 1929, 13, 553—557).—1% "Neosalutan" is quantitatively precipitated from solution by sulphuric acid at 50—60°, leaving in solution toxic oxidation products, which reduce iodine. A "toxicity number" is proposed, being the number of c.c. of *N*-iodine solution necessary to oxidise the toxic soluble constituents of 1 g. of the preparation in question; the toxicity number usually found is 0.06—0.10, but one of 0.20, representing 0.8% of toxic arsenic, has no noticeable toxic action on animals, whilst at a value of 0.30 half the animals injected die. The same method can be applied without modification to "neosalvarsan," whilst derivatives of salts of aminohydroxyarsenobenzene with formaldehyde-sulphuric acid possess normally a higher toxicity number.

R. TRUSZKOWSKI.

Metabolism during lead poisoning. A. CARNI (Trud. Mat. Ukrain. gosud. Inst. pat., 1928, 6, 227—234).—In chronic poisoning of dogs and cats by oral administration of lead-protein the nitrogen elimination was greater than the nitrogen absorption, but the nitrogen metabolism was qualitatively unchanged. Azotæmia gradually develops. After 1 month the alkali reserve decreased; the blood-inorganic phosphorus increased, and the acid-soluble decreased.

CHEMICAL ABSTRACTS.

Distribution of colloidal lead in the tissues after intravenous injection. W. J. DILLING and E. F. HAWORTH (J. Path. Bact., 1929, 32, 753—763).—The lead is concentrated first in the large

phagocytic cells of the spleen and occasionally in the endothelial cells; much is collected in the Kupfer cells of the liver. Some is found in the alveolar wall cell of the lungs and the leucocyte-like cells of the inter-alveolar spaces. There is much lead in the kidneys. Excretion in the urine, bile, and alimentary tract is variable.

CHEMICAL ABSTRACTS.

**Determination of small quantities of lead with special reference to urine and biological materials.** A. G. FRANCIS, C. O. HARVEY, and J. L. BUCHAN (*Analyst*, 1929, **54**, 725—735).—To an aliquot portion of the urine (100 c.c.) nitrosyl-sulphuric acid is gradually added with amyl alcohol to prevent frothing. After boiling to one third the volume, concentrated nitric acid is added and final traces of organic matter are removed by boiling. The solution is diluted, the silica filtered off, volatilised, and the residual liquid added to the original solution. Citric acid, a copper solution (2 mg. of copper per c.c.), and a few drops of "masked" methyl-orange solution are added, and concentrated ammonia is run in until the colour changes from grey to green, after which hydrogen sulphide is passed for 1 hr. The sulphides are collected and the filter-paper is destroyed by wet combustion, when the lead and copper are present as sulphates. Lead peroxide is then deposited on a platinum anode and separated as sulphate, which is washed with alcohol and concentrated sulphuric acid and dissolved in ammonium acetate. A suitable proportion of this solution is transferred to a Nessler cylinder and to it and to a control solution are added potassium cyanide solution, ammonia, water, and 2 drops of sodium sulphide solution. A solution containing 0.01 mg. of lead per c.c. is run into the control solution until a match is obtained, the exact match being made with a fresh control, to which 1 c.c. less of the lead solution is added, and the sulphide added last. With biological materials the nitrosylsulphuric acid is omitted. Large quantities of iron salts in the electrolyte must be avoided. Lead ranging from 0 to 0.133 mg. per litre was found in 55 samples of normal urines.

D. G. HEWER.

**Absorption by animals of mercury from contaminated air.** A. STOCK and W. ZIMMERMANN (*Biochem. Z.*, 1929, **216**, 243—248).—The amounts of mercury absorbed by guinea-pigs which were caused to breathe the air charged with small amounts of mercury are determined. The amounts of mercury retained after breathing the air for one day in one case amounted to 53  $\gamma$ , but did not increase with further exposure. The amount of mercury stored in the body decreased very slowly when the animal was placed in mercury-free air, after 3—4 weeks one half and after 5 weeks one quarter of the mercury remaining. The mercury accumulated in the liver and particularly in the lungs. The amount of mercury retained by the stomach, intestine, muscle, blood, and bones was strikingly low and was quickly and completely lost when the animal was placed in mercury-free air.

P. W. CLUTTERBUCK.

**Fatty degeneration of the liver in phosphorus poisoning.** E. MISLOWITZ and E. L. LOEWY (*Biochem. Z.*, 1929, **216**, 362—366).—The increase of ether-soluble phosphorus of the liver in phosphorus

poisoning is due to an increased infiltration of this material (cf. Gubser, A., 1928, 1156; Loewy, A., 1927, 792; 1928, 325).

P. W. CLUTTERBUCK.

**Influence of irradiation on the iodine and bromine fractions of the animal body, especially after administration of iodine.** L. PINCUSSEN and W. ROMAN (*Biochem. Z.*, 1929, **216**, 336—361).—An electrodialyser is described and used to separate thyroxine and salts. Bromine is a normal physiological constituent of the white mouse. The mean iodine, bromine, and chlorine contents of the white mouse are 3.42, 10.11, and 514.9 mg. per 100 g. of dry material, respectively. The water content of the animal is 67.3%. The ratio of organic to inorganic iodine is 1.85, of non-dialysable to dialysable bromine 0.624, and of chlorine 0.297. When 8.5 mg. of iodine as sodium iodide is injected into the mouse, the bromine content is decreased and the chlorine content remains unchanged. By injection of inorganic iodine, the organic iodine is at first increased. Irradiation by the mercury lamp decreases the ratio of organic to inorganic iodine in both normal and injected animals, increases the organic bromine at the expense of the inorganic, and has no effect on the distribution of chlorine.

P. W. CLUTTERBUCK.

**Kinetics of enzyme reactions: Schütz's law.** E. A. MOELWYN-HUGHES, J. PACE, and W. C. M. LEWIS (*J. Gen. Physiol.*, 1930, **13**, 323—334).—Theoretical deductions of Schütz's law on the basis of the law of mass action (cf. Northrop, A., 1924, i, 1267) and on the basis of Langmuir's adsorption theory (cf. A., 1917, ii, 19) are given. Attention is directed to the possible error which may arise if Schütz's constant is used to calculate the critical increment. The true critical increment for an enzymic reaction is equal to twice the critical increment calculated from Schütz's constant if the heat of decomposition of the hydrolysis products—enzyme complex is neglected. The true critical increment of the tryptic hydrolysis of caseinogen at 30° and 40° at  $p_H$  8.9 is 14,400 g.-cal.

C. C. N. VASS.

**Structure and enzyme reactions. VIII. Physical state of the sorbent.** S. J. PRZYŁECKI and M. GURFINKEL (*Biochem. J.*, 1930, **24**, 179—189).—In the system oil—starch—amylase, starch undergoes adsorption at the water—oil interface to an extent of 26.3% from 1% and 34.2% from 0.5% solutions in the presence of 5 g. of oil. The presence of 1.4% of propyl alcohol or of 0.71% of butyl alcohol reduces adsorption to about one half. About 68% of the adsorbed starch is deposited as a precipitate from emulsions of oil in starch solution on the resolution of the emulsion. The adsorption of amylase on oil is very small, not exceeding 5%. The precipitated starch at the surface does not react with amylase. In the ovalbumin—starch—amylase system starch undergoes adsorption to about 63% on the protein membranes present in the foam formed when ovalbumin solutions are shaken. The addition of alcohol leads to elution of starch. A portion of the adsorbed starch is deposited as a precipitate on the resolution of the foam. Amylase is adsorbed to the extent of about 30%. If the protein is absent the velocity of hydrolysis is only 3.5% more if the system is shaken;

without shaking retardation amounts to 12.7%, whilst when amylase is added 24 hrs. after shaking it amounts to 52%. The degree of inhibition due to ovalbumin is proportional to the extent to which it is coagulated. In the system caseinogen-glycogen-amylase, when the caseinogen is coagulated in the presence of glycogen the latter is occluded within the precipitate and is thereby protected from the action of amylase in the medium, only 24% of the adsorbed glycogen being hydrolysed. The occluded glycogen is not eluted by alcohols. In the system gelatin-starch-amylase the inhibitive effect on the hydrolysis of starch due to the presence of gelatin increases with concentration of the latter and is greater at 25° than at 37°.

S. S. ZILVA.

**Combined effect of salivary, pancreatic, and malt amylases on starch.** P. RONA and J. HEFTER (Biochem. Z., 1930, 217, 113—124).—Starch could not be converted into dextrose by the combined action of any two of the three amylases: salivary, pancreatic, malt, and hence the results of Pringsheim and Leibowitz (A., 1926, 715) have not been confirmed.

W. MCCARTNEY.

**$\beta$ -Glucosidase. I. Fission of amygdalin.** R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1929, 79, 591—602).—Amygdalin is now known to be a  $\beta$ -*D*-mandelonitrile glucoside in which the sugar complex is gentiobiose, and the three enzymes formerly supposed to be necessary for its complete hydrolysis, viz., amygdalase, prunase, and oxynitrilase, may be reduced to two, for  $\beta$ -glucosidase can split off both dextrose residues in turn, yielding first prunasin and finally mandelonitrile. This conclusion is based on a study of the relative rates of liberation of dextrose and hydrogen cyanide in the action of emulsin and autolysed yeast juice on amygdalin. J. H. LANE.

**$\beta$ -Glucosidase. II. Hydrolysis of cellobiose.** R. WEIDENHAGEN.—See this vol., 301.

**Application of the mass action law to the enzymic decomposition of sucrose.** R. WEIDENHAGEN and E. LANDT.—See this vol., 301.

**Lactic acid formation in muscle extracts. V. Comparison between soluble starch and glycogen in respect of lactic acid formation and phosphoric ester accumulation. VI. Influence of irradiation on lactic acid formation and phosphoric ester accumulation from glycogen.** D. STIVEN (Biochem. J., 1930, 24, 169—171, 172—178).—V. During the first 40—50 min. of incubation the rate of lactic acid formation and the rate of phosphoric ester accumulation in the presence of extracts from the perfused skeletal muscle are greater with glycogen than with soluble starch. At the end of 2 hrs., however, the lactic acid formation from soluble starch is practically the same as that from glycogen.

VI. In twelve of thirteen experiments it has been possible to increase the rate of lactic acid formation from glycogen if the muscle extract be irradiated before incubation. In one case the rate of lactic acid formation in the irradiated sample was three times that in the control. Irradiation leads also to alteration of the phosphoric ester accumulation. The shorter irradiations resulted in an increase of the

extent of the ester accumulation, the longer irradiations produced a decrease. The highest rates of lactic acid formation coincide with a decrease of the ester accumulation. In only one case was the lactic acid formation decreased after long irradiation and in this case the ester accumulation was almost completely inhibited.

S. S. ZILVA.

**Enzymic hydrolysis of diphosphoglyceric acid.** H. KOBAYASHI (J. Biochem. Japan, 1929, 11, 173—181).—With taka-phosphatase, but not with kidney phosphatase, the optimal  $p_H$  differs for  $\alpha$ - and  $\beta$ -glycerophosphate. Kidney phosphatase hydrolyses  $\alpha\beta$ -diphosphoglyceric acid to the extent of 70% at  $p_H$  8.0 in 24 hrs. at 37°. With taka-phosphatase this ester is hydrolysed optimally at  $p_H$  5.6, as are  $\alpha$ - and  $\beta$ -glycerophosphates, but with the purified enzyme the hydrolysis takes place equally well at  $p_H$  2.9 or 5.5, with minimal activity at  $p_H$  4.0. The second peak in the curve at about  $p_H$  3.0 is attributed to the hydrolysis of the  $\beta$ -glycerophosphate, so that the specific hydrolysis is different for the  $\alpha$ - and  $\beta$ -esters.

CHEMICAL ABSTRACTS.

**Enzymic hydrolysis of different phosphoric esters.** K. ASAKAWA (J. Biochem. Japan, 1929, 11, 143—172).—The optimal  $p_H$  differs for taka-phosphatase and kidney-phosphatase and for the different esters.

CHEMICAL ABSTRACTS.

**Malt pectinase.** J. J. WILLAMAN (Arkiv Kemi, Min., Geol., 1929, 10, A, No. 3, 4 pp.).—Pectinase preparations from two different samples of malt were identical in activity, as measured by their rate of hydrolysis of commercial citrus pectin. After heating at 100° for 10 min. the enzyme still possesses some activity. By precipitation first with 50% and then with 87% alcohol, a more active material is obtained.

K. V. THIMANN.

**Mechanism of oxidative processes. XXII. Mode of action of oxidases and peroxidases.** H. WIELAND and H. SUTTER (Ber., 1930, 63, [B], 66—75; cf. A., 1928, 921).—The oxidase action is determined by volumetric measurement of the oxygen absorbed during the dehydrogenation of quinol or pyrocatechol. The absolute activity of the potato-enzyme varies within very wide limits according to the variety. The activity of the enzyme in the skin is about four times as great as in the skin-free tuber. In spite of a large excess of quinol and oxygen the rate of absorption of the gas diminishes with the time. This effect is not due to the benzoquinone produced, but is attributable to the direct action of oxygen on the enzyme. Hydrocyanic acid has a restricting influence. The sensitiveness of the phenol-oxidase of apple towards oxygen is greater than that of the potato-enzyme, whereas hydrocyanic acid has a less marked influence. The phenolases of cherry, radish, and green pea also appear to be sensitive towards oxygen. Comparison of the behaviour of the skin and substance extracts of potato towards quinol and nitrate indicates the probability that two different enzymes are involved.

The behaviour of horse-radish peroxidase towards pyrogallol has been examined in the presence of ethyl hydrogen peroxide, ethyl peroxide, dihydroxymethyl peroxide, peracetic acid, and disuccinyl peroxide.



The activation of peroxides appears to require the presence of at least one hydroxyl group. Disubstituted peroxides are completely inactive. Since the monosubstituted compounds lag far behind hydrogen peroxide it is probable that they have scarcely any biological significance and that the behaviour of peroxides in this respect must be discussed solely with reference to the parent compound. H. WREN.

**Mechanism of action of the oxidoreductases.** K. SHIBATA (Acta Phytochim., 1929, 4, 373—379).—The theory of oxidases, peroxidases, and catalases is discussed and the view is expressed that the essential action is the activation of water or of hydrogen peroxide. Certain complex metal salts exhibit, not only oxidase, but also peroxidase and catalase activity, and the view that they are analogous to the natural enzymes is supported by the fact that mutual interference may occur when both are present simultaneously. W. O. KERMACK.

**Oxidase-like actions of certain complex metal salts.** Y. SHIBATA and K. SHIBATA (Acta Phytochim., 1929, 4, 363—371).—The oxidation of myricetin in aqueous alcoholic solution is much accelerated by the presence of many complex cobalt-ammine salts as well as by certain complex salts of nickel, zinc, cadmium, chromium, and silver. The catalytic actions of these salts resemble those of the natural enzymes as they are inhibited by acidity of the medium, by boiling, and by certain chemical substances, e.g., cyanides, hydroxylamine, and mercuric chloride. The catalytic action is also inhibited by the presence of certain cobaltammine salts which themselves are inactive.

W. O. KERMACK.

**Catalase action of organically-combined iron.** H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1929, 10, B, No. 5, 6 pp.).—Pyratin, prepared from hæmin by Schumm (A., 1928, 1263), decomposes hydrogen peroxide about 20 times as rapidly as hæmin. Its activity decreases with time, and also in high concentrations of hydrogen peroxide. The activity is rapidly reduced by treatment with hydrogen sulphide. The catalase action of hæmin, hæmo-chromogen, and derivatives is closely connected with their iron content (cf. this vol., 302).

K. V. THIMANN.

**Lipase.** H. VON EULER and S. GARD (Arkiv Kemi, Min., Geol., 1929, 10, A, No. 2, 7 pp.).—The liver of the rat and pig was freed from fat, extracted first with acetone, then with equal parts of acetone and ether, and finally with ether, dried, and powdered. The lipase was then extracted with glycerol, and the extract centrifuged. The action of this lipase solution at  $p_H$  8 on monobutylin, ethyl acetate, and glycine ethyl ester in the presence of albumin and calcium chloride was examined. The results were compared with the lipolysis produced by hydrochloric acid. The hæmolyses produced by this extract, by blood-serum, and by intestinal mucosa were also compared.

K. V. THIMANN.

**Stereochemical specificity of esterases. I. Affinity of liver-esterases for optically active alcohols.** D. R. P. MURRAY and C. G. KING (Biochem. J., 1930, 24, 190—198).—The *l*-forms of methyl-

*n*-hexylcarbinol, phenylmethylcarbinol, and methyl- $\beta$ -phenylethylcarbinol inhibit sheep-liver esterase about four to five times as strongly as the *d*-forms. On the other hand, with rabbit-liver esterase there is no difference in the inhibiting action of the *d*- and *l*-alcohols.

S. S. ZILVA.

**Asymmetric esterification caused by the esterase of pig pancreas.** P. RONA and R. AMMON (Biochem. Z., 1930, 217, 34—41).—When powdered pig pancreas acts on mixtures of water, isoamyl alcohol, and *d*-, *l*-, or *dl*-lactic acid the amyl ester of the *d*-acid is formed more rapidly than are the esters of the *l*- and *dl*-acids.

W. MCCARTNEY.

**Stereochemical specificity of taka-esterases.** P. RONA, R. AMMON, and M. WERNER (Biochem. Z., 1930, 217, 42—49).—Measurements of dissociation and hydrolysis constants show that the compound of taka-diastrase with the methyl ester of *l*-mandelic acid is hydrolysed twice as rapidly as is the corresponding *d*-compound and that the affinity of the taka-diastrase for the *d*-ester is five times as great as it is for the *l*-ester. The quantitative investigation of the optical specificity of the taka-esterases is now complete.

W. MCCARTNEY.

**Arginase method for arginine determinations; analysis of proteins.** A. HUNTER and J. A. DAUPHINEE (J. Biol. Chem., 1930, 85, 627—665).—Fresh liver, finely minced, is extracted by shaking for 10 min. with an equal volume of 75% glycerol, the mixture is heated in a water-bath to 58° for 5 min., cooled, and filtered; the filtrate contains 80—100 units of arginase per c.c., the unit being the amount of enzyme required to liberate 0.5 mg. of carbamide-nitrogen from 10 mg. of arginine in 30 min. at 37°. A stable solid preparation of the enzyme may be obtained by making the extraction with water, and evaporating the filtered extract in thin layers in an air-current. Conditions are described for the recovery of 99.4  $\pm$  0.1% of the theoretical amount of ammonia from carbamide by means of urease; application of this technique to the solution resulting from the action of arginase on arginine enables the latter to be determined with an error of 0.5%. The method has been applied to the determination of arginine in protein hydrolysates either directly or after precipitation with phosphotungstic acid. A correction is made if necessary for the deaminising effect of the liver extract on other amino-acids. The arginine contents of the following proteins have been thus determined: gelatin 15.48, caseinogen 7.99, edestin 26.7, gliadin 4.78, globin 7.72, fibrin 14.31, ovalbumin 10.36%.

C. R. HARRINGTON.

**Substrate in peptic synthesis of protein.** H. BORSOOK, D. A. MACFADYEN, and H. WASTENEYS (J. Gen. Physiol., 1930, 13, 295—306).—Peptic digests of egg-white show a marked decrease in the amount of synthesis which can be effected by pepsin in the concentrated digests, with the lengthening of the period of digestion. The amount of protein synthesised is independent of the  $p_H$  to which the digest is exposed in the absence of pepsin. Synthesis can also be effected by pepsin in concentrated solutions of proteose or peptone, but the protein differs from the plastein synthesised from the whole digest. The cessation

of synthesis by pepsin in a digest is due to the attainment of a true equilibrium, since after removal of the synthesised protein the residual digest on concentration affords more protein, providing it still contains the specific complex which results from primary hydrolysis of the protein molecule by pepsin.

C. C. N. VASS.

**Enzymic proteolysis.** V. P. RONA and H. A. OELKERS (Biochem. Z., 1930, 217, 50—112).—When solutions of egg-albumin were treated with pepsin there was a slight increase in the osmotic pressure during the period before chemical action began, and when it did begin the osmotic pressure fell. In the case of caseinogen and trypsin, during the same period, the increase in osmotic pressure was great and only when decomposition of the protein had proceeded to a considerable extent did the pressure begin to fall. The osmotic pressure of egg-albumin solutions did not increase as a result of the action of trypsin. These results confirm the views previously advanced concerning the changes which occur in the period before decomposition of proteins by enzymes begins.

W. MCCARTNEY.

**Caseinogen-splitting action of papain, and mechanism of the acceleration by hydrogen cyanide.** S. SATO (J. Fac. Agric. Hokkaido Imp. Univ., 1929, 24, No. 4, 101—151).—The quantity of caseinogen digested in unit time is proportional to the concentration of papain. The velocity coefficient of the unimolecular reaction gradually becomes maximal and then decreases, the maximum value being attained earlier for larger amounts of papain. The temperature coefficient varies from 4.0 at 40—50° to 0.6 at 80—90°; the optimal  $p_H$  is 6.5. Appreciable amounts of amino-acids are not formed. The activating action of potassium cyanide is attributed to that of hydrogen cyanide molecules; removal of hydrogen cyanide with air decreases the velocity to the original value.

CHEMICAL ABSTRACTS.

**Origin of inosinic acid.** M. V. BUELL (J. Biol. Chem., 1930, 85, 435—445).—Aqueous extracts of the muscles of the ox, pig, rabbit, and of man (but not of the rat) have the power of deaminising adenine nucleotide to give inosinic acid. The deamination proceeds most rapidly at  $p_H$  6.0 and more readily with adenine nucleotide from muscle than with that from yeast. The results explain the occurrence of inosinic acid and also that of hypoxanthine in muscles which lack adenase.

C. R. HARRINGTON.

**Uricase and its action.** S. J. PRZYLECKI (Biochem. J., 1930, 24, 81).—The uricolytic activity of the author's uricase preparation purified by dialysis in the presence of antiseptics such as thymol is due to bacterial action (cf. A., 1928, 1055).

S. S. ZILVA.

**Mechanism of alcoholic fermentation.** A. N. LEBEDEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1199—1201).—Polemic.

**Selective fermentation of dextrose and lævulose by brewer's yeast.** H. IVEKOVICH (Biochem. J., 1930, 24, 4—5; cf. A., 1927, 592; Hopkins, A., 1928, 1158).—Dextrose is fermented 1.78 times as rapidly as lævulose.

S. S. ZILVA.

**Decreasing rate of fermentation.** O. RAHN (J. Bact., 1929, 18, 207—226).—The assumption that the decrease in the rate of fermentation caused by products of fermentation is proportional to their concentration divided by the limiting concentration leads to a formula giving a fermentation constant which represents the rate corrected for retardation by the products. For alcoholic fermentation,  $Kt = \log_e 2L/(2L-x)$ , where  $t$  is the time,  $L$  the limiting concentration of alcohol, and  $x$  the amount of sugar decomposed; for lactic fermentation  $Kt = Y \log_e L(L-x)$ , the factor  $Y$  representing the number of acting yeast-cells. In both alcoholic and lactic fermentations the relationship between the rate of fermentation and the amount of product added is linear.

CHEMICAL ABSTRACTS.

**Formation of pyruvic acid as an intermediate phase in the alcoholic degradation of sugars. Isolation of pyruvic acid as the chief product of fermentation.** C. NEUBERG and M. KOBEL (Biochem. Z., 1929, 216, 493—496).—By the action of an acetone-dried preparation of a bottom yeast on magnesium hexosediphosphate, a yield of 90% of pyruvic acid may be obtained providing that the correct proportion exists between the substrate and enzyme concentration, the latter being greater than is necessary for the production of methylglyoxal, but less than is necessary to bring about complete fermentation in the experimental time.

P. W. CLUTTERBUCK.

**Phosphoric esters of alcoholic fermentation.** R. ROBISON and W. T. J. MORGAN (Biochem. J., 1930, 24, 119—132).—Methods are described for the separation and investigation of the phosphoric esters produced during fermentation of sugars by yeast preparations. Sources of error in the conclusions reached from the results obtained with the aid of these and other methods are discussed. The distribution of total esterified phosphorus among the four known esters, estimated by the application of these methods, is given for a number of fermentation experiments with yeast-juice, zymin, and dried yeast. Some indication has been obtained of the presence of a fifth ester, but this can at most form only a very small proportion of the fermentation products. The effect of varying the rate of addition of phosphate on the relative proportions of the different esters has been studied. Hexosemonophosphate was obtained in maximum yield when the fermentation was rapid and inorganic phosphate was in considerable excess. Trehalosemonophosphate, on the other hand, increased in amount when the fermentation was continued for some time after the addition of phosphate, but again decreased if the fermentation was prolonged. A sparingly soluble crystalline form of barium trehalosemonophosphate is described.

S. S. ZILVA.

**Enzymic carbohydrate degradation.** R. NILSSON (Arkiv Kemi, Min., Geol., 1929, 10, B, No. 1, 6 pp.).—Fermentation of dextrose in presence of phosphates, by a mixture of co-zympase, zymophosphate, and yeast which has been washed free of co-zympase, produces carbon dioxide and a hexosemonophosphate, the barium salt,  $\alpha_D + 14.9^\circ$ .

of which corresponds with the formula  $C_6H_{11}O_5PO_4Ba$  (see Euler, Myrbäck, and Runejelm, A., 1928, 1158). Sodium fluoride suppresses the reaction.

K. V. THIMANN.

**Problems of affinity.** H. VON EULER and R. NILSSON (Arkiv Kemi, Min., Geol., 1929, 10, A, No. 4, 7 pp.).—The insoluble residue left when yeast is washed with water contains an invertase. The effect of phenol on the rate of inversion of sucrose by this invertase and by the water-soluble invertase was determined, the percentage inhibition being the same in each case. Phenol also exercises considerable inhibition on the action of mutase on acetaldehyde. The conception is developed that the inhibition or poisoning produced by phenol and by protoplasmic poisons of the toluene type is due to the poison affecting the affinity between enzyme and substrate.

K. V. THIMANN.

**Peroxidase reaction during alcoholic fermentation.** G. WOKER and E. BLUM-SAPAS (Biochem. Z., 1930, 217, 236—252).—The colours produced and the times required for them to reach their maxima when mixtures of yeast and dextrose solution and of yeast and water were tested, immediately after preparation or after intervals of from 1 hr. to 3 weeks, for the presence of acetaldehyde with *p*-phenylenediamine and hydrogen peroxide, have been observed. The results showed that acetaldehyde was always produced, although it appeared much earlier in the case of the yeast-dextrose mixture than in that of the yeast-water mixture.

W. MCCARTNEY.

**Effects of certain chemical compounds on the course of gas production by baker's yeast.** S. E. BRANHAM (J. Bact., 1929, 18, 247—264).—A simple gas meter is described. With mercuric chloride, mercurochrome, metaphen, and hexylresorcinol the greatest amount of gas was formed at dilutions causing relatively slight initial inhibition; with chloramine-*T*, tincture of iodine, and sodium hypochlorite there was sudden activity at dilutions causing complete inhibition for 1—2 hrs. Mercuric or sodium chloride at high (non-inhibitory) dilution caused a transient initial stimulation, whilst silver nitrate caused no increase of fermentation.

CHEMICAL ABSTRACTS.

**Chemical investigation of "bios."** I. B. T. NARAYANAN (Biochem. J., 1930, 24, 6—18).—A method of fractionation of "bios" from hydrolysed yeast based on the removal of impurities at various stages with baryta, lead acetate, alcohol, silver, and platinic chloride, and on the precipitation of the active principle with phosphotungstic acid is described. Doses of this concentrate of the order of 0.01 mg./c.c. stimulate the growth of yeast. This preparation is more active than those obtained by Eddy (A., 1925, i, 342) and Miller (Science, 1924, 59, 1927). Inositol is not an essential unit of "bios" (cf. Eastcott, A., 1928, 1056). The latter is not identical with vitamin-*B*, from which it can be separated. S. S. ZILVA.

**Acid production, respiration, oxidase reaction, and reducing power of various species of *Aspergillus*.** H. TAMIYA and T. HIDA (Acta Phytochim., 1929, 4, 343—361).—A large number of species of *Aspergillus*, cultivated under definite conditions, have been examined in respect of the quantity and nature

of the acids produced, the extent of the respiration, the indophenol-oxidase reaction, and the power of reducing methylene-blue with and without the addition of succinic acid. Amongst the acids observed were gluconic acid, citric acid, and oxalic acid, as well as kojic acid.

W. O. KERMACK.

**Utilisation of micro-organisms for human food materials.** VIII. Proteins. IX. Nucleic acid. X. Carbohydrates of the mycelium of *Aspergillus oryzae*. R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, 32, 243—244B, 245B, 245—247B).—VIII. The protein is obtained in 0.35% yield from the mycelium by extraction with 1% sodium hydroxide solution and precipitation with dilute acetic acid. It contains N 14.78, P 1.77, ash, 2.66%, S trace. Acid hydrolysis of the protein yields about 4% of reducing sugars, chiefly glucosamine. Repeated digestion of the residual mycelium with pepsin in 1% hydrochloric acid solution yields a peptone containing 17% N (of which 10.1% is free amino-nitrogen), 0.59% of ash, but no phosphorus. It is soluble in water or dilute alcohol and is precipitated by phosphotungstic acid, copper hydroxide, and lead acetate. The nitrogen distribution determined by Van Slyke's method and the amounts of several amino-acids of the protein, peptone, and mycelium are tabulated.

IX. The nucleic acid contains N 13.16, P 7.01%, and yields on hydrolysis guanine, adenine, hypoxanthine, and probably uracil. Of the total nitrogen content in the mycelium 15.8% is nucleic acid-nitrogen.

X. From the alcoholic extract of the dried mycelium mannitol and trehalose were isolated, whilst mannose, levulose, trehalose, an unidentified polysaccharide, and considerable quantities of dextrose and glucosamine were identified in the residual syrup. The ratio of the fermentable reducing sugars to the unfermentable was 1:2.7. Amylose (cf. Schmidt, A., 1925, i, 368) and glycogen were isolated as water-soluble polysaccharides. Treatment of the protein-free residues (VIII) with 10% sodium hydroxide solution and precipitation of the filtrate with hydrochloric acid, gave a substance which yielded, on hydrolysis with 2.5% hydrochloric acid, 35.5% of reducing sugars, chiefly glucosamine, whilst hydrolysis with 75% hydrochloric acid yielded 80.6% of reducing sugars.

C. C. N. VASS.

**Utilisation of micro-organisms for human food materials.** XIV—XVI. Culture of *Aspergillus oryzae*. III. Relation between the hydrogen-ion concentration of the medium and the yield of mycelium. IV. Influence of sodium chloride, sodium sulphate, and sugar concentration on the growth of the mycelium. V. Relation between the duration of culture, yield and nitrogen content of mycelium, and sugar concentration. R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, 32, 306B, 307B, 308B).—III. Two optimum  $pH$  values for the growth of the mycelium in a given synthetic medium in which the carbohydrate is supplied as sucrose, dextrose, dextrin, or soluble starch, and nitrogen as ammonium chloride or nitrate, potassium nitrate, or urea, are obtained; the values

found are 4.5 and 5.6, which lie on either side of the isoelectric point of the mycelium (cf. Robbins, A., 1924, i, 475), which appears to be at about  $p_H$  5.0. *A. oryzae* is capable of growth over the range  $p_H$  1.8—9.0.

IV. The maximal yield of mycelium is obtained, using the foregoing synthetic medium in the presence of sodium chloride or sulphate, when the concentration of the latter is 0.5%; the yield decreases with increasing salt concentration and growth is inhibited by concentrations greater than 10%. The yields of mycelium produced by 40—60 hrs. culture in media containing 1—5% of sugar are nearly constant, but decrease with higher sugar concentrations; for a period of 10 days' culture in the presence of 1% of sugar the economical coefficient is 39.8%, whilst in the presence of 3—10% of sugar the coefficient is nearly constant, ranging from 27.0 to 29.9%.

V. The yield of mycelium, produced by *A. oryzae* growing in a synthetic medium in which sucrose was the sole source of carbon and urea a source of nitrogen, increases rapidly from the 2nd to the 6th day, remains nearly constant for 2 days, and gradually decreases to about one half the maximum at the 17th day. The economical coefficient is highest at the 3rd day (30.2%), and decreases gradually to 9.2% at the 17th day. The nitrogen content of the mycelium decreases gradually, from 5.89% at the 2nd to 3.02% at the 17th day. C. W. SHOPPEE.

**Action of micro-organisms on the odorous principle of rhizoma iridis.** A. VON LINGELSHEIM (Arch. Pharm., 1930, 268, 1—7).—When a culture of *Trichoderma* and related fungi, obtained originally from *Iris pallida*, is grown on a medium containing powdered iris the original characteristic violet odour is destroyed and a strong terpene odour develops. Similar observations have been made during the decay of various species of violet plants, the growth of the fungus being observed simultaneously, and it is suggested that the irone present in the plant is converted into a terpene derivative (?  $\alpha$ -pinene) by the action of the micro-organism. In support of this view it is found that when traces of oil of violets, an aqueous extract of the oil, or even of artificial ionone are added to cultures of the fungi, the characteristic violet odour disappears and is replaced by a terpene odour. The significance of this change and of the reverse change of a terpene into a violet odour, which has been observed in human urine, is discussed.

J. W. BAKER.

**Soluble enzymes secreted by the *Hymenomyces*. Antioxygenic function of hydrocarbons and terpenes.** L. LUTZ (Compt. rend., 1930, 190, 218—220).—Pinene, limonene, caryophyllene, cymene, and styrene exert in sunlight a considerable antioxygenic effect as shown by the decolorisation of methylene-blue contained in the media on which six species of the fungi were grown. Cincole had no effect on the oxidising powers of the fungi (cf. A., 1926, 869).

C. C. N. VASS.

**Metabolism of anaerobes. IV. Nature of the volatile acids produced by *Cl. histolyticum* from proteins.** W. S. STURGES, L. B. PARSONS, and E. T. DRAKE (J. Bact., 1929, 18, 157—167).—Cultures

grown in buffered pork in glass bombs thrice evacuated to the vapour pressure of water and sealed in a vacuum were acidified and the gases removed; carbon dioxide, ammonia, and acetic acid were present in the molar ratio 1 : 2 : 2. This ratio cannot be accounted for by the decarboxylation of dicarboxylic amino-acids preceded or followed by reductive deamination, or of monocarboxylic acids, or the degradation of chains by oxidative processes.

CHEMICAL ABSTRACTS.

**Reduction phenomena in the lactic acid fermentation.** W. N. SCHAPOSHNIKOV and J. P. ZACHAROV (Biochem. Z., 1929, 216, 325—329).—Methylene-blue, potassium nitrate, and sulphur introduced into fermentation mixtures sown with pure cultures of *B. Delbrücki* were reduced to leuco-base, nitrite, and hydrogen sulphide, respectively.

P. W. CLUTTERBUCK.

**Influence on bacterial viability of various anions in combination with sodium.** F. W. FABIAN and C. E. A. WINSLOW (J. Bact., 1929, 18, 265—291).—Experiments on the viability of *Escherichia coli* showed that the stimulating effect of various sodium salts at low concentration was a direct function of the sodium content, and that inhibition at higher concentration depends on the sodium and hydrogen-ion concentrations. If the latter are favourable, the phosphate ion stimulates growth. Assumption of antagonism or specific salt effect in such cases is frequently unnecessary.

CHEMICAL ABSTRACTS.

**Degradation of carbohydrate by *B. coli*. Isolation of methylglyoxal.** C. FROMAGEOT (Biochem. Z., 1929, 216, 467—474).—Magnesium hexosediphosphate on digestion at 37° with an alcohol-ether dry glycolase preparation of a culture of *B. coli* gave methylglyoxal in 89.72% yield.

P. W. CLUTTERBUCK.

**Quantitative conversion of methylglyoxal into pure *d*(-)-lactic acid by *B. fluorescens*.** E. WIDMANN (Biochem. Z., 1929, 216, 475—478).—*B. fluorescens* converts methylglyoxal rapidly and quantitatively into optically pure *d*(-)-lactic acid.

P. W. CLUTTERBUCK.

**Nitrifying bacteria.** D. W. CUTLER (Nature, 1930, 125, 168).—A new group of organisms has been discovered which produces nitrite when grown in a culture containing 0.06% NaCl, 0.002%  $CaCl_2$ , 0.005%  $MgSO_4$ , 0.03% of potassium hydrogen phosphate, 0.1% of sucrose, and an ammonium salt. The organisms isolated from a sugar-beet effluent filter-bed produce nitrite more freely from ammonium lactate, whilst those isolated from soil prefer the phosphate. Nitrite formation occurs over a wide  $p_H$  range from 4.5 to 7.9. The new organisms have characteristics distinct from those of *Nitrosomonas* and *Nitrosococcus*.

L. S. THEOBALD.

**Chemotherapy of tuberculosis. II.** G. MEISSNER and E. HESSE (Arch. exp. Path. Pharm., 1930, 147, 339—359; cf. A., 1928, 1286).—Tubercle bacilli are stained in the peritoneal cavity of the mouse or in guinea-pig serum only by certain dyes which are basic in nature and therefore positively charged. This fact has been correlated with the

negative charge which tubercle bacilli bear, when suspended in serum under the same conditions. In addition to the dyes previously employed, about 2000 compounds have been tested by Wright's method as to their bacteriostatic action with reference to tubercle bacilli growing in blood. The compounds include salts of 48 elements and certain other metallic compounds and 145 alkaloids and alkaloidal derivatives. The inorganic salts are inactive, but of the alkaloids conessine and harmine are active as well as certain derivatives of quinine, viz.,  $\alpha$ -isoquinine, ethylapocuinine, and aminohydroquinine. Eucupin, optochiu, and vuzin are inactive. The activity of indamine-blue in promoting the cure of guinea-pigs lightly infected with tuberculosis has been confirmed.

W. O. KERMACK.

**Lipins of tubercle bacilli.** X. Lipin fractions from avian tubercle bacilli. XI. Phosphatide fraction from avian tubercle bacilli. XII. Lipin fractions from bovine tubercle bacilli. R. J. ANDERSON and E. G. ROBERTS (J. Biol. Chem., 1930, 85, 509—517, 519—528, 529—538).—X. Moist avian tubercle bacilli (3515 g. of dry material) were extracted successively with a mixture of alcohol and ether and with chloroform. The alcohol-ether solution was evaporated under diminished pressure and the final aqueous suspension was extracted with ether; some wax which separated was added to the chloroform extract. The material extracted by ether was separated into acetone-soluble fat (77.3 g.) and phosphatide (79.7 g.); the chloroform extract yielded 379.5 g. of wax, and the aqueous solution 3.61 g. of polysaccharide.

XI. Figures are given for the constituents yielded by the above-mentioned phosphatide on hydrolysis. This phosphatide resembles in composition that obtained from human tubercle bacilli (A., 1927, 1114), except that it contains less ether-soluble and more water-soluble constituents than the latter.

XII. Bovine tubercle bacilli (3941 g. of dry material) were extracted by the method described above for the avian bacilli, and yielded acetone-soluble fats (131.7 g.), phosphatide (60.5 g.), wax (336 g.), and polysaccharide (40.3 g.).

C. R. HARRINGTON.

**Chemical changes accompanying the growth of avian tubercle bacilli on Long's synthetic medium.** A. G. RENFREW, S. L. BASS, and T. B. JOHNSON (Amer. Rev. Tuberculosis, 1929, 20, 114—121).—The copper reduction curve suggests that the organism does not produce the same carbohydrate combination as does the human tubercle bacillus.

CHEMICAL ABSTRACTS.

**Chemical changes accompanying the growth of timothy bacilli on Long's synthetic medium.** S. L. BASS and T. B. JOHNSON (Amer. Rev. Tuberculosis, 1929, 20, 122—127).—Timothy and avian tubercle bacilli form sugar of low reducing power, whilst the reducing power of the sugar formed in human tubercle bacilli is variable and increases to a maximum. The same sugar combination does not function in the three organisms.

CHEMICAL ABSTRACTS.

**Action of formaldehyde, hydrogen peroxide, and white phosphorus on tuberculin.** J. F. HEYMANS and C. HEYMANS (Compt. rend. Soc. Biol., 1929, 101, 153—155; Chem. Zentr., 1929, ii, 1018).—Tuberculin, which is not decomposed by the above reagents, is exceptional among proteins.

A. A. ELDRIDGE.

**The water-soluble substance of Friedländer's bacillus in relation to the identity of antibodies.** C. E. LIM and T. J. KUROCHKIN (Chinese J. Physiol., 1929, 3, 409—418).—Guinea-pigs could not be sensitised to a solution of the soluble specific substance of Friedländer's bacillus by injecting them with the precipitate obtained when a solution of soluble specific substance is mixed with homologous antiserum. Guinea-pigs could not be passively sensitised by the administration of immune serum from which the antibody had been removed by precipitation with a solution of the soluble specific substance. A similar result was obtained with serum from which the agglutinins had been removed by adsorption. The complement-fixing properties of the serum decreased with increased removal of precipitin, but complete absence of complement-fixing power was never attained. It is concluded that the agglutinating, precipitating, and complement-fixing substances in immune serum are probably identical.

W. O. KERMACK.

**Composition of diphtheria toxin-antitoxin floccules.** J. R. MARRACK and F. C. SMITH (Proc. Roy. Soc., 1930, B, 106, 1—19).—Spectrophotometric observations on the ultra-violet absorption curves of solutions of the floccules produced by the interaction of preparations of diphtheria toxin and of antitoxin (in such a proportion as to give most rapid flocculation) are consistent with the view that the floccules consist essentially of pseudoglobulin. Experiments on the flocculation by various salts of dispersions of these floccules in distilled water indicate that the pseudoglobulin is in the denatured condition. The presence of unspecific protein in the mixtures of toxin and antitoxin does not increase the precipitate obtained, which further is largely independent of the conditions employed. It appears therefore that the precipitate consists essentially of the active substances and not of unspecific material. The percentage of lipin in the floccules was likewise small.

W. O. KERMACK.

**Penetrative power of the bactericidal rays in the ultra-violet as emitted by carbon.** DE W. VORSTER (J. Dental Res., 1929, 9, 641—651).—Gentian-violet, methylene-blue, cosin (1 in 100), or mercurochrome (1 in 4000) used as sensitiser decreases the germicidal action of the rays of carbon on *Staphylococcus aureus*. Saliva is opaque to the rays.

CHEMICAL ABSTRACTS.

**Negative staining of bacteria.** W. C. DORNER (Stain Tech., 1930, 5, 25—27).—Attention is directed to the usefulness of Burri's Indian ink technique and of nigrosine. When these substances are applied to a liquid on a slide which is subsequently dried, a uniform dark film, in which the bacteria remain unstained, is produced.

H. W. DUDLEY.

**Hæmatein, its advantages as a stain.** S. I. KORNHAUSER (Stain Tech., 1930, 5, 13—15).—Mayer's

"hæmalum" stain is preferred to the usual hæmatoxylin mixtures.

H. W. DUDLEY.

**Mechanism of staining.** II. A. E. STEARN and E. W. STEARN (*Stain Tech.*, 1930, 5, 17—24).—A discussion of the rôle of adsorption and chemical combination in connexion with the processes of staining.

H. W. DUDLEY.

**Equilibria and "automatins."** H. ZWAARDEMAKER (*Arch. Néerland. Physiol.*, 1929, 14, 565—591).—An equi-radioactive equilibrium demonstrated by the cessation of heart beat has been obtained in an isolated frog's heart when perfused (a) alternately with two Ringer solutions, the one containing an  $\alpha$ -, the other a  $\beta$ -ray source, (b) with a Ringer solution containing a radioactive element supplying one kind of rays and irradiated externally with the opposite kind of rays, (c) with an admixture of the perfusion fluids obtained by perfusing the heart with two Ringer solutions which contain sources of  $\alpha$ - and  $\beta$ -rays or have been irradiated by such rays, and (d) when the heart has been simultaneously irradiated by two opposed sources of  $\alpha$ - and  $\beta$ -rays. When the heart is at rest "automatinogen" is given off to the perfused liquid. Irradiation externally or by dissolved radioactive sources converts "automatinogen" into two radioactive antagonistic substances termed  $\alpha$ - and  $\beta$ -"automatins." The free energy furnished to the heart by irradiation is 1 micro-erg per sec. per g., but since the greater part of this energy reaches water molecules and protoplasm, it is considered that the "automatins" are produced by an autocatalytic chain reaction as evidenced by the latent period following irradiation. The heart frequency is a function of the concentration of the potassium, the intensity of the irradiation, and the quantity of "automatin" produced. Curves, resembling adsorption curves, are given showing the concentration of potassium as opposed to thorium, uranium, ionium, and radon for equi-radioactive equilibrium. Choline, eosin, nicotine, and *d*-adrenaline in the presence of calcium stimulate the formation of  $\beta$ -automatin from potassium, whilst histamine, ephedrine, fluorescein, trypanflavin, and *l*-adrenaline activate uranium; these substances do not modify the duration of the latent period.

C. C. N. VASS.

**Heart hormone. Action of active substances.** R. RIGLER and F. TIEMANN (*Pflüger's Archiv*, 1929, 222, 450—459; *Chem. Zentr.*, 1929, ii, 1551).—The chief agent in the "substances actives" is unspecific, and apparently belongs to the histamine class of substances.

A. A. ELDRIDGE.

**Adrenaline therapy.** A. J. ANTHONY (*Arch. exp. Path. Pharm.*, 1930, 148, 93—101).—Subcutaneous administration of adrenaline or ephedrine, or oral administration of ephedrine, increases the respiratory quotient immediately, and usually also the blood-pressure and blood-sugar.

K. V. THIMANN.

**Effect of extracts of suprarenal cortex on the blood-calcium.** L. MIRVISH and L. P. BOSMAN (*Brit. J. Exp. Biol.*, 1929, 6, 350—354).—An extract of suprarenal cortex lowered the blood-calcium by 30% in 24 hrs. It is similar in action to the hormone of the ovary.

E. BOYLAND.

**Effect of testicular extracts on blood-calcium.** L. MIRVISH and L. P. BOSMAN (*Brit. J. Exp. Biol.*, 1929, 6, 355—359).—The injection of the alcoholic extract of testis into rabbits produces a fall in blood-calcium.

E. BOYLAND.

**Pressor substance from bull's prostate gland.** J. B. COLLIP (*Trans. Roy. Soc. Canada*, 1929, [iii], 23, V, 165—168).—Extracts of bull's prostate gland exert a pressor effect similar to that of adrenaline, although the return to normal blood-pressure is more gradual in the former. Subcutaneous injection of prostatic extracts produces hyperglycemia in rabbits, and its effect on the isolated uterus of the rat is similar to that of adrenaline.

P. G. MARSHALL.

**Preparation of œstrin.** G. F. MARRIAN (*Nature*, 1930, 125, 90—91).—The yields of œstrin can be greatly increased by acidification of urine before ether extraction. Losses during initial saponification can be minimised by saturating the saponified mixture with carbon dioxide before extraction with ether. The most potent preparation of œstrin obtained by introducing these modifications of method had an activity of  $8 \times 10^6$  mouse units per g.

L. S. THEOBALD.

**Crystalline "menformon."** E. LAQUEUR, E. DINGEMANSE, and S. KOBER (*Nature*, 1930, 125, 90; cf. A., 1929, 850).—Colourless platelets, recrystallisable from 70% alcohol, subliming at 130—150° and 0.01 mm., have been obtained. The crystals (C 78.61%, H 8.25%) are similar to those described by Doisy and by Butenandt (this vol., 118), and yield the same X-ray spectrum as that given by earlier preparations. The degree of spreading on water indicates a carbon chain of not more than 25 atoms. Other crystals containing a hydroxyl group (cf. Marrian, A., 1929, 1495) were encountered during the purification of the original material. Since a substance of greater activity ( $14 \times 10^6$  units per g.) has been produced in certain cases it is still not certain that the crystalline menformon now obtained is the pure hormone.

L. S. THEOBALD.

**Ovarian hormone and blood-cholesterol.** S. MORI and M. REISS (*Endokrinol.*, 1928, 1, 418—421; *Chem. Zentr.*, 1929, ii, 1551—1552).—Injection of "hormovar" into rats caused an increase in blood-cholesterol which depended on the dose.

A. A. ELDRIDGE.

**Cow's ovaries during pregnancy.** G. F. CARLAND, F. W. HEYL, and E. F. NEUPERT (*J. Biol. Chem.*, 1930, 85, 539—547).—During pregnancy the concentration of œstrin increases in the corpus luteum and decreases in the remaining ovarian tissue; simultaneously the neutral fat of the corpus luteum increases, whilst the phospho- and sulpho-lipids decrease; no change was observed in the cholesterol of the corpus luteum or in any lipin constituents of the rest of the ovary.

C. R. HARRINGTON.

**Insulin. I. Standardisation with white mice.** H. HORSTERS and H. BRUGSCH (*Z. ges. exp. Med.*, 1929, 65, 569—573; *Chem. Zentr.*, 1929, ii, 1021).—The conditions which must be observed in the test are described, and the limiting values obtained for commercial preparations are recorded.

A. A. ELDRIDGE.



**Insulin in human organs.** H. BRUGSCH (Z. ges. exp. Med., 1929, 65, 574—593; Chem. Zentr., 1929, ii, 1021).—The pancreas contains 10—100 Toronto units; in only one (case of death from starvation) practically none was found. Other values (for average weight of organ) are: heart 70—900, kidneys 110—300, muscle 1600—3150, liver 68—605 Toronto units.

A. A. ELDRIDGE.

**Decomposition of aqueous solutions of insulin by heat.** E. TROCELLO (Rass. Clin. Terap. Sci. Aff., 1928, 27, 504—505; Chem. Zentr., 1929, ii, 1311).—Solid insulin was kept without change at 37—40° for 1 yr., whilst an aqueous solution kept at 42° became completely inactive in 3 months.

A. A. ELDRIDGE.

**Increase of insulin content of blood after reflex stimulation of vagus.** H. VAN GOOR (Arch. Néerland. Physiol., 1929, 14, 535—548).—In rabbits stimulation of the vagus causes a decrease in the sugar content of the blood, shown by Ahlgren's technique to be due to the secretion of insulin. An analogous condition occurs in man on prolonged respiration in a closed system.

C. C. N. VASS.

**Insulin and glycæmin.** III. O. LOEWI (Klin. Woch., 1929, 8, 391—393; Chem. Zentr., 1929, ii, 441).—It is no longer considered that glycæmin, as well as lack of insulin, is always of causal significance of the appearance of hyperglycæmia.

A. A. ELDRIDGE.

**Influence of insulin on narcotised animals.** H. HORSTERS and H. BRUGSCH (Arch. exp. Path. Pharm., 1930, 147, 193—210).—Administration of narcotics to rabbits inhibits the convulsions accompanying insulin hypoglycæmia, independently of any effect of the narcotic on the blood-sugar level.

W. O. KERMACK.

**Effect of insulin on the amylolytic activity of saliva and blood.** T. GAYDA (Arch. Sci. biol., 1928, 12, 197—202; Chem. Zentr., 1929, ii, 1421).—The action of insulin is accompanied by a marked increase in the amylolytic activity of saliva, but not of the blood-serum.

A. A. ELDRIDGE.

**Appearance of sugar in urine after injection of insulin.** E. WIECHMANN (Deut. Arch. klin. Med., 1929, 164, 172—174; Chem. Zentr., 1929, ii, 1312).—In jaundice without diabetes 18 g. of dextrose were excreted per day after treatment with insulin.

A. A. ELDRIDGE.

**Effect of thyroid gland and pancreas on the carbohydrate exchange of the liver.** R. SIEGEL (Klin. Woch., 1929, 8, 1069—1071; Chem. Zentr., 1929, ii, 1702).—The sugar content of the liver of white mice 1 min. after death was 347 mg. per 100 g., rising in 10 min. to 851 mg. Injection of thyroxine a few hours before death accelerated the hydrolysis of the glycogen, the sugar content of the liver rising in 10 min. to 1020 mg. per 100 g., whilst injection of insulin maintained subnormal values. Metabolic disturbance in diabetes and the effect of lack of insulin on the action of the thyroid gland are discussed.

A. A. ELDRIDGE.

**Preparation of two active and specific thymus substances, and their effect on the lime and phosphate content of rabbit's serum.** A.

NITSCHKE (Z. ges. exp. Med., 1929, 65, 637—650; Chem. Zentr., 1929, ii, 1172).—Fresh calf's thymus, finely divided, was stirred with an equal quantity of 10% acetic acid and the mixture heated at 70°. The  $p_H$  of the cooled liquid was adjusted to 8—9 with sodium hydroxide, and then with hydrochloric acid to the isoelectric point of the protein. An equal volume of alcohol was added, the mixture was filtered after 3 hrs., and 80% of the filtrate was evaporated. Injection of the extract causes a fall in the serum-calcium and -phosphorus of the rabbit.

A. A. ELDRIDGE.

**Vitamin-A in animals.** B. VON EULER and H. VON EULER (Arkiv Kemi, Min., Geol., 1929, 10, B, No. 3, 6 pp.).—The serum of the ox, rat, pig, and a young healthy man gave the antimony trichloride reaction for carotenoid or vitamin-A, whilst the serum of the guinea-pig and an old man gave negative results. Extracts of ox liver give a strong positive reaction, corresponding with 168 Lovibond units per g. of fresh liver. In rats, the pale red liver gives a stronger reaction than the normal reddish-brown liver.

K. V. THIMANN.

**Relative vitamin-A value of the body and liver oils of certain fish.** B. AHMAD and J. C. DRUMMOND (Biochem. J., 1930, 24, 27—36).—The colorimetric and biological values for vitamin-A obtained with a number of fish-body and -liver oils agreed within reasonable limits. This is contrary to Schmidt-Nielsen's findings (Kon. Norsk. Videnskab., 1, Nos. 15, 29, 63; 2, No. 13), possibly on account of differences in technique and of his attempt to express results of the biological test, which is liable to wide variations, in terms of the units proposed by the U.S. Pharmacopœia.

S. S. ZILVA.

**Antimony trichloride reaction for vitamin-A.** P. KARRER, B. VON EULER, and H. VON EULER (Arkiv Kemi, Min., Geol., 1929, 10, B, No. 2, 6 pp.).—The antimony trichloride reaction of Carr and Price (A., 1926, 870) is specific for the group of carotenoid substances, for which it is a group reaction. The comparative intensity of blue coloration produced is as follows, carotene being taken as 100; bixin 160, xanthophyll 41,  $\gamma$ -crocin 350, dihydro- $\alpha$ -crocin 240. Measurements of the principal spectroscopic bands are given. The reaction is ascribed to the presence of a system of conjugated double linkings.

K. V. THIMANN.

**Antimony trichloride reaction for vitamin-A.** E. R. NORRIS and A. E. CHURCH (J. Biol. Chem., 1930, 85, 477—489).—The colour reaction described by Carr and Price (A., 1926, 870) has been studied in detail. The colour produced by a chloroform solution of the unsaponifiable matter of cod-liver oil is composed of blue and green in the ratio of 1:0.4 Lovibond unit; on keeping, it fades completely without the development of a red colour. The colour is not affected by saturated fatty acids and oils, or by traces of light petroleum or ethylene dichloride; in presence of oleic acid or of unsaturated oils, however, the rate of fading is increased and the linearity of the relationship between concentration of extract and intensity of colour is destroyed. With purified preparations of vitamin-A it is important to work at sufficiently

low concentrations in order to obtain quantitative results.

C. R. HARRINGTON.

**Vitamins-A and -D. I—VII.** W. KERPPOLA (Skand. Arch. Physiol., 1929, 56, 173—180, 181—187, 188—195, 196—200, 201—206, 207—209, 210—215; Chem. Zentr., 1929, ii, 1050—1051).—I. The colour reactions given by cod-liver oil and various condensation substances, and variations produced by ultra-violet irradiation, oxidation, or removal of saponifiable constituents, are described.

II. The antimony trichloride reaction is not given by extracts of the lungs and liver of rats maintained on a diet free from vitamin-A.

III. Under certain conditions the reactions of cod-liver oil parallel those of ergosterol.

IV. The antimony trichloride colour reactions of portions of a number of food-plants have been studied.

V. The unsaponifiable fraction of cod-liver oil affords a chromogen, m. p. 145.5° (acetate, m. p. 111°), forming triclinic crystals similar to those of cholesterol.

VI. Chloroform extracts of human and animal organs have been tested by the antimony trichloride reaction.

VII. The same reaction has been applied to a chloroform extract of human blood-serum.

A. A. ELDRIDGE.

**Absorption spectra in relation to vitamin-A.** R. A. MORTON, I. M. HEILBRON, and F. S. SPRING (Biochem. J., 1930, 24, 136—140; cf. Rosenheim and Webster, A., 1929, 1202).—Whilst the absorption curve attributed to vitamin-A has not so far been resolved, that of dehydroergosterol shows three distinct bands at 342, 326, and 311  $\mu$ , and an inflexion at about 297  $\mu$ . Further, the intensity of absorption of dehydroergosterol is not greater than one sixth of that shown by the absorbing constituent of liver oils. Rosenheim and Webster's criticism of the selective absorption of liver oils being used as a criterion for vitamin-A is contested also on general grounds.

S. S. ZILVA.

**Hypervitaminosis-A. I. Effects of an over-dose of biosterol on the salt metabolism of rabbits.** T. MUNEHISA (Sei-i-kwai Med. J., 1929, 48, No. 5, 57—81).—Elimination of calcium, phosphorus, magnesium, and nitrogen was increased by hypodermic administration of biosterol to rabbits. Injection of olive oil into controls produced smaller increases in salt metabolism, but pathological symptoms were absent.

CHEMICAL ABSTRACTS.

**Vitamin-B content of grass seeds in relationship to manures.** M. J. ROWLANDS and B. WILKINSON (Biochem. J., 1930, 24, 199—204).—Grass seed from a soil manured with dung is richer in vitamin-B than seeds from a similar soil manured with artificial manure. An alcoholic extract of pig's dung contains vitamin-B.

S. S. ZILVA.

**Concentration of vitamin-B<sub>2</sub>.** B. T. NARAYANAN and J. C. DRUMMOND (Biochem. J., 1930, 24, 19—26).—The active principle obtained by precipitation of the hydrolysate or the alcoholic extract of yeast by lead acetate is adsorbed by fuller's earth over a range of  $p_H$  extending from 6.8 to 0.1, the adsorption increasing as the acidity is raised. The

vitamin cannot, however, be removed from the adsorbent by extraction with baryta, acid 50% alcohol, alkaline 50% alcohol, or hot dilute hydrogen chloride at  $p_H$  6.8. Unsatisfactory results were obtained with "norit" as an adsorbent. The vitamin is almost completely precipitated from the lead acetate fraction by 70% alcohol after previously clearing the solution with 50% alcohol. The stability of vitamin-B<sub>2</sub> to heat, acids, and alkalis is confirmed. It is not destroyed by hydrogen peroxide or nitrous acid (cf. Levene, A., 1928, 1405; Chick, A., 1929, 853), nor is it appreciably soluble in butyl alcohol.

S. S. ZILVA.

**Heat-stability of the (anti-dermatitis, "anti-pellagra") water-soluble vitamin-B<sub>2</sub>.** H. CHICK and M. H. ROSCOE (Biochem. J., 1930, 24, 105—112).

—Vitamin-B<sub>2</sub> from yeast or yeast extract is much more stable at high temperatures in acid ( $p_H$  5.0—7.0) solutions than when the reaction is alkaline. The extract obtained by boiling the yeast with 0.01% acetic acid is more suitable than yeast itself, owing to the formation of toxic substances in the latter during heating, especially when the reaction is alkaline. No loss in the vitamin potency takes place on heating yeast at  $p_H$  5.0 for 2 hrs. at 90—100°. A loss of 50% was recorded on heating the yeast for 4—5 hrs. at 123°. At  $p_H$  3.0 the loss was the same both with yeast and yeast extract. At  $p_H$  9.5—10 about 30% of the vitamin originally contained in the yeast extract is lost in 10 days at the ordinary temperature; on heating for 2 hrs. at 98—100° ( $p_H$  8.3) the loss is about 50%, and on autoclaving for 4—5 hrs. at 122—125° ( $p_H$  8.3—10) between 75 and 100%.

S. S. ZILVA.

**Further evidence for a third accessory "B" factor.** V. READER (Biochem. J., 1930, 24, 77—80; cf. A., 1929, 1203).—Further evidence is produced for the existence of this factor. It is present in the mercuric sulphate precipitate of the Kinnersley and Peters process for the concentration of vitamin-B<sub>1</sub>.

S. S. ZILVA.

**Lactic acid and lactacidogen in the organism during avitaminosis-B in the dog.** K. TANAKA (Fol. endocrin. Japon., 1928, 4, 39—40).—Lactic acid in the dog's jugular vein and carotid artery is increased during avitaminosis-B; it is increased in muscle and decreased in the liver. The weight and the actual and percentage iodine contents of the thyroid gland are increased.

CHEMICAL ABSTRACTS.

**Antiscorbutic potency of apples.** M. F. BRACEWELL, E. HOYLE, and S. S. ZILVA (Biochem. J., 1930, 24, 82—90).—Bramley's Seedling was markedly more active than a number of other varieties of apples which differ among themselves comparatively very much less in their vitamin-C content. There was no indication that the character of the soil, the age of the tree, or the season has any bearing on the antiscorbutic activity of the apple. Bramley's Seedlings picked from the same tree 14 days before the normal crop are approximately of the same antiscorbutic activity. There was little loss in the vitamin-C content of apples stored at 1° in the air or at 10° in a mixture of carbon dioxide, nitrogen, and oxygen for about 3 months. The activity of the gas-stored apples deteriorated, however, to a greater extent than

that of the cold-stored apples. Imported dessert apples showed a higher activity when the time elapsing between the picking of the fruit and the testing was shorter. There was no indication of any very marked difference in activity which could be correlated with the difference in variety amongst the imported varieties. Heating of Bramley's Seedlings in their skins scarcely affected their antiscorbutic activity.

S. S. ZILVA.

**Vitamin-C content of fresh sauerkraut and sauerkraut juice.** B. CLOW, A. L. MARLATT, W. H. PETERSON, and E. A. MARTIN (*J. Agric. Res.*, 1929, 39, 963—971).—Experiments in which 10, 5, and 2.5 g. daily of fresh raw sauerkraut were fed per animal to guinea-pigs for 60 days, and 10 g. of sauerkraut juice for 75 days, indicate that the 5 g. level of fresh sauerkraut prevented the development of scurvy, whilst a similar quantity of the juice cured animals with definite symptoms of the disease. One half the vitamin-C content of cabbage is lost in making sauerkraut.

E. HOLMES.

**Preparation and properties of vitamin-C fractions from lemon juice.** H. L. SIPPLE and C. G. KING (*J. Amer. Chem. Soc.*, 1930, 52, 420—423).—Decitration of lemon juice by treatment with lead acetate, subsequent removal of lead with phosphoric acid, concentration of the residual solution below 50°, and precipitation of solid material with alcohol, causes no loss in vitamin-C activity of the alcohol-free solution. When decitrated lemon juice containing lead acetate is brought to  $p_H$  7.4—7.6 with ammonia, a lead complex which contains practically all the vitamin is precipitated. Dissolution of this complex in acetic acid and reprecipitation causes a diminution in the total solids of the lead-free preparation. The extraction of such a lead-free preparation with *n*-butyl alcohol removes colouring matter only, and evaporation of the residual aqueous solution gives a 98% preparation, purified further by dissolution in 98% alcohol and treatment with ether, whereby inactive material (mainly ammonium salts) is precipitated. Evaporation of the alcoholic ethereal solution gives solid material (0.56 mg.  $\equiv$  1 c.c. of original juice), which on extraction with ether is deprived of inactive, amorphous material. The final preparation (0.28 mg.  $\equiv$  1 c.c. of original juice) is chiefly carbohydrate in nature. All experiments are carried out in an atmosphere of nitrogen at relatively low temperature. Lead acetate cannot be replaced by barium acetate, nor can sodium hydroxide be used in place of ammonia, in the above purification.

H. BURTON.

**Preservation of the antiscorbutic vitamin in lemon juice.** J. WILLIAMS and J. W. CORRAN (*Biochem. J.*, 1930, 24, 37—50).—Potassium metabisulphite inactivates the antiscorbutic vitamin in lemon-juice at 15—18° at measurable velocity. Lemon-rind oil, although not such a good preservative against fermentation, has a less destructive action on the antiscorbutic potency, 0.07% of rind oil having a less injurious effect in this respect than 0.275%. Lemon-juice adjusted with hydrochloric acid to  $p_H$  1.6 preserves its antiscorbutic activity for 14 months at the ordinary temperature, the zone of optimum stability lying between 1.6 and 2.2. At  $p_H$  1.4 and

below, the vitamin is very much less stable. Sodium benzoate, formic acid, and oil of cloves exert a destructive action on vitamin-C. Sucrose does not preserve the vitamin, whilst there are indications that dextrose may.

S. S. ZILVA.

**Possible preparation of highly active ergosterol (vitamin-D) from raw coffee.** L. VON NOEL and F. DANNMEYER (*Strahlenther.*, 1929, 32, 769—771; *Chem. Zentr.*, 1929, ii, 1707).—The unsaponifiable fraction of coffee oil, having  $[\alpha] -150^\circ$ , contained an unstable crystalline substance,  $[\alpha] -200^\circ$ , which with digitonin gives no compound insoluble in alcohol; on absorption of oxygen and diminution of rotatory power, however, it tends to form such a compound. The spectrum is that of irradiated ergosterol, but on exposure to air becomes that of unirradiated ergosterol.

A. A. ELDRIDGE.

**Cereals and rickets. III. Rachitic properties of maize, wheat, and oats; effect of irradiation and of mineral supplements.** H. STEENBOCK, A. BLACK, and B. H. THOMAS (*J. Biol. Chem.*, 1930, 85, 585—606).—On diets composed for the most part of wheat, oats, or yellow maize, rats showed deficient calcification, the deficiency increasing in the order mentioned; satisfactory calcification was obtained in all cases when the cereals were irradiated. Supplementation of the non-irradiated cereals with calcium carbonate (the optimum amount being 1%) improved the calcification markedly; simultaneous supplementation with phosphoric acid had little or no effect. Of the three cereals the oats were consumed least satisfactorily, probably owing to deficiency of vitamin- $B_1$  and  $-B_2$ , particularly of the latter.

C. R. HARINGTON.

**Origin of chlorophyll and its relationship to the blood pigments.** F. M. SCHERTZ (*Science*, 1929, 70, 258—259).—A discussion of Noack and Kiessling's work (*A.*, 1929, 727).

L. S. THEOBALD.

**Electrical effects accompanying the decomposition of organic compounds; relation to photo-synthesis and plant nutrition.** M. C. POTTER (*Zentr. Bakt. Par.*, 1929, II, 78, 56—65; *Chem. Zentr.*, 1929, ii, 759).—Catalysis and synthesis in living plants are always accompanied by *E.M.F.*, which is a sign of vitality. Gases liberated by organic compounds are activated; the quantity of ionised carbon dioxide is important in photo-synthesis. The difference between catalytic and synthetic enzymes is discussed.

A. A. ELDRIDGE.

**Physiology of fruit. I. Changes in respiratory activity of apples during senescence at different temperatures.** F. KIDD and C. WEST (*Proc. Roy. Soc.*, 1930, B, 106, 93—109).—The amount of respiration of ripe apples after picking rises to a peak of about 1.5 times the original value and then falls. The time of reaching the peak varies inversely with the temperature, the temperature coefficient of the carbon dioxide production being about 5.4 for a rise of 20°, whilst that for the rate of protoplasmic change involved is considerably higher. Death from fungal disease supervenes after about the same amount of carbon dioxide has been evolved at all temperatures.

K. V. THIMANN.

**Limiting factors in carbon dioxide assimilation.** T. H. VAN DEN HONERT (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1008—1020).—The carbon dioxide assimilation by a filamentous alga belonging to the genus *Hormidium* has been investigated to determine the relation between assimilation velocity and the factors temperature, light intensity, and carbon dioxide concentration. The assimilation velocity is directly proportional to the light intensity up to an arbitrary intensity 1.99. Above this value the effect of increasing illumination becomes increasingly small, a doubling of the intensity at the value 6.18 causing only a 5% increase in assimilation velocity. The influence of rise of temperature is greater the greater is the illumination intensity. At low carbon dioxide concentrations the assimilation velocity is proportional to the concentration. The assimilation process may be reduced to a catenary process on the assumptions that it consists of (a) a diffusion process by which the carbon dioxide is transferred from the external medium to the chloroplast, (b) a photochemical process, and (c) a dark chemical process. F. G. TRYHORN.

**Importance of oxygen in the formation of urea in mushrooms.** N. N. IVANOV and M. I. SMIRNOVA (Zhur. exp. Biol. Med., 1929, **11**, 79—89).—Urea is produced in mushrooms only in presence of oxygen, although in hydrogen the urea content remains unaltered. In the absence of oxygen ammonia is not absorbed from its salts. CHEMICAL ABSTRACTS.

**Effect of summer and winter temperatures on the catalase of pine-needles; reply to criticism.** F. C. GREEN, M. E. M'ENDARFER, O. S. ORTH, and W. E. BUDGE (Proc. Roy. Irish Acad., 1929, **39**, B, 156—159).—The catalase content of pine needles (*Pinus strobus*), gathered when the temperature was below 0°, was 5—6 units and remained constant when the needles were stored at -5°. When kept at 22° the catalase content rose to 10—11 units, and at 35° to 42 units (cf. Doyle and Clinch, A., 1928, 1408). J. H. BIRKINSHAW.

**Enzyme chemistry of heredity.** H. VON EULER and H. NILSSON (Arkiv Kemi, Min., Geol., 1929, **10**, B, No. 6, 6 pp.).—Young buds of barley have a considerable catalase content, which is restricted to the coleophyll. Of two Mendelian varieties, one containing chlorophyll (dominant) the other white (recessive), the former has the higher catalase content,  $K \times 10^{-3}$  at 0° in 10-day seedlings being about 45 for the green and from 7 to 23 in the white. This is the first instance of enzyme activity occurring as a Mendelian factor. K. V. THIMANN.

**Reducing power of the roots of Gramineae: reduction of calcium nitrate.** III. G. SANI (Atti R. Accad. Lincei, 1929, [vi], **10**, 197—201; cf. A., 1920, i, 209).—The reduction of calcium nitrate by pulped maize roots is inhibited by small proportions of potassium hydroxide, chloroform, or formaldehyde, and also by heating or drying. In small quantity, citric acid enhances the action, but sulphurous acid is without effect. The reaction of the medium changes from acid to alkaline during the reduction, the ultimate arrest of the change being probably due to the alkalinity. T. H. POPE.

**Evolution of nitrogen during germination.** R. BONNET (Bull. Soc. Chim. biol., 1929, **11**, 1025—1061).—A more detailed account of work already published (A., 1929, 1204).

**Histochemical investigation of the tanning material in the leaves of *Carpinus betulus* at different times.** A. NIETHAMMER (Biochem. Z., 1929, **216**, 462—466).—Considerable amounts of tannins are present in the leaves of *C. betulus* during the whole growth period and are detectable in both the epidermis and the parenchyma.

P. W. CLUTTERBUCK.

**Variation of the cellular permeability of a ligneous plant during growth.** B. SOYER (Compt. rend., 1930, **190**, 205—207).—The permeability of the wood and the leaf of the oak to a solution of potassium nitrate has been measured from May to October. The cell permeability was found to be complementary to the large spring and autumn metabolic activities.

C. C. N. VASS.

**Microchemical reactions for the study of permeability in plants.** A. NIETHAMMER (Mikrochem., 1929, **7**, 314—317).—The microscopical examination of wheat grains which had been soaked in various solutions for different periods of time showed that whilst copper sulphate, mercury chlorophenoxide, and mercury toluenesulphonamide did not penetrate to the interior of the grain, and mercuric sulphate and chloride did so only after a prolonged period of treatment, nickel sulphate and nitrate readily penetrated completely. Potassium thiocyanate resembled the nickel salts in this respect, whilst potassium sulphate could be detected in the embryo only after treatment for 20 hrs.

H. F. HARWOOD.

**Anatomy and microchemistry of the fruit of *Gardenia florida*, L., and other species of *Gardenia* and comparison with the fruit of *Randia dumetorum*, Lam. (*Gardenia dumetorum*, Roxb.).** T. MUNESADA (Arch. Pharm., 1930, **268**, 13—22).—Mainly morphological. A detailed account of the action of various chemical reagents on the different tissues of the fruits of six species of *Gardenia*.

J. W. BAKER.

**Preparation of large microtome sections of hard woods.** H. NIESEMAN (Arch. Pharm., 1930, **268**, 23—24).—The technique of the preparation of large microtome sections of hard woods is described in detail, together with staining processes.

J. W. BAKER.

**Cell walls in wood. I. Structure of the cell wall and distribution of chemical constituents.** G. W. SCARTH, R. D. GIBBS, and J. D. SPIER (Trans. Roy. Soc. Canada, 1929, [iii], **23**, V, 269—279).—By the use of differential solvents the distribution of cellulose, lignin, and pectin has been studied, although the presence of pectin cannot be precluded in the middle lamella from the evidence obtained. In general, those parts which stain more readily with phloroglucinol-hydrochloric acid have a greater resistance to sulphuric acid (e.g., the middle lamella, ray cells, etc.). The presence of hydrochloric acid does not accelerate the rate of removal of lignin by glycerol  $\alpha$ -monochlorohydrin, although it does when ethylene glycol or glycerol is used as solvent. At

ph 5.59 and 4.63 the middle lamella and secondary wall can be distinguished by differential staining. Lignin extraction reduces the tendency to differential staining.

P. G. MARSHALL.

**Cell walls in wood. II. Effect of solvents on permeability of red spruce heartwood.** G. W. SCARTH and J. D. SPIER (Trans. Roy. Soc. Canada, 1929, [iii], 23, V, 281—288).—Untreated air-dried "sapwood" was found to be freely permeable to water, whilst "heartwood" was not permeable to any extent even at a pressure of 100 lb. per sq. in. A very slight increase in the permeability of heartwood was observed after previous boiling in water for 12 hrs. Prolonged extraction with alcohol-benzene mixture, xylene, acetone, etc., to remove resins, followed by boiling water, produced no increased permeability beyond that effected by boiling water alone. Extraction with lignin solvents was equally ineffective.

P. G. MARSHALL.

**Hemicelluloses. I. Hemicelluloses of wheat bran.** F. W. NORRIS and I. A. PREECE (Biochem. J., 1930, 24, 59—66).—Hemicellulose of wheat bran yields four fractions chemically and physically distinct, two of them containing small amounts of uronic acid residues. It was found from hydrolysis experiments that hemicellulose  $B_2$  appears to be a glucosan, whilst the other fractions are largely composed of pentose residue. A method of preparation and purification of hemicellulose is described and is based on the following principle. After removing pectin and lignin from the bran, the hemicelluloses are extracted with sodium hydroxide. Hemicellulose  $A$  is precipitated by acetic acid from the extract, hemicellulose  $B$  by a half volume of acetone from the mother-liquor, and hemicellulose  $C$  by further treatment with acetone. Hemicellulose  $B$  is resolved into hemicelluloses  $B_1$  and  $B_2$ .

S. S. ZILVA.

**Variations in the composition of the fresh branches of *Amelanchier vulgaris*, Moench.** M. BRIDEL and J. RABATÉ (J. Pharm. Chim., 1930, [viii], 11, 49—55).—See this vol., 121.

**Variation of the colour of plants during drying.** Oroberol, a chromogen obtained from *Oberus tuberosus*, L. M. BRIDEL and C. CHARAUX (Compt. rend., 1930, 190, 202—204).—When the leaves are air-dried or exposed to ether vapour they assume a bluish-black colour due to the action of a soluble enzyme on the principal chromogen following plasmolysis. *O. tuberosus* contains two glucosides, *oroboside*, which is hydrolysed by emulsin, and a *glucoside* hydrolysed by rhamnodiastase. The chromogen *oroberol*,  $C_{18}H_{14}O_8$ , m. p. 290°, is isolated from green dried leaves by extraction with boiling 60% alcohol, removal of the alcohol, filtration, and precipitation with sulphuric acid; the precipitate is dissolved in ether, the solution dried and evaporated to dryness, and the residue dissolved in boiling water, from which *oroberol* crystallises. It is optically inactive, and a reducing agent. The colours of its solutions in acid and alkali and with ferric chloride are recorded.

C. C. N. VASS.

**Corylopsin, a crystalline constituent of the bark of *Corylopsis spicata*.** S. HATTORI (Acta Phytocchim., 1929, 4, 327—341).—Corylopsin is ob-

tained in about 5% yield from the bark of *C. spicata* by extraction with 40% alcohol, filtration from tannin-like material which separates after partial concentration, and further evaporation of the alcohol until a thin syrup remains, from which corylopsin,  $C_{13}H_7O_2(OMe)(OH)_6 \cdot H_2O$ , needles from dilute alcohol, is obtained. When recrystallised, it has m. p. 239° after melting with frothing at 145—150° followed by resolidification,  $[\alpha]_D -41.6^\circ$  in methyl alcohol; it reduces Fehling's solution and ammoniacal silver nitrate, decolorises potassium permanganate solution and bromine water, and exhibits the properties of a phenol. It contains a lactone ring and forms a *penta-acetyl* derivative,  $C_{13}H_8O_3(OMe)(OAc)_5$ , m. p. 208—209°,  $[\alpha]_D -33.85^\circ$  in chloroform. Methylation by diazomethane yields dimethylcorylopsin,  $C_{13}H_7O_2(OMe)_3(OH)_4 \cdot 2H_2O$ , m. p. 198—199°, which when oxidised by potassium permanganate in alkaline solution yields an acid,  $C_{10}H_3O_4(OMe)_3$ , m. p. 260—262°, and a lactone,  $C_9H_3O_2(OMe)_3$ , m. p. 76—77°. On treatment with bromine, corylopsin yields a compound,  $C_{14}H_{16}O_9Br_2$ , m. p. 84—85°, and with hydrobromic acid forms an additive compound,  $C_{14}H_{17}O_9Br$ , m. p. 156—157°. Mixed m. p. determinations show that corylopsin and dimethylcorylopsin are respectively identical with bergenin and methylbergenin (cf. Tschitschibabin *et al.*, A., 1929, 574).

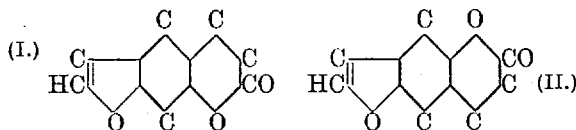
W. O. KERMACK.

**Fluorescent glucosides of *Diervilla diervilla* and *Symphoricarpos occidentalis*.** D. R. McCULLAGH, C. H. A. WALTON, and F. D. WHITE (Trans. Roy. Soc. Canada, 1929, [iii], 23, V, 159—163).—Stems of *S. occidentalis* (wolfberry) are extracted with 85% alcohol and the alcohol is removed, the residue being taken up in water and treated successively with neutral and basic lead acetates. The basic lead precipitate is then decomposed, but all attempts to crystallise the product (a glucoside contaminated with some dextrose) failed. From the products of hydrolysis with hydrochloric acid *æsculetin* (4 : 5-dihydroxycoumarin) was isolated, and showed the typical blue fluorescence in aqueous solution. The glucoside in *Diervilla* (bush honeysuckle) extract can be obtained crystalline (long needles losing water of crystallisation at 201—205°). It gives a more green fluorescence in alcoholic ammonia than *æsculin*. From the hydrolysis products *acetylfraxetin* (m. p. 193—195°) was obtained. The glucoside is therefore *fraxin* (glucoside of the monoethyl ether of trihydroxycoumarin).

P. G. MARSHALL.

**Constituents of the white dittany (*Dictamnus albus*).** H. THOMS and C. DAMBERGIS (Arch. Pharm., 1930, 268, 39—48; cf. A., 1923, i, 639).—From the light petroleum extract of the residue obtained by evaporation of an 85% alcoholic extract of dittany root is isolated a crystalline lactone *fraxinellone*,  $C_{14}H_{16}O_3$ , m. p. 117°,  $[\alpha]_D^{25} -38.39^\circ$ . A further quantity is obtained from the accompanying oil after hydrolysis with alcoholic potassium hydroxide, evaporation, precipitation of acidic and lactic substances with dilute sulphuric acid, and removal of acids with sodium carbonate, and from the balsam fraction in which a small quantity of dictamnolactone is also found, the amount of the latter substance present

being much less than that in the samples of dittany previously examined (*loc. cit.*). Bromination of fraxinellone gives a monosubstituted bromo-derivative,  $C_{14}H_{15}O_3Br$ , m. p. 130°. Although no methoxyl or carbonyl groups can be detected in fraxinellone itself, it is converted by heating with acetic anhydride saturated with hydrogen chloride in a sealed tube at 160—170° into *fraxinellone methyl ketone*,  $C_{16}H_{18}O_4$ , m. p. 169—170°,  $[\alpha]_D^{25} -47.50^\circ$  (p-nitrophenylhydrazone, m. p. 198°), probably by the replacement of a hydrogen of the  $\cdot CH$  group adjacent to the hetero-atom by an acetyl group in a manner similar to that which occurs with coumarin (UNGER, private communication). A further similarity to coumarin is found in the reduction of fraxinellone with sodium and alcohol (the reaction being completed in a sealed tube at 160—180°), when phenolic and non-acidic products are obtained, similar treatment of coumarin yielding coumarin and o-ethylphenol. Oxidation of fraxinellone with various reagents gave no identifiable products, whilst ozonolysis gives an acid and a substance which reduces silver nitrate and forms a p-nitrophenylhydrazone and a semicarbazone. From a comparison of the reactions of fraxinellone and other substances isolated from the *Rutaceae*, xanthotoxin and bergapten, it is considered probable that the new lactone possesses the carbon skeleton I or II.



The composition previously assigned to dictamnolactone is confirmed and, like fraxinellone, it is converted similarly into *dictamnolactone methyl ketone*,  $C_{18}H_{20}O_6$ , m. p. 168° (sinters 155°). From the aqueous solution obtained after evaporation of the alcohol from the original dittany root extract, chloroform extracts dictamnine [hydrochloride, m. p. 195°; chloroplatinate, sinters 210°, not melting at 250° (cf. *loc. cit.*, m. p. 152°); picrolonate, m. p. 178°; chloroaurate, m. p. 152°, decomp. 171°], whilst from the residual aqueous solution potassium bismuth iodide precipitates trigonelline and choline. J. W. BAKER.

**Demonstration of formation of formaldehyde in living plants during chlorophyllic photosynthesis, by means of dimethyldihydroresorcinol.** G. POLLACCI and M. BERGAMASCHI (Atti R. Accad. Lincei, 1929, [vi], 10, 687—689).—Experiments with the aquatic plant, *Elodea canadensis*, in presence of "dimedon" (cf. Klein and Werner, A., 1926, 439), show that formaldimedon is formed when the conditions for photosynthesis under the influence of chlorophyll are fulfilled. Although the dimedon exerts a narcotic influence on the plants, these are not killed but retain their power of assimilation. T. H. POPE.

**New amino-compound in the jack bean and a corresponding new enzyme.** I. M. KITAGAWA and T. TOMIYAMA (J. Biochem. Japan, 1929, 11, 265—271).—See this vol., 121.

**Enzymic substance contained in koji made of rice in different degrees of its polishing.** M. ITO (J. Biochem. Japan, 1929, 11, 111—141).—The koji-enzyme is produced by the reciprocal action of the

*Aspergillus oryzae* and the rice material itself in presence of water. The composition of the ash, carbohydrate, and nitrogenous substances, respectively, is important in determining the starch-liquefying, carbohydrate-hydrolytic, and protein-splitting activity of the enzyme. Koji made from rice in different phases of polishing has different qualities and enzymic activities.

#### CHEMICAL ABSTRACTS.

**Purification of soya-bean protein. II. Influence of water on purification by lower alcohols.** M. MASHINO (J. Soc. Chem. Ind. Japan, 1929, 32, 312B; cf. A., 1928, 436).—The amount of carbohydrate extracted from crude soya-bean protein by aqueous methyl or ethyl alcohol increases with increasing dilution until it reaches a maximum at 70% or at 40% alcohol, respectively. The crude protein extracted also increases with increasing dilution, about threefold and tenfold with the respective solvents. C. W. SHOPPEE.

**Protein content of grass, chiefly meadow fox-tail (*Alopecurus pratensis*), as influenced by frequency of cutting.** F. T. SHUTT, S. N. HAMILTON, and H. H. SELWYN (J. Agric. Sci., 1930, 20, 126—134).—Work during two seasons shows that the protein content of herbage and its digestibility increase with shortening of the period between cuttings, due in the first season to the fact that protein decreases with age, but in the second to incursion of white Dutch clover. Total yields of protein and dry matter per acre tend to decrease with frequency of cutting. E. HOLMES.

**Protein content of grass as related to stage of growth.** F. T. SHUTT (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 133—140).—The results are given of a comparison, for two seasons, of protein and fibre content, and total dry matter and protein in the crops from four plots of pasture cut (a) weekly, (b) fortnightly, (c) every three weeks, and (d) for hay with aftermath. The young grass in (a), (b), and (c) contained 21, 19, and 17% of protein and 19, 21, and 22% of fibre, respectively, in the first season, and in the second season 29, 23, and 21% and 17, 19, and 20%. The increase in protein was associated with an increase of white Dutch clover. Plot (d) gave 10 and 13% of protein, and 29 and 27% of fibre. The total yield of protein per acre was highest from (c) in the first season, and in the second season it was about equal from (a), (b), and (d) and least from (c). Plot (d) gave the highest yield of dry matter, and this yield appears to be inversely proportional to the frequency of cutting. The essential value of the close grazing system lies in furnishing throughout the season pasturage rich in protein of a particularly digestible and nutritious character. R. K. CALLOW.

**Extracts from the woolly-pod milkweed, *Asclepias eriocarpa*.** J. F. COUCH (Amer. J. Pharm., 1929, 101, 815—821).—The poisonous constituent is a complex organic acid, insoluble in water, acids, chloroform, and ether, soluble in aqueous alkalis and in alcohol, non-glucosidal, and non-haemolytic; it contains no amino-group. It is present as a salt which is extracted by hot water; addition of barium hydroxide precipitates the barium



salt from the extract, the precipitate is treated with sulphuric acid to liberate the organic acid, which is extracted by sodium carbonate solution and then reprecipitated by addition of hydrochloric acid.

S. I. LEVY.

**Unsaponifiable matter of ego oil.** M. TSUJIMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 324B).—Ego oil (from the seeds of *Styrax japonica*),  $d_4^{20}$  0.9387,  $n_D^{20}$  1.4814, affords 7.1% of unsaponifiable matter, containing 1.7% of sterols and a substance ("egonol"),  $C_{18}H_{18}O_5$ , m. p. 116° (monoacetyl derivative, m. p. 107°), which contains one methoxyl group. Egonol adds rather less than 2 atoms of bromine in ethereal solution, giving a compound, m. p. 164°; catalytic hydrogenation experiments were inconclusive, and a semicarbazone could not be obtained.

C. W. SHOPPEE.

**Detection of oil in twigs.** R. HAYNES (Stain Tech., 1930, 5, 29).—The penetration of oil applied to dormant twigs was demonstrated by cutting sections about 20  $\mu$  thick which were stained with Sudan IV and then with methylene-blue. The oil is distinguished as brilliant red droplets, very much larger than those of the naturally occurring fat. H. W. DUDLEY.

**Chemical and physical variations of waters of the strait of Georgia in relation to phytoplankton.** A. H. HUTCHINSON, C. C. LUCAS, and M. MCPHAIL (Trans. Roy. Soc. Canada, 1929, [iii], 23, V, 177—187).—The period of greatest diatom quantity normally follows the period of lowest salinity, and the most favourable conditions for phytoplankton growth occur in the 10-yard region, where mixing of the sea-water and Fraser river water takes place. Abundance of phytoplankton lowers the soluble silica and phosphates. P. G. MARSHALL.

**Influence of oxygen on the volatilisation of iodine.** P. DANGEARD (Compt. rend., 190, 131—133).—The emission of iodine by fresh sea-weeds has been examined both in air and in an atmosphere of nitrogen, and is found to be diminished and finally inhibited in the latter. External oxygen is therefore necessary for the volatilisation of iodine. This explains why the most active types of *Laminaria* are found in the most highly aerated waters and why the activity is greater in air than in water.

P. G. MARSHALL.

**Mineral content of the jujube.** M. P. BENOV (J. Agric. Res., 1929, 39, 949—951).—Comparative data are given for the mineral constituents on a moisture-free basis, and of the ash, of dates, seeded raisins, and the jujube or Chinese date, *Zizyphus jujuba*, Mill. E. HOLMES.

**Titanium in cryptogams.** G. BERTRAND and C. VORONCA-SPIRT (Bull. Soc. chim., 1930, [iv], 47, 102—104).—See A., 1929, 1113.

**Copper as an element necessary to plants.** A. QUINTAROLI (Annali Chim. Appl., 1929, 19, 467—469).—The importance of so-called catalytic elements such as iron, manganese, copper, zinc, and arsenic to animal nutrition is discussed, these elements apparently exerting a function analogous to that of the vitamins. Determinations of the proportions of copper and manganese in about 300 Italian soils of different origins and types show that, in general, the

proportion of manganese is ten times that of copper. In the more vital organs of plants, however, the proportion of copper is of the same order as, and often in excess of, that of manganese. In any one plant organ, the amount of copper is comparatively high in the early stages of growth, but it diminishes gradually as the organ ages; the manganese, on the other hand, continuously accumulates. Such organs as seeds, leaves, buds, filiform roots, etc. contain appreciably more copper than secondary organs such as trunks, branches, and shells. T. H. POPE.

**Phosphorus-containing constituents of plants.**

**V. Solubility of the phosphorus-containing constituents of rye embryos.** Z. KOEHLER (Bull. Acad. Polonaise, 1929, B, 237—254).—Air-dried rye embryos have a mean total phosphorus content of 3.11% (calculated as phosphorus pentoxide), whilst that of defatted embryos is 3.548%. Of this latter quantity about 11% corresponds with mineral phosphorus pentoxide, whilst 44% is accounted for as phytic phosphorus pentoxide (cf. A., 1927, 1227). When the defatted embryos are extracted with distilled water about 69% of the total phosphorus passes into the extract. When the extracting liquid is hydrochloric acid the quantity of phosphate in the extract decreases to a minimum of 19% with 0.05% acid and then increases again with increasing concentrations of acid, being 71.42% with 5.0% acid. Dilute sodium hydroxide solution extracts rather less phosphorus than does distilled water. With very dilute acid, distilled water, or alkaline solution, the extracts contain a considerable quantity of plant-proteins, which partly account for the increase in the phosphorus extracted with acid more dilute than 0.05%. W. O. KERMACK.

**Starch-liquefying action of sandal leaf extracts.** B. N. SASTRI (J. Indian Inst. Sci., 1929, 12, A, 251—252).—Healthy leaf extract contains more of the starch-liquefying principle than diseased leaf extract. P. G. MARSHALL.

**Aucuba or yellow mosaic of the tomato plant: reaction of infected juice.** W. F. BEWLEY and B. J. BOLAS (Nature, 1930, 125, 130).—A marked action occurs when the expressed juice from a tomato plant is mixed with an aqueous colloidal solution of tomato chlorophyll; a brown colour develops with apparent destruction of the chlorophyll. The reaction is sensitive to light and is accelerated by an intensity of 800 ft.-candles at 30°. L. S. THEOBALD.

**Spike disease of sandal (*Santalum album*, Linn.). VI. Nitrogen metabolism in healthy and spiked sandal leaves.** N. NARASIMHAMURTHY and M. SREENIVASAYA (J. Indian Inst. Sci., 1929, 12, A, 153—163).—Increases in total water-soluble nitrogen, in basic nitrogen, and in total amino-nitrogen are characteristics of the diseased leaves when compared with normal leaves. E. A. LUNT.

**Spike disease of sandal (*Santalum album*, Linn.). VII. Factors influencing diastatic activity. VIII. Composition of leaf-tissue fluids. IX. Composition of stem-tissue fluids. B. N. SASTRI and M. SREENIVASAYA. X. Seasonal variations in healthy and diseased trees.**

A. V. V. IYENGAR (J. Indian Inst. Sci., 1929, **12**, A, 233—238, 239—244, 245—250, 295—305).—VII. Dialysis of enzyme extracts produces a greater loss of activity in spiked than in healthy leaves. The greater enzymic activity of diseased extracts is due mainly to a decrease in calcium (121.5 mg. per 100 c.c.), increase in phosphate and amino-nitrogen, and increased buffering power with a lower  $p_H$ . Activators are present in spiked leaf extracts, but no inhibitors are found in healthy leaf extracts.

VIII. Healthy leaves give a greater percentage of tissue fluid than diseased leaves, and the fluid has a higher content of ash and calcium, together with a lower content of maltose and reducing sugars.

IX. Spike disease causes variations in composition of the stem-tissue fluid similar to those occurring in leaf-tissue fluid. The high gradient of calcium concentration from stem to leaf tends to disappear after onset of the disease, showing that the mechanism of transport is impaired.

X. The highest ash values are recorded towards the end of the hot spring for the fluid from both diseased and healthy trees, the increase in silica content being particularly marked in disease. The electrical conductivity of diseased tissue fluid is greater than that of fluid from healthy trees. P. G. MARSHALL.

Chemotherapy of organic dyes in plant diseases. G. TRUFFAUT and I. PASTAC (Compt. rend., 1929, **189**, 1013—1015).—Dyes kill parasitic fungi by a process of staining following penetration of the protoplasm. In laboratory experiments Raulin's culture medium is used (with varying additions of dye) and inoculated with *Rhizopus nigricans* or *Penicillium glaucum*. Malachite-green alone is ineffective in preventing growth, as the high surface tension prevents penetration. Soaps and sulphuric acid cannot be used to reduce the surface tension on account of their susceptibility to chemical reagents, but some adhesives recently introduced (eucarnite, iporite, etc.) are effective. Crystal-violet is harmful to the healthy leaves of plants, but auramine kills the parasite without damage to the plants, two or three treatments with the dye solution at intervals of three days being usually sufficient. Wheat blighted by *Tilletia foetens* and *Triciti* is rendered healthy by 2 hrs.' immersion in the dye solution followed by drying; the germinating power is not impaired. P. G. MARSHALL.

Double electrode for micro-determination of hydrogen-ion concentration. L. SMOLIK (Biochem. Z., 1930, **217**, 216—217; cf. A., 1926, 927).—The apparatus has been modified so that determinations can be made using two or three drops of liquid. W. MCCARTNEY.

Silver chloride electrode in contact with Ringer's solution. J. W. LANGELAAN (Arch. Néerland. Physiol., 1929, **14**, 592—597).—The Ag|AgCl electrode, in contact with Ringer's solution, behaves as a reversible chlorine electrode which is insensitive to the sodium hydrogen carbonate of the solution, to dissolved carbon dioxide, and to small amounts of lactic and nitric acids. The value

calculated for the potential of the half-cell with reference to the normal hydrogen electrode as zero is 0.287 volt. C. C. N. VASS.

Micro-determination of iodides in the presence of other salts. J. F. REITH (Biochem. Z., 1929, **216**, 249—268).—A number of methods for the micro-determination of iodine are comparatively investigated. The sensitivity of the iodine-starch reaction, the possibility of the oxidation of hydrogen iodide by air, and the influence of  $p_H$  and concentration of potassium iodide on the thiosulphate titration of very dilute iodide solutions are investigated. Curves summarise the disturbances caused by the presence of nitrites and bromides with the different methods. P. W. CLUTTERBUCK.

Determination of volatile substances. G. GAZENKO (Biochem. J., 1930, **24**, 55—56).—A description of a closed system in which the air is continuously circulated, by means of a pump, until the volatile substance in the solution to be analysed has been completely transferred to, and absorbed in, an appropriate standard solution. H. W. DUDLEY.

Importance of sublimation for pharmacological investigation. E. KEESER and J. KEESER (Arch. exp. Path. Pharm., 1930, **147**, 360—365).—Compounds such as barbituric acid derivatives and other hypnotics and certain alkaloids when injected into a rabbit may be recovered from the brain by careful sublimation, the crystals so obtained being identified by their shape and by micro-chemical reactions. W. O. KERMACK.

Modifications in Mendel and Goldscheider's colorimetric determination of lactic acid. H. J. FUCHS (Biochem. Z., 1930, **217**, 405—408; cf. A., 1926, 212; 1929, 110).—The special sulphuric acid specified by the above authors may be replaced by the ordinary pure acid if the concentration of the veratrol solution is raised from  $\frac{1}{3}\%$  to 20%. Under these conditions the determination is twice as sensitive without losing its specificity. K. V. THIMANN.

Micro-detection of fats. A. NIETHAMMER (Biochem. Z., 1930, **217**, 436—439).—In a modification of the author's method (A., 1929, 1114) the fat is sublimed off directly from the tissue, and the fatty acids of which it consists are identified by their characteristic microcrystalline appearance, of which examples are given. The method can be used for following the changes during ripening of seeds. K. V. THIMANN.

Determination of sucrose by Hanes' modification of the Hagedorn-Jensen method. E. H. CALLOW (Biochem. J., 1930, **24**, 57—58).—The sucrose is inverted and is determined by Hanes' modification (A., 1929, 478). The quantity of invert-sugar present is obtained from a curve giving the relationship of this sugar to the thiosulphate equivalent of the ferri-cyanide reduced. S. S. ZILVA.

Determination of uric acid. L. T. MARGOLIN and S. F. BUCHTEYEV (Zhur. exp. Biol. Med., 1929, **11**, 110—113).—The stability of the sodium cyanide solution used in Benedict's method was examined.

CHEMICAL ABSTRACTS.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

APRIL, 1930.

### General, Physical, and Inorganic Chemistry.

**Bohr's theory of the hydrogen spectral series.** J. JAHZADNICEK (Z. Physik, 1930, 59, 723—724).—A logical presentation of Bohr's original theory.

A. B. D. CASSIE.

**Continuous spectra of hydrogen in relation to the Balmer and Paschen series.** D. CHALONGE and N. T. ZÉ (Compt. rend., 1930, 190, 425—427; cf. A., 1929, 963).—With increase in pressure from 0.3 to 23 mm. in a tube of hydrogen excited by successive similar highly-condensed discharges, the energy distribution curve of the radiations approaches a limit at 18 mm., the secondary spectral lines (of molecular origin) visible at 0.3 mm. having practically disappeared. It was shown that the energy of the continuous spectrum of the Balmer series is distributed uniformly between 3800 and 2600 Å., whilst the continuous spectrum of the Paschen series examined at 20 mm. pressure forms an intense continuous background extending to a (calculated) limit at 9546 Å. It is suggested that the continuous radiation observed at low pressures is the superposition of the continuous spectra of the hydrogen molecule and atom, the latter alone being stable at higher pressures.

J. GRANT.

**New connexion between the absorption spectrum of hydrogen and the many-lined spectrum.** O. W. RICHARDSON (Proc. Roy. Soc., 1930, A, 126, 487—510).—A number of band systems have been found which end on Dieke and Hopfield's *C* level (A., 1927, 89). These systems all have initial states which are identical with one or other of the initial states of the bands which end on the  $2p^1\Sigma$  level (Dieke and Hopfield's *B* level, previously called  $2^1S$ ). The wave numbers of the lines are tabulated. All the five known electronic levels with principal quantum number 4 which go down to  $2p^1\Sigma$  also give rise to bands (in the yellow-green region) with transitions to the *C* state. So far only the  $0' \rightarrow 0''$  bands have been found. Of the levels with principal quantum number  $<4$  which go down to  $2p^1\Sigma$ , bands are found (in the infra-red) which represent transitions from  $3^1A$ ,  $3^1C$ ,  $3^1K$ , and  $3^1O$  to the *C* state. In all cases the  $0' \rightarrow 0''$ ,  $1' \rightarrow 1''$ , and  $2' \rightarrow 2''$  bands occur, and in  $3^1A$  and  $3^1C$  the  $3' \rightarrow 3''$  bands are also represented. The bands in general have *P*, *Q*, and *R* branches, but usually a *P* or *R* branch is weak or missing. A detailed analysis of the bands is made and the electronic transitions of  $H_2$  are considered.

L. L. BIRCUMSHAW.

**Complex  $4d$  of the helium molecule.** E. FERMI (Atti R. Accad. Lincei, 1929, [vi], 10, 515—

517).—From the theory of perturbations the differences between the  $4d$  terms of the helium molecule are calculated and shown to be in good agreement with experiment.

O. J. WALKER.

**Intensity maxima in the continuous helium spectrum.** (Miss) J. M. DEWEY (Physical Rev., 1930, [ii], 35, 155—157; cf. A., 1929, 224).—The displacements of the maxima of continuous atomic spectra to the red have been attributed to stray fields set up by ions and free electrons (cf. A., 1928, 807). The positions of the maxima in the continuous spectrum of helium were measured, using a hot cathode are, in which measurements of ion concentration were made with an exploring electrode. The calculated displacements of the maxima are smaller than those observed; this is probably due mainly to the error in the electron concentration introduced by the discharge avoiding the neighbourhood of the exploring electrode.

N. M. BUGH.

**Intensities of lines in the helium spectrum as a function of the pressure and electron velocity. II.** W. ELENBAAS (Z. Physik, 1930, 59, 289—305; cf. Peteri and Elenbaas, A., 1929, 732).—Data are recorded for the intensities and polarisation of the following lines in the helium spectrum at pressures of 0.04 and 0.1 mm. when excited by electrons from 28 to 250 volts under conditions such that the current density was maintained constant at 0.002 amp. cm.<sup>-2</sup>: 6678, 5876, 5048, 5016, 4922, 4713, 4472, 4438, 4388, 4144, 4121, 4026, 3965, and 3889 Å. R. W. LUNT.

**Intensity measurements in the band spectrum of nitrogen.** W. R. VAN WIJK (Z. Physik, 1930, 59, 313—319).—In the pressure range  $3 \times 10^{-3}$  to 30 mm. the ratio of the statistical weight of the inverse to the direct rotational terms has the constant value 2 independent of the nature of the exciting discharge for the negative nitrogen bands. Measurements with the positive band give the same value for this ratio in the case of the resolved lines of the *R* branch. The intensities in the *R* branches are governed by a Boltzmann distribution law.

R. W. LUNT.

**Intensity measurements in the nitrogen band spectrum.** W. R. VAN WIJK (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1243—1247).—The negative bands are emitted by the positive molecular ion, the more complicated second positive bands by the neutral molecule. To determine the frequency law for the molecular rotational states, intensity measurements were made in the negative bands each of which consists of a *P* and *R* branch only. The

frequency function for the  $n$ th initial state, derived from the intensity measurements, is plotted on a logarithmic scale against  $n(n+1)$ , which is proportional to the rotational energy of the  $n$ th state. The resulting straight line indicates that the frequency function is an exponential function of the rotational energy. Alternating intensities of band lines are illustrated and their explanation is discussed; the value  $h/2\pi$  is found for the nuclear spin, and is confirmed by measurements of the intensities of doublet components of the 3371 Å. band in the second positive nitrogen bands. N. M. BUGH.

**Dissociation energy of oxygen determined from the pre-dissociation of sulphur dioxide.** V. HENRI (Nature, 1930, 125, 275).—The heat of dissociation of oxygen calculated from data previously obtained from the absorption spectra of sulphur vapour and of sulphur dioxide is 126,400 g.-cal., in good agreement with the value obtained from the pre-dissociation of nitrogen peroxide (this vol., 272). L. S. THEOBALD.

**Intensity ratios of the forbidden O III lines in the spectra of the planetary nebulae and novae.** W. GROTRIAN (Z. Physik, 1930, 60, 302—306).—An explanation of the intensity ratios of the forbidden O III lines  $\lambda$  4363, 4959, and 5007 Å. in the spectra of the planetary nebulae and the novae is sought. The conclusion is reached that the life period of the metastable  $^1S_0$  state of the  $O^{++}$  ion must be shorter than that of the  $^1D_2$  state. The absolute values of the life periods cannot be calculated from the data available. For the analogous lines in the N II spectrum,  $\lambda$  5755, 6548, and 6584 Å., the intensity ratios are quite similar to those for the O III lines. A. J. MEE.

**Atmospheric oxygen band at 7600 Å. (A group).** R. M. BADGER and R. MECKE (Z. Physik, 1930, 60, 59—68).—The A group band at 7600 Å. has been photographed and measured. A detailed description of the experimental procedure is given. The wave-lengths and frequencies of the components of the P and R branches of the band are tabulated and compared with results of previous investigators. From considerations of the intensity relationships of the band components, the structure of the band is investigated. Calculated values for the separation of the band lines are in good agreement with observed values. The combination relationships are discussed and it is shown that the band represents a  $^1\Sigma^- - ^3\Sigma^-$  combination as suggested by Mulliken.

W. R. ANGUS.

**Series of combination lines in the neon spectrum.** N. RYDE (Z. Physik, 1930, 59, 836—846).—The combination lines of neon occurring in an electric field have been investigated by the Stark and Lo Surdo methods, and the work of Foster and Rowles (A., 1929, 615) has been extended considerably. More than 100 "forbidden" lines between the wave-lengths 5800 and 4250 Å. have been observed and identified, and for some combinations of the type  $p-nf$  and  $p-ng$  the wave-lengths in the absence of a field have been found by extrapolation. Knowing the  $p$ -terms, it is possible to evaluate the Bergmann and "ultra-Bergmann" terms. Considerably weaker electric fields have been used than those employed by

Foster and Rowles (the field never exceeded 53 kilovolts per cm.). This made possible the observation of certain weak lines which disappear in strong fields, but limited the dispersion that could be used. A square law effect of the field has been demonstrated in the case of several  $n-np$  combination lines.

E. B. ROBERTSON.

**Probable band spectrum of neon.** D. G. DEHAVALÉ (Nature, 1930, 125, 276).—A number of bands in the red apparently due to neon molecules were obtained a year ago when using a neon discharge tube working under a transformer discharge. The bands disappeared when an induction coil was used. They showed no head and consisted of a number of lines at equal frequency intervals; the Q branch was absent, only the P and R branches being developed. The bands appeared at approximately 7393, 7208, 7063, 6963, and 6847 Å. L. S. THEOBALD.

**Intensity relations for alkali doublets.** E. FERMI (Z. Physik, 1930, 59, 680—686).—Theory gives the ratio of the intensity of the alkali doublet components in the principal series as 2 : 1. Experimental results, particularly for caesium, depart from this rule. This discrepancy is explained. A. B. D. CASSIE.

**Actinic strength and spectrum temperature of magnesium ribbon burning in air and of magnesium flash-light.** J. M. EDER (Z. wiss. Phot., 1930, 27, 337—343).—The actinic strength of magnesium burning in air is 413 units (referred to 1 mg. of magnesium and compared with the actinic effect of a standard candle on a silver bromide gelatin emulsion expressed in m.-sec.). The value of 48 found by Beck and Eggert (*ibid.*, 1927, 24, 374) is too low. In pure oxygen the actinic strength of magnesium is almost twice as great. Agfa flash-light powders (magnesium + thorium nitrate) have values of 200—300. The corresponding spectrum temperatures are: magnesium (in air) 3700° Abs., (in oxygen) 4000°; flash-light 3000—3100° Abs. (cf. Arens and Eggert, A., 1928, 1295). O. J. WALKER.

**Spectrum of silicon hydride.** C. V. JACKSON (Proc. Roy. Soc., 1930, A, 126, 373—392).—The conditions most favourable for the production of the silicon hydride band extending from about 4100 to 4200 Å. have been investigated, and photographs have been taken of the spectrum of the arc in hydrogen at pressures between 3 and 9 cm. of mercury. A general catalogue is given of the wave-lengths, intensities, wave-numbers, and classification of all the observed lines in the band. The lines have the wide spacing characteristic of hydride spectra, and lines due to vibrational transitions (0,0) and (1,1) have been identified. The (0,0) band possesses P, Q, and R branches, of which the Q branches are the strongest, whilst only the Q branches appear in the (1,1) band, which is much fainter than the (0,0). The band is of the doublet type and bears a marked resemblance to the CH 4300 Å. band. The electronic doublet separation is, however, much larger than that of CH and the  $\sigma$  type doubling is much smaller. The double origins of the band are approximately at  $v = 24,102$  and  $24,226$  cm.<sup>-1</sup> In addition to the twelve main branches, two satellite branches are found. The analysis indicates that, as with the 4300 CH

band, there is no combination defect present in the silicon hydride spectrum. A notable feature of the band structure is the very rapid decline in intensity of the lines of all the branches after reaching a fairly flat maximum. Some interesting perturbations are found in the lower members of the *P*, *Q*, and *R* branches, which take the form of unexpected fine doubling of some of the lines. The carrier of the spectrum is considered, from theoretical and experimental reasons, to be an unstable molecule  $\text{SiH}$ . The electronic transition is  $^2D \rightarrow ^2P$ , the  $^2P$  level being inverted.

L. L. BIRUMSHAW.

**Luminescence of argon in a side branch of a discharge tube.** I. M. FREEMAN (*Z. Physik*, 1930, 59, 635–637).—A spectroscopic examination has been made of the luminescent glow in a side branch of an argon discharge tube. The spectrum contains lines of both the “blue” and “red” spectra, and is similar to the so-called “white” spectrum. The intensity relations in the several series show that recombination of ions and electrons is of considerable importance in such a side tube.

J. W. SMITH.

**Distribution of intensity in the lines of diffraction spectra, particularly in the iron lines.** P. H. BRODERSEN (*Z. Physik*, 1930, 60, 43–58).—The grating and source of illumination both influence the distribution of intensity in a spectral line. Single lines appear multiple in the photometer record of a plate that is not accurately in the focal plane. This is shown to be a property of the spherical mirror, and so affects all lines equally. The source of light has three influencing factors: (i) Doppler broadening, which leaves the intensity distribution symmetrical; (ii) Stark effect, due to intense electric fields near the poles of an arc, which may give an unsymmetrical intensity distribution; (iii) pressure effect, which leaves the intensity symmetrical but diffuse. Tables showing the errors likely to arise from these causes are given.

A. B. D. CASSIE.

**Secondary standards between 3600 and 3000 Å. in the iron spectrum.** H. PRESENTIN (*Z. Physik*, 1930, 60, 125–136).—Attempts to obtain suitable light sources for interferometer measurements in this region are described. Preliminary values for iron lines are given.

A. B. D. CASSIE.

**Near infra-red spectra of iron, lanthanum, calcium, barium, strontium, magnesium, and their compounds.** J. QUERBACH (*Z. Physik*, 1930, 60, 109–124).—The spectra were photographed with a Rowland grating of dispersion 2.62 Å. per mm., using the plates described by Lucg (this vol., 396). Tables of observed wave-lengths—not always in agreement with results of other workers—are given. Heads in four groups of lanthanum oxide bands and in eight groups of barium fluoride bands were measured, and fit formulae that are given. Bands were also obtained for calcium chloride, fluoride, and bromide, for strontium chloride, fluoride, and bromide, and for magnesium chloride.

A. B. D. CASSIE.

**Anomalous dispersion in band spectra.** E. SEGURÉ (*Atti R. Accad. Lincei*, 1929, [vi], 10, 590–594).—The absorption spectrum of iodine vapour at a temperature slightly above the ordinary has been

measured between 5100 and 5800 Å. The bands show a characteristic festoon structure for which a theoretical expression is derived from the relation between refractive index and the number of dispersion electrons for a given wave-length.

O. J. WALKER.

**Spark spectrum of iodine.** W. KERRIS (*Z. Physik*, 1930, 60, 20–42).—The spark spectrum of iodine was investigated with a Rowland grating, using aluminium iodide, which dissociates under the influence of the discharge, and aluminium electrodes. The resolving power of the grating was sufficient to separate lines differing by 0.12–0.14 Å. The wave-lengths and intensities are compared with those obtained by other investigators. Comparing with an arc spectrum analysis by Turner, the author found lines with a constant difference of  $7600 \pm 5$ , but does not consider them to be arc lines.

J. E. MILLS.

**Regularities in the arc spectrum of hafnium (Hf I).** W. F. MEGGERS and B. F. SCRIBNER (*Bur. Stand. J. Res.*, 1930, 4, 169–175).—Regularities among lines characterising the first spectrum of hafnium (Hf I) have been discovered. Combinations of seven low energy levels with higher excited states account for more than 200 lines. Inner quantum numbers have been assigned to the energy levels and a tentative identification of the seven low levels is suggested.

C. J. SMITHELLS.

**Structure of the first spark spectrum of mercury (Hg I).** G. DÉJARDIN and R. RICARD (*Compt. rend.*, 1930, 190, 427–429).—Paschen's classification of this spectrum (A., 1928, 677) has been modified by the use of the electrodeless discharge (Bloch, A., 1923, ii, 350), and the unclassified lines in the interval 8000–1850 Å. have been shown to fall into two categories of about 50 lines each. (1) Lines belonging to the Hg III spectrum (cf. McLennan, McLay, and Crawford, A., 1928, 1167). (2) First order spark spectrum lines of the group  $E_1'$ , distinguishable from those of the group  $E_1$  by their higher excitation potentials (cf. Valasek, A., 1928, 1167). Lines attributed to the doubly-ionised atom (Hg III) constitute the two groups 5746, 4–3358, 78 and 4212, 22–2769, 22, having the same separation (12,367 cm.<sup>-1</sup>) and corresponding with ( $6p^3F_4 - 6p^3F_3$ ).

J. GRANT.

**Causes of the mercury bands.** S. MROZOWSKI (*Z. Physik*, 1930, 60, 410–413).—Previous work on the ordering of the mercury bands is completed and discussed. The atomic excitation has no effect on the primary spectrum, but plays a very important part in the production of bands.

A. J. MEE.

**Extension of the spectrum of Tl II.** S. SMITH (*Physical Rev.*, 1930, [ii], 35, 235–239; cf. A., 1929, 1119; McLennan and others, *ibid.*, 366).—Spectrograms were made for the range 1900–8000 Å. of the spectrum of Tl II using the metal in a hollow cathode discharge in helium. Newly-found terms  $6s8d^3D_{2,3,1}$ ,  $6s8d^1D_2$ ,  $6s9s^3S_1$ ,  $6s10s^3S_1$ ,  $6s6f^3F_{2,3,4}$ ,  $6s7f^3F$ , and an unclassified term  $2_3^0$  are reported. Absolute term values are calculated from the sequence  $6s6d^3D_2$ ,  $6s7d^3D_2$ ,  $6s8d^3D_2$ ; the ionisation potential is found to be 20.3 volts. Term values, 58 newly-classified lines, and 14 new multiplets arising from the fine structure of the terms are tabulated.

N. M. BLIGH.

**Second spark spectrum of lead.** A. S. RAO and A. L. NARAYAN (*Z. Physik*, 1930, **59**, 687—689).—The work of Smith (A., 1929, 113) on the series regularities in this spectrum is compared with that of K. R. Rao and the present authors (A., 1928, 1067). There is good agreement between the results, except in the assignment of the combination  $1^3P-1^3S$ , but it would appear that Smith uses the present authors'  $1^3S_1$  as  $1^3P_1$ . Arguments are advanced for the authors' view, by comparison with the irregular doublet series of Hg I, Tl II, and Pb III. Interchanging Smith's  $1^3S_1$  and  $1^3P_1$  levels brings the two sets of results into complete agreement.

An attempt has been made to identify the singlet spectrum, and a table is given of the lines resulting from the combinations of singlet terms and the intercombinations of singlet and triplet terms.

E. B. ROBERTSON.

**Spectrum of the sunlit auroral rays.** C. STORMER (*Nature*, 1930, **125**, 305; cf. A., 1929, 1120).—A reply to Vegard (this vol., 5). L. S. THEOBALD.

**Stellar absorption lines.** O. STRUVE and C. T. ELVEY (*Nature*, 1930, **125**, 308—309).

**Direct measurement of the shape and width of infra-red spectral lines.** H. BECKER (*Z. Physik*, 1930, **59**, 583—600).—Three of the higher-frequency lines of the hydrogen chloride band at  $1.75\ \mu$  were investigated at 3, 5, 7, 9, and 11 atm. pressure. The method of obtaining these pressures and the precautions necessary to eliminate false bands are described. The shape of the lines is best represented by the function  $1/(1+x^2)$ , where  $x$  is proportional to  $v-v_0$ . The five factors, damping, Doppler effect, intramolecular Stark effect, Lorentz collision broadening, and resonance between neighbouring molecules generally determine the width of a line; at  $1.75\ \mu$  the last two are alone effective. The Lorentz effect increases as the pressure, whilst the resonance effect increases as its square root. At high pressures, the former appears greatest, and  $1.87\ \text{\AA}$ . is the estimated line width due to this effect. The molecular diameter effective in these collisions is then  $10.7\ \text{\AA}$ .

A. B. D. CASSIE.

**Occurrence of a continuous spectrum in the blue and ultra-violet at metal surfaces.** F. ROTHER and W. M. COHN (*Naturwiss.*, 1930, **18**, 155—156).—At the place where a stream of electrons impinges on a metallic surface in a vacuum a bluish-grey glow appears. In a high vacuum a similar but very bright glow can be made to spread over the entire anode surface. Using a hollow cylinder of thorium as anode and a tungsten wire inserted axially as cathode and connecting the electrodes to a high-tension supply, the entire surface emits a bright blue light which is perfectly continuous over the whole spectral range from the blue to the ultra-violet limit of the quartz spectrograph. The spectrum shows its maximum intensity at  $450\ \mu\mu$ . With a high-vacuum arrangement the massive thorium anode becomes red hot, but the intensity distribution indicates the superposition of a temperature radiation on the blue glow which retains its intensity unchanged. The effect is believed to have importance in astrophysics.

R. A. MORTON.

**Series spectra of the lightest elements in the extreme ultra-violet.** A. ERICSON and B. EDLEN (*Z. Physik*, 1930, **59**, 656—679).—A vacuum spectrograph with which spark spectra can be photographed as far as about  $100\ \text{\AA}$ . is described. Some preliminary results are given for the series spectra of the five lightest elements up to and including boron, but it is doubtful whether any lines of helium were obtained.

E. B. ROBERTSON.

**Relative intensities of super-multiplet lines.** J. H. BARTLETT, jun. (*Physical Rev.*, 1930, [ii], **35**, 229—234; cf. this vol., 5; Houston, A., 1929, 480).—Theoretical. A simple method for constructing wave functions for the case of (*jj*) coupling is described. The ordinary multiplet intensity formulæ may be modified to give the relative intensities in a super-multiplet for (*jj*) coupling, and on application to the transition  $(2p)^2 \rightarrow 2p3s$  give results in agreement with those previously found for this case. The sum rules hold generally for non-equivalent electrons, and are examined for the above transition.

N. M. BUGH.

**Theory of light emission of canal rays.** R. SEELIGER (*Naturwiss.*, 1930, **18**, 155).—It is suggested as a working hypothesis that collisions of the second kind play an important part in the emission of light in and from canal rays. Support is lent to this view from the fact that mercury vapour emits the stationary spectrum under any canal-ray bombardment, whilst gases cannot be excited in this way; the low excitation potentials of mercury in conjunction with the idea of inelastic collisions provide a rational basis for this result.

R. A. MORTON.

**Fine structure and the wave-length separation of the  $K_\beta$  doublet in the molybdenum X-ray spectrum.** S. K. ALLISON and J. H. WILLIAMS (*Physical Rev.*, 1930, [ii], **35**, 149—154).—A nomenclature for describing the possible positions of the double X-ray spectrometer is suggested. Experiments on the separation of the  $K\beta$  doublet of molybdenum show that if the line  $K\beta'$  (cf. Davis and Purks, A., 1928, 451) exists, its intensity is less than one tenth that of  $\beta_1$  at 43—46 kilovolts. An average of eight determinations of  $\Delta\lambda$  for  $\text{Mo}K_{\beta_1\beta_2}$  gives  $0.572 \pm 0.003\ \text{\AA}$ .

N. M. BUGH.

**Diffraction of electrons by a molecule.** H. MARK and R. WIERL (*Naturwiss.*, 1930, **18**, 205).—The diffraction of high-speed electrons by metal foils differs essentially from X-ray scattering in two respects. With X-rays, the reciprocal effect is between the light wave and the charge, whilst with electrons the stronger effect between charge and lattice potential is responsible; the relation of the times of exposure for photographing the scattering of electrons and of X-rays by the same substance is as 1 : 10,000. Also the atomic nucleus plays a part in electron scattering. The possibility of obtaining internal molecular interference through the scattering of electrons by a gaseous stream has been considered and it was found that the vapours of chloroform and carbon tetrachloride gave two distinct interference bands, whereas water vapour gave a diffuse scattering. From the results for carbon tetrachloride the distance between the chlorine atoms has been evaluated. The



value obtained is 3.14 Å., in good agreement with the value, 3.3 Å., which Debye, Bewilogua, and Erhardt (Physikal. Z., 1929, 30, 84) obtained from considerations of X-ray scattering by carbon tetrachloride. W. R. ANGUS.

**J-Phenomenon in X-rays.** N. S. ALEXANDER (Proc. Physical Soc., 1930, 42, 82—96).—Evidence for and against the existence of the *J*-phenomenon and its relation to the Compton effect are reviewed critically. The work of Barkla and others was repeated, using heterogeneous radiations of various degrees of hardness from gas and Coolidge bulbs, filtered by aluminium and copper, and unfiltered, with scatterers of aluminium, paper, and paraffin wax. No evidence of the *J*-phenomenon was obtained, indicating that the necessary special experimental conditions were not realised (cf. Gaertner, A., 1927, 911). N. M. BLIGH.

**Scattering of X-rays by gases. II.** G. HERZOG (Helv. phys. Acta, 1929, 2, 217—256; Chem. Zentr., 1929, ii, 2149).—The scattering of X-rays in hydrogen, carbon monoxide, nitrogen, ethane, acetylene, argon, nitrous oxide, and carbon dioxide has been compared with that in air. The scattering coefficient increases with the wave-length and differs for gases with the same electronic number. The intensity of scattering by molecules is not the sum of that by the atoms. A. A. ELDRIDGE.

**New kind of photo-cell.** B. LANGE (Physikal. Z., 1930, 31, 139—141).—Radiation strikes a plane metallic collector and the liberated photo-electrons traverse a very thin layer of a unipolar half conductor which is in close contact with a second plate of metal. A cell with copper electrodes and a film of cuprous oxide between the plates is very sensitive to radiations between 500 and 1500  $\mu$ , the spectral sensitivity curve showing a sharp maximum at 800  $\mu$ . The new cell has many advantages, as may be seen from a comparison with alkali cells. The threshold wave-length of the new cell is 6600  $\mu$  as against 600  $\mu$ ; the work of release for an electron is 0.19 as against 2.0 volts, whilst the quantum yield is 22.5 as against 2.04 coulombs per g.-cal. R. A. MORTON.

**Electron counting tube.** A. K. DAS and K. WÖLCKEN (Physikal. Z., 1930, 31, 136—139).—An improved Geiger-Müller electron counting tube is described, with details concerning the circuit. The sensitivity of the method has been determined in relation to the  $\gamma$ -rays of radium. The mass absorption coefficient  $\mu/Q$  for these radiations in lead and also the variation of radiation intensity with distance are in conformity with earlier work. R. A. MORTON.

**Probability and critical potentials for the formation of multiply-charged ions in mercury vapour by electron impact.** W. BLEAKNEY (Physical Rev., 1930, [ii], 35, 139—148).—A series of  $i/m$  curves was constructed for electron velocities from 35 to 350 volts, which show maxima for the ions  $Hg^+$ ,  $Hg^{2+}$ ,  $Hg^{3+}$ ,  $Hg^{4+}$ , and  $Hg^{5+}$ . By plotting the areas under the peaks as a function of the electron velocity and extrapolating to zero, the ionising potentials for single impact were found to be 10.4, 30, 71, 143, and 225 volts, respectively. Curves are given

for the fraction of the total positive ion current carried by each type of ion as a function of the electron velocity, and for the fraction of the total number of ions carrying one, two, three, four, and five charges; at 400 volts the values are 77, 16.5, 4.4, 1.3, and 0.8%, respectively. The probability of ion formation and the effective cross-section of the mercury atom towards an ionising collision are obtained from curves of the number of each type of ion, per electron, per cm. path, per mm. pressure at 0° as a function of the electron velocity (cf. Compton, A., 1926, 769; Jones, A., 1927, 708). N. M. BLIGH.

**Effect of nitric oxide on the photo-electric sensitivity of potassium.** R. FLEISCHER and H. TEICHMANN (Z. Physik, 1930, 60, 317—319).—The effect of the addition of nitric oxide on the photo-electric sensitivity, the long-wave photo-electric limit, and the selective maximum of potassium was investigated. The nitric oxide was left in contact with the potassium for 15 min. and was then pumped out. There was a great increase in the photo-electric sensitivity in the ultra-violet. The experiments described may serve for the construction of a potassium cell strongly sensitive to the ultra-violet. A. J. MEE.

**Photo-effect in the K shell of the atom, with special reference to the acceleration of the photo-electron.** A. SOMMERFELD and G. SCHUR (Ann. Physik, 1930, [v], 4, 409—432).—Mathematical. Wentzel has obtained a distribution function for photo-electrons symmetrical with regard to the direction of the incident polarised light. When short wave-length light is dealt with, however, an extra term must be added which makes the function unsymmetrical. This additional term involves a displacement  $\gamma$ . The size of this may be compared with that ( $\gamma_0$ ) given by the classical theory, and based on the pressure of light. Wentzel's work gives  $\gamma = \gamma_0$ . With the necessary corrections the application of wave-mechanics gives  $\gamma = 2\gamma_0$ . Thus the photo-electron receives on the average double the number of forward impulses that it receives from the radiation. Experimental work, as far as it concerns the K shell of different atoms, is in agreement with this conclusion. A. J. MEE.

**Direction distribution of photo-electrons of the L shell.** G. SCHUR (Ann. Physik, 1930, [v], 4, 433—442).—Mathematical. A continuation of the foregoing work for the L shell (cf. preceding abstract). A. J. MEE.

**Non-stationary treatment of the photo-effect.** H. BETHE (Ann. Physik, 1930, [v], 4, 443—449).—Mathematical. There has been some discrepancy between the results of the "stationary" and "non-stationary" treatment of problems by wave-mechanics. The Dirac method is here used to apply the non-stationary treatment to the photo-effect. The phenomenon can be completely described by the method, which yields results similar to those of the stationary treatment. A. J. MEE.

**Surface heat of charging.** K. F. HERZFELD (Physical Rev., 1930, [ii], 35, 248—258; cf. Tonks, A., 1928, 1068; Bridgman, *ibid.*, 213).—Mainly mathematical. The surface heat of charging and the

temperature variation of the photo-electric threshold are connected with the deviation of the thermionic emission constant from the theoretical value, and the effect is explained as being partly due to thermal expansion of the material and the dependence of the work function on the volume. N. M. BLIGH.

**Ionisation in the upper atmosphere ; variation with longitude.** E. O. HULBERT (Physical Rev., 1930, [ii], 35, 240—247; cf. *ibid.*, 1929, [ii], 34, 1167).—Theoretical. Changes in the ionisation in the upper atmosphere with longitude are calculated theoretically. An expression is found for the variation during daylight of the maximum electron density with latitude and longitude, which gives skip distances of short wireless waves approximately in agreement with observation. N. M. BLIGH.

**Neutralisation of space charge by positive ions in caesium vapour.** V. E. WHITMAN (Bur. Stand. J. Res., 1930, 4, 157—167).—The neutralisation of space charge by positive ions formed by photo-electric ionisation of caesium vapour, for higher pressures and lower voltages than those used by Kingdon (Physical Rev., 1923, [ii], 21, 408), was studied as a function of pressure, light intensity, anode voltage, and cathode emission. An empirical relation,  $I/\Delta i = K(i + \Delta i)$ , where  $I$  is the intensity of light,  $\Delta i$  the change in anode current  $i$ , was found to fit the experimental results if the constant  $K$  is chosen appropriately. C. J. SMITHIELLS.

**Excitation function of mercury collision luminosity.** K. SIEBERTZ (Physikal. Z., 1930, 31, 141).—The intensities of the mercury lines 4047, 4078, 4358, and 5461 Å., excited by collisions with electrons of known velocity from 10.6 to 15 volts at intervals of 0.2 volt, have been determined from photographic records by means of a registering photometer. The intensity/voltage curves all exhibit two maxima. The second maximum is more sensitive to pressure changes than the first and is regarded as a recombination effect. Polarisation can at most modify the results in a quantitative sense only. R. A. MORTON.

**Dissociation by collision with positive ions.** A. LEIPUNSKI and A. SCHECHTER (Z. Physik, 1930, 59, 857—863).—Ions of the alkali metals, when of sufficient energy, may dissociate hydrogen molecules. The energy required for activation indicates that this dissociation is a process secondary to the excitation of hydrogen molecules. A. B. D. CASSIE.

**Unsymmetrical angular distribution of doubly-reflected electrons.** E. RUPP (Naturwiss., 1930, 18, 207).—Electrons incident successively at small angles at two gold surfaces show a polarisation effect when their velocity is sufficiently high, and the results agree qualitatively with Mott's theory. A. B. D. CASSIE.

**Power of reflexion and reflexion polarisation of electron waves.** W. ALEXANDROW (Z. Physik, 1930, 60, 387—394).—Mathematical. Using Frenkel's method the reflexion phenomena of electron waves are calculated from the assumption of a constant potential change at the boundary between two media. A. J. MEE.

**Reflexion of electron waves at thin sheets.** W. ALEXANDROW (Z. Physik, 1930, 60, 395—401).—Mathematical. The subject is treated from the point of view of wave-mechanics, making use of Frenkel's work. A. J. MEE.

**Ionic mobilities in chlorine and in chlorine-air mixtures.** L. B. LOEB (Physical Rev., 1930, [ii], 35, 184—192; cf. A., 1928, 809, 932).—With additional precautions and using chlorine carefully dried and purified from hydrogen chloride, the values of the mobilities in pure chlorine for positive and negative ions were 0.654 and 0.510 cm./sec. per volt/cm., respectively, in agreement with the work of Mayer (cf. A., 1926, 878; 1927, 1001), and contrary to the theory of Loeb and Condon. A study of mixtures of dry air and chlorine showed that less than 0.1% of chlorine reduced the negative ion mobility below that of the positive ion. The positive mobilities were little affected by the presence of chlorine molecules, the ions obeying Blanc's law, but the lowering of the negative ion mobility must be due to the formation of large and stable chlorine-molecule clusters about the ion, by an unexplained electrochemical mechanism, and not to the existence of an unsymmetrical dipole of large moment in the chlorine molecule. N. M. BLIGH.

**Optical determination of the effective cross-section of helium atoms for slow electrons.** L. S. ORNSTEIN and W. ELENBAAS (Z. Physik, 1930, 59, 306—312).—By suitable choice of experimental conditions the mean free path of slow electrons in helium can be derived from observations of the diminution of the light emission of helium, when exposed to electrons of velocities from 30 to 70 volts in a field-free space, as a function of the distance from the electron source. The value thus obtained is 0.70 cm., corresponding with an effective diameter of  $14.3 \text{ cm.}^2 \text{ cm.}^{-3}$ , whilst that given by Ramsauer is  $9 \text{ cm.}^2 \text{ cm.}^{-3}$ . R. W. LUNT.

**Resistance to motion through gases of metallic particles of high density.** F. EHRENHART and E. WASSER (Z. Physik, 1930, 59, 727—730).—A discussion of experimental results and their deviation from the Stokes-Cunningham law, which applies to particles of radius much greater than the mean free path of the gas molecules, and from the Knudsen-Weber law, which applies to particles of radius comparable with the mean free path of the gas. A. B. D. CASSIE.

**Determination of the law of resistance to motion through gases for gold particles of  $1$  to  $2 \times 10^{-5} \text{ cm.}$**  M. SLOPKOVITZER (Z. Physik, 1930, 59, 754—770).—Ehrenhaft's condenser method was used, and a valid resistance law obtained. The charge on each particle varied from 1.04 to  $3.96 \times 10^{-10}$  o.s.u. A. B. D. CASSIE.

**Determination of the resistance law for submicroscopic platinum particles of the order of  $10^{-5} \text{ cm.}$**  S. VIRTEL (Z. Physik, 1930, 59, 771—806).—Platinum particles of uniform structure were obtained from an electric arc. The results and their deviations from the linear and exponential resistance laws are discussed. A. B. D. CASSIE.

**Magnetic moment of the atomic nucleus.** E. FERMI (*Z. Physik*, 1930, **60**, 320—333; cf. Hargreaves, A., 1929, 972).—Theoretical. By calculating the theoretical hyperfine structure of the alkali atoms and comparing with the experimental values, the magnetic moment of the nucleus can be calculated. The method was applied to sodium and caesium of which the hyperfine structure was known (cf. Jackson, A., 1929, 1). The hyperfine structure of rubidium has recently been investigated (cf. Filippov and Gross, A., 1929, 365), and the same method can be applied.

A. J. MEE.

**Diamagnetism of halogen ions.** G. FOEX (*Compt. rend.*, 1930, **190**, 481—483).—The ionic susceptibilities of the halogens have been calculated as  $\frac{8}{7}$ ths of the atomic susceptibility deduced from Pascal's determinations (cf. A., 1911, ii, 367), and the values obtained agree within the limits of experimental error with the recent determinations of Weiss (this vol., 277). The method assumes that the orbits of the seven valency electrons of the halogen atom are not affected by the arrival of the eighth electron, and that this last has a similar orbit; also that the susceptibility is not altered by the union of the two atoms to form the molecule. C. A. SILBERRAD.

**Pseudo-components of hydrogen.** A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 603—609).—See A., 1929, 982.

**Pseudo-components of hydrogen. II, III.** A. SMITS (*Physikal. Z.*, 1930, **31**, 172—177, 178—180; cf. A., 1929, 982).—II. The hydrogen system is treated from the point of view of the phase rule. Pressure-composition and temperature-composition curves are given for the system.

III. The conditions of equilibrium of the hydrogen components (para and ortho) are discussed. It is difficult to say when the state of inner equilibrium has been reached. It is only by the use of certain catalysts that it is possible to ensure that a quantity of hydrogen remains in inner equilibrium during a slow temperature change, or some other physical change.

A. J. MEE.

**A third chlorine isotope.** H. BECKER (*Z. Physik*, 1930, **59**, 601—602).—A third satellite to each absorption line of the hydrogen chloride rotation-vibration spectrum is satisfactorily explained on the assumption of an isotope of mass 39.

A. B. D. CASSIE.

**Photometry of mass-spectra and the atomic weights of krypton, xenon, and mercury.** F. W. ASTON (*Proc. Roy. Soc.*, 1930, **A**, 126, 511—525).—With the ultimate aim of investigating the problem of the evolution of matter a study has been made of the relative abundance of isotopes of complex elements. Although it is impossible to obtain a mixture of elements which may be regarded as a fair sample of cosmic matter, it is, on the other hand, practically impossible to obtain a mixture of isotopes which is not a fair sample of a complex element. Details are given of a method by which it is possible to deduce, with fair accuracy, the relative abundance of isotopes from the photometry of their lines in mass-spectra, and numerical results are given for the 6 isotopes of krypton, 9 of xenon, and 7 of mercury.

The isotopic moment of an element is defined as being the sum of the products (abundance)  $\times$  (distance from the mean mass number on the mass scale) for all the isotopes, and is not only roughly proportional to the error to be expected in an atomic weight calculated from the mass-spectrum, but is also an accurate measure of the ease with which the atomic weight may be altered, per unit, artificially by such methods as diffusion or free evaporation. The calculated values of the isotopic moments for krypton, xenon, and mercury are 0.87, 1.71, and 1.40, respectively, whilst the corresponding at. wts., worked out from the abundance results, are  $83.77(5) \pm 0.02$ ,  $131.27 \pm 0.04$ , and  $200.62(6) \pm 0.05$ . That of mercury is in good agreement with the accepted value, but the values for krypton and xenon are very much higher than those in use. It is suggested that those deduced from the densities are about 1% too low, and should be redetermined.

L. L. BIRCHUMSHAW.

**Activation of matter.** G. REBOUL (*Compt. rend.*, 1930, **190**, 374—375; cf. this vol., 129).—The value of  $\lambda$  for the radioactivity induced as previously described (0.0003) being independent of the nature of the metal and conditions of experiment, it is inferred that it must be due to the surrounding medium. Electrified points in that medium act as nuclei of condensation for a pre-existent emanation which then deposits on the metal plate. C. A. SILBERRAD.

**Emission of  $\alpha$ -particles from radioactive nuclei exposed to short-wave radiation.** G. I. POKROVSKI (*Z. Physik*, 1930, **59**, 427—432).— $\alpha$ -Particles have a probability of crossing a nuclear potential barrier the maximum energy of which exceeds that of the particle. The probability of this event is increased if the energy of the  $\alpha$ -particle is increased. Experiment shows that  $\gamma$ - and even X-radiation supply energy enough to increase the emission of  $\alpha$ -particles.

A. B. D. CASSIE.

**Capture of electrons by  $\alpha$ -particles.** A. H. BARNES (*Physical Rev.*, 1930, [ii], **35**, 217—228).—Previous work (cf. A., 1929, 971) is described in detail, and is extended by the use of a second tube allowing a reduction of the time of passage of an  $\alpha$ -particle through the electron stream, the detection of scintillations due to singly-charged and neutral particles, and variation of the velocity of the  $\alpha$ -particle. Single and double electron captures have been observed. For double capture the sum of the kinetic energies due to each electron corresponds with the energy of the quantum states of parhelium and orthohelium types of atom; there is indication of the previously unobserved ground state of orthohelium. For capture to occur the electron must have, due to some external field, a kinetic energy which with respect to the nucleus is either zero or equal to the energy of one of the quantum states of the atom. It was shown that capture takes place in less than  $3 \times 10^{-10}$  sec. in a region of electron density of the order  $10^7$  electrons per c.c.

N. M. BLYTH.

**Radioactivity of various metals from old roofing.** A. BOUTARIC and (Mlle.) M. ROY (*Compt. rend.*, 1930, **190**, 483—485; cf. Maracineanu, A., 1928, 455).—Four samples of lead, two of zinc, and one of

copper sheeting that had been on roofs for periods of 20—95 years were examined. The aluminium base plate of a Szilard electrometer was replaced by plates of the above, and the velocity of discharge noted. When the side of the metal sheeting not exposed to the air was uppermost the rate of discharge was practically the same as with the aluminium (0.3—1.5 in arbitrary units), but with the exposed side uppermost the rate is 3—7. Further, if that side is slightly scraped all radioactive effect is found in the scrapings only. Various explanations are discussed, and it is considered that the most probable cause is fixation of radioactive material from the atmosphere.

C. A. SILBERRAD.

**Existence of unknown disintegration product of radium with penetrating  $\gamma$ -radiation.** O. ERBACHER and H. KÄDING (Z. physikal. Chem., 1930, B, 6, 368—370).—No evidence for the existence of a disintegration product of radium of short life, emitting penetrating  $\gamma$ -rays, as postulated by Peters and Weil (A., 1929, 1124), could be obtained.

J. A. V. BUTLER.

**Foundation of Nernst's hypothesis of the formation of radioactive elements on the basis of wave-mechanics. II.** J. KUDAR (Z. Physik, 1930, 60, 292—297; cf. A., 1929, 621).—Mathematical. The physical meaning of the complex characteristic value for the atom is discussed on the basis of the theoretical resonance phenomenon discovered by Fowler and Wilson. There seems to be a fairly certain basis for the Nernst hypothesis that if an  $\alpha$ -particle approaches an atomic nucleus with a velocity of characteristic value not possessed by the nucleus, the  $\alpha$ -particle is taken up by the nucleus without opposition. A difficulty in Gamow's theory is mentioned.

A. J. MEE.

**Supposed transmutation of lead.** (Mlle.) S. MARACINEANU (Compt. rend., 1930, 190, 373—374).—A reply to Fabry and Dubreuil (this vol., 271).

C. A. SILBERRAD.

**Concentration measurement in monatomic hydrogen, oxygen, and nitrogen.** E. WREDE (Z. Physik, 1929, 54, 53—73).—In principle the method adopted consists in measuring a pressure in equilibrium with the mixture containing monatomic gas. A relatively wide tube connects the vessel containing the mixture with a McLeod gauge; provided the connecting tubing is long enough to prevent monatomic gas reaching the gauge, this indicates the total pressure,  $p_E$ , in the mixture at the temperature  $T_E$ , that is the sum of the partial pressures of monatomic gas  $p_1$ , and undissociated gas  $p_2$ . A second McLeod gauge is connected to the mixture through a small orifice; any monatomic gas which streams through this orifice is rapidly catalytically combined on a metal surface. At equilibrium there is thus a pressure difference established across the orifice; the pressure read on the gauge side is denoted by  $p_0$ , the corresponding temperature being  $T_0$ . It is shown that the pressures are related according to the expression:  $0.293p_1 = p_E[1 - (p_0/p_E)\sqrt{T_E/T_0}]$ . The conditions governing the choice of orifice dimensions are discussed at length; pressures in the range 0.125—0.175 mm. were employed, and for these an orifice

0.02 mm. diam. and 3—4 mm. in length was used. The tube containing the mixed gases and those leading to the McLeod gauges were immersed in a constant-temperature bath in order to eliminate any difference between  $T_E$  and  $T_0$ ; control measurements with neon and undissociated nitrogen established that this condition had been attained. For direct-current discharges in hydrogen (0.13 mm.) the concentration of monatomic gas rises approximately exponentially to a limiting value of  $p_1/p_E = 0.90$  as the mean current density in the tube (25 mm. diam.) is increased to 0.033 amp. cm.<sup>-2</sup> With alternating currents smaller concentrations are found.

In nitrogen, under similar pressure conditions, discharges excited by alternating potentials when suitable capacities were connected in parallel with the discharge tube produced about 2% atomic nitrogen. Periodic discharging of a condenser (50 joules per discharge) through the gas produced mean concentration of monatomic gas of 30—35%. If the periodic discharging be superimposed on a relatively weak alternating-current discharge the yield is diminished by half; this is attributed to the processes  $N + N_2^+ \rightarrow N_3^+$ ,  $N_3^+ + N \rightarrow N_2 + N_2^+$ . In oxygen at pressures of the order of 0.15 mm. a concentration of 25% of monatomic gas is readily attained by direct- or alternating-current discharges of mean density  $0.3 \times 10^{-3}$  amp. cm.<sup>-2</sup>; at higher current densities the yield of monatomic gas is somewhat increased, but disturbing effects set in which are thought to be similar to the "recombining" effect of some discharges observed now in the case of nitrogen. The life period of monatomic oxygen is shown to be one third to one half that of monatomic nitrogen.

R. W. LUNT.

**Concentration measurements in monatomic hydrogen, nitrogen, and oxygen.** P. HARTECK (Z. Physik, 1929, 54, 881; cf. A., 1929, 253; Wrede, preceding abstract).—Independent use of the method of determining the concentration of hydrogen atoms is claimed.

A. J. MEE.

**Dirac's wave-mechanical theory of the electron and its revision in terms of field theory.** C. LANZOS (Physikal. Z., 1930, 31, 120—130).—A theoretical discussion of Dirac's theory in relation to the unitary field theory.

R. A. MORTON.

**Quantum defect and ultimate lines of the elements of the iron period.** M. A. CATALÁN (Anal. Fis. Quím., 1930, 28, 83—100).—The quantum defects of the elements from calcium to zinc, calculated from the values of the Rydberg denominators, exhibit for the different electronic states a regular increase. The relationship between the intensities of the ultimate lines and the spark limits is discussed; the intensity of an ultimate line is proportional to the difference between the spark limit of the transition from which it arises and the adjacent spark limit.

H. F. GILBE.

**Structure of molecular states from atomic states and dissociation into these.** W. WEIZEL (Z. Physik, 1930, 59, 320—332).—A general rule is given for determining molecular terms from terms of the separated atoms. This rule includes those of Herzberg and Hund as special cases. Molecular

terms may in general be allocated in more than one way, and dissociation has corresponding possibilities. Molecules in a given state may dissociate into atoms in several different states. Examples are hydrogen and helium.

A. B. D. CASSIE.

**Some new results of atomic physics and atomic chemistry.** E. BRÜCHE (Z. angew. Chem., 1930, 43, 1—6).—A review of recent work and theories with especial reference to the sphere of activity of atoms.

A. R. POWELL.

**Anomalous behaviour of the nitrogen nucleus.** R. DE L. KRONIG (Naturwiss., 1930, 18, 205).—The anomalous behaviour of the nitrogen nucleus is very probably due to the fact that it not only behaves according to statistical laws, but also possesses an abnormal resultant angular momentum.

W. R. ANGUS.

**Ratio of the masses of the proton and electron.** H. GREINACHER (Z. Physik, 1930, 60, 285—291).—Mathematical. Using Fürth's method (cf. A., 1929, 1360), but with a different assumed electron structure, a value for the ratio of the masses of the proton and electron is found.

A. J. MEE.

**Quantum mechanics of energy transitions.** H. KALLMANN and F. LONDON (Z. Physik, 1930, 60, 417—419).—Polemical. Frenkel's work gives an effective cross-section for the molecule of  $10^{-10}$  cm.<sup>2</sup>, which is about a million times that given by the gas-kinetic method.

A. J. MEE.

**Possibility of establishing the magnetic moments of free electrons.** F. KNAUER (Z. Physik, 1930, 59, 807—811).—A theoretical consideration of the possibility of measuring the magnetic moments of free electrons by means of a beam of electrons by compensating the deviation in an electric field. With this fundamental arrangement it should be possible to measure the magnetic moments experimentally, given uniformity of velocity with magnitude and direction.

J. FARQUHARSON.

**Measurement of weak ultra-violet intensities.**

E. WEYDE, W. FRANKENBURGER, and W. ZIMMERMANN (Naturwiss., 1930, 18, 206—207).—Leucocyanide solutions of triphenylmethane dyes become intensely coloured on exposure to ultra-violet light. A leucocyanide solution of crystal-violet was irradiated with monochromatic light from a mercury arc and the amount of colouring determined colorimetrically by comparison with a solution of known concentration. Measurements were made throughout the absorption range and at temperatures from  $-6^{\circ}$  to  $36^{\circ}$ . This method is used as a means of measuring very weak ultra-violet intensities.

W. R. ANGUS.

**Spectrum of boron monoxide.** W. SCHEIB (Z. Physik, 1930, 60, 74—108).—The spectrum from a carbon arc fed with borax, photographed between 3600 and 7000 Å. with a concave grating, was found to contain bands ascribed by Mullikan to boron monoxide. The spectrum consists of three band systems, the  $\alpha$ -double bands, the  $\beta$ -single bands, which are both degraded towards the red, and the combination bands degraded towards the violet. Tables are given for rotation lines in the respective *P*, *Q*, and *R* branches, and the results are discussed.

A. B. D. CASSIE.

**Intensity relationships of NO bands.** R. SCHMID (Z. Physik, 1930, 59, 850—856).—A comparison of the direct intensity measurements of the  $\gamma$  band (band head at  $\lambda=2477$  Å.) with the intensity distributions calculated from Hill and Van Vleck's formulae. The relative intensities of the  $\beta_1$ ,  $\gamma_1$ , and  $\delta_1$  band heads lying in the far ultra-violet are likewise discussed.

W. R. ANGUS.

**Dispersion frequencies of alkali halide crystals in the Schumann region.** R. HILSCH and R. W. POHL (Z. Physik, 1930, 59, 812—819).—The condensation method (cf. A., 1929, 1214) was used to obtain thin crystalline layers of the chloride, bromide, and iodide of lithium, sodium, potassium, rubidium, and caesium. A double monochromator was used to obtain absorption spectra up to 160 m $\mu$ . Absorption spectra are similar for the same halide of different metals. The results are discussed, but the theoretical significance of several maxima for each halide is obscure.

A. B. D. CASSIE.

**Light absorption of nitrophenols. II. In acid solutions (and in organic solvents). III. In concentrated salt and alkali solutions.** J. EISENBRAND and H. VON HALBAN (Z. physikal. Chem., 1930, 146, 101—110, 111—130; cf. this vol., 272).—II. The absorption spectra of mono- and di-nitrophenol and of picric acid have been measured in acid solutions. In this case the change in the light absorption due to the introduction or removal of nitro-groups is the same as was found in alkaline solutions, and is independent of whether the nitrophenol is in the dissociated or undissociated form. There are considerable differences between the spectra of undissociated nitrophenols and those of the corresponding nitroanisoles. The first absorption band of nitrophenols is principally due to the nitro-group, the second one to the benzene nucleus.

III. Considerable differences are observed in the absorption bands of nitrophenols in concentrated alkali and salt solutions compared with those in dilute solutions. In salt solutions the bands are displaced, but the regular change due to introduction of nitro-groups is maintained. In the concentrated alkali solutions, however, the regularity found with dilute solutions no longer holds, but there is a relationship between the acidic strength of the nitrophenol and the spectral effect of the salt or alkali. In the case of picric acid, with increase of alkali concentration a new long wave-length band appears, which resembles the absorption band of trinitrobenzene in alkaline solution. Extinction coefficient measurements indicate a value of  $10^{-15}$  to  $10^{-16}$  for the "second dissociation constant" of picric acid.

O. J. WALKER.

**Absorption spectra of diphenyl and some derivatives.** T. C. C. ADAM and A. RUSSELL (J.C.S., 1930, 202—206).—The absorption spectra of the following compounds have been examined: diphenyl, 2- and 4-nitro-, 4-amino-diphenyl and its hydrochloride, 4-fluoro-, 4-chloro, and 4-bromo-, 4-diphenyl-, 4'-nitro-4-diphenyl-, and 2-2'-diphenyl-diphenyl. The results support the view that valency oscillation takes place but does not involve the 4-position, since the same band is shown by the 4-derivatives as by diphenyl

itself, minor disturbances alone being observed. The 2-derivative and more especially the 2-2''-derivative give extremely shallow bands, due to a suppression of the valency oscillation by the introduction of these groups. M. S. BURR.

**Spectrochemistry of rufin and its derivatives.** C. DIÉRE, C. BAUMELER, and A. SCHNEIDER (Compt. rend. Soc. Biol., 1928, 99, 722—725; Chem. Zentr., 1929, ii, 1799).—The absorption spectrum of the orange-red pigment of *Arion rufus* and the effect of addition of acid or alkali are described.

A. A. ELDRIDGE.

**Tesla-luminescence spectrum of benzene.** I. A. BLACK (Nature, 1930, 125, 274).—Of 110 bands recorded for the Tesla-luminescence spectrum of benzene, 87 can be represented by the formulae  $\nu = 38613 + 924n' - 161n'' - 994n'''$ ;  $\nu = 37547 + 924n' - 161n'' - 986n'''$ ;  $\nu = 36476 + 924n' - 160n'' - 990n'''$ , where  $n'$ ,  $n''$ , and  $n'''$  have integral values from 0 to 6 (cf. Shapiro, A., 1929, 1127).

L. S. THEOBALD.

**Ultra-violet absorption spectrum of chlorophyll.** D. VAN GULIK (Ann. Physik, 1930, [v], 4, 450—452).—The ultra-violet absorption of chlorophyll has been measured using a continuous spectrum. Curves were drawn connecting the absorption coefficient,  $E$ , with the wave-length, and the absorption constant,  $A$ , with the wave-length. There are two minima in the visible spectrum, and in the ultra-violet there is a deep minimum before the actual "end" absorption occurs. It is a question whether in plant life this latter absorption contributes to the assimilation, or whether it merely serves to protect certain cells from the injurious effect of the rays.

A. J. MEE.

**Behaviour of natural and artificial pearls in ultra-violet light.** J. A. A. LEROUX, E. RAUB, and K. W. FRÖHLICH (Z. Physik, 1930, 60, 307—312).—It is possible to distinguish between natural and artificial pearls by the use of ultra-violet light. The apparatus is described. The method depends on the determination of the presence of a natural pearl nucleus. An examination of the form of the transmitted light enables this to be done. In no case does an artificial pearl give the same type of diagram as a natural pearl.

A. J. MEE.

**Infra-red transmissivity of thin sputtered films and of organic substances below  $3\mu$ .** E. RÜTTEN (Z. Physik, 1930, 60, 1—12).—The transmissivity of a number of sputtered films and organic substances has been investigated by a fluorite prism spectrometer in the region 0.7— $3.0\mu$  in the hope of finding suitable filters for infra-red photography. The preparation of films sputtered on glass plates is described, and films of selenium, tellurium, carbon, silver, and gold were studied. The transmission of a selenium film is 80% throughout the whole range. Tellurium and carbon films gave characteristic "colloidal" curves and showed increased transmission as the wave-length increased. The author's results for carbon do not agree with results previously obtained for allotropic modifications. The transmissivity of silver and gold varied according to the colour of the films obtained. The inability of exactly

reproducing metal films makes their application as filters difficult.

Various dyes have been investigated also. Filters were prepared by dipping films of gelatin in 1% solution of the dye for 5—10 min., then thoroughly washing with water. Cellophane and asphalt also were investigated as "dye-carriers." Filters were prepared with a variety of dyes. Filters impregnated with dilute solutions of the dyes showed that the strong absorption of visible light was soon superseded by good transmission of infra-red radiation. A nigrosine-gelatin filter was practically impervious at 1.1 and transmitted 80% between 2.0 and  $2.6\mu$  and would therefore make a very serviceable filter for this region. W. R. ANGUS.

**Infra-red absorption and the structure of very thin sputtered metal films.** T. DREISCH and E. RÜTTEN (Z. Physik, 1930, 60, 69—73; cf. preceding abstract).—Gold and silver films have been prepared in atmospheres of hydrogen, nitrogen, and carbon dioxide and it is shown that the colour of the film is independent of the atmosphere in which it is sputtered, but depends on the duration of sputtering, the current strength, and the thickness of the film. When parts of the mirror were considerably heated during preparation these parts displayed a different colour from the cool portions. As the wave-length is increased the transmissivity of the thinner films increases, whereas the thicker films show a decrease of transmission. One curve is obtained for a gold film which does not alter with increasing wave-length. This is attributed to a superposition of two curves characteristic of different modifications of the metal. The curves obtained for the very thin films are similar to the curve which Coblenz obtained for colloidal silver. It is therefore suggested that the sputtered particles of thin films are colloidal. The results agree with Falkenhagen's theory that, in sputtering, colloidal particles are deposited until a certain concentration of the metal is reached, after which the deposited particles are metallic.

W. R. ANGUS.

**Sensitising photographic plates, and photographs of some near infra-red spectra.** P. LUEG (Z. Physik, 1930, 60, 13—19).—Treatment with dicyanine gives cloudy plates. Neocyanine is sensitive to radiation of wave-length between 6000 and  $9000\text{Å}$ . The necessary treatment is described. These plates may be used up to  $10,000\text{Å}$ . if first treated with dilute sulphuric acid. Some photographs are reproduced, and the arcs used are described.

A. B. D. CASSIE.

**Methods of excitation of Raman spectra.** R. W. WOOD (Trans. Faraday Soc., 1930, 26, 99—100).—An apparatus suitable for use with small quantities of liquid is described. R. CUTHILL.

**Method of observing the Raman effect in liquids.** J. ZAHNADNÍČEK and B. VLACH (Z. Physik, 1930, 60, 402—404).—An arrangement of apparatus for investigation of the Raman spectra of liquids is described. With benzene and water, the Raman lines and bands appeared on both sides of the spectral line  $4358\text{Å}$ . after 2 and 15 hrs.' exposure, respectively. A. J. MEE.



**Constitution of liquid ammonia.** A. DADIEU and K. W. F. KOHLRAUSCH (Naturwiss., 1930, 18, 154—155).—Raman spectra indicate a frequency of  $2920\text{ cm}^{-1}$  for liquid or gaseous methane and  $1340$ ,  $1620$ ,  $3000$ ,  $3080\text{ cm}^{-1}$  are frequencies characteristic of liquid or gaseous ethylene. Gaseous ammonia exhibits one frequency at  $3330\text{ cm}^{-1}$ , but in the liquid state frequencies near  $1070$ ,  $1580$ , and  $3200$ — $3400\text{ cm}^{-1}$  (3 lines) are shown. It is calculated that the linking  $\text{H}_3\text{N}\cdot\text{NH}_3$  corresponds with the frequency  $1070$ , the compound  $\text{H}_3\text{N}\cdot\text{NH}_3$  with the  $1580$  frequency, and the X-H linking with frequencies between  $2900$  and  $3400\text{ cm}^{-1}$ . Hence liquid ammonia is regarded as a mixture of the dimeric compound with quinquivalent nitrogen, and a dimeric form in which the  $\text{NH}_3$  groups are held together by secondary valencies or in which the nitrogen is quadrivalent.

R. A. MORTON.

**Theory of molecular scattering of light in crystals (classical theory).** L. MANDELSTAM, G. LANDSBERG, and M. LEONTOWITSCH (Z. Physik, 1930, 60, 334—344).—The scattering of light in crystals is explained as being due to alterations in the elastic oscillations of the crystal. On scattering the frequency of the light changes. If the oscillation belongs to the acoustic spectrum of the crystal the frequency change is small and dependent on the direction of scattering. If it belongs to the infra-red spectrum the case of combination scattering occurs, where the frequency change is relatively large and practically independent of the direction of scattering. The results thus theoretically obtained are compared with those found experimentally by Cabannes (A., 1929, 378) and by Menzies (*ibid.*, 1361) with quartz.

A. J. MEE.

**Quantum theory of molecular scattering of light in solid bodies.** I. TAMM (Z. Physik, 1930, 60, 345—363).—Theoretical. Progressive, not stationary waves are here considered, thus enabling the calculation to be applied easily to actual conditions used in observing scattering and avoiding the introduction of special limiting conditions. The method of Dirac is applied. If the idea of an "elastic quantum" is used, analogous to a light quantum, a number of the results of calculations using quantum mechanics can be formulated. Some simple observations on light scattering are mentioned which are quite analogous to the Compton effect. The connexion between the scattering and the results of the Heisenberg-Pauli treatment is discussed (*ibid.*, 1929, 56, 1). The amount of scattering calculated to a first approximation deviates from that calculated on the classical theory only by the dependence of the Stokes' scattering on temperature, where the observed results favour the quantum theory treatment. A. J. MEE.

**Scattering of light in crystals at high temperatures.** II. G. LANDSBERG and L. MANDELSTAM (Z. Physik, 1930, 60, 364—375; cf. A., 1929, 9).—The intensity of the satellites of the combination scattering in quartz between  $295^\circ$  and  $810^\circ\text{ Abs.}$  was investigated. Besides the well-known increase in intensity of the violet satellites there is also an increase in intensity of the red. There is qualitative agreement with theory. A. J. MEE.

**Relationship between intensity, polarisation, and angle of scattering for Raman radiation.** G. I. POKROVSKI and E. A. GORDON (Ann. Physik, 1930, [v], 4, 488—492).—Investigations were carried out with water and benzene by two methods. In the first the scattered light was photographed by means of a large quartz spectrograph and the spectrum measured by a microphotometer. In the second the scattered light was measured directly by a modified Weber's photometer. Both methods gave the same results. In certain cases the light is not symmetrically scattered, but a phenomenon can be observed which is similar to the Mie effect. A. J. MEE.

**Variations of crystal polychroism under the action of the magnetic field.** R. BRUNETTI (Atti R. Accad. Lincei, 1929, [vi], 10, 585—590).—A review of the author's previous papers (cf. A., 1928, 1077; 1929, 1126) claiming priority over the interpretation given by Becquerel (cf. A., 1929, 1134) of the action of a magnetic field on the absorption lines of crystals of the rare earths. O. J. WALKER.

**Chemiluminescence in the oxidation of fluorescent and non-fluorescent substances by hydrogen peroxide and ozone.** N. N. BISWAS and N. R. DHAR (Z. anorg. Chem., 1930, 186, 154—158).—Oxidation of various organic compounds, e.g., dyes, tannin, and gallic acid, by hydrogen peroxide or ozone in the presence of ferrous sulphate is accompanied by a feeble glow visible in a dark room. The glow becomes stronger with rise of temperature and, up to a certain limit, with increase in the concentration of the solution, but becomes feebler or disappears when the concentration is still further increased. An alcoholic suspension of gelatinous silica containing adsorbed neutral-red exhibits a glow when treated with ozonised oxygen. A. R. POWELL.

**Limit of accuracy of the cosine law of molecular radiation.** F. KNAUER and O. STERN (Z. Physik, 1930, 60, 414—416).—Polemical in reply to Mayer (cf. A., 1929, 490). A. J. MEE.

**Photo-electric effect and decoloration and excitation of alkali halides.** A. SMAKULA (Z. Physik, 1930, 59, 603—614).—A quantitative investigation is made of the absorption of light by crystals of sodium and potassium chlorides possessing coloration of the first kind, and of the resulting excitation and decoloration. The maximum absorption constant and width of absorption band are measured photo-electrically at very low intensities so that there is no observable excitation or decoloration; then a known number of light-quanta lying in a narrow frequency band is absorbed by the crystal so as to produce excitation and decoloration. The maximum absorption constant is found to have decreased, and if there is strong excitation there is increased absorption for the long waves. To reverse the excitation, long-wave light of great intensity is passed through the crystal, and the absorption band determined. From the classical electron theory the number of optically active electrons originally present and the number rendered inactive by the decoloration and by the excitation are calculated from the three absorption bands. The highest values for excitation were found

in natural crystals and in synthetic crystals at low temperatures, and by making observation at  $-186^{\circ}$  excitation was obtained in potassium chloride crystals for the first time. Sodium chloride crystals with or without traces of thallium to produce phosphorescence were investigated at various temperatures. In all the above cases, with small light energies, about one quantum of light was necessary for the removal of each optically active electron, independent of the wave-length of the absorbed light or of the temperature of the crystal. The simple numerical relation found is taken as proving that coloration of the first kind is caused by single alkali atoms and not by colloidal aggregates.

H. A. JAHN.

**Photo-electric effect with benzene and its derivatives.** R. DANTINNE and A. MOLLE (Bull. Soc. chim. Belg., 1929, 38, 435—442).—Solid benzene gives a pronounced photo-electric effect, but with the liquid no effect is observed unless the liquid is agitated, which suggests that molecular orientation plays an important part in producing the effect. Examination of solid benzene derivatives in alcoholic solution and of liquid derivatives shows that the intensity of the effect depends on both the character and position of the substituent groups. For very dilute solutions of a given solute the intensity is proportional to the concentration.

R. CUTHILL.

**Photoconductivity in dielectric liquids.** W. H. ELLER (J. Opt. Soc. Amer., 1930, 20, 71—80).—The influence of light of wave-length greater than about 2300 Å. on the conductivity of paraffin oil, *n*-tetradecane, diisomyldodecane, *n*-decane, *n*-octane, and isooctane has been studied. Threshold values of the wave-lengths necessary to produce ionisation were found to correspond with the absorption limits of the liquids. Both these quantities increase on ascending the series of hydrocarbons. The slowness of recombination indicates that the mobilities of the ions are small.

C. W. GIBBY.

**Ionisation of dicyanogen by slow electrons.** K. E. DORSCH and H. KALLMANN (Z. Physik, 1930, 60, 376—378).—The ionisation processes occurring with dicyanogen were investigated. The ions  $(\text{CN})_2^+$ ,  $\text{C}_2^+$ ,  $\text{CN}^+$ , and  $\text{C}^+$  were found to be present. Atomic ions of nitrogen were not observed, and  $\text{N}_2^+$  ions were found in traces only where there was a weak glow and a high potential. The amounts of the different ions formed are greatly dependent on pressure and potential. The dependence on potential is shown by the unequal form of the intensity/potential curve. For electrons of potential 50 volts and small pressure, the intensity ratios of the ions are  $\text{C}^+ : \text{C}_2^+ : \text{CN}^+ : \text{C}_2\text{N}_2^+ = 1.5 : 1 : 2 : 12$ .

A. J. MEE.

**Ionisation in fuel vapours during slow combustion in air.** F. GILL (Trans. Faraday Soc., 1930, 26, 49—61).—When the vapour of hexane or carbon disulphide is undergoing slow phosphorescent combustion in air (cf. A., 1928, 1335) there is no detectable ionisation of the gas mixture at temperatures up to  $400^{\circ}$ , and it is calculated that if ions are actually present their amount must be too small to be a cause of the reactivity. The results are also similar if substances inhibiting the phosphorescence, such as lead tetraethyl and iron carbonyl, are present.

With hydrogen-air mixtures, appreciable ionisation occurs, but only immediately before violent self-ignition at relatively high temperatures. The depression of the ignition temperature by nitrogen peroxide cannot be accounted for by ionisation effects, and ionisation cannot be detected in the reaction between hydrogen and nitrogen peroxide in absence of air.

R. CUTHILL.

**Dielectric properties of ionised gases and the high-frequency discharge.** H. GUTTON (Ann. Physique, 1930, [x], 13, 62—129; cf. A., 1929, 742).—Ionised gas was subjected to a high-frequency field, between the plates of a condenser as a resonator, tuned with an oscillator. The resonance current and the current in the ionised gas were measured for various pressures, and the resonance wave-length, conductivity, and dielectric constant of the gas were calculated. The convection current in the gas, due to the movement of the ions, is additional to the displacement current, and modifies the apparent dielectric constant, the value of which is less than unity for feeble ionisation, and increases with rise of field frequency. It was found that  $\lambda^2 N^{0.75}$  is a constant, where  $\lambda$  is the resonance wave-length and  $N$  the number of ions per c.c. The variation of the dielectric constant and absorption is explained by a characteristic electronic period, which was investigated by the application of a magnetic field. Two resonance periods were found, analogous to the doubling of an absorption band in the Zeeman effect and leading to a value for  $e/m$  corresponding with that for the electron. Eccles' theory of the propagation of radio-telegraphic waves and the ionised layers of the upper atmosphere is discussed in the light of the above results.

N. M. BLIGH.

**Rochelle salt as a dielectric.** C. B. SAWYER and C. H. TOWER (Physical Rev., 1930, [ii], 35, 269—273).—Braun tube oscillograms were made at various temperatures with a condenser having as dielectric Rochelle salt slabs cut perpendicular to the *a*-axis. Saturation and hysteresis were observed. The dielectric constant of the slabs may reach a value of 18,000. Curves are given for the variation of mechanical and electrical saturation with temperature. When the salt is excited with alternating potentials the resulting mechanical deformation shows certain peculiarities. Clear half-crystals have been grown up to 45 cm. long and 2 kg. weight.

N. M. BLIGH.

**Variation of electric moment in homologous series.** H. A. STUART (Physikal. Z., 1930, 31, 80—83).—The electric moment ( $\mu \times 10^{18}$ ) for aliphatic alcohols is constant near 1.66 and for aliphatic ketones near 2.72. The nitriles exhibit increasing values, from hydrogen cyanide 2.65 to valeronitrile 3.84, whilst the ethers show values decreasing from 1.29 for dimethyl ether to 0.85 for dipropyl ether. For methyl, ethyl, and propyl chlorides the values are 1.89, 2.08, and 1.87, respectively. The variations can be accounted for on the basis of polarisation of  $\text{CH}_2$  and  $\text{CH}_3$  groups by the binding moments characteristic of the different homologous series, since the power to rotate freely is restricted through definite regions of minimal potential energy.

R. A. MORTON.

**Symmetry relations of molecules from the point of view of their electric moment. Diphenyl group.** E. BRETSCHER (Helv. phys. Acta, 1929, 2, 257—270; Chem. Zentr., 1929, ii, 2155).—Measurements ( $\pm 0.01\%$ ) of the dielectric constants of the following substances dissolved in benzene were made: methyl diphenate, *oo'*-diacetoxy-, *oo'*-dimethoxy-, *oo'*-dinitro-, *oo'*-diamino-, *oo'*-dichloro- (20% yield from *o*-chloriodobenzene and copper powder at 220—290°, and distillation in a vacuum), and *pp'*-dicyano-diphenyl. The results for the electric moments indicate deformation owing to free rotation. The difference between the values for ethylene oxide and diphenyl ether is related to the angle between the valencies of the oxygen atom. A. A. ELDRIDGE.

**Molecular and atomic volumes. XXII.  $\gamma$ -Aluminium oxide and spinels.** W. BILTZ and A. LEMKE [with K. MEISEL]. **XXIII. Alkyl compounds of metals and metalloids.** W. BILTZ and A. SAPPER (Z. anorg. Chem., 1930, 186, 373—386, 387—391; cf. A., 1928, 936).—XXII. The properties of the four known modifications of alumina are tabulated and discussed, and those of  $\gamma$ -alumina have been studied in detail. The densities and solubilities in acid have been determined for specimens of hydrated alumina prepared by precipitation, when heated at different temperatures between 500° and 1400°, the nature of the material at the various stages being checked by X-ray examination.  $\gamma$ -Alumina is recognisable at temperatures up to 750°, its density ( $25^\circ/4^\circ$ ) being 3.42. Above 1000° the material is corundum, whilst the intermediate temperatures represent a range of transition. The absorption of moisture on exposure to air by the  $\gamma$ -modification amounts to more than 10%, but is too small to be detected when the substance has been heated sufficiently to ensure complete transformation into corundum. The solubility in concentrated hydrochloric acid runs parallel with the absorption of water. The higher chemical activity of the  $\gamma$ -modification is attributed to the relative looseness of its crystal lattice. The discrepancies hitherto found between the mol. vols. of spinels when calculated additively from those of the constituent oxides, and when observed directly, are due to the use of the mol. vol. of corundum: satisfactory agreement is obtained when the value for  $\gamma$ -alumina is substituted. Similarly, the mol. refractions of the spinels are additive if  $\gamma$ -alumina is assumed to be a constituent.

**XXIII.** The mol. vols. of alkyl compounds of silicon, germanium, tin, lead, zinc, cadmium, and mercury calculated from the at. vols. of the nuclear elements and the radical vols. obtained by difference, correspond closely with the values determined experimentally. Constitutive effects are observed with distannanes, disilanes, and bistrimethyl-lead pentane.

F. L. USHER.

**Chemical forces, constitution of the atom, and refractive data.** K. FAJANS (Anal. Fis. Quím., 1930, 28, 22—46).—A general survey, with special reference to molecular refraction and the deformation of ions.

H. F. GILLBE.

**Absorption and rotatory dispersion of tartaric acid.** G. BRUHAT and R. LEGRIS (Ann. Physique,

1930, [x], 13, 5—61).—A more detailed account of work already published (this vol., 10, 18).

**Influence of alkali molybdates on the rotatory power of dextrose.** E. DARMOIS and J. MARTIN (Compt. rend., 1930, 190, 294—296).—The change in rotatory power observed by Tanret (A., 1921, i, 498) on adding ammonium molybdate to dextrose is probably due to the existence of compounds of the two. The formation of such compounds has been studied by determining the rotatory powers of a series of solutions containing dextrose, molybdic acid, and sodium hydroxide or ammonia. The maximum rotation is obtained when the ratio NaOH/MoO<sub>3</sub> lies between 1 and 2. A constant value for the rotation is reached only after about an hour, but it makes no difference to the value whether  $\alpha$ - or  $\beta$ -glucose is used, or an equilibrium mixture of the two. The solutions had the composition *P* mols. of dextrose (5 g.), *nP* mols. of molybdic acid, and *xP* mols. of sodium hydroxide in 100 c.c. If *n* is constant and *x* variable, the limiting rotation increases with *x* to a maximum and then falls. When *x* = 2*n* the rotation and rotatory dispersion are those of  $\alpha\beta$ -glucose. The compound formed has evidently a  $p_H$  of maximum stability. The maximum rotation increases with the value of *n* and the compound is more stable in the presence of an excess of molybdic acid. Under these conditions the rotatory dispersion is greater than that of either  $\alpha$ - or  $\beta$ -glucose, which confirms the conclusion that a compound exists, and, on the analogy of molybdomalic and -tartaric compounds, its composition is probably [MoO<sub>3</sub>.*m*C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>].Na. On the basis of earlier investigations, the value of *m* is probably 2 (cf. A., 1926, 1201). The fact that time is required for the attainment of equilibrium in the case of dextrose, but not in that of tartaric or malic acid, supports the hypothesis put forward by other investigators that there is a reactive form of dextrose of which the equilibrium quantity present in dextrose solutions is only small. Experiments with boric acid and borates appear to lead to similar conclusions. The rate of change of rotation with time in the molybdate solutions suggests that it depends on a reaction which is unimolecular with respect to dextrose. The addition of a salt, e.g., ammonium chloride, greatly modifies the rate of mutarotation.

M. S. BURR.

**Influence of boric acid and borates on the rotatory power of tartaric acid.** E. DARMOIS (Compt. rend., 1930, 190, 371—373).—Whilst boric acid has no effect on the rotatory power of ethyl tartrate even at 40°, borax affects it at that temperature, and the metaborate does so at 20°. By examining the rotatory power of various mixtures of ethyl tartrate with sodium metaborate and extrapolating to zero time it is inferred that a compound NaBO<sub>2</sub>.C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.Et<sub>2</sub> exists initially, but undergoes very rapid dissociation (cf. Lowry, this vol., 135).

C. A. SILBERRAD.

**Parachor and chemical constitution. XIV. Tellurium compounds.** F. H. BURSTALL and S. SUGDEN (J.C.S., 1930, 229—234).—The parachors of the following bivalent tellurium compounds have been determined: diphenyl telluride, dianisyl

telluride, *di-n-butyl telluride* (preparation described), phenoxtellurine, *di-2-p-phenetyl telluride*, and *di-p-phenetyl ditelluride*. The values obtained give a mean constant for tellurium of 79.4, which lies satisfactorily between the constants for iodine and antimony. The oxygen family of elements thus shows the same steady increase of atomic parachor with atomic number as other groups, *e.g.*, the halogens. The parachors for the two stable quadrivalent compounds diphenyl and *di-p-anisyl telluridichlorides* have also been determined and are in good agreement with the hypothesis that the molecule contains two singlet linkings. Data obtained by Lowry and Gilbert (A., 1929, 1218) for dialkyltelluride dihalides are also in general agreement with this view. The electronic formulæ of the isomerides of this series are discussed.

M. S. BURR.

**Natural periodic system of non-ionogenic compounds.** J. N. FRERS (Z. anorg. Chem., 1930, 186, 145—153).—Theoretical. It is shown that all compounds which do not form ions as well as all ions which themselves do not further dissociate may be arranged in a natural periodic system according to the number of electrons attached to the central atom, assuming that in complex ions all the atoms with the exception of the central atom are electrically neutral. The electronic number of an electrically neutral compound is the same as the atomic number of the central atom, but that of an ion is greater or less than this by the number of negative or positive charges respectively which it holds. The compounds are then arranged in the periodic system in families, all of which have the same electronic number as the atomic number of one element in the periodic table. In every family, therefore, the central atoms should have an equal number of outer electrons and a similar configuration; hence they should all have the same maximum valency. Examples are given of families related to at least one element of the eight groups of the periodic table.

A. R. POWELL.

**Value of measurements on oil particles of radius  $3.4\text{--}11.4 \times 10^{-5}$  cm. by the Ehrenhaft method, and a determination of their errors.** H. FEINER (Z. Physik, 1930, 59, 731—753).—The probable errors in Mattauch's results (*ibid.*, 1925, 32, 439) are calculated. His results fit the empirical Knudsen-Weber resistance law better than the Stokes-Cunningham law. Comparison of errors for oil and selenium particles shows that oil is more trustworthy.

A. B. D. CASSIE.

**Multiple crystal X-ray spectrograph.** J. W. M. DUMOND and H. A. KIRKPATRICK (Rev. Sci. Instr., 1930, 1, 88—105).—An X-ray spectrograph has been constructed in which a concave Rowland grating is made by arranging fifty small slips of calcite on an arc of a circle about 1 m. in diameter. Detailed instructions for adjusting the instrument are given, and its application to the study of the Compton effect is described.

C. W. GIBBY.

**X-Ray interferences with isomeric molecules.** P. DEBYE [with L. BEWLOGUA and F. EHRHARDT] (Physikal. Z., 1930, 31, 142).—X-Ray interference produced by scattering in the vapour state provided a method for measuring certain distances between

atoms. Thus the distances between chlorine atoms in the dichloroethylenes are: *cis*-form 3.6 Å., *trans*-form 4.1 Å.; in ethylidene chloride and ethylene chloride the distances are 3.4 and 4.4 Å., respectively.

R. A. MORTON.

**Röntgen analysis of copper amalgams.** N. KATOH (Bull. Chem. Soc. Japan, 1930, 5, 13—16; cf. this vol., 22).—By a repetition of the X-ray examination of a copper amalgam (24.1% Cu) the existence of the  $\gamma$ -phase was confirmed. The dimension of the lattice is given as  $a = 9.399$  Å. in place of the earlier value of 9.401 Å. No evidence of the  $\alpha$ -form was found in a specimen tempered at 100° for 48 hrs.

F. G. TRYHORN.

**Occurrence of oriented recrystallisation in aluminium.** W. G. BURGERS (Z. Physik, 1930, 59, 651—655).—In distinction to the conception derived from previous work on the subject it is shown that the recrystallisation of aluminium is not anomalous, but that the new crystals exhibit anisotropy in their orientation, especially after relatively strong deformation. The extent of the orientation is influenced by the deformation which precedes the recrystallisation.

W. R. ANGUS.

**Mechanism of the change of space-lattice in different modifications of crystals.** H. SHÖJI (Proc. Imp. Acad. Tokyo, 1929, 5, 447—449).—Theoretical. Lattice changes corresponding with plastic deformation are discussed and illustrated for a number of substances. For free change of lattice between two crystal modifications the atoms or molecules most firmly bound in the planes of greatest cohesion move in groups. The transformation can occur slowly through slip-like deformation along planes other than these, and for some optically active substances by a spring-like deformation of the lattice. Amorphous-crystalline transformations, and those due to small or simple lattice change corresponding with elastic deformation, are discussed.

N. M. BLIGH.

**Crystal structure of the anhydrous iodides of bivalent metals.** I. Iodides of cobalt, iron, and manganese. A. FERRARI and F. GIORGI (Atti R. Accad. Lincei, 1929, [vi], 10, 522—527).—The iodides have typical cadmium iodide structure with the following dimensions: cobalt,  $a$  3.96,  $c$  6.65; iron,  $a$  4.04,  $c$  6.75; manganese,  $a$  4.16,  $c$  6.82;  $d_{\text{calc}}$  5.75, 5.39, and 5.01, respectively. A fresh determination of the lattice dimensions of lead iodide gives  $a$  4.53,  $c$  6.92,  $d_{\text{calc}}$  6.22.

O. J. WALKER.

**Crystal structure of normal carbonates of cobalt and nickel.** A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1929, [vi], 10, 594—598).—Normal cobalt carbonate has a rhombohedral structure of the calcite type with a unit cell containing four molecules:  $a$   $5.91 \pm 0.005$  Å.,  $\alpha$   $103^\circ 22'$ ,  $d_{\text{calc}}$  4.24. Normal nickel carbonate could not be prepared.

O. J. WALKER.

**Crystal structure of aluminium fluoride.** A. FERRARI and A. SCHERILLO (Gazzetta, 1929, 59, 927—930).—X-Ray examination of aluminium fluoride shows that it has a characteristic hexagonal lattice not found in any other compound. The dimensions are  $a$  4.92,  $c$  6.25 Å.;  $d_{\text{calc}}$  3.22.

O. J. WALKER.

**Crystal structure and sensitiveness to shock of rubidium and barium azides.** P. GUNTHER, J. PORGER, and P. ROSBAUD (*Z. physikal. Chem.*, 1930, **B**, **6**, 459—480).—X-Ray measurements indicate that rubidium azide forms tetragonal-holohedral crystals belonging to the space-group  $D_{4h}$ . The dimensions of the elementary cell containing the molecule  $RbN_3$  are  $a$  4.497,  $c$  3.707 Å. The coordinates are Rb,  $1/2$   $1/2$   $1/2$ ; N, 000; 2N, 00 $\bar{u}$ , 00 $\bar{u}$  with  $u=0.30_4$ ;  $d$  (X-ray) is  $2.7876 \pm 0.0006$ . Contrary to previous observations, barium azide crystallises in the monoclinic systems and belongs to one of the space-groups  $C_{2h}$  or  $C_{2v}$ . The elementary cell contains 10 molecules and has the dimensions  $a$  6.22,  $b$  29.29,  $c$  7.02 Å.;  $d$  (X-ray) is  $2.9365 \pm 0.0025$ . The sensitiveness to percussion of the two azides has been determined. The greater sensitiveness of rubidium azide compared with sodium azide appears to be related to a greater compression of the nitrogen in the former, resulting in a smaller stability of the azide radical. N. M. BLIGH.

**Space lattice of diethylphthaloyl ketone.** H. MARK and H. MEHNER (*Z. Krist.*, 1927, **65**, 461—468). H. MARK (*ibid.*, 1929, **70**, 516; *Chem. Zentr.*, 1929, ii, 2014).—The unit cell of the ditetragonal-bipyramidal crystals ( $a$  7.25,  $c$  20.47 Å.) contains 4 mols.; the space-group is  $D_{4h}$ . A. A. ELDRIDGE.

**Thermal study of the magnetic properties of the rare earths.** A. DUPERIER (*Anal. Fis. Quím.*, 1930, **28**, 47—55).—The previous work (cf. A., 1929, 982) has been extended and measurements have been made with a different type of apparatus, whereby the magnetic susceptibility is calculated from the force experienced by the material when placed in a non-uniform magnetic field. For holmium oxide the susceptibility has been redetermined between 293° and 697°, and the calculated value of  $\Delta$  in the modified Curie-Weiss equation is 13.5. Determinations with ytterbium sulphate, for which the Curie-Weiss equation is not valid, yield for  $\Delta$  in the modified equation 82.1. The results for thallium sulphate are not concordant and this is ascribed to the presence of impurities. H. F. GILLBE.

**Diastereoisomerism and crystal symmetry of ephedrine.** H. EMDE and F. SPÄNHÄUER.—See this vol., 470.

**Mechanical and magnetic factors influencing the orientation and perfection of bismuth single crystals.** A. GOETZ (*Physical Rev.*, 1930, [ii], **35**, 193—207).—A growing crystal is expected to be very sensitive to any mechanical stress (cf. A., 1929, 1220; Kapitza, A., 1928, 825). To decide whether the sensitive region is in the solid part of the growing crystal or in the liquid state a method is described for the production of single metal crystals of any size and shape in absence of external influences or under a strong magnetic field. Conditions under which seed-crystals transfer their orientation to a rod are studied. Experiments with artificially distorted seeds show that crystalline units must exist in the liquid state, are destroyed at about 10° above the m. p., and are probably identical with elementary crystal units (cf. Zwicky, A., 1929, 630). Crystals in the three main orientations to the directions of a magnetic field when

grown, one half with, the other half without the field, were relatively unchanged in orientation in absence of secondary influence. Otherwise the crystals showed preference for an orientation in which the direction of the smallest diamagnetic susceptibility was parallel to the lines of force, supporting the assumption of a "block phase" slightly above the m. p. N. M. BLIGH.

**Paramagnetic rotation of the plane of polarisation in uniaxial rare-earth crystals.** H. A. KRAMERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 1176—1189).—Theoretical. Becquerel has shown (cf. A., 1929, 1134) that certain magnetic properties of absorption lines in uniaxial rare-earth crystals indicate that the metallic ions are in a strong electric field. Atomic theory is applied to an investigation of the magnetic rotation of the plane of polarisation in these crystals, taking into account the electric field. It is shown that if this field is of cylindrical symmetry it leads to Ladenburg's formula for the rotation of the plane of polarisation when the crystal axis and magnetic field are parallel. Possible values of the generalised Landé factor in the formula are examined with the help of Hund's theory. In special cases when the magnetic field is perpendicular to the crystal axis, the rotation obeys the formula. A modification of the formula is deduced for a small deviation from symmetry of a parallel field at low temperatures. N. M. BLIGH.

**Paramagnetic rotation of the plane of polarisation in crystals of tysonite and xenotime.** H. A. KRAMERS and J. BECQUEREL (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 1190—1198).—The theory of rotation of the plane of polarisation previously developed (cf. preceding abstract) is applied to rare-earth crystals (cf. A., 1929, 1134). Results for tysonite (lanthanum cerium fluoride) agree with the view that the rotation is due to the cerium ions; the structure of the lattice being unknown, certain assumptions are made concerning the electric field in the crystal. The approximate electric field for xenotime (yttrium erbium gadolinium phosphate) is calculated, the lattice structure being known, and experimental results (cf. following abstracts) are in agreement with the modified rotation formula (cf. preceding abstract) and lead to the conclusion that the rotation is probably due to the gadolinium ions. The wider significance of the theory is discussed. N. M. BLIGH.

**Paramagnetic rotatory power of the crystals of xenotime at very low temperatures and the paramagnetic saturation.** J. BECQUEREL and W. J. DE HAAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 1199—1205; cf. A., 1929, 1134).—To eliminate in the measurement of the rotation of xenotime difficulties caused by perturbations due to the multiplicity of bands in the visible region and their large Zeeman effect, wave-lengths were chosen at 5615-66 and 5780-1 Å. A special method is described for avoiding difficulties due to the strong double refraction of the crystal. Five series of measurements of rotation produced by the principal absorption in the ultra-violet were made: one at 14.34°, three at the temperature of liquid helium under atmospheric pressure, and one at 1.38° Abs. Results are tabulated for

plotting (cf. following abstract), and deductions therefrom are discussed.

N. M. BLIGH.

**Experimental verification of the theory of the paramagnetic rotatory polarisation in the crystals of xenotime.** J. BECQUEREL, W. J. DE HAAS, and H. A. KRAMERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1206—1211).—Using the data obtained for xenotime (cf. preceding abstract) curves are given for the magnetic rotation plotted against  $H/T$ , where  $H$  is the magnetic field intensity, and  $T$  the absolute temperature, and are compared with the theoretical curves. The modified rotation formula previously deduced is satisfactorily verified, and the most probable value of the active magnetic moment is found to be 7 magnetons, that of the gadolinium ion.

N. M. BLIGH.

**Electrical properties of galena crystals.** F. REGLER (Physikal. Z., 1930, 31, 168—172).—The change in form of galena crystals under the action of an electric field was investigated, and the effect of pressure of the contact on the conductivity was found. The curve connecting the pressure with the current flowing under a given potential is frequently a hysteresis curve. The conductivity increases with the pressure. The crystal does not obey Ohm's law, but the deviations in the case of galena may be explained as a consequence of variable transition resistance. The great effect of temperature on the crystal is noted.

A. J. MEE.

**Orienting influence of magnetic field, wall and reciprocal action on the swarms of liquid crystalline *p*-azoxyanisole.** A. VAN WYK (Ann. Physik, 1929, [v], 3, 879—933).—The crystallo-optical behaviour in convergent, linearly polarised light of a glass cell filled with liquid crystalline *p*-azoxyanisole has been studied in relation to the strength of a magnetic field, the lines of force being disposed at right angles to the cell walls. For each wave-length of light and each temperature of the material, a series of field strengths are recorded, for which by observation between crossed Nicol prisms a figure similar to that observed with a crystal plate cut vertically to the axis can be obtained. The field strength depends on temperature and on wave-length. For field strengths other than those recorded the figures are ill-defined, unsymmetrical, and exhibit a tendency to disappear completely. The phenomenon is partly a wall effect, since preliminary treatment with sodium hydroxide results in a new series of field strengths for optimal definition of the figure, whereas treatment with sulphuric acid results in the appearance of sharp figures at lower field strengths with an increase in sharpness as the field strength is increased, instead of the disappearance of the figure. The phenomenon is traced to a joint action of the known orienting power of the walls and of the field, both sides of the vessel having a layer of material regularly disposed in the wall plane. The optical thickness of the wall-layer  $\delta$  is given by  $\delta = K/H^\alpha$ ,  $K$  being a constant for the cell,  $H$  the strength of the magnetic field, and  $\alpha$  a constant (0.93) characteristic of the substance studied. The rôle of wave-length is also discussed. On the assumption that the orienting effect of the field on the swarms arises from anisotropic

polarisability  $\delta = K/H$  is in satisfactory agreement with experiment; on the other hand the assumption of a dipole character for the swarms leads to the expression  $\delta = K/(H)^\frac{1}{2}$ , in much less satisfactory accord with experiment.

R. A. MORTON.

**Law of linear crystal growth.** G. MASING (Wiss. Veröff. Siemens-Konz., 1929, 8, [2], 144—156).—A review of recent work on the laws governing crystallisation of molten materials is followed by a theoretical and mathematical discussion of Tamman's law of linear crystal growth. It is shown that this law most nearly represents the known facts assuming that the temperature at the boundary between liquid and crystal is that of the m. p. of the substance, an assumption which is only approximately true.

A. R. POWELL.

**Polymorphism of potassium nitrate.** F. C. KRACEK (J. Physical Chem., 1930, 34, 225—247).—At 128.02° and 82 megabars potassium nitrate exists in three forms I, II, and III. The forms I and II are in equilibrium at 127.66° and 1 megabar and the reaction is reversible in the presence of small amounts of water. With dry potassium nitrate, form III appears metastably at 1 megabar and is in metastable equilibrium with I at 126.1°. On heating, II passes into I directly, whilst on cooling I changes metastably to III which then inverts to II in a reaction which is truly monotropic. Above 82 megabars pressure III has a region of stability between definite temperature limits; the pressure-temperature diagram for moist potassium nitrate has been determined for pressures up to 300 megabars. The specific volume of I exceeds that of II by 0.00484 cm.<sup>3</sup>/g. at 50 megabars, whilst the volume changes accompanying the transitions II  $\rightarrow$  III and III  $\rightarrow$  I at 151 and 251 megabars pressure are -0.0087 and -0.0091 cm.<sup>3</sup>/g. for the former, and 0.0134 and 0.0133 cm.<sup>3</sup>/g. for the latter, respectively, at the corresponding equilibrium temperatures. The heats of inversion are 10.40 g.-cal./g. for II  $\rightarrow$  I, 5.52 g.-cal./g. for III  $\rightarrow$  I, and -4.97 g.-cal./g. for II  $\leftarrow$  III at the ordinary pressure. The hysteresis limits are given and the conditions for the metastability of KNO<sub>3</sub>-III at the ordinary pressure are discussed.

L. S. THEOBALD.

**Spreading of electrical waves in metals.** F. WALTER (Wiss. Veröff. Siemens-Konz., 1929, 8, [2], 115—125).—Theoretical and mathematical. Expressions are deduced from Maxwell's fundamental equations for the rate of spreading of a plane electrical wave in metals, for the resulting distribution of the current and electromagnetic field, and for other electrical quantities.

A. R. POWELL.

**Measurement of weak alternating currents by tellurium-platinum thermoelements.** A. TEICHMANN (Z. Physik, 1930, 59, 615—622).—The method is a refinement of previous methods employed in measuring weak alternating currents and is much more sensitive. The experimental arrangement is discussed.  $\beta$ -Tellurium was used in making the elements and its preparation and properties are discussed.

W. R. ANGUS.

**Resistance changes in stretched nickel wires.** R. S. BEDI (Physikal. Z., 1930, 31, 180—182).—The



variation of resistance of nickel wires under different conditions of stretching was investigated. The resistance decreased up to the elastic limit, and the resistance minimum coincided with the elastic limit. If taken through a cycle of stretching, the extension-resistance curve for the outward section was above that for the inward section provided that the extension was not taken above the elastic limit. If the latter is the case various types of curve are obtained according to the degree of stretching. Similar results are obtained with copper, iron, and steel wires, below the elastic limit, but when a permanent deformation is produced the behaviour is different. An explanation is attempted on the basis of change of atomic structure.

A. J. MEE.

**Specific heats of gases at high pressures. I. Method and apparatus at room temperature.** N. W. KRASE and B. H. MACKAY (J. Amer. Chem. Soc., 1930, **52**, 108—115).—A constant-temperature continuous-flow adiabatic calorimeter and auxiliary apparatus for measuring specific heats of gases up to 1000 atm. at the ordinary temperature is described. Sources of error are discussed. Heat losses by conduction and radiation are balanced by electrical heating. Results are reproducible to within 0.5%.

J. G. A. GRIFFITHS.

**M.-p. curves of hydrogen, neon, nitrogen, and argon.** F. SIMON, M. RUHEMANN, and W. A. M. EDWARDS (Z. physikal. Chem., 1930, **B**, 6, 331—342; cf. A., 1929, 1372).—The m. p. of hydrogen, neon, and nitrogen from 0 to 5000 kg. per sq. cm. and of argon from 0 to 3400 kg. per sq. cm. have been determined. The measurements are in good agreement with the formula  $\log(p+a)=C/T+b$ , where  $a$ ,  $b$ , and  $c$  are constants. There is a close connexion between the values of  $a$  and the internal pressures as determined by Stefan's equation. The densities of solid hydrogen, nitrogen, and argon have been calculated by means of the Clausius-Clapeyron equation. J. A. V. BUTLER.

**Latent heat of vaporisation of associated liquids. II.** K. M. STACHORSKI (J. Russ. Phys. Chem. Soc., 1929, **61**, 1743—1749).—A theoretical consideration of phenomena connected with the vaporisation of associated liquids, both alone and in solution.

R. TRUSZKOWSKI.

**Normal b. p. of oxygen.** W. H. KEESOM, (MISS) H. VAN DER HORST, and (MISS) A. F. J. JANSEN (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1167—1170).—In view of divergent existing values, the b. p. of oxygen was determined, using the helium thermometer which was employed for the fundamental pressure coefficient of helium (cf. A., 1928, 697), the value for which is taken as 0.0036611, and the value obtained by van Agh and Onnes (cf. A., 1926, 231) for the thermal expansion of glass. The mean normal b. p. was found to be  $-182.97 \pm 0.010^\circ$ .

N. M. BLIGH.

**Revision of classical [kinetic] theory of collision effects in gases.** J. FRENKEL (Z. Physik, 1930, **59**, 640—648).—The failure of the classical conception of the mean free path to account for persistence of velocity and of the Sutherland theory when applied to atomic hydrogen is mentioned. It is proposed that Einstein's idea of a frictional coefficient  $f$  for

single molecules is more fundamental than that of the mean free path, for with it treatment of persistence of velocity is possible and the coefficients of diffusion and viscosity and heat conduction can be calculated from it. The method of deriving this coefficient from the collision area treated as a function of the angular deflexion of the molecule considered is given, and the integration of the resulting expression shown to be difficult except in the simple classical case of rigid spheres. An approximate expression for  $f$ , of the same type as that derived from the classical theory, is derived by the wave-mechanics theory (cf. this vol., 132) of the collision of two atoms considering only their repulsive energy. It is shown that chemical forces can be allowed for by a simple modification of the formula and that this modified formula shows that  $f$  remains finite at small velocities, whereas on the Sutherland theory it would become infinite. A preliminary formula for the treatment of van der Waals' attractive forces is given. H. A. JAHN.

**Rate of vaporisation and vapour pressure: method of measuring the specific area of a surface.** F. J. WILKINS (Nature, 1930, **125**, 236).—In determining the rate of vaporisation from unit area of a metallic filament Langmuir's assumption that the specific equals the apparent area is, in general, unjustifiable, since irregularities of atomic dimensions are present in all surfaces. The vapour pressures determined by Langmuir's method are too large by a given factor,  $A$ , which in the case of tungsten or molybdenum is shown by deviations of the chemical constants from the theoretical to be large. For tungsten the specific area is 5 times the apparent and for molybdenum it is 20 times the apparent.  $A$  is a measure of the area accessible to condensing molecules of the vaporising solid. Since  $A=p'/p$ , where  $p'$  is the vapour pressure calculated from the rate of vaporisation and  $p$  is the true vapour pressure, it can be determined with fair accuracy by using Knudsen's effusion method for  $p$ .

L. S. THEOBALD.

**General formulæ for calculating the at. or mol. heat and sp. heat of elements and their compounds in the solid state. I.** MAYDEL (Z. anorg. Chem., 1930, **186**, 289—323; cf. A., 1929, 386).—Previous work has been completed by supplementing Kopp's law so as to permit the calculation or correction of at. heats. "Effective" at. heats have been calculated for gaseous elements and for special groups such as CN, CO<sub>2</sub>, CO, and OH, from consideration of a large number of compounds containing them. In general, the values obtained are lower than those calculated from the sp. heats of the gases. The existence of such effective at. heats for special structures explains why certain isomerides possess different sp. and mol. heats. Deviations from Kopp's law occur at low temperatures.

F. L. USHER.

**Vapour-pressure curves and the calculation of van der Waals'  $a$  constants for metals and salts.** R. LORENZ and W. HERZ (Z. anorg. Chem., 1930, **186**, 165—170; cf. A., 1929, 648).—Mathematical. Van der Waals' constant  $a$  for metals can be calculated from a knowledge of the b. p. of the metal if the b. p.

and vapour-pressure constant  $A$  of silver are known. The same applies to the value of  $a$  for halides if the b. p. and value of  $A$  are known for sodium chloride.

A. R. POWELL.

**Relation between the gas pressure and translational energy of the gas molecule.** K. SCHAPOSCHNIKOW (Z. Physik, 1930, 59, 725—726).—The expression  $p = E_{\text{trans.}}/3$  of Anderson (this vol., 25) for the pressure of light-quanta gas is shown to be incorrect, the correct expression being  $p = E/3$ .

H. A. JAHN.

**Density of crystals after cooling under pressure.** G. TAMMANN and E. JENCKEL (Z. anorg. Chem., 1930, 186, 141—144).—The density of crystalline substances is not altered by subjecting them to a high pressure at a temperature 10—30° below their m. p., although the density of amorphous glassy substances is thereby increased. This difference in behaviour is to be expected.

A. R. POWELL.

**Standard materials for expansion measurements with solids up to 1400°.** W. M. COHN (Ann. Physik, 1930, [v], 4, 493—512).—By means of apparatus described the use of certain substances as standard materials for extension measurements by the comparison method up to 1400° was tested. The substances used were quartz glass, zirconia, and other ceramics. Quartz glass and zirconia can be used up to 1000°, whilst other refractory materials can be used up to 1200° and 1400°.

A. J. MEE.

**Thermodynamic properties of ammonia. I. Compressibility of and an equation of state for gaseous ammonia. Vapour pressure of liquid ammonia.** J. A. BEATTIE and C. K. LAURENCE (J. Amer. Chem. Soc., 1930, 52, 6—14).—An extension of previous work on the pressure-volume-temperature behaviour of ammonia. Existing vapour-pressure data (A., 1918, ii, 60; 1920, ii, 370) are confirmed. The authors' data for the range 20—95 c.c./g. and 75—325° are reproduced, with a mean deviation of 0.077%, by inserting the values  $A_0 = 8250$ ,  $a = 10$ ,  $B_0 = 2.005$ ,  $b = 11.223$ ,  $c = 280 \times 10^6$  (units: atm., c.c./g., °Abs.) in the Beattie-Bridgeman equation of state (A., 1927, 819) and the data of Meyers and Jessup (Refrig. Eng., 1925, 11, 345) are reproduced to within 0.155%.

J. G. A. GRIFFITHS.

**Chemical forces, molecular attraction, and viscosity of monatomic gases.** J. FRENKEL and N. SEMENOV (Z. Physik, 1930, 59, 638—639).—Exception is taken to the common view that chemical forces of attraction, owing to their rapid decrease with increase of distance, have little influence on the van der Waals attractive forces. It is shown that the van der Waals constant  $a$  is practically independent of the manner in which the attractive forces vary with distance. Treating monatomic hydrogen as composed of Sutherland molecules, a large value for the effective collision area and therefore of the temperature coefficient of viscosity is predicted, in disagreement with Harteck's experimental result. This is explained partly by the inaccuracy of Harteck's results and partly by the inadequate treatment of the repulsive molecular forces in the Sutherland theory. Experimental work on this point is in progress.

H. A. JAHN.

**Determination of viscosity of very small quantities of liquid with the aid of the Brownian movement.** R. FÜRTH (Z. Physik, 1930, 60, 313—316).—By observing the motion of a single particle in a small quantity of liquid the viscosity of the medium can be found. The horizontal component of the Brownian movement of the particle was used, there being no currents of any marked size in the small amount of liquid used. The theory of the accuracy of the process is worked out. If a series of 300 readings of the time taken by the particle to traverse a given distance be taken, the viscosity can be calculated to within about 5%.

A. J. MEE.

**Condensation of vapours by adiabatic expansion of mixtures of them with air in connexion with change of entropy during vaporisation.** N. V. TANCOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1833—1848).—The condensation of water vapour from air on the adiabatic expansion of the mixture takes place relatively more readily at higher than at lower temperatures, pointing to a smaller entropy change under these conditions. In general, for all liquids, the smaller is the entropy change, the more readily does condensation take place. Liquids may be classified into two groups: those, such as water or alcohols, which always possess nuclei for drop formation in their vapour, and those, such as hydrocarbons, chloroform, and ether, which possess these nuclei only in the liquid itself, so that they are present in the vapour only if a stream of air is passed through the liquid.

R. TRUSZKOWSKI.

**Evaporation of binary mixtures. II.** M. S. VREVSKI and G. P. FAERMAN (J. Russ. Phys. Chem., 1929, 61, 1897—1904).—The latent heat of evaporation of mixtures of hydrogen chloride and water at 78° and 21° was determined by Vrevski's compensatory method (A., 1927, 733). The values found are in satisfactory agreement with those calculated from the formula  $l = l_2(1-x') + (dq'/dn_1) \cdot x' + (dq''/dn_2)(1-x')$ , where  $l$  is the latent heat of evaporation of 1 g. of liquid and  $l_2$  that of 1 g. of water,  $x'$  is the concentration in g. of hydrogen chloride in the saturated vapour,  $dq'/dn_1$  is the heat of dissolution in water of 1 g. of hydrogen chloride, and  $dq''/dn_2$  is the heat of dissolution in hydrogen chloride of 1 g. of water. The composition of the vapour determined experimentally agrees with that calculated from the formula  $x'/(1-x') = (l-l_2-dq''/dn_2)/(dq'/dn_1-l_2)$ .

R. TRUSZKOWSKI.

**Evaporation of binary mixtures. III.** M. S. VREVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1875—1895).—The expression  $L = x'L_1 + (1-x')L_2 + x'W_1 + (1-x')W_2$  is deduced, in which  $L$ ,  $L_1$ , and  $L_2$  are respectively the latent heats of condensation of a binary vapour mixture containing  $x'$  g.-mol. of one constituent and  $1-x'$  of the other, and of the pure components, and  $W_1$  and  $W_2$  are the differential heats of dilution per mol. of each liquid. The above equation is verified for mixtures of ethyl alcohol and water, methyl alcohol and water, and nitric acid and water.

R. TRUSZKOWSKI.

**Azeotropism in binary systems consisting of an alcohol with an amine, a nitro-derivative, an ether, or water.** M. LECAT (Z. anorg. Chem.,

1930, 186, 119—140).—Tables are given showing the b. p. of the constituents, the b. p. of the azeotropes and their composition, and the heat effect observed on mixing the components of the systems in azeotropic proportions for numerous binary systems comprising an alcohol with an amine, a nitro-derivative, an ether, or water. If the difference between the b. p. of the constituents is  $\Delta$  and the depression of the b. p. in the case of the azeotropic mixture  $\delta$ , the points representing these functions for compounds of the same type often lie on a parabolic curve of the second or third degree. In the case of the system alcohol-amine (69 systems examined) no such curves can be represented, as the chemical properties of the amines play too large a part in the determination of the composition and b. p. of the azeotropic mixtures. The same remark applies to the system alcohol-nitro-derivative (70 systems) with the exception of that involving nitromethane (17 systems), which can be represented by the equation  $\delta = 8.9 - 33\Delta_1 + 67\Delta_1^3$  where  $\Delta_1 = \Delta/100$ . For the system ethyl ether-alcohol (12 systems)  $\delta = 7.2 - 38.3\Delta_1 + 43\Delta_1^2$ ; similar equations apply for systems with other ethers. The systems comprising glycol with various alcohols (19 examined) give a curve with two branches the equations to which are  $\delta_n = 24.2 - 70\Delta_1 + 51\Delta_1^2$  and  $\delta_n = 24.2 - 58.5\Delta_1 + 40\Delta_1^2$  for  $\Delta_1 < 0.7$ . In the 27 systems examined for water-alcohol mixtures the two branches are represented by the equations  $\delta_n = 12 - 80\Delta_1 + 120\Delta_1^2$  and  $\delta_n = 12 - 30.6\Delta_1 + 29\Delta_1^2 - 10\Delta_1^3$  for  $\Delta_1 < 1.05$ . In both the above cases  $\delta_n$  is asymptotical to the  $\Delta$  axis.

A. R. POWELL.

**Composition of constant-boiling hydrochloric acid at pressures of 50 to 1220 mm.** W. D. BONNER and A. C. TITUS (J. Amer. Chem. Soc., 1930, 52, 633—635).—Using a method similar to that of Foulk and Hollingsworth (A., 1923, 482) the compositions and densities of various hydrochloric acid solutions of constant b. p. at pressures between 50 and 1220 mm. have been determined and are tabulated. Since the density increases almost linearly with the concentration of hydrochloric acid, it is possible to prepare constant-boiling acid at any convenient pressure and measure its density at 25°. From this the percentage of hydrochloric acid in the solution is given by  $(\Delta - 0.9966)/0.004912$ , thus avoiding the necessity of measuring the pressure, and avoiding errors from variations of the latter during the preparation of the acid.

J. W. SMITH.

**Relations between the behaviour during distillation of a binary system and the shape of the temperature-vapour pressure curves of the components.** M. LECAT (Atti R. Accad. Lincei, 1929, [vi], 10, 649—653).—The conditions which determine whether a given binary system will be azeotropic or not are discussed. A simple notation is suggested for describing the azeotropism of such systems.

O. J. WALKER.

**Effect of temperature on molecular surface energy of binary mixtures.** I. W. F. SEYER and W. S. PECK (J. Amer. Chem. Soc., 1930, 52, 14—23).—The surface tensions (capillary tube method) and densities of liquid sulphur dioxide and of mixtures of sulphur dioxide and benzene have been determined

between  $-50^\circ$  and  $100^\circ$ . The results indicate that liquid sulphur dioxide is associated below  $20^\circ$  (cf. Stowe, A., 1929, 381) and that molecular association occurs in the mixtures. There is no evidence of compound formation in the f.-p. curve, which indicates the existence of a eutectic (m. p.  $-77.5^\circ$ ) containing 6% by weight of benzene.

J. G. A. GRIFFITHS.

**Hardness of silver-rich copper-silver alloys.** M. HANSEN (Z. anorg. Chem., 1930, 186, 41—48).—Hardness measurements of silver alloys with 0.68—10.22% Cu after prolonged annealing at various temperatures and quenching confirm the solubility curve of copper in silver previously established by conductivity measurements and micrographic analysis (B., 1929, 753).

A. R. POWELL.

**Resistance thermometry at the temperatures of liquid helium.** W. H. KEESOM and J. N. VAN DEN ENDE (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1171—1175).—With the object of finding an alloy the resistance of which changes sufficiently in the temperature range of liquid helium to serve as a resistance thermometer, the resistances of alloys of platinum-silver, platinum-10% iridium, brass, phosphor-bronze, and "technically pure" platinum were measured at  $0^\circ$  and at the temperatures of liquid air, hydrogen, and helium. In the liquid helium region the change of resistance with temperature is too small, except in the case of phosphor-bronze, for thermometric purposes. The change for non-annealed phosphor-bronze is nearly linear and much larger than for any other alloy, and is practically uninfluenced by a magnetic field.

N. M. BLIGH.

**Entrainment of polonium, as chloropoloniate, by ammonium chloroplumbate.** M. GUILLOT (Compt. rend., 1930, 190, 590—592).—The addition of ammonia to a mixture of polonium chloride and a saturated solution of chloroplumbic acid  $H_2[Pb^{IV}Cl_6]$  in the presence of excess of chlorine and of hydrochloric acid precipitates fine yellow octahedral-cubic crystals of  $(NH_4)_2[Pb^{IV}Cl_6]$  and its isomorph  $(NH_4)_2[Po^{IV}Cl_6]$ . Determinations of the lead and polonium contents of the crystals and mother-liquors obtained with varying quantities of ammonia showed that the ratio of the polonium contents of the crystalline and liquid phases is a linear function of the ratio of the lead contents up to the value 5 of the latter. Above this the polonium ratio falls rapidly owing to the surface portions of the crystals being richer in polonium than their centres. The fact that the fine-textured precipitate of lead chloride produced under the same conditions of acidity in the presence of polonium entrains none of the latter, indicates that the above phenomena are due to the analogous structures of the lead and polonium salts, and not to adsorption.

J. GRANT.

**Dependence of concentration of saturated mixed crystals on temperature.** G. TAMMANN and W. OELSEN (Z. anorg. Chem., 1930, 186, 257—288).—A number of binary systems in which one of the components is ferromagnetic and the other non-ferromagnetic have been examined by measuring the force exerted on a small specimen placed in a magnetic field of known strength and gradient. The magnetic

susceptibility of alloys of this nature bears a linear relation to the proportion of the ferromagnetic component present as such, but the susceptibility of mixed crystals containing a small proportion of the ferromagnetic substance is negligibly small; hence in a series of susceptibility-composition curves the points where the extrapolated lines intersect the composition axis represent the composition of the saturated mixed crystals. By examining in this way specimens chilled from various temperatures, the dependence of composition on temperature can be determined. The mixtures studied were those of cobalt with copper, lead, silver, bismuth, and mercury, of nickel with silver, lead, and mercury, and of iron with copper, lead, silver, bismuth, cadmium, and mercury. The results obtained for the variation of solubility of one of the components with temperature are satisfactorily represented by the formula  $\log s = a/T + b$ . Values of the constants  $a$  and  $b$  are given for several of the systems studied.

F. L. USHER.

**Method of finding molecular constitution of certain liquid and solid intermetallic solutions.** F. H. JEFFERY (Trans. Faraday Soc., 1930, 26, 86—89).—For a dilute binary liquid solution (molar fraction of the solute  $=n$ ) in equilibrium with a dilute solid solution of the same components in which the molar fraction of the solute is  $n'$ , the equation  $\log(1-n') - \log(1-n) = L/RT - L/RT_0$ , where  $L$  is the latent heat of fusion of the solvent and  $T_0$  its f. p. and  $R$  and  $T$  have their usual significance, has been derived. Application of this equation to the data previously obtained for liquidus and solidus compositions in solutions of lead in tin and tin in lead (A., 1927, 1030; 1928, 366) shows that in both liquidus and solidus no compounds are formed and the molecules of both components are monatomic at temperatures near the liquidus. Similar conclusions are also reached from new data obtained for solutions of cadmium in tin.

R. CUTHILL.

**Solubilities of helium, neon, and argon in water and organic solvents.** A. LANNUNG (J. Amer. Chem. Soc., 1930, 52, 68—80).—The solubilities (Bunsen and Ostwald  $l$  coefficients) of helium, neon, and argon in water, methyl alcohol, ethyl alcohol, acetone, benzene, cyclohexane, and cyclohexanol have been determined for the range 15—37°. In each solvent helium has the least solubility and argon the greatest. The solubility in water decreases with rise of temperature. The converse is true for organic solvents, and from the linear relation between  $\log_{10} l$  and  $1/T'$  (which does not hold for water) the heats of dissolution ( $u$ ) at constant volume are calculated. The relation  $-\log_{10} a = 0.3 + u(\text{g.-cal.})/3000$  is obtained (where  $l = ae^{u/RT}$ ) for monatomic and diatomic molecules and the organic solvents.

J. G. A. GRIFFITHS.

**Solubility of sodium thiocyanate in alcohol.** J. R. PARTINGTON (J.C.S., 1930, 181; cf. Hughes and Mead, A., 1929, 1375).—Attention is directed to values previously published (A., 1927, 1020).

S. K. TWEEDY.

**Effect of one salt on solubility of another in ethyl alcohol solution.** IV. F. S. HAWKINS and J. R. PARTINGTON (Trans. Faraday Soc., 1930, 26, 78—86).—The effect of lithium perchlorate on the

solubility of sodium iodide in anhydrous alcohol at 25° has been determined and found to agree with the equation  $-\frac{1}{2} \log R = 3\alpha(\sqrt{2\mu} - \sqrt{2\mu_0}) + \beta c$  (cf. A., 1928, 1182), but not with the equation  $-\log f = A\sqrt{2\mu} + B\mu$  (Brönsted, A., 1927, 1027).

R. CUTHILL.

**Apparatus for determination of solubility.** A. N. CAMPBELL (J.C.S., 1930, 179—180).—A wide-mouthed bottle,  $A$ , is provided with a bung and inverted over a similar bunged bottle,  $B$ . Through the bungs passes a 3-mm. tube packed with glass wool and having a constriction at the end just within  $A$ , as well as a narrow tube drawn out to an S-shaped capillary at the bottom of  $B$ . Solid and solvent are placed in  $B$ ; after dissolution the apparatus is inverted in the thermostat, whereupon solution filters through the 3-mm. tube into  $A$ , which is then detached, closed, and weighed.

S. K. TWEEDY.

**Solutions of salts in pure acetic acid. II. Solubilities of acetates. III. Zinc acetate and sodium zinc acetate.** A. W. DAVIDSON and W. H. McALLISTER (J. Amer. Chem. Soc., 1930, 52, 507—519; 519—527).—II.  $f$ . p.-composition curves have been obtained for binary systems consisting of acetic acid and potassium, ammonium, lithium, lead, barium, and calcium acetates, and additive compounds have been isolated. Solvation is most marked and the solubility is greatest for the acetates of the most electro-positive metals. Of the additive compounds only the  $\text{MOAc} \cdot \text{HOAc}$  compounds of potassium and ammonium have true m. p. In acetic acid solution acetates behave as bases towards indicators, restoring neutrality after addition of dry hydrogen chloride. Water and ammonia behave in the same manner. A method of preparation of pure ammonium acetate is detailed, and the m. p. of this compound, previously uncertain, has been found to be 112—113°.

III. The  $f$ . p.-composition curves for solutions of zinc acetate in pure acetic acid and in acetic acid containing up to about 7 mol.-% of sodium acetate have been determined. The solubility of zinc acetate at constant temperature increases with the sodium acetate concentration so long as the zinc acetate is the stable phase. On the appearance of the ternary phase  $\text{Zn}(\text{OAc})_2 \cdot 2\text{NaOAc} \cdot 4\text{HOAc}$ , however, the solubility decreases with increasing sodium acetate concentration. This is compared with the analogous system zinc hydroxide-sodium hydroxide-water. Some reactions of zinc and of its acetate and other salts with various reagents in dry acetic acid solution are described.

J. W. SMITH.

**Determinations of the solubilities of radium salts.** O. ERBACHER (Ber., 1930, 63, [B], 141—156).—For the detailed account of the experimental procedure the original memoir should be consulted. The recorded values for the solubility (g. per 100 g. of solution) in water at 20° and the specific contraction for radium bromide, chloride, and nitrate are respectively 41.4 g. and 0.0010, 19.7 g. and 0.0015, and 12.2 g. Deduction of the solubility of radium salts by extrapolation from the data for the alkaline-earth metals is not permissible, since it leads to values differing widely from those found experimentally. There is no simple relationship between the difference

in solubility of barium and radium salts and the degree of enrichment in radium in the crystals resulting from fractional crystallisation. A notably greater enrichment is observed with the bromides than with the chlorides, although the difference in solubility is somewhat smaller with the former than with the latter substances. With the nitrates a distinct but not great enrichment is observed, thus affording an unusual instance of the accumulation of the more freely soluble component in the crystals obtained by fractionation of two salts with the same anion which presumably form an unbroken series of mixed crystals with one another.

H. WREN.

**Theory of supersaturated salt solutions.** E. N. GAPON (J. Russ. Phys. Chem. Soc., 1929, 61, 1721—1727).—It is shown on theoretical grounds that for every degree of supersaturation there must be a limiting weight of crystal below which seeding does not provoke crystallisation. Three classes of supersaturated solutions may exist—stable, metastable, and labile, according to whether the result of seeding is exclusively growth of the crystals added, both this and the formation of new centres of crystallisation, or, finally, exclusively precipitation of crystals, without growth. The concentrations at which these types of supersaturated solutions exist are constant for any given solute.

R. TRUSZKOWSKI.

**Induction period in the crystallisation of supersaturated solutions.** E. N. GAPON (J. Russ. Phys. Chem. Soc., 1929, 61, 1729—1741).—The length of the induction period in the crystallisation of supersaturated solutions is given by the expression  $IC^{n-1} = \text{const.}$ , where  $C$  is the concentration of the solute and  $n$  the order of the reaction, determined by the number of ions into which the given solute is dissociated, but dependent also on whether the reaction is one of spontaneous or of catalytically induced crystallisation. The above expression is verified for both cases, as well as for double decomposition with precipitation of the product. The energy of activation of molecules calculated from the induction constant is smaller than that calculated from the velocity of crystallisation.

R. TRUSZKOWSKI.

**Adsorption of gases by solids.** A. GANGULI (J. Physical Chem., 1930, 34, 665—668).—Theoretical. From a consideration of the data of other workers, it is concluded that for gases the heats of adsorption and of sublimation are equal to Póányi's maximum adsorption potential. Adsorption is then supposed to be essentially a process of condensation at the surface, the adsorbed substance being present generally as a unimolecular layer of solid at the interface forming adsorption compounds similar to but more complex than the solid solution.

L. S. THEOBALD.

**Sorption of gases on crystal faces.** J. B. M. HERBERT (Trans. Faraday Soc., 1930, 26, 118—127).—The rate of sorption at 0° and at constant pressures between 8 and 718 mm. has been determined for ammonia and sulphur dioxide on sodium chloride and for ammonia on sapphire. The results for sodium chloride are consistent with the hypothesis that the complete isotherm for any pressure within the range studied is S-shaped. Different portions of the curve

are covered by the observations at different pressures. Contrary to expectation, a longer time is required to approach sorption equilibrium on a crystalline face than on a non-crystalline one. Desorption is more rapid than sorption, but very far from instantaneous. In no case was equilibrium sufficiently approached even after a month to permit of extrapolation to the equilibrium value.

F. G. TRYHORN.

**Adsorption by chemically active surfaces.** S. N. CHAKRAVARTI and K. C. SEN (Z. anorg. Chem., 1930, 186, 357—364).—The adsorption by freshly-precipitated zirconium hydroxide of a series of fatty acids and of a series of substituted benzoic acids increases with the ionisation constant of the acid. The capillary activity of the adsorbed acid is outweighed by the chemical attraction between it and the adsorbent.

F. L. USHER.

**Adsorption of ferric chloride by crystalline barium sulphate.** (Mlle.) L. DE BROUCKÈRE (Bull. Soc. chim. Belg., 1929, 38, 409—421).—Measurement of the adsorption of ferric chloride by barium sulphate indicates that micelles and complex ions and molecules are adsorbed much more readily than simple ions and molecules. Thus from a pure aqueous solution of ferric chloride much more than one equivalent of iron is adsorbed per equivalent of chlorine, the ratio falling, however, with increasing dilution, probably as a result of the decrease in size of the micelles. With solutions containing free hydrochloric acid, the ratio exceeds 1 when micelles are present and is less than 1 when they are absent. For a given salt concentration the ratio decreases continuously with increasing acid concentration, tending towards the value 0.6 : 1, which would correspond with the formula  $H_4Fe_2Cl_{10}$ , whilst the actual quantity of substance adsorbed first falls to a minimum and then rises again, the destruction of the micelles by the acid being more than compensated for in the more concentrated solutions by the formation of chloro-ferric complexes. The fact that ferric chloride is adsorbed to a much greater extent than the chlorides of other trivalent metals is therefore attributed to the presence of micelles.

R. CUTHILL.

**Special selective adsorption of Japanese acid clay.** S. UENO (J. Soc. Chem. Ind. Japan, 1930, 33, 35—37B).—It has been previously shown that Japanese acid clay adsorbs soaps from oil solutions. It has now been found that the acid value of the oil is increased by this treatment to a figure considerably above that of the original oil or of the earth. Apparently the basic constituent of the soap is adsorbed to a greater extent than the acid. Tests are described in which solutions of sodium stearate, oleate, linoleate, etc. in such oils as olive oil or linseed oil were heated at 120° with the clay for a few minutes and then filtered, with the result stated.

C. IRWIN.

**Mixed adsorbents.** N. A. SCHILOV, M. M. DUBININ, and S. A. TOROPOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1765—1776).—See A., 1929, 1376.

**Adsorption in solvent mixtures.** II. E. ANGELESCU and V. N. COMĂNESCU (Kolloid-Z., 1930, 50, 114—116).—Measurements of the adsorption of picric acid by carbon from solutions in alcohol-water,

alcohol-toluene, and alcohol-xylene mixtures confirm the conclusions reached from previously reported work (A., 1928, 581).  
E. S. HEDGES.

**Adsorption from solutions and polarity of the solvent.** E. HEYMANN and E. BOYE (Naturwiss., 1930, 18, 157).—The adsorption of solutes on carbon, using various solvents, has been studied. For fatty acids, benzoic acid, and frequently for iodine, the power of adsorbing decreases with increasing dipole moment of the solvent. In other cases (especially amines) the rule no longer holds. The polarity of solvent molecules influences not only adsorption but also the molecular state of the solute and as a result changes in dipole moment occur. The deformation polarisation must also be taken into account; in the homologous series of alcohols having a practically constant dipole moment the adsorbability of the solute decreases with increasing molecular polarisation of the solvent. The results with mixed solvents show that if both constituents are non-polar, the relation between adsorption and composition is linear. If one solvent is polar, two possibilities arise: (a) the curve for molecular polarisation is not very different from a straight line (e.g., chloroform-benzene, chlorobenzene-benzene, toluene-benzene) and the adsorption curve is of a similar type; (b) the polarisation curve shows a maximum and the adsorption curve a minimum, frequently at roughly the same composition (e.g., alcohol-benzene, alcohol-carbon tetrachloride, acetone-carbon tetrachloride).

R. A. MORTON.

**Variation of the surface tension of aqueous solutions of certain dyes with time.** J. C. GHOSH and S. C. DUTT (J. Indian Chem. Soc., 1929, 6, 903—910).—The method of Rhode (Ann. Physik, 1906, [iv], 19, 935) has been applied to the measurement of changes in the surface tensions of aqueous solutions of dyes on keeping. With pure water and with aqueous solutions of diamond-fuchsin and methylene-blue there was no change in surface tension with time, but very considerable diminutions were observed over periods of about 3 hrs. with rhodamine-B, crystal-violet, Bismarck-brown, and malachite-green. The lowering of the surface tension through dissolution of dyes of the latter class for similar concentrations is much higher than with the former group. The gradual change in surface tension of these dye solutions is attributed to the increasing surface concentration of the micelles with time, and a theoretical equation is developed on a kinetic basis expressing the change of surface tension with time. The experimental results obtained are in accordance with this theory.

J. W. SMITH.

**Structure of surface films. XIV. Esters of fatty acids; evidence of flexibility in the long chains. XV. Amines.** N. K. ADAM (Proc. Roy. Soc., 1930, A, 126, 366—372, 526—541; cf. this vol., 257).—I. The surface films formed on water by the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-octyl, and *n*-hexadecyl esters of palmitic acid have been examined and curves showing the relation between area per mol. and lateral compression or surface pressure are reproduced. When the alkyl chain is not more than 4 carbon atoms long, the temperature low, and the com-

pression high, condensed liquid films with the usual area of about 20.5 sq. Å. at no compression can be obtained. It is considered that in these films the alkyl chain continues the direction of the acidic chain down into the water. With longer alkyl chains, or at higher temperatures or lower pressures, the esters form liquid expanded films, of area about 85 sq. Å. at no compression, with the molecules held to the water by the oxygen-containing groups in the centre, both chains pointing generally upwards, but oscillating violently through a number of angles of tilt. This hypothesis is confirmed by measurements with glycol dilaurate, which is almost certain to form an expanded film with both the chains in motion; stable films are formed, indistinguishable from those of octyl palmitate, except for a lower tendency to collapse under compression. With very long alkyl chains (as in *n*-hexadecyl palmitate) solid films with an area of about 41 sq. Å. are formed, and the structure is clearly that of two long chains packed closely side by side and pointing nearly vertically upwards. The results afford clear evidence for the flexibility of long hydrocarbon chains; additional evidence for this is discussed.

II. Measurements are recorded on unimolecular surface films of a number of long-chain amines,  $C_nH_{2n+1}NH_2$  (where *n* is 14, 16, 17, 18, or 20), on aqueous solutions of acidity varying from 0.1*N*-alkali to 0.1*N*-acid, buffered solutions being used for most of the intermediate acidities. Owing to the difficulty of using the free bases, the hydrochlorides were employed, comparative measurements yielding proof that the same results are obtained with the latter as with the former. The adequacy of a benzene-alcohol mixture as a solvent from which substances can be conveniently spread on a surface is also established. The results indicate that the  $p_H$  of the solution on the acid side of neutrality is of little importance, but that the structure of the films is highly dependent on the nature of the acid radical. The amines form salts with the acids, and the structure of the films of the phosphates, sulphates, hydrochlorides, acetates, phthalates, and benzenesulphonates are all very different. Similar results are obtained on the phthalate buffer and on the much more acid benzenesulphonic acid, probably owing to the similarity in constitution of the amine benzenesulphonates and phthalates. In most cases the expanded films on the acid side are "gaseous," but the amount of lateral adhesion between the molecules varies very much in different series, the acetates having very much less adhesion than the hydrochlorides. On alkaline solutions the condensed films of the amines are solid and of the simple "close-packed chain" type, of area 20.5 sq. Å. per mol. at no compression. Lyons and Rideal's recent theory of interlocking chains (A., 1929, 875) is criticised; the present results do not confirm their value of 26 sq. Å. for the area per mol. of the amines.  
L. L. BIRCHUMSHAW.

**Osmosis of liquids. III.** F. A. H. SCHREINERMAKERS (J. Gen. Physiol., 1930, 13, 335—347).—Theoretical. A discussion of the importance of the nature of the membrane which is permeable to more than one substance.  
C. C. N. VASS.



**Membrane and osmosis. III.** F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 1152—1158).—Theoretical.

**Dipole measurements of organic molecules in benzene solution. III.** O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1930, **B**, **6**, 441—445; cf. this vol., 134, 275).—The dipole moments of benzylideneacetone and dibenzylideneacetone in benzene are both  $3.3 \times 10^{-18}$  e.s.u. The increase of this value above that for acetone is to be attributed to the influence of the aromatic group on the moment of the carbonyl group and not to a large atomic polarisation which, otherwise, would have to be postulated. For phthalaldehyde, isophthalaldehyde, and terephthalaldehyde the values are 4.50, 2.86, and  $2.35 \times 10^{-18}$  e.s.u., respectively. The first two values are in good agreement with the theory of the vector addition of the moments of disubstituted benzene derivatives. On the same basis, however, the value of the third should be zero. The following dipole moments have also been determined: furfuraldehyde,  $3.57 \times 10^{-18}$ ; nitrobenzene,  $3.22 \times 10^{-18}$ ; *p*-benzoquinone,  $0.67 \times 10^{-18}$  e.s.u. M. S. BURR.

**Application of the differential ebullioscope to the investigation of the volatility of dissolved substances.** E. BUREŠ (Coll. Czech. Chem. Comm., 1930, **2**, 70—76).—See this vol., 31.

**Ebullioscopic investigations of the molecular equilibria of resorcinol in barium chloride solutions.** F. BOURION and E. ROUYER (Compt. rend., 1930, **190**, 303—305).—In continuation of the authors' investigations of the molecular state of resorcinol in various salt solutions (cf. A., 1927, 515; 1928, 233; 1929, 396), measurements have been made of the b.-p. elevations of solutions of resorcinol in 0.25*M*- and 0.6125*M*-barium chloride solutions. The results indicate that there is an equilibrium between simple and double and also between simple and triple molecules of resorcinol. The b.-p. constant is greater than for water and increases with the concentration of barium chloride. It is also greater than for potassium chloride solution of the same equivalent concentration, of the same order as for sodium and calcium chlorides, and smaller than for lithium chloride. The equilibrium coefficients of the resorcinol molecules are of the same order of magnitude as in solutions of potassium, sodium, and calcium chlorides, but, for the triple molecules, the coefficient is appreciably smaller than in lithium chloride solutions. Divergence of the b.-p. constants of barium chloride from that of water is to be explained by the adsorption of water by the salt ions. M. S. BURR.

**Cryoscopic study of paraldehyde in aqueous solution and in solutions of potassium chloride.** F. BOURION and E. ROUYER (Compt. rend., 1930, **190**, 585—587).—Cryoscopic measurements indicate that paraldehyde (1.67—10.90%) exists in water at 0° and in an aqueous 0.5*M*-solution of potassium chloride (K., 23.0) as the trimeride of acetaldehyde (C<sub>2</sub>H<sub>4</sub>O)<sub>3</sub>. It depolymerised in 1.225*M*-potassium chloride solution to an extent which increases as its concentration decreases. J. GRANT.

**Cryoscopic examination of mixtures of electrolytes.** P. I. GONTSCHAROV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1513—1561).—Mixtures of pairs of solutions of the following substances: hydrochloric acid, acetic acid, and potassium, lithium, and calcium chlorides, have been examined cryoscopically. A cryoscopic coefficient,  $\Delta/(\delta_1 + \delta_2)$ , is proposed in which  $\Delta$  is the observed depression of f. p., and  $\delta_1 + \delta_2$  the sum of the depressions of the individual salts in solution. The cryoscopic coefficient has in most cases a value greater than unity (the maximum observed value is 1.250 in the case of solutions containing *M*-hydrochloric acid and *M*-calcium chloride, whilst the lowest value found is 0.998 for solutions containing 0.1*M*-hydrochloric acid and 0.05*M*-calcium chloride). All the salts examined possess the same cryoscopic properties, independently of whether the given salt is hydrated in solution or not. The deviation from unity of the cryoscopic coefficient is relatively greater with electrolytes of smaller ionic volume. The value of the cryoscopic coefficient of a given system corresponds very closely with that of its activity coefficient, measured electrometrically. Jones' formula (Z. physikal. Chem., 1890, **6**, 405) does not agree with the experimental results. Direct measurement of the dielectric constant of aqueous solutions of electrolytes shows that the value of this constant is smaller than that of the pure solvent. The following theory of the action of electrolytes on the properties of solutions is proposed. In the first stage, hydration of ions or formation of spheres of influence around ions leads to the exhaustion of available molecules of free water; with increasing concentration of the electrolyte, dehydration of ionic hydrates or diminution of ionic spheres of influence supervenes and depolymerisation of water complexes may also occur.

R. TRUSZKOWSKI.  
**Tendency to association of amino-acids in aqueous solution.** M. FRANKEL (Biochem. Z., 1930, **217**, 378—388).—F.-p. and b.-p. measurements show that glycine, *D*-arginine, and *L*-dihydroxyphenylalanine are associated to the maximum extent of 1.18, 1.4, and 1.6%, respectively, in concentrated aqueous solutions. Alanine, leucine, and valine behave normally and *L*-asparagine shows very slight association. The refractive index of concentrated solutions of glycine and *L*-asparagine is lower than that calculated from the data for dilute solutions, and this is also held to indicate association. K. V. THIMANN.

**Osmotic pressure in concentrated solution.** S. KANEKO (J. Soc. Chem. Ind. Japan, 1930, **33**, 24—25B).—The equations  $d\bar{v}/dp = \bar{v}x - d\alpha/dc$ ,  $P = (RT/\bar{v}) \times \log_e f_0/f_1$ ,  $\bar{v} = M(V - x \cdot dv/dx)$  are derived in which  $\bar{v}$  is the partial molal volume,  $P$  the pressure,  $\alpha$  compressibility of solution,  $c$  concentration in g.-mol.,  $f_0$  and  $f_1$  are the fugacities of the pure solvent and of the solvent in the solution,  $M$  is the mol. wt. of the solvent,  $v$  its mol. volume, and  $x$  the mol. fraction of the solute. C. W. GIBBY.

**Viscosity of solutions of electrolytes.** B. N. FINKELSTEIN (Physikal. Z., 1930, **31**, 130—135).—Theoretical. An attempt has been made to develop a generalised form of the Einstein theory applicable

to strong binary electrolytes dissolved in a dipolar solvent such as water.

R. A. MORTON.

**Theory of viscosity of solutions of strong electrolytes.** B. N. FINKELSTEIN (Physikal. Z., 1930, 31, 165—167; cf. Falkenhagen and Dole, A., 1929, 1389).—Mathematical. The relation between the viscosity and the concentration of a solution of a strong electrolyte is found to involve two independent factors, one of which is represented by the deformation of the ionic atmosphere, whilst the other is made up of two parts, each of which can be derived from an expression involving the first power of the concentration.

A. J. MEE.

**Change of volume on neutralisation. II.** J. J. SASLAVSKI and E. G. STANDEL (Z. anorg. Chem., 1930, 186, 171—175; cf. A., 1929, 759).—The changes in volume on mixing equivalent weights of sodium hydroxide and hydrochloric, hydrobromic, formic, and acetic acids, and on mixing equivalent quantities of ammonia with hydrochloric, formic, and acetic acids, have been measured. The magnitude of the increase in volume in the first series increases with the concentration of the solutions to a flat maximum, then decreases. In the second series the contraction varies linearly with the concentration, being as great as 9% for 18*N*-ammonia-formic acid solutions.

A. R. POWELL.

**Refractometry. XIII. Methods of refractometry and the refractivity-concentration relations of perchloric acid.** K. FAJANS and M.-L. GRESSMANN (Z. physikal. Chem., 1930, 146, 309—313; cf. A., 1929, 1385; Hantzsch and Dürigen, *ibid.*).—Measurements of the refractivity of perchloric acid solutions have been repeated and earlier results are confirmed. The method of weight-dilution is at least as accurate as direct titration.

F. L. USHER.

[Methods of refractometry and the refractivity-concentration relations of perchloric acid.] F. DÜRIGEN and A. HANTZSCH (Z. physikal. Chem., 1930, 146, 314; cf. preceding abstract).—The accuracy of the weight-dilution method is recognised and the existence of a minimum mol. refraction at about 18 mol.-%  $\text{HClO}_4$  is admitted.

F. L. USHER.

**Absorption spectra of mixtures of dilute solutions of copper sulphate and sodium sulphite in the red and ultra-violet.** J. C. GHOSH and S. N. CHAKRAVARTI (J. Indian Chem. Soc., 1929, 6, 823—825).—0.002*M*-Copper sulphate solution, which appears almost colourless to the eye in layers 1 cm. thick, develops a perceptible greenish-blue coloration on mixing with sodium sulphite solution. This increase in absorption coefficient in the red is attributed to an unstable intermediate complex formed by the action of copper sulphate with sodium sulphite. This complex must decompose fairly quickly, since the colour disappears after some time. Mixtures of copper sulphate and sodium sulphite solutions show no exaltation in the extinction coefficient in the ultra-violet between 260 and 296  $\mu$ . It is suggested that the inertness of copper sulphate towards the photochemical oxidation of sodium sulphite is accounted for by this last fact, whilst its catalytic

action on the dark oxidation of sodium sulphite may be explained by the pronounced exaltation of extinction coefficients of the mixtures of these two salts in the red and infra-red regions.

J. W. SMITH.

**Extinction coefficient of mixtures of copper sulphate with dextrose, glycerol, and sodium formate in the ultra-violet as experimental evidence in favour of the formation of unstable intermediate compounds. IV.** J. C. GHOSH and S. N. CHAKRAVARTI (J. Indian Chem. Soc., 1929, 6, 871—877).—Measurements have been made of the extinction coefficients at various wave-lengths in the ultra-violet region of mixtures of alkaline copper sulphate solutions with dextrose, glycerol, and sodium formate, in order to determine whether the hypothesis of the formation of intermediate compounds prior to photochemical decomposition is supported by such measurements. Using copper sulphate in the form of Fehling's solution, the experimental data obtained could be explained quantitatively on the basis of an equilibrium between copper sulphate and dextrose and copper sulphate and glycerol as reactants and the intermediate complex formed by the loose combination of one molecule of each reactant, and on the assumption of a definite value of the molecular extinction coefficients for each wave-length for the intermediate complex. With Benedict's solution, however, the molecular extinction coefficient must be assumed to be constant for all wave-lengths.

J. W. SMITH.

**Condition of strong electrolytes in concentrated solution. III. Tetra-alkylammonium nitrates.** H. VON HALBAN and J. EISENBRAND (Z. physikal. Chem., 1930, 146, 294—308; cf. A., 1928, 590).—The nitrate absorption band at 300  $\mu$  can be displaced toward either the ultra-violet or the red by varying the cation. The lower members of the alkali metal group displace the band towards the violet, and those of higher at. wt., including substituted ammonium cations, towards the red. In experiments with tetraethyl- and tetrapropyl-ammonium nitrates in chloroform, methyl-alcoholic, and aqueous solution the largest effects were obtained in chloroform and the smallest in water. The results are discussed. Displacement toward the ultra-violet is probably due to the formation of an absorbing complex between the cation and the nitrate ion, and displacement toward the red to molecular association or complex formation.

F. L. USHER.

**Homology of  $\text{BeF}_4''$  and  $\text{SO}_4''$  ions from chemical, structural, and crystallographic points of view.** P. B. SARKAR and N. RAY (J. Indian Chem. Soc., 1929, 6, 987—990).—In solutions of the double fluorides  $2\text{KF} \cdot \text{BeF}_2$  and  $2\text{NH}_4\text{F} \cdot \text{BeF}_2$  the beryllium is a constituent of a complex ion, because beryllium hydroxide is only incompletely precipitated by ammonia from these solutions, and also because electrolysis of these solutions produces a gradual and marked increase in the concentration of beryllium at the anode, although part of the beryllium is precipitated as hydroxide at the cathode. It is therefore assumed that in aqueous solutions of these salts the  $\text{BeF}_4''$  ion exists, although partly dissociated into  $\text{Be}''$  and  $4\text{F}'$ . This ion, being isosteric

and isoelectric with the sulphate ion, may be expected to show a close relation with it in physical and chemical properties. This is observed in the molecular volumes of the ammonium salts and the isomorphism of the potassium salts. Both potassium and ammonium beryllium fluoride form double salts with the sulphates of bivalent elements which are monoclinic and isomorphous with the double sulphates, and also form alums with aluminium sulphate.

J. W. SMITH.

**Comparison of some physical constants of [sodium] thiocyanate, azide, and nitrite solutions.** P. GÜNTHER and W. PERSCHKE (J.C.S., 1930, 100—104).—Reasons are given for doubting Cranston and Livingstone's conclusions (A., 1926, 458) that the anions in azide and cyanate solutions have the same spatial structures. In an endeavour to determine the structure of the thiocyanate ion by Cranston and Livingstone's method the sp. gr. (20°), viscosities (20°), specific refractivities ( $n_D^{25}$ ), and molecular conductivities of sodium thiocyanate, azide, and nitrite solutions up to 3M were determined. The results show that no conclusions can be reached from such measurements as to the similarity or dissimilarity of the atomic structures of the ions investigated, Cranston and Livingstone's results being considered fortuitous.

S. K. TWEEDY.

**Electrokinetic potential of diaphragms.** N. SCHÖNFELDT (Wiss. Veröff. Siemens-Konz., 1929, 8, [2], 97—106).—The electrokinetic potential of a single ceramic diaphragm is given by  $\zeta = \zeta_0(1 + \alpha i)$ , where  $\zeta_0$  is the initial potential rise in the electrical double layer of the diaphragm,  $i$  is the current density, and  $\alpha$  a constant depending on the material of the diaphragm and the solution. In the case of systems with two diaphragms the potential of the diaphragm system is the mean of that of the more strongly negatively-charged cathodic and the less strongly negatively-charged anodic diaphragm.

A. R. POWELL.

**Influence of current density and organic diaphragms on the electro-osmosis of an electrolyte containing sucrose.** W. HILLER and N. SCHÖNFELDT (Wiss. Veröff. Siemens-Konz., 1929, 8, [2], 107—114).—The inversion of sucrose by the acid formed in the electro-osmosis of potassium chloride solution contained between two diaphragms of "mako," quinone-leather, and chrome-gelatin has been determined. Practically no inversion occurred with the last-named, the potassium and chlorine ions being removed almost simultaneously by electro-osmosis, so that the solution remained almost neutral throughout the test; with quinone-leather slight inversion occurred with current densities of 0.5 and 0.25 amp./cm.<sup>2</sup> and with "mako" considerable inversion at all current densities. The potentials of the three diaphragms decreased in the order "mako," quinone-leather, chrome-gelatin, i.e., in the order of decreasing inversion. In general the acidity of the solution increased with increase of current density for a current flow of 1 amp.-hr. and decreased with increase of current density for 12 amp.-hrs.

A. R. POWELL.

**Sedimentation equilibria of colloidal particles.** N. JOHNSTON and L. G. HOWELL (Physical Rev.,

1930, [ii], 35, 274—282).—The distribution of colloid particles under the influence of gravity has been examined with special precautions to eliminate spurious effects. Gold sols were prepared, using Zsigmondy's device for obtaining particles of uniform size, by the reduction of gold chloride by phosphorus dissolved in ethyl alcohol, and the nuclei enlarged in two steps by the reduction of gold chloride on to particles by hydrogen peroxide. The sols were allowed to settle for several days in a deep quartz cell in a carefully controlled thermostat bath; the steady state was determined by taking ultramicroscopic counts on different days. The observed distribution agrees with the exponential law. N. M. BLIGH.

**Determination of distribution curve of polydisperse colloidal systems.** C. E. MARSHALL (Proc. Roy. Soc., 1930, A, 126, 427—439).—Various methods of using the centrifuge for the determination of the distribution curve of polydisperse systems containing all sizes of particles of colloidal dimensions are discussed, and the existing methods are shown to be clumsy and inaccurate. A new method of using the high-speed laboratory centrifuge, applicable within the range  $2\mu$ —20  $\mu$ , is described in detail. The method consists in centrifuging a thin layer of the polydisperse system on top of a column of the dispersion medium (a concentrated aqueous solution of sucrose or carbamide). The influence of the nature of the lower column and of the method of dispersion is discussed. The method is found to be trustworthy to about 1% under conditions suitable for clays, which is comparable with the accuracy of existing methods for fractions greater than  $2\mu$ . As an example of the application of the new method to clay problems, the variations in the degree of dispersion of bentonite have been studied under different conditions. The results indicate that clays are much more sensitive to alkali than has hitherto been supposed, and that they can undergo partial coagulation without the total clay percentage being much altered.

L. L. BIRCUMSHAW.

**Flotation and  $p_H$ . II. Flotation of hydrophilic powders and  $p_H$ .** D. TALMUD and N. M. LUBMAN (Kolloid-Z., 1930, 50, 159—162; cf. A., 1929, 881).—Investigation of the dependence of flotation on hydrogen-ion concentration for oxides, carbonates, and sulphates of metals has shown that the maximum flotation for oxides (excepting silica) and carbonates is in the neighbourhood of neutrality. No definite relation was found for sulphates. The relations for mixtures of powdered substances are very complicated and cannot be expressed in general form.

E. S. HEDGES.

**Flotation and electric charge of precipitates.** D. TALMUD and N. M. LUBMAN (Kolloid-Z., 1930, 50, 163—164).—To investigate the relation between flotation and the charge on the particles, use has been made of the fact that silver iodide precipitates prepared by exact chemical titration are uncharged, those having a slight excess of potassium iodide are negatively charged, and those having a slight excess of silver nitrate are positively charged. Tendency to flotation is at a maximum when the interfacial charge is at a minimum.

E. S. HEDGES.

**Behaviour of hydrophilic and hydrophobic powders in benzene-water mixtures.** D. TALMUD (*Z. physikal. Chem.*, 1930, 146, 315—318).—Preliminary. The hydrophilic powder calcium carbonate settles more quickly in dry than in damp benzene. The sediment in the latter case is flocculent and more voluminous than in the former. Lead sulphide also settles more quickly in the dry liquid, but the volume of the sediment is substantially the same in each case. Further addition of water makes the powders stick to the glass walls, from which they can be removed by oleic acid or by forming a three-phase emulsion by the addition of still more water. These phenomena are not observed with the hydrophobic powder ash-free charcoal. F. L. USHER.

**Colloid crystallisation states of naphthalene.** N. VON WEIMARN (*Kolloid-Z.*, 1930, 50, 164—166).—When concentrated aqueous sugar solutions are mixed at low temperatures with alcoholic naphthalene solutions, the naphthalene passes into a state of colloidal crystallisation. At  $-14^{\circ}$  and with 60% sugar solution this state may last for 15 min., after which the particles form secondary aggregates. The mean dispersity of the crystal particles increases with increase in the viscosity of the medium. The coagulation curve passes through a minimum with increasing concentration. E. S. HEDGES.

**New effect of light on matter.** V. POSPIŠIL (*Physikal. Z.*, 1930, 31, 65—78).—Light of suitable intensity after passing through a screen of water results in a 40% increase in the average (displacement)<sup>2</sup> of soot particles of diameter  $0.4$ – $0.6\ \mu$  as compared with the values for weak illumination. The larger particles are only weakly excited by radiation in the optical region. The relative effects on the movement vary as a first approximation inversely as the viscosity of the liquid medium. The action of optical radiation is lessened by intense infra-red irradiation. The enhancing of Brownian movement by means of light is a kind of luminescence in the region of molecular thermal motion. The fact that light sources relatively stronger in emitting high frequencies are more effective than ordinary electric lamps supports this view. Brownian movement, as enhanced by natural light, exhibits in a plane vertical to the light axis the same circular symmetry as the natural Brownian heat movement. The mean square of the displacement is always linearly proportional to the time. In linearly-polarised light the excited movement does not show circular symmetry. The mean (displacement)<sup>2</sup> along the axis falling in the light plane is always greater than that in the axis at right angles to this direction. The enhancement of Brownian movement takes place in the plane of polarisation of the light. R. A. MORTON.

**Radiation and Brownian movement.** V. POSPIŠIL (*Physikal. Z.*, 1930, 31, 78—80).—The square of the mean displacement for a single quantum impulse on a dark particle suspended in a medium of defined viscosity is calculated and a comparison made with ordinary Brownian movement data. The considerations are applied to the enhancing action of light (cf. preceding abstract). R. A. MORTON.

**General colloid chemistry. XXV. Constitution of colloidal gold.** F. EIRICH and W. PAULI (*Kolloidchem. Beih.*, 1930, 30, 113—162).—An extensive experimental study of the conditions governing the stability of gold sols prepared by the electrical disintegration method has been made. The influence of glass vessels is considerable and Jena glass should always be used. In experiments on the preparation of gold sols in very dilute hydrochloric acid solutions it was found that between  $3 \times 10^{-4}N$  and  $10^{-5}N$ -hydrochloric acid the stability of the sol increases with the concentration of the acid; the stability decreases with increasing duration of the dispersion process. The behaviour of sols towards the addition of electrolytes and also towards centrifuging was studied. The addition of small quantities of hydrochloric acid or potassium chloride has a stabilising effect, chlorine water stabilises only at a concentration less than  $10^{-4}N$ , sulphuric acid and gold chloride diminish the stability or flocculate the sol. Similar sols prepared in very dilute sulphuric acid were less stable and coagulated completely in less than 24 hrs., but the rate of coagulation was retarded by the addition of hydrochloric acid. Sols of gold in dilute potassium sulphate solutions were also prepared, but were very unstable. Sols prepared in the purest conductivity water are exceedingly unstable, but are rendered more stable by the addition of dilute hydrochloric acid and particularly by a mixture of  $10^{-4}N$ -hydrochloric acid and  $5 \times 10^{-5}N$ -chlorine water; very dilute sulphuric acid hastened the coagulation. Gold sols were also prepared in dilute solutions of chlorine, potassium chloride, bromide, and iodide, but it was not possible to obtain sols in dilute potassium fluoride solutions. All the sols gave Zsigmondy's blue ring test with ammonia, indicating the presence of gold compounds in the particles. The influence of carbon dioxide and of potassium hydrogen carbonate on the stability of sols prepared in dilute potassium hydroxide was examined. For the preparation of sols of gold in potassium thio-sulphate solutions a relatively concentrated solution is necessary and the experiment does not succeed at dilutions greater than  $5 \times 10^{-4}N$ . The sols are generally brown and hydrogen sulphide is also present. Gold sols in potassium nitrate cannot be prepared unless the concentration of the salt is greater than  $10^{-3}N$ . The surface compounds on the particles of gold are discussed. E. S. HEDGES.

**Ferric oxybromide hydrosols.** A. W. THOMAS and (Miss) E. R. HAMBURGER (*J. Amer. Chem. Soc.*, 1930, 52, 456—463).—A series of ferric oxybromide hydrosols has been prepared and measurements were made of the viscosities, electrical conductivities, and sodium sulphate liminal values (*i.e.*, the average in millimols. of the amount of salt which just fails to precipitate and the amount which just does precipitate the sol under given conditions). All the sols were pressure-dialysed until the desired iron/bromide ratio was obtained, and then diluted to a concentration of about 400 milliequiv. of iron per litre. As in the case of ferric oxychloride hydrosols (cf. A., 1924, ii, 50) as the ratio iron/halide diminishes the viscosity increases, whilst the liminal value and the con-

ductivity decrease. Ferric oxybromide hydrosols have higher conductivities than ferric oxychloride sols of similar iron/halide ratio, but lower viscosities. They are less readily salted out than the corresponding oxychloride sols. The properties of ferric oxybromide sols change more rapidly with time than those of the oxychloride sols, indicating that the micelles undergo hydrolysis more readily and to a greater extent than those of latter sols. J. W. SMITH.

**Osmotic pressure of solutions of cellulose nitrate.** J. DUCLAUX and R. NODZU (Rev. gén. Colloid., 1929, 7, 385—392).—The osmotic pressure of cellulose nitrate solutions falls with the concentration and the "true molecular weight" can only be obtained by extrapolating the osmotic pressure-concentration curve to zero concentration, and this involves measurements at extreme dilutions. The apparent mol. wt. varies with the kind of cellulose nitrate; for preparations having the same content of nitrogen, the mol. wt. is greater the more viscous is the solution. The value varies with the solvent and is not strongly influenced by the presence of inorganic matter. In cellulose nitrates of different degrees of nitration the apparent mol. wt. determined by osmotic pressure measurements is proportional to the chemical mol. wt. E. S. HEDGES.

**Reactions between hydrophilic sols.** II. W. J. LESLEY (Trans. Faraday Soc., 1930, 26, 69—78).—The reaction of silicic acid sol with albumin sol at various  $p_H$  values is similar to that with gelatin sol (A., 1929, 1382), but silicic acid and agar do not react. With silicic acid and glycine, too, there is no precipitation, and with tyrosine or 8-hydroxyquinoline the precipitate formed in presence of silicic acid differs only in appearance from that produced in its absence, containing little or no silica. It is therefore concluded that with these substances such precipitation as there is arises simply from the normal variations in solubility with change in  $p_H$ .

R. CUTHILL.

**Effect of electrolytes on the inversion of emulsions.** H. V. TARTAR, R. E. LOTHROP, and G. F. PETTENGILL (J. Physical Chem., 1930, 34, 373—378; cf. A., 1929, 506).—Sodium chloride inverts emulsions of water with benzene, xylene, chloroform, or carbon tetrachloride when sodium oleate or stearate, but not sodium laurate, is used as emulsifying agent. Emulsions prepared with potassium stearate, oleate, laurate, or pelargonate are not inverted by potassium chloride; only oil-in-water emulsions are obtained. Ethyl ether gives only oil-in-water emulsions. The emulsions with the laurates are less stable than those prepared with the oleates and stearates. A rise in temperature favours the oil-in-water type, whilst a fall favours the water-in-oil type. The conductivity method for determining emulsion type gives results in agreement with those of the Briggs drop method. L. S. THEOBALD.

**Optimum conditions for the formation of silica gel from alkali silicate solutions.** I. R. C. RAY and P. B. GANGULY (J. Physical Chem., 1930, 34, 352—358; cf. Flemming, A., 1902, ii, 646).—The optimum conditions for the formation of silica gel by the action of hydrochloric or sulphuric

acid or ferric chloride on alkali silicate solutions have been investigated. For a given concentration of alkali silicate gel formation is confined to a narrow range of  $p_H$  and a U-shaped curve enclosing the region of gel formation and symmetrical about the neutral point is obtained when the concentration of silicate is plotted against  $p_H$ . With sulphuric acid the region of gel formation is less sharply defined than with hydrochloric acid. The setting of a silica gel is accelerated by ultra-violet light. The addition of ferric chloride to sodium silicate does not readily give a gel at the ordinary temperature, but at 60° gel formation is rapid. An excess of ferric chloride yields no gel; a part of the precipitate originally formed is dissolved. An arrangement for the production of silica gels from dilute solutions is described.

L. S. THEOBALD.

**Soap films and colloidal behaviour.** A. S. C. LAWRENCE (J. Physical Chem., 1930, 24, 263—272).—The nature of soap films is discussed. The film-forming capacity and the colloidal properties of soap solutions result from the peculiar form of the soap molecules, the isolated position of the single water-soluble group in an insoluble molecule being the origin of both properties. L. S. THEOBALD.

**Factors controlling the type of water-soap-oil emulsions.** V. E. WELLMAN and H. V. TARTAR (J. Physical Chem., 1930, 34, 379—409).—When aqueous solutions of sodium stearate or palmitate of sufficiently high initial concentration are placed in contact with organic liquids such as benzene, toluene, carbon tetrachloride, etc., a transfer of soap across the interface takes place in amounts depending on the original concentration of the soap and on the organic liquid used. The transferred soap appears to be almost entirely in the gel condition. This important property has been previously overlooked in the study of emulsions. These results together with those of other workers indicate that the distribution of soap emulsifiers between the immiscible phases of emulsions is a factor determining the type of emulsion; it is independent of the metal involved. The behaviour of emulsions of sodium stearate, palmitate, or oleate with benzene or carbon tetrachloride shows further that the distribution of soap is controlled by factors such as temperature, phase-volume relationships, mechanical treatment, and presence of electrolytes, which influence solubility and wetting power. Oil-in-water emulsions are stabilised by soaps present chiefly in the aqueous phase and the soaps are probably colloidal at the interfaces of such emulsions. Soaps which are more easily wetted by the "oil," or are chiefly in the colloidal condition in the non-aqueous phase, temporarily stabilise water-in-oil emulsions. Low interfacial tension aids dispersion but must be accompanied by a substance capable of forming permanent films round the droplets in order that the emulsion may be stable. L. S. THEOBALD.

**Behaviour of colloidal particles at an electrode.** M. SHIKATA and N. HOSAKI (J. Soc. Chem. Ind. Japan, 1929, 32, 361—362B).—The discharge potential of a colloidal particle is determined entirely by the nature of the inorganic ions in solution.

F. J. WILKINS.

**Distribution of crystalloids in colloidal systems similar to cytoplasm.** B. ZAWADZKI (*Acta Biol. Exp.*, Warsaw, 1929, 4, 119—149).—Sugars (sucrose, maltose, dextrose, galactose, and levulose) in solutions of egg-white or -yolk are shown cryoscopically to be dissolved exclusively in the "free" water of the system. Determination of the concentration of sugar in such systems, as compared with that in pure water, allows the volume of "free" and of "bound" water to be evaluated. Carbamide is distributed over the water of the whole system, and the same applies to sodium and potassium chlorides; these salts do not undergo sorption by the colloids present. Calcium and magnesium chlorides are in solution both in the "free" and the "bound" water of egg-yolk solutions, and are, further, sorbed by the colloidal constituents of this system.

R. TRUSZKOWSKI.

**Kinetics of coagulation.** A. M. PATEL and B. N. DESAI (*Trans. Faraday Soc.*, 1930, 26, 128—133).—The effects of impurities and of concentration on the velocity of coagulation in the presence of an electrolyte have been studied in the case of thorium hydroxide sol, using the photo-electric cell method (A., 1928, 948, 950). With increasing time of dialysis the coagulation-time curves tend to become less and less S-shaped. In sols dialysed for 14 days an S-shaped curve is not obtained at any concentration of added electrolyte (sodium chloride), even with a concentrated sol. The S-shaped curves also disappear with increased dilution of the sol. It thus appears that a proper control of the purity and the concentration of the colloid is necessary to demonstrate the auto-catalytic nature of the coagulation.

F. G. TRYHORN.

**Influence of temperature on "rapid" coagulation of gold hydrosol.** P. J. R. BUTLER (*J. Physical Chem.*, 1930, 34, 656—664; cf. Davies, A., 1929, 393).—For gold sols thermo-senscence (*loc. cit.*) persists even under conditions of rapid coagulation, i.e., when sufficient coagulant is present completely to discharge all sol particles. This indicates that thermo-senscence is accompanied by a decrease in the range of attraction,  $\rho$ , postulated by Smoluchowski as existing around each sol particle; this results from an actual decrease in size of the sol units. Data for the region of rapid coagulation show that the effect of temperature is accounted for by a change in viscosity of the system as is demanded by Schmoluchowski's theory. The ratio of  $\beta_{80^\circ}/\beta_{25^\circ}$  found is 2.87—3.08 as against 2.96 demanded by the theory. An apparatus for measuring coagulation accurately over periods of 20 sec. is described.

L. S. THEOBALD.

**Influence of lyophile colloids on the precipitation of salts. Agar-agar and lead iodide.** II. T. R. BOLAM (*Trans. Faraday Soc.*, 1930, 26, 133—144; cf. A., 1928, 126).—Electrometric potential measurements show that the activity of iodide ion in unpurified agar gel containing potassium iodide is slightly less than in an aqueous solution of the salt of the same concentration. The agar reduces considerably the activity of lead ion in lead nitrate solutions. Purification of the agar by washing and by treatment with alcohol is without appreciable

effect on the value of the activity of the iodide ion, but reduces considerably the inhibition of the activity of the lead ion. Similar measurements show that agar inhibits the precipitation of lead iodide from suitable mixtures of lead nitrate and potassium iodide. Purified agar possesses this inhibitory power to a considerable degree.

F. G. TRYHORN.

**Silicic acid gels. II. Hydrogen-ion concentration and cataphoresis of the gel-forming mixtures. III. Effect of non-electrolytes on the time of setting of the gel-forming mixtures.** M. PRASAD and R. R. HATTIANGADI (*J. Indian Chem. Soc.*, 1929, 6, 893—902, 991—1000; cf. A., 1929, 1235).—I. A study of the hydrogen-ion concentrations of gel-forming mixtures of sodium silicate and acetic acid has been made. Cataphoresis experiments show the existence of colloidal particles in these mixtures, the particles being positively charged in acid media and negatively charged in alkaline. The minimum time of setting of gels always occurs at above  $p_H$  7. Since gel formation probably occurs through coagulation of the silicic acid sol, the time of setting may be expected to be a minimum at the isoelectric point of the sol particles. However, if zero *P.D.* on the particles is indicated by the neutrality of the mixtures, then in mixtures setting in minimum time there must be some small negative contact potential on the particles. This critical contact potential rises with rising concentration of the mixture. When mixtures are alkaline the  $p_H$  values increase during and after gelation, indicating that some change, probably hydrolysis of some unchanged sodium silicate, takes place even after the gel has set. On the other hand, acidic mixtures show no such change, suggesting that only the neutralisation of the positive charge by the anions present in the mixture is taking place. Contrary to the Schulze-Hardy law, hydrochloric acid and acetic acid are better coagulants of the positive sol than sulphuric acid. The general conclusion is reached that the time of setting of a gel depends mainly on the density of charge on the particles and on the effective concentration of coagulating agent present, as well as on factors such as viscosity and interfacial tension.

II. The effect of addition of methyl, ethyl, or propyl alcohol, acetone, or pyridine on the time of setting of silicic acid sols has been investigated. In an alkaline medium, in which the colloidal particles carry a negative charge, the addition of non-electrolytes decreases the time of setting of either a dialysed or an undialysed sol. In a moderately acid medium, where they are positively charged, their addition increases the time of setting, i.e., they exert a protective influence on the particles. Pyridine is exceptional, since it hastens coagulation even in moderately acid mixtures. These effects cannot be explained by the diminution of the dielectric constant of the mixtures and hence by the change in charge on the colloid particles unless the influences are all specific. Although it is thought probable that the alcohols and acetone may stabilise the positively charged sol by increasing the density of the charge, it is suggested that hydration may bear an important rôle in deter-



mining the stability of the highly hydrated positively charged particles of silicic acid in acid media.

J. W. SMITH.

Colloidal condition of cholesterol, cholesteryl ester, and lecithin. I. Preparation of cholesterol and lecithin sols. Coagulation experiments; coagulation swelling values at different  $p_H$ ; coagulation velocity measurements and precipitation by electrolytes. II. Electrokinetic measurements. The  $\zeta$ -potential and the cataphoretic velocity of migration of cholesterol sols. III. [with N. TAVASTSYERNA.] The electric properties of cholesterol and lecithin sols. Measurements of the electrical conductivity and dielectric constant. IV. Dialysis of colloidal cholesterol and lecithin. V. Cholesterol gels, swelling experiments, and the permeability of the gels obtained. I. REMESOV (Biochem. Z., 1930, 218, 86—133, 134—146, 147—156, 157—172, 173—190).—I. A method for the preparation of pure sols of cholesterol (free and esterified) and of lecithin is described and the highest concentrations attained are given. The coagulation limit for cholesterol sols is at  $p_H$  4, for the ester sol at  $p_H$  2, and for lecithin sols at  $p_H$  6.2 (hydrolecithin) and 5.6 (lecithin). Optimum coagulation (isoelectric point) of lecithin sols is at  $p_H$  2.8—2.0. Native protein, some carbohydrates, especially dextrose, some enzymes and certain alkaloids, especially nicotine, act as sensitisers of these sols, whereas bile inhibits. Sensitisation of lecithin sols is accompanied by displacement of the coagulation swelling and of the coagulation optimum. The course of precipitation by alcohol of both sols is autocatalytic in character and stands in close relationship to the lowering of the dielectric constant of the medium. When precipitation by electrolytes is carried out in presence of dextrose, the coagulation velocity curve loses completely its autocatalytic character.

II. The sols of cholesterol, its ester, and of lecithin are electronegatively charged, the  $\zeta$ -potential for cholesterol sol being 27.3 millivolts. Dilution of the sol increases both the stability and the  $\zeta$ -potential of the sol. The critical potential varies with the  $p_H$ , so that the  $\zeta$ -potential falls to null values at  $p_H$  values corresponding with the coagulation values. Dextrose and albumin charge the sols, the protein at its isoelectric point and dextrose at a  $p_H$  approximating to the corresponding coagulation value of the sol. Characteristic  $\zeta$ - $c$  curves obtained by electrolyte (alkaline and alkaline-earth metals) precipitation of cholesterol sols sensitised by addition of dextrose indicate that dextrose under certain conditions can affect the colloidal character of the sols.

III. The specific conductivity of cholesterol and lecithin sols decreases with decrease of concentration but again increases at very small concentrations. The dielectric constant of these sols shows the opposite behaviour on dilution. In presence of dextrose, however, the conductivity increases and the dielectric constant decreases with decreasing sol concentration.

IV. Cholesterol and cholesteryl ester sols diffuse through a semi-permeable membrane, the maximum dialysis of the former being at  $p_H$  7.8 and of the latter at 6.2. In presence of dextrose, the dialys-

ability of cholesterol is increased and the maximum displaced to the alkaline side in proportion to the dextrose concentration. The cholesterol and dextrose of a mixture diffuse in inverse relationship, the maximum dialysis of cholesterol occurring with a minimum of dextrose. The presence of an undialysable fraction of cholesterol and sugar was detected, probably due to the formation of a glycolipin. Serum-cholesterol of normal rabbits and of rabbits fed with cholesterol is completely undialysable.

V. A method for the preparation of cholesterol gels of different concentrations in isoelectric gelatin is described. The swelling minimum of these gels lies at  $p_H$  4.2 (against  $p_H$  4.7 for pure gelatin). Dextrose and carbamide promote swelling of cholesterol. The results are treated mathematically in order to test the formula of Póányi (A., 1914, ii, 721; 1915, ii, 235) in respect to the relationship of adsorption, swelling, and osmotic pressure. The course of swelling of these gels at different  $p_H$  resembles closely that of several biological objects, e.g., the aorta, the swelling minimum of which is at  $p_H$  4.0. Dextrose exerts considerable effect on the permeability of cholesterol gels.

P. W. CLUTTERBUCK.

Physical conditions affecting the setting of gelatin and the bearing of the results on the theory of gel formation. (MISS) W. B. PLEASS (Proc. Roy. Soc., 1930, A, 126, 406—426).—Cooling and heating curves for gelatin solutions of 1.0—10.0% concentration over a temperature range of about 0—50° indicate that heat is evolved on setting and absorbed on melting. At temperatures below about 20°, and for concentrations of gelatin between 10.0 and 2.5%, the rate of cooling is independent of the concentration. Gelation curves are reproduced, showing the minimum concentrations of solutions of gelatin over a range of hydrogen-ion concentration from  $p_H$  0.5 to 11.5 which will set to a gel after keeping for 48 hrs. at constant temperatures of 0°, 12°, 18°, and 25°, respectively. At all temperatures from 0° to 25° the gelation curves exhibit a minimum at the isoelectric point corresponding with about 0.5% of gelatin, but in the isoelectric zone the gelatin is turbid, the systems appear to be unstable, and the gelatin tends to separate from the solution. At 18° or lower, the setting curve exhibits a broadly defined maximum in the acid zone at  $p_H$  2.3—2.6, with a gelatin concentration of 1.2%, followed, between  $p_H$  2.3 and 1.3, by a steady decrease in the concentration of gelatin necessary for gelation. In the alkaline zone, the setting curve slowly rises from  $p_H$  5.0 to 10.0, whilst in the strongly acid and alkaline solutions gelation is inhibited. A rise in temperature causes a decrease in the gelling power of a gelatin solution, more pronounced at temperatures above 18°. At 25°, 1.5% solutions will set only between  $p_H$  4.2 and 5.5. Maximum turbidity occurs in 2.0% gels of  $p_H$  4.8—5.1 at temperatures of 18° or less. At 8.0% the gels are just opalescent and at 10% quite transparent, whilst solutions of 0.2—0.1% concentration are just slightly opalescent. The flocculation of gelatin occurs most rapidly in 1.0% solutions. In a long discussion of the results it is pointed out that there is a striking similarity between the form of the

setting curves, the swelling curves for leaf gelatin in solutions of hydrochloric acid and sodium hydroxide (Jordan Lloyd and Pleass, A., 1928, 119), and the curves for the rate of ice crystallisation in super-cooled gelatin gels of 2.0–4.0% concentration at  $-3^\circ$  over the  $p_H$  range 1.0–10.0 (Callow, A., 1925, ii, 777). The results are interpreted by postulating a change on cooling from a solution of gelatin in water to one of water in gelatin, with the formation of a framework of gelatin and evolution of heat. Turbidity is the indication of heterogeneity, one phase being hydrated gelatin and the other a dilute solution of water in gelatin. In acid or alkaline systems the gelatin combines with less water than in the isoelectric system, and there is an increase in the free water and a decrease in the strength of the gel.

L. L. BIRCHMURSHAW.

**Swelling of gelatin in acids.** E. SAUER and E. KLEVERKAUS (Kolloid-Z., 1930, 50, 130–141).—The following improvements on Fisher's method of measuring the swelling of gels are described. Gelatin powder was put into a graduated tube and allowed to swell in a continuously renewed supply of the swelling agent; the height of the swollen gel in the tube was measured after centrifuging for a definite time in order to expel the enclosed liquid; the experiments were conducted under the shortest possible time conditions so as to eliminate as far as possible the dissolution of the gelatin by the swelling liquid. Kuhn's observation (A., 1922, i, 183), that the maximum swelling is reached at low concentrations of strong acids and at high concentrations of weak acids, was confirmed. The true swelling maximum is always at a somewhat lower concentration of acid than that given in the literature, because in previous work, where the swelling liquid has not been renewed, a reduction in concentration of the acid has not taken place. The amount of acid contained by the swollen gel is proportional to the concentration of acid in the swelling liquid and is uninfluenced by the swelling curve. Although the total amount of acid in the swollen gel is greater than in an equal volume of the swelling liquid, the hydrogen-ion concentration in the swollen gel is actually greater than in the swelling liquid, indicating that the acid bound in the gel is less dissociated. For a number of acids there is a relation between the swelling maximum and hydrogen-ion concentration, which is independent of the degree of dissociation of the acid.

E. S. HEDGES.

**Swelling of the gel composed of cholesterol, lecithin, and gelatin.** J. CALÁBEK and V. MORÁVEK (Kolloid-Z., 1930, 50, 141–147).—The swelling of gelatin, gelatin-lecithin, and gelatin-lecithin-cholesterol has been studied. In solutions more acid than  $p_H$  4.35, gels with an excess of lecithin swell most, but at  $p_H$  8.00 gels with an excess of cholesterol swell the most. Lecithin displaces the isoelectric point of gelatin to the acid side. Gels with 0.3% of cholesterol show a new maximum of swelling between  $p_H$  5.00 and 7.00. Cholesterol and lecithin may act in regard to swelling either in an antagonistic or an additive sense, according to the hydrogen-ion concentration of the solution. At  $p_H$

5.4 to 5.7 the gels swell more in calcium chloride than in potassium chloride solution, and the swelling is even less in the mixed electrolytes.

E. S. HEDGES.

**Capillarity. XIII. Behaviour of true and colloidal solutions in capillaries on evaporation.** K. SCHULTZE (Kolloid-Z., 1930, 50, 106–113).—A study has been made of the relations between evaporation and diffusion in capillaries containing methylene-blue, night-blue, gelatin, agar, and silicic acid, respectively. In most cases, periodic structures are formed in the capillaries. These may be related to the "pectographs" described by Bary (A., 1929, 136).

E. S. HEDGES.

**Plant colloids. XXIII. Erythro-substances.** M. SAMEC and M. BLINC (Kolloidchem. Beih., 1930, 30, 163–196).—Experiments have been directed at the properties of substances in starch which give with iodine a blue colour and a red colour respectively. The following properties of starch solutions were examined: effect of ageing on the stability of the solution, effect of precipitating agents, degree of dispersion in water and in formamide, viscosity and the variation of viscosity with the content of alkali, electrical conductivity, hydrogen-ion concentration, behaviour towards alkali. These properties have been related to the phosphorus and nitrogen contents of the starch. The difference in the state of aggregation of amylo- and erythro-substances indicated by ultramicroscopical examination is traced to a difference in the surface development of the particles. Drying and swelling experiments and chemical analysis do not suggest that water plays a special rôle, and as a working hypothesis it is suggested that there is a difference in the relative adsorption of hydroxyl radicals, a supposition which agrees well with the differences in the relations of amylo- and erythro-substances towards fermentation.

E. S. HEDGES.

**Colloids from the biological and thermodynamical points of view.** V. COFMAN (Rev. gén. Colloid., 1929, 7, 337–351, 406–414).—An attempt is made to apply to colloidal systems the laws applicable to gases and molecular solutions by finding what properties are truly analogous to pressure, volume, and temperature. For the pressure factor the swelling pressure of gels is taken, the volume factor is the volume of the colloidal system minus the volume of the colloidal particles themselves (corresponding with the term  $V-b$  in van der Waals' equation), and consideration of the variation of surface tension with hydrogen-ion concentration leads to the replacement of the temperature factor by the hydrogen-ion concentration. Measurements of the surface tension of solutions of sodium oleate at various hydrogen-ion concentrations have been made and indicate that between the values  $p_H$  5.5 and 9.0 the surface tension is a linear function of  $p_H$ . The surface tension is also proportional to the surface concentration. The spontaneous dispersion of colloids is compared with the boiling of liquids. These ideas are developed in an application of the Carnot cycle to colloidal systems, replacing the usual variables by the analogous factors, and the efficiency of "colloid

machines" working between two limits of hydrogen-ion concentration is considered, and the importance of such a study in relation to muscular action is indicated. The entropy of colloidal systems is discussed. Some measurements of the swelling pressure of gels have been carried out by balancing the swelling pressure against the osmotic pressure of a sugar solution. This was done by placing cubes of 20% gelatin in sugar solutions varying in concentration between 0.5 and 50% and determining by means of weighing whether water passed to or from the gel.

E. S. HEDGES.

**Proteins and electrolytes. Thermochemical investigations.** E. HEYMAN (Kolloid-Z., 1930, 50, 97—105).—The reactions between proteins and electrolytes are discussed from the point of view of adsorption and chemical combination through residual valency, and the difficulties of differentiating these two types of binding, both experimentally and theoretically, are pointed out. Measurements of the heat of reaction of hydrochloric acid, potassium, calcium, aluminium, and zinc chlorides, ferric chloride and hydroxide, and silver nitrate with albumin and glutin have been made and some additional measurements were carried out with glycine. The results for hydrochloric acid, potassium and calcium chlorides, and silver nitrate indicate heats of reaction of less than 1000 g.-cal. and suggest an adsorption process rather than a true chemical reaction. A molecular compound is formed between potassium chloride and glycine, and the heat of reaction is about 1700 g.-cal., being much greater than the values obtained with albumin or glutin (200—300 g.-cal.). The heats of reaction of ferric, aluminium, or zinc chlorides with the proteins have negative values (about —2000 g.-cal.), a fact which is attributed to hydrolysis of the complexes. In the system glycine-ferric chloride, the production of ferric hydroxide was shown experimentally.

E. S. HEDGES.

**Special cases and transition phenomena in the thixotropy of ferric oxide sols.** W. HELLER (Kolloid-Z., 1930, 50, 125—130).—An investigation of the thixotropy of ferric hydroxide sols has shown that with decreasing coagulation value the concentration of sol and of electrolyte necessary for the appearance of thixotropy steadily falls. More concentrated, sensitive sols are the more readily thixotropic and the gels formed are more transparent. Particularly unstable ferric oxide sols set in time to "thixolabile" gels, which are regarded as a transition form. An attempt is made to connect the phenomena of thixotropy and syneresis.

E. S. HEDGES.

**Formation of Liesegang rings and the peptisation effect of the gel.** L. N. MUKHERJEE and A. C. CHATTERJI (Kolloid-Z., 1930, 50, 147—159).—Directions are given for the preparation of periodic structures of a number of insoluble sulphates, ferrocyanides, ferricyanides, cyanides, phosphates, and silicates in silicic acid gel. Although in most of these cases the general rule was observed that with decreasing concentration of the diffusing electrolyte the distance between the bands increases, exceptions were noticed in the cases of zinc, nickel, and ferrous

cyanides, nickel ferricyanide, and cobalt ferrocyanide, where an effect similar to that reported by Hedges and Henley (A., 1928, 1323) for periodic structures of arsenious sulphide was noted. Experiments on the effect of diffusing excess of one of the reagents into a gel containing the reagents in equivalent proportions showed that in general one of the reagents is always more effective than the other in producing periodic structures, suggesting that these structures are produced by a true coagulation process. When the gel already contains silver chromate as a sol, the diffusion of salts of thorium, cerium, aluminium, lead, barium, zirconium, titanium, silver nitrate, and sodium phosphate causes periodic coagulation; the authors do not agree therefore with the view that release of supersaturation by the diffusion of a common ion (Hedges, Chem. and Ind., 1929, 48, 233) may be the cause of the production of the precipitate, and they maintain that it is a true coagulation. The experiments support the view that the formation of this type of periodic structure is due to the coagulation of a peptised sol.

E. S. HEDGES.

#### Effect of temperature on the isoelectric point.

I. I. SHUKOV and V. F. MATUSEVITSCH (J. Russ. Phys. Chem. Soc., 1929, 61, 1683—1689).—The isoelectric point of 0.5—2.0% gelatin remains constant at  $p_H$  5.28 during the interval 30—40°. In acid solution, the  $p_H$  is constant over this temperature interval, but in alkaline solution it is slightly lower at the higher temperature.

R. TRUSZKOWSKI.

**Magnetophotophoresis and electrophotophoresis.** F. EHRENHART (Compt. rend., 1930, 190, 263—265).—Observations have been made on the influence of magnetic and direct or alternating electric fields on the transverse and longitudinal movements of particles of radius  $10^{-4}$  to  $10^{-5}$  cm., illuminated by a beam of light.

J. GRANT.

**Swelling of cellulose and its affinity relations with aqueous solutions. I. Experiments on the behaviour of cotton cellulose and regenerated cellulose in sodium hydroxide solution, and their theoretical interpretation.** S. M. NEALE (J. Text. Inst., 1929, 20, T373—399).—Swelling, absorption, and heat of reaction phenomena of cotton and regenerated cellulose in contact with sodium hydroxide solutions have been investigated and a theory is advanced to explain the effects observed both by the author and by previous workers. It is assumed that cellulose, behaving as a very weak monobasic acid, forms a sodium salt to an extent increasing with the concentration of the sodium hydroxide. Excess alkali diffuses into the mechanically separable cellulose phase in amount determined by Donnan's thermodynamic equation of membrane equilibrium, and the resulting unequal distribution of ions causes osmosis, which distends the cellulose until the osmotic pressure is balanced by the forces arising from the cohesion of the gel. If the sodium hydroxide solution be replaced by a large excess of water, the cellulose sodium salt is hydrolysed, the osmotic pressure falls, and the cellulose, although recovered chemically unchanged, is permanently distorted if the osmotic pressure has been sufficiently high. The theory accounts for the fact that the swelling of the

cellulose is greatest in solutions of moderate concentration, and that it is greater, and the optimum concentration lower, at low temperatures. Taking the experimental values of the absorption of water from the sodium hydroxide solution as basis, it predicts accurately the corresponding alkali sorptions over the concentration range 0.5–23 molal. Over the whole range of sodium hydroxide concentrations up to saturation the curve for heat of reaction of regenerated cellulose is in fair quantitative agreement with the theoretical postulate of salt formation according to the law of mass action. With purified cotton less heat is liberated except in the concentration range where the swelling of the cotton hairs is great, whilst mercerised cotton occupies an intermediate position. These differences between the forms of cellulose are explained in terms of an "accessibility factor," which is always near to unity for viscose cellulose, and for cotton increases as the material swells. The theoretical aspects of the distribution of sodium hydroxide between cellulose and water, the behaviour of cellulose as a solid colloidal acid, osmotic pressure relations, effects of temperature, etc., and the assumptions and approximations involved in the elaboration of the theory, are discussed.

B. P. RIDGE.

**Elastic properties of wool in organic liquids.** J. B. SPEAKMAN (Trans. Faraday Soc., 1930, 26, 61–69).—Hydroxylic compounds with small molecules are unique among organic liquids in the marked influence which they exert on the elastic properties of the wool fibre, the potential energy of extension, for instance, being much reduced. This effect is probably due both to their adsorption on polypeptide linkings of adjacent molecules and to solvolysis of anhydride linkings. Saturated aliphatic monohydric alcohols higher in the series than *n*-propyl alcohol are, however, comparatively inert and are adsorbed only very slightly, from which it is concluded that the capillary spaces in the fibres are of approximately the same size as the propyl alcohol molecule.

R. CUTHILL.

**Plastic and pseudo-plastic flow.** A. DE WAELE (J. Rheology, 1930, 1, 139–147).—Pseudo-plastic substances are instanced by cellulose nitrate sols, gelatin gelatin sol, some liquid-liquid emulsions, etc., and are distinguished from plastic substances by exhibiting no observable yield point or rigidity, whilst indicating departure from Poiseuille's law when examined plastometrically. The relation between shearing stress and rate of shear is discussed for these types of systems. It is concluded that departure from the state of true molecular dispersion in fluids is attended by departure from linearity in the stress-shear relation, the function being, in part at least, parabolic. This parabolic curve may simulate linearity at its upper points. True plastic systems resemble pseudo-plastic systems at a rate of shear above a certain critical value, the rigidity component manifesting itself at low values of shear. Rigidity vanishes progressively as the rate of shear increases.

E. S. HEDGES.

**Manipulation of jelly strength testing apparatus.** G. SPENCER (J. Physical Chem., 1930, 34, 654–655).—Details of manipulation and testing of

the apparatus previously described (this vol., 160) are given.

L. S. THEOBALD.

**Pectographic examination of solutions of dyes.** P. BARY (Compt. rend., 1930, 190, 488–490; cf. A., 1929, 136).—Pectographs have been prepared for eleven dyes from solutions in water, alcohol, and acetone. The deposits were of three types: *A* crystalline, *B* continuous sheet (gelatinous), and *C* small isolated points, type *B* characterising a lyophile and type *C* a lyophobic colloid. In most cases mixtures of two types occurred, and deposits of types *B* or *C* gradually changed to *A*. Type *B* occurs most frequently, and tends especially to predominate as the mol. wt. increases.

C. A. SILBERRAD.

**Relation between acids and pectin in jelly formation.** G. SPENCER (J. Physical Chem., 1930, 34, 410–417).—The data of Tarr (Univ. Del. Expt. Sta. Bull. No. 134, 1923) on the effect of various acids on the  $p_H$  value of a 1% pectin sol are discussed. It is claimed that pectin does not reduce, but increases the hydrogen-ion concentration as a result of preferential anion adsorption. Pectin has no buffering action.

L. S. THEOBALD.

**Temperature of flames, and their content of atomic hydrogen.** G. RIBAUD (Compt. rend., 1930, 190, 369–371).—Using Bjerrum's figures (A., 1912, ii, 540) for specific heat and the degree of dissociation of carbon dioxide and water, Langmuir's value (A., 1926, 550) for the degree of dissociation and 100,000 g.-cal. for the heat of dissociation of  $H_2$ , the temperatures of the flames in the reactions (i)  $H_2 + O$ , (ii)  $C_2H_2 + 5O$ , and (iii)  $C_2H_2 + 2O$  are calculated to be (i) 2850°, (ii) 3200°, and (iii) 2975°, the last agreeing sufficiently well with Henning and Tingwaldt's figure 3100° (A., 1928, 826). If the dissociation of  $H_2$  be ignored the figures are (i) 3050°, (ii) 3780°, and (iii) 3875°. The fractions of  $H_2$  dissociated are calculated as (i) 0.26, (ii) 0.65, and (iii) 0.28, whilst the actual percentages of atomic hydrogen in the flames are approximately (i) 10, (ii) 13.5, and (iii) 17 (by volume).

C. A. SILBERRAD.

**Equilibrium between nitrogen and carbon dioxide in the electric arc.** H. V. TARTAR and J. L. HOARD (J. Amer. Chem. Soc., 1930, 52, 156–163; cf. Krase and Mackey, A., 1928, 1324).—In the synthesis, by the electric arc, of nitric oxide from air, carbon dioxide acts largely as a diluent. The reaction  $N_2 + 2CO_2 = 2NO + 2CO$  in the electric arc has been investigated. Some nitrogen peroxide was formed. When 65 milliamp. were passed through mixtures of nitrogen and carbon dioxide at 760 mm. the best yield of nitric oxide was 1%, in comparison with 6% from air under similar conditions. Decrease of pressure did not change the equilibrium. The yield of nitric oxide rose 30–40% when the current was increased by 50%.

J. G. A. GRIFFITHS.

**Equilibria in sulphur dioxide solutions.** W. B. CAMPBELL and O. MAASS (Canad. J. Res., 1930, 2, 42–64).—The vapour pressures and densities of sulphur dioxide solutions have been measured between 20° and 120°, and the conductivities between 5° and 110°. The values ( $\times 10^3$ ) of the apparent dissociation

constant  $[H^+][HSO_3^-]/[H_2SO_3]+[SO_2]$  are  $0^\circ$  31.3,  $20^\circ$  19.6,  $25^\circ$  17.3,  $40^\circ$  11.4. The true dissociation constant of sulphurous acid,  $[H^+][HSO_3^-]/[H_2SO_3]$ , is at least as large as 0.031.

C. W. GIBBY.

**Dissociation constants of some inorganic acids from solubility measurements.** W. V. BHAGWAT and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 807—822).—The dissociation constants of hypophosphorous, chromic, hydrofluoric, iodic, titanous, antimonous, boric, vanadic, tungstic, and molybdic acids have been determined from the solubilities of benzoic, carbonic, and acetic acids in solutions of their sodium and potassium salts (cf. A., 1929, 135). The formula  $K = K_1 a(c-b+a)/(b-a)^2$  (where  $a$  is the solubility of the sparingly soluble acid in water,  $b$  its solubility in the salt solution of concentration  $c$ ,  $K$  the dissociation constant of the unknown acid, and  $K_1$  that of the sparingly soluble acid) is specific for monobasic acids. Taking into consideration the basicity of the acid of which the dissociation constant is required, and allowing for incomplete ionisation of the various substances used, a general expression is deduced for the  $n$ th dissociation constant of an acid. Assuming that the salts ionise completely and that the weak acids do not ionise, this becomes  $K_n = nKa_1nc - (b-a)/(b-a)^2$ . If the acid for which the dissociation constant  $K$  is assumed is monobasic, this becomes identical with the first equation above. The circumstances that the dissociation constant continues to increase with dilution of the salt solution and that the more dilute is the acid solution the lower is the value of the dissociation constant of the unknown acid have been explained on this basis. J. W. SMITH.

**Equilibria involving complex ions of silver and the free energy of silver compounds.** M. RANDALL and J. O. HALFORD (J. Amer. Chem. Soc., 1930, 52, 178—191).—Solubilities of silver bromide, iodide, and thiocyanate in aqueous potassium thiocyanate at  $25^\circ$  are recorded. From solubility measurements, the free energy changes at  $25^\circ$  are determined:  $AgCl(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + Cl^- + 2H_2O(l)$ , 3472 g.-cal.;  $\frac{1}{2}Ag_2O(s) + 2NH_4OH(aq.) = Ag(NH_3)_2^+ + OH^- + 1.5H_2O(l)$ , 674 g.-cal.;  $AgCN(s) + HCN(aq.) = H^+ + Ag(CN)_2^-$ , 6038 g.-cal.;  $AgCl(s) + 2HCN(aq.) = Ag(CN)_2^- + 2H^+ + Cl^-$ , 11,902 g.-cal. From the solubilities of precipitated and hexagonal silver iodide in aqueous potassium cyanide at  $25^\circ$ , the free energy changes are:  $AgI(ppt.) + 2CN^- = Ag(CN)_2^- + I^-$ , -3201 g.-cal.;  $AgI(ppt.) = AgI(hex.)$ , -531 g.-cal. Other free energy changes are calculated from existing data. Standard free energy of formation is computed for:  $Ag(SO_3)_2^{3-}$ , -226,545 g.-cal.;  $Ag(NH_3)_2^+$ , -4003 g.-cal.;  $HAg(CN)_2$ , 72,047 g.-cal.;  $AgCN(s)$ , 38,499 g.-cal.;  $Ag(CN)_2^-$ , 72,047 g.-cal. J. G. A. GRIFFITHS.

**Distribution of ammonia between toluene and aqueous silver ammonia chloride and hydroxide, and of hydrogen cyanide between benzene and aqueous hydrogen silver cyanide.** M. RANDALL and J. O. HALFORD (J. Amer. Chem. Soc., 1930, 52, 192—194).—It is deduced from these determinations that the activity coefficient of ammonia in aqueous silver ammonia chloride and of hydrogen cyanide in aqueous hydrogen silver cyanide is unity at  $25^\circ$ .

J. G. A. GRIFFITHS.

**Internal equilibrium in sulphur. II. Amorphous sulphur ( $S_A$ ) as a gel and the Tyndall effect in liquid sulphur.** D. L. HAMMOCK and M. ZVEGINTZOV (J.C.S., 1930, 273—277).—Previous observations (A., 1928, 956) indicated that, in certain circumstances, molten sulphur can be chilled without the separation of amorphous sulphur ( $S_A$ ), and that, unlike solid  $S_A$ , it then remains miscible with carbon disulphide and other solvents. Experiment has shown that  $S_A$  itself is readily soluble in various solvents above  $120^\circ$ , although, under the conditions of the experiments, transformation into soluble  $S_A$  could not have taken place. In explanation, it is suggested that  $S_A$  is a gel and this appears to be confirmed by the fact that the Tyndall effect is observed in pure molten sulphur. This view removes the difficulty in accounting for the observation that, although  $S_A$  is metastable with respect to crystalline sulphur, the latter is much more soluble. M. S. BURR.

**Iron-nitrogen system.** S. EPSTEIN, H. C. CROSS, E. C. GROESBECK, and I. J. WYMORE (U.S. Bur. Stand. J. Res., 1929, 3, 1005—1027).—The iron-nitrogen alloys obtained by heating electrolytic iron in ammonia have been investigated by thermal, micrographic, and X-ray analysis and the data obtained have been incorporated into a tentative iron-nitrogen diagram using the diagrams of Sawyer (B., 1923, 933) and Fry (*ibid.*, 1074) as a basis. Three nitride layers have been observed for which the compositions  $Fe_2N$ ,  $Fe_4N$ , and  $Fe_6N$  are suggested; the last-named has a face-centred cubic structure and  $Fe_4N$  a hexagonal close-packed structure. In the diagram the eutectoid horizontal is placed at  $600^\circ$  and a peritectoid horizontal at  $675^\circ$  is found in alloys with 3—6% N. Between 4 and 6% N the alloys consist of ( $Fe_6N + Fe_4N$ ) and between 6 and 11% N of ( $Fe_4N + Fe_2N$ ). In specimens of steel containing 2.5% Al, 0.85% Mo, and 0.25% C nitrided at  $500$ — $700^\circ$  only one nitride layer was observed; this had a hexagonal close-packed structure and appeared yellowish in the microstructure. A. R. POWELL.

**Equilibrium diagram of [the system] nickel and chromium.** S. NISHIGORI and M. HAMASUMI (Sci. Rep. Tôhoku Imp. Univ., 1929, 18, 491—502).—The fact that chromium has a body-centred and nickel a face-centred cubic lattice indicates that the previously accepted equilibrium diagram of the nickel-chromium system, which postulates a continuous series of solid solutions with a minimum at  $1295^\circ$ , is incorrect. This has been confirmed by thermal and micrographical analysis. The results of this work show that there are two series of solid solutions forming a eutectic with 50% Cr, m. p.  $1320^\circ$ . The solid solubility of nickel in chromium rises from 8% at  $20^\circ$  to 36% at the eutectic temperature and that of chromium in nickel from 35 to 46%. Extrapolation of the liquidus and solidus at the chromium end indicates that the m. p. of pure chromium is not less than  $1650^\circ$ . X-Ray examination failed to prove the existence of any allotropic transformation in chromium, hence no eutectoid change was found in the system. A. R. POWELL.

**High-temperature equilibrium between silicon nitride, silicon, and nitrogen.** W. B. HINCKE

and L. R. BRANTLEY (J. Amer. Chem. Soc., 1930, 52, 48—52).—The reaction  $\text{Si}_3\text{N}_4 = 3\text{Si} + 2\text{N}_2$  has been studied between 1606° and 1802° Abs. The equilibrium pressures are represented by  $2.3 \log_{10} p(\text{atm.}) = 19.75 - 44,500/T$ , whence the free energy change at 1 atm. is 176,300—78,357 g.-cal. J. G. A. GRIFFITHS.

**Heterogeneous equilibria in mixtures of water, ether, and a metallic salt.** (MLLE.) O. GUÉMPÉL (Bull. Soc. chim. Belg., 1929, 38, 443—477).—The equilibria in the ternary systems composed of water and ether and uranyl nitrate, zinc iodide, or cadmium iodide have been studied and the results represented diagrammatically. R. CUTHILL.

**Effect of  $p_H$  on the precipitation of zinc ammonium phosphate.** T. R. BALL and M. S. AGRUSS (J. Amer. Chem. Soc., 1930, 52, 120—124).—Quantitative precipitation of zinc as zinc ammonium phosphate occurs between  $p_H$  6.4 and 6.9. The precipitate is not crystalline beyond  $p_H$  7.0. The precipitating agent (5—10 g. of ammonium chloride, 10 c.c. of 2*N*-sodium or ammonium acetate, 10 c.c. of 10% diammonium hydrogen phosphate in 150 c.c. of solution) has  $p_H$  7.5, but heating on the water-bath for 2 hrs. causes an automatic adjustment of  $p_H$ . Outside the range  $p_H$  5.1—7.7 precipitation is very incomplete. J. G. A. GRIFFITHS.

**Quaternary system water, sodium chloride, sulphate, and nitrate.** A. CHRÉTIEN (Caliche, 1929, 11, 195—201).—See A., 1929, 1388.

**Equilibria between water and the nitrates and sulphates of sodium and potassium.** E. CORNEC, H. KROMBACH, and A. SPACK (Caliche, 1929, 11, 202—225).—A more detailed account of work already published (A., 1929, 767).

**Prediction of phase equilibria by application of the theory of thermodynamic potential.** J. J. VAN LAAR (Chem. Weekblad, 1930, 27, 66—74).—Mathematical. Thermodynamic considerations are applied to the vapour pressure of pure substances and of binary mixtures, and especially to the vapour pressure of water containing dissolved gas at high pressures. The osmotic pressure of dilute solutions is also discussed. H. F. GILLBE.

**Calculation of the fugacities of a solution.** C. VAN LERBERGHE (Bull. Acad. roy. Belg., 1930, [v], 16, 94—102; cf. A., 1928, 1096).—Mathematical. Experimental partial molal volume data can be used in the formula deduced in the previous paper to calculate the fugacities of the constituents of a liquid mixture. O. J. WALKER.

**De Donder's chemical kinetics, and stable and metastable equilibria.** R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], 16, 73—83).—Mathematical. The conditions of equilibrium to which De Donder's theory (this vol., 277) leads are discussed. O. J. WALKER.

**Thermodynamics of systems with several equilibria.** N. VON RASCHEVSKY (Z. Physik, 1930, 59, 562—563; cf. A., 1929, 509; this vol., 25).—To illustrate the theory already put forward, the system resulting from the dissolution of two substances *A* and *B*, between which a reversible reaction takes place,  $A \rightleftharpoons B$ , is investigated. If the solution is not dilute

the opposing effect of the dissolved molecules must be taken into account. Assuming the presence of collision forces decreasing rapidly with distance, and of attractive forces, weaker, but also decreasing with distance, such a system can have several equilibria, and should show the hysteresis phenomena referred to in previous work. A. J. MEE.

**Thermodynamics of caoutchouc. I. Caoutchouc as a system of two phases.** L. S. ORNSTEIN, (MISS) J. G. EYMERS, and J. WOUDE (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1235—1242).—A method is described for the simultaneous measurement of the stress and strain in the cross-section of caoutchouc for a range of short-period extensions. Indications of a phase change are obtained, the transition point being displaced by change of temperature. From the Clapeyron equation a change in length for constant stress is indicated, and this is shown by experiment to be about 5%, from which the heat of transition is calculated as  $4 \times 10^{-3}$  g.-cal. per unit volume. The linear expansion of raw caoutchouc is found to be positive, which must cause a cooling effect on straining; the observed heating effect is attributed to hysteresis. N. M. BLIGH.

**Limiting heats of dissolution of hydrated sodium thiosulphate and magnesium sulphate.** J. PERREU (Compt. rend., 1930, 190, 429—431).—The mean values obtained by the direct and indirect methods (cf. A., 1929, 1238) are in good agreement viz., —7.50 for sodium thiosulphate and —4.16 g.-cal. for magnesium sulphate. Specific heat data for solutions of the former at 14—34° are also recorded. J. GRANT.

**Thermochemistry of the compounds in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . II. Heat of dissolution of calcium hydroxide in hydrochloric acid.** T. THORVALDSON and W. G. BROWN (J. Amer. Chem. Soc., 1930, 52, 80—87).—Calcium hydroxide prepared by treating calcium oxide with: (a) steam at 150°, (b) water vapour at 21°, (c) water vapour at 21° (but unlike *a* and *b* not dried over calcium oxide), had heats of dissolution in  $\text{HCl} \cdot 200\text{H}_2\text{O}$  at 20° of 551.0, 554.0, and 550.8 g.-cal. per g. of  $\text{CaO}$ , respectively. Corresponding heats of wetting with saturated calcium hydroxide solution at 20° were 1.0, 3.3, and 0.5 g.-cal. per g. of  $\text{CaO}$ . Calcium hydroxide *b* retained the form of the original calcium oxide and absorbed water more readily than the *a* form, which consisted of microscopic plates and prisms. J. G. A. GRIFFITHS.

**Heats of combustion and formation of aromatic nitro-compounds.** W. H. RINKENBACH (J. Amer. Chem. Soc., 1930, 52, 115—120).—Heats of combustion of 21 aromatic nitro-compounds have been determined: nitronaphthalene, 6878.3 g.-cal./g. (const. vol.); 1:5-dinitronaphthalene, 5298.9; 1:8-dinitronaphthalene, 5286.1; 1:3:8-trinitronaphthalene, 4223.9; *m*-nitroaniline, 5463.9; 2:4-dinitroaniline, 3933.9; *s*-trinitroaniline, 2962.2; 2:3:4:6-tetranitroaniline, 2411.1; *p*-nitrophenol, 4900.0; 2:4-dinitrophenol, 3526.7; picric acid, 2687.2; 4:6-dinitro-2-aminophenol, 3408.3; *p*-nitrobenzaldehyde, 5250.6; *s*-trinitrobenzaldehyde, 3035.0; *s*-trinitrotoluene, 3598.9; 2:4:6-trinitrophenylmethylaminoamine, 2924.4; 2:4:6-



trinitro-*m*-xylene, 4039.4; 2:4:6-trinitroresorcinol, 2202.8; 2:4:6-trinitroanisole, 3236.1; *s*-trinitrochlorobenzene, 2609.4; hexanitrodiphenylamine, 3011.7; *m*-dinitrobenzene, 4149.4. Existing values for seven of these compounds (Garner and Abernethy, A., 1921, ii, 435) suggest that the new values may be 0.7% low. Heats of formation and nitration are calculated.

J. G. A. GRIFFITHS.

**Heat of formation and constitution of compounds of cobaltous halides with amines.** W. HIEBER and F. MÜHLBAUER (Z. anorg. Chem., 1930, 186, 97—118).—The heats of formation of compounds of cobaltous chloride, bromide, and iodide with aniline, pyridine, hydrazine, ethylenediamine, and *o*-phenylenediamine have been determined. The results show that the evolution of heat per mol. of amine added decreases as complete saturation is approached. The heat of formation of the hydrazine compounds approximates to that of the ethylenediamine compounds, showing that 1 mol. of hydrazine occupies two co-ordination places; on the other hand, *o*-phenylenediamine behaves co-ordinatively as a univalent compound. Comparison of the heat of formation of the cobaltous halide amines from solid halide and gaseous amines shows close similarity in the figures for the corresponding pyridine, aniline, and ammonia derivatives. In the case of the hexapyridine cobaltous iodide compound the heat evolution is 8.5 g.-cal. per mol. of pyridine, which is about the same as that for the tetrapyridine chloride; the hexapyridine chloride and bromide are unknown, as they would have a lower heat of formation than this. For a similar reason compounds with more than 4 mols. of aniline or 2 mols. of hydrazine are unknown. The following compounds are described:

$\text{CoBr}_2 \cdot 2\text{NH}_2\text{Ph}$ ;  $\text{CoBr}_2 \cdot 3\text{en}$ ;  $\text{CoBr}_2 \cdot 1.5\text{en}$ ;  $\text{CoCl}_2 \cdot \text{en}$ ;  $\text{CoCl}_2 \cdot 3\text{en}$ ;  $\text{CoI}_2 \cdot 2\text{NH}_2\text{Ph}$ ;  $\text{CoI}_2 \cdot 3\text{en}$ ;  $\text{CoI}_2 \cdot 6\text{C}_5\text{H}_5\text{N}$ ;  $\text{CoI}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ .

A. R. POWELL.

**Conductometric behaviour of sodium chloride solutions.** F. GIORDANI and T. MARESCA (Gazzetta, 1929, 59, 878—891).—Measurements have been made of the viscosities and conductivities of 0.5–4.5*N*-solutions of sodium chloride between 10° and 60°. The results are used to calculate the Ghosh expression  $K = \log 1/\alpha \div C^{-1.3}$ . For a given temperature the values of  $K$  decrease with increase of concentration. In the dilute solutions  $K$  increases with rise of temperature, but in the more concentrated solutions decreases with rise in temperature. The results are in general agreement with the theory of Ghosh, but indicate the existence of some cause which tends to make the increase of the dielectric constant of the medium with the concentration greater than that calculated from the internal pressure.

O. J. WALKER.

**Conductometric behaviour of sodium hydroxide solutions.** F. GIORDANI and T. MARESCA (Gazzetta, 1929, 59, 892—904; cf. preceding abstract).—Similar measurements have been made for *N*- to 6*N*-solutions of sodium hydroxide for the same temperature range. The calculated values of  $\alpha$ , the degree of dissociation, are very nearly equal to the corresponding values for sodium chloride at like concentrations, and do not vary much with the temper-

ature. The curve of  $K$  plotted against the concentration passes through a minimum.

O. J. WALKER.

**Conductometric behaviour of solutions of sodium chloride and hydroxide.** F. GIORDANI and T. MARESCA (Gazzetta, 1929, 59, 905—913; cf. preceding abstracts).—The viscosities and conductivities of solutions containing both sodium chloride and sodium hydroxide have been measured between 10° and 60°. The experimental values of the conductivity satisfy fairly well an expression, based on the Ghosh theory, for the conductivity of solutions containing two binary uni-univalent electrolytes with a common ion, if the variation of the mobility of the ions with viscosity of the medium is taken into account.

O. J. WALKER.

**Supposed maximum in the molecular conductivity of certain electrolytes.** A. BERTHOUD (Helv. Chim. Acta, 1930, 13, 17—21).—It is suggested that the supposed maximum in the molecular conductance curves of certain electrolytes arises from experimental errors introduced through the methods used in diluting the electrolyte solutions. Measurements of the conductance at dilutions from 125 to 4000 litres, in which special precautions were adopted in the diluting process, fail to show maxima in the cases of benzenesulphonic acid, trichloroacetic acid, picric acid, potassium permanganate, sodium ammonium hydrogen phosphate, normal potassium phosphate, and sodium chromate.

F. G. TRYHORN.

**Non-aqueous solutions and the conductivity of typical binary salts.** P. WALDEN (Bull. Soc. chim., 1930, [iv], 47, 1—45).—A lecture.

C. W. GIBBY.

**Solubilities and conductivities of inorganic and organic compounds in hydrogen fluoride.** K. FREDENHAGEN and G. CADENBACH (Z. physikal. Chem., 1930, 146, 245—280).—Fluorides are more soluble in hydrogen fluoride than in water and yield the same ions in each. Chlorides, bromides, iodides, cyanides, and azides are either insoluble or, as in the case of the alkali and alkaline-earth salts, decompose into a fluoride and the corresponding acid. The halogen acids are not appreciably soluble nor do they yield ions. Most of the solutions are good conductors, comparable with the best conductors in aqueous solution, and solutions of such widely differing compounds as water, potassium fluoride, silver fluoride, alcohols, and organic acids lead to the same value of  $\Lambda_\infty$ , viz., about 260. The only anion present is  $\text{F}'$ , and its high rate of migration compared with that of the cations  $\text{H}_3\text{O}^+$ ,  $\text{R}\cdot\text{CO}_2\text{H}_2^+$ , or  $\text{R}\cdot\text{OH}_2^+$  probably accounts for the constant value of  $\Lambda_\infty$ . In some cases  $\text{H}_3\text{O}^+$  and  $\text{F}'$  are the only conductors present, e.g.,  $\text{R}\cdot\text{OH} + 2\text{HF} = \text{RF} + \text{H}_3\text{O}^+ + \text{F}'$ . The observations are explained by Fredenhagen's theory of affinity. Existing data on the solubility of various compounds in hydrogen fluoride have been supplemented and corrected.

F. L. USHER.

**Conductivity of hydroxides and alkoxides of alkali metals (lithium, sodium, potassium) in methyl, ethyl, *n*-propyl, isobutyl, and isoamyl alcohols.** M. HŁASKO, M. KADENACÓWNA, and A. SALITÓWNA (Rocz. Chem., 1930, 10, 1—70).—The

molecular and limiting conductivities and the conductivity coefficients of lithium, sodium, and potassium hydroxides in the above alcohols have been determined, as well as those of the three corresponding methoxides in methyl alcohol, and of sodium *n*-propoxide in *n*-propyl alcohol. The mobilities of the following ions in methyl alcohol at 25° are: Li<sup>+</sup> 30.7, Na<sup>+</sup> 38.1, K<sup>+</sup> 47.3, OH<sup>-</sup> 59.7, and OMe<sup>-</sup> 56.7; in ethyl alcohol, Li<sup>+</sup> 14.7, Na<sup>+</sup> 19.2, K<sup>+</sup> 22.4, and OH<sup>-</sup> 22.3. The conductivity coefficients increase in the order LiOH, NaOH, KOH, and the differences between the values obtained augment as the dielectric constant of the medium diminishes. The ionic radii calculated from the Debye-Hückel formula are of the order of 10<sup>-8</sup> cm., and increase as the dielectric constant of the medium diminishes. For a given medium the radius increases as the at. wt. of the ion diminishes.

R. TRUSZKOWSKI.

**Conductivity of magnesium ethyl iodide in ethereal solution.** N. V. KONDYREV and A. K. SUZI (J. Russ. Phys. Chem. Soc., 1929, 61, 1913—1922).—A different degree of association is found for each separate concentration of magnesium ethyl iodide in ethereal solution. The quantity of magnesium iodide formed as a by-product in the preparation of magnesium ethyl iodide increases with the volume of ether taken as solvent. Magnesium iodide is present as MgI<sub>2</sub>·2Et<sub>2</sub>O, and not as a complex salt with magnesium ethyl iodide.

R. TRUSZKOWSKI.

**Potential of metals in pure liquids.** E. TOPORESCU (Compt. rend., 1930, 190, 300—302).—If two different metals are placed in contact with certain pure liquids there is a difference of potential set up between the two metals. This difference of potential, which may be zero in some cases, does not appear to bear a direct relationship to the dielectric constant of the liquid. The behaviour of zinc and platinum in the series of alcohols from methyl to amyl alcohol inclusive has been investigated. The potential is found to depend on the preliminary treatment of the surface of the zinc, a polished surface giving a lower value than one scratched by a file. The potential also decreases towards a limiting value with time. When measurements were made under comparable conditions the values obtained increased gradually from 0.517 volt in methyl alcohol to 0.692 volt in amyl alcohol. The values of the dielectric constants for the same alcohols fall from 33.2 to 16.0. The product of the degree of association of the alcohol and the molecular volume increases with the potential. It is suggested that there is a relationship between the potential obtained and the molecular structure of the liquid.

M. S. BURR.

**Potential of lead-lead ion.** M. RANDALL and (Miss) J. Y. CANN (J. Amer. Chem. Soc., 1930, 52, 589—592).—The potential of the lead-lead ion electrode has been determined by measurements of the lead (in saturated amalgam)-lead nitrate electrode, combined by flowing liquid junctions of lead nitrate-potassium nitrate, and potassium nitrate-potassium chloride with a silver-silver chloride electrode. The standard potential of the lead ion is found to be 0.1203 volt, and the free energy of formation -5551 g.-cal. at 25°.

J. W. SMITH.

**Antimony electrode for determination of hydrogen-ion concentration. I. Standardisation of an antimony electrode in buffer solutions and calculation of  $p_H$ .** A. ITANO (Ber. Ohara Inst. landw. Forsch., 1929, 4, 273—277).—A stick of metallic antimony 7 mm. in diameter and 40 mm. long, smoothed with emery and soldered to a copper lead, is used as the electrode. In Clark's and in Kolthoff's buffer solutions this electrode gives results very close to those of the hydrogen electrode.

O. J. WALKER.

**Büilmann's quinhydrone electrode. IV. Comparative study of quinhydrone and hydroquinhydrone electrodes.** A. ITANO and S. ARAKAWA (Ber. Ohara Inst. landw. Forsch., 1929, 4, 255—264).—In presence of dextrose, alcohol, ammonia, and various buffer solutions the quinhydrone electrode gives more satisfactory values of  $p_H$  than the hydroquinhydrone electrode (both compared with the hydrogen electrode) if the readings are taken within 1 minute after adding the quinhydrone. In general, lower values are obtained with the hydroquinhydrone electrode, especially when  $p_H$  is greater than 7. In conjunction with the above electrodes the simplified saturated calomel electrode gives slightly larger  $p_H$  values (about 0.05) than the standard 0.1*N*-electrode.

O. J. WALKER.

**Tables of  $p_H$  values corresponding to *E.M.F.* measurements with hydroquinhydrone, quinhydrone, hydrogen, and antimony electrodes against 0.1*N*- and saturated calomel and quinhydrone standard electrodes.** A. ITANO (Ber. Ohara Inst. landw. Forsch., 1929, 4, 199—253).—The calculated values of *E.M.F.* and  $p_H$  at 18° are tabulated for the complete  $p_H$  range. Tables for temperature correction are also given.

O. J. WALKER.

**Comparison method for determining ionisation constants with a quinhydrone reference electrode.** H. D. KIRSCHMAN, B. WINGFIELD, and H. J. LUCAS (J. Amer. Chem. Soc., 1930, 52, 23—28).—By a potentiometric comparison method which largely eliminates variable liquid junction potentials, the Ostwald ionisation constants of benzoic acid and *p*-cyanobenzoic acid are found to be 6.7 × 10<sup>-5</sup> and 3.1 × 10<sup>-4</sup>, respectively (cf. Valby and Lucas, A., 1929, 1384; and others). The cell employed is Pt, 0.09*N*-KCl + 0.01*N*-HCl + quinhydrone(satd.)|0.09*N*-KCl + *xN*-HA + quinhydrone(satd.), Pt, where *xN*-HA represents concentrations of hydrochloric acid between 0.02*N* and 0.0003*N* in one series of experiments and the corresponding concentrations of the acids to be studied in the other series. J. G. A. GRIFFITHS.

**Application of the quinhydrone electrode to solutions of phenols and cresols.** P. E. ROLLER (J. Physical Chem., 1930, 34, 367—372).—The quinhydrone electrode has been used to determine the  $p_H$  of approximately 0.1*M*-solutions of phenol and the cresols, and the dissociation constants have been calculated on the assumption that the number of phenol or cresol ions is equal to that of the hydrogen ions.

L. S. THEOBALD.

**Oxidation-reduction potential  $r_H$ .** J. BARBAUDY (Chim. et Ind., 1930, 23, 14—29).—A review

of the theory of oxidation-reduction potentials, based mainly on the work of Clark and other workers, and of the applications to biochemical problems.

O. J. WALKER.

**Oxidation potential of the lead dioxide electrode in perchloric acid solution.** D. J. BROWN and J. C. ZEMMER (J. Amer. Chem. Soc., 1930, 52, 1-6).—The standard oxidation potential of lead dioxide in solutions of unit hydrogen-ion activity is computed to be 1.467 volts at 25° from determinations of the *E.M.F.* of the cells  $(\text{Pt}), \text{PbO}_2 | 0.1-0.0001N\text{-Pb}(\text{ClO}_4)_2, 0.1-0.001N\text{-HClO}_4 | \text{H}_2, (\text{Pt})$ . It is suggested that the high values obtained with freshly-prepared lead dioxide electrodes are due to physical strains, and the decrease of potential after the period of stability is due to the formation of lead ions. The period of stability is increased by plating the electrode slowly. Fluctuations of the potential of the hydrogen electrode in lead chlorate solutions are proportional to the concentration of lead ions and become negligible when that is less than  $0.01M$ .

J. G. A. GRIFFITHS.

**Effect of hydrogen-ion concentration on the electrode potential of iron.** A. L. McAULAY and G. L. WHITE (J.C.S., 1930, 194-199).—The equilibrium electrode potential at the surface of pure iron in air-free solutions of varying  $p_{\text{H}}$  has been investigated. The variation of potential with  $p_{\text{H}}$  may be represented by two intersecting straight lines, increase of potential with  $p_{\text{H}}$  being less rapid in the alkaline region. The same relation is obtained in the alkaline region whether the anion in the buffer is chloride or phosphate, but in the acid part it is specific for each anion. It is, however, practically independent of concentration. The results are reproducible up to  $p_{\text{H}}$  10, above which a film of oxide is probably formed. The results are discussed and it is suggested that the iron is probably behaving as a hydrogen electrode showing overvoltage. Experiments have also been made in solutions which were not air-free. The results were complicated and not reproducible. In phosphate solutions there exists a definite critical  $p_{\text{H}}$  (between 7.5 and 8.5) on the alkaline side of which the equilibrium potential of a freshly-ground electrode ultimately reaches  $-0.3$  volt, and on the acid side  $-0.8$  volt. In chloride solutions no such critical  $p_{\text{H}}$  is observed.

M. S. BURR.

**Concentration cells in ethyl alcohol. IV. Mixtures of sodium and potassium iodides.** J. R. PARTINGTON and H. G. SIMPSON (Trans. Faraday Soc., 1930, 26, 147-154; cf. A., 1929, 269).—The *E.M.F.* of the cells  $\text{Ag}|\text{AgI}, \text{NaI}, 0.1N\text{-(NaI + KI)}, 0.01N\text{-AgI}|\text{Ag}$ , and  $\text{Ag}|\text{AgI}, \text{NaI}, 0.1N\text{-(NaI + KI)}, 0.02N\text{-AgI}|\text{Ag}$  in ethyl-alcoholic solution has been measured for a series of mixtures of sodium and potassium iodides. At the concentrations employed the isohydric principle does not hold in alcoholic solution. The activity coefficient of sodium iodide in these solutions depends on the concentration of the potassium iodide in the solution and not solely on the total concentration of the mixture as postulated by G. N. Lewis for the activity coefficient of a strong electrolyte in a dilute solution of mixtures of strong electrolytes of the same valency type.

F. G. TRYHORN.

**Behaviour of glass electrodes of different compositions.** D. A. MACINNES and M. DOLE (J. Amer. Chem. Soc., 1930, 52, 29-36; cf. Hughes, A., 1928, 370; Elder, this vol., 50).—The suitability of specially prepared glasses for electrodes (A., 1929, 673) has been investigated with respect to potentials in the diaphragm, resistance, and trustworthiness in alkaline solution. The best of the glasses studied has the composition  $\text{SiO}_2$  72,  $\text{Na}_2\text{O}$  22,  $\text{CaO}$  6%. The *P.D.* between an electrode of this glass and the hydrogen electrode is constant in solutions of  $p_{\text{H}}$  as great as 9.5, although this limit is lower in concentrated salt solutions. Different, but steady *P.D.* were observed in solutions of higher  $p_{\text{H}}$ . The substitution of lithium or potassium for sodium gives rise to inferior electrodes. Hard glasses show large variable potentials in the diaphragm and high resistances, and are untrustworthy in alkaline solutions.

J. G. A. GRIFFITHS.

**Influence of magnetic field and electrolyte agitation on electrolytic potential.** V. SIHVONEN and G. KERKÄNEN (Suomen Kem., 1929, 2, 54-60).—The true field action of a medium strength electromagnet on an electrode potential is only seldom apparent. In addition to the known paramagnetic positive effect of a concentrated ferric salt solution on an iron electrode, a negative diamagnetic effect is also observed when an iron magnet encased in copper is placed in a concentrated cupric ammonium chloride solution. The true magnetic potential variations appear and disappear gradually in contradistinction to the momentary oscillation-like effect on the potential caused by movement of the electrode during magnetisation. Violent agitation of the electrolyte generally makes more positive an annular electrode which has an active interior surface and is made of a metal less noble than hydrogen.

S. K. TWEEDY.

**Polarisation phenomena.** F. GIORDANI and B. FOCACCIA (Gazzetta, 1929, 59, 914-926).—An oscillographic method for measuring the potential at an electrode during polarisation and depolarisation is described. Preliminary measurements showing the anodic and cathodic behaviour of smooth platinum electrodes in 30% potassium hydroxide solution are recorded.

O. J. WALKER.

**Overvoltage in the electrolytic production of hydrogen.** E. BAARS (Sitzungsber. Ges. Beförd. ges. Naturwiss., 1928, 63, 213-320; Chem. Zentr., 1929, ii, 1779-1780).—There is no minimum value of the hydrogen overvoltage in the sense of a value which varies with the material of the electrode and deviates from the thermodynamic deposition potential. The overvoltage increases logarithmically with increasing current density. At constant current density the overvoltage (except at mercury electrodes) increases with the duration of electrolysis. Diminution of the overvoltage on opening the polarising circuit is logarithmic, with a specific velocity coefficient for each metal equal to that for its increment with increasing current density. The potential of the cathode is related linearly to the number of hydrogen atoms in its surface, this being always smaller than would form a unimolecular layer. Hence the gas-film theory is rejected.

A. A. ELDRIDGE.

**Photochemical transformations and photo-electric cells.** S. SCHLIVITCH (Compt. rend., 1930, 190, 302—303).—It has been observed (A., 1929, 1393) that the combination: Pt[urarine solution]|Pt gives a different *E.M.F.* after illumination according to whether it is under atmospheric pressure or under reduced pressure. This may be accounted for by oxidation. After successive periods of illumination under atmospheric pressure the *E.M.F.* is reduced. This may be explained by supposing that the photo-oxidation process is not reversed in the dark. If glycerol is present, however, the same *E.M.F.* is obtained after each illumination, due to hydrogenation of the oxidised product by the glycerol in the dark, thus giving a pseudo-reversible reaction. The cell may thus be regarded as a photo-electric accumulator. It has also been shown that the *E.M.F.* varies with the amount of oxygen dissolved in the solution.

M. S. BURR.

**Application of effects associated with electrodes of unequal surface to observations on the formation of colloidal systems.** A. DUMANSKI and T. A. GRANSKAYA (J. Russ. Phys. Chem. Soc., 1929, 61, 1819—1831).—Schtschukarev's observation (cf. A., 1916, ii, 172) that a *P.D.* is set up between two plates of platinum of unequal size when these are immersed in a solution in which some reaction is proceeding is applied to the study of the formation of ferric hydroxide gel, the *P.D.* disappearing with the disappearance of ferric ions from solution on the progressive addition of ammonia solution. Characteristic S-shaped curves are obtained for this system, whilst under analogous conditions different curves are obtained with copper sulphate or aluminium chloride. This difference is due probably to change of valency of iron.

R. TRUSZKOWSKI.

**Velocity of a bimolecular reaction in a homogeneous system.** S. C. HORNING (J. Physical Chem., 1930, 34, 427—428).—A theoretical derivation of the equation for the velocity of a reaction from the simplest assumptions.

L. S. THEOBALD.

**Exact method of ascertaining the bimolecular course of a chemical reaction.** K. SANDVED (Forh. Kong. Norske Vidensk. Selskab., 1930, 2, 159—162).—Theoretical. A more exact method of determining the order of a reaction from observations of its early stages is described and applied to bimolecular reactions.

J. A. V. BUTLER.

**Reaction between hydrogen and oxygen.** D. ALEXÉEV and D. AVANESSOV (Z. Physik, 1930, 59, 864—871).—Mixtures of oxygen and hydrogen have been exploded at various temperatures and pressures in an apparatus described. The extent of the reaction (or explosion) wave in a mixture of the gases is a typical chain reaction. Several probable courses are discussed. From the fact that this reaction wave is not propagated at certain definite temperatures and pressures, the maximum time during which an excited atom may retain its energy can be calculated. It has been found, from a study of the extent of the flame reaction in a hydrogen-oxygen mixture, that this is possible so long as the distance of the oxygen molecule does not exceed a limiting value. Calculations of the

probable "life" of an excited hydrogen atom give the probable value of  $10^{-9}$  sec. W. R. ANGUS.

**Gaseous combustion.** W. A. BONE (Nature, 1930, 125, 274—275).—A discussion of David and Davies' view (this vol., 166). L. S. THEOBALD.

**Limits of combustion of inflammable mixtures of vapour and air at low pressures.** E. BERL and E. HARTMANN (Z. physikal. Chem., 1930, 146, 281—293; cf. B., 1927, 546).—The range of combustion over which explosion is possible becomes narrower with decreasing pressure for mixtures of air with ether, acetone, hexane, cyclohexane, or benzene, and no reaction takes place below a certain limiting pressure. This critical ignition pressure decreases with increase in the energy of ignition, with increasing ease of oxidation of the vapour, and with rise of temperature. Dilution with nitrogen always narrows the combustion region.

F. L. USHER.

**Extinction of methane flames by water vapour.** H. F. COWARD and J. J. GLEADALL (J.C.S., 1930, 243—248).—The limits of inflammability of methane-air mixtures containing water vapour have been determined. The effect of water lies between that of carbon dioxide and that of nitrogen (cf. A., 1926, 805). The order of the extinctive effect of the six diluent gases (carbon tetrachloride, carbon dioxide, water, nitrogen, helium, and argon) is that of their molecular heat capacities, with the exception of helium, the abnormal position of which is ascribed to its high thermal conductivity. The effect of water is rather greater than would be expected from its specific heat, owing to the absorption of heat in the dissociation of complex water molecules.

J. A. V. BUTLER.

**Theory of flame motion.** P. J. DANIELL (Proc. Roy. Soc., 1930, A, 126, 393—405).—For the horizontal propagation of flame through a still mixture in circumstances such that the pressure produced by the combustion is freely vented into the atmosphere, it is shown that, when certain assumptions are made and cooling is neglected, the velocity  $\bar{V}$  relative to the unburned gas is given by the formula  $\bar{V}^2 = \text{constant} \times kf/c\rho$ , where  $k$  is the conductivity,  $f$  the rate of reaction,  $c$  the specific heat, and  $\rho$  the density. The constant is non-dimensional and depends on the temperature of ignition, the heat of reaction, and the manner in which the reaction takes place. Cooling introduces a term which reduces the velocity, and the analysis shows that if the cooling is sufficiently great the propagation of flame is impossible. There is thus a positive lower limiting velocity as well as an upper ideal limit for a given mixture under various conditions of cooling. A variation of the mixture produces a variation in the rate of reaction  $f$  and affects  $\bar{V}$  through this term.

L. L. BIRUMSHAW.

**Influence of an electric field on the combustion of gases.** A. E. MALINOVSKI and F. A. LAVROV (Z. Physik, 1930, 59, 690—696).—The influence of an electric field on the velocity of propagation of flame in explosive mixtures of methane, ethylene, and acetylene, respectively, with deficiency of air has been investigated. Under these conditions carbon is deposited on the negative pole. A lowering

of the velocity of propagation was observed in the neighbourhood of the saturation point of the conductivity curve. This effect increased in the order methane, ethylene, acetylene, *i.e.*, with increasing carbon content of the flame; in the last case it led to the complete stoppage of combustion. Similar experiments with mixtures of hydrogen and air led to no positive results.

J. W. SMITH.

**Thermal decomposition of ozone.** H. J. SCHUMACHER and G. SPRENGER (*Z. physikal. Chem.*, 1930, **B**, 6, 446—458).—The thermal decomposition of ozone has been investigated in an apparatus which prevented contact of the ozone with any material other than glass or quartz. The velocity coefficient, calculated on the basis of a bimolecular reaction, increases as the reaction proceeds. This is interpreted as indicating that a purely bimolecular reaction is taking place uninfluenced by the oxygen present or by the walls of the vessel. In addition, however, there is a unimolecular reaction which is probably heterogeneous and takes place at the walls of the container. The theory of the bimolecular decomposition of ozone is discussed.

M. S. BURR.

**Thermal reaction between bromine and ozone.** B. LEWIS and H. J. SCHUMACHER (*Z. physikal. Chem.*, 1930, **B**, 6, 423—440).—Investigations previously described (A., 1929, 1156, 1395) have been continued at different temperatures. At higher temperatures, above 15°, the reaction takes place in the gaseous phase and can be explained most satisfactorily as a chain reaction. Under certain conditions an explosion takes place. Experiments at temperatures ranging from -12° to 13°, and for different partial pressures of bromine and ozone, confirm previous results. These results are explained by supposing that the period of induction observed (*cf.* A., 1929, 1395) is due to the formation and condensation of bromine oxide. After practically all the bromine has been deposited as solid bromine oxide on the walls of the vessel the rate of reaction appears to become constant if sufficient ozone is present. Actually, some of the oxide, the fraction depending on the temperature, decomposes, giving oxygen. The other decomposition product rapidly reacts with more ozone, reproducing the original quantity of bromine oxide, which again decomposes. There is thus taking place in the solid phase a first order reaction which is the first of its kind to be observed. The temperature coefficient of the reaction between 0° and 10° is now given as 3.15 for 10°.

M. S. BURR.

**Low-temperature oxidation. II. Ignition of some hydrocarbons in oxygen.** J. S. LEWIS (*J.C.S.*, 1930, 58—74; *cf.* A., 1929, 655).—A simple preliminary apparatus has been used to determine the conditions for explosion of mixtures of some hydrocarbons and oxygen. The conditions determining the explosion of these mixtures on progressive heating are (a) a sufficiently rapid rise of temperature; a more rapid rate of heating tends to raise the ignition temperature of mixtures of paraffins and oxygen, the effect being less with richer mixtures, but this is not shown in the case of the olefines; (b) adequate concentration of oxygen, and (c) a concentration of hydrocarbon above a certain minimum, which rises

rapidly with the mol. wt. in the paraffin series, *i.e.*, rises with the instability towards oxygen. Unsaturated hydrocarbons require to be present in high concentration and to be heated rapidly in order that explosion be brought about. Rich mixtures show a minimum explosion temperature, but with paraffinic hydrocarbons the explosion is a mild one of low note and often there is an absence of flame and no carbon deposit. Maximum violence is attained when the proportions approach those for complete combustion. There are so many disturbing factors in the determination of the relative ignition temperatures that the measurement of the "lag" in the case of equimolecular concentrations at some point above the ignition temperature is preferable as a measure of ignitibility. The results obtained are discussed critically with reference to the chain mechanism of the reactions. It is suggested that the successive stages in the combustion of paraffins are: (a) primary dehydrogenation yielding unsaturated hydrocarbons; (b) combination of the latter with oxygen to give unstable peroxides, and (c) decomposition of the peroxides *per se* to aldehydes, which are further oxidised to water and oxides of carbon if the mixtures are rich in oxygen. The explosion temperatures determined in the usual way are raised by materials which inhibit oxidation or reduce auto-oxidation, *e.g.*, lead tetraethyl, because they diminish the number of fresh chains formed in unit time, whereas promoters of oxidation by surface action raise the ignition temperature either by removing one of the intermediate products, or, according to the chain mechanism, by increasing the rate of deactivation.

J. W. SMITH.

**Effect of ethane and nitrogen on the rate of thermal decomposition of azomethane at low pressures.** H. C. RAMSPERGER (*J. Physical Chem.*, 1930, **34**, 669—671; *cf.* A., 1927, 737).—The combined effects of ethane and nitrogen produced during the thermal decomposition of azomethane at low pressures (1 mm.) are shown to be sufficient to maintain the rate of reaction at its initial value; the main effect is due to ethane. The results are discussed in the light of reaction rate theories previously advanced (A., 1927, 833).

L. S. THEOBALD.

**Rate of formation of fumaric acid in molten malic acid.** P. HERASYMENKO and Z. TYVOŇUK (*Coll. Czech. Chem. Comm.*, 1930, **2**, 77—82).—Heyrovsky's polarographic method has been applied to the determination of fumaric acid in the mixture resulting from the melting of malic acid. The sensitivity of the saturation currents towards slight changes in the rate of dropping of the cathodic mercury was overcome by registering on the same polarogram the rate of fall of the saturation currents in the solution under analysis and in a mixture containing a known amount of fumaric acid. Measurements were made at 137° and 157°. The fused mass becomes turbid when more than 20% of fumaric acid has been formed. From a study of the loss of water from the mass and from acidity changes it is found that the production of fumaric and malomalic acids is simultaneous. The velocity of formation of fumaric

acid in a mixture of 97.06% of malic acid and 2.94% of fumaric acid is  $7.85 \times 10^{-6}$  at  $137^\circ$  and  $6.37 \times 10^{-5}$  at  $157^\circ$ . The calculated critical increment is approximately 37,000 g.-cal. The coefficient for the velocity coefficient  $K = 10^{11} \times e^{-37000/RT}$  is of the same order as those found for other unimolecular reactions.

F. G. TRYHORN.

**Variation with temperature of the relative rates of hydrolysis of glucosides.** E. A. MOELWYN-HUGHES (J. Gen. Physiol., 1930, 13, 317—321).—Since the ratio of the velocity coefficients for the hydrolysis of any two glucosides determined at the same temperature varies with the temperature unless both hydrolyses possess the same critical increment (cf. A., 1929, 405), deductions from previously reported work which neglected this fact require revision, particularly in the comparison of the rates of hydrolysis of glucosides by acids at high temperatures and by enzymes at comparatively low temperatures. The critical increments for 17 sugars are tabulated.

C. C. N. VASS.

**Phosphoric acid. I. Decomposition of formic acid by means of phosphoric acid.** J. H. WALTON and H. M. STARK (J. Physical Chem., 1930, 34, 359—366).—At  $120^\circ$ , sodium formate yields, with an excess of phosphoric acid, formic acid which is quantitatively decomposed into carbon monoxide, and water. Measurements of the rate of gas evolution show that, after a period of induction, the reaction is unimolecular. The temperature coefficient is 1.82 approximately, and  $k \times 10^3 = 257$ . The reaction is inhibited by the addition of small amounts of water and of certain soluble phosphates and the relation between  $k$  and the amount of water present is exponential. Sulphuric acid accelerates the reaction. The active agent is not the ortho-, meta-, or pyro-acid; another form of phosphoric acid is considered to be responsible for the dehydration of formic acid.

L. S. THEOBALD.

**Time course of the heat effects in rapid chemical changes. I. Apparatus and methods. II. Reactions of acids, bases, amino-acids, and proteins.** F. J. W. ROUGHTON (Proc. Roy. Soc., 1930, A, 126, 439—469, 470—486).—I. The method of Hartridge and Roughton (A., 1925, ii, 47) for studying the velocity of very rapid chemical reactions has been modified for the measurement of the amount of heat liberated in rapid reactions within periods of 0.01 sec. or less from the beginning of the reaction. Special precautions are taken to ensure that the reagents (about 4 litres are required of each), their containers, delivery tubes, mixing chamber, and observation tube are all at the same temperature during the experiment. Three different types of thermocouple are used. An extensive test of the physical sources of error involved in the measurement of temperature of rapidly moving fluids by means of thermojunctions, including heat conduction effects, fluid friction effects, thermo-elastic effects, and local temperature effects in the neighbourhood of the thermo-junction, indicates that it is possible to measure the absolute temperature of the fluid travelling down the observation tube to an accuracy of 0.001°. This is supported by measurements of the

heat of neutralisation of hydrochloric acid by sodium hydroxide. Further experiments show that the method is equally applicable for determining the temperature gradients in the observation tube, when the reaction under investigation is slow enough to "occupy" more than the first 2 or 3 cm. of the tube. The temperature difference between two points in the observation tube in such circumstances is measurable to an accuracy of about 0.0002°. It is proved that any possible error arising from stagnant films in the neighbourhood of the thermo-junction is negligible. A further improvement of the sensitivity of the method to 0.0001° is being worked out.

II. The claims advanced for the method described above are justified by a study of the time relationships of the heat evolved in the following rapid reactions: (a) the neutralisations of typical acids and bases (strong and weak); (b) the reactions of glycine with acids, bases, and buffers; (c) the reactions of the blood proteins with acids and bases, and (d) a single experiment on the reaction between carbon monoxide and haemoglobin. The experimental observations confirmed the expectation that, of the above reactions, only those of carbonic acid with bases, of hydrogen carbonate with acid, and of haemoglobin with carbon monoxide would fail to show completion of the heat change within 0.01—0.015 sec. In the case of (d), a definite temperature gradient was observed down the observation tube, and the heat accompanying the reaction is spread out over a period of about 0.05 sec. The physico-chemical and physiological implications of the results obtained are discussed.

L. L. BIRCUMSHAW.

**Temperature coefficients of the decomposition of acetonedicarboxylic acid in water.** E. O. WING (J. Physical Chem., 1930, 34, 596—597; cf. A., 1928, 963).—The velocity of decomposition of acetonedicarboxylic acid in aqueous solution has been measured at  $0^\circ$ ,  $10^\circ$ ,  $20^\circ$ ,  $30^\circ$ , and  $40^\circ$ . The values of the critical increment calculated by means of the Arrhenius equation are constant over the range  $0—60^\circ$ .

L. S. THEOBALD.

**Velocity of the decomposition of diazo-compounds in water. III.** E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1929, 32, 352—357B; cf. this vol., 300).—The influence of added sodium hydrogen carbonate or of sodium acetate on the velocity of decomposition of benzenediazonium chloride in water at  $0^\circ$  has been studied. In both cases the added salt causes an initial rapid decomposition which subsequently decreases and follows a unimolecular law. The influence of temperature on the rate of decomposition has also been studied over the range  $0—30^\circ$ ; the results satisfy the Arrhenius equation.

F. J. WILKINS.

**Velocity of the reaction between halogeno-carboxylic acids and sulphites. I.** H. J. BACKER and W. H. VAN MELS (Rec. trav. chim., 1930, 49, 177—194).—The reaction between the potassium salt of a halogeno-acid and potassium sulphite has been studied quantitatively in 0.1N-solution at  $25^\circ$  by iodometric determination of the unchanged sulphite at definite time intervals with the view of elucidating the effect of the nature and position of the halogen



atom, the polar and steric influence of alkyl and negative substituent groups and other halogen atoms on the course and velocity of the reaction  $XHal + K_2SO_3 \rightarrow X \cdot SO_3K + KHal$ , and the concurrent side reactions of reduction and hydrolysis. The following experimental results were obtained, the discussion of which is deferred to a later paper. Under the above conditions the value of the bimolecular velocity coefficient  $K$  (concentration in g.-mols. per litre; time in minutes) for monochloro-, monobromo-, and monoiodo-acetic,  $\alpha$ -chloro-,  $\alpha$ -bromo-,  $\alpha$ -iodo-,  $\beta$ -chloro-,  $\beta$ -bromo-, and  $\beta$ -iodo-propionic, and  $\alpha$ -bromo-*n*-butyric acids is, respectively, 4.61, 454, 793, 0.160, 13.4, 25.2, 0.532, 20.5 (0.5% decomposition of acid occurs), 32.6 (5% decomposition), and 4.5 (3.5% hydrolysis)  $\times 10^{-3}$ . With  $\alpha$ -bromo-isobutyric acid the velocity of hydrolysis of the bromo-acid greatly exceeds that of sulphonation ( $K$  not constant);  $\alpha$ -bromo-*n*-valeric acid suffers 6.5% decomposition ( $K = 2.34 \times 10^{-3}$ );  $\alpha$ -bromo-*iso*-valeric acid reacts exceedingly slowly ( $K = 0.037 \times 10^{-3}$ ), 26% of the bromo-acid undergoing hydrolysis during the 15 days over which measurements were continued; whilst with  $\alpha$ -bromo-*n*-hexoic acid the large amount of hydrolysis destroys the constancy of the velocity coefficient for sulphonation ( $K = \text{approx. } 1.5 \times 10^{-3}$ ). With the halogenodicarboxylic acids, bromomalonic, bromoethylmalonic, and monobromosuccinic acid, no sulphonation occurs, the main reaction being the reduction  $XHal + K_2SO_3 + H_2O = XH + HHal + K_2SO_4$ , the value of  $K$  not being constant. Potassium chlorosulphoacetate does not react with potassium sulphite even at 45°, but in a phosphate-buffered solution ( $p_H$  6.7–6.43) the value of  $K$  for the corresponding bromo-derivative is  $67 \times 10^{-3}$ . Reduction also occurs, the velocity increasing in an acid medium, and in the presence of an equimolar quantity of potassium carbonate (maximum  $p_H$  possible, 5.6) the value  $9.1 \times 10^{-3}$  is obtained for the reduction velocity coefficient of the reaction  $SO_3K \cdot CHBr \cdot CO_2K + K_2SO_3 + K_2CO_3 + H_2O \rightarrow SO_3K \cdot CH_2 \cdot CO_2K + K_2SO_4 + KHCO_3$ . Similarly, in slightly alkaline solution (to prevent the occurrence of reduction) the value of  $K$  for the sulphonation reaction with dichloro-, and chlorobromo-acetic acids is, respectively, 0.117 and  $3.31 \times 10^{-3}$ . The reactions with dibromoacetic,  $\alpha\alpha'$ -dibromopropionic, and  $\alpha\beta$ -dibromopropionic acids are complicated by side reactions, the approximate values of  $K$  being 2, 0.2, and  $3.2 \times 10^{-3}$ , respectively. In a phosphate-buffered solution  $\alpha\beta$ -dibromosuccinic acid gives  $K = 31.6 \times 10^{-3}$ , which probably applies to the reaction  $(\cdot CHBr \cdot CO_2K)_2 + K_2SO_3 + H_2O = (\cdot CH \cdot CO_2K)_2 + K_2SO_4 + 2HBr$ , followed by  $(\cdot CH \cdot CO_2K)_2 + KHSO_3 = CH(SO_3K)(CO_2K) \cdot CH_2 \cdot CO_2K$ . The velocity of the original sulphonation reaction is decreased by substitution of sodium or ammonium sulphite for the potassium salt, the values of  $K$  for the reaction of potassium, sodium, and ammonium sulphites with potassium bromoacetate being, respectively, 454, 418, and  $400 \times 10^{-3}$ . The ratio of the velocity coefficients for chloro-, bromo-, and iodo-acetic acid, however, is approximately the same with all three alkali sulphites, the values being, respectively, 1:98:172 ( $K$ ); 1:101:176 ( $Na$ ), and 1:104:174 ( $NH_4$ ).

J. W. BAKER.

**Relative reactivities of some Grignard reagents with a miscellany of compounds.** H. GILMAN, L. L. HECK, and N. B. ST. JOHN (Rec. trav. chim., 1930, 49, 212–215).—The relative velocities of reaction of several Grignard reagents with compounds of different types have been determined by refluxing the compound with a 10–20% deficiency of the Grignard reagent in ether and observing the time ( $t$ ) required for the reaction mixture to give a negative colour test (Gilman and Heck, A., 1929, 922) for the latter reagent. With azobenzene the values of  $t$  (hours) for various  $RMgX$  compounds are as follows:  $X = Cl$ ,  $R = n$ - and *tert*-Bu 0.25,  $X = Br$ ,  $R = n$ -Bu 1.5, *iso*-Bu 40, *sec*-Bu 0.25, cyclohexyl 0.25,  $CHPh:CH \cdot 4.0$ ,  $Ph$  168, *p*- $MeC_6H_4$  > 33,  $X = I$ ,  $R = Me$  6,  $Et$  0.58,  $Pr$  2.5, *n*-Bu 2.5. With all the Grignard reagents investigated the reaction with benzaldehyde was very rapid,  $t$  having a value 0.08 hr. in all cases. The values of  $t$  for the reaction of magnesium *n*-butyl bromide and magnesium phenyl bromide with the following compounds are, respectively, ethyl sulphate > 20, > 20; benzyl chloride 23.0, 31.0; ethyl cinnamate 0.1, 0.12; nitrobenzene, acetophenone, styryl methyl ketone, and phenylcarbimide, less than 0.08 in all cases; cupric chloride 21.5, 0.16; *o*-nitrotoluene 0.19, 0.26; nitrocymene 0.36, 1.43; 2-nitro-*p*-xylene 0.50, 1.37; *o*-chloronitrobenzene 0.23, 0.33; 2:5-dichloronitrobenzene 0.22, 0.21; and 1-nitronaphthalene 0.53, 1.46. Reaction between various Grignard reagents and esters of benzoic acid is almost instantaneous.

J. W. BAKER.

**Factors affecting the rate of Grignard reactions.** H. GILMAN and E. L. ST. JOHN (Rec. trav. chim., 1930, 49, 222–225).—The effect of concentration, temperature, solvents, and catalysts on the velocity of reaction between a nitrile (usually benzonitrile) and magnesium *n*-butyl bromide has been studied. The velocity is increased by increased concentration and by rise in temperature, the following being the number of hours required for the completion of the reaction (colour test) between 0.12 mol. of benzonitrile and 0.1 mol. of magnesium *n*-butyl bromide at the respective temperatures: 33°, 4.36; 57°, 0.46; 73°, 0.17; boiling di-*n*-butyl ether, 0.06. The effect of a large number of catalysts was tried. Chlorobenzene has a definitely accelerating influence, whilst lead tetraethyl had a pronounced retarding effect on the above reaction, but no effect on the velocity of interaction of *n*-valeronitrile and magnesium phenyl bromide.

J. W. BAKER.

**Chemical kinetics of systems hydrogen peroxide-electrocolloids.** H. DAMIANOVITCH and O. F. F. NICOLA (Anal. Assoc. Quím. Argentina, 1929, 17, 142–188).—The loss of activity of colloidal solutions of gold and platinum when employed in the catalytic decomposition of hydrogen peroxide has been studied by measurement of the decline in the velocity of decomposition with time. The decay of the activity appears to follow an exponential time law, and is ascribed to irreversible aggregation of the colloidal particles, resulting in a diminution of the active surface. Adsorption complexes, which retard the decomposition process, may also be formed.

H. F. GILLBE.

**Action of hydrogen under high pressure on metallo-organic compounds.** I. V. N. IPATIEV, G. A. RAZUBAIEV, and I. F. BOGDANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1791—1799).—Lead tetraethyl, tetramethyl, and tetraphenyl are quantitatively converted into lead and hydrocarbon by the action of hydrogen at 60 atm. at 225—250° for 24 hrs., lead tetraphenyl being the most stable. In the absence of hydrogen prolonged heating at 200° is without effect on the methyl and phenyl compounds, whilst 11% of the ethyl derivative undergoes decomposition, no free lead being, however, formed. The velocity of decomposition by hydrogen increases rapidly with increase of pressure up to 60 atm., after which it remains constant. The velocity is greatest during the first 24 hrs. of reaction, after which the remaining traces of compound are only very slowly decomposed. The use of different solvents did not affect the velocity of decomposition above 200°; below this temperature the best results were obtained with benzene.

R. TRUSZKOWSKI.

**Reduction of cupric sulphide by hydrogen at various temperatures.** K. FISCHBECK and O. DORNER (Z. anorg. Chem., 1930, 186, 365—372).—The variation of the velocity of the above reaction with time and temperature has been followed by titrating the hydrogen sulphide produced. Cupric sulphide prepared by precipitation behaves differently from that made by the interaction of metallic copper and sulphur dissolved in carbon disulphide. The heat of activation of the substance prepared by the second method, calculated by means of the author's formula (A., 1929, 1389), is 30.2 kg.-cal. per mol. of hydrogen sulphide formed.

F. L. USHER.

**Dehydration of copper sulphate pentahydrate.** W. E. GARNER and M. G. TANNER (J.C.S., 1930, 47—57).—The rates of dehydration of single crystals of copper sulphate pentahydrate in a vacuum have been measured at a series of temperatures between 20° and 56°. Crystals of known weight and surface area were activated by rubbing with the powder of the monohydrate, after which treatment partial dehydration leads to the formation of a core of pentahydrate, the surfaces of which are parallel to the original surfaces of the crystal. At the higher temperatures the rate of loss of water per unit area of the interface between the pentahydrate and the dehydration product was practically constant, but in some experiments at the lower temperatures it decreased as dehydration proceeded. Below 46° the dehydrated product is the monohydrate, which remains as a pseudomorph which loses water only very slowly. At 56° the trihydrate is first formed, and this decomposes only when all the pentahydrate has disappeared. It then gives up its water at a slow constant rate. The logarithm of the velocity coefficient per unit area of interface plotted against the reciprocal of the absolute temperature gives a straight line. The critical increment of the process is 10,300 g.-cal., and  $\mu=2.77$ , corresponding with one of the vibration frequencies of the water molecule. However, it is considered that since the pressure of water vapour at the interface is probably appreciable, the rates measured may not be the true rates of evaporation, and the critical increment may

not be the true value for the unit process which occurs at the interface.

J. W. SMITH.

**Velocity of dehydration of gypsum at different temperatures.** P. P. BUDNIKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1713—1716).—The velocity of dehydration at 40°, 100°, and 140° of synthetic gypsum is smaller than that of natural gypsum and the curves expressing this velocity have a more distinct halt at the point corresponding with the formation of polyhydrate in the latter than in the former case. At 160°, the curves coincide over the first period of dehydration, and no break in the curves is evident.

R. TRUSZKOWSKI.

**Velocity of hydration of dehydrated gypsum.** P. P. BUDNIKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1717—1720).—Hydration by water vapour of both natural and synthetic gypsum, previously dehydrated at 140°, proceeds rapidly up to the formation of polyhydrate, after which it is retarded as a result of the covering of the polyhydrate grains by a colloidal gel. Polyhydrate formation is complete 1—2 sec. after immersion of dehydrated gypsum in water; further hydration then ceases for a short time, after which dihydrate is rapidly formed. The velocity of hydration during this period varies inversely with the time during which the gypsum was dehydrated.

R. TRUSZKOWSKI.

**Homogeneous catalysis of gaseous reactions.** K. CLUSIUS and C. N. HINSHELWOOD (Nature, 1930, 125, 311).—The homogeneous decomposition of diisopropyl ether catalysed by iodine can be represented by the equation  $(\text{CHMe}_2)_2\text{O} = \text{Me}_2\text{CO} + \text{CH}_2\text{Me}_2$ . Various alkyl iodides and, to a smaller extent, bromides (methyl, ethyl, and isopropyl iodides, hydrogen, ethylene, ethyl, and isopropyl bromides), but not chlorides, also catalyse this reaction. The catalytic mechanism involving the transfer of a hydrogen atom within the molecule is a general one; the atom transferred is in each case attached to the carbon atom adjacent to the oxygen.

L. S. THEOBALD.

**Influence of hydrogen and water vapour on ignition of carbon monoxide.** A. SMITHELLS, H. WHITAKER, and T. HOLMES (J.C.S., 1930, 185—194).—The concentrations of hydrogen and water vapour required, in a mixture of carbon monoxide and oxygen in their combining proportions, to effect their combination by an electric spark have been determined. The gas mixtures, containing hydrogen and water vapour respectively, were contained in two eudiometers and a spark was passed simultaneously through the two. In mixtures not subjected to prolonged drying containing 0.03—0.06% of hydrogen or water vapour, hydrogen was effective in causing the ignition, but not water. The minimum concentrations required to promote combustion are estimated to be 0.03% of hydrogen and 0.12% of water vapour. The catalytic activity of hydrogen was greatly reduced by long drying of the gaseous mixture, so that the superior effectiveness of hydrogen itself appears to be due to the presence of small quantities of water vapour.

J. A. V. BUTLER.

**Acid and salt effects in catalysed reactions.** XXIII. Catalytic activity of acid salts with

reference to the catalytic effects produced by potassium hydrogen oxalate in the acetone-iodine reaction. H. M. DAWSON and J. E. SMITH (J.C.S., 1930, 79—85; cf. A., 1929, 889; this vol., 42).—The velocity of reaction between acetone and iodine in the presence of potassium hydrogen oxalate has been determined over a range of concentrations of the latter salt and the results have been applied to the elucidation of the constitution of solutions of acid salts. At a concentration above 0.1M the reaction velocity is approximately a linear function of the concentration, but for the more dilute solutions it falls much more rapidly than would be expected from this linear relation. The observed results can be expressed by the equation  $v = k_1[H^+] + k_{H_2Ox}[H_2Ox] + k_{HOx}[HOx] + k_{Ox'}[Ox']$ , and it is shown that the departure from the linear law is due to the circumstance that  $[H^+] = \sqrt{K_1 K_2}$  at higher concentrations and  $[H^+] = \sqrt{K_2(c - [H^+])}$  at lower concentrations. Observations with solutions maintained at constant ionic strength by the addition of potassium chloride give closely similar results and show that inert salt effects, in so far as they have not been allowed for, are of very minor significance. J. W. SMITH.

Decomposition of sulphite-quinol solutions and action of aged solutions. J. PINNOW (Z. wiss. Phot., 1930, 27, 344—360; cf. A., 1912, i, 849).—The oxidation of sulphite-quinol solutions to form dark-coloured products is represented by a series of reactions. For the protection of sulphite solutions from oxidation by molecular oxygen a mixture of  $\alpha$ - and  $\beta$ -quinoldisulphonates is more effective than quinol. The catalytic action of copper in the oxidation process is discussed.

O. J. WALKER.

Inhibition of chemical reactions. III. Inhibition by sulphur of the atmospheric oxidation of benzaldehyde. K. C. BAILEY (J.C.S., 1930, 104—116).—The oxidation by atmospheric air or oxygen of benzaldehyde in an unshaken vessel, with and without the presence of traces of sulphur (inhibitor), has been studied. The velocity of the oxidation process is approximately proportional to the area of the liquid-gas interface and independent of the area of the liquid-solid interface. When the solid surface is nearer to the oxygen, the velocity of reaction in light is slightly diminished. The velocity of oxidation is reduced by 70% by the addition of 1 part of sulphur in  $10^5$ , whilst further addition of sulphur has a much smaller effect on the velocity. This effect is analogous to that of pyridine on the esterification of ethyl alcohol and acetic acid (A., 1928, 718), and it is suggested that the cause may be the same, viz., that the portion of the reaction which is readily affected is a surface reaction, whilst the portion not readily affected is a homogeneous reaction. Shaking the vessel increases the rate of reaction, and the velocity of oxidation increases with the rate of shaking, i.e., with the rate of diffusion of oxygen. The view suggested is that the reaction chain usually begins at the liquid surface, where it is more readily interrupted by an inhibitor concentrated there than when it begins in the homogeneous phase where the concentration of inhibitor

is lower. The reduction of velocity with diminishing depth of the liquid is attributed to earlier interruption of the reaction chain by collision with the solid surface. J. W. SMITH.

Catalytic reduction of nitric oxide. A. J. BUTTERWORTH and J. R. PARTINGTON (Trans. Faraday Soc., 1930, 26, 144—147).—Hydroxylamine and ammonia are formed in small amounts when a mixture of nitric oxide and hydrogen is brought into contact with platinised platinum in the presence of dilute hydrochloric acid. The amounts are variable and the two substances are formed probably by independent reactions. It is suggested that reaction occurs between the nitric oxide and the hydrogen protons in contact with the platinum,  $NO + H^+ \rightarrow NOH$ , followed by  $NOH + 2H^+ \rightarrow NH_2OH$  and  $NO^+ + 5H^+ \rightarrow NH_4OH$ . F. G. TRYHORN.

Preferential catalytic oxidation of carbon monoxide in the presence of hydrogen. I. Activity of two water gas conversion catalysts, of copper oxide, of manganese dioxide, and of a mixture of these oxides. II. Activity of two-component hopcalites. W. E. KUENTZEL (J. Amer. Chem. Soc., 1930, 52, 437—444, 445—455).—I. The preferential catalytic oxidation of carbon monoxide by oxygen in the presence of hydrogen and carbon dioxide and a large excess of water vapour (which acts as a catalytic poison towards the oxidation of hydrogen) has been investigated, using as catalysts promoted iron oxide, promoted cobalt oxide, copper oxide, manganese dioxide, a mixture of manganese dioxide and copper oxide, and a five-component hopcalite. The commercial promoted iron and cobalt oxide catalysts are of little use as preferential catalysts; they act principally as water-gas conversion catalysts and the presence of oxygen in the gas mixture has little effect on the products. Copper oxide at first oxidises both carbon monoxide and hydrogen, with reduction of the catalyst, leading to a diminution in activity, especially towards the oxidation of the hydrogen, but it is not efficient for removal of more than 1% of carbon monoxide. Manganese dioxide is also too readily reduced. The 60 : 40 (by wt.) mixture of manganese dioxide and copper oxide is the most satisfactory of the preferential oxidation catalysts tested. It shows more than 81% efficiency at 150° even after being heated at higher temperatures. At 175°, 96% efficiency is obtained over a period of 37 hrs. The hopcalite is much inferior, showing serious reduction with a resulting efficiency of only about 50%.

II. The activities of commercial hopcalities as preferential catalysts for the oxidation of carbon monoxide in converted water-gas have been investigated. Using a gas mixture containing 1.3% CO, 49.0% H, and 1.5% O, 97—98% of the influent carbon monoxide can be oxidised catalytically by free oxygen at 160—195° in presence of 3 vols. of steam to 1 vol. of gas at 1000 dry gas space velocity. The catalyst always suffers a loss in available oxygen through both thermal dissociation and reduction by the hydrogen and carbon monoxide, resulting in a decrease in catalytic activity. As the gases contained no catalytic poisons, it is concluded that the

loss of activity is due entirely to loss of oxygen. Attempts to restore the activity by treatment with dry air or with air mixed with steam at 190° and at 160° were only partly successful, the activity at 190° being improved, but that at 160° being still very low. Decreasing the steam content to a 2:1 ratio improved the efficiency. The rapid and efficient dissipation of the heat of reaction is very important; the catalysts were shown to be much less effective in glass than in copper vessels on this account. The steam assists the reaction in this respect, as well as specifically inhibiting the reduction of the catalyst and the oxidation of hydrogen. J. W. SMITH.

**Mechanism of catalytic action of metals and metal oxides.** L. V. PISARSHEVSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1609—1634).—The catalytic action of metals or their oxides in heterogeneous systems is supposed to be due partly to adsorption, and partly to the existence of "electronic isomerism." A dynamic equilibrium is presumed to exist, on the surface of the catalyst, between "passive" and "active" atoms; these differ in their labile electronic content, and the possession of a labile electron confers catalytic properties to an atom.

R. TRUSZKOWSKI.

**Magneto-analytical investigations on cobalt oxide catalysts for the oxidation of carbon monoxide at the ordinary temperature.** F. MERCK and E. WEDEKIND (Z. anorg. Chem., 1930, 186, 49—74).—The magnetic susceptibilities of preparations of cobaltic oxide for use in the catalytic oxidation of carbon monoxide have been measured after drying for varying periods at different temperatures in oxygen. The results indicate that the catalyst consists of a mixture of the hydroxide  $\text{CoO}(\text{OH})$  and the oxide  $\text{Co}_3\text{O}_4$ , but neither of these compounds alone is catalytically active. It is suggested that the catalysed reaction occurs at the phase boundaries, as there are indications from X-ray examination that the cobaltic oxide in the  $\text{Co}_3\text{O}_4$  lattice is superficially reduced by dilute carbon monoxide. The magnetic susceptibility of catalysts increases during the conversion of the hydroxide into the oxide, reaching a maximum of  $32 \times 10^{-6}$  with pure  $\text{Co}_3\text{O}_4$ , but this value varies only slightly with the amount of available oxygen. During the conversion there appears to be an active intermediate condition characterised by variation of the susceptibility with the strength of the magnetising field; this condition disappears on ageing or on sintering and is of no importance in the catalytic action. A. R. POWELL.

**Sulphuric acid catalysis. IV. So-called arsenic poisoning.** B. NEUMANN and H. JÜTTNER (Z. Elektrochem., 1930, 36, 87—96).—The catalytic influence of various materials which are usually regarded as "poisons" on the reaction  $\text{SO}_2 + \text{O} \rightarrow \text{SO}_3$  has been investigated by comparison of the percentage conversion at various temperatures with that obtained with a platinum catalyst. Arsenic pentoxide shows a maximum conversion of 54% at 660°, the action being due to a reversible reduction and re-oxidation of the catalyst. Arsenic tri- or pentoxide therefore behaves as an activator when admixed with oxide catalysts of which the rate of reduction

and reoxidation is slow; thus with a ferric oxide catalyst the maximum conversion is raised from 69.5% to 78.5% and occurs 63° lower when arsenic oxide is added, but for vanadium pentoxide, which has a high reduction velocity, addition of arsenic pentoxide has no effect. With metallic vanadates, e.g., silver vanadate, the poisoning effect of arsenic is immediately apparent. A platinum-asbestos catalyst containing arsenic pentoxide shows after a preliminary heating at 300° a gradual rise in the percentage conversion, the maximum, at about 575°, and the subsequent course of the curve being very near the conversion values obtained with pure platinum; after regeneration the material behaves at temperatures above 450° in a manner almost identical with that of platinum. Analogous results are obtained when elementary arsenic is added to the platinum catalyst, but in neither case can the activity of the unpoisoned catalyst at low temperatures be attained by regeneration. Selenium exerts an influence very similar to that of arsenic on platinum, but to a much smaller extent. Addition of arsenic pentoxide to silver reduces its activity almost to zero, i.e., to a value far below that of either component.

H. F. GILLBE.

**Influence of the carrier on the catalytic activity of metal-carrier catalysts. II.** T. SABALITSCHKA and K. ZIMMERMANN (Ber., 1930, 63, [B], 375—380; cf. A., 1927, 427).—The hydrogenation of fumaric acid has been investigated in the presence of (a) blood charcoal which has adsorbed palladium chloride and subsequently been treated with hydrogen, (b) barium sulphate mixed with palladium hydroxide and treated with hydrogen, (c) sugar charcoal shaken with palladium obtained by reducing the chloride, and (d) palladium wool prepared according to Lockemann and Picher (Z. Hyg., 1927, 108, 125). Charcoal and barium sulphate as carriers can depress the catalytic activity of the metal, this occurring invariably when they are added to palladium suspended in an aqueous medium or adsorbed on wool; the degree of depression increases with the amount of carrier. Even when the metal is distributed throughout the carrier by adsorption its activity may be less than that of the freely-suspended substance although, in itself, the distribution of the metal on the carrier increases its catalytic activity (*loc. cit.*). The contradictory effects of the carrier on the catalytic activity necessitate the observance of an optimal mass relationship of metal to carrier in producing a catalyst of maximal activity. An excess of carrier depresses the activity. Facilitation of hydrogenation is not observed, owing to the additional amount of the gas absorbed when charcoal saturated with hydrogen is brought into contact with similarly saturated palladium in an atmosphere of hydrogen. Diminution of the catalytic activity due to the carrier cannot be completely explained by the adsorption of fumaric acid by the carrier. It probably has its origin in a coating caused by adsorption between the active metallic centres and the carriers or in the blocking of the active centres.

H. WREN.

**Catalytic addition of hydrogen.** G. BREDIG (Ber., 1930, 63, [B], 488).—The general view that

reactions in which finely-divided metals act as catalysts proceed according to a simple logarithmic formula has not been expressed by the author (cf. Krestinski and Perssianzewa, this vol., 319).

H. WREN.

**Oxidation of mercury vapour at glowing platinum.** Y. OKAYAMA (Z. physikal. Chem., 1930, B, 6, 355—367).—The velocity of oxidation of mercury vapour by oxygen at the surface of heated platinum has been determined, allowance being made for the oxidation of platinum itself. The rate of the reaction is practically independent of the mercury pressure, but increases with the oxygen pressure, and is proportional to the amount adsorbed according to Langmuir's equation.

J. A. V. BUTLER.

**Catalytic "coupling" of manganese dioxide with phosphoric or sulphuric acid as an oxidising agent. Effect of acidity on the oxidation of butyric acid with hydrogen peroxide.** E. J. WITZEMANN (J. Amer. Chem. Soc., 1930, 52, 640—646).—When butyric acid is treated with hydrogen peroxide in presence of varying amounts of phosphoric, sulphuric, or boric acid, no change in the peroxide concentration is found until manganese dioxide (or porous earthenware) is added (cf. A., 1922, i, 6); the amount of acetone formed during the catalysed oxidation rises with increased acidity. Manganese dioxide and phosphoric acid (in small concentrations) react with hydrogen peroxide thus:  $2\text{H}_3\text{PO}_4 + 3\text{MnO}_2 + 3\text{H}_2\text{O}_2 = \text{Mn}_3(\text{PO}_4)_2 + 3\text{O}_2 + 6\text{H}_2\text{O}$ . With increased concentration of the acid only a portion of it reacts in this way, suggesting that with low acid concentrations a complex is formed between the peroxide and the acid. It is suggested that the manganese dioxide acts on this complex. The butyric acid is largely oxidised to acetone, carbon dioxide, and a small amount of acetic acid.

H. BURTON.

**Heterogeneous decompositions. II.** H. DOHSE (Z. physikal. Chem., 1930, B, 6, 343—354; cf. A., 1929, 1231).—The decomposition of *n*- and *iso*-propyl alcohols and *n*-, *iso*-, and *tert*-butyl alcohols at the surface of bauxite at various temperatures has been studied, both with and without the presence of barium oxide to remove the water formed. The heats of activation in the two cases differ by about 13,000 g.-cal., which is also the heat of adsorption of water. The product  $k \cdot e^{Q/RT}$ , where  $k$  is the velocity coefficient of the reaction and  $Q$  the heat of activation, is the same for the different alcohols, showing that the active surface area is the same in each case. The velocity of decomposition on bauxite of surface layers of alcohols of different thicknesses has been determined. The time for half-decomposition remains constant below a certain thickness, at which 2 to  $3 \times 10^{19}$  molecules are adsorbed per g. of bauxite. This is regarded as the number of active catalysing centres.

J. A. V. BUTLER.

**Catalytic dehydration of saturated aliphatic alcohols by alkali hydrogen sulphates.** J. B. SENDERENS and J. ABOULENC (Compt. rend., 1930, 190, 150—152).—According to the temperature of reaction saturated aliphatic alcohols yield ethers and/or hydrocarbons with sodium hydrogen sulphate but are almost unaffected by potassium hydrogen

sulphate (cf. A., 1929, 695). *iso*Amyl, *n*-amyl, and octyl alcohols yield both classes of substance, whilst *n*-heptyl and cetyl alcohols yield the ethers at low temperatures and the hydrocarbons above 175° and 250°, respectively. Methyl, ethyl, propyl, *isopropyl*, and *isobutyl* alcohols (b. p. 66—108°) distil unchanged.

J. GRANT.

**Decomposition of chloropicrin by heating in contact with metals.** A. D. PETROV and A. O. SAVELEV (J. Appl. Chem., Moscow, 1929, 2, 629—632).—Metals have little catalytic action; such action is least with iron or lead and greatest with brass. The rate of decomposition at the b. p. (112.7°) is 10 times that at 100°.

CHEMICAL ABSTRACTS.

**Electrolytic charging of metals with hydrogen.** H. O. VON SAMSON-HIMMELSTJERNA (Z. anorg. Chem., 1930, 186, 337—356).—The differences observed by Tammann and Schneider (A., 1928, 701) in the amounts of hydrogen produced electrolytically at hard and soft iron cathodes have been traced to recombination of the hydrogen and oxygen developed, a process the rate of which depends on the type and nature of the cathode. With copper, silver, or gold cathodes, similarly, normal volumes of hydrogen are produced when contact with anodic oxygen is prevented. On the other hand, adsorption of hydrogen occurs at cathodes of cerium or lanthanum. The oxygen loss at a gold anode is greatly in excess of the hydrogen loss, and the production of temper colours indicates that the gold is oxidised. Changes in the structure of a palladium surface when hydrogen is absorbed, and the dependence of the amount of hydrogen taken up and of the velocity of absorption on the orientation of the crystals, have been studied. Experiments have been made to show the influence of pressure and of a low temperature on the absorption of electrolytic hydrogen by palladium.

F. L. USHER.

**Reactions occurring at the electrodes in electrolysis, and some metallic compounds produced.** A. P. ROLLET (Ann. Chim., 1930, [x], 13, 137—252).—In the electrolysis with alternating current of dilute aqueous solutions of alkali or sulphuric acid with gold or platinum electrodes or of dilute solutions of alkali with silver electrodes, no gas is evolved until the current density exceeds a certain limiting value. It thus appears that at low current densities the products of electrolysis are fixed by the electrodes, decomposition being therefore followed by recombination, and this view is confirmed by the observation that a silver electrode is alternately coated with oxide and with powdery metal. With increase in the current density, however, a point is ultimately reached at which the electrodes are unable to fix all the oxygen liberated during half a cycle, and the excess is therefore given off, as is also the hydrogen above the amount equivalent to the oxygen fixed. Gold, nickel, cobalt, iron, copper, and lead behave like silver, oxygen being fixed to a much greater extent than hydrogen, whereas with platinum and palladium the reverse is the case. Similar results are also obtained when soluble electrodes are used; e.g., in the electrolysis of sulphuric acid solutions with nickel electrodes oxygen is evolved when the current

density exceeds a certain critical value. In no circumstances, however, does any kind of decomposition occur unless the maximum *E.M.F.* in the cycle exceeds the decomposition tension for water with the particular electrodes used. The critical current density in the electrolysis of potassium hydroxide solutions to which carbon dioxide is being added changes discontinuously when the amount of carbon dioxide is just sufficient to convert the whole of the alkali into the normal salt if the electrodes consist of one of the metals which fix oxygen, from which it would appear that several degrees of oxidation are possible. It has, in fact, proved possible to study the oxidation by combining such an electrode, anodically polarised with a direct current, with a reference electrode and observing the *E.M.F.*-current strength relationship when this cell is allowed to discharge. The formation of the oxide  $\text{Ag}_2\text{O}_3$  on a silver electrode has thus been demonstrated, and similar experiments with accumulator plates have yielded results supporting the theory that lead subsulphate is formed on the negative plate at discharge, but no definite evidence of the presence of  $\text{Pb}_2\text{O}_5$  on the charged positive plate could be obtained (cf. Féry, A., 1919, ii, 263; B., 1926, 497). In the Edison accumulator, the active material on the charged nickel plate is mainly nickel dioxide if the alkali concentration exceeds about 6*N*.

R. CUTHILL.

**Oxidation at platinum anodes of cathodically reduced chromic acid solutions.** S. TAKEGAMI (Bull. Chem. Soc. Japan, 1930, 5, 16—24).—The oxidation and reduction occurring at platinum electrodes during the electrolysis with low current densities at 30° of chromic acid solutions (containing small amounts of sodium sulphate) have been measured by comparing the amounts of oxygen and hydrogen evolved at these electrodes with those formed in a series coulombmeter. Although in no case was a visible film noticed at the anode the view is adopted that such a film is present, since the oxidation diminishes in the early stages of electrolysis, particularly at low current densities (0.01 amp.). At higher densities (0.05 amp.) the oxidation falls to zero in about 100 min. and thereafter rises to irregular values. Normally the oxidation should increase with time, parallel with the increase in  $\text{Cr}^{+++}$  ion concentration. No connexion was traced between the extent of oxidation and the  $\text{Cr}^{+++}$  ion concentration. This is due probably to the rupture of the film through the evolution of oxygen, the extent of such rupture being uncontrollable by the conditions of the experiment.

F. G. TRYHORN.

**Electrolytic reduction of acid molybdenum solutions. I.** F. FOERSTER, E. FRICKE, and R. HAUSSWALD (Z. physikal. Chem., 1930, 146, 81—100).—The equilibria  $\text{Mo}^{\text{VI}}\text{O}_2^{++} + 2\text{H}^+ \rightleftharpoons \text{Mo}^{\text{VO}} + \text{H}_2\text{O} + \oplus$  and  $\text{Mo}^{\text{VO}} + 2\text{H}^+ \rightleftharpoons \text{Mo}^{\text{III}} + \text{H}_2\text{O} + 2\oplus$  have been studied by measuring the potentials of platinum, iridium, and gold electrodes in 2, 4, and 8*N*-hydrochloric acid solutions containing varying ratios of  $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$  and  $\text{Mo}^{\text{V}}/\text{Mo}^{\text{III}}$ , respectively, the total molybdenum concentration being 0.5 at. The observed values show considerable deviations from

the theoretical potentials calculated only from concentration changes, especially in the case of platinum and gold electrodes. The equilibria between the various valency stages of molybdenum are discussed.

O. J. WALKER.

**Electrolytic reduction of acid molybdenum solutions. I (cont.).** F. FOERSTER, E. FRICKE, and R. HAUSSWALD (Z. physikal. Chem., 1930, 146, 177—231; cf. preceding abstract).—The static potentials of  $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$  and of  $\text{Mo}^{\text{V}}/\text{Mo}^{\text{III}}$  have been determined for varying proportions of the constituents, in 8*N*-, 4*N*-, and 2*N*-hydrochloric acid, and compared with the reduction potentials obtaining during the electrolytic processes  $\text{Mo}^{\text{VI}} \rightarrow \text{Mo}^{\text{V}}$  and  $\text{Mo}^{\text{V}} \rightarrow \text{Mo}^{\text{III}}$ . The reduction is accompanied by considerable polarisation which decreases with increasing acidity. In both series of measurements the same results are obtained with platinum, iridium, or gold electrodes, and with hydrochloric or sulphuric acid, whence it is inferred that the polarisation is due to the molybdenum. As with chromate solutions, the course of the reduction is influenced by the formation round the electrodes of porous diaphragms composed of oxides or basic salts of the electrolyte and its immediate reduction product. The exact nature of these diaphragms is unknown; they are, however, so thin that the theoretical current yield of the process is maintained although the necessary *E.M.F.* is greatly increased.

F. L. USHER.

**Temperature effect at working electrodes.** F. FICHTER (Helv. Chim. Acta, 1930, 13, 89—99).—Numerous examples are quoted of anodic reactions which occur during electrolysis at temperatures near the ordinary but require rather high temperatures when carried out in the usual chemical way. It is suggested that the former cases are explicable on the assumption of a thin zone or layer of relatively high temperature existing near the surface of the electrode from which there is a steep temperature gradient towards the bulk of the electrolyte and the electrode itself. By this assumption it is possible to account for the rapid decomposition of the diacyl peroxides and the organic per-acids immediately after their formation at cooled anodes, as well as for numerous types of synthesis to which electrochemical methods are applicable. Should the assumption of these zones of high temperature in what are usually regarded as isothermal systems prove untenable the explanation of the disparity in the conditions under which one and the same reaction can occur must be sought on some fundamentally new basis.

F. G. TRYHORN.

**Energy considerations in the electro-deposition of metals.** I. W. WARK.—See B., 1930, 200.

**Electrochemical oxidation of *o*-toluenesulphonamide to saccharin.** F. HALLA (Z. Elektrochem., 1930, 36, 96—98).—The electrochemical oxidation of *o*-toluenesulphonamide to saccharin has been studied, using platinum, lead, gold, tin, and mercury anodes. Gold and platinum give good yields of approximately the same order, whereas with lead and tin only traces of saccharin are formed: a mercury anode causes amalgamation of the cathode. The use of alternating current does not appreciably alter the yields.

H. F. GILLBE.



**Action of the silent discharge on oils, fats, and fatty acids. III. Influence of temperature, voltage, polar distance, and pressure of gaseous medium.** Y. IWAMOTO (*J. Soc. Chem. Ind. Japan*, 1929, **32**, 359—361B).—When fatty acids are subjected to the action of the silent discharge in the presence of hydrogen, both polymerisation and reduction occur simultaneously. The higher is the temperature (below 100°), the more intense is the action of the discharge. Further, the discharge is the more effective the greater is the voltage between 5000 and 20,000 volts. From experiments at 20,000 volts the effect of the discharge appears to be inversely proportional to the distance between the poles. With pressures of gas less than 10 mm. the effect of the discharge increases with decreasing pressure. At higher pressures the reverse obtains.

F. J. WILKINS.

**Photochemical and photo-electric measurement of submarine illumination.** W. R. G. ATKINS and H. H. POOLE (*J. Marine Biol. Assoc.*, 1930, [ii], **16**, 509—514).—The absorption coefficients of water in the English Channel down to depths of 40 m. have been determined by the authors' uranyl oxalate method (A., 1929, 1249). The results are compared with those obtained by photo-electric measurements.

C. W. GIBBY.

**Oxidation and photo-oxidation of alkali and ammonium thiocyanates.** B. S. SHARMA (*Z. anorg. Chem.*, 1930, **187**, 237—240).—The precipitate obtained by oxidising a solution of ammonium thiocyanate with hydrogen peroxide is of a variable composition and when ignited leaves a residue of ferric oxide. The photo-oxidation proceeds most readily in 44% solution and is promoted by traces of iron but hindered when the concentration of the latter exceeds a certain value. Hydrocyanic and sulphuric acids were found among the products of decomposition.

F. L. USHER.

**Development of colour by photochemical change in concentrated solutions of ammonium thiocyanate.** B. S. SHARMA (*J.C.S.*, 1930, 308—309).—The colour is not developed in purified solutions of ammonium thiocyanate and is dependent on the presence of iron. It is considered that the colour is not due to the formation of ferric thiocyanate, since it disappears in the dark, but to the formation of a loose compound of ferrous thiocyanate, oxygen, and probably some ammonium thiocyanate.

J. A. V. BUTLER.

**Photochemical formation of carbonyl chloride.** S. LENHER and G. K. ROLLEFSON (*J. Amer. Chem. Soc.*, 1930, **52**, 500—506).—A new mechanism is proposed for the photochemical reaction between carbon monoxide and chlorine. It is suggested that in the reaction at the ordinary temperature the chlorine molecule is dissociated by light, and that a molecule  $\text{COCl}$  is formed by triple collision between a chlorine atom, a carbon monoxide molecule, and a chlorine molecule which takes up sufficient energy to stabilise the  $\text{COCl}$  molecule. On collision with another chlorine molecule the latter then gives carbonyl chloride and a chlorine atom, whilst on collision with a chlorine atom carbon monoxide and mole-

cular chlorine are regenerated. The inhibiting action of oxygen and the photo-sensitised formation of carbon dioxide are explained in the same way as in the mechanism suggested by Bodenstein, Wagner, and Lenher (A., 1929, 894), with which this mechanism is compared. The high-temperature formation of carbonyl chloride is attributed to the triple collision of a chlorine atom with a carbon monoxide molecule and a chlorine molecule yielding carbonyl chloride directly ( $\text{CO} + \text{Cl} + \text{Cl}_2 = \text{COCl}_2 + \text{Cl}$ ). J. W. SMITH.

**Photochemical studies. X. Electronic and photochemical decompositions of potassium chlorate.** J. G. MEILER and W. A. NOYES, jun. **XI. Quantum efficiency of ozone formation in the fluorite region.** W. E. VAUGHAN and W. A. NOYES, jun. (*J. Amer. Chem. Soc.*, 1930, **52**, 527—533, 559—568).—X. An attempt has been made to investigate the decomposition of potassium chlorate on bombardment with slow electrons. With an accelerating potential of 22 volts definite evidence of decomposition is obtained, but the high experimental errors do not permit of any being detected at lower voltages. It is calculated that probably the effect would not be decisive unless short reaction chains, 10—100 molecules in length, were initiated by the bombardment. Photochemical decomposition of potassium chlorate to give potassium chloride and oxygen can be brought about by radiation of wavelength less than 2800 Å., but the threshold could not be determined accurately. The quantum efficiency at 2537 Å. is of the order of 1/100. The two series of experiments are considered not to be contradictory, since the activating processes are probably different in the two cases.

**XI. Determinations of the quantum efficiency of ozone formation in radiation transmitted by fluorite** indicate a value of  $2.0 \pm 0.3$ . This is approximately the value to be expected from theoretical considerations, although a slightly higher value would not be impossible.

J. W. SMITH.

**Effect of light on silver chloride in chemical analysis.** G. E. F. LUNDELL and J. I. HOFFMAN (*Bur. Stand. J. Res.*, 1930, **4**, 109—114).—Errors resulting from the exposure to light of silver chloride during analytical work have been investigated. Exposure during precipitation causes positive errors if silver is in excess, and negative errors if hydrochloric acid is in excess, of the order of 0.1%. Exposure of dry precipitates has little effect.

C. J. SMITHELLS.

**Becquerel effect. III.** I. LIFSCHITZ and S. B. HOOGHOUTD (*Z. physikal. Chem.*, 1930, **146**, 145—172; cf. A., 1929, 514).—A satisfactory measure of the Becquerel effect in an electrode-electrolyte system can be obtained by determining the *E.M.F.* of the closed cell, electrode|electrolyte|non-polarisable electrode, in the dark and on exposure to light. A method for determining the difference ( $\pi$ ) of the two values is described, and illustrated in the case of various electrolytes, e.g., copper and uranyl salts, and dyes.  $\pi$  is dependent on the nature of the electrolyte, temperature, intensity and wave-length of the light, but is independent of the external and internal resistance of the cell, the nature of the non-

polarisable electrode, the duration of exposure to light, the polarisation and electrode potentials, the shape and size of the electrode, and the volume of the exposed solution. O. J. WALKER.

**Photochemical interaction of acetaldehyde and oxygen.** E. J. BOWEN and E. L. TRETZ (J.C.S., 1930, 234—243).—When gaseous, liquid, or dissolved acetaldehyde containing oxygen is exposed to ultra-violet light, a peroxide is formed. It is also formed in the dark when liquid acetaldehyde is shaken with oxygen, and is comparatively stable. The rate of reaction in the gas and in solution is proportional to the square root of the light intensity and to the acetaldehyde concentration, but independent of the oxygen concentration. The reaction is essentially the same at different wave-lengths within the acetaldehyde absorption band. The behaviour is explained by a chain reaction involving the formation of peracetic acid as the first product. In solution peracetic acid reacts according to the equations  $\text{CH}_3\cdot\text{CO}_3\text{H} + \text{CH}_3\cdot\text{CHO} = 2\text{CH}_3\cdot\text{CO}_2\text{H}$ ;  $\text{CH}_3\cdot\text{CO}_3\text{H} + \text{CH}_3\cdot\text{CO}_2\text{H} = \text{CH}_3\cdot\text{CO}\cdot\text{O}_2\cdot\text{CO}\cdot\text{CH}_3$ . When added to solutions of aldehyde in hexane, alcohol acts as an inhibitor and the reaction becomes proportional to the light intensity. The action of several anti-knock substances on the reaction has been studied. They do not all act as inhibitors of the reaction. J. A. V. BUTLER.

**Oxidation of oils in the presence of irradiated sterols.** E. COUTURE (Compt. rend., 1930, 190, 532—533).—Linseed and cod-liver oils are catalytically oxidised by irradiated sterols, a sterol possessing a marked specific action on the oil from which it has been extracted. The oxidation occurs equally in air or in an atmosphere of nitrogen; the catalytic process is dependent on light, but is unaffected by filtration of the incident rays through Wood's glass. C. W. SHOPPEE.

**Decomposition of cholesterol *in vitro* by X-rays.** A. H. ROFFO and L. M. CORREA (Strahlen-ther., 1929, 33, 537—541; Chem. Zentr., 1929, ii, 2019).—The decomposition of cholesterol in solution in chloroform, carbon tetrachloride, or iodoform by X-rays is due to the oxidising action of chlorine or bromine liberated from the solvent. A. A. ELDRIDGE.

**Chemical effects of X-rays and the energy relations involved.** G. L. CLARK and (Miss) L. W. PICKETT (J. Amer. Chem. Soc., 1930, 52, 465—479).—Experiments have been carried out with the object of determining what types of reactions are sensitive to X-radiation, and to study the energy relations involved. Anthracene, dianthracene, maleic acid, fumaric acid, ferric sulphate, methylene-blue, triphenylmethane, diphenylmethane, and azoindigo were all unchanged in X-rays of effective wave-length 0.24 Å. A 40% oxidation of ferrous sulphate in sulphuric acid to ferric sulphate, and slight reaction between iodine and benzene were observed, whilst sucrose showed slight inversion, especially in the presence of lead nitrate, the effect of this salt being probably due to the change of  $p_{\text{H}}$ . The condensation of aldehydes with aldehydes is affected only very slightly or not at all by X-rays, whereas the condensation of aldehydes with ketones is markedly

catalysed. It is concluded that sensitivity to ultra-violet light is no criterion of sensitivity to X-radiation of this wave-length and that the reactions most affected are those involving oxidation in aqueous solution. The decomposition of potassium iodide and of potassium nitrate under the action of X-rays has been studied in detail, with special attention to the energy relation of the changes. In both cases, the decomposition in a vacuum is a straight-line function of the intensity of the radiation, but with potassium iodide it takes place more readily in the presence of oxygen, whereas the decomposition of potassium nitrate is independent of the oxygen pressure. The formation and subsequent decomposition of hydrogen peroxide is not essential for oxidation in aqueous solution, although it may play a contributory part in the total effect. The effects of X-rays and of ultra-violet radiation on these two salts are additive. Only 0.8% of the energy absorbed by potassium nitrate appears as chemical dissociation. Colloidal lead as used in the Blair-Bell treatment for cancer is not coagulated by X-rays, but is stabilised to a slight extent. It does not catalyse chemical reactions in X-rays. Hence its effect in the tissues is probably a specific chemical effect rather than the action of producing secondary radiation. The coagulation of colloidal clays by X-rays depends on the traces of organic matter present.

J. W. SMITH.

**Temperature coefficient of the synthesis of hydrogen chloride by light and by  $\alpha$ -radiation.** S. C. LIND and R. LIVINGSTON (J. Amer. Chem. Soc., 1930, 52, 593—608).—The temperature coefficients of the photochemical (white light) and radiochemical syntheses of hydrogen chloride are identical within the limits of experimental error. In both cases the temperature coefficient varies with the sensitivity of the reacting system, having a value of 1.10 for an average chain length of  $2 \times 10^3$  and rising to a flat maximum of about 1.20 for an average chain length of  $8 \times 10^4$ . It is shown qualitatively that the temperature coefficient is about 10% higher when green light (filtered through nickel sulphate) is used as the source of activation. Using monochromatic light of 4358 Å. the yield per ion pair and the yield per quantum are approximately equal. This is not in agreement with the measurements of Porter, Bardwell, and Lind (A., 1926, 1111), whose results are discussed in the light of more recent investigations. A mechanism of the activation by means of  $\alpha$ -particles is suggested.

J. W. SMITH.

**Routine preparation of conductivity water. II.** J. M. STUART and F. WORMWELL (J.C.S., 1930, 85—87; cf. A., 1927, 1045).—A modification has been developed of the conductivity water still described previously. The tin condensing column is fixed vertically above a tinned copper steam trap, the water being condensed in an annular space formed by a short inner tin tube. All soldered joints in the condensing column are made with pure tin. The form of air-purification train now used consists of four columns, 3 cm. in diameter and 45 cm. high, containing glass beads and joined by short lengths of rubber tubing, which does not affect the conductivity of the water. The advantages claimed for the modified

design are low cost, great strength and compactness, ease of erection and working, and durability.

J. W. SMITH.

**Chemical inertia of the rare gases. I. Action of helium on platinum.** H. DAMIANOVICH (Anal. Asoc. Quím. Argentina, 1929, 17, 95—141).—Under the action of an alternating electric discharge between platinum electrodes in helium at low pressures the metal is corroded and dark grey laminated crystals are formed and deposited on the walls of the vessel. The substance decomposes in a vacuum slowly at the ordinary temperature, and more rapidly as the temperature is raised, leaving a residue of platinum. Ultra-violet photomicrographs and X-ray diagrams indicate that the material has a different structure from that of the residue obtained after its decomposition. The quantity of helium "fixed" varies from 14 to 34 c.c. per g. of platinum, and the velocity of fixation from 0.5 to 0.15 c.c./min., being maximal at about 100°. The mechanism of the formation of the new substance is uncertain, but it may represent a type of combination midway between that of ordinary compounds and that of co-ordinate compounds.

H. F. GILLBE.

**Alteration of crystalline sodium sulphide.** H. PECKER (J. Pharm. Chim., 1930, [viii], 11, 147—150).—Samples of crystalline sodium sulphide which had been kept for long periods in sealed containers were found to have been partly or completely transformed into crystalline sodium thiosulphate and/or a liquid containing this salt, sodium hydroxide, and a little sodium sulphate, with traces of free sulphur. Ammonium hydrogen sulphide decomposes, similarly, into ammonia, ammonium thiosulphate, and sulphur.

H. E. F. NOTTON.

**Extraction of rubidium and caesium from carnallite. II.** G. JANDER and F. BUSCH (Z. anorg. Chem., 1930, 187, 165—176; cf. B., 1929, 641).—A new method of extraction, starting from "artificial" (*i.e.*, once recrystallised) carnallite, is described. The product of a second recrystallisation is dissolved in hot dilute hydrochloric acid, and the solution on cooling deposits a part of its potassium chloride. The residual liquid is treated at 60—70° with a solution of sodium silicomolybdate, which precipitates the rubidium and caesium along with some potassium. The mixture of complex salts is converted into chlorides by heating in a current of hydrogen chloride, the molybdenum volatilising as hydroxychloride. The chloride mixture is dissolved in 2.5*N*-hydrochloric acid and precipitated in three fractions with 96% alcohol, the crystals obtained containing more than 50% of rubidium chloride along with potassium chloride, but no caesium chloride. The filtrate is then concentrated and treated with a hydrochloric acid solution of antimony trichloride, when more than half the caesium present is precipitated as the double chloride in a state of purity. The mother-liquor is added to the appropriate solution in a subsequent operation.

F. L. USHER.

**Oxidations with fluorine. XIV. Solutions of silver salts.** F. FICHTER and A. GOLDACH (Helv. Chim. Acta, 1930, 13, 99—102).—Fluorine precipitates from solutions of silver nitrate, sulphate,

perchlorate, and fluoride lustrous black crystalline compounds of silver peroxide with the respective salts. The greatest yield is obtained with concentrated silver nitrate solutions, the product corresponding on analysis with the formula  $\text{AgNO}_3 \cdot 2\text{Ag}_2\text{O}_4$ .

F. G. TRYHORN.

**Action of acetaldehyde, chloral hydrate, and mannitol on silver thiocyanate and the insoluble silver halides in presence of strong bases.** L. VANINO (Z. anal. Chem., 1930, 79, 369—371).—Silver chloride and silver thiocyanate are readily reduced to metal by treatment with potassium hydroxide and one of the above-mentioned reducing agents. The silver bromide and iodide must be repeatedly heated with concentrated potassium hydroxide solution and either chloral hydrate or mannitol in order to bring about their reduction; acetaldehyde cannot be employed in these cases, owing to the formation of aldehyde resin.

H. F. HARWOOD.

**Reduction by charcoal of heavy metal salts in solution.** E. HEYMANN, K. SALOMON, and R. KIEFFER (Z. anorg. Chem., 1930, 187, 97—111).—Auric chloride solution is reduced quantitatively to the metal by wood charcoal in the cold. This is explained by supposing that the auric chloride is hydrolysed and that the auric hydroxide is more strongly adsorbed than the acid. This is supposed to react with the carbon in the interface, yielding gold and carbon dioxide. The extraction of gold by the Plattner process is discussed in relation to those observations. Similarly, ferric chloride solutions are reduced by charcoal to ferrous chloride. The reducing action of specimens of charcoal which had been treated in different ways was investigated, including that of very pure carbon produced from carbon tetrachloride and mercury according to the method of Tammann (A., 1921, ii, 450). Experiments with this last specimen showed that the reducing action is not due to the presence of small traces of organic impurity, which charcoals generally contain. It is assumed that only such carbon atoms are oxidised as are connected with the active spots on the charcoal surface. Graphite has a slight reducing action of this type.

Oxygen at 20—100° is able to oxidise carbon suspended in an aqueous solution of ferric chloride, especially when a compound is added (*e.g.*, potassium iodide or platinised charcoal) which accelerates the re-oxidation of ferrous chloride to ferric chloride. Similar experiments with copper sulphate and chrome alum yielded only negative results.

J. W. SMITH.

**Magnesium carbonates. I. Basic magnesium carbonates.** H. MENZEL and A. BRÜCKNER (Z. Elektrochem., 1930, 36, 63—87).—The nature of the precipitates obtained from solutions of magnesium salt on addition of alkali hydrogen carbonate, carbonate, and hydroxide both separately and simultaneously has been studied under widely varying conditions of temperature, dilution, and composition of the precipitating agent. The precipitates are at first amorphous and finely divided, but when kept in contact with the mother-liquor they become crystalline, and the X-ray spectra have in many cases been determined. The existence of the following substances,

of definite composition and lattice structure, has been established:  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$ , precipitated by hydrogen carbonate or carbonate when not added in excess;  $\text{Mg}(\text{OH})_2$ , precipitated by an excess of hydroxide-carbonate mixture;  $5\text{MgO} \cdot 4\text{CO}_2 \cdot \text{aq.}$ , precipitated under widely varying conditions, and often contaminated by magnesium hydroxide or carbonate, which may be either mechanically mixed or present as solid solutions. This latter material, which is the essential constituent of all the basic magnesium carbonates obtained by precipitation, may be prepared also by hydrolysis of the normal carbonate by hot water. Although part of the water contained by the air-dried precipitate is merely adsorbed, it is not possible to remove this water in the ordinary manner without loss of chemically combined water, but on treatment with anhydrous liquid ammonia or with acetone at  $0-20^\circ$  the compound  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 6\text{H}_2\text{O}$  is obtained; desiccation of the hexahydrate over sulphuric acid yields slowly and reversibly the pentahydrate  $5\text{MgO} \cdot 4\text{CO}_2 \cdot 5\text{H}_2\text{O}$ . By heating at  $250^\circ$  the ratio  $5\text{MgO} : 4\text{CO}_2$  and the crystalline structure are practically unchanged, although the water content then corresponds approximately with the trihydrate. Discussion of the structure of the basic carbonates leads to the formulæ  $[\text{Mg}(\text{MgCO}_3 \cdot \text{H}_2\text{O})_4](\text{OH})_2$  and  $[\text{Mg}(\text{MgCO}_3 \cdot \text{H}_2\text{O})_4](\text{OH})_2 \cdot \text{H}_2\text{O}$  for the penta- and hexa-hydrates, respectively. H. F. GILLBE.

**Fundamental synthesis of calcium aluminates and their hydration.** IV. S. NAGAI and R. NAITO (J. Soc. Chem. Ind. Japan, 1930, 33, 17—19B).—Calcium aluminate was prepared by heating calcium carbonate and alumina in the ratio  $3\text{CaO} : \text{Al}_2\text{O}_3$  and the free and combined oxides in the product were determined. At  $1100-1250^\circ$  the primary product is  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ , but at higher temperatures this is converted into  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ , a result similar to those obtained with other ratios ( $5 : 1$  and  $3 : 5$ ). A small proportion of the compound  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  was also first formed but eliminated by further heating. The compound  $5\text{CaO} \cdot \text{Al}_2\text{O}_3$  was also converted by heating into  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  with separation of free lime. C. IRWIN.

**Hydration of the aluminates of calcium.** I. New crystalline form of tricalcium aluminate. T. THORVALDSON and N. S. GRACE (Canad. J. Res., 1929, 1, 36—47).—Tricalcium aluminate formed by heating alumina with calcium carbonate at  $1370^\circ$  forms the hydrate  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  when heated at  $150^\circ$  with steam in an autoclave. This compound forms isotropic crystals,  $n_D 1.604$ , which are slightly hygroscopic; at  $275-300^\circ$  the stable hydrate ( $+1.5\text{H}_2\text{O}$ ) is formed and at  $1000^\circ$  the last traces of water are expelled. At  $750-900^\circ$  decomposition into free lime and the aluminate  $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$  occurs, but recombination ensues after heating at above  $1000^\circ$  or by heating in steam at  $150^\circ$ .

A. R. POWELL.

**Action of nitrogen peroxide and of nitric oxide on calcium carbonate and lime.** E. BRINER, J. P. LUGRIN, and R. MONNIER (Helv. Chim. Acta, 1930, 13, 64—75).—The action of liquid and gaseous

nitrogen peroxide at temperatures between  $15^\circ$  and  $400^\circ$  and for periods between 5 and 624 hrs. on calcium carbonate and oxide, and that of nitric oxide on these substances at  $400^\circ$ , have been studied. Both in the liquid and the gaseous states dry nitrogen peroxide reacts with calcium carbonate according to the equation  $\text{CaCO}_3 + 3\text{NO}_2 = \text{Ca}(\text{NO}_3)_2 + \text{CO}_2 + \text{NO} + 27 \text{ kg.-cal.}$  The amount of nitrogen peroxide absorbed is proportional to the time of contact, and the rate of absorption increases rapidly with rise of temperature. With lime both nitrate and nitrite are formed with the liberation of nitric oxide, but the absorption is irregular by reason of the pasty nature of the product. At  $400^\circ$  nitric oxide does not react with calcium carbonate and is decomposed only to a very slight extent by lime. Under conditions in which the solid may be stirred nitrogen peroxide, in 10% concentration in air, is better absorbed by calcium carbonate than by lime. The use of calcium carbonate in the recovery of nitrous gases is suggested.

F. G. TRYHORN.

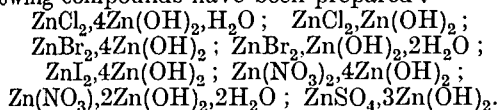
**Action of nitrogen peroxide on calcium phosphate.** E. BRINER and J. P. LUGRIN (Helv. Chim. Acta, 1930, 13, 76—80).—Neither liquid nor gaseous nitrogen peroxide has appreciable action on dry calcium phosphate, even with periods of contact of 35 days. In the presence of traces of water the action is represented by  $3\text{NO}_2 + \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} = \text{Ca}(\text{NO}_3)_2 + 2\text{CaHPO}_4 + \text{NO}$ , and, with a greater amount of water, by  $6\text{NO}_2 + \text{Ca}_3(\text{PO}_4)_2 + 2\text{H}_2\text{O} = \text{CaH}_4(\text{PO}_4)_2 + 2\text{Ca}(\text{NO}_3)_2 + 2\text{NO}$ . No nitrite is formed in either case, any nitrous acid formed either decomposing to give nitric acid,  $3\text{HNO}_2 = \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$ , or being oxidised by the nitrogen peroxide,  $\text{HNO}_2 + \text{NO}_2 = \text{HNO}_3 + \text{NO}$ . F. G. TRYHORN.

**Action of sulphur dioxide on calcium carbonate and calcium phosphate.** E. BRINER and R. MONNIER (Helv. Chim. Acta, 1930, 13, 80—85).—No action even after months of contact is observed between sulphur dioxide in the gaseous or liquid states and dry calcium carbonate at the ordinary temperature. A relatively rapid reaction represented by  $2\text{CaCO}_3 + 3\text{SO}_2 = 2\text{CaSO}_4 + \text{S} + 2\text{CO}_2 + 74 \text{ kg.-cal.}$  occurs at  $95^\circ$ . If water is present sulphite is formed by simple replacement. No reaction occurs between calcium phosphate and sulphur dioxide at the ordinary temperature, but at higher temperatures a reaction, represented by the equation  $2\text{Ca}_3(\text{PO}_4)_2 + 3\text{SO}_2 = 2\text{CaSO}_4 + 2\text{Ca}_2\text{P}_2\text{O}_7 + \text{S}$  occurs.

F. G. TRYHORN.

**Decomposition of solids in liquids.** I. Basic zinc salts. W. FEITKNECHT (Helv. Chim. Acta, 1930, 13, 22—43).—The formation of basic zinc salts when zinc oxide or hydroxide is left for prolonged periods in contact with solutions of zinc salts has been investigated chemically and by means of X-ray analysis. In general well-defined basic salts are formed in which the ratio  $\text{ZnO/zinc salt}$  is  $4 : 1$  if the anion is univalent, and  $3 : 1$  in the case of the single bivalent anion investigated. In the intensively dried, more basic compounds with the exception of the chloride the ratio  $\text{ZnO/H}_2\text{O}$  is  $1 : 1$ , the water being present in the hydroxide form. Further water of

the zeolitic type can apparently be present. The following compounds have been prepared:



Equilibrium between the basic salt and hydroxide occurs with the different salts at the following concentrations: sulphate 0.0015*N*, chloride 0.04*N*, nitrate 0.067*N*, bromide 0.234*N*, and iodide 0.74*N*. The equilibrium between the basic salt I and basic salt II occurs in 14*N*-solution for the chloride and bromide, and in 7.5*N*-solution for the nitrate. The basic halides are considerably soluble in the corresponding salt solutions, the solubility increasing up to the equilibrium value for the system basic-acid salt. An X-ray examination of the compounds with 3 and 4 mols. of zinc hydroxide indicated that the hydroxide is present in the  $\alpha$ -form. The crystal forms of the compounds are in agreement with this assumption. It appears that these zinc compounds cannot satisfactorily be represented as co-ordination compounds, but that the salt ions are arranged in layers between others of zinc hydroxide molecules, and that three or four hydroxide molecules can be associated with a single salt ion without greatly altering the unit cell. As the univalent ion increases in size the symmetry of the crystalline form decreases. In the series containing 1 mol. of zinc hydroxide the symmetry decreases with the replacement of chloride by bromine.

F. G. TRYHORN.

**Subhalides of homologues of mercury.** G. VON HEVESY and E. LÖWENSTEIN (Z. anorg. Chem., 1930, 187, 266—272).—The solubilities of cadmium in molten cadmium chloride, bromide, and iodide, of mercury in mercuric iodide, and of zinc and magnesium in their respective chlorides have been determined. Cadmium dissolves in molten cadmium chloride as a subchloride analogous to calomel, but stable only when liquid. On solidification the subchloride reverts to a mixture of the ordinary chloride and the metal. The tendency to form a subhalide increases with increasing size of the cation. Addition of an alkali halide to the fused mass hinders the formation of mercurous iodide and of cadmium subchloride.

F. L. USHER.

**Hydrides of boron.** B. D. STEELE and J. E. MILLS (J.C.S., 1930, 74—79).—Aluminium and cerium borides have been prepared by fusion of the metal powders with finely-divided boron oxide, the reaction in the latter case being carried out in a rapid stream of hydrogen. On treatment with acids these give small yields of boron hydrides, but these, on low-temperature fractionation and analysis, proved to be the same as those produced from magnesium boride,  $\text{B}_4\text{H}_{10}$  being the chief constituent, probably together with  $\text{B}_5\text{H}_9$  and  $\text{B}_6\text{H}_{10}$ .

J. W. SMITH.

**Blanc's alumina.** N. PARRAVANO and E. OSORATO (Atti R. Accad. Lincei, 1929, [vi], 10, 475—480).—By decomposition of aluminium chloride hexahydrate between 180° and 450° an apparently amorphous form of alumina is obtained. It gives no X-ray spectrum, but shows the double refraction

characteristic of non-monometric crystalline substances, and is considered to be in the semi-crystalline state. On being heated above 540° it is converted into a form which is definitely crystalline and is probably rhombohedral or hexagonal. The change in form is accompanied by an increase in density from 2.2 to 3.5. Above 950° the second form changes to corundum with a corresponding increase in the density to 3.9.

O. J. WALKER.

**Thermal decomposition of rare earth [tri]-halides.** G. JANTSCH (Naturwiss., 1930, 18, 155).—Whilst the m. p. of chlorides in the lanthanum series falls from lanthanum to europium the iodides vary as follows: neodymium tri-iodide melts at 775°, the praseodymium salt at 733°, and samarium tri-iodide begins to liberate iodine at 816—824°. The preparation of bivalent salts by means of gaseous reducing agents is troublesome owing to the necessity for rigid exclusion of moisture and oxygen. Thermal decomposition in a high vacuum seems likely to be more effective. Under a pressure of 0.01 mm. samarium tri-iodide begins to dissociate at 560° and at 750° the formation of samarium di-iodide is complete.

R. A. MORTON.

**Compact fused silicon and the density of this element.** C. BEDEL (Compt. rend., 1930, 190, 434—435).—A mixture of 30-mesh silicon with 10% of potassium fluosilicate covered with a thin layer of the latter and heated gradually in a quartz tube to the fusion point (1500°) is converted into a compact form of silicon which, however, may contain microscopic cavities. It contains 98.94% Si and has  $d_4^{20}$  2.307, the corresponding values for silicon from aluminium and zinc being 2.326 and 2.329, respectively, and 2.330 for fused silicon, powdered and washed with hydrofluoric acid.

J. GRANT.

**Germanium. II. Compounds of germanium with nitrogen.** R. SCHWARZ and P. W. SCHENK (Ber., 1930, 63, [B], 296—300; cf. A., 1929, 1407).—Addition of a solution of germanium tetrachloride in ether at -80° to liquid ammonia at the same temperature results in the formation of ammonium chloride, which is removed by repeated washing with liquid ammonia, and *germanium imide*,  $\text{Ge}(\text{NH})_2$ , a white, amorphous powder very readily decomposed by atmospheric moisture into germanium dioxide and ammonia. When heated in nitrogen at about 150°, the compound loses ammonia and yields *germanam*,  $\text{Ge}_2\text{N}_3\text{H}$ , stable below about 300°. At higher temperatures, *germanium nitride* is produced; this substance dissociates into its components when ignited. The latter type of decomposition occurs to some extent at much lower temperatures so that specimens of the nitride are usually coloured brown by the finely-divided metal. The formation of germanium tetra-amide has not been observed.

H. WREN.

**Preparation of pure metals of the titanium group by thermal decomposition of their iodides.** II. Zirconium. III. Hafnium. J. H. DE BOER and J. D. FAST (Z. anorg. Chem., 1930, 187, 177—189, 193—208; cf. A., 1926, 699).—II. The reduction of zirconium compounds by various methods has been studied in detail. The action of sodium on zirconium

tetrachloride at 850° yielded a partly sintered powder which after conversion into the tetraiodide gave a compact ductile specimen of the metal. Reduction of the oxide with a mixture of calcium or magnesium and sodium is also satisfactory, but it is necessary to purify the calcium by sublimation. A mixture of sodium and barium chloride gave a very finely-divided metal and the final product was impure and brittle. The product of the interaction of sodium and potassium fluozirconate was pure and ductile. The influence of common impurities on the preparation and properties of the metal has also been investigated. Iron is comparatively unimportant, since, even when present in the materials used, it usually cannot be detected in the final product. Silicon and aluminium, however, must be very completely removed from the materials before the reduction is carried out. Hydrogen, oxygen, and nitrogen form with the hot metal compounds which dissolve in it and profoundly modify its properties. Zirconium containing dissolved oxide is brittle and has a higher m. p. and a lower temperature coefficient of electrical conductivity than the pure metal.

III. Starting from an oxide rich in hafnium, direct reduction of the oxide is more advantageous than conversion into the chloride, since in the latter process fractionation occurs and the product contains less hafnium than the original material. Purified calcium gives a better product than magnesium. Reduction of the tetrachloride with sodium is satisfactory if the former is prepared from the crude metal instead of from the oxide. Reduction of a specimen of oxide of 100% purity with calcium and sodium and subsequent treatment by the iodide process gave a metal which was not ductile and was of too low a density, but on chlorinating the metal thus obtained, reducing the resulting chloride with sodium, and repeating the iodide process, a satisfactory specimen was obtained. Mechanical and electrical properties of the pure metal having m. p. about 2500° Abs.,  $d$  13.31, are described.

F. L. USHER.

**Preparation of pure hafnium salts.** J. H. DE BOER and J. BROOS (*Z. anorg. Chem.*, 1930, **187**, 190—192; cf. *A.*, 1927, 954).—The precautions necessary to ensure the absence of impurities which may give rise to volatile and dissociable iodides are described in detail. The preparation is carried out by means of the hydrofluoric acid-borax and the sulphuric acid methods previously described.

F. L. USHER.

**Mechanism of precipitation processes in which compounds of bromine with lead are formed.** Z. KARAOGLANOV and D. TSCHAWDAROV (*Z. anorg. Chem.*, 1930, **187**, 273—288).—The precipitation of lead salts by alkali bromides under various conditions has been studied in order to determine the part played by univalent complex lead cations. The precipitate obtained by mixing aqueous solutions of potassium bromide and lead acetate has the composition  $Pb(OH)Br$ , even when the liquid contains 0.5*N*-acetic acid, but normal lead bromide is formed in the presence of 0.2*N*-hydrobromic acid. The normal bromide is also formed if lead nitrate is used instead of the acetate. The probable sequence is:  $Pb^{++} + Br^- \longrightarrow PbBr^+$ ;  $PbBr^+ + AcO^- \longrightarrow Pb(OAc)Br$ ;  $Pb(OAc)Br + H_2O \longrightarrow Pb(OH)Br + HOAc$ . The acet-

ate bromide is stable only in glacial acetic acid. Normal lead bromide is converted into hydroxybromide by solutions of potassium acetate, partly into chlorobromide by alkali chlorides, and completely into the normal iodide by potassium iodide.

F. L. USHER.

**Preparation of pure nitrogen.** P. HARTECK (*Ber.*, 1930, **63**, [B], 427—429).—Pure nitrogen is obtained by passing ammonia over nickel powder heated at 1000° in a quartz tube. Any residual ammonia is frozen by liquid air. The separation of nitrogen from hydrogen depends on the freezing of the former substance by evaporating liquid air. Hydrogen retained by the solidified nitrogen is mostly removed by exhaustion, the remainder being eliminated by evaporation and re-condensation with loss of about 10% of the nitrogen.

H. WREN.

**Preparation and properties of pure nitric acid.** K. P. MISHCHENKO (*J. Appl. Chem.*, Russia, 1929, **2**, 521—525).—The acid is distilled four times at 25—40°/25—40 mm. in Creighton's apparatus from which rubber connexions have been eliminated; it is then blown for 1.5—2 hrs. in the cold with dry air free from carbon dioxide. The pure acid is entirely stable only below -41°; it has  $d_4^{25}$  1.52150,  $d_4^{20}$  1.54786, and f. p. slightly above -41.1°.

CHEMICAL ABSTRACTS.

**New phosphonium salt.** V. EVRARD (*Natuurwetensch. Tijds.*, 1930, **12**, 6—11).—Phosphine gives with concentrated perchloric acid a crystalline precipitate, too hygroscopic and too easily dissociated for direct analysis. By indirect analysis of the wet crystals and the mother-liquor, the formation of phosphonium perchlorate was established. The compound readily explodes, and is too unstable for use in the proposed synthesis of the phosphine analogue of hexamethylenetetramine.

S. I. LEVY.

**Action of sulphuric acid on thiocyanates.** B. S. SHARMA (*J. Amer. Chem. Soc.*, 1930, **52**, 581—582).—The precipitate formed by treating ammonium thiocyanate solutions with sulphuric acid varies in composition according to the concentrations of the thiocyanate and acid solutions used. All attempts to obtain these precipitates in a pure state have failed. The more concentrated is the sulphuric acid used the lower is the sulphur content of the precipitate. From a study of the sulphur and carbon contents of the precipitates under varying conditions it is concluded that the sulphuric acid, besides its hydrolysing effect, also has an oxidising influence on thiocyanates, this effect being the more marked the more concentrated is the acid.

J. W. SMITH.

**Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. IX. Relations of metatungstates to para- and monotungstates in solution.** G. JANDER and W. HEUKESHOVEN (*Z. anorg. Chem.*, 1930, **187**, 60—74; cf. *A.*, 1929, 281, 664).—When sodium tungstate solution is titrated conductometrically with hydrochloric acid (cf. Jander and Pfundt, *A.*, 1929, 652) the curve of the conductivity plotted against the acid added shows two sharp breaks, corresponding with the addition of 7 and 9 hydrogen ions, respectively, to each six tungstate ions. These are explained by supposing



the reactions to be  $6\text{WO}_4^{''} + 7\text{H}^+ \rightleftharpoons \text{HW}_6\text{O}_{21}^{''''} + 3\text{H}_2\text{O}$  and  $\text{HW}_6\text{O}_{21}^{''''} + 2\text{H}^+ \rightleftharpoons \text{H}_3\text{W}_6\text{O}_{21}^{''''}$ . The ion  $\text{HW}_6\text{O}_{21}^{''''}$  gives rise to paratungstates. This view suggests that metatungstates in solution are also salts of a hexatungstic acid, but that they are more acidic salts than paratungstates, and must be formulated  $\text{M}_3(\text{H}_3\text{W}_6\text{O}_{21})$ . When boiling alkali tungstate solutions are conductometrically titrated with mineral acids, breaks are obtained in the curve corresponding with the addition of 6 and 9 hydrogen ions, respectively, to each 6 monotungstate anions. This is explained by supposing that at the higher temperature the residual hydrogen atom of the paratungstic acid dissociates. Thermometric titration of alkali tungstate solutions leads to similar results. There is a sharp difference between the light absorption of monotungstate solution in the spectral region 2000—4000 Å. and that with the solution acidified to  $p_{\text{H}}$  6.2 when a paratungstate would be forming, but little further change is observed as far as  $p_{\text{H}}$  3.3. The difference in structure between para- and metatungstic acid solutions is discussed in relation with these observations.

J. W. SMITH.

**Complex uranyl fluorides.** F. OLSSON (Z. anorg. Chem., 1930, 187, 112—120).—With organic bases, uranyl fluoride forms double salts of three different types, viz.,  $\text{MUO}_2\text{F}_3 \cdot n\text{H}_2\text{O}$ ,  $\text{M}(\text{UO}_2)_2\text{F}_5 \cdot n\text{H}_2\text{O}$ , and  $\text{M}(\text{UO}_2)_3\text{F}_7 \cdot n\text{H}_2\text{O}$ . The first of these is analogous to the sodium compound prepared by Bolton (Ber. Preuss. Akad., 1866, 31, 299) but the other types are new to sexavalent uranium compounds. Besides primary bases, secondary, tertiary, and quaternary organic bases give sparingly soluble double uranyl fluorides. All the double fluorides which have been prepared are yellow, stable in air, and relatively insoluble in dilute hydrofluoric acid as well as in water.

J. W. SMITH.

**Behaviour of metallic oxides and silicates in chlorine.** R. WASMUEH (Z. angew. Chem., 1930, 43, 98—101, 125—129).—Measurements have been made of the temperatures at which reactions begin between chlorine and a number of metallic oxides and silicates, with and without the addition of carbon. In the absence of carbon no reaction occurs with silica up to 1100°, whilst with 25% of carbon present reaction commences at about 850°. Aluminium oxide begins to react at about 850° in the absence of carbon, and at about 700° when it is present. Ferric oxide alone reacts at about 525°, and at 500° with a greater velocity in the presence of carbon. The presence of sulphide or phosphide in iron oxide reduces the initial reaction temperature to 250°. Ferrous oxide, alone, or with additions of sulphide, phosphide, or carbon, reacts above 150°. Under the same conditions reactions begin with manganous oxide at 200°. No action, with or without carbon, was obtained with the oxides of chromium, tungsten, nickel, or cobalt. Grünerite and fayalite, with and without carbon addition, react at 300° and 150°, respectively. No reaction was obtained with rhodonite, tephroite, and high-temperature slag.

The above results all refer to decomposition without loss of oxygen. In all the cases mentioned decomposition with loss of oxygen begins at a higher tem-

perature, usually from 100° to 300° higher than those recorded above.

F. G. TRYHORN.

### Manganites, manganates, and permanganates.

**I. Potassium manganite.** A. S. COCOSINSCHI (Z. anorg. Chem., 1930, 186, 176—180).—Fusion of potassium permanganate with potassium chloride at 600° yields the compound  $\text{K}_2\text{O} \cdot 2\text{MnO}_2$ , which loses more potash on further heating, the proportion falling from 29.21% at 600° to 18.57%  $\text{K}_2\text{O}$  at 1100°. These manganites are slowly hydrolysed by water with the formation of complex acids of the general formula  $\text{H}_2\text{Mn}_n\text{O}_{2n+1}$ ; the presence of these acids is held to be the origin of the water found in the potassium manganites described by Rousseau (A., 1892, 569).

A. R. POWELL.

**Iridescent films as reaction products of the slow hydrolysis of ferric chloride.** H. ZOCHER and W. HELLER (Z. anorg. Chem., 1930, 186, 75—96).—Slow hydrolysis of 0.1—8% solutions of ferric chloride, extending over months or even years in the case of the more dilute solutions, results in the formation of anisotropic sediments of decreasing sol character with increasing concentration of the solution. From solutions with 0.3—1.0% of ferric chloride these sediments have the properties of a tactosol of the type of Zocher's ferric oxide iridescent films. The lustre and purity of these films on the non-iridescent precipitates first formed increase with decreasing concentration of the solution during hydrolysis and their formation proceeds more rapidly in diffused light and by slightly raising the temperature above the ordinary. During ageing the tactosols undergo changes characterised by an increase in the periodicity of the films to a maximum and in the order of the film colours and a decrease in the lustre of the films. On dilution with water the films immediately peptise to a turbid anisotropic sol. Dialysis of the original ferric chloride even for a short time inhibits the formation of the tactosol. Evidence is adduced to show that the formation of the films is dependent on the concentration of the hydrogen and chlorine ions.

A. R. POWELL.

**Complex compounds of chloroferric acid with organic sulphur compounds.** The analogy of gold and iron compounds. P. C. RAY and P. C. MUKHERJEE (Z. anorg. Chem., 1930, 187, 121—126).—On condensing ferric chloride with ethyl sulphide and with 1:4-dithian the compounds  $\text{HFeCl}_4 \cdot \text{Et}_2\text{S} \cdot \text{H}_2\text{O}$  and  $\text{HFeCl}_4 \cdot (\text{C}_2\text{H}_4\text{S})_2 \cdot 4\text{H}_2\text{O}$ , respectively, are formed. These give such definite acidic reactions and the conductivities and their concentrated aqueous solutions are so high that they must yield hydrogen ions. An unsuccessful attempt was made to prepare the potassium salt of the former by fractional crystallisation of a concentrated mixture of the acid with potassium chloride. The addition of strong bases such as ammonia or aniline to this acid produces a precipitate of ferric hydroxide. Weak bases such as pyridine, quinoline, or o-toluidine completely displace the ethyl sulphide radical, and the following compounds were obtained,  $\text{Fe}_2\text{Cl}_6 \cdot \text{C}_5\text{H}_5\text{N} \cdot 4\text{EtOH}$ ;  $\text{Fe}_2\text{Cl}_6 \cdot \text{C}_9\text{H}_7\text{N} \cdot 4\text{EtOH}$ ;  $\text{Fe}_2\text{Cl}_6 \cdot \text{C}_7\text{H}_7\text{NH}_2 \cdot 3\text{EtOH}$ . The alcohol was introduced during the purification process. These reactions are explained by supposing that the

hydrochloric acid is removed first by the base, after which the base replaces the ethyl sulphide. Thus, unlike the corresponding platinum compounds, which are reduced from the quadri- to the ter- or bi-valent state by bases, the valency of the iron compounds is not changed under these conditions. J. W. SMITH.

**Preparation and properties of some complexes of cobalt with cyclic amines, which may be employed as specific reagents for polysulphides.** J. BEATO and M. DE LOS D. BRUGGER (Anal. Fis. Quím., 1929, 27, 822—831).—By the action of diacetyldioxime and aniline on an alcoholic solution of cobaltous chloride in presence of air a dark crystalline compound is formed, of which an aqueous or alcoholic solution yields a characteristic violet coloration when warmed with a solution of a polysulphide, and a similar coloration with the ferrocyanide ion in the cold. An identical reaction with polysulphides is given by the analogous *o*- and *p*-toluidine complexes. Substitution of diacetyldioxime by benzaldoxime or by formaldoxime does not appear to yield similar complexes. H. F. GILLBE.

**Dissociation of carbonic acid and its action on metallic nickel under pressure.** E. MÜLLER and A. LUBER (Z. anorg. Chem., 1930, 187, 209—230).—Aqueous carbonic acid reacts with nickel reversibly and the concentration of dissolved metal is accurately reproducible for a given temperature and partial pressure. From the amount of nickel in solution it is calculated that under a pressure of 50 atm. and at the ordinary temperature the concentration of  $\text{H}_2\text{CO}_3$  is 0.386 g. per litre, and the hydrogen-ion concentration of the solution, determined by means of indicators, is  $1.25 \times 10^{-3}$ . The affinity constant for the first stage of dissociation is  $2.46 \times 10^{-4}$ . Nickel is dissolved in the form of hydrogen carbonate, which could not be obtained as a solid. The crystalline compounds  $\text{NiCO}_3$  and  $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$  were prepared in a pure state. F. L. USHER.

**Platinum arsenide.** L. WÖHLER (Z. anorg. Chem., 1930, 186, 324—336).—Platinum diarsenide has been prepared by heating a mixture of the elements in a closed tube at 270°. The reaction is explosive, but can be moderated by using a large excess of arsenic which is afterwards removed in a stream of carbon dioxide at 500°. The residual grey powder resembles natural sperrylite and is attacked with difficulty by concentrated nitric acid or by aqua regia. The product of the interaction of arsine and platinum chloride or potassium chloroplatinite in solution is a mixture of variable composition. The compound  $\text{PtAsOH}$  described by Tivoli was not obtained. F. L. USHER.

**Constitution of tetrammineplatinum salts.** A. HANTZSCH and F. ROSENBLATT (Z. anorg. Chem., 1930, 187, 241—265).—Among a large number of platinum tetrammine salts which have been prepared and examined the following are described: *tetrapyridineplatinum thiocyanate*, *acetate*, and *oxalate*; *tetradimethylamineplatinum picrate* and *nitrate*; *diethylenediamineplatinum oxalate*, *carbonate*, *perchlorate*, *bromide*, and *platinocyanide*; *cis-diamminodipyridineplatinum picrate*; *trans-diamminodipyridineplatinum picrate* and *chloride*. From the results of measure-

ments of the electrical conductivity of these and other salts previously described, and of their absorption spectra, it is concluded that they possess six coordinatively bound groups, and not four as has hitherto been assumed. They should therefore be formulated as pseudo-salts of the type  $[\text{Pt}(\text{NH}_3)_4\text{X}_2]$ . These pseudo-salts can be dissolved to some extent unchanged in non-dissociating solvents with low solvating power such as chloroform or ether, but in solvents such as water, alcohol, or acetone they are unstable and readily converted into stable salts of the type  $[\text{Pt}(\text{NH}_3)_4(\text{solvent})_2]\text{X}_2$ . The pseudo-salts under other conditions readily lose 2 mols. of ammonia or amine and yield diammino-compounds.

F. L. USHER.

**New type of complex platinum compounds. Ter- and quinque-valent platinum. II.** P. C. RAY and S. C. S. GUPTA (Z. anorg. Chem., 1930, 187, 33—48; cf. Ray and Bose-Ray, A., 1929, 433).—The action of dimethyl disulphide on chloroplatinic acid in aqueous solution in a closed tube at 100° leads to the formation of the compound  $\text{PtCl}_3\text{Me}_2\text{S}_2 \cdot \text{H}_2\text{O}$ . The molecule of water is only loosely bound, and on keeping in a vacuum desiccator over sulphuric acid the compound  $\text{PtCl}_3\text{Me}_2\text{S}_2$  is formed. Dehydration is also almost complete in 14 hrs. at 115—120°. The compound is practically insoluble in ordinary organic solvents, but is rather more soluble in dimethyl disulphide. This solvent, however, is unsuitable for either mol. wt. or conductivity measurements. In the preparation chlorine is liberated; this is also observed in other cases and leads to the general conclusion that under these conditions platinum possesses a greater affinity for sulphur than for chlorine. By the action of bases on this compound the following compounds are formed: by the action of a 33% solution of methylamine at 0°,  $\text{Pt}_5\text{Cl}_4\text{Me}_2\text{S}_2 \cdot 5\text{MeNH}_2$ ; with hydrazine hydrate,  $\text{Pt}_5\text{Cl}_4\text{Me}_2\text{S}_2 \cdot 2\text{NH}_2 \cdot \text{NH}_2 \cdot 2\text{H}_2\text{O}$ ; with piperidine,  $\text{Pt}_5\text{Cl}_4\text{Me}_2\text{S}_2 \cdot 3\text{C}_5\text{H}_{11}\text{N}$ ; with anhydrous ethylamine at 0°,  $\text{Pt}_9\text{Cl}_7\text{Me}_2\text{S}_2 \cdot 5\text{EtNH}_2$ ; with allylamine,  $\text{Pt}_6\text{Cl}_7\text{Me}_2\text{S}_2 \cdot 5\text{C}_3\text{H}_5\text{NH}_2$ ; with phenylhydrazine,  $\text{Pt}_{11}\text{Cl}_8\text{Me}_2\text{S}_2 \cdot 4\text{NH}_2 \cdot \text{NHPh}$ . Thus different bases lead to different degrees of reduction, as with the ethyl analogues. The last compound is analogous to the missing type in the ethyl series. The conclusion is reached that with organic bases the compounds  $\text{PtCl}_3\text{R}_2\text{S}_2$  yield compounds containing always an odd number of platinum atoms, and only one chlorine atom per molecule. All platinum atoms of the odd members of the series must be regarded as tervalent, whilst with the even members one platinum atom is quinquevalent and the others are tervalent, or else two are quadrivalent and the others tervalent.

By the action of dimethyl disulphide on chloroplatinic acid made into a thick paste with water in a sealed tube, a dark orange compound  $\text{PtCl}_3 \cdot 2\text{Me}_2\text{S}_2$  is formed. The mol. wt. of this compound, determined by the cryoscopic method in naphthalene, corresponds with the simple formula. It is assumed that the co-ordination number of the metal is 4, with one atom of chlorine outside the complex,  $[\text{Pt}(\text{Me}_2\text{S}_2)_2\text{Cl}_2]\text{Cl}$ . Treatment of dimethyl disulphide with excess of chloroplatinic acid, washing away excess of this reagent, refluxing with alcohol,

and extracting with molten naphthalene led to the isolation of a compound,  $\text{Pt}_2\text{Cl}_5 \cdot 4\text{Me}_3\text{S}_2$ . When a solution of this compound in cold acetone was concentrated slowly, dark orange plates of  $\text{PtCl}_2 \cdot 2\text{Me}_3\text{S}_2$  were first obtained. This is regarded as the neutral  $\text{PtCl}_2(\text{Me}_3\text{S}_2)_2$ . The action of pyridine and ethylamine on  $\text{PtCl}_2 \cdot 2\text{Me}_3\text{S}_2$  yields the compounds  $\text{PtCl}_2 \cdot 4\text{C}_5\text{H}_5\text{N}$  and  $\text{PtCl}_2 \cdot 4\text{EtNH}_2$ , respectively. J. W. SMITH.

**Quantitative spectroscopic analysis of solutions.** A. CORSI (Nuovo Cim., 1929, 6, 275—280; Chem. Zentr., 1929, ii, 2700).—The "line length" of an element (Occhialini, A., 1929, 734) varies with the concentration of the element in the electrode as well as with the resistance of the circuit; hence it can be applied to the determination of an element in a solution of a salt. A. A. ELDRIDGE.

**Systematic indirect analysis.** I. P. FUCHS (Z. anal. Chem., 1930, 79, 417—451).—A detailed review of the methods of indirect analysis. The theoretical principles are discussed, and the degree of accuracy attainable is indicated. Tables are given illustrating a number of typical methods, and comprising also the factors required for the calculation of the results. H. F. HARWOOD.

**Designation of the sensitivity of analytical reactions.** F. L. HAHN (Mikrochem., 1930, 8, 75—76).—It is suggested that the sensitivity of any particular reaction should be accurately defined by stating both the smallest amount (expressed in  $\gamma$ ) detectable of the given substance, and the limiting concentration for the test, the latter value being expressed in terms of  $\gamma \text{ cm.}^{-3}$  H. F. HARWOOD.

**Determination of concentration of hydrogen peroxide solutions.** M. HAIGHT (J. Chem. Educ., 1929, 6, 2234).—The hydrogen peroxide solution (1 c.c.) is introduced by means of a curved pipette into a fermentation tube filled with strongly ammoniacal copper sulphate solution, the oxygen evolved being collected in the graduated arm.

#### CHEMICAL ABSTRACTS.

**Determination of small amounts of iodine in organic material rich in iron.** K. WÜLFERT (Mikrochem., 1930, 8, 100—105).—The determination of iodine in organic material by the usual method of ignition with potassium carbonate (cf. A., 1929, 1323) leads to low results in the presence of much colloidal ferric hydroxide, owing to the incompleteness with which the material is wetted by the solution. It is recommended to treat the weighed quantity of substance with four to five times its weight of potassium hydroxide dissolved in a little water, and to heat until complete decomposition results, as shown by the flocculation of the ferric hydroxide. Carbon dioxide is then passed in to carbonate the excess of alkali, the whole is transferred to an iron dish, and the determination finished in the usual way.

H. F. HARWOOD.

**Oxidation of iodide ion by persulphate ion.** III. Iodometric determination of persulphates. C. V. KING and E. JETTE (J. Amer. Chem. Soc., 1930, 52, 608—610).—The amount of iodine liberated from iodide by potassium persulphate in neutral solution agrees to 1 part in 1000 parts with that liberated by

an equivalent amount of potassium permanganate in acid solution. Persulphate is therefore recommended as a standard oxidising agent in iodometric determinations. The iodine liberated in alkaline solution is invariably 2—5 parts in 1000 lower than the amount liberated in neutral solution. The same is found when a solution of iodine in potassium iodide is made alkaline and then acidified. This is explained by supposing that hypiodous acid or hypiodite ion decomposes in some manner such that part of the iodine does not reappear on acidifying.

J. W. SMITH.

**Determination of sulphate in the presence of aluminium fluoride.** H. GINSBERG (Z. angew. Chem., 1930, 43, 21—24).—Unsatisfactory results for sulphate are obtained by precipitation with barium chloride in a solution containing a large excess of fluoride. The following method is therefore recommended: 1—2 g. of finely-powdered cryolite or aluminium fluoride is intimately mixed with 5—7 g. of zinc dust and the mixture placed in a porcelain crucible, covered with 3—5 g. of zinc dust and a layer of sodium carbonate 1—2 cm. thick, and heated slowly during 20—30 min. up to 900° with the point of a blowpipe flame applied only to the bottom of the crucible, which is allowed to project through a hole in an asbestos pad. After cooling, the contents of the crucible are placed in a distillation flask together with 1—2 g. of a mixture of equal parts of calcined precipitated alumina and silica (to retain hydrofluoric acid). A current of carbon dioxide is passed through the apparatus and dilute hydrochloric acid is added to the flask through a dropping funnel until decomposition is complete. The hydrogen sulphide evolved is collected in 0.1N-iodine and the excess titrated with thiosulphate. A. R. POWELL.

**Supposed influence of copper in the determination of sulphur in iron and steel.** H. PINSL.—See B., 1930, 195.

**Oxalate method of determining titre of hyposulphite using borax.** N. A. TANANAEV and N. A. LAZARKEVITSCH (J. Russ. Phys. Chem. Soc., 1929, 61, 1909—1912).—20 C.c. of approximately 0.1N-hyposulphite solution are evaporated to dryness with 2 c.c. of hydrochloric acid, and ignited to drive off sulphur. The residue is dissolved in 10 c.c. of water, 0.5 c.c. of saturated barium chloride solution is added, and the solution is evaporated to dryness and feebly ignited. The residue is extracted with 10 c.c. of water and the barium sulphate separated by filtration, using about 25 c.c. of water for washing. 2 G. of oxalic acid are added to the filtrate, which is then evaporated to dryness, the residue redissolved in 10 c.c. of water, the solution again evaporated, and this operation is once again repeated. In this way, the final residue is freed from chlorides, and consists of oxalic acid and of the oxalates of sodium and barium. Excess of oxalic acid is removed by sublimation, and oxalates are then converted into carbonates by ignition. The final residue is extracted by water, and barium carbonate separated by filtration. The filtrate, containing sodium carbonate, is titrated, using acid standardised against borax.

R. TRUSZKOWSKI.

**Action of hydrogen peroxide on thiocyanates.** F. SCHUSTER (Z. anorg. Chem., 1930, 186, 253—256).—The sulphur in thiocyanates is completely oxidised to sulphate by 30% hydrogen peroxide in hot alkaline solution, whilst the nitrogen is converted mostly into ammonia, although a small amount of nitrate is formed. For the quantitative analysis of thiocyanates, 0.1—0.2 g. is heated with 50 c.c. of 0.5*N*-potassium hydroxide and 5 c.c. of 30% hydrogen peroxide for 1 hr. on the water-bath, the solution is boiled for 15 min., acidified with hydrochloric acid and treated with barium chloride, and the precipitate collected, ignited, and weighed. For the determination of chloride and thiocyanate together the sum is ascertained by titration with silver nitrate and the thiocyanate in a separate portion as described above. If cyanide is also present all three acids are determined by means of silver nitrate, thiocyanate is determined by oxidation to sulphate, and chloride by precipitation with silver nitrate after destruction of cyanogen compounds with hydrogen peroxide.

A. R. POWELL.

**Ceric sulphate as a volumetric oxidising agent.** XII. Determination of tellurous acid. XIII. Determination of mercurous mercury. H. H. WILLARD and (MISS) P. YOUNG (J. Amer. Chem. Soc., 1930, 52, 553—556, 557—559).—XII.—A rapid method for the determination of tellurium is based on the oxidation of tellurous acid by excess of standard ceric sulphate in presence of chromic sulphate as catalyst, and electrometric titration of the excess of ceric sulphate with standard ferrous sulphate solution. The oxidation is quantitative over wide ranges of concentration of acid, excess of ceric sulphate, chromic acid, and tellurous acid, and over wide variations in the time of action and volume of solution. Selenious acid does not interfere if the sulphuric acid concentration at the time of oxidation is not too high, and cupric salts are without effect. The use of chromic sulphate as catalyst in other oxidations in which ceric sulphate alone is not effective is suggested.

XIII. Mercurous mercury can be determined by oxidation in a hot sulphuric acid solution by means of standard ceric sulphate solution, the excess of which is determined by electrometric titration with standard ferrous sulphate solution. A large excess of ceric salt should be used and allowed to act in hot solution for 30—60 min. The acidity of the solution should not be too great. A moderate amount of perchloric acid causes no interference, but nitric acid produces a slight effect. A large amount of mercuric mercury does not interfere if a blank correction is made for its slight action on ceric sulphate. J. W. SMITH.

**Sensitive reaction with apomorphine [for the detection of nitrites].** F. PAVELKA (Mikrochem., 1930, 8, 46—52).—*apomorphine* gives in acetic acid solution a bluish-green colour with nitrites (but not with nitrates) which can be extracted by many organic solvents, forming a violet solution. In order to utilise this reaction as a test for nitrous acid, the solution is acidified with 2—3 drops of 50% acetic acid, and 1—2 mg. of *apomorphine* are added. The whole is heated almost to boiling, allowed to cool, and extracted with ethyl acetate. One part of nitrite ion

in  $15 \times 10^6$  parts suffices to give a distinct violet coloration. Ferric salts interfere, but their effect can be overcome by using phosphoric in place of acetic acid to acidify the solution. Nitrates may be detected in the presence of nitrites by removing the latter from an acetic acid solution by the addition of sodium azide, and subsequent boiling. After cooling, zinc is added and the solution tested as above for nitrite after keeping for 10 min. One part of nitrate ion in  $10^7$  parts can thus be detected. The reaction may be used conversely as a test for *apomorphine*, of which less than  $10^{-7}$  g. in 1 c.c. can be detected.

H. F. HARWOOD.

**Threefold colour reaction with nitrous acid.** P. ZYWNEV (Z. anal. Chem., 1930, 79, 389—390).—A slightly acid solution of a nitrite gives with an aqueous extract of walnut kernels a fiery red colour, which turns transitorily violet, then blue, and finally yellow; if the nitrite solution is strongly acid the yellow colour is produced immediately. By this reaction 0.003 g. of potassium nitrite in a litre can be detected, and the name "juglin" is proposed for the specific tanning material present in the walnuts to which the colour is due. H. F. HARWOOD.

**Potentiometric titrations of phosphates, arsenates, and arsenites with silver nitrate.** M. H. BEDFORD, (MISS) F. R. LAMB, and W. E. SPICER (J. Amer. Chem. Soc., 1930, 52, 583—588).—The potentiometric titration of phosphates, arsenates, and arsenites with silver nitrate has been carried out successfully by using 0.1*N*-sodium or -potassium hydroxide for a secondary titration to keep the solution at a constant low hydrogen-ion concentration. The phosphate determination gave the least sharp end-point. J. W. SMITH.

**Sensitive reaction for arsenic acids and its use in distinguishing between methylarsinates and cacodylates.** J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1929, 67, 84—87; Chem. Zentr., 1929, ii, 2230).—With sulphuric acid (33%) and a few drops of 10% potassium iodide solution, mono-alkyl- and -aryl-arsinic acids give di-iodo-alkyl- or -aryl-arsines, sparingly soluble in hot water. After decolorisation of the ethereal extract with sodium sulphite the iodo-derivatives may be isolated and characterised. Cacodylic acid is reduced to cacodyl oxide, which is detected by its odour. A. A. ELDRIDGE.

**Micro-determination of carbon by sulphochromic oxidation and of nitrogen by treatment with sulphuric acid.** A. BORVIN (Bull. Soc. Chim. biol., 1929, 11, 1269—1409).—The previous work of the author (cf. A., 1928, 1064; 1929, 204, 954, 1257, 1323) and of others on the micro-determination of carbon is reviewed in detail. In addition, an accurate method for the micro-determination of carbon in urine containing volatile constituents in small amounts only is described. Methods for freeing sulphuric acid from small amounts of carbon and for the micro-determination of carbon in organic liquids are described in detail. Non-volatile liquids are treated as in the case of solids (cf. A., 1929, 1323), but volatile liquids are weighed in a sealed ampoule which is introduced into the oxidising mixture of sulphuric acid and silver chromate. Satisfactory results for a

wide range of aliphatic and aromatic liquids have been obtained.

In the decomposition of nitrogenous organic material by sulphuric acid for both macro- and micro-analyses the results now obtained show that heating for at least 1 hr. after decolorisation of the acid is essential for the complete conversion of the nitrogen into ammonia in many cases, *e.g.*, hippuric acid. Even in the absence of oxidising agents or of nitrate or nitrite, organic substances which usually lose no nitrogen do so when the proportion of potassium sulphate used in the attack is varied. In general, too great a proportion of potassium sulphate should be avoided. For general use it is recommended that a few mg. of the organic substance should be heated with 1 c.c. of sulphuric acid and 0.1 g. each of potassium sulphate, crystalline copper sulphate, and mercuric oxide. If necessary, 2 or 3 drops of alcohol are added to produce slight carbonisation and after decolorisation is complete (5–10 min.) heating is continued for 1 hr. This method of attack gives good results for solids of protein-like nature, but for pyridine, antipyrine, and alkaloids the results are too low. Data comparing this method with the micro-Dumas, micro-Deniges, and Pregl methods for desiccated powders obtained from pulverised organs are reproduced; the last-named methods give results which are slightly low.

The micro-determination of nitrogen in urine is discussed and further results show that the micro-Dumas method carried out on the dry residue obtained by evaporating urine in a vacuum over sulphuric acid gives values in good agreement with those of the micro-Kjeldahl method, using oxalate or mercury-copper catalysts. Catalysis by copper sulphate alone gives results which are slightly low (5%). A similar conclusion is reached for the determination of the non-protein-nitrogen of blood defecated by colloidal iron oxide and by tungstic, phosphotungstic, and molybdic acids; when trichloroacetic acid is present, however, the copper-mercury catalysis becomes untrustworthy.

L. S. THEOBALD.

Qualitative analysis of cations without the use of hydrogen sulphide. D. STROHAL (Arh. Hemiju, 1930, 4, 14–16).—A number of corrections to the tables comprised in the previous paper on this subject (A., 1928, 723) are given.

H. F. HARWOOD.

Application to analytical chemistry of certain derivatives of fluorene. L. GUGLIAMELLI and C. RUIZ (Anal. Asoc. Quim. Argentina, 1929, 17, 189–208).—Various precipitation and coloration reactions of diaminofluorene are described, and its behaviour in relation to its structure is discussed.

H. F. GILLBE.

Determination of alkalis in waters and in silicates by a semi-microchemical method. K. L. MALJAROV (Mikrochem., 1930, 8, 63–71).—The water (2–10 c.c.) is evaporated to dryness with sulphuric acid at a temperature not exceeding 350°. The residue is treated with water, the solution diluted to a concentration of 0.1%, and the sulphuric acid, heavy metals, and magnesium are removed by the addition of a slight excess of barium hydroxide. The

filtered solution is treated with ammonium carbonate and ammonia, filtered after 2 hrs., and the filtrate evaporated to dryness on the steam-bath. The whole is moistened with water, again evaporated, and the residue finally heated for 1 hr. on the steam-bath. The dry mass is dissolved in water, methyl-orange is added, and the alkalis are determined by titration with 0.3*N*-hydrochloric acid. In the case of silicates, the material (0.3–0.4 g.) is decomposed by hydrofluoric and sulphuric acids and the analysis then carried out as described above. The method may be employed for the determination of alkalis in glass and porcelain containing alumina, zinc and lead oxides, and boric acid.

H. F. HARWOOD.

Systematic spot-analysis. II. K. HELLER [with Z. FLEISCHMANS] (Mikrochem., 1930, 8, 33–40; cf. A., 1929, 900).—A scheme is given for the systematic qualitative analysis by spot reactions of alloys containing silver, lead, tin, antimony, cadmium, bismuth, iron, aluminium, chromium, cobalt, nickel, manganese, and zinc. An analysis can be made on 10 mg. of material, and requires only 40–60 min., as against 2–3 hrs. by the usual methods. The tests for aluminium and zinc are, however, not very sensitive, and fail to afford positive evidence of these metals in the presence of other elements of the ammonium sulphide group.

H. F. HARWOOD.

Colorimetric determination of minute amounts of calcium. A. ASTRUC, M. MOUSSERON, and (Mlle.) N. BOUVISSON (Compt. rend., 1930, 190, 376–377).—The calcium is precipitated as tungstate, which is converted by an acid (*e.g.*, hydrochloric, but not phosphoric) into tungstic acid, and this into an acid solution of potassium tungstate, which is reduced by a freshly-prepared standard solution of titanous chloride. The tungsten content of the blue solution thus produced is determined colorimetrically by comparison with a standard solution, and the amount of calcium calculated therefrom. Good results were obtained with amounts as small as 0.5 c.c. of a solution containing 0.32 g. of calcium ion per litre.

C. A. SILBERRAD.

Pyrophosphate method for determination of magnesium. S. S. MIHOLIC (J.C.S., 1930, 200–202).—The conversion of magnesium ammonium phosphate into magnesium pyrophosphate takes place completely below 480° and precipitates obtained by the pyrophosphate method of determining magnesium can be ignited at this temperature. The use of Gooch or Jena sintered glass crucibles is satisfactory.

J. A. V. BUTLER.

Viscose as a qualitative reagent. J. V. TAMCHYNA (Chem. Listy, 1930, 24, 31–34).—Lead salts give a red coloration with viscose solution at concentrations greater than 1 in 200,000, bismuth gives a reddish-brown coloration at the same dilution, copper at dilutions of above 1 in 400,000 gives a brown coloration, and cobalt at concentrations of not less than 1 in 170,000 gives a greenish-brown colour. When lead and copper are present together, the latter should first be transformed into cuprocyanide, whilst when lead and bismuth are together, lead should be precipitated as sulphate, which is coloured red by the addition of viscose.

R. TRUSZKOWSKI.

**Detection and determination of lead in "ethyl" petrol.** H. KIEMSTEDT.—See B., 1930, 229.

**Volumetric determination of copper.** W. ORLIK and W. TRETZE (Chem.-Ztg., 1930, 54, 174—175).—Owing to the high cost of the ordinary iodide method for determining copper when a large number of analyses have to be made, the method of Bruhns (A., 1918, ii, 276) has been critically investigated, and the following procedure is now recommended. The alloy (0.5 g.) is dissolved in 10 c.c. of a mixture of somewhat diluted nitric and sulphuric acids, and the solution evaporated to fuming; 25 c.c. of water are added, followed by 25 c.c. of a solution containing 50 g. of potassium thiocyanate and 6 g. of potassium iodide in 1000 c.c. The whole is then titrated with thiosulphate in the usual way, starch being used as an indicator. The end-point is very sharp, even in artificial light, and the volume of the solution may vary within wide limits without affecting the accuracy of the results. The method can be employed directly for the determination of copper in a large number of its alloys. Silver and mercury must be absent. Iron up to 0.2% does not interfere, but if larger amounts are present a few grams of sodium pyrophosphate must be dissolved in the solution before the addition of the thiocyanate. The results are excellent, and are practically identical with those obtained by the electrolytic method.

H. F. HARWOOD.

**Volumetric determination of copper by potassium cyanide.** M. LORA Y TOMAYO (Anal. Fis. Quim., 1930, 28, 63—75).—Copper may be satisfactorily determined in alkaline tartrate solutions by titration with potassium cyanide solution until decolorisation takes place. As it is difficult to observe the end-point with accuracy, an excess of potassium cyanide solution is added, and, after adjusting the  $p_H$  of the solution to about 9.3—9.6, for which process thymolphthalein may be used, the excess of potassium cyanide is titrated with silver nitrate solution.

H. F. GILLBE.

**Colorimetric determination of copper.** A. B. SHAKHKELDIAN (J. Appl. Chem., Russia, 1929, 2, 475—482).—Tananaev's test (J. Russ. Phys. Chem. Soc., 1928, 60, 453) is employed quantitatively and its sensitivity increased. To each solution of copper (as sulphate; the standard contains 3 mg. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per litre) are added 3% sodium salicylate solution (10 c.c.), ammonia solution ( $d$  0.9, 10 c.c.), 3 c.c. of a colourless 0.1% solution of benzidine in 20% acetic acid, and 1—1.5 c.c. of 1% potassium hydroxide solution. The solutions, after dilution to 100 c.c., are compared in a colorimeter. The determination must be completed within 5 min., since the colour is unstable. It may alternatively be matched against an acidified solution of methyl-orange. Alkali and alkaline-earth metals, but not silver, may be present; heavy metals are first removed by boiling with ammonia.

CHEMICAL ABSTRACTS.

**Action of oxidising agents on metallic mercury. Analytical applications.** P. FLEURY and J. MARQUE (J. Pharm. Chim., 1930, [viii], 11, 150—157; cf. A., 1929, 1095, 1266, 1426).—Finely-divided mercury, precipitated in presence of barium sulphate,

is quantitatively oxidised by 0.01*N*-permanganate and a little sulphuric acid at 100° to a mercuric salt. It reduces ferric salts in hydrochloric acid at the ordinary temperature, and the phosphomolybdate reagent of Fontès and Thivolle (A., 1921, ii, 563) at 100° in presence of hydrochloric acid and sodium chloride, subsequent titration with permanganate showing that a mercurous salt is formed in each case. These reactions provide alternatives to the iodometric method previously given for determining mercury.

H. E. F. NOTTON.

**Determination of mercury as metal by reduction with hydrazine or stannous chloride.** H. H. WILLARD and A. W. BOLDYREFF (J. Amer. Chem. Soc., 1930, 52, 569—574).—Of the reagents tested for the reduction of mercury salts to the metal, hydrazine hydrate in ammoniacal solution and stannous chloride in hydrochloric acid were found to be the most satisfactory. The conditions for the accurate gravimetric determination of mercury after reduction by these reagents are given. The most satisfactory method of drying the precipitate is to wash with pure acetone, afterwards drying in air at the ordinary temperature. A small but calculable volatility correction has to be applied to the determination, which then leads to results correct to 0.1%. The presence of iron, cadmium, bismuth, copper, lead, antimony, nitrate, and sulphate does not interfere with the accuracy of the measurement when reduction is carried out with stannous chloride.

J. W. SMITH.

**Determination of aluminium by hydrazine carbonate.** A. JÍLEK and J. LUKAS (Coll. Czech. Chem. Comm., 1930, 2, 63—69).—A quantitative precipitation of aluminium as a basic carbonate from slightly acidic solution is obtained by means of a solution of hydrazine carbonate containing free hydrazine. After precipitation in the cold, the precipitate is heated for 1 hr. on the water-bath, when it becomes easy to filter and wash. It is washed with warm water, or, if alkali salts are present, with neutral ammonium nitrate solution, and ignited to the oxide.

F. G. TRYHORN.

**Detection of ferrocyanides and ferricyanides together with thiocyanates.** T. PAVOLINI (Annali Chim. Appl., 1929, 19, 561—562).—The dilute solution of the alkali salts acidified with a slight excess of dilute hydrochloric acid is treated with excess of ammonium molybdate solution, brown molybdenyl ferrocyanide being precipitated. The liquid is shaken with fine asbestos, filtered by suction through a perforated funnel covered with asbestos, and the residue is washed twice with cold acidified water. The precipitate is dissolved in ammonia solution and the liquid saturated with hydrogen sulphide and acidified with dilute sulphuric acid. The brown molybdenum sulphide is filtered off and the filtrate freed from hydrogen sulphide and treated with ferric chloride solution; Prussian blue is thus precipitated if the original solution contained a ferrocyanide. The filtrate from the molybdenyl ferrocyanide is treated slowly with excess of a hydrochloric acid solution of stannous chloride and immediately with ether, with which it is shaken from time to time.



Intense carmine coloration of the ethereal layer indicates the presence of thiocyanate. If brown, the residual liquid contains ferrieyanide, which may be confirmed in the same way as ferrocyanide (see above).

T. H. POPE.

**Detection and determination of cobalt in presence of nickel.** A. LIEBERSON (J. Amer. Chem. Soc., 1930, 52, 464—465).—The reduction by cobalt salts of arsenophosphotungstic acid in presence of cyanide, producing cobalticyanide and intensely blue tungstous acid, enables cobalt to be detected colorimetrically in the presence of 300—400 times its weight of nickel, and to be rapidly and accurately determined in traces as small as 0.25 or 0.5 mg. in presence of ten times its weight of nickel. Stannous tin, manganese, ferrous iron, mercurous mercury, copper, and sulphide are interfering ions and must not be present. A number of other metallic ions may interfere with the quantitative test if present in appreciable amounts (four to five times the concentration of the cobalt) owing to the formation of a turbid solution.

J. W. SMITH.

**Separation of cobalt and nickel for determination of these metals.** M. G. SCHUSTER (J. Pharm. Chim., 1930, [viii], 11, 97—101).—Precipitation is effected by sodium hydroxide in presence of hydrogen peroxide; the precipitate is treated with ammonia and ammonium chloride, which dissolves the cobalt quantitatively.

S. I. LEVY.

**Quantitative analysis of mixtures of nickel and cobalt.** S. GLASSTONE and J. C. SPEAKMAN (Analyst, 1930, 55, 93—102).—A sound theoretical basis for Rupp and Pfenning's method of determining nickel and cobalt (A., 1910, ii, 458) has been supplied by electrometric titrations of the metals with potassium cyanide using nickel and cobalt indicator-electrodes. Small amounts of cobalt in the presence of various amounts of nickel may be determined by treating about 5 c.c. of solution containing from 0.0005 to 0.005 g. of cobalt with about 0.5 g. of sodium perborate, 10—15 c.c. of 2*N*-sodium hydroxide solution, and about 15 c.c. of water. After boiling for 10 min. and cooling quickly, 4—10 c.c. of 0.1*N*-potassium iodide solution, a few crystals of sodium carbonate, and 10—15 c.c. of 8*N*-sulphuric acid are added, and the liberated iodine in the clear solution is titrated with sodium thiosulphate solution. A blank titration is necessary. Results of analysis for solutions containing varying quantities of nickel and cobalt by Rupp and Pfenning's method for the total amounts of the metals, and by the above method for the cobalt, show a satisfactory agreement with actual compositions.

D. G. HEWER.

**Determination of tungsten, chromium, and vanadium in high-speed tool steels.** W. BRÜGGMANN.—See B., 1930, 243.

**Colorimetric determination of tin.** R. HANSEN (Chem.-Ztg., 1930, 54, 143).—The neutral or slightly acid solution (10 c.c.) is treated with a drop of bromine to convert all the tin into the stannic condition, and 5 c.c. of a freshly-prepared solution of hydrogen sulphide are added. After being kept some hours at the ordinary temperature the liquid is compared colorimetrically with standards containing

known amounts of stannic sulphide. A further portion of 5 c.c. is then treated as above with hydrogen sulphide, and 5 c.c. of concentrated hydrochloric acid are added; any stannous sulphide at once dissolves, and the residual stannic sulphide can be determined as before, the difference between the two determinations representing the stannous tin. The results are somewhat high, but are satisfactory for quantities of tin ranging from 1 to 5 mg.

H. F. HARWOOD.

**Reaction of iodate and quadrivalent vanadium in alkaline solutions.** J. B. RAMSEY and A. ROBINSON (J. Amer. Chem. Soc., 1930, 52, 480—483).—A rapid reaction occurs between vanadyl sulphate and potassium iodate in hot alkaline solution according to the equation  $6\text{VOSO}_4 + \text{KIO}_3 + 18\text{KOH} = 6\text{KVO}_3 + 6\text{K}_2\text{SO}_4 + \text{KI} + 9\text{H}_2\text{O}$ . A method of determining vanadium by using this reaction has been developed, and yields results correct to 0.1%. Oxygen must be removed from the solution and excluded during the reaction. Phosphate catalyses the reaction to a considerable extent.

J. W. SMITH.

**Complete analysis of antimony ores, regulus, and alloys.** H. BLAHETEK.—See B., 1930, 195.

**Spectroscopic determination of bismuth in copper.** B. A. LOMAKIN (Z. anorg. Chem., 1930, 187, 75—96).—By photometric measurement of the ratios of the intensities of bismuth lines to those of neighbouring copper lines, it has been shown possible to determine spectroscopically the bismuth content of copper. The alloy is used as the electrodes of a direct-current arc, the spectrum of which is observed photographically and the spectrogram studied by means of a microphotometer. The maximum blackening of the photographic plate in the bismuth line increases linearly with the logarithm of the bismuth content of the alloy. This is explained theoretically. With alloy specimens tested containing 1.25—0.000625% Bi the mean square deviations between the true and measured values varied from 18% to 5.5% according to the time of exposure, longer periods of exposure being associated with a more stable mean voltage on the arc.

J. W. SMITH.

**Determination of platinum in rocks.** R. GANS, C. KRUG, and E. HEUSELER (Mitt. Labor. Preuss. Geol. Landesanst., 1922, No. 3, 18 pp.; Chem. Zentr., 1929, ii, 2080).

**Micro-catalytic detection of the platinum metals.** F. L. HAHN (Mikrochem., 1930, 8, 77—80).—A small conical depression is made in a strip of asbestos paper by pressure with a rounded glass rod. A drop of the solution under examination is placed in the hollow, and the whole carefully heated over a Bunsen flame, and allowed to cool. A stream of hydrogen is then permitted to impinge on the spot thus formed, when a visible glowing takes place if the solution contained only  $4 \times 10^{-5}$  part of platinum. The presence of large amounts of many other metals does not inhibit the reaction, but arsenic interferes if present in quantity fifty times that of the platinum. The reaction is even more sensitive with palladium, which may be detected at a concentration of  $1 \times 10^{-5}$ .

H. F. HARWOOD.

**Gravimetric determination of ruthenium.** R. GILCHRIST (Bur. Stand. J. Res., 1929, 3, 993—1004).—The solution of the chloride obtained by heating ruthenium tetroxide with hydrochloric acid is diluted, so that it contains less than 0.2 g. per 150 c.c., and treated at the b. p. with a 10% solution of sodium hydrogen carbonate until the black precipitate suddenly coagulates. Further carbonate is added until bromocresol-purple shows the solution to be feebly alkaline; after boiling for 5–6 min. the precipitate is collected, washed with a hot 1% solution of ammonium sulphate, then with a cold 2.5% solution of the same reagent, dried slowly and heated, gently at first, then more strongly, reduced and cooled in hydrogen, and weighed as ruthenium. If the original solution contains ruthenium trichloride it must be treated with chlorine water prior to the above treatment. Solutions containing ruthenium amines or nitrosochlororuthenates are not precipitated by sodium hydrogen carbonate. Very dilute solutions of ruthenium chloride, but not of the nitrosochloride, give a characteristic green or bluish-green colour when treated with hydrochloric acid and thiocarbamide.

A. R. POWELL.

**Fluorescence microscope made from simple materials.** M. HAITINGER (Mikrochem., 1930, 8, 81–88).—A description is given of the construction of an apparatus which is adapted for use with any ordinary microscope in order to permit of the observation of fluorescence phenomena. A mercury-vapour lamp is employed as the source of ultra-violet light.

H. F. HARWOOD.

**Determination of the shade and intensity of colour of liquids.** E. LEIKOLA and W. KERPPOLA (Skand. Arch. Physiol., 1929, 56, 261–264; Chem. Zentr., 1929, ii, 1944).—The liquid is examined in a comparator and compared with a series of tints prepared from nitrate (6%), potassium dichromate (0.1%), nickel sulphate (15%), and copper sulphate-ammonia (5 pts. 10% with 95 pts. 5%) solutions.

A. A. ELDRIDGE.

**Apparatus to measure colour temperature of incandescent lamp filaments.** C. H. SHARP (J. Opt. Soc. Amer., 1930, 20, 62–70; cf. Campbell, *ibid.*, 1925, 177; 1926, 38).—A rotating celluloid disc, half red, half blue, is placed between the lamp and a caesium photo-electric cell. The latter, which is sensitive over the whole spectrum, is connected to an amplifying circuit so that a galvanometer deflects one way or the other, according as the effect of the red or of the blue light is the greater. A combination of red and blue is found at which the effects of the two colours balance, and the colour temperature is found by substituting a standard lamp and adjusting the voltage applied to it until a balance is again obtained.

C. W. GIBBY.

**Replacement of the sodium flame for polarimeter illumination by electric light, using a filter.** C. WILHELM (Chem.-Ztg., 1930, 54, 194).—Combination filters of dyed gelatin have been prepared for use in conjunction with a 40- or 60-watt electric lamp as a source of monochromatic light, the maximum of such filters coinciding almost exactly with the sodium line. A much greater illumination of the field is thus obtained than is possible when the

ordinary sodium flame is employed, and the filters themselves show no alteration after 12 months' use.

H. F. HARWOOD.

**Errors due to capillary in reading the mercury thermometer.** C. E. GUILLAUME (Arch. Sci. Phys. nat., 1930, [v], 12, 1–10).—The effect on the accurate reading of a thermometer of the alteration in the shape of the meniscus as the mercury is rising or falling is discussed with special reference to determinations of the pressure coefficient, and exemplified by such determinations by both the method of varying changes of temperature and that of varying pressures. Where readings can be made under the best conditions a scale of 1 cm. per degree is advised, capillary effect being then negligible.

C. A. SILBERRAD.

**Laboratory muffle furnaces.** H. WEMMER (Chem.-Ztg., 1930, 54, 184).—The advantages of a muffle heated by gas on the surface-combustion principle over the usual gas and electric muffle are enumerated. Rapid heating to 1500° and a high efficiency are claimed but no details of the construction are given.

A. R. POWELL.

**Small gas muffle furnace.** A. SULFRIAN (Chem. Fabr., 1930, 34–35).—This furnace, which holds one crucible, is formed of refractory enclosed in sheet metal. The upper half is removable entire and the triangle is constructed of V2A steel. It is durable and there is no risk of fragments flaking off inside.

C. IRWIN.

**Universal heater for laboratory and melting operations.** E. BEISENHERZ (Chem.-Ztg., 1930, 54, 118).—A device for heating crucibles is described and illustrated.

W. O. KERMACK.

**Facilitating filtration.** A. PARLOW (Chem.-Ztg., 1930, 54, 183).—To ensure complete filling of the stem of the filter with liquid the paper is folded at an angle of 93–98° instead of the usual 90° and the corner of the thicker side is torn (not cut) off. The fibrous edges prevent ingress of air into the stem and filtration is thus accelerated.

A. R. POWELL.

**Vacuum-jacketed Twisselmann extractor.** A. VERHEIN (Chem. Umschau, 1930, 37, 61).—A modified form of Twisselmann extractor which is suitable for use with high-boiling liquids is described; the lower part of the tube leading to the condenser is fitted with a vacuum-jacket, which also protects the solvent-container from overheating. The apparatus is easily adaptable for quantitative fractional distillation.

E. LEWKOWITSCH.

**Laboratory overflow centrifuge.** SPROCKHOFF (Chem.-Ztg., 1930, 54, 124).—The centrifuge is designed for the separation of small quantities of sediment from large volumes of liquid. It has a central continuous feed with two funnels, a cover, and a stationary jacket into which the liquid overflows.

C. IRWIN.

**Instrument for sampling marine muds.** H. B. MOORE and R. G. NEILL (J. Marine Biol. Assoc., 1930, [ii], 16, 589–594).—The sampler consists of a glass tube open at both ends, held vertically in a heavy brass body. The instrument sinks into the mud under its own weight, and when it stops the top is closed by a valve.

C. W. GIBBY.

**Apparatus for rapid electrometric titration.**

R. G. NEILL (J. Marine Biol. Assoc., 1930, [ii], 16, 519—527).—The apparatus consists essentially of a standard quinhydrone half-element joined by a salt bridge to the acid solution, which contains quinhydrone and a gold electrode. Potentiometric readings are carried out with the aid of a telephone and interrupter.

C. W. GIBBY.

**Mercury cathode cell for the determination of minute quantities of arsenic.** T. CALLAN and R. T. P. JONES (Analyst, 1930, 55, 90—92).—The cathode cell consists of a glass flat-bottomed tube with an aperture, covered by parchmentised paper, in the side about 6 mm. from the bottom. This covering acts as a low-resistance diaphragm between anolyte and catholyte. Purified mercury is placed in the bottom of the tube with the surface just below the aperture, and electrical connexion is made by a narrow glass tube with a platinum wire sealed into the lower end, placed inside the cell, and projecting through the rubber stopper closing it. Copper wire makes contact with the end of the platinum wire inside the tube by means of a short column of mercury and forms the negative terminal. The electrolyte or test solution is introduced through a tap funnel, and an exit tube with a small hole near the bottom connects with the purifying tube of the mercuric chloride or Marsh-Berzelius type of arsenic detector. The cathode cell is immersed in the electrolyte of the anode cell, and the anode consists of lead foil welded to a short length of stout platinum wire. No poisoning of the mercury cathode was observed, but the mercury is purified as a precaution by spraying through dilute nitric acid.

D. G. HEWER.

**Modified vacuum-walled adiabatic calorimeter.** B. C. HENDRICKS, J. H. DORSEY, R. LEROY, and A. G. MOSELEY, jun. (J. Physical Chem., 1930, 34, 418—426).—The apparatus described consists essentially of a Dewar vessel containing mercury-in-glass thermometers and a heating element, the whole being immersed in a thermostat. Satisfactory tests were obtained by determining the heats of dissolution of  $\alpha$ -glucose and sucrose. The specific heats of 3*N*. and 6*N*. sodium hydroxide were found to be 0.8913 at 21.7° and 0.8455 at 21.5°, respectively. These values fall into line with data for more dilute solutions.

L. S. THEOBALD.

**Inorganic stopcock lubricant.** H. N. STEPHENS (J. Amer. Chem. Soc., 1930, 52, 635—636).—A stopcock lubricant better than either moist phosphoric oxide or moist metaphosphoric acid is obtained by dissolving 18 g. of metaphosphoric acid in 35 g. of 85% orthophosphoric acid containing a drop or two of concentrated nitric acid by heating at 300° for some time. By varying the proportions of the components the viscosity of the lubricant can be varied over a wide range. Taps which "freeze" with this lubricant can be freed by warming. They must, of course, be mercury-sealed or otherwise protected from atmospheric moisture.

J. W. SMITH.

**Regulator allowing rapid changes in the temperature setting of the thermostat.** M. J. POLISSAR (J. Amer. Chem. Soc., 1930, 52, 636—637).

—A new type of vapour-pressure thermostat regulator is described. The bulb is evacuated excepting for the liquid and its vapour, and this is shut off by a mercury U-tube which connects on the other side with a long tube inclined at an angle of about 45° and having wires sealed through its wall at intervals along its length. This also is evacuated from the upper end and sealed off from the atmosphere. The whole is connected to an iron bar which can be rotated so as to adjust the inclination of the long tube to the vertical. By connexion to a suitable wire through the wall and by inclination at a suitable angle this regulator will work at any desired temperature, always providing that a suitable liquid is chosen.

J. W. SMITH.

**Apparatus for determination of volatile compounds [by adsorption with activated carbon].**

R. KATTWINKEL (Chem. Fabr., 1930, 33).—The apparatus which serves for stripping the enriched activated carbon consists of a steam generator, above it a nest of parallel vertical superheater tubes heated by a ring burner, and an insulated jacket containing the carbon tube around which the products of combustion pass. This apparatus, which is compact and entirely of metal construction, is connected to a condenser and overflow measuring burette.

C. IRWIN.

**Microburette.** A. WÖHLK (Dansk Tidsskr. Farm., 1930, 4, 38—40).—A simple form of microburette is described.

H. F. HARWOOD.

**Rapid evaporation.** III. H. N. NAUMANN (Biochem. Z., 1930, 217, 409—420; cf. this vol., 314).—An apparatus suitable for rapid evaporation or rapid vacuum distillation with quantitative collection of the distillate is described.

K. V. THIMANN.

**Simple aid to vacuum distillation.** G. M. SCHWAB (Z. angew. Chem., 1930, 43, 155—156).—From Trouton's rule it may be shown that at  $T=\infty$  the limiting vapour pressure of any liquid is  $4.9 \times 10^7$  mm. This point is now plotted on logarithmic-hyperbolic co-ordinates paper (abscissa =  $1/x$ , ordinate =  $\log y$ ). The straight line joining this point to the known point will give the b. p. at any other pressure. Examples show that results are accurate to within a few degrees.

C. IRWIN.

**Vacuum-distillation apparatus.** F. FRIEDRICH (Chem.-Ztg., 1930, 54, 144).—In the usual forms of vacuum-distillation apparatus the effects of the height of the column of vapour of the liquid under treatment and the friction of the vapour itself in retarding the distillation are disregarded. A description is given of an apparatus constructed so that the above factors are both reduced to a minimum.

H. F. HARWOOD.

**Calculation of absolute viscosity from data secured by means of the torsion viscosimeter.** R. WHITAKER and B. L. HERRINGTON (J. Dairy Sci., 1929, 12, 456—463).—The equation  $V = [KR/(2A - R)] - K'$ , where  $V$  is the viscosity in centipoises,  $R$  the degrees of retardation,  $A$  the distance from the initial point to the point of rest of the ball, and  $K$  and  $K'$  are constants, is derived for the Mojonier-Doolittle viscosimeter. Errors of about 3% were recorded.

CHEMICAL ABSTRACTS.

## Geochemistry.

**Salinity interchange between sea-water in sand and overflowing fresh water at low tide.** D. M. REID (J. Marine Biol. Assoc., 1930, [ii], 16, 609—614).—Measurements have been made of the change in salinity of sand on a beach when a stream of fresh water is flowing over it. The change extends to a depth of only a few inches. C. W. GIBBY.

**Seasonal changes in the nitrite content of sea-water.** W. R. G. ATKINS (J. Marine Biol. Assoc., 1930, [ii], 16, 515—518).—The nitrite content of sea-water may be used as an indication of the rapid conversion of ammonium salts into nitrates. C. W. GIBBY.

**Composition and classification of Italian mineral waters.** D. MAROTTA and C. SICA (Annali Chim. Appl., 1929, 19, 529—560).—The data furnished refer to both potable and spa waters. T. H. POPE.

**Muds of the Clyde Sea area. I. Phosphate and nitrogen contents.** H. B. MOORE (J. Marine Biol. Assoc., 1930, [ii], 16, 595—607).—The phosphate and total nitrogen contents of Clyde Sea mud have been determined at 33 stations at 5-cm. intervals down to 20—30 cm. below the surface. The phosphate contents at depths of less than 40 m. all lie close together, and diminish with increasing depth in the mud. The nitrogen content also diminishes with increasing depth. Points at which the tides are strong generally have low nitrogen and phosphate contents. C. W. GIBBY.

**Rôle of silicon, aluminium, and iron in the weathering of the earth's crust.** H. HARRASSOWITZ (Z. angew. Chem., 1930, 43, 185—190).—Silica, alumina, and ferric oxide play various rôles in the weathering process according to climatic conditions. In cold and wet climates acid humus is formed and dissolves all bases, leaving a sand of high silica content. In warm moist climates acids are no longer formed; the bases give rise to gels which build up loam, red earth, or laterite. In tropical climates with a dry season alternations of acidity occur with corresponding reactions in which crystalline phases can be distinguished. In dry climates alkaline conditions are usual; in deserts iron and silica are prevalent, in steppes the oxides form gels giving rise to black earth. Bauxite is produced from scillitic loam by removal of silica under pressure and alkaline conditions. C. IRWIN.

**X-Ray examination of Japanese acid clay.** N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1930, 33, 29—31b).—Three samples of this clay from different localities were each elutriated into five portions and examined separately. A definite series of diffraction lines characteristic of all the samples was obtained. These were not identical with the diffraction lines of silica-gel,  $\alpha$ -quartz, kaolinite, or other compounds examined and it was concluded that the principal constituent of the clay must be an unknown crystalline substance. C. IRWIN.

**Concretions of manganese ore from the Zeller lake [Upper Austria].** H. LASCH (Min. Petr. Mitt., 1930, 40, 294—296).—Concretions the size of

a man's head were dredged from depths of 18—22 m. at two spots where there was also evidence of springs of carbon dioxide. They consist of sandy marl with a black crust of wad, psilomelane, and limonite. Analysis of the crust gave  $\text{MnO}_2$  13.92,  $\text{MnO}$  2.86,  $\text{Fe}_2\text{O}_3$  37.68,  $\text{SiO}_2$  19.10,  $\text{H}_2\text{O}$  18.32%, etc. They are evidently formed by the metasomatic replacement of calcium carbonate by manganese and iron from carbonated springs. L. J. SPENCER.

**Sagvandites and their formation by the syntaxis of dolomite rocks.** T. F. W. BARTH (Min. Petr. Mitt., 1930, 40, 221—234).—Additional remarks to a previous paper (A., 1928, 1210). Sagvandites are igneous rocks containing primary magnesite with enstatite, and they occur in association with basic eruptive rocks and dolomitic sediments. It is suggested that they have originated by the assimilation (syntaxis) of dolomite by the basic magma. L. J. SPENCER.

**Basalt from "Cucchiara Zeppara" near Guspini (Sardinia).** G. MARTINEZ (Atti R. Accad. Lincei, 1929, [vi], 10, 665—670).—A description and analysis of a basaltic rock from the above region. O. J. WALKER.

**Eucrase from the Valle Aurina.** A. CAVINATO (Atti R. Accad. Lincei, 1929, [vi], 10, 656—664).—The physical, optical, and crystallographic properties of eucrase ( $d$  3.038) from the Valle Aurina in the upper Adige district are described and shown to be identical with those of eucrase from Villa Rica (Brazil). The analysis gave:  $\text{SiO}_2$  40.78,  $\text{Al}_2\text{O}_3$  34.46,  $\text{Fe}_2\text{O}_3$  0.97,  $\text{FeO}$  0.44,  $\text{BeO}$  16.54,  $\text{CaO}$  0.22,  $\text{MgO}$  0.55,  $\text{H}_2\text{O}+$  6.15,  $\text{H}_2\text{O}-$  0.13,  $\text{F}$  0.12, total (less O for F) 100.31%. This confirms the formula  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{BeO} \cdot \text{H}_2\text{O}$ . O. J. WALKER.

**Occurrence of copper in French Western Soudan.** R. FURON (Compt. rend., 1930, 190, 383—384).—Sandstone impregnated with copper in the form of malachite and chrysocolla has been discovered between Sirakoro and Sici, near Niore, in French Western Soudan. A sample has yielded 12% of metal. The whole area from Turugombe to Yerere is mineralised, and contains much magnetite. C. A. SILBERRAD.

**Antamokite, a new gold silver telluride.** A. D. ALVIR (Philippine J. Sci., 1930, 41, 137—139).—Antamokite, from Antamok, Philippine Islands, is a gold silver telluride, containing no lead antimony or copper;  $H$  2—3. C. W. GIBBY.

**Pacificite.** T. F. W. BARTH (J. Wash. Acad. Sci., 1930, 20, 60—68).—The name pacificite is suggested for anemousite-basalt, anemousite being a plagioclase carrying carnegieite in solid solution. Pacificite is otherwise free from feldspathoids, and is thus heteromorphous with tephrite or basanite according as olivine is absent or present. Analyses and detailed descriptions are given for two pacificites found in the Hawaiian Islands. C. W. GIBBY.

**Active disperse formations of Tua-Muyun.** I. KURBATOV (J. Russ. Phys. Chem. Soc., 1929, 61,

1651—1659).—The vanadium, copper, calcium, silica, alumina, and sulphur contents of Tua-Muyun ores are smaller at lower than at higher levels, whilst the contrary is the case with the uranium, iron, and barium contents. R. TRUSZKOWSKI.

**Iodine content of coal.** E. WILKE-DÖRFURT and H. RÖMERSPERGER (Z. anorg. Chem., 1930, 186, 159—164).—Ignition of a mixture of powdered coal and potassium carbonate results in loss of iodine by volatilisation. Good results are obtained by heating 30 g. of finely-powdered coal with 1.5 g. of potassium carbonate and 400 c.c. of 50% alcohol for 8 hrs. at 270—280° in an autoclave whereby all the

iodine is rendered soluble. The solution is filtered and evaporated to dryness, the residue heated gently to carbonise organic matter and extracted with water, and the carbon separated by filtration; this procedure is repeated until a colourless filtrate is obtained in which the iodine is determined volumetrically by Winkler's method (A., 1917, ii, 501). The iodine content of twelve mid-European coals was found to vary from 0.85 to 11.17 mg. per kg. but no relation could be established between the age of a coal and its content of iodine. It is calculated that, based on a consumption of 1200 million tons of coal per annum, about 7 million kg. of iodine are returned to circulation on the earth's surface. A. R. POWELL.

## Organic Chemistry.

**Fixation of ozone by unsaturated compounds.** G. BRUS and G. PEYRESBLANQUES (Compt. rend., 1930, 190, 501—503).—The forms of ozonisation curves (cf. A., 1929, 72) indicate that treatment of unsaturated hydrocarbons with ozonised oxygen (3—9% O<sub>3</sub>) affords the normal ozonides, and enables the number of double linkings to be calculated. Perozonide formation appears to occur subsequently, probably by addition of an atom of oxygen to the ozonide grouping (cf. Harries, A., 1912, i, 407). In the case of unsaturated ketonic compounds, the formation of ozonide peroxides occurs subsequently to that of the normal ozonides by addition of an atom of oxygen at the keto-group. C. W. SHOPPEE.

**Action of halogen compounds on ethylene derivatives.** J. J. CERDEIRAS (Anal. Fis. Quim., 1930, 28, 56—62).—It is recommended that the results of all determinations of the halogen absorption coefficient of unsaturated organic substances as, e.g., in the Wijs and Hübl methods, be expressed in terms of iodine. The advantages of a solution of iodine monochloride in alcohol over the solutions usually employed are described; provided that water be entirely absent, the solution is comparatively stable, and the reaction with unsaturated compounds takes place more readily, 40 min. usually being sufficient. Three different classes of reaction are considered: (1) the halogen addition corresponds with the theoretical; (2) the absorptive capacity is influenced by the structure of the compound; (3) substituted and additive derivatives are simultaneously produced. For the two latter classes the iodine value should be compared with the catalytic hydrogenation value.

H. F. GILLBE.

**Production of acetylene from methane. I. Cracking under vacuum.** P. K. FROLICH, A. WHITE, and H. P. DAYTON. **II. Cracking in the electric arc.** P. K. FROLICH, A. WHITE, R. R. UHRMACHER, and L. T. TUFTS.—See B., 1930, 173.

**Action of nitric acid on acetylene.** A. QUILICO and M. FRERI (Gazzetta, 1929, 59, 930—941).—The formula of the acid C<sub>2</sub>H<sub>3</sub>O<sub>3</sub>N (cf. Testoni and Mascarelli, A., 1901, i, 494), m. p. 149°, obtained when acetylene is passed slowly through fuming nitric acid, is confirmed. The acid reacts readily with diazo-

methane and -ethane, giving the *methyl*, b. p. 100—101°/12 mm., and *ethyl* esters, b. p. 110°/1 mm. The *amide*, C<sub>3</sub>H<sub>2</sub>ON·CO·NH<sub>2</sub>, has m. p. 142° and the phenylhydrazine salt, m. p. 176°, no phenylhydrazone being formed. Hydroxylamine is without action on the acid, which gives no coloration with ferric chloride. When boiled with alcoholic potassium hydroxide, the acid yields, among other products, oxalacetic acid, which was separated as its *p*-nitrophenylhydrazone, m. p. 190—195° (decomp.), whilst the use of sodium ethoxide instead of alcoholic potassium hydroxide gives pyruvic acid, the *p*-nitrophenylhydrazone of which has m. p. 187°. From these results and those obtained by Testoni and Mascarelli, it is concluded that this acid is isooxazole- $\alpha$ -carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}\begin{matrix} \text{O} \\ \parallel \\ \text{CH}\cdot\text{CH} \end{matrix}$ .

T. H. POPE.

**Law of periodicity.** V. P. PETRENKO-KRITSCHENKO [with V. OPOLSKI, M. DIAKOVA, and LOZOVY] (J. Russ. Phys. Chem. Soc., 1929, 61, 1777—1789).—The reactivity of halides of various methane derivatives containing other substituents, such as methyl, phenyl, or nitro- or carboxyl groups, with colloidal silver solutions, with certain exceptions, varies periodically with the number of halogen atoms in the molecule. In general, there are three types of curve connecting the reactivity of halogen in organic derivatives with the number of halogen atoms, the reagents being alkoxides, piperidine, silver nitrate, or silver sol. In type I, reactivity varies periodically, according to the order  $\text{RX} > \text{RX}_2 < \text{RX}_3 > \text{RX}_4$ ; in type II the order is  $\text{RX} > \text{RX}_2 > \text{RX}_3 < \text{RX}_4$ , whilst in type III it is  $\text{RX} < \text{RX}_2 < \text{RX}_3$ . R. TRUSZKOWSKI.

**Test for distinguishing primary, secondary, and tertiary saturated alcohols.** H. J. LUCAS (J. Amer. Chem. Soc., 1930, 52, 802—804).—The lower aliphatic tertiary alcohols react immediately with hydrochloric acid, whilst secondary alcohols on treatment with 6 volumes of a solution of zinc chloride (1 mol.) in hydrochloric acid (1 mol.) give chlorides within 5 min. at 26—27°. Primary alcohols do not react with either of the reagents. The presence of a secondary or tertiary alcohol in a primary alcohol can be detected provided the concentration is not too low. Allyl alcohol resembles a secondary alcohol.

H. BURTON.

### Preparation of allyl alcohol and allyl chloride.

A. DEWAELE (Bull. Soc. chim. Belg., 1930, 39, 40—42).—In the preparation of allyl alcohol ("Organic Syntheses," I, 15) the yield is increased from 45—47% to 66% in the following manner. The initial fraction, b. p. up to 195°, is redistilled until the thermometer registers 103°. The residue is added to the residue of the fraction of b. p. 195—260° after treatment as previously described (*loc. cit.*) and the whole redistilled with the thermometer in the liquid. The fraction of b. p. 200—260° (a further evolution of carbon dioxide occurs at 220°) is added to the glycerol residues and redistilled with formic acid. The fraction of b. p. below 200° contains glyceryl formate and monoallyl-glycerol, whilst hydrolysis of the fraction of b. p. 190—210° with methyl-alcoholic hydrogen chloride gives propylene glycol and trimethylene glycol. Allyl alcohol is converted into allyl chloride in 85—90% yield by saturating 250 g. of allyl alcohol, to which 1.5 g. of copper chloride has been added, four times with hydrogen chloride at 0° at 24-hr. intervals. The liquid separates into two layers and the supernatant layer, after drying with calcium chloride, distills completely at 46—47°/758 mm. J. W. BAKER.

**Mobile anion tautomerism. IV. Stability of  $\alpha$ - and  $\gamma$ -alkylallyl alcohols and their esters. 2:4-Dimethylcinnamyl alcohol.** H. BURTON (J.C.S., 1930, 248—252).—When a solution of either methylvinylcarbinyl, b. p. 69.5—70.5°/8 mm.,  $n_{D_{20}}^{25}$  1.46390, or crotyl trichloroacetate, b. p. 86—86.5°/9 mm.,  $n_{D_{20}}^{25}$  1.47596, in acetic anhydride is boiled for 6 hrs., the same mixture of about 55% of the former and 45% of the latter ester is obtained. Prévost's failure to effect interconversion (A., 1928, 1211) is considered to be due to unsuitable experimental conditions. Esterification of trichloroacetic acid with butylvinylcarbinol (*p*-nitrobenzoate, m. p. 24—25°) could not be accomplished as profound decomposition occurs at 100°. Magnesium *n*-hexyl bromide and acetaldehyde give  $\alpha$ -*n*-hexylallyl alcohol ( $\Delta^{\alpha}$ -nonen- $\gamma$ -ol), b. p. 89°/12 mm., separable from the reaction mixture by way of its *p*-nitrobenzoate, m. p. 36—37°. The last-named ester is not isomerised in boiling acetic anhydride (cf. A., 1928, 880).  $\alpha$ -isoAmylallyl alcohol (acetate, b. p. 83—84°/18 mm.) has b. p. 73—74°/16 mm.

Magnesium *m*-4-xylyl iodide and acetaldehyde afford a poor yield of  $\alpha$ -*m*-4-xylylallyl alcohol, b. p. 129—131°/12 mm. (*phenylcarbimide* derivative, m. p. 105—106°), which on acetylation and subsequent hydrolysis gives 2:4-dimethylcinnamyl alcohol, b. p. 162—164°/19 mm. (acetate, b. p. 168—170°/17 mm.; *phenylcarbimide* derivative, m. p. 82—83°). H. BURTON.

**An ethylenic erythritol [ $\Delta^{\gamma}$ -hexene- $\alpha\beta\epsilon\zeta$ -tetrol].** LESPIEAU and BOURGUEL (Compt. rend., 1930, 190, 378—380).—Hexinene- $\alpha\beta\epsilon\zeta$ -tetrol, m. p. 114° (cf. A., 1922, i, 103), in presence of colloidal platinum absorbs 1 mol. of hydrogen, yielding  $\Delta^{\gamma}$ -hexene- $\alpha\beta\epsilon\zeta$ -tetrol, m. p. 80—82°. From crude hexinene- $\alpha\beta\epsilon\zeta$ -tetrol, probably containing a mixture of isomerides, no crystalline product could be isolated.  $\alpha\zeta$ -Dimethoxy- $\Delta^{\gamma}$ -hexene- $\beta\epsilon$ -diol, b. p. 151°/5 mm., is obtained similarly. R. K. CALLOW.

**Photochemical reactions among derivatives of *o*-nitrobenzylidenacetals. IV. Tri-*o*-nitrobenzylidenemannitol.** I. TANASESCU and E. MACOVSKY (Bull. Soc. chim., 1930, [iv], 47, 86—93).—*o*-Nitrobenzaldehyde and mannitol in presence of 75% sulphuric acid yield a crystalline, m. p. 75°, and a viscous form of tri-*o*-nitrobenzylidenemannitol. In presence of hydrogen chloride at 120° the viscous form is the main product; it is converted into the crystalline isomeride by repeated recrystallisation from alcohol. A structure is suggested. On insolation in benzene tri-*o*-nitrobenzylidenemannitol is rapidly converted into a *disisonitroso*-derivative, m. p. 120°, which yields a *dibenzozate*, m. p. 90°, and on hydrolysis with nitric acid and addition of acetone yields an indigo, but could not be hydrolysed to  $\gamma\delta$ -*o*-nitrobenzylidenemannitol (cf. A., 1926, 726). R. BRIGHTMAN.

### Thermal decomposition of aliphatic ethers.

K. KASHIMA (Bull. Chem. Soc. Japan, 1930, 5, 25—42).—A quantitative examination of the products formed by the thermal decomposition of ethyl, *n*-propyl, *n*-butyl, *n*-amyl, and ethyl *n*-butyl ethers and *n*-amyl alcohol in the presence of small grains of Japanese acid clay at 350—400° under standard conditions has been made. The main products are the corresponding olefines, alcohols, and water, together with small amounts of aldehydes, esters, carbon monoxide, hydrogen, oxygen, and paraffin hydrocarbons, traces of free carbon being deposited on the catalyst. Since the molecular ratio olefine/water is always approximately 2 : 1, it is assumed that the main decomposition is the reaction  $(CH_3R \cdot CH_2)_2O \rightarrow 2CHR \cdot CH_2 + H_2O$  (I), the formation of alcohols being represented by  $(CH_3R \cdot CH_2)_2O \rightarrow CHR \cdot CH_2 + CH_3R \cdot CH_2 \cdot OH$  (II). The proportion of alcohol formed is greater the lower is the temperature, but above 300° only small quantities are produced, reaction I predominating. With *n*-butyl ether a mixture of  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -butene is obtained, the latter predominating, with ethyl *n*-butyl ether the quantity of butylene and ethyl alcohol formed is larger than that of ethylene and butyl alcohol, whilst with *n*-amyl alcohol a mixture of  $\alpha$ - and  $\beta$ -amylenes is obtained.

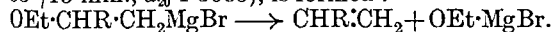
J. W. BAKER.

**Synthesis of  $\beta$ -bromoalkyl ethers and their use in further syntheses.** L. C. SWALLEN and C. E. BOORD (J. Amer. Chem. Soc., 1930, 52, 651—660).—Bromination of ethyl  $\alpha$ -chloroethyl ether affords ethyl  $\alpha\beta$ -dibromoethyl ether, b. p. 90—91°/20 mm.,  $d_{20}^{25}$  1.7350, and not the  $\alpha$ -chloro- $\beta$ -bromo-derivative as stated by Madinaveitia and Puyal (A., 1918, i, 373). Treatment of this dibromo-ether with magnesium alkyl (R) bromides affords  $\beta$ -ethoxyalkyl bromides,  $OEt \cdot CHR \cdot CH_2Br$ . The following are described:  $\beta$ -ethoxy-*n*-propyl, b. p. 138°,  $d_{20}^{25}$  1.2706;  $\beta$ -ethoxy-*n*-butyl, b. p. 166°,  $d_{20}^{25}$  1.2317;  $\beta$ -ethoxy-*n*-amyl, b. p. 176°,  $d_{20}^{25}$  1.2929;  $\beta$ -ethoxyisoamyl, b. p. 172°,  $d_{20}^{25}$  1.2183;  $\beta$ -ethoxy-*n*-hexyl, b. p. 85—87°/15 mm.,  $d_{20}^{25}$  1.1573, and  $\beta$ -ethoxyisoheptyl bromides, b. p. 93—95°/15 mm.,  $d_{20}^{25}$  1.1286.  $\beta$ -Ethoxyethyl iodide, b. p. 154.5—155° (corr.),  $d_{20}^{25}$  1.7032, is obtained from the chloro-compound and sodium iodide in alcohol. The following chlorides are prepared either by alkylation of ethylene chlorohydrin or from ethyl  $\alpha\beta$ -di-



chloroethyl ether and the requisite magnesium alkyl bromide:  $\beta$ -methoxy- and -ethoxy-ethyl;  $\beta$ -ethoxy-*n*-propyl, -butyl, and - $\beta$ -phenylethyl. Treatment of these chlorides with methyl-alcoholic potassium hydrogen sulphide at 65–90° affords the corresponding mercaptans, the following being described:  $\beta$ -ethoxyethyl, b. p. 125.5–125.8°,  $d_{20}^{25}$  0.9479 [mercurichloride, m. p. 152–153.5° (decomp.); corresponding disulphide, b. p. 161°/33 mm.,  $d_{20}^{25}$  1.0510; acetone condensation product, b. p. 134°/7 mm.,  $d_{20}^{25}$  1.0044];  $\beta$ -ethoxy-*n*-propyl, b. p. 134–134.5°,  $d_{20}^{25}$  0.9238 [mercurichloride, m. p. 121–123° (decomp.)], and  $\beta$ -ethoxy-*n*-butyl, b. p. 156–157°,  $d_{20}^{25}$  0.9177 (mercurichloride, m. p. 86–87° (decomp.); corresponding disulphide, b. p. 135°/8 mm.,  $d_{20}^{25}$  1.0013).  $\beta\beta'$ -Diethoxydiethyl sulphide has b. p. 229° (corr.),  $d_{20}^{25}$  0.9840. Oxidation of  $\beta$ -ethoxyethyl mercaptan with dilute nitric acid affords impure  $\beta$ -ethoxyethanesulphonic acid (sodium salt; impure chloride, b. p. 118–122°/26 mm.).

$\beta$ -Ethoxy-*n*-butyl bromide and ethyl sodiomalonate give the ethyl ester, b. p. 146–150°/12 mm., of  $\beta$ -ethoxy-*n*-butylmalonic acid (calcium salt), which on thermal decomposition at 180° affords  $\gamma$ -ethoxy-*n*-hexoic acid, b. p. 138–140°/8 mm.,  $d_{20}^{25}$  0.9816 (barium salt + H<sub>2</sub>O). Ethyl  $\beta$ -ethoxyethylmalonate,  $d_{20}^{25}$  1.0430, and  $\omega$ -ethoxyphenetole,  $d_{20}^{25}$  1.0057, are obtained similarly.  $\beta$ -Ethoxyethyl-, b. p. 262–263° (corr.),  $d_{20}^{25}$  1.0156, and  $\beta$ -ethoxybutyl-anilines, b. p. 264–269° (corr.),  $d_{20}^{25}$  0.9830, are prepared from aniline and the chloride and bromide, respectively. When  $\beta$ -ethoxyisheptyl bromide is treated with magnesium in ether,  $\Delta^1$ -isoheptene, b. p. 85° (dibromide, b. p. 95°/13 mm.,  $d_{20}^{25}$  1.5083), is formed:



H. BURTON.

Reaction for acetic acid. D. KRÜGER and E. TSCHIRCH (Pharm. Zentr., 1930, 71, 145–148).—See this vol., 62.

J. W. BAKER.

Conjugated systems. III. Chlorination of  $\beta$ -vinylacrylic acid. I. E. MUSKAT and B. C. BECKER (J. Amer. Chem. Soc., 1930, 52, 812–818).—Vinylacrylic acid absorbs 2 atoms of chlorine (under various conditions) forming  $\gamma\delta$ -dichloro- $\Delta^1$ -pentenoic acid, b. p. 153°/10 mm. (ozonolysis product  $\alpha\beta$ -dichloropropaldehyde), which undergoes thermal decomposition into the lactone, previously obtained from the  $\gamma\delta$ -dibromo-acid (this vol., 321). Treatment of the dichloro-acid with sodium hydroxide solution at about 0° affords  $\gamma$ -chlorovinylacrylic acid, m. p. about 94°, which is readily polymerised. This absorbs 2 atoms of chlorine in chloroform solution, yielding  $\gamma\delta$ -trichloro- $\Delta^1$ -pentenoic acid, b. p. 162°/8 mm., m. p. 132° (ozonolysis product  $\alpha\beta$ -trichloropropaldehyde).  $\alpha\beta$ -Trichloropropionic acid has m. p. 60° (lit. 50–52°). An electronic structure is suggested for conjugated systems.

H. BURTON.

Action of silent discharge on saturated fatty acids. Y. IWAMOTO (J. Soc. Chem. Ind. Japan, 1930, 33, 25–27B).—Decoic, lauric, palmitic, and stearic acids were polymerised by the action of the silent discharge for 30–100 hrs. in an atmosphere of hydrogen into viscous liquid acids having iodine value

5–8, lower saponification and neutralisation values, and higher values for  $d$  and  $\mu$ .

C. IRWIN.

Fatty acids associated with wheat starch. L. LEHRMAN (J. Amer. Chem. Soc., 1930, 52, 808–811).—Hydrolysis of wheat starch with hydrochloric acid (cf. A., 1929, 1040) gives 0.95% of a mixture of palmitic (35%), oleic (41%), and linoleic acids (24%); no glycerol is formed. During the oxidation of a mixture of oleic and linoleic acids with alkaline potassium permanganate the latter acid is converted into tetrahydroxystearic acid before the former is acted on.

H. BURTON.

Soaps of the fatty acids of the oleic acid series. I. Sodium physeterate. M. HIROSE and T. SHIMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 22–24B).—Physeteric acid  $\text{CH}_3 \cdot [\text{CH}_2]_7 \cdot \text{CH} \cdot \text{CH} \cdot [\text{CH}_2]_3 \cdot \text{CO}_2\text{H}$ , obtained from sperm oil contained 6% of myristic acid shown by its iodine value. The drop numbers and surface tension of solutions of the sodium soap in various concentrations are given and also the “lathering power.” The high drop numbers indicate the formation of a true solution. The general soap characters are unexpectedly good.

C. IRWIN.

Catalytic reduction of  $\alpha$ - and  $\beta$ -elaeostearic acids under the influence of nickel. J. BÜSEKEN, J. VAN KRIMPEN, and P. L. BLANKEN (Rec. trav. chim., 1930, 49, 247–256).—Catalytic reduction, with hydrogen under the ordinary pressure with a nickel catalyst deposited on diatomaceous earth, of pure specimens of ethyl  $\alpha$ -elaeostearate, b. p. 169–170.5°/cathode vacuum,  $n_D^{25}$  1.5043, and ethyl  $\beta$ -elaeostearate, b. p. 170°/cathode vacuum,  $d^{25}$  0.9032,  $n_D^{25}$  1.5078, has been repeated with improved apparatus (due to W. D. Cohen) and the previous results (A., 1927, 1169) have been confirmed. Progressive reduction follows Thiele's rule and in each case the products are, successively, ethyl  $\Delta^8$ -octadecadienoate, hydrolysed to the acid, m. p. 28–29° (ozonolysis yields hexoic and sebacic acids), and ethyl  $\Delta^8$ -octadecenoate, hydrolysed to the acid, m. p. 38.5°, identical with vaccenic acid obtained by Bertram (Diss., Delft, 1928) (ozonolysis gives heptonic and nonane- $\alpha$ -dicarboxylic acid). Bertram's method for the separation of saturated fatty acids from unsaturated acids (*loc. cit.*) gives low results for the proportion of saturated acids present unless the acid solution is heated to the fusion point of the fatty acids and then immediately extracted with light petroleum.

J. W. BAKER.

Synthetic gadoleic and selacholeic acids. V. VESELY and L. K. CHUDŽILOV (Coll. Czech. Chem. Comm., 1930, 2, 95–107).—Ethyl oleate is reduced to oleyl alcohol, which is converted into the bromide; this latter is condensed with ethyl sodiomalonate and the dibasic acid so obtained loses carbon dioxide on distillation, yielding, together with the *trans*-isomeride, a small quantity of *cis*-eicosenoic acid identical with gadoleic acid (cf. Bull. A., 1906, i, 925). An identical synthetic process employing elaidic acid yields *trans*-eicosenoic acid identical with gadelaidic acid, m. p. 53–54° (amide, m. p. 90–91°), obtained by the isomerising action of nitrous acid on gadoleic acid. Gadoleic and gadelaidic acids are, therefore, formulated as the *cis*- and *trans*-forms of the acid

$\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CH}\cdot\text{CH}\cdot[\text{CH}_2]_6\cdot\text{CO}_2\text{H}$ . In the final stage of the synthesis, during the distillation, a degradation product, (?) *hexatriacontadiene*, m. p. 48—49°, is formed which can be isolated from the higher fractions.

Similarly, from erucic acid, by way of erucyl alcohol and *erucyl bromide*, b. p. 232—239°/10 mm., *cis*-tetracosenoic acid, m. p. 44—45° (*amide*, m. p. 87—88°), identical with Tsujimoto's selacholeic acid (B., 1926, 712), and from brassidic acid through *brassidyl alcohol*, m. p. 53—54°, b. p. 239—243°, and *brassidyl bromide*, m. p. 25—26°, b. p. 246—249°, *trans*-tetracosenoic acid (*amide*, m. p. 98—99), probably identical with selachelaidic acid (*loc. cit.*), have been obtained. The degradation product obtained in this synthesis from the higher fractions is (?) *tetra-tetracontadiene*,  $\text{C}_{44}\text{H}_{88}$ , m. p. 60—62°.

T. H. MORTON.

**Space configuration of molecules. Ultra-violet absorption of alkylmalonic acids.** (MME.) P. RAMART-LUCAS and F. SALMON-LEGAGNEUR (Compt. rend., 1930, 190, 492—495).—The absorption curves of the malonic acids,  $\text{CHR}(\text{CO}_2\text{H})_2$  ( $\text{R}=\text{Me}$ ,  $\text{Et}$ ,  $\text{Pr}^i$ ,  $\text{Bu}^i$ ,  $\text{Bu}^s$ , and heptyl), are displaced towards the visible, as compared with that of malonic acid; the curves of the corresponding acids,  $\text{CR}_2(\text{CO}_2\text{H})_2$ , exhibit a shift toward the ultra-violet in relation to those of the monoalkylated acids. By contrast, the absorption curves of the dialkyl diethylmalonates lie nearer the visible than those of the corresponding monoalkyl esters. Different space configurations are attributed to the mono- and di-alkylmalonic acids, and the acids and their esters.

C. W. SHOPPEE.

**Reactions of malonic esters with formaldehyde.** I. K. N. WELCH (J.C.S., 1930, 257—261).—Ethyl malonate condenses with formaldehyde (formalin) in presence of dilute sodium hydroxide at  $p_{\text{H}}$  8—9 and below 50°, forming *ethyl di(hydroxymethyl)malonate*, m. p. 52—53° (*bisphenylcarbimide* derivative, m. p. 161°; *sulphite*, b. p. 166°/20 mm., prepared by the action of thionyl chloride in ether). In presence of a larger excess of ethyl malonate the condensation product is probably ethyl hydroxymethylmalonate, which cannot be distilled owing to the ease with which it loses water, forming ethyl methylenemalonate. The above dihydroxy-ester is converted by boiling hydriodic acid ( $d$  1.71) into  $\alpha$ -iodomethylacrylic acid, m. p. 106—107°, reduced by red phosphorus and hydriodic acid to isobutyric acid. Ethyl malonate and the dihydroxy-ester condense in presence of a small amount of piperidine, triethylamine, or alcoholic potassium hydroxide, yielding a mixture of ethyl methylenedimalonate and ethyl pentane- $\alpha,\alpha,\gamma,\gamma$ -hexacarboxylate; the amount of the latter ester is decreased by using a larger amount of ethyl malonate. Ethyl malonate and ethyl methylenemalonate condense in presence of a small amount of piperidine, forming ethyl methylenedimalonate, which undergoes similar condensation to the above hexacarboxylate. Ethyl ethylmalonate and formaldehyde in presence of dilute sodium hydroxide give *ethyl ethylhydroxymethylmalonate*, b. p. 105—107°/4 mm. (*phenylcarbimide* derivative, m. p. 63—64°). H. BURTON.

**cis-trans-Ethenoid transformation.** G. R. CLEMO and S. B. GRAHAM (J.C.S., 1930, 213—215).—

The transformation of methyl maleate (method of preparation from maleic anhydride, methyl alcohol, and sulphuric acid given) into methyl fumarate is catalysed by ammonia and primary or secondary amines, but not by tertiary amines. It is suggested that the first stage of the transformation is the production of a co-ordinate linking between the basic hydrogen and carbonyl oxygen atoms. This would produce a mobility in the electronic system constituting the double linking, and lead to an unstable complex in which both the ethylenic carbon atoms would be positive and surrounded by only seven electrons. A parallel mechanism is suggested for the catalytic action of primary and secondary amines in the Knoevenagel reaction (A., 1895, i, 48).

H. BURTON.

**Polymerisation and ring formation. IV. Ethylene succinates.** W. H. CAROTHERS and G. L. DOROUGH (J. Amer. Chem. Soc., 1930, 52, 711—721).—The neutral ethylene succinate, m. p. 102°, prepared from succinic acid and an excess of ethylene glycol (A., 1929, 1165), is a chain polymeride containing 23 structural units per mol. terminated by hydroxyl groups. When heated with succinic anhydride at 175—180° it furnishes an acidic *ethylene succinate* ( $M$  3110), m. p. 98° (*sodium salt*, m. p. 104°), and with *p*-bromobenzoic anhydride affords a *di-p-bromobenzoate*, m. p. 93°. When ethylene glycol is heated with a 20% excess of succinic acid first at 200—210° and then at 200—210°/vac., and the product fractionally precipitated, three acidic *ethylene succinates*, m. p. 73°, 82°, and 90°, respectively (*sodium salts*, m. p. 91°, 97°, and 100°, respectively), are formed. The degrees of polymerisation are 6, 9, and 12, respectively. When ethylene glycol (1 mol.) is heated with succinic acid (0.33 mol.) at 174—180° (bath) and then at 250°/0.015 mm., 0.07 mol. of impure  $\beta$ -hydroxyethyl succinate, b. p. 176—180°/0.001 mm. (*di-p-nitrobenzoate*, m. p. 90—91°; *bisphenylcarbimide* derivative, m. p. 113°), is obtained. Ethylene glycol and a neutral, polymeric ethylene succinate are produced by heating this ester slowly in a vacuum. Tilitcheev's statement (A., 1926, 713) that the ethylene succinate, m. p. 129—130°, obtained by thermal decomposition of the polymeric ester, m. p. 88—89°, is dimeric, is confirmed; the dimeride is postulated as a 16-membered ring compound.

When ethylene succinate, m. p. 102°, and ethylene sebacate, m. p. 78°, are fused together, the product formed can be separated into its original constituents by extraction with benzene (*cf. loc. cit.*). The ester formed from ethylene glycol and equivalents of succinic and sebacic acids has m. p. 38—40° ( $M$  1540), and is homogeneous, indicating that it is a mixed polymeride, and demonstrating the absence of any reversible relationship of association between it and the two corresponding simple polymerides. The mol. wts. of the polymeric ethylene succinates are found to be the same when determined either by chemical or osmotic methods; this is considered to be evidence against an association theory of the structure of poly-esters.

H. BURTON.

**Synthesis of pilopinic acid and structure of pilocarpine.** A. E. TSCHITSCHIBABIN and N. A. PREOBASCHENSKI (Ber., 1930, 63, [B], 460—470).—

Ethyl ethylsuccinate and ethyl formate in presence of absolute-alcoholic sodium ethoxide afford ethyl formylethylsuccinate (cf. Carrière, A., 1922, i, 319) (probably a mixture of isomerides), which is reduced by aluminium in moist ether to a mixture of isomeric ethyl ethylmalates. When heated, the mixture loses alcohol and affords a mixture of the esters of the stereoisomeric ethylparaconic (pilopinic) acids. By combination of fractional distillation and freezing the mixture is separated into the liquid ester,  $C_9H_{14}O_4$ , b. p. 276—276.5°/751 mm.,  $d_4^{20}$  1.1085, and the solid ester, m. p. 48.5—49°, b. p. 283°/751 mm. The former ester is hydrolysed to an acid,  $C_7H_{10}O_4$ , prisms, m. p. 87.5—88°, b. p. 184—185°/7.5 mm., whereas the acid from the latter ester crystallises in needles, m. p. 90—91°, and passes at 180° into the acid of m. p. 87.5—88°. The relationship of the acids from the crystalline and liquid esters resembles that of pilocarpine to isopilocarpine. The stable ethylparaconic acid is resolved into its optical antipodes by strychnine in aqueous solution, whereby the alkaloidal salt of the *l*-acid is the more sparingly soluble. The homogeneous *l*-acid has m. p. 105.5°,  $[\alpha]_D^{25}$  —58.06° in water, whereas the *d*-acid has m. p. 105.5°,  $[\alpha]_D^{25}$  +58.92°. For pilopinic acid obtained by the oxidation of isopilocarpine Jowett (J.C.S., 1903, 83, 463) records m. p. 104°,  $[\alpha]_D^{25}$  +36.1°. Repetition of Jowett's work followed by purification of the acid thus obtained through the strychnine salt shows that oxidation is accompanied by racemisation and yields an acid, m. p. 105.5°,  $[\alpha]_D^{25}$  +58.93°, identical with the synthetic product. The labile acid from the crystalline ester has been resolved into its optical antipodes by crystallisation of the brucine salt, but the homogeneity of the active acids is not fully established.

The analogy in the relationships of pilocarpine to isopilocarpine and of the labile to the stable acid shows that Jowett's pilopinic acid is configuratively related to isopilocarpine and not to pilocarpine. It is therefore designated *d*-isopilocarpine acid. It is equally certain that the labile, dextrorotatory acid corresponds with the labile pilocarpine and hence may be named *d*-pilopinic acid. This acid must be formed by the oxidation of pilocarpine and can be obtained when the conditions which lead to its isomerisation to the stable acid are avoided.

H. WREN.

**Determination of uronic acids.** A. D. DICKSON, H. OTTERSON, and K. P. LINK (J. Amer. Chem. Soc., 1930, 52, 775—779).—The method is a modification of that of Lefèvre and Tollens (A., 1908, ii, 74); the apparatus and procedure are described in detail. Complete decarboxylation of uronic acids is only accomplished by hydrochloric acid (*d* 1.06) at 135—140° (bath) after 5 hrs.

H. BURTON.

**Sugars. IX.** H. KILIANI (Ber., 1930, 63, [B], 369—374; cf. A., 1928, 741).—The isolation of the basic copper and calcium salts of the acid  $C_7H_{10}O_{10}$  obtained by the action of potassium cyanide on potassium *l*-mannosaccharate is supplemented by the preparation of the crystalline zinc salt and of the free acid which is too hygroscopic to permit analysis and appears to be a mixture of mirror isomerides. The reaction has therefore been extended to the more

accessible double lactone of *d*-mannosaccharic acid, the preparation of which is described in detail. The conversion of *d*-mannose into *d*-mannoheptonic acid is fully recorded.

*d*-Mannosaccharic acid yields a diamide,  $[\alpha]_D$  —5.9° in aqueous glycerol (1 : 1 by vol.); the corresponding value for the *l*-diamide is +6.1°. Like *l*-mannosaccharic acid, the *d*-acid gives two distinct series of salts (cf. A., 1926, 940), one type obtained directly from the double lactone, the other through the diamide; the potassium, zinc, cadmium, and calcium compounds are described. Decomposition of the calcium salt from the diamide by aqueous oxalic acid regenerates the double *d*-lactone.

H. WREN.

**Aldehydic reactions of dithiocarboxylic acids.** M. H. WUYTS (Bull. Soc. chim. Belg., 1930, 39, 58—66; cf. A., 1929, 1176).—The course of the reaction between dithiocarboxylic acids,  $R \cdot CS_2H$ , with carbonyl reagents such as phenylhydrazine ( $R' = NPh$ ) and semicarbazide ( $R' = NH \cdot CO \cdot NH_2$ ) depends on the nature of the group *R*. When this group is aliphatic or alicyclic the normal thioacyl derivative is formed thus:  $R \cdot CS_2H + NH_2R' \rightarrow R \cdot CS \cdot NHR' + H_2S$  (1), but if it is aromatic complete elimination of sulphur occurs with the formation of the derivative of the corresponding aldehyde,  $R \cdot CS_2H + NH_2R' \rightarrow R \cdot CH \cdot NR' + S + H_2S$  (2), accompanied by reaction (1) if an aliphatic side-chain is attached to the *ortho* position. Thus by the action of phenylhydrazine on the appropriate dithio-acid in ether at about —25° the unstable phenylhydrazine salt is formed which decomposes when the temperature is allowed to rise, giving thioacetyl-, m. p. 82°; thiophenylacetyl-, m. p. 89° (together with a trace of a substance, m. p. 112—117°), and thiocyclohexanonecarboxyl-, m. p. 129—130°, phenylhydrazine. By heating semicarbazide hydrochloride with the acid and pyridine, dithio-*p*-toluic, -benzoic, and - $\alpha$ -naphthoic acids yield, respectively, *p*-tolualdehyde, benzaldehyde, and  $\alpha$ -naphthaldehyde-semicarbazone, m. p. 227—228° (decomp.), but with dithiocyclohexanecarboxylic acid the product is dithiocyclohexanecarboxylsemicarbazide, m. p. 173—174°. With hydroxylamine the product may be either the oxime of the corresponding aldehyde or the nitrile. Thus dithio-*o*-toluic and  $\alpha$ -naphthoic acids give, respectively, *o*-tolualdehyde, and  $\alpha$ -naphthaldehydeoxime, m. p. 97.5°, whilst dithiocyclohexanecarboxylic and dithiophenylacetic acids give a mixture of the nitrile and the oxime, accompanied, in the latter case, by a trace of the acid amide.

J. W. BAKER.

**Methylation with formaldehyde.** H. EMDE (Apoth.-Ztg., 1929, 44, 1125—1127; Chem. Zentr., 1929, ii, 2318).—That *N*-methylation with formaldehyde depends on the change:  $2H \cdot CHO \rightarrow MeOAc \rightarrow H \cdot CO_2H + MeOH$  is supported by the fact that on careful distillation of aqueous formaldehyde solution with aqueous ammonia much methyl formate is produced; moreover, when paraformaldehyde is heated with aqueous hydrogen chloride considerable quantities of methyl chloride and formic acid are obtained. The formation of methylamine from ammonium chloride and formaldehyde is considered to be due to interaction of methyl chloride with the

ammonium chloride, or to the reactions:  $\text{NH}_4\text{Cl} + \text{H}\cdot\text{CHO} \rightarrow \text{NH}_2\cdot\text{CH}_2\cdot\text{OH} + \text{HCl}$ ;  $\text{NH}_2\cdot\text{CH}_2\cdot\text{OH} + \text{HCl} + \text{H}\cdot\text{CO}_2\text{H} \rightarrow \text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}, \text{HCl}$  (hypothetical)  $\rightarrow \text{NH}_2\text{Me}, \text{HCl} + \text{CO}_2$ . A. A. ELDRIDGE.

**Action of formaldehyde on potassium ferrocyanide in aqueous solutions. I—IV.** T. KIRIGAKUBO (J. Soc. Chem. Ind. Japan, 1929, 32, 357—359B).—By the action of formaldehyde on potassium ferrocyanide, potassium glycollate and glycollamide are formed either separately or together, depending on the experimental conditions. The gases evolved during the reaction are ammonia, hydrogen, and nitrogen, the first in considerable quantities. F. J. WILKINS.

**Condensation of isobutaldehyde.** V. GRIGNARD and N. ILIESCO (Compt. rend., 1930, 190, 556—559).—Self-condensation of isobutaldehyde in an equal volume of ether with 15% aqueous potassium hydroxide at  $-15^\circ$  gives a 60% yield of  $\beta$ -hydroxy- $\alpha\alpha$ -trimethylvaleraldehyde (Urbain, A., 1896, i, 590), b. p.  $79^\circ/6$  mm.,  $95$ — $96^\circ/14$  mm.,  $d_4^{20}$  0.954,  $n_D^{20}$  1.44717 (oxime, b. p.  $136$ — $137^\circ/14$  mm.; phenylurethane, m. p.  $63^\circ$ ). This aldol decomposes when distilled under ordinary pressure and on keeping becomes very viscous, the increase in its saponification value from 0 to 144.9 after 14 months indicating the occurrence of a Cannizzaro reaction. Formation of the crystalline product obtained by Brauchbar (A., 1897, i, 137) was not observed. Similar condensation of isobutaldehyde at  $10^\circ$  gives a 52% yield of the isobutyrate, b. p.  $104$ — $106^\circ/6$  mm.,  $d_4^{20}$  0.952,  $n_D^{20}$  1.44847, of  $\beta\beta$ -trimethyl- $n$ -pentane- $\alpha\gamma$ -diol, m. p.  $50.5^\circ$ , b. p.  $234^\circ/737$  mm.,  $d_4^{20}$  0.937,  $n_D^{20}$  1.45127 (diacetate, b. p.  $141$ — $142^\circ/20$  mm.,  $d_4^{20}$  0.972,  $n_D^{20}$  1.43332) (Lieben, A., 1896, i, 403), which is obtained on hydrolysis. The same ester, together with some isobutaldehyde, is also obtained by condensation of  $\beta$ -hydroxy- $\alpha\alpha$ -trimethylvaleraldehyde with 15% aqueous potassium hydroxide at  $-15^\circ$ . Dehydration of this aldol with concentrated potassium hydroxide at  $28$ — $30^\circ$  (Grignard and Abellmann, Bull. Soc. chim., 1910, 7, 638) gives a 35% yield of (?) $\alpha\alpha$ -trimethyl- $\Delta^2$ -pentenaldehyde, b. p.  $149$ — $150^\circ$ ,  $61$ — $62^\circ/14$  mm.,  $d_4^{20}$  0.871,  $n_D^{20}$  1.44707 (Fossek, A., 1884, 37) together with small quantities of the dimeride, b. p.  $127$ — $130^\circ/8$  mm., and the trimeride, b. p.  $156$ — $162^\circ/8$  mm., to which the structures  $\text{CHR} \begin{smallmatrix} \diagup \text{O} \diagdown \end{smallmatrix} \text{CHR}$  and  $\text{O} \begin{smallmatrix} \diagup \text{CHR} \diagdown \text{O} \end{smallmatrix} \text{CHR}$  [ $\text{R} = \text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2$ ], respectively, are assigned. Contrary to the results of Kirchbaum (A., 1904, i, 473), self-condensation of isobutaldehyde with solid potassium hydroxide at the ordinary temperature gives a mixture of  $\beta\gamma$ -dihydroxy- $\alpha\alpha\gamma\gamma$ -pentamethylheptaldehyde, b. p.  $188$ — $189^\circ/34$  mm. (29% yield), and its dehydration product,  $\beta$ -hydroxy- $\alpha\alpha\gamma\gamma$ -pentamethyl- $\Delta^2$ -heptenaldehyde, b. p.  $151$ — $153^\circ/34$  mm.,  $d_4^{20}$  0.903,  $n_D^{20}$  1.45207 (63% yield). Similar condensation with 50% potassium hydroxide gives the last-named aldehyde, the  $\text{C}_9$  aldol, the above isobutyrate, and traces of an unidentified substance, b. p.  $169$ — $175^\circ/18$  mm. J. W. BAKER.

**Synthesis of methyl  $n$ -octyl ketone.** K. MURAKAMI (Sci. Rep. Tōhoku, 1929, 18, 639—642).—Addition of an ethereal solution of heptaldehyde to a

well-stirred mixture of acetone and 5% sodium hydroxide solution below  $10^\circ$ , affords methyl  $\beta$ -hydroxyoctyl ketone, b. p.  $136.5$ — $137.5^\circ/15.5$  mm., and a small amount of  $\beta\beta'$ -dihydroxydioctyl ketone, m. p.  $90$ — $91^\circ$ . When the former ketone is heated with 0.01—0.02% of its weight of iodine at  $100^\circ$  and then distilled, methyl  $\Delta^2$ -octenyl ketone, b. p.  $101.5$ — $102.5^\circ/15.3$  mm. [semicarbazone, m. p.  $110$ — $111^\circ$  (lit.  $149^\circ$ )], is obtained. This is reduced catalytically (platinum-black) in ethereal solution to methyl  $n$ -octyl ketone. H. BURTON.

**Acylolins. I. Acetoin and its dimerides.** W. DIRSCHERL and E. BRAUN (Ber., 1930, 63, [B], 416—422).—Observations of the ultra-violet absorption spectrum of monomeric acetoin indicates the presence of the carbonyl group and hence of the preponderating, if not exclusive, existence of the keto-form,  $\text{COMe}\cdot\text{CHMe}\cdot\text{OH}$ , in the monomeride (cf. Bergmann and Ludewig, A., 1924, i, 490). In alcohol, the two dimerides of acetoin give almost the same extinction curve as the monomeride. Dissolution in alcohol does not cause fission of the dimerides, since they can be recovered crystalline after some hours and mol. wt. determinations of the isomeride of higher m. p. in the boiling solvent give normal values which decrease only when ebullition is prolonged. In the two crystalline forms the two acetoin molecules must therefore be united in such a manner that the keto-group and, consequently, the whole acetoin molecule remains unchanged in its main valency arrangement. The structure  $[\text{Me}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OH}]_2$  is therefore proposed. The possibility that groups other than carbonyl can give a similar extinction curve is negated by observations with epichlorohydrin and triacetylglucose anhydride. A dioxan structure is excluded, since dioxan itself is non-absorbent. Two ethereal oxygen atoms attached to the same carbon atom do not cause absorption as shown by the behaviour of methoxyacetaldehyde dimethylacetal. The dimeric methylacetal of acetoin does not exhibit the characteristic ketonic absorption, and hence is regarded as a dioxan derivative,  $\text{O} \begin{smallmatrix} \diagup \text{CHMe}\cdot\text{CMe}(\text{OMe}) \diagdown \\ \diagdown \text{CMe}(\text{OMe})\cdot\text{CHMe} \diagup \end{smallmatrix} \text{O}$ ; this view is in harmony with its relatively difficult depolymerisation. The dimeric acetoin has m. p.  $85^\circ$  and  $95^\circ$ , respectively, when very slowly heated (cf. Diels and Stephan, A., 1907, i, 1000), m. p.  $95^\circ$  and  $125^\circ$ , respectively, when very rapidly heated (cf. von Pechmann and Dahl, A., 1890, 1234). The transformation temperature of the dimerides into the monomeride appears, therefore, to lie below the m. p. H. WREN.

**Catalytic reduction of  $O$ -alkylated oximes.** L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1930, 52, 669—679).—Catalytic reduction of  $O$ -alkylketoximes in presence of platinum oxide and aqueous alcoholic hydrochloric acid affords varying amounts of the alkoxyamine hydrochlorides,  $\text{OAlk}\cdot\text{NH}\cdot\text{CRR}'$ , ammonium chloride, ketones, and alcohols. Thus  $O$ -methyl-diethyl and -dipropyl ketoximes furnish  $\gamma$ -methoxylaminopentane (48%), b. p.  $124^\circ$  [chloroplatinate, m. p.  $161^\circ$  (decomp.)]; phenylcarbamide derivative, m. p.  $59^\circ$ ; phenylthiocarbimide derivative, m. p.  $57^\circ$ ], and  $\delta$ -methoxylaminoheptane (38%), b. p.

164—166°, 88—89°/60 mm. (*phenylcarbimide* derivative, m. p. 109°), respectively. *O*-Methyl- and -ethyl-acetoximes afford  $\beta$ -methoxylaminopropane (17%), b. p. 76° [*chloroplatinate*, m. p. 183° (decomp.); *phenylcarbimide* derivative, m. p. 73°], and  $\beta$ -ethoxyaminopropane (4%), b. p. 78° [*chloroplatinate*, m. p. 174° (decomp.)], respectively.  $\beta$ -Methoxylaminopropane is also formed by the hydrolysis of *ethyl N*-methoxy-*N*-isopropylcarbamate, b. p. 164—167°/734 mm. (from *ethyl N*-methoxycarbamate and isopropyl iodide in presence of methyl-alcoholic sodium methoxide), with alcoholic potassium hydroxide. Similarly, *ethyl N*-methoxy-*N*- $\gamma$ -amylcarbamate, b. p. 196°, furnishes  $\gamma$ -methoxylaminopentane. Reduction of *O*-methylacetaldoxime gives a quantitative yield of ammonium chloride, whilst *O*-methylbenzaldoxime affords benzylamine and dibenzylamine [hydrochloride, m. p. 263° (corr.; lit. 256°)]. Methoxylamine hydrochloride gives ammonium chloride, and the formation of this in the above reductions is probably due to the intermediate production of alkoxyamine hydrochlorides from the *O*-alkylketoximes or aldoximes.

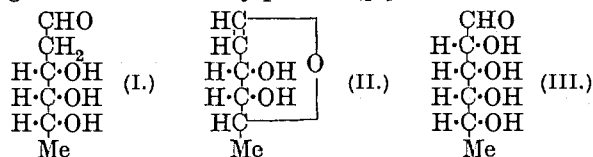
Reduction of *O*-ethylacetaldoxime in presence of acetic anhydride furnishes ethyl acetate and acetethylamide.

H. BURTON.

**Carbohydrate of thymonucleic acid.** P. A. LEVENE, L. A. MIKESKA, and T. MORI (J. Biol. Chem., 1930, 85, 785—787).—Repetition of the work of Levene and Mori (A., 1929, 1277) shows that the previous observations were erroneous, and that the carbohydrate of thymonucleic acid is, in fact, *d*-2-deoxyribose. 1-2-Deoxyribose (from arabinol,  $[\alpha]_D^{25} -263.5^\circ$  in chloroform) had  $[\alpha]_D^{25} +91.7^\circ$  to  $+40.5^\circ$  in pyridine; when heated it softened at 67°, melted at 80°, and cleared at 154°; the *phenylbenzylhydrazone* had m. p. 125—126°,  $[\alpha]_D^{25} +17.5^\circ$  in pyridine. On oxidation with hypiodite the deoxyribose gave an acid,  $[\alpha]_D^{25} +8.5^\circ$  (*barium salt*,  $[\alpha]_D^{25} -0.43^\circ$ ), which yielded a lactone,  $[\alpha]_D^{25} -12.2^\circ$ . C. R. HARRINGTON.

**Configuration of digitoxose.** F. MICHEEL (Ber., 1930, 63, [B], 347—359).—Digitoxose has been shown by Kiliani (A., 1922, i, 224) to be a 2:6-deoxyhexose in which application of Hudson's rules enables the position of the hydroxyl groups attached to carbon atoms 3 and 4 to be fixed. The arrangement round the C5 atom has been elucidated by Windaus and Schwartz (Nachr. Ges. Wiss. Göttingen, 1926), who isolated, by oxidation of Cloetta's anhydrodigitoxose (A., 1921, i, 39), a compound which they regarded as *l*-altromethylose. This last-named compound is not identical with the *l*-altromethylose of Freudenberg and Raschig (A., 1929, 427). Repetition of Kiliani's work confirms the observations of this author. Explanation of the discrepancy is found in the examination of the aldomethtetose obtained by the action of ozone on Cloetta's anhydrodigitoxose. Since the *p*-bromophenylosazone of this compound is not identical with that derived from *l*-lyxomethylose (cf. Votoček, A., 1917, i, 250) and the hydroxyls attached to the carbon atoms 3 and 4 in digitoxose (2 and 3 in the methyltetose) are in the *cis*-position, the product must necessarily be a ribomethylose. This view is confirmed by the identity of its phenylosazone and

*p*-bromophenylosazone with those derived from *d*-arabomethylose. It is thus shown that the hydroxyls attached to the carbon atoms 4 and 5 in digitoxose are in the *cis*-position, and since those in 3 and 4 are also similarly placed (as shown by oxidation) the structures I and II are assigned to digitoxose and anhydrodigitoxose. The methylpentose ( $[\alpha]_D -1.0^\circ$  in water;



equilibrium value) must be either a *d*-altromethylose or *d*-allomethylose. The former view is excluded, since it is not the antipode of *l*-altromethylose and the compound is regarded as *d*-allomethylose (III). Comparison of the constants of the phenylosazones of the methylpentose and *l*-altromethylose shows the substances to be antipodes. It therefore appears that Hudson's rule is not valid for digitoxonic acid or digitoxosecarboxylolactone.

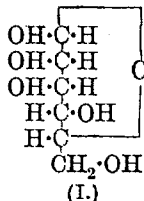
Anhydrodigitoxose is converted by acetic anhydride and pyridine into the diacetate, m. p. 47—50°,  $[\alpha]_D^{25} +387^\circ$  in chloroform, which is transformed by ozone in acetic acid and subsequent treatment with zinc dust into the non-crystalline diacetyl-*d*-ribomethylose,  $[\alpha]_D$  about  $+43^\circ$  in chloroform. The diacetyl compound is hydrolysed and transformed into the *p*-bromophenylosazone, m. p. 160—161°,  $[\alpha]_D^{25} \pm 0^\circ$ , and phenylosazone, m. p. 173—174°,  $[\alpha]_D^{25} -63.2^\circ$  in pyridine and alcohol (2:3), of *d*-ribomethylose. Diacetyl-*l*-rhamnal is successively ozonised, hydrolysed, and converted into the *p*-bromophenylosazone, m. p. 160—161°,  $[\alpha]_D^{25} \pm 0^\circ$ , and phenylosazone, m. p. 172—174°,  $[\alpha]_D^{25} +66.0^\circ$  in pyridine and alcohol (2:3), of *l*-arabomethylose. Acetobromo-*d*-glucosomethylose is transformed by zinc dust and acetic acid into diacetyl-*d*-rhamnal,  $[\alpha]_D^{25} -68.5^\circ$  in chloroform, which is transformed into the *p*-bromophenylosazone, m. p. 160—161°,  $[\alpha]_D^{25} \pm 0^\circ$ , and phenylosazone, m. p. 172—174°,  $[\alpha]_D^{25} -65^\circ$  in pyridine and alcohol (2:3), of *d*-arabomethylose identical with the compounds derived from the methyltetose from digitoxose. H. WREN.

**Absorption measurements in the ultra-violet with the thermo-column and their application to problems of sugar chemistry.** F. GOOS, H. H. SCHLUBACH, and G. A. SCHRÖTER (Z. physiol. Chem., 1930, 186, 148—156).—The ultra-violet absorption of some dextrose derivatives was tested by a method described. Pure dextrose,  $\alpha$ -methylglucoside in water, and pentamethylglucose in alcohol, showed no absorption band at 2800 Å., but pentamethylglucose with a free aldehydic group in ethereal solution showed a greatly increased general absorption in the ultra-violet and a band at 2800 Å. This indicates that dextrose freshly dissolved in water is present as the aldehyde only in minimal amount. The pyranoid ring shows only slight spectrographic differences from the furanoid structure. J. H. BIRKINSHAW.

**Configuration of  $\alpha$ - and  $\beta$ -forms in the sugar series.** F. MICHEEL and H. MICHEEL (Ber., 1930, 63, [B], 386—393).—The action of trimethylamine on  $\alpha$ -acetobromoglucose and  $\alpha$ -acetobromogalactose

yields salts of quaternary bases, which, by reason of their optical activity, are probably  $\beta$ -forms. Since the substituents attached to carbon atoms 1 and 2 in the sugars are in the *cis*-position, the quaternary salts are *trans*-compounds. The *trans*-compound, 1-chloro-3:4:6-triacetyl-2-trichloroacetylglucose, on the other hand, does not yield a quaternary base with trimethylamine under any conditions. If, however, the conditions are such that the trichloroacetyl group becomes displaced, the 1-chloro-3:4:6-triacetylglucose becomes isomerised gradually to the  $\alpha$ -form, which yields a *trans*-compound with trimethylamine. Acetochloro- $\alpha$ -D-mannose, acetobromo- $\alpha$ -D-mannose, m. p. 48–50°,  $[\alpha]_D^{20} +122.1^\circ$  in chloroform, and acetobromo- $\alpha$ -L-rhamnose do not afford quaternary ammonium salts and hence belong to the *trans*-type ((?)2:3:4:6-tetra-acetylmannose, m. p. 159–160°,  $[\alpha]_D^{19} -24.2^\circ$  in chloroform, is obtained as by-product). Acetobromo- $\beta$ -L-arabinose gives trimethyltriacetyl-L-arabinosidoammonium bromide,  $[\alpha]_D^{20} +27.6^\circ$  in water.  $\alpha$ -Acetochlorofructose,  $[\alpha]_D^{20} +41^\circ$ , reacts unusually vigorously with trimethylamine, but the instability of the quaternary salt inhibits its isolation, whereas  $\beta$ -acetochlorofructose,  $[\alpha]_D^{20} -160^\circ$  in chloroform, is unaffected.

The configurations for the  $\alpha$ - and  $\beta$ -forms of the sugars investigated, as deduced from their behaviour towards trimethylamine, agree with those deduced from the considerations of Haworth and Hirst (A., 1928, 740); they are also in harmony with the results of Böeseken's measurements (A., 1921, i, 843) except in the case of  $\alpha$ -D-mannose to which the configuration I is ascribed. H. WREN.



**Numerical relationships in the fructose series.** H. H. SCHLUBACH and G. A. SCHRÖTER (Ber., 1930, 63, [B], 364–367).—Difficulties are encountered in applying Hudson's methods in the fructose series, since the differences in the activities of the compounds of the  $\alpha$ -series in different solvents are unusually great, whereas smaller differences are observed in the  $\beta$ -series, and hence the magnitude of the increment depends greatly on the choice of solvent. A universal solvent has not been discovered. The following specific rotations are recorded: methylfructoside,  $\alpha +46.5 \pm 1^\circ$  in water,  $+92.7 \pm 1^\circ$  in ethyl alcohol,  $+91 \pm 3^\circ$  in ethyl acetate;  $\beta -172 \pm 0.5^\circ$  in water,  $-172.7 \pm 1^\circ$  in ethyl alcohol,  $-164 \pm 4^\circ$  in ethyl acetate; tetra-acetylmethylfructoside,  $\alpha +45.5 \pm 0.5^\circ$  in chloroform,  $+57 \pm 0.5^\circ$  in ethyl alcohol,  $+44.3 \pm 0.5^\circ$  in ethyl acetate;  $\beta -124 \pm 1.5^\circ$  in chloroform,  $-118 \pm 1.5^\circ$  in ethyl alcohol,  $-123 \pm 1.5^\circ$  in ethyl acetate; tetramethylmethylfructoside,  $\alpha +16.7 \pm 1.5^\circ$  in water,  $+83.7 \pm 1^\circ$  in chloroform,  $+90 \pm 1.5^\circ$  in ethyl alcohol,  $+93 \pm 2.5^\circ$  in ethyl acetate;  $\beta -149.8 \pm 0.8^\circ$  in water,  $-137 \pm 0.7^\circ$  in chloroform,  $-124.5 \pm 1^\circ$  in ethyl alcohol,  $-113.7 \pm 1^\circ$  in ethyl acetate. The conclusion is reached that the increments calculated from the values of the aldose series cannot be applied in the ketose series, in which the values are markedly higher.

$\alpha$ -Methylfructoside, m. p. 102°, is conveniently prepared by hydrolysing its tetra-acetyl derivative with ethyl-alcoholic dimethylamine. H. WREN.

Oroboside, a new glucoside hydrolysed by emulsin, extracted from *Orobis tuberosus*, L., and its products of hydrolysis, dextrose and orobol. M. BRIDEL and C. CHARAUX (Compt rend., 1930, 190, 387–389; cf. this vol., 383).—Oroboside,  $\text{C}_{21}\text{H}_{40}\text{O}_{11}$ , m. p. 220–221°,  $[\alpha]_D^{20} -61.29^\circ$  (anhydrous) in pyridine, is hydrolysed by dilute acid or slowly by emulsin to give dextrose and orobol,  $\text{C}_{15}\text{H}_{10}\text{O}_6$ , m. p. 270.5°, which is probably a tetrahydroxyflavone, with at least two adjacent hydroxyl groups. Colour reactions are described. R. K. CALLOW.

**Action of mercury salts on acetohalogeno-sugars. II. Conditions for the formation of  $\alpha$ -phenylcellobioside.** G. ZEMPLÉN and Z. S. NAGY (Ber., 1930, 63, [B], 368; cf. Zemplén, A., 1929, 683).—The presence of aluminium filings is not necessary for the preparation of hepta-acetyl- $\alpha$ -phenylcellobioside from acetobromocellobiose, phenol, and mercuric acetate in benzene. The amount of mercuric salt employed should be rather less than that required to convert the liberated hydrogen bromide into mercuric bromide, but a considerable quantity of hydrogen bromide diminishes the yield of hepta-acetyl- $\alpha$ -phenylcellobioside owing to its decomposing action. With larger amounts of mercuric acetate the production of hepta-acetylcellobiose is facilitated. H. WREN.

**Sinistrin A [dilævan] as product of the degradation of inulin.** H. H. SCHLUBACH and H. ELSNER (Ber., 1930, 63, [B], 362–364).—Depolymerisation of inulin ("album nach Kiliani") in glycerol (cf. Vogel and Pictet, A., 1928, 276) affords a dilævan apparently identical with sinistrin A obtained by Schlubach and Flörshiem (A., 1929, 914) from *Scilla maritima*. Products other than those obtained by the Swiss chemists appear to be derived for "Inulin high purity" (Digestive Ferments Co.). Treatment of the depolymerised material with methyl sulphate and alkali hydroxide yields the trimethyl derivative of a complex, inulin-like polymerisation product, m. p. 106–114°,  $[\alpha]_D^{20} -37.9^\circ$  in chloroform, hydrolysed by alcoholic oxalic and hydrochloric acids to 3:4:6-trimethyl- $\gamma$ -fructose, b. p. 115°/0.01 mm.,  $n_D^{20} 1.4640$ ,  $[\alpha]_D^{20} +28.2^\circ$  in chloroform (osazone, m. p. 79–81°), identical with the product obtained by Haworth and Learner from inulin (A., 1928, 510) and by Schlubach and Flörshiem (*loc. cit.*) from sinistrin A.

H. WREN.  
**Constitution of starch and cellulose.** H. PRINGSHEIM (Suomen Kem., 1930, 3, 1–9).—A lecture. T. H. MORTON.

**Cellulose. XXXVI. Determination of mol. wt. in glacial acetic acid.** K. HESS (Ber., 1930, 63, [B], 518–534).—The customary purification of acetic acid by fractional distillation followed by fractional solidification is adequate for the determination of the mol. wt. of "normal substances," but not for those of cellulose derivatives. Better specimens are obtained by careful fractional distillation, using Hahn's apparatus (A., 1910, ii, 183). Sufficient criteria of the suitability of specimens of the acid are afforded by the m. p. (highest recorded m. p. 16.65  $\pm 0.02^\circ$ ) and specific conductivity which may not exceed  $k_{18} = 3.24 \times 10^{-8}$ . The properties of the best



specimens remain unchanged by prolonged preservation in the presence of magnesium perchlorate, boron triacetate, or anhydrous copper sulphate, followed by direct distillation at  $20^{\circ}/>0.005$  mm. into the freezing apparatus. The cryoscopic behaviour of acetone-soluble cellulose acetate (cellite) in glacial acetic acid of three grades (all sufficiently pure for "normal substances") in an apparatus permitting measurements to less than  $\pm 0.0015^{\circ}$  and with supercooling regulated to  $0.25-0.4^{\circ}$  gives exactly reproducible results for individual specimens, but the behaviour of different samples is irregular and the relationship of cellulose acetate to glacial acetic acid appears complex. In very dilute solution fibrous and Ost's cellulose triacetate and trimethylcellulose give disproportionately great depressions which increase markedly with increasing concentration; the effect can scarcely be ascribed to minute traces of water introduced with the specimens. With amylose acetate there is no evidence of the existence of particles of mol. wt. 288. With inulin acetate the apparent mol. wt. is 1200, but the actual value cannot be deduced. The earlier explanation of the large depressions with "customary acetic acid" must be abandoned. With the hexa-acetyl-biosan of Hess and Friese, scarcely any depression is observed with a 0.014% solution. Between 0.19 and 0.569% the depression increases proportionally with the concentration and corresponds with the mol. wt. 554-587 (theory 576). The depressions range from  $0.013^{\circ}$  to  $0.040^{\circ}$  and are strictly reproducible, the undercooling ( $0.4-0.6^{\circ}$ ) being sufficiently great to permit rapid registration by the thermometer as closely as possible to the true f. p. With concentrations exceeding 0.569% there is only a slight increase of the depression, indicating the probable saturation concentration of the molecular-disperse phase.

The biosan acetate is closely related to cellulose acetate. Cellulose fibre treated at above  $70-80^{\circ}$  affords the biosan acetate, whereas below this temperature cellulose acetate I results. Similarly, the biosan acetate separates from solutions above a certain temperature [about  $80^{\circ}$  for pyridine, about  $30^{\circ}$  for chloroform-methyl alcohol (1:1)], whereas below this limit cellulose acetate I is deposited. The biosan acetate appears to be derived from hydrocellulose. Cellulose acetate I appears to be an equilibrium mixture of acetates, one of which is derived from hydrocellulose, whereas the other is formed from a carbohydrate closely related to that of the natural cellulose. In solution in organic media, cellulose acetate gives a mixture of two components of which the equilibrium is dependent on temperature and nature of solvent. In the solution of cellulose acetate, morphological factors must also be considered. The assumption that the properties of natural cellulose fibres are even approximately identical with those of chemically pure cellulose is erroneous.

H. WREN.

[Determination of mol. wt. in glacial acetic acid.] K. FREUDENBERG and E. BRUCH (Ber., 1930, 63, [B], 535-536).—A reply to Hess (preceding abstract; cf. Freudenberg and others, this vol., 198). The authors maintain their view that the biosan acetate in 0.2% solution does not show the

properties of a molecular-disperse substance and the irregularities establish the unsuitability of freezing acetic acid or, more generally, of the cryoscopic method for the determination of the true mol. wt. of this substance, since it is very great. The conditions selected by Hess are arbitrary. The main source of uncertainty lies in the delay of crystallisation; if this can be avoided, data approaching the actual mol. wt. may be expected.

H. WREN.

Intermediate products of the hydrolysis of cellulose and chemical determination of their mol. wt. M. BERGMANN and H. MACHEMER (Ber., 1930, 63, [B], 316-323).—All isolable products of the degradation of celluloses acetates reduce alkaline iodine solution and the iodine consumption is an accurate and reproducible measure of the free aldehydic groups and the mol. wt. of the compounds. The acetyl groups are removed from the acetylated compound by sodium hydroxide and the product, without isolation of the carbohydrate, is immediately oxidised with iodine. The quantity of 0.1N-iodine solution required by 1 g. of substance is termed the iodine number. Since the number for aldohexoses and aldopentoses is 111 and 133, respectively, these types of sugar can be readily distinguished analytically, which is impossible by the copper method. The mol. wt. is calculated from the expression  $M=20,000 \div \text{iodine number}$ . The iodine consumption of ketoses and non-reducing saccharides and sugar anhydrides is so slight that the compounds cannot be mistaken for aldoses or sugars with free aldehydic group. Technical cellulose acetate is degraded with hydrogen bromide in glacial acetic acid; the product is separated by hot methyl alcohol in acetylsaccharide A [analogous to the acetylcellobiose anhydrides of Bergmann and Knehe (A., 1925, i, 1384)] and acetylsaccharide B. Determination of the iodine numbers of the respective materials indicates in them the presence of mixtures of polysaccharides containing, as an average, 8 or 9-11 hexose residues. The product obtained by the acetolysis of cellulose according to Hess and Friese (A., 1927, 44) is separated into a number of fractions which appear to contain 8-13 hexose residues. The establishment of the polysaccharide nature of the more complex products of the degradation of cellulose and the presence in them of non-glucosidic, aldehydic groups indicates the possibility of reaction with phenylhydrazine to yield hydrazone or osazone and the probable variation of the amount of phenylhydrazine with the length of the chain. Acetylsaccharide A is converted by phenylhydrazine at  $130^{\circ}$  into a compound containing 2.4% N, whereas Hess and Friese's mixture yields a product with 1.5% N.

H. WREN.

Integral relationship between cellulose and the less soluble xylan in the structural element of red beech (*Fagus sylvatica*). E. SCHMIDT, K. MEINEL, K. NEVROS, and W. JANDEBEUR (Cellulose-chem., 1930, 11, 49-68).—When beechwood meal is delignified by chlorine dioxide and sodium sulphite in the usual manner, the residue is not gravimetrically stable to repeated treatment with the reagents. This may be assigned to excessive alkalinity of the

sulphite; by maintaining the  $p_H$  between 6.8 and 7.5 during treatment with the latter lignin may be removed quantitatively in 6–8 operations with a loss of but 0.2% of the structural carbohydrate at each stage. The cell-wall constituents so obtained consist of a hemicellulose containing carboxyl ("easily soluble xylan"), a less soluble xylan, and cellulose proper. The distribution of the pentosan content of this structural material has been investigated by the determination of the loss of weight which occurs in samples dried at  $78^\circ/0.0002$  mm. when extracted with sodium hydroxide solutions of varying concentrations. The hemicellulose is completely soluble in 0.04–0.2% sodium hydroxide and amounted, in the various samples of beechwood examined, to 15.3–27.4%. At this concentration the less soluble xylan is not attacked, but may be completely removed by treatment with 5% sodium hydroxide. Loss of cellulose is prevented by the use of a 5% sodium hydroxide solution containing 3% of sodium chloride. In all cases the relation of the cellulose to the less soluble xylan was found to be in the ratio of 3 mols. of glucose anhydride ( $C_6H_{10}O_5$ ) to 1 mol. of xylose anhydride ( $C_5H_8O_4$ ). This relationship is independent of the geographical origin of the beech and is found both in 8- and 80-year wood, in sapwood, and in heartwood. It is suggested that both the xylan and the cellulose are integral parts of the structural material and that their formation is interdependent. This stoichiometric relation has been confirmed by determination of the pentosan content by the production of furfuraldehyde by distillation with hydrochloric acid and also by the isolation of the xylan from the alkaline liquors.

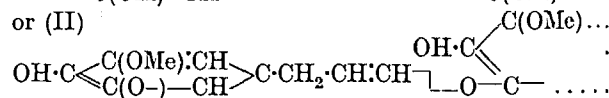
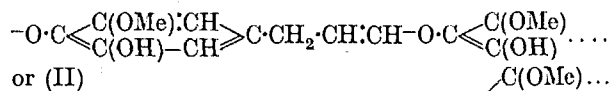
The complete drying of cellulose, which has previously been extracted with alkali, produces a further fraction (about 2%) which is soluble in 5% sodium hydroxide solution. T. H. MORTON.

**Methylation of beechwood and hydrolysis of the methylated product.** Beechwood lignin. A. VON WACEK (Ber., 1930, **63**, [B], 282–296; cf. A., 1928, 1227).—The mixture of cellulose methyl ethers soluble in water obtained previously (*loc. cit.*) is converted by methyl-alcoholic hydrogen chloride under pressure into 2:3:6-trimethylglucose, m. p. 114–115°. Isolation of the cellulose ethers from the methylated wood is effected also by Cross and Bevan's method. The product, however, still contains materials which are soluble in acetone. The products obtained after the Friedrich hydrolysis (*loc. cit.*) contains material which can be removed by Cross and Bevan's process and hence methyl-lignin is present which cannot be brought into solution by hydrolysis. Repeated chlorination of the hydrolytic product, followed by prolonged treatment of the residue with boiling acetone, leaves a colourless mixture of non-homogeneously methylated cellulose.

The percentage of methoxyl (26.5) in the methyl-lignin described previously (*loc. cit.*) is unexpectedly low and appears to be caused by long preservation of the acetone solution previous to precipitation. Methyl-lignin from freshly-prepared acetone solution uniformly contains 33–35% OMe, raised by exhaustive methylation to 35.2%. Methyl-lignin, pre-

cipitated from cold, freshly-prepared solution in acetone, cannot be hydrogenated in acetone or acetic acid with or without pressure. Under drastic conditions, the methoxyl content becomes greatly reduced.

A scheme is elaborated according to which the phenols of beechwood tar may be regarded as arising from 2:6-dimethoxy-4-allylphenol. The possibilities are examined that the residue of this substance may be present in lignin in the form (I)



Treatment of primary methyl-lignin with sodium ethoxide under pressure at 150–160° results in its conversion to the extent of 60–70% into an oil soluble in ether, a part of which (15–20% of the primary methyl-lignin) can be distilled in a vacuum. The distillate can be separated by alkali hydroxide into a soluble and an insoluble portion, from which crystals occasionally separate in very small amount. The neutral oil rapidly decolorises permanganate, thus rendering probable the presence of a double linking. It contains 35.16% OMe, whereas 31.41% is present in the alkali-soluble portion. The neutral oil is oxidised by permanganate to 3:5-dimethoxybenzoic acid. The methoxyl groups are therefore present in the *meta*-position to one another, thus supporting the formula I (see above). Since the comparatively mild conditions of the degradation appear to exclude the possibility of the formation of aromatic compounds during the process, the presence of such a complex in beechwood lignin seems to be placed beyond doubt.

H. WREN.

**Lignin. IV. Lignin from oat hulls.** M. PHILLIPS (J. Amer. Chem. Soc., 1930, **52**, 793–797).—The hulls are extracted first with 2% alcoholic sodium hydroxide at the ordinary temperature and then with 4% aqueous sodium hydroxide at 100°. The lignin from the alcoholic extract contains three hydroxyl (*triacetate*) and four methoxyl groups (Zeisel; Kirpal and Bühn, A., 1914, ii, 497; 1916, ii, 154); it has the composition  $C_{40}H_{46}O_{16}$ . The lignin (*triacetate*) from the aqueous extract also contains three hydroxyl and four methoxyl groups; it has the composition  $C_{42}H_{40}O_{16}$ . Phenyltrimethylammonium iodide has m. p. 231.6° (corr.; lit. 211–212°). H. BURTON.

**De-alkylation of tertiary amines by organic acids.** J. VON BRAUN and K. WEISSBACH (Ber., 1930, **63**, [B], 489–497).—The reaction of acid anhydrides with tertiary bases resembles that of acid chlorides, but takes place so slowly that it cannot be utilised in determining tenacity series. With organic acids de-alkylation takes place more slowly than with cyanogen bromide, but can readily be conducted in such a manner as to elucidate the sequence in which the individual alkyl residues are eliminated. The tenacity series determined in this manner at about 200° coincides with that obtained by the use of cyanogen bromide, but the neighbouring residues are

not so sharply differentiated from one another under the more drastic experimental conditions.

The acids employed are acetic, palmitic, benzoic, and  $\beta$ -phenylpropionic; operations in sealed tubes are necessary only with acetic acid. The product is dissolved in ether and shaken successively with alkali and acid. The neutral portion contains the *N*-acyl derivatives and, usually, ester derived from the acid and eliminated alcohol. With acetic acid and aromatic bases small amounts of basic acetophenone derivatives and of diphenylmethane compounds (produced from formaldehyde derived from the liberated methyl alcohol) are formed. The open-chain monoamines examined include methylethylaniline, ethylpropylaniline, benzylmethylaniline, benzyldimethylamine, dimethyl- $\epsilon$ -phenyl-*n*-amylamine, dimethyl-*n*-octylamine, and dimethyl-*n*-decylamine. The following compounds appear to be new:  $\beta$ -phenylpropionmethylanilide, b. p. 146—148°/0.3 mm.; palmitmethylanilide, b. p. 228—230°/0.5 mm., m. p. 37—38°;  $\beta$ -phenylpropionmethylanilide, b. p. 150—152°/0.3 mm.;  $\beta$ -phenylpropionbenzylanilide, b. p. 218—220°/0.2 mm.;  $\beta$ -phenylpropionmethyl-*n*-decylamide, b. p. 172—176°/15 mm.; benzomethyl-*n*-decylamide; diethyl-*n*-octylamine, b. p. 98°/13 mm. (non-crystalline hydrochloride; very hygroscopic methiodide);  $\beta$ -phenylpropionmethyl-*n*-octylamide, b. p. 172—175°/13 mm.

2-Methyltetrahydroisoquinoline is converted by boiling  $\beta$ -phenylpropionic acid into 2- $\beta$ -phenylpropionyltetrahydroisoquinoline, b. p. 190—192°/0.2 mm.; a similar change occurs with benzoic acid. Under like conditions, tropane affords benzoylnortropine, b. p. 204—205°/14 mm., m. p. 94—95°, and  $\beta$ -phenylpropionylnortropine, b. p. 176—178°/0.4 mm.

Tetramethyldiaminodiphenylmethane and  $\beta$ -phenylpropionic acid give the compound  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , b. p. 260—264°/0.3 mm.; the corresponding triethyl derivative, b. p. about 265°/0.2 mm., is hydrolysed to triethyldiaminodiphenylmethane, b. p. 255—258°/14 mm. (non-crystalline hydrochloride; picrate, m. p. 145°).

Ethyl  $\beta$ -o-dimethylaminophenylpropionate, b. p. 150—152°/16 mm., is converted by successive treatment with hydrochloric acid and sodium acetate into  $\beta$ -o-dimethylaminophenylpropionic acid, which passes when heated into *N*-methylhydrocarbostyryl (cf. Mayer and others, A., 1928, 1257). H. WREN.

By-products obtained in the reduction of phenylhydrazones to primary amines. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1929, 61, 1309—1315).—During the reduction of phenylhydrazones by aluminium amalgam, besides the primary amines, a certain amount of the secondary amines, together with aniline, are obtained as by-products. Methyl ethyl ketone phenylhydrazone gave diisobutylamine (which was precipitated as the diphenylthiocarbamide derivative, m. p. 144—145°, by the addition of phenylthiocarbimide); the phenylhydrazone of isovaleraldehyde gave diisoamylamine (diphenylthiocarbamide derivative, m. p. 148—149.5°); diphenylcarbamide derivative, m. p. 230—230.5°), and heptaldehydephenylhydrazone yielded diheptylamine, b. p. 271—275° (diphenylthiocarbamide deriv-

ative, m. p. 150—151°; diphenylcarbamide derivative, m. p. 225—225.5°). In the course of all three reactions, some aniline was produced. M. ZVEGINTZOV.

Condensation of  $\beta\gamma$ -diaminobutane with carbon disulphide. L. ZAHLOVA (Coll. Czech. Chem. Comm., 1930, 2, 108—111).—The first product obtained by the condensation of diaminobutane and carbon disulphide in alcoholic solution is  $\beta$ -amino-butane- $\gamma$ -dithiocarbamic acid, m. p. 144°, which very easily loses hydrogen sulphide in the formation of *s*-dimethylethylenethiocarbamide,  $\begin{matrix} \text{CHMe}\cdot\text{NH} \\ \text{CHMe}\cdot\text{NH} \end{matrix} > \text{CS}$ , m. p. 198°. This latter is stable and yields in aqueous solution the insoluble salts,  $\text{C}_5\text{H}_{10}\text{N}_2\text{S}\cdot\text{HgCl}_2$  and  $(\text{C}_5\text{H}_{10}\text{N}_2\text{S})_2\cdot\text{PtCl}_4$ . T. H. MORTON.

Hexamethylenetetramine. I. Hexamethylenetetramine and hydrogen peroxide. II. Action of halogens. D. MAROTTA and M. E. ALESSANDRINI (Gazzetta, 1929, 59, 942—946, 947—954).—I. When treated in acetic acid solution with hydrogen peroxide, hexamethylenetetramine undergoes hydrolysis to methyleneimine and trihydroxytrimethylamine, the latter then undergoing further change into the insoluble hexamethylenetriperoxide-diamine (cf. Baeyer and Villiger, A., 1900, i, 627). This reaction of hexamethylenetetramine confirms the formula  $\text{N}(\text{CH}_2\cdot\text{N}\cdot\text{CH}_2)_3$  attributed to it by Cambier and Brochet (A., 1895, i, 262).

II. The action of bromine or iodine on hexamethylenetetramine dissolved in various solvents gives rise to additive compounds containing (1) two and (2) four halogen atoms, which are loosely bound. The action of chlorine, however, appears to give highly unstable chloro-substituted hexamethylenetetramines, which decompose into ammonium chloride and chlorinated hydrocarbons. T. H. POPE.

Acetylation of amino-acids by keten. M. BERGMANN and F. STERN (Ber., 1930, 63, [B], 437—439).—The difference between the rate of reaction of keten with water and amino-acids is so great that the latter compounds can be advantageously acetylated with the reagent in aqueous solution. The carboxyl group may be neutralised by alkali, thus permitting the use of freely soluble alkali salts. Even in the absence of alkali the freely soluble glycine and sparingly soluble leucine are readily acetylated. The following examples are cited: glycine to aceturic acid; *dl*-alanine, *dl*-leucine, *dl*-phenylalanine, *l*-tyrosine, and *d*-glutamic acid to their acetyl derivatives. In absence of alkali, *o*- and *p*-aminophenol give their *N*-monoacetyl derivatives in good yield. H. WREN.

Superfluous stereoisomerides of  $\gamma$ -amino- $\beta$ -hydroxy-*n*-butyric acid. M. BERGMANN and M. LISSITZIN (Ber., 1930, 63, [B], 310—313).—The *l*- $\gamma$ -benzamido- $\beta$ -hydroxybutyric acid I,  $[\alpha]_D -7.2^\circ$ , of Tomita and Sendju (A., 1927, 1058) is not homogeneous, since it can be separated by crystallisation from alcohol into fractions of widely differing specific rotation. This is true also for the corresponding *d*-acid I so that, in accordance with theory, there are only two optically active (hydrated)  $\gamma$ -benzamido- $\beta$ -hydroxybutyric acids,  $[\alpha]_D -11.84^\circ$  and  $+10.0^\circ$  in water. The acids I are regarded as molecular com-

pounds of 1 mol. of active and 1 mol. of *dl* acid (and hence are designated *lld*- ( $[\alpha]_D -7^\circ$ ) and *ddl*- ( $[\alpha]_D +7^\circ$ ) -benzamido-hydroxybutyric acids) for the following reasons. The *l*-benzamido-acid II when polarised in 0.5*N*-sodium hydroxide is almost exactly thrice as active as the *l*-benzamido-acid I under the same conditions. The *dl*-benzamido-acid when air-dried is anhydrous, whereas the *l*-acid II is monohydrated; a simple mixture of the acids must therefore contain water of crystallisation, whereas the *l*-acid I is anhydrous. Crystallisation of a mixture of the *l*-benzamido-acid II with an equal or double quantity of the *dl*-acid from water yields a product having  $[\alpha]_D$  about  $-7^\circ$  in 0.5*N*-sodium hydroxide. The relationships with the *d*-benzamido-acid I are the same as with the *l*-acid I. The free amino-acids,  $[\alpha]_D -21^\circ$  and  $+18.3^\circ$ , are more or less individual antipodes. It is not established whether the acids,  $[\alpha]_D -3.4^\circ$  and  $+3.2^\circ$  respectively, are mixtures of the active acids and the *dl*-forms or complex molecular compounds.

H. WREN.

**Method of assigning optically active  $\alpha$ -amino-acids to the *d*- or *l*-series.** I. O. LUTZ and B. JIRGENSONS (Ber., 1930, 63, [B], 448—460; cf. A., 1929, 1283).—The standard material adopted is natural *L*-aspartic acid. For any particular acid, a constant weight of material is taken and the individual samples are treated with increasing amounts of acid or alkali. The graph is plotted showing the relationship between optical rotation of the solution and number of added molecules of hydrogen chloride or sodium hydroxide. The most characteristic portions of the curves are those lying in the acid region. With increasing concentration of acid the rotation increases in the positive sense for *lævo*-antipodes and in the negative sense for *dextro*-antipodes.

The following natural amino-acids all belong to the *lævo*-series: aspartic acid from asparagine; glutamic acid from vegetable protein; alanine from silk; leucine from casein; tyrosine from silk; cystine from hog's bristles. *L*-Anilinosuccinic, *l*-*o*-toluidinosuccinic, and *l*-*p*-phenetidinosuccinic acids belong to the *lævo*-series whereas *d*-methylaminosuccinic acid belongs to the *dextro*-group. The acids are obtained from *l*-bromosuccinic acid and the requisite base.

H. WREN.

**Aminohydroxy-acids.** W. J. N. BURCH (J.C.S., 1930, 310—312).—Treatment of glutaconic acid with a large excess of hypochlorous acid and subsequent neutralisation with barium hydroxide affords barium  $\alpha$ -chloro- $\beta$ -hydroxyglutarate. When the free chloro-hydroxy-acid is treated with methyl-alcoholic ammonia, ammonium dihydroxyglutaramate (the free acid reduces ammoniacal silver nitrate) is produced. Crotonic acid and a 25% excess of hypochlorous acid afford a product, which with methyl-alcoholic ammonia at  $120^\circ$  yields probably a mixture of  $\beta$ -amino- $\alpha$ -hydroxy- and  $\alpha$ -amino- $\beta$ -hydroxy-butyric acids (silver and cinchonine salts) (cf. Dakin, A., 1922, i, 143). Similarly, tiglic acid furnishes  $\alpha$ -amino- $\beta$ -hydroxy- $\alpha$ -methylbutyric acid (silver and brucine salts) and the isomeric  $\beta$ -amino-acid; acrylic acid gives serine and isoserine, whilst maleic acid affords hydroxy-aspartic acid (cf. Dakin, loc. cit.).  $\alpha$ -Chloro- $\beta$ -hydr-

oxyglutaric acid is not converted into hydroxy-glutamic acid by Gabriel's method. H. BURTON.

**Action of organo-magnesium compounds on aliphatic dialkylamides.** (Mlle.) M. MONTAGNE (Ann. Chim., 1930, [x], 13, 40—135).—Partly a more detailed account of work previously abstracted (A., 1926, 942; 1928, 510, 992). The following appears to be new. Propiondiethylamide (1 mol.) reacts with ethereal magnesium ethyl bromide (2.4 mols.) yielding ethane, diethyl ketone (25% of amide used),  $\gamma$ -diethylamino- $\gamma$ -ethylpentane (25%), b. p.  $81-82.5^\circ/13$  mm. [picrate, m. p.  $96^\circ$ ; perchlorate, m. p.  $180^\circ$  (decomp.); chloroaurate, m. p.  $138^\circ$ ], and a small amount of a substance, b. p.  $142-148^\circ/13$  mm. When reaction is accomplished in boiling benzene the yields of ketone and base are 12 and 33%, respectively. Propiondiethylamide and magnesium ethyl iodide do not react to any appreciable extent. Butyrdiethylamide and magnesium ethyl bromide (no reaction occurs with the iodide) in ether or benzene give about 45% of ethyl propyl ketone and 21—22% of  $\gamma$ -diethylamino- $\gamma$ -ethylhexane; addition of ethyl bromide to the reaction mixture does not cause the formation of a higher homologue (cf. loc. cit.). The hydrochloride of the last-named compound decomposes at  $140-150^\circ$  into diethylamine hydrochloride and  $\gamma$ -ethyl- $\Delta^8$ -hexene (nitrosate, m. p. about  $85^\circ$ ). Butyrdimethylamide and ethereal magnesium ethyl bromide furnish 26% of ethyl propyl ketone and 33% of  $\gamma$ -dimethylamino- $\gamma$ -ethylhexane, b. p.  $73-74^\circ/13$  mm. (picrate, m. p.  $137^\circ$ ); the hydrochloride of this decomposes at  $200-220^\circ$  into  $\gamma$ -ethyl- $\Delta^8$ -hexene. The hydrobromide of  $\beta$ -diethylamino- $\beta$ -methylpentane (A., 1926, 942) (obtained in increased yield from butyrdiethylamide and magnesium methyl iodide in propyl ether or benzene) decomposes at  $190-195^\circ$  into diethylamine hydrobromide and  $\beta$ -methyl- $\Delta^8$ -pentene [nitrolaniline, m. p.  $98^\circ$  (lit.  $86^\circ$ )], identical with the hydrocarbon obtained by dehydration of  $\beta$ -methylpentan- $\beta$ -ol. Nonodiethylamide, b. p.  $167-169^\circ/16$  mm., reacts with 2.5 mols. of magnesium ethyl bromide in ether or benzene forming 53 or 25% of ethyl octyl ketone and 12 or 43% of  $\gamma$ -diethylamino- $\gamma$ -ethylundecane, b. p.  $161-163^\circ/15$  mm. (picrate, m. p.  $57^\circ$ ), respectively. Butyrdimethylamide and magnesium methyl iodide in propyl ether afford, in addition to the normal  $\beta$ -dimethylamino- $\beta$ -methylpentane, some  $\gamma$ -dimethylamino- $\gamma$ -methylhexane, b. p.  $161-163^\circ$  (picrate, m. p.  $153-154^\circ$ ; chloroaurate, m. p.  $122^\circ$ ; chloroplatinate, blackens without melting at  $230^\circ$ ) (cf. A., 1928, 510), synthesised as follows.

$\alpha$ -Methyl- $\alpha$ -ethylvaleramide is converted by bromine and potassium hydroxide solution into  $\alpha$ -methyl- $\alpha$ -ethylbutylcarbamide, b. p.  $160-161^\circ$ , and *s*-di- $\alpha$ -methyl- $\alpha$ -ethylbutylcarbamide, m. p.  $182-183^\circ$ . The carbimide is stable towards alcoholic potassium hydroxide, but is transformed by hydrochloric acid into  $\gamma$ -amino- $\gamma$ -methylhexane, b. p.  $131-132^\circ$  (picrate, m. p.  $155^\circ$ ). Methylation of this yields the above tertiary base.  $\alpha\alpha$ -Dimethylvaleramide affords similarly *s*-di- $\alpha\alpha$ -dimethylbutylcarbamide, m. p.  $155^\circ$ , hydrolysed by Jeffreys' method (A., 1899, i, 730) to  $\beta$ -amino- $\beta$ -methylpentane, b. p.  $101-103^\circ$  (picrate,

m. p. 166°).  $\alpha$ -Methyl- $\alpha$ -ethylbutylcarbamide and as-phenyl- $\alpha$ -methyl- $\alpha$ -ethylbutylcarbamide have m. p. 115° and 117°, respectively.

Magnesium methyl iodide and benzyl chloride in a relatively small amount of toluene form *p*-benzyl-toluene, b. p. 153—154°/16 mm., oxidised to *p*-benzoyl-benzoic acid; in presence of a relatively large amount of toluene, ethylbenzene, dibenzyl, and ethane are produced. Dehydration of methylethylpropyl-carbinol affords a mixture of  $\gamma$ -methyl- $\Delta^{\beta}$ -hexene (nitrolaniline, m. p. 122°) and  $\gamma$ -methyl- $\Delta^{\gamma}$ -hexene.

H. BURTON.

Formation of cyanic acid and carbamide by oxidation of carbon and its derivatives in presence of ammonia. G. LANDE (Compt. rend., 1930, 190, 435—438).—A number of organic compounds have been oxidised by permanganate in ammoniacal solution, in some cases in presence of copper, and the formation of carbamide, and, in nearly every case, of cyanate, has been demonstrated (cf. Fosse, A., 1922, i, 117). The compounds treated include alkaloids, heterocyclic compounds (including furfuraldehyde, and pyridine in presence of copper), alkyl halides, and hydrocarbons (including aromatic hydrocarbons in presence of copper).

R. K. CALLOW.

Structure of the isomeric methyl ferrocyanides. S. GLASSTONE (J.C.S., 1930, 321).—It is suggested that the so-called methyl ferrocyanide has the structure  $[\text{Fe}(\text{Me}\cdot\text{NC})_4(\text{CN})_2]$ , with the four neutral Me·NC groups co-ordinated to the iron atom, and the two valency electrons of the atom shared with the cyano-groups; the substance should be a non-electrolyte. Since it is of the type  $\text{MX}_4\text{A}_2$ , it can exist in *cis*- and *trans*-modifications, and Hartley's  $\alpha$ -form (J.C.S., 1910, 97, 1725; 1911, 99, 1549; 1913, 103, 1196) corresponds with the *cis*-compound. The substance  $\text{Me}_6\text{Fe}(\text{NC})_6\text{I}_2$ , obtained from the  $\alpha$ -form and methyl iodide is probably  $[\text{Fe}(\text{Me}\cdot\text{NC})_6]\text{I}_2$ .

H. BURTON.

Valency limit with phosphorus cyanides and thiocyanates. H. GALL and J. SCHÜPPEN (Ber., 1930, 63, [B], 482—487).—Phosphorus tricyanide is conveniently prepared by heating phosphorus trichloride with silver cyanide in a sealed tube at 100°, removal of excess of the trichloride under diminished pressure, and sublimation of the tricyanide from the residue at 130—150°/vac. It is hydrolysed by an excess of ice-cold water to hydrocyanic and phosphorous acids with a little phosphorus hydride. If a little water is used at the ordinary temperature, solid phosphorus hydride is gradually deposited. Phosphorus pentachloride and silver cyanide in a current of nitrogen at 130° afford phosphorus tricyanide and cyanogen. Phosphorus pentacyanide is prepared by heating the tricyanide with cyanogen at 80° under pressure; its existence is established by tensimetric measurements. Phosphorus trithiocyanate, b. p. 141°/0.3 mm., m. p. (indef.) -4°, is obtained in 30% yield from phosphorus trichloride and mercury thiocyanate in presence of anhydrous carbon tetrachloride. It is only slowly hydrolysed to alkali phosphite and thiocyanate with very little hydrogen sulphide by alkali hydroxide at the atmospheric temperature. Phosphorus pentachloride

and mercury thiocyanate give free thiocyanogen which rapidly becomes polymerised.

The valency limit in the case of the phosphorus halides appears to be determined by the limiting value of total covering, whereby with increasing zero volume of the halogen (cf. Biltz, A., 1928, 572) the position of the valency limit shifts from five to three. The order thus deduced is F, Cl, Br, CN, I, SCN, which agrees with Birckenbach's sequence except with regard to the position of thiocyanogen.

H. WREN.

Highly polymerised substances. XIX. Polymeric silicic esters. E. KONRAD, O. BÄCHLE, and R. SIGNER (Annalen, 1929, 474, 276—295).—The reaction whereby alkyl orthosilicates are obtained from silicon tetrachloride and the appropriate alcohol (Ebelman, Annalen, 1846, 57, 319; Friedel and Crafts, Ann. Chim., 1866, [iv], 9, 32) also affords variable quantities of high-boiling, viscous products, which result from the presence of water in the alcohol, and are also obtained by distillation of the alkyl orthosilicate with water. Treatment of 1 mol. of methyl orthosilicate with 0.5 mol. of water leads to the almost exclusive formation of the disilicic ester  $[(\text{MeO})_3\text{Si}]_2$  (I); the use of 1 mol. of water furnishes a practically quantitative yield of a polymeric silicic ester, of mol. wt. approximately 10,000. By assuming that the action of the water is purely hydrolytic and leads to an infinite series of consecutive reactions, ultimately producing homogeneous molecules of the type  $(\text{MeO})_3\text{Si}\cdot\text{O}\cdot[\text{Si}(\text{OMe})_2\cdot\text{O}]_x\cdot\text{Si}(\text{OMe})_3$  (II), an expression,  $p=n/(n-m)$ , is given defining  $p$  ( $=x+2$ ), the degree of polymerisation produced by the action of  $m$  mols. of water on  $n$  mols. of ortho-ester. A series of experiments employing silicon tetrachloride, methyl orthosilicate, and I, with varying values of  $m$  and  $n$ , give products the molecular complexity of which (determined cryoscopically in benzene) is in complete agreement with the value of  $p$ , calculated from the above expression.

The polymerisation process is not an association, but a chemical phenomenon depending on hydrolysis and condensation. In the large silicic ester molecules atomic union occurs by normal covalent linkings between definite atoms. The following are described: *methyl disilicate*, b. p. 195—205°/760 mm.,  $d^{20}$  1.122,  $\eta$  0.019; *trisilicate*, b. p. 248—258°/760 mm.,  $d^{20}$  1.163,  $\eta$  0.038; *tetrasilicate*, b. p. 170—195°/12 mm.,  $d^{20}$  1.197,  $\eta$  0.074; *pentasilicate*, b. p. 207—215°/12 mm.,  $d^{20}$  1.222,  $\eta$  0.116; *hexasilicate*, b. p. 230—250°/12 mm.,  $d^{20}$  1.230,  $\eta$  0.170; *octasilicate*, b. p. 190—205°/0.002 mm.,  $d^{20}$  1.256,  $\eta$  0.318; *nonasilicate*, b. p. 205—220°/0.002 mm.,  $d^{20}$  1.260,  $\eta$  0.375; *decasilicate*, b. p. 220—240°/0.002 mm.,  $d^{20}$  1.270,  $\eta$  0.508.

C. W. SHOPPEE.

Peculiarity in the formation of the nitrile-esters of dicarboxyglutaconic acid. Y. URU-SHIBARA (Bull. Chem. Soc. Japan, 1930, 5, 1—13; cf. A., 1928, 49, 1356).—By a study of the condensation of eight pairs of sodiomethylene compounds  $\text{CHNaX}\cdot\text{Y}'$  with ethoxymethylene compounds  $\text{CXY}\cdot\text{CH}\cdot\text{OEt}$  in dry ether it is shown that one or more of four types of compounds,  $\text{CXY}\cdot\text{CH}\cdot\text{CHX}\cdot\text{Y}'$  (I),  $\text{CX}\cdot\text{Y}'\cdot\text{CH}\cdot\text{CHXY}$  (II),  $\text{CX}\cdot\text{Y}'\cdot\text{CH}\cdot\text{CHX}\cdot\text{Y}'$  (III), and  $\text{CXY}\cdot\text{CH}\cdot\text{CHXY}$  (IV) ( $\text{X}, \text{X}', \text{Y}, \text{Y}' = \text{CN}, \text{CO}_2\text{Me}, \text{or } \text{CO}_2\text{Et}$ ), may result

from each condensation. The following mechanism, based on the occurrence of retrograde Michael reactions, is proposed:  $CXY:CH \cdot OEt + CH_2X'Y' \rightarrow I + EtOH$ ;  $I + CH_2X'Y' \rightarrow CH(CHX'Y')_2(CHXY) \rightarrow I + CH_2X'Y'$  or  $II + CH_2X'Y'$  or  $III + CH_2X'Y'$ ;  $I$  or  $II + CH_2XY \rightarrow CH(CHXY)_2(CHX'Y') \rightarrow I + CH_2XY$  or  $II + CH_2XY$  or  $IV + CH_2X'Y'$ . The numbers in parentheses in the following details refer to these types of condensation products. Condensation of ethyl ethoxymethylenecyanoacetate and methyl sodiocyanoacetate gives, after decomposition of the sodium compound, a mixture, m. p.  $193^\circ$ , of the semihydrates of the two isomeric methyl ethyl  $\alpha\gamma$ -dicyanoglutaconates (I and II), crystallisation of the sodio-derivative from alcohol affording the *semihydrate*, m. p.  $190^\circ$ , of the hitherto unknown isomeride (probably II). Condensation of methyl ethoxymethylenecyanoacetate and ethyl sodiocyanoacetate gives only the isomeric semihydrate, m. p.  $196^\circ$ , which is also the sole product when the condensation is carried out in alcoholic solution. Ethyl ethoxymethylenemalonate and ethyl sodiocyanoacetate give ethyl  $\alpha\gamma$ -dicyanoglutaconate (III) and the oily ethyl  $\gamma$ -cyano- $\alpha$ -carbethoxyglutaconate (II), partly converted into a *substance*, m. p.  $199^\circ$ , probably ethyl 2:6-dihydroxypyridine-3:5-dicarboxylate. Ethyl ethoxymethylenecyanoacetate and ethyl sodiomalonate give ethyl  $\alpha\gamma$ -dicyanoglutaconate (IV), ethyl  $\alpha\gamma$ -dicarbethoxyglutaconate (III), and the above pyridine derivatives, indicating the formation of ethyl  $\gamma$ -cyano- $\alpha$ -carbethoxyglutaconate (I). Ethyl ethoxymethylenemalonate and sodiomalononitrile give the *sodio*-derivative of ethyl  $\gamma\gamma$ -dicyano- $\Delta^8$ -propylene- $\alpha\alpha$ -dicarboxylate (II), (since on acidification it is converted into ethyl  $\gamma\gamma$ -dicarbamyl- $\Delta^8$ -propylene- $\alpha\alpha$ -dicarboxylate) and ethyl  $\alpha\alpha$ -dicyano- $\Delta^8$ -propylene- $\gamma\gamma$ -dicarboxylate (I). Ethoxymethylenemalononitrile and ethyl sodiomalonate give ethyl  $\alpha$ -sodio- $\gamma\gamma$ -dicyano- $\Delta^8$ -propylene- $\alpha\alpha$ -dicarboxylate (I) (isolated as the dicarbamyl derivative), and ethyl  $\alpha\gamma$ -dicarbethoxyglutaconate (III). Ethyl ethoxymethylenecyanoacetate and sodiomalononitrile afford a mixture, not readily separated, of ethyl  $\alpha\gamma$ -dicyanoglutaconate (IV) and (?) ethyl  $\alpha\gamma\gamma$ -tricyano- $\Delta^8$ -propylene- $\alpha$ -carboxylate (II), whilst the last-named is the sole product of the condensation of ethoxymethylenemalononitrile and ethyl sodiocyanoacetate.

J. W. BAKER.

**Equilibria studies of organomagnesium halides.** Irreversible reaction between organomagnesium halides and halogen acids. H. GILMAN and J. A. LEERMAKERS (Rec. trav. chim., 1930, 49, 208—211).—The irreversibility of the reaction  $R.MgX + HX \rightarrow RH + MgX_2$  has been proved by long heating of a mixture of magnesium bromide or iodide with triphenylmethane, diphenylmethane, and phenylacetylene in ether-benzene solution at  $65$ – $70^\circ$  in a current of carbon dioxide. In no case did the issuing gas give a precipitate with silver nitrate nor could any trace of a carboxylic acid  $R \cdot CO_2H$  be detected. High percentage recovery of the hydrocarbons was effected.

J. W. BAKER.

**Effect of some amino-compounds on the sensitive colour test for reactive organometallic compounds.** H. GILMAN and L. L. HECK (Rec. trav. chim., 1930, 49, 218—221).—The authors'

colour test (A., 1928, 160) for the detection of an excess of a Grignard reagent in a reaction mixture is affected by the presence of some amines, for example, pyrrole, and to a smaller extent by di-*n*-butylamine and diallylamine, although in these cases a colour is obtained in the aqueous layer when an excess of the Grignard reagent is present. The test is not affected by diethylamine, aniline, methylaniline, benzylaniline, diphenylamine, and piperidine. J. W. BAKER.

**Reaction between sulphonyl chlorides and organomagnesium halides.** H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1929, 51, 3501—3508).—The various explanations of the reaction between sulphonyl chlorides and Grignard reagents (Hepworth and Clapham, J.C.S., 1921, 119, 1188; Wedekind and Schenk, A., 1921, i, 664) are criticised. Under the conditions now used, the chief products isolated from aromatic sulphonyl chlorides and magnesium aryl or aralkyl halides are sulphones, sulphinic acids, and halides. The reactions taking place are probably (i)  $Ar \cdot SO_2Cl + R \cdot MgX \rightarrow Ar \cdot SO_2 \cdot R + MgXCl$ , (ii)  $Ar \cdot SO_2Cl + R \cdot MgX \rightarrow RCl + Ar \cdot SO_2 \cdot MgX \xrightarrow{H_2O} Ar \cdot SO_2H$ . The formation of sulphide is noted using Hepworth and Clapham's experimental conditions (heating of the reaction mixture). The reaction mixtures were not heated during the present investigation.

H. BURTON.

**Metallo-organic complexes.** I. L. KONDAKOV, F. BALAS, and L. VIT (Chem. Listy, 1930, 24, 1—8, 26—31; cf. this vol., 200).—*tert*-Amyl alcohol when heated in a sealed tube with zinc chloride yields  $\beta$ -methyl- $\Delta^8$ -butene, and double compounds of zinc chloride with amyl alcohol or with water, viz.,  $[Cl_2Zn(OH)_2]_2H_2$ ,  $[Cl_2Zn(OC_5H_{11})_2]_2H_2$ , and  $[Cl_2Zn(OH)(OC_5H_{11})]_2H_2$ . With  $\beta$ -methyl- $\Delta^8$ -butene zinc chloride yields the complex  $2ZnCl_2 \cdot C_5H_{10}$ , which can also be prepared by the decomposition of  $ZnCl_2 \cdot 2C_5H_{11} \cdot OH$ .  $\beta$ -Methyl- $\Delta^8$ -butene on heating with platinous chloride yields a complex,  $2PtCl_2 \cdot C_5H_{10}$ , whilst with palladous chloride the complex  $PdCl_2 \cdot C_5H_{10}$ , decomposing at  $85$ – $90^\circ$ , is obtained.

R. TRUSZKOWSKI.

**Tin methyl derivatives.** V. Action of tin sodium trimethyl on methylene chloride. C. A. KRAUS and A. M. NEAL (J. Amer. Chem. Soc., 1930, 52, 695—701).—Tin sodium trimethyl and methylene chloride react in liquid ammonia forming *di(trimethylstannyl)methane*,  $(SnMe_3)_2CH_2$ , b. p.  $199$ – $201^\circ$ , converted readily by iodine in chloroform into methylene iodide and tin trimethyl iodide. When treated with sodium in liquid ammonia, it furnishes tin sodium trimethyl and methane; addition of ammonium bromide to the reaction product causes evolution of hydrogen, formed by the interaction of sodamide and trimethylstannane. According to the concentration and state of division of the last-named reactants, tin sodium trimethyl, trimethylstannylamine, and hydrogen, or tin sodium trimethyl and ammonia, are produced. Tin trimethyl and sodamide give tin sodium trimethyl and trimethylstannylamine.

H. BURTON.

**Organometallic compounds with tertiary alcohol radicals.** I. *tert*-Butyl and *tert*-amyl compounds of tin. E. KRAUSE and K. WEINBERG



(Ber., 1930, 63, [B], 381—385).—The action of tin tetrachloride on magnesium *tert.*-alkyl chlorides is accompanied by reduction which proceeds to the formation of the dark-coloured dialkyl compounds. If the tetrachloride is kept in excess, unsaturated compounds result in unimportant amount, but reaction proceeds only to the tin dialkyl dihalide.

Tin tetrachloride is converted by magnesium *tert.*-butyl chloride (the bromide and iodide are unsuitable) followed by successive treatment with bromine and potassium hydroxide into *tin di-tert.-butyl dihydroxide*. It is transformed by the requisite halogen acid into *tin di-tert.-butyl dibromide*, b. p. 128°/14 mm., and *dichloride*, m. p. 42°, decomp. 241°. *Tin di-tert.-butyl difluoride*, decomp. 254°, is obtained from the bromide and aqueous-alcoholic potassium fluoride. With an excess of magnesium *tert.*-butyl chloride the dichloride affords *tin tri-tert.-butyl chloride*, b. p. 132°/12 mm., m. p. +4°; converted in the usual manner into the corresponding *fluoride*, decomp. above 257°, and *hydroxide*, m. p. 153° after softening at 53°, decomp. above 156°. The last-named compound yields *tin tri-tert.-butyl bromide*, b. p. 137°/12 mm., and *iodide*, b. p. 147·5°/12 mm., m. p. 21°. *Tin di-tert.-butyl hydroxychloride*, m. p. 156—170° after softening at 147°, decomp. 254°, and the *hydroxybromide*, m. p. 149—152° after softening at 135°, decomp. above 269°, are obtained as by-products during the preparation of the trialkyl derivatives. The following substances are prepared by analogous methods: *tin di-tert.-amyl dibromide*, b. p. 166°/13 mm., m. p. -12·5°, *dichloride*, b. p. 153°/12 mm., *di-iodide*, b. p. 186°/12 mm. (partial decomp.), m. p. -14·5°, *difluoride*, decomp. 264° after softening and darkening above 229°, *dihydroxide*, m. p. 200°, decomp. above 204°.

H. WREN.

Action of hydrogen under high pressure on organo-metallic compounds. I. Action of hydrogen on organo-metallic lead compounds,  $\text{PbR}_4$ . V. N. IPATIEV, G. A. RAZUBAIEV, and I. F. BOGDANOV (Ber., 1930, 63, [B], 335—342).—The action of hydrogen under high pressure and at elevated temperature on lead tetraphenyl, tetraethyl, and tetramethyl results in irreversible displacement of the metal and production of hydrocarbon,  $\text{PbR}_4 + 2\text{H}_2 \rightarrow \text{Pb} + 4\text{RH}$ . Deposition of the metal from the tetraphenyl compound in benzene commences at about 150° and becomes quantitative at 250°, the change occurring mainly at 175—225°. From lead tetraethyl about 15% of the metal is displaced at about 100° and complete decomposition is attained at 225°. Incipient action with lead tetramethyl occurs above 125°, the complete action taking place at 250°. The tenacity sequence of the hydrocarbon residues thus differs somewhat from that observed by Grüttner and Krause (A., 1917, i, 256). In the absence of hydrogen, lead tetraphenyl and tetramethyl remain unchanged at 200°; lead tetraethyl suffers partial decomposition with separation of a white precipitate. Under small pressure, increase of pressure has a marked effect on the deposition of lead from the tetraphenyl compound, but further increase has little influence when the pressure is already high. Under standard conditions the bulk of the displaced metal separates during

24 hrs., after which the influence of time is not so pronounced. The solvent (benzene, acetone, alcohol, light petroleum) has little influence. Lead tetraphenyl remains unchanged when heated with water, whereas lead tetramethyl undergoes hydrolysis with separation of a white, crystalline precipitate.

H. WREN.

Stereochemical isomerides and halogeno-derivatives of *cyclohexane-1:3-diol* (resorcitol). L. PALFRAY and B. ROTHSTEIN (Compt. rend., 1930, 190, 189—191).—Hydrolysis of the *trans*-dibenzoate, m. p. 123·5°, of *cyclohexane-1:3-diol* (cf. A., 1929, 1064) with alcoholic potassium hydroxide at 160° affords the *trans-diol*, m. p. 115·5°; the *cis*-dibenzoate, m. p. 65·5°, yields the *cis-diol*, m. p. 84·5°. The *trans-diol* has also been obtained by seeding an acetone solution of commercial resorcitol at -15°. Treatment of resorcitol with hydrochloric acid yields a 1:3-dichloro*cyclohexane*, b. p. 80°/13 mm., which when cooled to -15° affords a solid dichloride, m. p. 102° which is not depressed on admixture with 1:4-dichloro*cyclohexane* (A., 1929, 1441). Hydrobromic acid affords a product, b. p. 115°/15 mm., which, when cooled to -15°, gives two 1:3-*dibromocyclohexanes*, m. p. 112° and 48° which are not depressed on admixture with the two dibromo-compounds from quinitol. The 1:3- and 1:4-dihalides are considered to be identical and the phenomenon of pseudomigration is proposed to account for their inter-conversion.

C. C. N. VASS.

Characteristic of cyclic compounds. P. PETRENKO-KRITSCHENKO (Ber., 1930, 63, [B], 536—537).—The communication of Loevenich and others (this vol., 200) confirms the author's views of the unique nature of aromatic compounds (A., 1925, ii, 1122).

H. WREN.

Trinitroethylbenzenes. J. N. E. DAY (J.C.S., 1930, 252—256).—*p*-Acetamidoethylbenzene (the free base is prepared in 19·5% yield by the Clemmensen reduction of *p*-aminoacetophenone) is converted by an excess of nitric acid (*d* 1·5) into the 3:5-dinitro-derivative (cf. Brady, Day, and Allam, A., 1928, 626). Diazotisation of 3:5-dinitro-4-aminoethylbenzene and subsequent treatment with sodium nitrite and copper sulphate solutions gives 3:4:5-trinitroethylbenzene, m. p. 92·5°, which with alcoholic methylamine and hydrazine hydrate yields 3:5-dinitro-4-methylamino-, m. p. 73°, and 3:5-dinitro-4-hydrazino-ethylbenzene, m. p. 85°, respectively. Oxidation of 2:3- and 2:5-dinitro-4-aminoethylbenzenes (*loc. cit.*) with Caro's acid furnishes the corresponding 4-nitroso-derivatives, m. p. 80—81° and 111—112°, respectively. These are oxidised by warm nitric acid (*d* 1·42) to 2:3:4-trinitro-, m. p. 80° (also obtained by direct nitration of 2:3-dinitroethylbenzene), and 2:4:5-trinitro-ethylbenzenes, m. p. 40°, respectively. 2:4-Dinitro-3-methylamino-, m. p. 92—93° (corresponding 3-hydrazino-derivative, m. p. 149°), and 2:4-dinitro-5-methylamino-ethylbenzenes, m. p. 149° (corresponding 5-hydrazino-derivative, m. p. 141°), are also described. Alcoholic solutions of the trinitro-compounds give colorations with dilute sodium hydroxide solution.

Nitration of *p*-aminoethylbenzene in presence of an excess of sulphuric acid at -8° to 0° affords the 2-nitro-

derivative, m. p. 45° (cf. Cline and Reid, A., 1928, 162). H. BURTON.

**Alkali metal derivatives of phenylated methanes and ethanes.** C. B. WOOSTER and N. W. MITCHELL (J. Amer. Chem. Soc., 1930, 52, 688—694).—Potassamide reacts with phenyl derivatives of methane and ethane in liquid ammonia only when the hydrocarbon has two phenyl groups and a hydrogen atom attached to the same carbon atom. Thus, reaction is observed with di- and tri-phenylmethanes,  $\alpha\beta$ -triphenylethane, and *s*-tetraphenylethane, but not with  $\alpha\alpha\alpha$ -triphenylethane, *as*-tetraphenylethane, toluene, ethylbenzene, tetraphenylmethane, and *s*-diphenylethane. Potassium in liquid ammonia reacts similarly, but a slight action on  $\alpha\alpha\alpha$ -triphenylethane and *as*-tetraphenylethane is noted. The last-named hydrocarbons are prepared from potassium triphenylmethide and methyl iodide or benzyl chloride, respectively, in liquid ammonia. Hexaphenylethane and potassium give an additive compound. Benzyl bromide and sodium in liquid ammonia afford a red solution of sodium benzyl, which reacts with benzyl bromide, forming dibenzyl (cf. Kraus and White, A., 1923, i, 466).

Successive introduction of three phenyl groups into methane causes a progressive increase in the ionisation of the resulting molecules. This is contrary to Kharasch and Marker's views (A., 1927, 165) but is in accordance with those of Lewis. H. BURTON.

**Highly phenylated aliphatic nitro-compounds.** E. P. KOHLER and J. F. STONE (J. Amer. Chem. Soc., 1930, 52, 761—768).—Magnesium phenyl bromide and  $\alpha$ -nitro- $\alpha\beta$ -diphenylethylene give the compound,  $\text{CHPh}_2\text{CPh}\cdot\text{NO}(\text{OMgBr})$ , which on acidification affords *aci*- $\alpha$ -nitro- $\alpha\beta\beta$ -triphenylethane, m. p. 91° (decomp.), purified through its sodium salt, m. p. 100—103°. Attempted methylation of this salt with methyl iodide gives phenyl diphenylmethyl ketoxime, also obtained by reduction of the *aci*-derivative with aluminium amalgam in moist ether. Treatment of the *aci*-compound with hydrochloric acid in ethereal solution affords phenyl benzhydryl ketone; no rearrangement into the true nitro-form occurs. When an aqueous solution of the above sodium salt is boiled for 1 hr.,  $\alpha$ -nitro- $\alpha\beta\beta$ -triphenylethane, m. p. 130°, is produced. This is extracted from an ethereal light petroleum solution with methyl-alcoholic sodium methoxide as the *aci*-sodium salt. The *aci*-derivative, its sodium salt, or, more conveniently, the above magnesium derivative and bromine give  $\alpha$ -bromo- $\alpha$ -nitro- $\alpha\beta\beta$ -triphenylethane, m. p. 185° (decomp.), which with methyl-alcoholic sodium methoxide affords  $\alpha$ -nitrotriphenylethylene, m. p. 170°, decomp. a few degrees above the m. p. This is oxidised by chromic and acetic acids or by ozone in chloroform to benzophenone, and reduced by zinc dust and acetic acid to phenyl benzhydryl ketone. The nitroethylene reacts with magnesium methyl, ethyl, and benzyl iodides, forming, *aci*- $\alpha$ -nitro- $\alpha\beta\beta$ -triphenylpropane, m. p. 120° (decomp.), *aci*- $\alpha$ -nitro- $\alpha\beta\beta$ -triphenyl-*n*-butane, m. p. 120° (decomp.), and *aci*- $\alpha$ -nitro- $\alpha\beta\gamma$ -tetraphenylpropane, m. p. 140° (decomp.), respectively. These resemble *aci*- $\alpha$ -nitro- $\alpha\beta\beta$ -triphenylethane in their properties, and they are not rearranged into the true nitro-derivatives, which

have m. p. 136° (decomp.), 138° (decomp.), and 136° (decomp.), respectively, by treatment with acids. When the sodium salt of *aci*- $\alpha$ -nitro- $\alpha\beta\beta$ -triphenylpropane is treated with methyl-alcoholic hydrochloric acid, 3 : 4 : 4'-triphenylisooxazoline, m. p. 142° (N-ethyl derivative ferrichloride,  $\left[\begin{smallmatrix} \text{CH}_2\cdot\text{O}\cdot\text{NEt} \\ \text{CPh}_2\text{---CPh} \end{smallmatrix}\right]\text{FeCl}_4$ , m. p. 110—111°), is produced. H. BURTON.

**Action of hydrocyanic acid, hydrogen chloride, and aluminium chloride on unsaturated hydrocarbons.** H. WIELAND and E. DORRER (Ber., 1930, 63, [B], 404—411; cf. Wieland and others, A., 1922, i, 1033; 1925, i, 779).—Since unsaturated compounds frequently react with aluminium chloride alone in various directions it has not been found generally possible to cause the hydrocyanic acid to react in an obvious manner. Thus styrene is rapidly removed from its action in the form of metastyrene. Stilbene yields a basic compound which has not been definitely characterised and a bimolecular hydrocarbon, presumably 1 : 2 : 3 : 4-tetraphenylcyclobutane, m. p. 118—119°. Triphenylethylene affords a halochromic additive compound with aluminium chloride and is not further changed. *as*-Diphenylethylene is partly polymerised to 1 : 1 : 3 : 3-tetraphenylcyclobutane, partly converted into  $\alpha\alpha$ -diphenylpropionitrile, b. p. 168—170°/10 mm., identified by hydrolysis to  $\alpha\alpha$ -diphenylpropionic acid, m. p. 172—173° ( $\alpha\alpha$ -diphenylpropionamide has m. p. 103—104°); *as*-diphenylethane is also produced. The intermediate formation of the compound  $\text{NH}\cdot\text{CH}\cdot\text{CPh}_2\cdot\text{CH}_2\text{Cl}$  is assumed. cycloHexene in presence of benzene affords phenylcyclohexane, formamidocyclohexane, b. p. 140—142°/10 mm., m. p. 39°, and two weak bases, m. p. 120—122° [hydrochloride, m. p. 242—244° (decomp.)] and 103—104° (hydrochloride, m. p. 166—172°). If carbon disulphide is used as solvent, cyclohexyl chloride and formamidocyclohexane result. Hydroxymethylene-camphor yields the substance  $(\text{C}_{11}\text{H}_{15}\text{O}_2)_3\text{Al}$ .

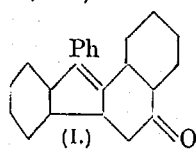
H. WREN.

**Diphenyl and its derivatives.** VI. L. MASCARELLI and D. GATTI [with E. JONA and V. LEONCINI] (Gazzetta, 1929, 59, 867—877; cf. this vol., 205).—As with nitro-derivatives of benzene (cf. Meyer, A., 1916, i, 134), so with those of diphenyl, the action of thionyl chloride at a suitable temperature effects replacement of the nitro-groups by chlorine atoms; at a low temperature the replacement may not affect all the nitro-groups, whilst at a high temperature substitution of the hydrogen atoms of the benzene nuclei may also occur. When treated in this way, 3 : 3'-dinitrodiphenyl gives 3 : 3'-dichlorodiphenyl (cf. Cain, J.C.S., 1904, 85, 7), 3-chloro-3'-nitrodiphenyl, m. p. 100—101°, and a compound (? polychlorodiphenyl), m. p. 188°. 2 : 2'-Dinitrodiphenyl gives 2 : 2'-dichlorodiphenyl (cf. Dobbie, Fox, and Gauge, J.C.S., 1911, 99, 1615). 4 : 4'-Dinitrodiphenyl gives 4 : 4'-dichlorodiphenyl, and a 4 : 4' : *x*-trichlorodiphenyl, m. p. 61° (after sublimation) or 55—56° (crystallised from acetic acid) (cf. Raudnitz, A., 1927, 453).

Decomposition of diphenyleneiodonium salts by heat has been investigated with the object of obtaining new diphenyl derivatives, especially 2 : 2'-dihalogenated

compounds containing two different halogens. Diphenyleneiodonium hydroxide gave no definite result. The *fluoride*, m. p. 166°, gives mainly tarry products; the *cyanide*, browning at about 130° and decomposing at 146°, decomposes violently when heated, giving only traces of white crystals; the double salts,  $C_{13}H_8NI.KCN$ , m. p. 175—180°, and  $C_{13}H_8NI.HCN$ , m. p. 120°, were prepared, as also were the following diphenyleneiodonium salts: *carbonate*, m. p. 163° (blackening at 135—140°); *sulphate*, m. p. 264°, decomp. 280—290°; *nitrate*, m. p. 230°; *benzoate*, browning at about 177°, m. p. 184°; *salicylate*, m. p. 188—189°. T. H. POPE.

**Syntheses of benzofluorene derivatives and ring closure to five-membered, carbocyclic rings by aluminium chloride.** E. CLAR [with E. HEMPEL] (Ber., 1930, 63, [B], 512—517; cf. this vol., 203).—Naphthalene and benzophenone chloride are converted by aluminium chloride in benzene into 9-phenyl-1:2-benzofluorene, m. p. 196° (cf. Ullmann and Mourawrew-Winogradoff, A., 1905, i, 642), also prepared by distillation of 3-hydroxy-9-phenyl-1:2-benzofluorene with zinc dust. If the benzene solution obtained at 0° as described above is boiled for 5 min. instead of 20 min., the product is 9-phenyl-3:4-benzofluorene, m. p. 135—138° (cf. Ullmann and co-worker, *loc. cit.*). Oxidation of 9-phenyl-1:2-benzofluorene with chromium trioxide in glacial acetic acid affords (?) 9-hydroxy-9-phenyl-2':3'-p-benzoquinono-1:2-fluorene, m. p. 154°, with small amounts of o-benzoylbenzoic acid. Addition of aluminium chloride to a solution of benzophenone chloride and  $\alpha$ -naphthol in benzene at 0° and subsequent heating of the mixture on the water-bath affords 3-hydroxy-9-phenyl-1:2-benzofluorene, m. p. 240° in a sealed capillary, also obtained similarly from 1-keto-1:4-diphenylmethylene-1:4-dihydronaphthalene (cf. Clough, J.C.S., 1906, 89, 774). It is oxidised by potassium persulphate or



sodium hypobromite in aqueous alkaline solution to (?) the compound I, m. p. 207°, and by chromium trioxide in boiling glacial acetic acid to 2-o-benzoylphenyl-1:4-naphthaquinone, m. p. 318—319°. 3-Bromo-2-o-benzoylphenyl-1:4-naphthaquinone, m. p. 224°, is described. H. WREN.

**ms-Alkylanthracenes and "transannular tautomerism."** IX. E. DE B. BARNETT, N. F. GOODWAY, and J. L. WILTSHIRE (Ber., 1930, 63, [B], 472—478; cf. this vol., 202).—Technical 1:8-dichloroanthraquinone is reduced by tin and hydrochloric acid in boiling glacial acetic acid to a mixture of 4:5- and 1:8-dichloro-9-anthrone which are separated from one another by treatment with acetone. 1:8-Dichloroanthrone is converted by magnesium methyl iodide into 1:8-dichloro-9-methyl-9:10-dihydroanthran-9-ol, m. p. 114°, transformed by hydrochloric acid in glacial acetic acid into 1:8-dichloro-9-methylanthracene, m. p. 127°. The last-named compound is transformed by bromine in carbon disulphide into 1:8-dichloro-10-bromo-9-methylene-9:10-dihydroanthracene, m. p. 209° (decomp.), which, with calcium carbonate and methyl alcohol, affords 1:8-dichloro-10-methoxy-9-methylene-

9:10-dihydroanthracene, m. p. 131°. Similarly, 1:8-dichloro-9-benzyl-9:10-dihydroanthran-9-ol, m. p. 164° after softening, passes by loss of water into 1:8-dichloro-9-benzylanthracene, m. p. 129°. The last-named substance appears to yield 1:8-dichloro-10-bromo-9-benzylidene-9:10-dihydroanthracene, m. p. 206° (decomp.), which affords 1:8-dichloro-10-methoxy-9-benzylidene-9:10-dihydroanthracene, m. p. 137—138°.

4:5-Dichloroanthrone and magnesium methyl iodide yield a difficultly purifiable dihydroanthranol, dehydrated to 4:5-dichloro-9-methylanthracene, m. p. 153°, transformed by bromine in carbon disulphide into 4:5-dichloro-9-bromomethylanthracene, m. p. 203—206° (decomp.), from which 4:5-dichloro-9-acetoxymethylanthracene, m. p. 164°, and 4:5-dichloro-9-methoxymethylanthracene, m. p. 179°, are derived. 4:5-Dichloro-9-benzyl-9:10-dihydroanthran-9-ol, m. p. 162°, and 4:5-dichloro-9-benzylanthracene, m. p. 162°, are described. 4:5-Dichloro-9- $\alpha$ -bromobenzylanthracene, m. p. 203° (decomp.), is converted into 4:5-dichloro-9- $\alpha$ -acetoxymethylanthracene, m. p. 155°, and 4:5-dichloro-9- $\alpha$ -methoxymethylanthracene, m. p. 145°. H. WREN.

**Mechanism of the formation of rubrene: new synthesis.** C. MOUREU, C. DUFRAISSE, and N. DRISCH (Compt. rend., 1930, 190, 548—550).—Phosphorus pentachloride converts phenyl  $\beta$ -phenylstyryl ketone into an unstable chloro-compound, which could not be isolated, since moisture readily reconverts it into the original ketone, but it loses 1 mol. of hydrogen chloride when heated with an alcoholic solution of potassium acetate, giving another, more stable, oil which is converted into pure, crystalline rubrene on heating (30% yield calc. on original ketone). Since the oily intermediates do not give the reactions (A., 1923, i, 921; 1927, 355) characteristic of the acetylenic derivative  $CPh_2Cl:C:CPh$  from which rubrene has previously been prepared (A., 1926, 945), the synthesis now described represents a new method for the formation of this hydrocarbon.

J. W. BAKER.

**Trianilinoethylene. I. Synthesis of trianilinoethylene and some of its derivatives.**

II. Reaction of sulphur on trianilinoethylene. R. SHIBATA (J. Soc. Chem. Ind. Japan, 1929, 32, 282B, 283—284B).—I. Condensation of trichloroethylene and aniline gives trianilinoethylene, m. p. 147° (decomp.) [hydrochloride,  $C_{20}H_{19}N_3 \cdot 2HCl$ , m. p. 167° (decomp.)]. The monoacetyl derivative, m. p. 123°, and the mono- and tetra-sulphonic acids were prepared.

II. Fusion of trianilinoethylene (5 parts) and sulphur (1 part) at 150° for 40 min. gives an orange mass from which have been isolated: dithio-oxanilide, m. p. 134.5—135°, a compound,  $C_{20}H_{19}N_3S$ , m. p. 102—104°, and a substance  $C_{14}H_{11}N_2$ , probably dianilinoethylene, m. p. 132.5°. Treatment of tritolylaminoethylene in the same way gave an alkali-soluble substance, m. p. 200°, and a compound, insoluble in alkali, m. p. 136—137°. Oxidation of dithio-oxanilide with an acetone solution of potassium permanganate at the ordinary temperature gave thio-oxanilide and oxanilide; oxidation with lead peroxide and acetic acid yielded phenylthiocarbimide and a substance  $C_{14}H_{10}N_2S_2$ , m. p. 137°. A. A. GOLDBERG.

**Action of chloretone and potassium hydroxide on aromatic primary bases.** G. BANTI (Gazzetta, 1929, 59, 819—834; cf. Passerini and Banti, A., 1929, 180).—The action of solid potassium hydroxide on an alcoholic solution of equimolecular proportions of aniline and trichloro-*tert.*-butyl alcohol gives  $\alpha$ -*anilino-isobutyranilide*, m. p. 155—157°, in poor yield. The low m. p. indicates the  $\alpha$ -position of the anilino-group. The formation of  $\beta$ -*anilinoisobutyric acid* by hydrolysis is attributed to simultaneous isomerisation. With excess of trichloro-*tert.*-butyl alcohol, the main product is  $\beta$ -*anilinoisobutyric acid*. *o*-Phenylenediamine, trichloro-*tert.*-butyl alcohol, and potassium hydroxide yield 2-*keto*-3 : 3-*dimethyltetrahydroquinoxaline*, m. p. 175—176°, which is partly converted by ring-fission into the unstable amino-acid by long boiling with hydrochloric acid. R. K. CALLOW.

**Imide and amide chlorides of non-aromatic acids.** IV. J. VON BRAUN and H. SILBERMANN (Ber., 1930, 63, [B], 498—502; cf. A., 1927, 547).—Imide chlorides,  $\text{CH}_2\text{R}\cdot\text{CCl}\cdot\text{NR}'$  and  $\text{CH}_3\cdot\text{CCl}\cdot\text{NR}'$  (R=hydrocarbon residue or halogen), are usually so unstable even when R' is an aromatic residue that a member of this class has not previously been isolated. If, however, a substituent is present in the *ortho*-position to the nitrogen atom in R', the product becomes stabilised. In this connexion the methoxyl group has little influence; methyl is less effective than chlorine and bromine, which have an almost equal action.

Acet-*o*-toluidide is converted by 1 mol. of phosphorus pentachloride at 0° into a mixture of *acet-o-tolylimide chloride*, b. p. 60°/0.1 mm., 95—97°/14 mm. (stable at the ordinary temperature and rapidly hydrolysed by water to acet-*o*-toluidide), and the hydrochloride of the amidine base,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CMe}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CCl}\cdot\text{CH}_2$ , m. p. 50°. The yield of imide chloride is diminished by prolongation of the reaction, whereas that of the hydrochloride is increased; more than 50% of imide chloride has not been obtained. *Chloroacet-o-tolylimide chloride*, b. p. 126—128°/13 mm., is obtained in rather better yield from chloroacet-*o*-toluidide. Aceto-*o*-chloroanilide yields *acet-o-chlorophenylimide chloride*, b. p. 111—114°/14 mm., and the chlorinated amidine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{CMe}\cdot\text{N}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{CCl}\cdot\text{CH}_2$ , m. p. 85°. Chloroacet-*o*-chloroanilide is converted slowly and almost quantitatively into *chloroacet-o-chlorophenylimide chloride*, b. p. 144—147°/14 mm., the stability of which is indicated by the difficulty of transforming it into dichloroacet-*o*-chlorophenylimide chloride. *o*-Bromoacetanilide affords *acet-o-bromophenylimide chloride*, b. p. 142—143°/12 mm., and the amidine,  $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}\cdot\text{CMe}\cdot\text{N}(\text{C}_6\text{H}_4\text{Br})\cdot\text{CCl}\cdot\text{CH}_2$ , m. p. 100°. *Chloroacet-o-bromophenylimide chloride* has b. p. 134—138°/0.5 mm. Chloroacet-*o*-aniside yields a small amount of the corresponding, very unstable imide chloride, whereas acet-*o*-aniside yields almost exclusively the hydrochloride from which the amidine,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CMe}\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CCl}\cdot\text{CH}_2$ , m. p. 78°, is isolated. H. WREN.

**Nitrous acid as a nitrating agent.** I. Nitration of dimethyl-*p*-toluidine. H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 277—280).—Nitrous acid nitrates dimethyl-*p*-toluidine in the *o*-position to

the dimethylamino-group, whereas in the normal nitration process the nitro-group enters the corresponding *m*-position. An explanation is advanced involving the formation of an additive complex of nitrous acid and dimethyl-*p*-toluidine, which renders the nitrogen atom of the nitrous acid less positive; hence the free nitrous acid in solution oxidises the acid part of the complex to nitric acid, being itself reduced to nitric and nitrous oxides. The 3-carbon atom being activated by formation of the complex, nitration occurs in this position (cf. Lapworth and Robinson, A., 1929, 546).

Dimethyl-*p*-toluidine when mixed with solid picric acid or an alcoholic solution of it develops an intense red colour, which soon becomes yellow, the *picrate*, m. p. 128°, crystallising. This may be due to the transient formation of the salt of the *aci*-form of the picric acid. Dimethyl-*p*-toluidine treated with sodium nitrate in aqueous hydrochloric acid gives a little *N*-nitrosomethyl-*p*-toluidine, m. p. 49.5° (Bamberger and Wulz, A., 1891, 1202, give m. p. 52—53°), and 3-*nitrodimethyl-p-toluidine*, red, m. p. 26°, in about 80% yield (*picrate* m. p. 129°). The orientation of this latter compound is established by its identity with the reaction product of 4-chloro-3-nitrotoluene and dimethylamine. When nitrated in concentrated sulphuric acid, dimethyl-*p*-toluidine gives 2-*nitrodimethyl-p-toluidine*, vermilion, m. p. 37° (*picrate*, m. p. 141—143°), in almost theoretical yield. *Dimethylaniline picrate*, m. p. 159°, *o-nitrodimethylaniline picrate*, m. p. 103°, and *m-nitrodimethylaniline picrate*, m. p. 119°, are described. H. A. PIGGOTT.

**Catalytic hydrogenation of fluorene and derivatives.** K. NAKAMURA (Proc. Imp. Acad. Tokyo, 1929, 5, 469—472).—Fluorenoneoxime is reduced by the calculated amount of hydrogen in presence of Adams' platinum catalyst to  $\alpha$ -9-*amino-hexahydrofluorene*, b. p. 130—131°/6 mm.,  $d_4^{25}$  1.026,  $n_D^{25}$  1.54108 (*hydrochloride*, m. p. 236°; *acetate*, m. p. 147—148°; *picrate*, m. p. 175°; *phenylurethane*, m. p. 213—214°; *chloroplatinate*, decomp. 203—204°; *chloroaurate*, decomp. 148—149°; *benzoyl derivative*, m. p. 170—171°), a  $\beta$ -modification, b. p. 134—135°/11 mm.,  $d_4^{25}$  1.044,  $n_D^{25}$  1.56189 (*hydrochloride*, m. p. 306°; *acetate*, m. p. 179—180°; *picrate*, m. p. 196—197°; *phenylurethane*, m. p. 253°; *chloroplatinate*, decomp. 232°; *chloroaurate*, decomp. 195°; *benzoyl derivative*, m. p. 223°; *acetyl derivative*, m. p. 202—203°), and hexahydrofluorene. Further hydrogenation, using an active catalyst, gives 9-*aminododecahydrofluorene* [*hydrochloride*, m. p. 323—324°; *acetate*, m. p. 189—190°; *picrate*, m. p. 210—211°; *hydrogen tartrate* (+MeOH), m. p. 191°; *chloroplatinate*, decomp. 238—239°; *benzoyl derivative*, m. p. 203—204°; *acetyl derivative*, m. p. 168—169°], more conveniently prepared by heating aminohexahydrofluorene with concentrated halogen acid at 150—160° for 6 hrs. The hexahydroamines contain one benzene nucleus intact, since they do not decolorise bromine in acetic acid and are oxidised by permanganate to *o*-phthalic acid, oxalic acid, carbon dioxide, and ammonia. The  $\alpha$ -base gives with acetyl chloride the acetyl derivative of the  $\beta$ -base and with benzoyl chloride equal amounts of the  $\alpha$ - and  $\beta$ -benzamido-derivatives. The ready

isomerisation suggests that the bases differ only in the configuration of the amino-group. Resolution of  $\alpha$ -9-aminohexahydrofluorene using tartaric acid gives d-,  $[\alpha]_D^{25} + 12.03^\circ$  [hydrogen tartrate, (+MeOH), m. p.  $206^\circ$ ], and l-,  $[\alpha]_D^{25} - 11.98^\circ$  (hydrogen tartrate, m. p.  $223-224^\circ$ ), forms. Hydrogenation of fluorene or, better, fluorenoneoxime with palladium oxide-palladium gives hexahydrofluorene. With the platinum catalyst fluorene gives mainly dodecahydrofluorene (cf. Ipatiev, A., 1909, i, 466).

H. E. F. NOTTON.

**Reduction of o-nitrotoluene.** P. S. VARMA and V. A. RAO (J. Indian Chem. Soc., 1929, 6, 915—924).—Good yields, up to 88%, of o-azoxytoluene are obtained when o-nitrotoluene is reduced with an excess of magnesium powder in a solution of equal volumes of saturated ammonium chloride and methyl or ethyl alcohol (cf. Zechmeister and Rom, A., 1926, 720); proportionally larger yields are obtained with ethyl alcohol. The ammonium chloride cannot be replaced by sodium or aluminium chlorides; the yield is diminished when ammonium sulphate is used. Varying amounts of the azoxy-derivative are formed with the following reducing agents: hydrogen sulphide in ammoniacal solution; zinc dust and ammonium chloride; zinc dust, aluminium wire, and stannous chloride in aqueous-alcoholic sodium hydroxide solution. o-Azotoluene is best prepared from o-nitrotoluene and zinc dust in alcoholic sodium hydroxide solution; 35—48% yields are obtained with sodium methoxide or ethoxide solutions. Reduction of o-nitrotoluene with aluminium powder and methyl-alcoholic sodium hydroxide solution or, better, of azotoluene with methyl-alcoholic ammonium sulphide affords hydrazotoluene (74—94% yield). Reduction of o-nitrotoluene with aqueous-alcoholic sodium disulphide gives a 70% yield of o-toluidine, also formed in 80% yield from the hydrazo-derivative, stannous chloride, and hydrochloric acid.

H. BURTON.

**1- and 2-Substituted semicarbazides.** 1- and 2-Benzylsemicarbazides. J. LEBOUCC (J. Pharm. Chim., 1930, [viii], 11, 200—207).—The substance, m. p.  $135^\circ$ , obtained from benzylhydrazine and potassium cyanate and described as 2-benzylsemicarbazide by Busch, Opfermann, and Walther (A., 1904, i, 628; cf. Curtius, 1900, i, 610), possesses this constitution, since it condenses readily with aldehydes and ketones and reacts with a second mol. of potassium cyanate to give benzylhydrazodicarboxylamide, m. p.  $265^\circ$  (Maquenne block). The electropolar nature of the substituent is regarded as determining the point of attack ( $\text{NH}_2$  or  $\text{NH}$ ) of the cyanate molecule in the production of substituted semicarbazides from substituted hydrazines; electronegative radicals such as phenyl direct attack on the  $\text{NH}_2$  group, whilst less electronegative groups such as methyl or ethyl determine reaction with the  $\text{NH}$  group. The following benzylsemicarbazones are described: benzaldehyde-, m. p.  $159.5-160^\circ$ ; cinnamaldehyde-, m. p.  $200^\circ$ ; anisaldehyde-, m. p.  $163.5-164^\circ$ ; acetone-, m. p.  $155^\circ$ ; cyclohexanone-, m. p.  $165^\circ$ ; pyruvic acid-, m. p.  $214^\circ$ .

C. W. SHOPPEE.

**Oxidation processes determined by normal diazohydrates.** A. ANGELI and Z. JOLLES (Atti

R. Accad. Lincei, 1929, [vi], 10, 320—322; cf. A., 1929, 1290).—Benzenediazonium chloride oxidises ferrous to ferric hydroxide, with formation of benzene, doubtless derived from the phenyldi-imide first formed; azobenzene; and phenyl azide, which probably results, together with aniline, from decomposition of the dimeride of phenyldi-imide. When treated with benzenediazonium chloride, hydrogen peroxide gives nitrogen and oxygen; hydroxylamine, a gas consisting almost entirely of nitrogen; potassium ferrocyanide, the ferricyanide; ammonium sulphide, a precipitate of sulphur.

T. H. POPE.

**Catalytic decomposition of diazo-compounds with copper sulphide.** J. S. P. BLUMBERGER (Rec. trav. chim., 1930, 49, 257—258).—The action of a moist, freshly prepared, paste of cupric sulphide on benzene-, toluene-, p-sulphobenzene-, and o-carboxybenzene-diazonium compounds gives a dark-coloured, resinous mixture of products and this reagent is, therefore, of no preparative value for the catalytic decomposition of diazonium compounds. Since cuprous sulphide behaves similarly it is inferred that the structure of cupric sulphide is  $\text{Cu}_2\text{S}\cdot\text{S}$ .

J. W. BAKER.

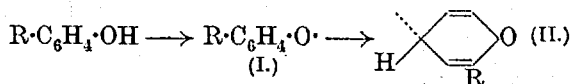
**Action of aluminium chloride and metallic aluminium on hydroxy-compounds.** I. T. POSTOVSKI and B. P. LUGOVKIN (J. Russ. Phys. Chem. Soc., 1929, 61, 1279—1284).—The thermal treatment of phenols in the presence of anhydrous aluminium chloride and metallic aluminium was investigated to ascertain the effect of catalytically cracking primary tars from brown coal, which are rich in phenolic compounds. Phenol itself, on boiling for 50 hrs. in presence of the catalyst, was almost entirely unchanged, a small quantity only of phenyl ether being formed. m-Cresol, under similar conditions, yielded 3:6-dimethylxanthene, m. p.  $200-201^\circ$ , together with a little di-m-tolyl ether, b. p.  $282-287^\circ$ . On boiling benzhydrol with metallic aluminium for 10 hrs., tetraphenylethane, m. p.  $207-208^\circ$ , and diphenylmethane, m. p.  $26-27^\circ$ , were obtained. Further boiling of the latter for 16 hrs. with aluminium gave only a small quantity of tetraphenylethane. With benzoin and benzyaniline, respectively, in the presence of metallic aluminium, lepidene (tetraphenylfuran), m. p.  $172^\circ$ , and a mixture of aniline and benzaldehyde were obtained.

M. ZVEGINTZOV.

**Univalent oxygen. V. Dehydrogenation of o-cresol.** S. GOLDSCHMIDT, E. SCHULZ, and H. BERNARD (Annalen, 1930, 478, 1—21).—When o-cresol in dilute, moist ethereal solution containing acetic acid is treated with excess of lead dioxide an intensely bluish-red product is formed; this is reduced to a colourless leuco-compound by phenylhydrazine or hydrazobenzene. The filtrate from the oxides of lead is run into phenylhydrazine. After removing excess of phenylhydrazine, o-cresol is removed by distillation in steam. Di-o-cresol (4:4'-dihydroxy-3:3'-dimethyldiphenyl) separates from the aqueous portion of the residue, and further amounts are obtained in the subsequent fractionation. It is oxidised by lead dioxide to 3:3'-dimethyl-4:4'-diphenoquinone, decomp.  $150^\circ$  without melting. The remainder of the

product is fractionated by extraction with light petroleum and distillation of the extracts. The *leuco-compound*,  $C_{21}H_{20}O_3$ , b. p. 186–195°/0.15 mm. (slight decomp.), decomp. 200°, is a resin which yields with lead dioxide the bluish-red product. The latter has the properties of an aroxyl (A., 1922, i, 1148). It is stable to atmospheric oxygen, reacts at low temperatures with hydrazobenzene, and is decolorised by triphenylmethyl. The equilibrium mixture of radical and dimeride appears to contain about 70–90% of the former, independently of the concentration.

The leuco-compound is soluble in sodium hydroxide, and contains one hydroxyl group (Zerevitinov). It is stable to hydriodic acid, but prolonged treatment with sodium-potassium alloy yields about 8% of *o*-cresol. It is probably, therefore, a hydroxy-derivative of a trinuclear aromatic ether. The formation of such a compound is explicable on the hypothesis that the oxidation of *o*-cresol proceeds according to the scheme:



followed by the formation from II of a dianthrone and finally a diphenol, or from I and II of a dehydrophenol and finally a hydroxydiphenyl ether. The last compound may then, for example, yield an aroxyl which condenses with II.

Two of the possible isomeric hydroxy-trinuclear ethers have been synthesised and found not to be identical with the leuco-compound. Fusion of *o*-cresol and 4-bromo-*o*-cresol methyl ether with potassium hydroxide and copper powder yields 4-methoxy-3:2'-dimethyldiphenyl ether, m. p. 44–44.5°, b. p. 170–179°/11 mm. Demethylation of this by boiling with hydriodic acid yields the 4-hydroxy-compound, m. p. 46°, b. p. 188–191°/11 mm., also obtained in poor yield, accompanied by di-*o*-cresol, from *o*-cresol and 4-bromo-*o*-cresol. An unstable blue colour is obtained by treatment of the hydroxy-ether with lead dioxide, indicating the formation of an aroxyl. Condensation with 4-bromo-*o*-cresol methyl ether yields 2-methoxy-5:5'-tritoly ether,  $C_6H_4Me \cdot O \cdot C_6H_4Me \cdot O \cdot C_6H_4Me \cdot OMe$ , m. p. 49.5–50°, b. p. 179–191°/0.3 mm. The latter reacts with lead dioxide to give a blue colour which fades, and finally a red colour. Condensation of *o*-cresol with 4:6-dibromo-*o*-cresol methyl ether yields 2-methoxy-3:5-di-*o*-tolyl oxytoluene, b. p. 165–177°/0.2 mm., which yields the hydroxy-ether, b. p. 173–181°/0.2 mm., which gives a weak reddish-yellow colour on oxidation. Condensation of 2-hydroxy-5:5'-tritoly ether with 4-bromo-*o*-cresol methyl ether yields 2-methoxy-5:5':5''-tetratoly ether, b. p. 220–238°/0.13 mm., which is demethylated to give a product which gives the same colour changes on oxidation as 2-hydroxy-5:5'-tritoly ether.

R. K. CALLOW.

[Action of potassium persulphate on *p*-cresol in neutral solution.] H. RAUDNITZ (Ber., 1930, 63, [B], 517–518).—In reply to Wolfenstein (Z. angew. Chem., 1929, 42, 1150), it is shown that the product of the action is 3:3'-di-*p*-cresol, m. p. 153° (cf. Pummerer and others, A., 1922, i, 1161).

H. WREN.

Variation of phenol coefficients in homologous series of phenols. C. E. COULTHARD, J. MARSHALL, and F. L. PYMAN (J.C.S., 1930, 280–291).—The phenol coefficients of homologous series of *p*-*n*-alkylphenols, 4-*n*-alkyl-*m*-cresols, 3- and 5-*n*-alkyl-*o*-cresols, and 4-*n*-alkylguaiacols have been determined by the Rideal-Walker method in dilute sodium hydroxide solutions. The values for the *p*-*n*-alkylphenols are in general much less than for the corresponding *n*-alkylcresols and those for the *n*-alkylguaiacols are comparatively trivial. In every case they rise to a maximum at the *n*-amyl compounds and then decrease. Of particular interest is 4-*n*-amyl-*m*-cresol on account of its high phenol coefficients against *B. typhosus* and various strains of *Streptococcus* and *Staphylococcus*, combined with a comparatively low toxicity. The requisite alkyl derivatives were all prepared by reduction of the corresponding ketones by Clemmensen's method, the latter being obtained by condensation of the appropriate acid and phenol, using zinc chloride (Nencki—I) or phosphoryl chloride (II), or by the isomerisation of phenyl esters by aluminium chloride (Fries—III) or zinc chloride (Pope—IV). The following new acylphenols were obtained by method I in yields of 5–10%: *p*-*n*-valeryl-, b. p. 210°/15 mm., m. p. 62–63°; *p*-*n*-hexoyl-, m. p. 63–64°; *p*-*n*-heptoyl-phenol, b. p. 220°/15 mm., m. p. 93–94° (benzoate, m. p. 92–93°). The Fries isomerisation (III) was used to obtain (yields good in general): *o*-*n*-butyrylphenol, b. p. 124–126°/14 mm., m. p. 8° (phenylhydrazone, yellow, m. p. 85–87°); *p*-*n*-butyrylphenyl benzoate, m. p. 106–107°; *o*-*n*-hexoylphenol, b. p. 145–147°, m. p. 22° (phenylhydrazone, m. p. 102–103°); *o*-*n*-heptoylphenol, b. p. 172–174°/20 mm., m. p. 24° (phenylhydrazone, m. p. 91–92°); 5-acetyl-*o*-tolyl benzoate, m. p. 79–80°; 3-*n*-butyryl-*o*-cresol, b. p. 143°/11 mm. (oxime, m. p. 87–88°; phenylhydrazone, m. p. 157–158°); 5-*n*-butyryl-*o*-cresol, b. p. 195–200°/15 mm., m. p. 132–133° (phenylhydrazone, m. p. 110°); 3-*n*-valeryl-*o*-cresol, b. p. 143–145°/15 mm., m. p. 18° (phenylhydrazone, m. p. 116–118°); 5-*n*-valeryl-*o*-cresol, b. p. 205°/15 mm., m. p. 103–104° (phenylhydrazone, m. p. 120–121°; benzoate, m. p. 72–73°); 3-*n*-hexoyl-*o*-cresol, b. p. 152–154°/15 mm., m. p. 23° (phenylhydrazone, m. p. 93–94°); 5-*n*-hexoyl-*o*-cresol, b. p. 200–205°/15 mm., m. p. 79–80° when free from benzene of crystallisation (benzoate, m. p. 59–60°); 3-*n*-butyryl-*p*-cresol-oxime, m. p. 96–97°, and -phenylhydrazone, m. p. 141–142°; 3-*n*-valeryl-*p*-cresol, made but not characterised by Wittig (A., 1926, 300), b. p. 144–145°/15 mm., m. p. 32–33° (phenylhydrazone, m. p. 113–115°); 3-*n*-hexoyl-*p*-cresol, b. p. 150–152°/15 mm., m. p. 19° (phenylhydrazone, m. p. 110–112°). Isomerisation of *m*-tolyl esters at the ordinary temperature in nitrobenzene solution gives mainly the 4-acyl-*m*-cresol, the yield of 6-compound being negligible. In this way were prepared the following acyl-*m*-cresols: 4-propionyl- (oxime, m. p. 103–104°); 6-*n*-butyryl-, m. p. 97–98°; 4-*n*-butyryl-, b. p. 142–144°/15 mm., m. p. 17° (oxime, m. p. 74–75°; phenylhydrazone, m. p. 95–97°); 4-*n*-valeryl-, b. p. 152–154°/15 mm., m. p. 16°; 4-*n*-hexoyl-, b. p. 162–164°/15 mm., m. p. 23–24° (phenylhydrazone, m. p. 92–93°), and 4-*n*-heptoyl-*m*-cresol, b. p. 172–



174°/15 mm., m. p. 18°. The yields of 4-compound varied from 84 to 93%. The following 4-acyl-guaiacols were obtained in a similar manner and isolated as aluminium chloride double compounds in yields of 50% and upwards: 4-*propionyl*-, b. p. 180—185°/15 mm., m. p. 61—62° (benzoate, m. p. 108—110°; *p*-nitrophenylhydrazones, m. p. 151—152°); 4-*n*-butyryl-, b. p. 185—195°/15 mm., m. p. 54—55° (benzoate, m. p. 75—77°; phenylhydrazones, m. p. 91—92°); 4-*n*-valeryl-, b. p. 195—197°/15 mm., m. p. 60—62° (benzoate, m. p. 85—87°); and 4-*n*-hexoyl-guaiacol, b. p. 212—215°/15 mm., m. p. 60—62° (benzoate, m. p. 54—55°); also 4-*n*-valerylpyrocatechol, b. p. 230—240°/15 mm., m. p. 143—144°, and 4-*n*-hexoylpyrocatechol, b. p. 240—250°/15 mm., m. p. 93—94°. The phosphoryl chloride method (II) was used for isoacetovanillone (phenylhydrazones, m. p. 102°; benzoate, m. p. 141—142°), 5-*propionyl*-guaiacol, m. p. 93—94° (benzoate, m. p. 96—98°), and 5-*n*-butyrylguaiacol, m. p. 81—82°. No new products are described as obtained by method IV.

These various acylphenols were reduced to alkyl-phenols with amalgamated zinc and dilute hydrochloric acid. *p*-*n*-Butylphenol, m. p. 12° (benzoate, m. p. 24—25°), *p*-*n*-amylphenol, m. p. 18°, 4-*n*-propyl-*m*-cresol, m. p. 16°, and 4-*n*-propylguaiacol, m. p. 16° are described in a crystalline form for the first time. New alkyl-phenols are: *p*-*n*-hexyl-, b. p. 155°/15 mm., m. p. 29° (benzoate, m. p. 24°); *o*-*n*-heptyl-, b. p. 163—165°/15 mm.; *p*-*n*-heptyl-, b. p. 165°/15 mm., m. p. 24° (benzoate, m. p. 32—33°); *p*-*n*-propylphenyl benzoate, m. p. 37—38°. New alkyl-*o*-cresols: 3-*n*-butyl-, b. p. 117—119°/15 mm., m. p. 14°; 5-*n*-butyl-, b. p. 127—129°/15 mm., m. p. 24°; 3-*n*-amyl-, b. p. 127—129°/15 mm., m. p. 32°; 5-*n*-amyl-, b. p. 137—139°/15 mm., m. p. 28°; 3-*n*-hexyl-, b. p. 139—141°/15 mm., m. p. 8°; 5-*n*-hexyl-, b. p. 147—149°/15 mm., m. p. 5°. New alkyl-*m*-cresols: 4-*n*-butyl-, b. p. 132—134°/15 mm., m. p. 18°; 4-*n*-amyl-, b. p. 137—139°/15 mm., m. p. 24°; 4-*n*-hexyl-, b. p. 147—149°/15 mm., m. p. 17°; 4-*n*-heptyl-, b. p. 153—155°/15 mm., m. p. 24°. New alkyl-*p*-cresols: 3-*n*-butyl-, b. p. 124—126°/15 mm., m. p. 19°; 3-*n*-amyl-, b. p. 135—137°/15 mm., m. p. 10°; 3-*n*-hexyl-, b. p. 148—150°/15 mm., m. p. 30°. New alkylguaiacols: 4-ethylguaiacyl benzoate, m. p. 58—59°; 5-ethyl-, b. p. 130—132°/15 mm., m. p. 35—36° (benzoate, m. p. 53°); 5-*n*-propyl-, b. p. 132—134°/15 mm., m. p. 21—22°; 4-*n*-amyl-, b. p. 155—157°/15 mm.; and 4-*n*-hexyl-guaiacol, b. p. 165—167°/15 mm. (benzoate, m. p. 82—83°).

H. A. PIGGOTT.

**Reduction of nitropyrocatechols.** J. E. FOGLESONG and I. L. NEWELL (J. Amer. Chem. Soc., 1930, 52, 834—837).—Nitration of pyrocatechol by Weselsky and Benedikt's method (A., 1882, 1200) affords an 80% yield of the 3- (5—8%) and 4-nitro-derivatives. Reduction of the 3-nitro-compound with tin and hydrochloric acid gives 3-aminopyrocatechol, m. p. 120—122° (decomp.) [hydrochloride, m. p. 196—202° after darkening at 160°; *N*-acetyl derivative, m. p. 124—125°; diacetyl derivative, m. p. 167—168°; triacetyl derivative, m. p. 97°], which is readily oxidised by air. The free base is isolated from the hydrochloride by decomposition with sodium hydrogen carbonate solution in an atmosphere of

carbon dioxide. 4-Aminopyrocatechol is prepared similarly. H. BURTON.

**Auto-oxidation reactions.** Oxidation of anethole [*isoeugenol* and *isosafole*]. N. A. MILAS (J. Amer. Chem. Soc., 1930, 52, 739—753).—An apparatus is described for the determination of the rate of absorption of oxygen in auto-oxidation reactions, particularly when gaseous products are being evolved during the change. Application of the method to anethole, *isoeugenol*, and *isosafole* shows that there is an abnormal decrease in the oxygen absorption rate before any appreciable amounts of the substances have been oxidised. The explanation suggested is that a rapid polymerisation occurs during the initial stages of the reaction. Addition of anthracene, anthraquinone, or phenanthraquinone causes an inhibition of the polymerisation and allows oxidation to proceed at a relatively high rate. With quinol and *p*-benzoquinone, both polymerisation and oxidation are inhibited during the early stages of the reaction; as soon as oxidation begins, polymerisation occurs also. Anthracene also inhibits the oxidation of anisaldehyde (formed intermediately from anethole) selectively, whilst it is oxidised inducedly to anthraquinone. Inhibitory constants of various substances are calculated from the relationship involving the maximum absorption rate, the concentration of the inhibitor, and the time necessary for the oxidation rate to reach a maximum value (cf. A., 1929, 1019). Anisaldehyde and anthracene have almost the same constant. Phenanthrene causes a slight acceleration of the auto-oxidation of anethole, although it is oxidised inducedly first to phenanthraquinone and then to diphenic acid. An inhibitor of the auto-oxidations studied is not necessarily a good reducing agent or an easily oxidisable substance. Thus, anthraquinone, which is unaffected during the oxidation of anethole, is a better inhibitor than anthracene, which is oxidised. H. BURTON.

**Brucine and strychnine salts of inositol-phosphoric acids.** N. SELIGSON (Arch. Pharm., 1930, 268, 104—113).—Previous work on inositol-phosphoric acids is criticised, particularly that of RATHER (A., 1917, i, 315; 1918, i, 212), whose "compounds" were certainly mixtures. The m. p. (actually temperatures of sintering or darkening) are not a criterion of purity, owing to decomposition. The m. p. given below are observed by plunging the capillary tube into a hot bath. The ratio C:P of the acids cannot be accurately determined in the salts directly. An analytical method is described for determining (a) the phosphorus in the salt, (b) the alkaloid liberated by ammonia and extracted by chloroform, and then (c) phosphorus, and (d) carbon, in aliquot portions of the residual solutions. In a vacuum the salts described retain 3H<sub>2</sub>O at the ordinary temperature and lose this at 100°. The solubility relations of brucine salts are more favourable than those of strychnine salts for the isolation of pure compounds, particularly of the hexaphosphoric acid.

Sodium phytate is prepared from phytin by a modification of Posternak's method (A., 1919, i, 426), the last traces of iron being removed by treatment of the solution with hydrogen sulphide in presence of

copper hydroxide and kaolin. The acidified solution is treated with the calculated amount of brucine, when *tetrabrucine inositolhexaphosphate*,  $C_6H_6(H_2PO_4)_6 \cdot 4Brucine \cdot 27H_2O$ , m. p. 214—217°, separates, which generally yields the *tribrucine salt* ( $+10H_2O$ ), m. p. 216—217°, when recrystallised from hydrochloric acid. Either of these yields, when brucine is added to the solution, the *hexabrucine salt* ( $+24H_2O$ ), m. p. 210—211°, treatment of which with chloroform appears to give soluble and insoluble modifications. The *hexastrychnine salt* ( $+11H_2O$ ), m. p. 210—211°, and a mixture of the *tetra-* and *pentastrychnine salts*, m. p. 230°, are also described.

R. K. CALLOW.

**Pairs of stereoisomeric amino-alcohols. Separate preparation of each isomeride.** M. Tiffeneau, J. Lévy, and E. Ditz (Compt. rend., 1930, 190, 57—59).—In continuation of previous work on glycols (McKenzie, Luis, Tiffeneau, and Weill, A., 1929, 1067), stereoisomerides of the amino-alcohols,  $OH \cdot CRR' \cdot CHMe \cdot NH_2$  have been separately prepared by varying the order of introduction of the radicals by the action of Grignard compounds on the amino-ketones  $R(or R') \cdot CO \cdot CHMe \cdot NH_2$ . In an attempt to extend this method to the preparation of stereoisomerides from ketones  $R(or R') \cdot CO \cdot CH_2 \cdot NH_2$ , only racemates were isolated.

Interaction of magnesium anisyl bromide and  $\alpha$ -aminopropiophenone hydrochloride yields  $\beta$ -amino- $\alpha$ -phenyl- $\alpha$ -anisyl- $n$ -propyl alcohol ( $\alpha$ -isomeride), m. p. 77—78° (hydrochloride, m. p. 264—266°; picrate, m. p. 198—199°). The  $\beta$ -isomeride, m. p. 74—75° (hydrochloride, m. p. 255—257°; picrate, m. p. 205°), is obtained from magnesium phenyl bromide and  $\alpha$ -amino- $p$ -methoxypropiophenone hydrochloride, m. p. 232° (prepared by reduction of oximino- $p$ -methoxypropiophenone with stannous chloride).  $\beta$ -Amino- $\alpha$ -phenyl- $\alpha$ - $p$ -tolyl- $n$ -propyl alcohol ( $\alpha$ -isomeride), m. p. 65—66° (hydrochloride, m. p. 249—250°; picrate, m. p. 209°), is obtained from magnesium  $p$ -tolyl bromide and  $\alpha$ -aminopropiophenone hydrochloride, and the  $\beta$ -isomeride, m. p. 95° (hydrochloride, m. p. 275°; picrate, m. p. 132°), from magnesium phenyl bromide and  $\alpha$ -amino- $p$ -methylpropiophenone hydrochloride, m. p. 247°.

R. K. CALLOW.

**Reactivity of atoms and groups in organic compounds. X. Measurement of the relative lability of linkings by rates of reactions and temperatures of decomposition. I. Hydrogen-oxygen linking in alcohols.** J. F. NORRIS and R. C. YOUNG (J. Amer. Chem. Soc., 1930, 52, 753—761).—Thermal decomposition of a series of triphenylmethyl alkyl and aralkyl ethers,  $CPh_3 \cdot OR$ , affords triphenylmethane and an aldehyde or a ketone (cf. A., 1925, i, 20) according as  $\cdot OR$  is a primary or secondary alcoholic residue. The temperature of decomposition is well defined and varies between 216° and 262°. The order of decreasing stability is found to be ( $R=$ ): methyl, ethyl,  $n$ -butyl, isoamyl,  $\beta$ -phenylethyl,  $n$ -propyl, isobutyl, benzyl, isopropyl, sec.-butyl. This order is identical (with one exception) with that previously determined (A., 1925, i, 626; 1927, 1166) from the velocities of the reactions between the alcohols,  $R \cdot OH$ , and  $p$ -nitrobenzoyl chloride; the

velocities are arranged in decreasing order of magnitude. The temperature of decomposition (242°) of triphenylmethyl ethyl ether is lowered appreciably by the addition of substances such as zinc oxide (205°), barium chloride (195°), potassium hydrogen sulphate (132°), and aluminium chloride (ordinary temperature); the new decomposition temperatures are given in parentheses. Similar results are found for triphenylmethyl methyl ether.

Aluminium chloride and triphenylmethyl ethyl ether react in carbon disulphide at the ordinary temperature, forming triphenylmethyl chloride, the additive compound,  $CPh_3Cl \cdot AlCl_3$ , and aluminium diethoxychloride,  $AlCl(OEt)_2$ . Ferric chloride and the same ether in carbon disulphide yield triphenylcarbinol and triphenylmethane. Triphenylmethyl acetate and aluminium chloride afford triphenylmethyl chloride, whilst with ferric chloride triphenylcarbinol is produced.

The following appear to be new: *triphenylmethyl n-butyl*, b. p. 212.8—213°/5 mm., *sec.-butyl*, b. p. 196—198°/5 mm., *isobutyl*, m. p. 51—53°, *isoamyl*, b. p. 205—205.5°/5 mm., *benzyl*, m. p. 103—104°, and  $\beta$ -phenylethyl ethers, m. p. 87.1—87.8°.

H. BURTON.

**Dehydrogenation by selenium. III. Dehydrogenation of ergosterol, cholic acid, and shellac.** O. DIELS and A. KARSTENS (Annalen, 1930, 478, 129—137).—Dehydrogenation of ergosterol with selenium, first at 250—280° and then at 320—360°, gives mainly the hydrocarbon  $C_{18}H_{16}$ , m. p. 125°, together with the hydrocarbon  $C_{25}H_{24}$ , m. p. 219°, both of which have been obtained previously from cholesterol (A., 1928, 169). Cholic acid furnishes chrysene (cf. A., 1927, 241), whilst shellac gives a paraffin hydrocarbon,  $C_{26}H_{54}$  (?), m. p. 68°. Varying amounts of oily products are also formed during the dehydrogenations.

H. BURTON.

**Ionisation constants and absorption spectra of ephedrine and  $\psi$ -ephedrine.** J. ABILDGAARD and H. BAGGESGAARD-RASMUSSEN (Dansk Tidsskr. Farm., 1930, 4, 30—38).—The picrates of these bases can be prepared by treating a 0.02*M*-solution of the hydrochloride with an equivalent quantity of a saturated solution of picric acid. *l*-Ephedrine picrate has m. p. 93—97°;  $[\alpha]_D - 38.6^\circ$ ; *ephedronine picrate*, m. p. 143—146°; *r*-ephedrine picrate, m. p. 145—147°; *d*- $\psi$ -ephedrine picrate, m. p. 145—147°,  $[\alpha]_D + 67.7^\circ$ . The *silicotungstates* of the above bases have the composition  $4C_{10}H_{15}ON \cdot 12WO_3 \cdot SiO_2 \cdot 2H_2O$ . The *l*-ephedrine salt forms a gummy mass, but the *r*-ephedrine and *d*- $\psi$ -ephedrine derivatives crystallise well. The ionisation constant at 18° of the equilibrium  $[C_{10}H_{15}ON]H^+ \rightleftharpoons C_{10}H_{15}ON + H^+$  has been determined by means of the Bjerrum-Arrhenius colorimeter, using thymol-blue and thymolphthalein as indicators. The absorption spectra of *l*- and *r*-ephedrine are identical; *d*- $\psi$ -ephedrine gives an absorption curve which shows a maximum lower than the others in the region  $\lambda$  2575 Å., but is otherwise quite similar.

H. F. HARWOOD.

**Diastereoisomerism. V. Diastereoisomerism and crystalline symmetry of ephedrine.** H. EMDE and F. SPÄNHÄUER (Helv. Chim. Acta, 1930,

13, 3—9).—Schwantke's determinations of the crystalline forms of the hydriodides of *l*-ephedrine and *d*- $\psi$ -ephedrine have been confirmed, and the measurements extended to the hydriodide of *r*- $\psi$ -ephedrine and the *O*-sulphuric ester of *d*- $\psi$ -ephedrine. *l*-Ephedrine hydriodide crystallises in enantiomorphic hemihedral forms in agreement with theory, and natural *r*- $\psi$ -ephedrine hydriodide in the holohedral form. The results for *d*- $\psi$ -ephedrine hydriodide and for the *O*-sulphuric ester of *d*- $\psi$ -ephedrine may be interpreted in terms of a holohedral form, without, however, ruling out the possibility of enantiomorphism as a result of a false holohedry combined with a hidden hemihedry. This is confirmed in the case of the *O*-sulphuric ester of *d*- $\psi$ -ephedrine by the pyroelectric properties of the crystals. The molecular rotations for *l*-ephedrine and *d*- $\psi$ -ephedrine hydriodide are, respectively,  $[M]_D^{20} -74.4^\circ$  and  $+126^\circ$ .

F. G. TRYHORN.

**Ephedrine.** H. EMDE (Arch. Pharm., 1930, 268, 83—103).—A review and bibliography.

R. K. CALLOW.\*

**Aromatic glycols.** DELUCHAT (Compt. rend., 1930, 190, 438—440).—The following di-( $\alpha$ -hydroxyalkyl)benzenes have been prepared by the interaction of magnesium methyl or ethyl bromide with the corresponding phthalaldehyde (cf. Nelken and Simonis, A., 1908, i, 348): *o*-di-( $\alpha$ -hydroxyethyl)-, m. p.  $105^\circ$ , *o*-di-( $\alpha$ -hydroxypropyl)-, m. p.  $70^\circ$ , *m*-di-( $\alpha$ -hydroxyethyl)-, m. p.  $98^\circ$ , *m*-di-( $\alpha$ -hydroxypropyl)-, m. p.  $67^\circ$ , *m*-di-( $\alpha$ -hydroxybenzyl)-, m. p.  $157^\circ$ , *p*-di-( $\alpha$ -hydroxyethyl)-, m. p.  $81^\circ$ , *p*-di-( $\alpha$ -hydroxypropyl)-, m. p.  $118^\circ$ , and *p*-di-( $\alpha$ -hydroxybenzyl)-benzene, m. p.  $172^\circ$ .

R. K. CALLOW.

**Electrolysis of solutions of alkali salts of polymethylenecarboxylic acids.** N. J. DEMIANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1861—1868).—The products of electrolysis of a solution of potassium cyclopropanecarboxylate, made alkaline with potassium carbonate and hydrogen carbonate, are allyl alcohol, acetaldehyde and its polymerides, and allyl cyclopropanecarboxylate. Using cyclobutanecarboxylic acid, the products are cyclobutanol, cyclobutyl cyclobutanecarboxylate, and cyclobutanone, whilst with cyclohexanecarboxylic acid, cyclohexanol and cyclohexanone are identified amongst the reaction products.

R. TRUSZKOWSKI.

**Trimorphism of *cis*-cinnamic acid.** A. W. K. DE JONG (Rec. trav. chim., 1930, 49, 216—217).—The double *cis*-*trans*-cinnamic acid in equilibrium with the acid of m. p.  $42^\circ$  has been obtained by concentration of a dilute solution of *cis*- and *trans*-cinnamic acids in light petroleum (b. p.  $50$ — $80^\circ$ ) which had remained for 8 days without crystallisation. The solution, when seeded with either the  $68^\circ$  or  $58^\circ$  acid, crystallised in these two forms respectively. Crystallographic measurements on this double acid give the same values as those obtained for the double acid in equilibrium with the  $58^\circ$  acid (this vol., 86). The identity of the three double acids establishes the trimorphism of *cis*-cinnamic acid. J. W. BAKER.

**Keto-lactol tautomerism. IV. Chemistry of 5-acetyl-1:1:2-trimethylcyclopentane-2-carboxylic acid.** Constitutions of the acid esters

of camphoric acid, and a synthesis of homo-epicamphor. M. QUDRAT-I-KHUDA (J.C.S., 1930, 206—213).—Both *ortho*- and *allo*-methyl hydrogen camphorates, m. p.  $77^\circ$  and  $86^\circ$ , respectively, hitherto believed to be structurally different, on conversion into acid chlorides and treatment with zinc methyl iodide give methyl 5-acetyl-1:1:2-trimethylcyclopentane-2-carboxylate, b. p.  $135^\circ/11$  mm.,  $d_4^{25}$  1.04555,  $n_D^{25}$  1.4733,  $[\alpha]_D^{25} +21.3^\circ$  in alcohol (*semicarbazone*, m. p.  $198^\circ$ ). The two acid chlorides, when brominated and poured into methyl alcohol, give methyl camphanate, Wreden's  $\omega$ -bromocamphoric anhydride (A., 1872, 895), camphanic acid, and methyl bromocamphorate, b. p.  $162$ — $164^\circ/12$  mm. (slight decomp.). Finally, the acid chloride of the *ortho*-ester with water is converted into the *allo*-ester. These facts taken in conjunction point strongly to the conclusion that the difference between the two esters is one of spatial configuration and not of structure.

5-Acetyl-1:1:2-trimethylcyclopentane-2-carboxylic acid, prepared by hydrolysing the ester with aqueous-alcoholic potassium hydroxide, has m. p.  $96^\circ$ ,  $[\alpha]_D^{25} +99.1^\circ$  in chloroform (*semicarbazone*, m. p.  $225^\circ$ ). This acid is most probably identical with the "aceto-camphenylcarboxylic acid" of Winzer (A., 1890, 1152). At the same time are produced an isomeric substance, b. p.  $186$ — $187^\circ/14$  mm., apparently the hydroxy-lactonic form of the acid (condensation product with semicarbazide acetate, m. p.  $172^\circ$ , isomeric with the above semicarbazone), and 1:8:8-trimethyldicyclopentane-2:4-dione, m. p.  $220^\circ$  to a red liquid, optically inactive. This diketone is obtained more conveniently by the use of sodium ethoxide. Both the acid and its hydroxy-lactone are practically unchanged by heating with acetyl chloride, the product being recovered as the monohydrated acid, m. p.  $73^\circ$  (cf. Winzer, *loc. cit.*). Acetic anhydride, however, yields

the unsaturated lactone,  $\begin{array}{c} \text{CH}_2\text{C}=\text{CMe} \\ | \quad | \\ \text{CMe}_2 \quad \text{O} \\ | \quad | \\ \text{CH}_2\text{CMe}-\text{CO} \end{array}$ , b. p.  $136^\circ/$

$22$  mm., m. p.  $62^\circ$ ,  $[\alpha]_D^{25} +77.7^\circ$  in chloroform. Reduction of the keto-acid, m. p.  $96^\circ$ , with sodium and alcohol gives methylcampholide, m. p.  $100$ — $101^\circ$ ,  $[\alpha]_D^{25} -44.8^\circ$  in chloroform. The diketone, m. p.  $220^\circ$ , reduced by Clemmensen's method, gives a mixture of a ketone, probably homoepicamphor (isolated as semicarbazone, m. p.  $220^\circ$ , from which the ketone could not be regenerated), and a semi-solid substance regarded as the corresponding keto-alcohol.

H. A. PIGGOTT.

**Phenylserines.** M. OESTERLIN (Metallbörse, 1929, 19, 1237—1238; Chem. Zentr., 1929, ii, 1398).—Forster and Rao's phenylisoserine (from  $\alpha$ -halogeno- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid and ammonia) is structurally isomeric with Erlenmeyer's phenylserine (from benzaldehyde and glycine); phenylglycidic acid is an intermediate product in its formation. Fourneau's phenylserine derivatives (from  $\alpha$ -halogeno- $\beta$ -hydroxy- $\beta$ -phenylpropionic esters and amines in benzene) are phenylisoserine derivatives. Hydrolysis of Fourneau's (identical with Forster and Rao's) amino-acid amide afforded an isomeric phenylisoserine. Phenylisoserine, from  $\alpha$ -bromo- $\beta$ -hydroxy- $\beta$ -phenylpropionic acid and ammonia, has m. p.  $230$ — $232^\circ$  (decomp.) (copper salt; toluene-*p*-sulphonyl

derivative, m. p. 189°); oxidation with permanganate gave phenyltoluene-*p*-sulphamidoacetic acid, m. p. 179°. Phenylglycidic acid yielded an acid, m. p. 224°, affording benzaldehyde and ammonia on oxidation. *N*-Methylphenylisoserine has m. p. 272° (decomp.), and *N*-dimethylphenylisoserine has m. p. 143°. Methyl phenylglycidate and ammonia afforded a product, m. p. 124°. Phenylisoserineamide has m. p. 200°; the isomeric phenylisoserine has m. p. 270—280° (decomp.). Phenylisoserinemethylamide has m. p. 153°.

A. A. ELDRIDGE.

**Lichen acids. I. Derivatives of  $\beta$ -orcinol.**  
A. ROBERTSON and R. J. STEPHENSON (J.C.S., 1930, 313—320).—The synthesis of a number of products obtained from the lichens is described, starting from  $\beta$ -orcinol, which has been prepared in quantity by an improved method. 2:4-Dimethylcarbonato-3:6-dimethylbenzaldehyde, m. p. 91°, prepared from  $\beta$ -oreylaldehyde and methyl chloroformate, on oxidation with permanganate yields 2:4-dihydroxy-3:6-dimethylbenzoic acid, the methyl ester of which occurs in atranorin and oak moss oil (Walbaum and Rosenthal, A., 1924, i, 758). The methyl ester may be prepared by heating a solution of the acid in methyl alcohol; the ethyl ester, similarly prepared, has m. p. 129°. The isolation of the acid from the natural methyl ester from atranorin is described for the first time. Partial methylation of  $\beta$ -oreylaldehyde by methyl iodide in acetone (Robertson and Robinson, A., 1928, 1020) is a convenient method for the preparation of rhizonaldehyde, also prepared by Sonn (A., 1917, i, 143) from  $\beta$ -orcinol monomethyl ether. Rhizonaldehyde condenses with  $\omega$ -methoxyacetoveratrone to give 3:7:3':4'-tetramethoxy-5:8-dimethylflavylum chloride, a dark green substance forming a dark red ferrichloride, m. p. 240—245° (sinters 236°). This confirms Pfau's orientation (A., 1928, 1241). Acetyl-rhizonaldehyde, m. p. 71°, on oxidation gives acetyl-rhizonic acid (2-acetoxy-4-methoxy-3:6-dimethylbenzoic acid, m. p. 146°), hydrolysed by 4% aqueous sodium hydroxide to rhizonic acid. 2-Hydroxy-4-methylcarbonato-3:6-dimethylbenzaldehyde, m. p. 110°, prepared from  $\beta$ -oreylaldehyde in a similar manner to the dicarbomethoxy-derivative, on methylation with methyl iodide and silver oxide gives the 2-methoxy-ether, m. p. 74—75°, which on hydrolysis with 4% methyl-alcoholic sodium hydroxide yields isorhizonaldehyde, also prepared by Pfau from  $\beta$ -orcinol monomethyl ether. This aldehyde does not condense with  $\omega$ -methoxyacetoveratrone to form a flavylum salt.

H. A. PIGGOTT.

#### Constitution of hydrangenol and phyllodulcin.

II. Y. ASAHINA and J. ASANO (Ber., 1930, 63, [B], 429—437; cf. A., 1929, 324).—The portion of the alcoholic extract of hydrangea flowers insoluble in water contains, in addition to hydrangenol, a compound soluble in sodium carbonate to which the name isohydrangenol has been applied by Asahina and Miyake (J. Pharm. Soc. Japan, 1916, No. 418), but for which, in recognition of its true acid properties, the restoration of the older term "hydrangic acid" is proposed. It is shown to be 3:4'-dihydroxystilbene-2-carboxylic acid in the following manner. It is readily isomerised to hydrangenol when heated.

It is converted by diazomethane into methyl 3:4'-dimethoxystilbene-2-carboxylate, m. p. 108° (corresponding acid, m. p. 121°), transformed by the successive action of ozonised oxygen and boiling water into a mixture of anisic acid and methyl hydrogen 3-methoxyphthalate. Reduction of hydrangic acid by sodium amalgam yields dihydrohydrangic acid (formerly deoxyhydrangenolic acid), which with methyl sulphate and alkali affords 3-hydroxy-4'-methoxy- $\alpha\beta$ -diphenylethane-2-carboxylic acid, m. p. 127°, oxidised by permanganate to  $\beta$ -*p*-anisylpropionic acid, m. p. 102—103°.

*m*-Methoxybenzaldehyde cyanohydrin is converted by ethereal magnesium *p*-anisyl bromide into 3:4'-dimethoxybenzoin, m. p. 60° (3:4'-dimethoxybenzil, m. p. 86°), transformed by successive treatment with zinc and hydrochloric acid in alcohol and hydriodic acid in glacial acetic acid into 3:4'-dihydroxy- $\alpha\beta$ -diphenylethane, m. p. 108°, isolated through the benzoyl derivative, m. p. 106°. The phenol is identical with the product obtained by Asahina and Miyake (*loc. cit.*) by the distillation of dihydrohydrangic acid.

Hydrangeol is soluble in alkali hydroxide or sodium carbonate and the yellow solution becomes colourless when treated with sodium amalgam, dihydrohydrangic acid being produced. *iso*Phyllodulcin is colourless in alkaline solution in which it cannot be reduced by sodium amalgam. *Hydrangeol monomethyl ether*, m. p. 122—123°, and *dimethyl ether*, m. p. 151°, yield colourless solutions in boiling alkali hydroxide from which the initial material is precipitated by acids; sodium amalgam is ineffective in alkaline solution.

Alcoholic solutions of *o*-hydroxy-carboxylic acids give a permanent bluish-violet colour after addition of a trace of ferric chloride, whereas their esters or lactones yield a transitory reddish-violet or red colour, thus affording a ready means of discrimination.

H. WREN.

**Syntheses in the hydroaromatic series. VII.**  
O. DIELS and K. ALDER [with E. PETERSEN and F. QUEBERITZ] (Annalen, 1930, 478, 137—154).—*cyclo*Hexadiene and acetaldehyde combine at 100° to give 2:5-endoethylene- $\Delta^3$ -tetrahydrobenzaldehyde, b. p. 84—85°/12 mm., the semicarbazone, m. p. 176—177°, of which is reduced by hydrogen in presence of colloidal palladium and alcohol, to the semicarbazone, m. p. 191—192°, of 2:5-endoethylenehexahydrobenzaldehyde, b. p. 98—99°/14 mm., m. p. 76—77°. Treatment of this with acetic anhydride and sodium acetate, and subsequent fission of the resulting enol acetate, b. p. 111—112°/15 mm., with ozone in presence of benzene and water (cf. A., 1929, 819) give 2:5-endoethylenecyclohexanone, m. p. 178—179° [semicarbazone, m. p. 204—205° (decomp.)]. This ketone is oxidised by warm fuming nitric acid to *cis*-hexahydroterephthalic acid. When *cyclo*hexadiene and dibromomaleic anhydride are condensed in benzene, 1:2-dibromo-3:6-endoethylene- $\Delta^4$ -tetrahydrophthalic anhydride, m. p. 252° with coloration, results. This is converted by treatment with zinc dust and acetic acid into 3:6-endoethylene- $\Delta^4$ -tetrahydrophthalic anhydride (A., 1928, 1018), and by hydrogen in presence of platinum-black and acetic acid into 3:6-endoethylene- $\Delta^1$ -tetrahydrophthalic anhydride, m. p.

158°. This arises by elimination of the bromine from the fully-reduced compound as hydrogen bromide. Ozonolysis of this anhydride in chloroform solution and oxidative fission of the ozonide with hydrogen peroxide solution afford *cis*-hexahydroterephthalic acid. Addition of both maleic and dibromomaleic anhydrides to cyclohexadiene occurs in the 1:4-positions of the conjugated double linkings. Reduction of *cis*-3:6-endoethylene- $\Delta^4$ -tetrahydrophthalic acid with hydrogen in presence of colloidal palladium and sodium carbonate solution affords *cis*-3:6-endoethylenhexahydrophthalic acid, m. p. 148—152° (decomp.; *anhydride*, m. p. 187°), converted by hydrochloric acid (*d* 1.19) at 180—190° into the *trans*-acid, m. p. 234°. Neither the *trans*-acid nor *trans*-3:6-endomethylenhexahydrophthalic acid gives anhydrides when treated with acetyl chloride; these results agree with Bredt's rule (A., 1924, i, 643). The 1:4-endoethylenecyclohexane ring system is strainless.

cyclopentadiene and dibromomaleic anhydride condense in ether, forming 1:2-dibromo-3:6-endomethylene- $\Delta^4$ -tetrahydrophthalic anhydride, m. p. 187—188°, which is converted by zinc dust and acetic acid into 3:6-endomethylene- $\Delta^4$ -tetrahydrophthalic anhydride (*loc. cit.*). Catalytic reduction (platinum-black) affords a compound,  $C_9H_8O_3Br_2$ , m. p. 198—200°, and 3:6-endomethylene- $\Delta^1$ -tetrahydrophthalic anhydride, m. p. 98—99° (isolated as the free acid, m. p. 212°). The last-named anhydride is converted by ozonolysis and subsequent oxidative fission into *cis*-cyclopentane-1:3-dicarboxylic acid. H. BURTON.

**Properties of conjugated compounds; additive formation of cyclohexenes.** E. H. FARMER and F. L. WARREN (Ber., 1930, 63, [B], 360—361; cf. A., 1929, 812).—A reply to Diels and Alder (*ibid.*, 1296). H. WREN.

**Bile acids. XXIX. Thermal decomposition of the simple bile acids.** H. WIELAND and V. WIEDERSHEIM (Z. physiol. Chem., 1930, 186, 229—236; cf. A., 1928, 1007).—Dehydronorcholene, treated with 3% perbenzoic acid in chloroform, gave *dehydronorcholene oxide*,  $C_{23}H_{36}O$ , m. p. 161—162°; by catalytic hydrogenation it yielded *dehydronorcholane*,  $C_{23}H_{38}$ ; m. p. 66—67°. Distillation of sodium cholanoate over soda-lime gave *norcholane*,  $C_{23}H_{40}$ , m. p. 101—103°. 7-Ketonorcholanic acid,  $C_{23}H_{36}O_3$  (sparingly soluble sodium salt), was obtained by oxidation of dehydronorcholane with potassium permanganate in acetic acid solution. 7:12-Diketocholelanic acid, m. p. 175—177°, prepared by reduction of dehydrocholic acid in alcoholic solution with zinc and hydrochloric acid and hydrolysis of the ester so produced, does not undergo any change on heating with 10% sodium hydroxide, unlike dehydroxydeoxycholic acid (A., 1926, 723). 7:12-Diketocholelanic acid heated in a stream of carbon dioxide yields 12-ketodehydronorcholene,  $C_{23}H_{34}O$ , m. p. 148—149°. The neutral portion of the distillate from cholic acid, from which cholatrienic acid had been removed, was a complex mixture, hydrogenation of which yielded some isolithocholic acid lactone. The acid fraction after hydrogenation yielded cholanilic acid and isolithocholic acid. Oxidation of the crude acid mixture gave 7-ketocholelanic acid. J. H. BIRKINSHAW.

**Action of bromine on phenolphthalein.** Further evidence of the tautomeric character of phenolphthalein. A. R. DAY (J. Amer. Chem. Soc., 1930, 52, 646—650).—When a solution of phenolphthalein in 3*N*-sodium hydroxide containing potassium bromide and bromate is acidified with hydrochloric acid, 5 mols. of bromine are consumed and a brownish-yellow precipitate is formed. When this is heated at 50—75° tribromophenol sublimes; the coloured residue, m. p. 229—236° (decomp.), is considered to be the impure acid,  $O:C_6H_2Br_2:CBR\cdot C_6H_4\cdot CO_2H$ . Dissolution of this acid in alcohol and slow evaporation of the solution gives the colourless lactone,  $\begin{matrix} CO\cdot C_6H_4\cdot CBR\cdot C_6H_2Br_2\cdot OH \\ | \\ O \end{matrix}$

m. p. 270—273° with some decomp. The formation of the coloured quinonoid derivative affords evidence of the quinonoid structure of phenolphthalein in alkaline solution. H. BURTON.

**Unsaturated ketonic acids. III. Behaviour of Pechmann dyes with amines.** Some diimino-ethers of diphenacylfumaric and diphenacylmaleic acids and their tinctorial properties. M. T. BOGERT and I. W. GREENBERG (Coll. Czech. Chem. Comm., 1930, 2, 83—94).—The so-called Pechmann dyes (A., 1882, 1074; cf. Bogert and Ritter, A., 1925, i, 36) yield with a primary amine ( $R\cdot NH_2$ ) in acetic acid solution, through an intermediate dilactamide, a di-imino-ether which is formulated  $\left( \begin{matrix} O \\ | \\ Ph\cdot C\cdot CH\cdot C\equiv N\cdot R \end{matrix} \right)_2$ .

By the use of the corresponding diacetones the stereoisomeric diphenacylfumaric and diphenacylmaleic NN'-diphenyldi-imino-ether were obtained by condensation with aniline. The preparation of pp'-diphenyldiphenacylfumaric dilactone from p-phenylbenzoylacrylic acid is described. It gives an intense green colour in concentrated sulphuric acid. Diphenacylfumaric di-imino-ethers were prepared by using the following amines: o-, m-, and p-toluidine, benzylamine,  $\alpha$ - and  $\beta$ -naphthylamine, m- and p-xylylene, o-, m-, and p-chloroaniline, 2:4-dichloroaniline, o-, m-, and p-bromoaniline, o-, m-, and p-aminophenol, 6-amino-m-cresol, o-, m-, and p-anisidine, o-, m-, and p-phenetidine, m- and p-nitroaniline, 4-nitro-o-toluidine, 4-chloro-3-nitroaniline, p-aminodithiylaniline, thio-p-toluidine, m- and p-phenylenediamine, m-tolylenediamine, benzidine, toluidine, pp'-diaminodiphenylmethane, glycine, alanine, leucine, ethyl  $\beta$ -aminocrotonate, m- and p-aminobenzoic acid, ethyl p-aminobenzoate, p-aminophenylacetic acid, p-aminophenylglycine, carbamide, p-aminoacetanilide, p-aminomethylacetanilide, sodium sulph-anilate, p-arsanilic acid, phenylhydrazine, p-aminoazobenzene, 2-amino-5-azotoluene, dehydrothio-p-toluidine, 5-amino-1-phenylbenzthiazole. These compounds are generally insoluble in the usual solvents and infusible. Some of those containing solubilising groups dye wool and silk violet shades fast to light.

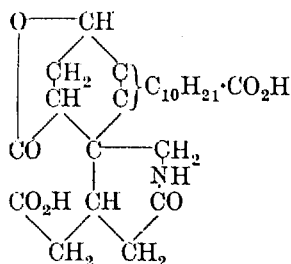
The Pechmann dye from  $\beta$ -benzoylacrylic acid generated on wool is fast to most dye tests except direct sunlight. T. H. MORTON.

**Constitution of a substance obtained by esterification of ferulic acid.** S. TANAKA (Sci.

Rep. Tôhoku, 1929, **18**, 619—623).—Treatment of ferulic acid with methyl alcohol and sulphuric acid affords a saturated ester,  $C_{23}H_{24}O_8$ , m. p. 165—165.5°, probably methyl 3:4(or 2:4)-di-(4-hydroxy-3-methoxyphenyl)cyclobutane-1:2(or 1:3)-dicarboxylate (dimethyl ether, m. p. 216—217°), hydrolysed to the corresponding acid,  $C_{20}H_{20}O_8$ , m. p. 251—251.5° (decomp.). Similar treatment with ethyl and *n*-propyl alcohols furnishes ethyl, m. p. 75.5—76.5°, and *n*-propyl ferulates, m. p. 78—79°.

H. BURTON.

**Bile acids. XXVI.** M. SCHENCK and H. KIRCHHOFF (Z. physiol. Chem., 1930, **186**, 271—279; cf. this vol., 89).—Oxidation of biliobanic acid followed by Beckmann inversion gave a product identical with one of the crystalline forms (form B, compact prisms)



of the lactone-lactam dicarboxylic acid,  $C_{24}H_{35}O_7N$  (annexed formula), shown previously to be formed by reducing the ketolactamtricarboxylic acid,  $C_{24}H_{35}O_8N$ , and lactone formation. Boiling form B with 25% hydrochloric acid yields the hydrochloride of form A (needles). Form A is converted into form B by boiling with acetic acid. When biliobanic acid oxime is treated with nitric acid the oximino-group at C7 is replaced by oxygen and biliobanic acid regenerated. There appears to be a transient formation of a nitroso-compound.

J. H. BIRKINSHAW.

**Isomerism of the oximes. XXXVII.** Allyl-*p*-nitrobenzaldoximes, *O*- and *N*-allylhydroxylamines, and sulphime *S*-ethers. O. L. BRADY and F. H. PEAKIN (J.C.S., 1930, 226—229).—In general resinous polymerisation products are obtained in attempts at the preparation of ethers from aldoximes and unsaturated alkyl halides. *p*-Nitrobenzaldoxime, however, gave crystalline *O*- and *N*-allyl ethers, not differing markedly in relative amounts from those of the methyl ethers. No crystalline products could be obtained with cinnamyl or styryl halides.  $\alpha$ -*p*-Nitrobenzaldoxime with sodium and allyl iodide gave  $\alpha$ -*O*-allyl-*p*-nitrobenzaldoxime, m. p. 75°, and *N*-allyl-*p*-nitrobenzaldoxime, m. p. 112° (hydrochloride, m. p. 61—64°), the *N*-allyl-oxime being also obtained from  $\beta$ -*p*-nitrobenzaldoxime. Benzhydroxamic acid with allyl bromide and sodium hydroxide gave *O*-allylbenzhydroxamic acid, m. p. 58°, which with alcoholic hydrochloric acid gave *O*-allylhydroxylamine hydrochloride, m. p. 172° (decomp.), which did not reduce Fehling's solution, and with *p*-nitrobenzaldehyde gave  $\alpha$ -*O*-allyl-*p*-nitrobenzaldoxime.  $\beta$ -Benzaldoxime on allylation gave an ether that could not be crystallised; the crude product on hydrolysis and removal of the regenerated aldehyde gave a solution that reduced Fehling's solution and formed *N*-allyl-*p*-nitrobenzaldoxime with *p*-nitrobenzaldehyde; it was therefore considered to contain *N*-allylhydroxylamine.

The sulphime *S*-ethers of Zincke and Farr (A., 1912, i, 763) are analogous to the oxime *O*-ethers, but attempts to obtain them in stereoisomeric forms

have not met with success. *o*-Nitrophenylsulphamine condensed with *m*-nitrobenzaldehyde to give *m*-nitrobenzylidene-*o*-nitrophenylsulphamine in one form only, m. p. 192°. Benzylidene-*o*-nitrophenylsulphamine was also prepared and found to be uniform. Neither was changed by exposure in benzene solution for 48 hrs. to the light of a quartz-mercury vapour lamp.

H. A. PIGGOTT.

**Possible existence of several dibenzylidenecyclopentanones.** R. CORNUBERT (Compt. rend., 1930, **190**, 440—442).—Distillation of 1:4-dibenzylidenecyclopentanone, m. p. 190°, at 267°/21 mm. causes a more or less complete change to an isomeride, m. p. 129°. When 1-methylcyclopentanone containing cyclopentanone is condensed with benzaldehyde in presence of hydrochloric acid, a yellow substance, m. p. 192°, is obtained, derived from the cyclopentanone. This may be a third isomeride or dibenzylidenecyclopentylidenecyclopentanone. It is hydrogenated in presence of nickel to give the dibenzyl compound, m. p. 37°, b. p. 230°/15 mm. (oxime, m. p. 145°; semicarbazone, m. p. 156—157°; tetrahydropyrone compound, m. p. 201—202°).

R. K. CALLOW.

**Interaction of sodamide and alkyl iodides with acetophenone and its homologues.** A. RUSSELL (J.C.S., 1930, 320).—Ethyl iodide reacts normally with sodio-*n*-propyl-*n*-butylacetophenone in a neutral solvent giving  $\alpha$ -ethyl- $\alpha$ -*n*-propyl- $\alpha$ -*n*-butylacetophenone in a yield greater than 50% (cf. Haller and Bauer, A., 1909, i, 108). Methyl iodide and sodioacetophenone interact normally in ether, but in benzene a polymeride of propiophenone, m. p. 96—98°, b. p. 300—320°/15 mm., is the sole product. It is unaffected by acids, alkalis (in which it is insoluble), permanganate, dichromate, and fusion with potassium hydroxide, and gives no methyl iodide in the Zeisel reaction; it may be  $O \begin{smallmatrix} \text{C} \text{Et} \text{Ph} \cdot \text{O} \\ \text{C} \text{Et} \text{Ph} \cdot \text{O} \end{smallmatrix}$ , the acetal structure accounting for its stability.

H. A. PIGGOTT.

**Phenacyl, *p*-chloro- and *p*-bromo-phenacyl esters of higher fatty acids.** R. M. HANN, E. E. REID, and G. S. JAMIESON (J. Amer. Chem. Soc., 1930, **52**, 818—820).—Phenacyl esters are prepared from phenacyl bromide and the sodium salt of the fatty acid in boiling aqueous alcohol containing a small amount of the free acid. The phenacyl esters of lauric, m. p. 48—49°; myristic, m. p. 56°; palmitic, m. p. 63°; stearic, m. p. 69°; arachidic, m. p. 85—86°, and lignoceric acids, m. p. 87—88°, are described. The corresponding *p*-chlorophenacyl esters have m. p. 70°, 76°, 82°, 86°, 86°, and 99—100°, respectively, and the corresponding *p*-bromophenacyl esters m. p. 76°, 81°, 86°, 90°, 89°, and 90—91°, respectively.

H. BURTON.

**Ammonolysis of ketones.** H. H. STRAIN (J. Amer. Chem. Soc., 1930, **52**, 820—823).—Aromatic and aryl alkyl ketones give small amounts of ketimines on treatment with ammonia at 180—200°. The yield is improved by carrying out the reaction in presence of the product formed by passing dry ammonia over aluminium chloride; this product is a good dehydrating agent. Thus, acetophenone and



liquid ammonia at 180° (cf. Blair, A., 1926, 277) afford 3% of acetophenoneimine; the yield is 30% in presence of the aluminium compound. Similarly, *p*-tolyl methyl ketone, fenchone, camphor, and benzophenone all furnish the corresponding imines. Benzil at 200° gives 40% of triphenyliminazole. Camphorimine is reduced by sodium and alcohol in presence of ether to bornylamine.

H. BURTON.

**Absorption and constitution of coloured acids, esters, and salts of indandione derivatives.** A. HANTZSCH and E. CZAPO (Z. physikal. Chem., 1930, 146, 131—144).—Comparison of the absorption spectra of yellow 3-methoxy-2-phenylindone, m. p. 78°, obtained best by the action of diazomethane on phenyloxindone in methyl alcohol, with those of the red, unstable indandione salts in alcoholic solution shows that the latter have not a simple enolic structure, but must be considered to be "conjugated" enolic salts in which the metal atom is linked to both the oxygen atoms. Those salts with colourless metallic and ammonium ions are all optically identical, with the exception of the substituted ammonium salts which are strongly associated in chloroform solution. Solutions of the free indandiones in alcohol and in water consist of equilibrium mixtures of colourless unchanged indandiones, yellow solvated oxindones, and red oxonium salts. The yellow salts of phenyloxindonecarboxylic esters are optically different from the above-mentioned red salts and have an unsymmetrical structure. The following salts of 2-phenyloxindone are described: sodium, +3H<sub>2</sub>O; potassium, +2H<sub>2</sub>O; thallium; cadmium, +2EtOH; ammonium; piperidinium; tetraethylammonium, and phenyltrimethylammonium; and of ethyl oxindonecarboxylate the strontium, +2½H<sub>2</sub>O, cadmium, thallium, tetraethyl- and tetrapropyl-ammonium salts.

O. J. WALKER.

**Auto-oxidation of  $\alpha$ -ketols in alkaline solution.** A. WEISSBERGER, E. STRASSER, H. MAINZ, and W. SCHWARZE (Annalen, 1930, 478, 112—128).—During the auto-oxidation of benzoin in aqueous-alcoholic potassium hydroxide solution (A., 1929, 1301), the benzoin ion and not the undissociated salt, OK·CHPh·COPh, reacts with oxygen. The rate is diminished by the addition of potassium chloride to the solution. Determinations of the velocities of auto-oxidation of *n*-butyrolin and 14 aroylarylcannabinols (with *m*- or *p*-substituents only) at 10° and 20°, using the method previously described (*loc. cit.*), show (with one exception) an analogy between the product of the dissociation constants of the two acids derived by oxidation of the ketol, and the rates of auto-oxidation. The velocity increases with increase in the strength of the acids. With *o*-substituted benzoin, steric hindrance factors cause a diminution in the rates of auto-oxidation to varying extents; they are, however, somewhat analogous to the dissociation constants of the acids.  $\alpha$ -Furfuroylphenylcarbinol is oxidised much less readily than furin or benzoyl- $\alpha$ -furylcarbinol. The following disubstituted benzoin are prepared by the usual cyanide condensation method: 4:4'-diethoxy-, m. p. 86—87°; 2:2'-diethoxy-, m. p. 68.5—69°, and 2:2'-dichloro-, m. p. 62—63°. The following are prepared from the re-

quisite magnesium aryl halide and aldehydecyano-hydrin: benzoyl-*p*-tolyl-, m. p. 116—117°; *p*-toluoyl-phenyl-, m. p. 109—110°; *p*-chlorobenzoylphenyl-, m. p. 88—89°; benzoyl-*p*-chlorophenyl-, m. p. 110—111°; benzoyl-*o*-ethoxyphenyl-, m. p. 81—82°; *o*-ethoxybenzoylphenyl-, m. p. 77—78°, and benzoyl-*o*-tolyl-carbinols, m. p. 64—65°.

H. BURTON.

**Methylation of the oximes of benzil. II. Monomethyl ethers of the benzildioximes.** O. L. BRADY and M. M. MUERS (J.C.S., 1930, 216—226).—*O*-Methyl- $\alpha$ -benzilmonoxime with hydroxylamine yields *O*-monomethyl- $\alpha$ -benzildioxime, m. p. 181—182° (acetyl compound, m. p. 107—108°; benzoyl compound, m. p. 167°), and  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime, m. p. 172° (acetyl compound, m. p. 80°; benzoyl compound, m. p. 79°). [The new configurations of Meisenheimer (A., 1922, i, 152) are used and in addition  $\alpha'$  indicates that the methylated oximino-group in the  $\gamma$ -dioxime is vicinal to, and  $\beta'$  that it is remote from, the phenyl group.] *O*-Methyl- $\beta$ -benzilmonoxime reacts only with difficulty and at the high temperature necessary (175—185° for 10 hrs.) gives only *O*-monomethyl- $\beta$ -benzildioxime, m. p. 177° (acetyl compound, m. p. 81°; benzoyl compound, m. p. 162°).  $\alpha$ -Benzildioxime on methylation yields a mixture of *O*- and *N*-monomethyl- $\alpha$ -benzildioximes; the latter (new) has m. p. 168°. The former, on further methylation, yields a mixture of *OO*- and *ON*-, and the latter a mixture of *ON*- and *NN*-dimethyl- $\alpha$ -benzildioximes (Brady and Perry, A., 1926, 171). The configuration of the monomethyl ethers is thus established.  $\alpha'$ -*O*-Monomethyl- $\gamma$ -benzildioxime yields *OO*-dimethyl- $\alpha$ -benzildioxime and *OO*-dimethyl- $\gamma$ -benzildioxime, m. p. 59°. *O*- and *N*-Ethers are distinguished by heating with hydriodic acid, methyl iodide and methylamine, respectively, being obtained. Methylation of  $\beta$ -benzildioxime yields *O*-monomethyl- $\beta$ -benzildioxime and *N*-monomethyl- $\beta$ -benzildioxime, m. p. 205° (decomp.):  $\gamma$ -benzildioxime yields the second as sole recognisable monomethylation product. *O*-Monomethyl- $\beta$ -benzildioxime yields *ON*- and *OO*-dimethyl- $\beta$ -benzildioxime; *N*-monomethyl- $\beta$ -benzildioxime yields *O*-methyl- $\beta$ -benzilmonoxime, probably by hydrolysis of *ON*-dimethyl- $\beta$ -benzildioxime.

*O*-Monomethyl- $\alpha$ -benzildioxime, boiled for 30 sec. with aniline, gives mainly  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime, but in addition the monomethyl ethers of the  $\beta$ - and  $\gamma$ -dioximes; longer boiling, or the action of hydrogen chloride in acetic acid, yields the  $\beta$ -compound as principal product.  $\alpha'$ -*O*-Monomethyl- $\gamma$ -benzildioxime also yields the  $\beta$ -compound. *OO*-Dimethyl- $\gamma$ -benzildioxime when boiled with concentrated hydrochloric acid yields *OO*-dimethyl- $\alpha$ -benzildioxime. *N*-Monomethyl- $\alpha$ -benzildioxime when boiled with aniline gives the anil (Auwers and Siegfeld, A., 1893, i, 354), but with dimethylaniline *N*-monomethyl- $\beta$ -benzildioxime.

*O*-Monomethyl- $\alpha$ -benzildioxime with phosphorus pentachloride undergoes the Beckmann change, yielding *N*-benzoyl-*O*-methylbenzamidoxime, m. p. 151° [identified by alkaline hydrolysis to benzoate and *O*-methylbenzamidoxime (Krüger, A., 1885, 895) and acid hydrolysis to benzamide and benzoic acid], and 3:5-diphenyl-1:2:4-oxdiazole (A., 1889, 1067).

The former is formed in proportionately larger quantity at 0° than at the ordinary temperature. The Beckmann rearrangement of  $\alpha'$ -O-monomethyl- $\gamma$ -benzildioxime yields  $\alpha$ -O-methylphenylglyoxalanilideoxime, m. p. 118—120°, yielding on hydrolysis aniline and an unidentified solid, m. p. 57—60°. Similarly, O-monomethyl- $\beta$ -benzildioxime yields  $\beta$ -O-methylphenylglyoxalanilideoxime, m. p. 152°, converted by boiling concentrated hydrochloric acid first into its  $\alpha$ -isomeride and then into hydrolysis products of the latter. It was synthesised by methylation of  $\beta$ -phenylglyoxalanilideoxime (A., 1893, 474) with methyl iodide and silver oxide. H. A. PIGGOTT.

**Nitration of 4:4'-dimethoxy- and 4:4'-diethoxy-benzophenones.** J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 153—164; cf. this vol., 90).—Nitration of 4:4'-dimethoxybenzophenone with absolute nitric acid in acetic anhydride at 0° gives the 3:3'-dinitro-derivative, m. p. 190° [identical with a specimen obtained by heating 4:4'-dichloro-3:3'-dinitrobenzophenone, m. p. 133° (Consonno, A., 1904, i, 676, gives 120°), with methyl-alcoholic sodium methoxide], but at the b. p. of the mixture or with absolute nitric acid alone at -15° the products are 3:3':5:5'-tetranitro-4:4'-dimethoxybenzophenone, m. p. 199° (similarly synthesised from the dichloro-tetranitro-compound; converted into 2:4:5-trinitroanisole only with difficulty), 2:4-dinitroanisole, and 3:5-dinitroanisole, the last two products being formed thus:  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \xrightarrow{\text{NO}_2, \text{OH}} p\text{-MeO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 + \text{C}_6\text{H}_4(\text{OMe})\cdot\text{CO}_2\text{H}$ , with subsequent nitration of the fission products. Similar results are obtained in the nitration of 4:4'-diethoxybenzophenone, the products being 3:3':5:5'-tetranitro-4:4'-diethoxybenzophenone, m. p. 194° (also synthesised), 2:4-dinitrophenetole, and 3:5-dinitro-4-hydroxybenzoic acid in absolute nitric acid at -15°, and 3:3'-dinitro-4:4'-diethoxybenzophenone, m. p. 159° (Consonno, loc. cit., gives 132°), in acetic anhydride at 0°. On the basis of these results and others cited from the literature it is concluded that replacement of groups in the benzene nucleus is hindered by the presence of nitro-groups in the *meta* position to such groups. By heating 3:3':5:5'-tetranitro-4:4'-dimethoxybenzophenone with the theoretical amount of the appropriate amine in alcoholic solution in a sealed tube at 100° the methoxy-group is replaced by the substituted amino-group, and thus are obtained 4:4'-diamino-, m. p. 324° (Consonno, loc. cit., gives 270°); 4:4'-dimethyl-, m. p. 230° (lit. 235°); 4:4'-diethyl-, m. p. 214°; 4:4'-di-n-propyl-, m. p. 156°; 4:4'-di-n-butyl-, m. p. 164°; 4:4'-di-n-amyl-, m. p. 130°; 4:4'-di-n-hexyl-, m. p. 121°; and 4:4'-di-n-heptyl-, m. p. 121°; -diamino-3:3':5:5'-tetranitrobenzophenones. The m. p. curve for these derivatives closely resembles that obtained for the corresponding benzil derivatives (van Alphen, loc. cit.), the m. p. tending to converge to 117° as the size of the alkyl group increases. J. W. BAKER.

**Syntheses of  $\beta$ -4-hydroxy-3-methoxyphenylethyl heptadecyl and nonadecyl ketones and 4-hydroxy-3-methoxystyryl nonadecenyl ketone.** T. OYAMADA (Sci. Rep. Tōhoku, 1929, 18, 625—637).

—Methyl heptadecyl ketone, obtained from ethyl hexadecylacetoacetate, condenses with vanillin in presence of aqueous-alcoholic potassium hydroxide forming 4-hydroxy-3-methoxystyryl heptadecyl ketone (+H<sub>2</sub>O), m. p. (anhydrous) 71—72°, reduced by hydrogen in presence of platinum-black and ether to  $\beta$ -4-hydroxy-3-methoxyphenylethyl heptadecyl ketone (I), m. p. 70.5—71.5°. Ethyl octadecylacetoacetate is hydrolysed with 20% sodium hydroxide solution to methyl nonadecyl ketone, m. p. 61—62° (semicarbazone, m. p. 130°), which is converted as above into 4-hydroxy-3-methoxystyryl (+H<sub>2</sub>O), m. p. (anhydrous) 79—80°, and  $\beta$ -4-hydroxy-3-methoxyphenylethyl nonadecyl ketones (II), m. p. 75.5—76.5°. Reduction of ethyl oleate with sodium and *n*-butyl alcohol in presence of toluene furnishes  $\Delta^1$ -octadecenyl alcohol, converted by treatment with red phosphorus and iodine into  $\Delta^1$ -octadecenyl iodide. Condensation of this with ethyl sodioacetoacetate and hydrolysis of the resulting product gives methyl  $\Delta^1$ -nonadecenyl ketone, m. p. 28.5—29.5° (semicarbazone, m. p. 106—107°), which condenses with vanillin forming a small amount of 4-hydroxy-3-methoxystyryl  $\Delta^1$ -nonadecenyl ketone (III), m. p. 52—54°. Catalytic reduction (platinum-black) of this in alcoholic solution affords II. The ketones I, II, and III are non-pungent. H. BURTON.

**Syntheses of 4'-nitro-2:4:6-trihydroxybenzophenone dimethyl ethers and 4'-amino-2:4:6-trimethoxybenzophenone.** M. YAMASHITA (Sci. Rep. Tōhoku, 1929, 18, 609—613).—The Hoesch condensation of *p*-nitrobenzonitrile with phloroglucinol dimethyl ether affords small amounts of 4'-nitro-2-hydroxy-4:6-dimethoxy-, m. p. 176.5—177°, and 4'-nitro-4-hydroxy-2:6-dimethoxy-benzophenones, m. p. 216—217°; the former of these compounds gives the boroacetic anhydride reaction (Dimroth, A., 1926, 297). 4'-Nitro-2:4:6-trimethoxybenzophenone, m. p. 170—170.5°, prepared by the addition of 40% sodium hydroxide solution to the trihydroxy-derivative in methyl-alcoholic methyl sulphate, is reduced by ferrous hydroxide to 4'-amino-2:4:6-trimethoxybenzophenone, m. p. 215.5° [hydrochloride, m. p. 193° (decomp.)]. H. BURTON.

**Steric hindrance in Hoesch reaction.** M. YAMASHITA (Sci. Rep. Tōhoku, 1929, 18, 615—618; cf. Orito, A., 1929, 929).—*o*-Nitrophenylacetonitrile and phloroglucinol condense in presence of ethereal hydrogen chloride and zinc chloride, forming a small amount of 2:4:6-trihydroxyphenyl 2-nitrobenzyl ketone, m. p. 202°. 2:4:6-Trihydroxyphenyl 3- and 4-nitrobenzyl ketones, m. p. 211—212° and 247°, respectively, are obtained in good yield from *m*- and *p*-nitrophenylacetonitrile, respectively. *m*-Nitrophenylacetonitrile and resorcinol yield 2:4-dihydroxyphenyl 3-nitrobenzyl ketone, m. p. 156.5°, but *p*-nitrophenylacetonitrile does not condense. H. BURTON.

**Substituted anilinoquinones.** M. COVELLO (Rend. Accad. Sci. Fis. Mat. Napoli, 1929, [iv], 35, 158—163).—The following compounds have been prepared by the interaction of the corresponding amines and acylaminobenzoquinones in boiling alcoholic solution: 3:5-dianilino-2:6-disuccinimido-decomp. without melting at 300°; 3:5-dianilino-2:6-diphthalimido-, m. p. 295—296°; 3:5-di-*p*-

*toluidino-2 : 6-disuccinimido-*, m. p. 204—205°; 3 : 5-*di-p-anisidino-2 : 6-disuccinimido-*, m. p. 240°; 3 : 5-*di-p-toluidino-2 : 6-diphthalimido-*, m. p. 264°; 3 : 5-*di-p-anisidino-2 : 6-diphthalimido-benzoquinone*, m. p. 278°.  
R. K. CALLOW.

**Acyl-*p*-quinones.** Contribution to the solution of the "Pechmann dyes" problem. M. T. BOGERT and H. P. HOWELLS (J. Amer. Chem. Soc., 1930, 52, 837—850).—1 : 4-Dimethoxybenzene, m. p. 56.8° (all m. p. are corr. except where stated otherwise), is converted by the Friedel-Crafts reaction with benzoyl chloride mainly into 2 : 5-dimethoxy-, m. p. 51.2°, or 2-hydroxy-5-methoxy-benzophenone, m. p. 84—85.5° (lit. 78—85°), according to the conditions used. The last-named compound is demethylated by a mixture of hydriodic acid, acetic acid, and acetic anhydride to 2 : 5-dihydroxybenzophenone, m. p. 125—126.1°, oxidised by sodium dichromate and dilute acetic and sulphuric acids to *benzoyl-p-benzoquinone*, m. p. 85—85.6°. This is converted by aniline in acetic acid into a *dianilino*-derivative, purplish-red crystals, m. p. 212.2—212.7°, and by acetic anhydride and a small amount of sulphuric acid at 40—50° into the *triacetate*, m. p. 137.7°, of *benzoylhydroxyquinol*, m. p. 129.1°. When the quinone is treated with sodium thiosulphate and acetic acid and then with potassium chloride a *potassium benzoylquinolthiosulphate*, decomp. about 240° without melting, is obtained. When this is treated with 2-amino-5-dimethylanilinetiosulphuric acid in 20% sodium carbonate solution, and then oxidised with air, a violet dye and a bluish-black, amorphous solid are obtained; the dye formation indicates that the benzoyl and thiosulphuric acid groups are not adjacent.

Quinol dibenzoate, benzoyl chloride, and aluminium chloride at 200—205° afford dibenzoylquinol, m. p. 210.5—211.1° (lit. 206—207°) [*dimethyl ether*, m. p. 124—124.5° (uncorr.)], after the product is hydrolysed with 15% alcoholic potassium hydroxide. This quinol is oxidised to (probably 2 : 5-) *dibenzoyl-p-benzoquinone*, m. p. 164—164.5°, which is converted by aniline in acetic acid into *anilindibenzoylquinol*, yellow, m. p. 234.9—236.8° after becoming orange at 225° and slight decomp. at 228°, and by acetic anhydride and sulphuric acid into the *triacetate*, m. p. 120—120.5°, of *dibenzoylhydroxyquinol*, m. p. 196.9—197.5° (uncorr.).

The dibenzoylquinol is oxidised less readily than the monobenzoylquinol in both acid and alkaline solution; the dibenzoylquinone is more easily reduced. Both quinones dye wool with a dark red shade (fast to acid; not fast to light or alkali). When dissolved in alkali hydroxide, both quinones give blood-red solutions.

The dibenzoyl-*p*-benzoquinone exhibits properties differing from those of the "Pechmann dye" formulated as this quinone by Koznievski and Marchlevski (A., 1906, i, 759). The results support Bogert and Ritter's configuration (A., 1925, i, 255).

H. BURTON.

1 : 4 : 1' : 4'-Tetrahydroxy-2 : 2'-dianthraquinonyl and furans derived therefrom. R. B. SCHMIDT, B. STEIN, and C. BAMBERGER (Ber., 1930,

63, [B], 300—309).—Quinizarin is converted by pyridine in alcohol at 60—70° into 1 : 4 : 1' : 4'-tetrahydroxy-2 : 2'-dianthraquinonyl, the eliminated hydrogen atoms being expended in reduction of a portion of the initial material to 1-hydroxyanthraquinone and its leuco-compound. The constitution of the compound is deduced from elementary analysis and determination of the acetyl groups in its tetraacetate. Contrary to Scholl, Schwinger, and Dischen-dorfer (A., 1920, i, 169), the compound  $C_{28}H_{14}O_8$  is correctly described in G.P. 146,223. 1 : 4 : 1' : 4'-Tetrahydroxy-2 : 2'-dianthraquinonyl is transformed by zinc chloride at 305—310° into 4 : 4'-dihydroxy-2 : 2'-dianthraquinonylene 1 : 1'-oxide, also prepared by heating the tetraacetate in nitronaphthalene at 260—270° and hydrolysis of the resulting *diacetate* by sulphuric acid.

Treatment of 1 : 4 : 1' : 4'-tetrahydroxy-2 : 2'-dianthraquinonyl with boiling nitronaphthalene affords 1 : 4 : 4'-trihydroxy-2 : 2'-dianthraquinonylene 3 : 1'-oxide, identical with the compound  $C_{28}H_{12}O_8$  described in G.P. 146,223. Its constitution is established by the production of a *triacetate* by the action of boiling pyridine and acetic anhydride on the completely amorphous material. In agreement with the authors' formulation, but contrary to Scholl (*loc. cit.*), the substance is unchanged by the prolonged action of zinc chloride. When distilled with zinc dust it yields (?) dianthrlyl in very small amount. If the hydroxyl groups are replaced by acetoxy-residues the oxidation does not occur, but acetic anhydride is lost with production of 4 : 4'-dihydroxy-2 : 2'-dianthraquinonylene 1 : 1'-oxide, the change also occurring in other media of high b. p., for example, anthracene and methyl-diphenylamine.

1 : 4 : 1' : 4'-Tetrahydroxy-2 : 2'-dianthraquinonyl is oxidised by manganese dioxide in fuming sulphuric acid (10%  $SO_3$ ) at -5° to 3 : 4 : 4'-trihydroxy-2 : 2'-dianthraquinonylene 1 : 1'-oxide, which, owing to the absence of a hydroxyl group in the quinizarin position, does not give a well-defined spectrum in boric and sulphuric acids; the *quinoline* salt is described.

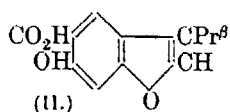
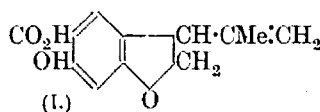
Reduction with sodium hyposulphite in presence of pyridine converts 1 : 4 : 1' : 4'-tetrahydroxy-2 : 2'-dianthraquinonyl into a *tetrahydro*-derivative, which in alkaline solution is not oxidised by air at the atmospheric temperature, although readily after being heated to 50—60°. It is converted by concentrated sulphuric acid at 150—140° into quinizarin and by sulphuric acid containing nitrite into the initial material.  
H. WREN.

**Colour reaction for ergosterol.** Differentiation of ergosterol and irradiated ergosterol. R. MESEMAECKER (Compt. rend., 1930, 190, 216—218).—Acetic anhydride and anhydrous zinc chloride added to a chloroform solution of ergosterol produce a rose coloration which changes into a stable green colour. If the chloroform solution has been exposed to ultra-violet light, only the green coloration, the intensity of which appears to be proportional to the duration of the exposure, is produced.

C. C. N. VASS.

**Vegetable, fish, and insect poisons. II. Rotenone, the physiologically active constituent**

of *Derris elliptica*. II. A. BUTENANDT and F. HILDEBRANDT (Annalen, 1930, 477, 245—268; cf. A., 1928, 1017).—*iso*Rotenone,  $[\alpha]_D^{25} + 8^\circ$  (Takei, A., 1928, 765), is converted by amyl nitrite and hydrochloric acid into *isorotenone*, decomp.  $254^\circ$ , whilst treatment with alcoholic potassium hydroxide in a current of hydrogen gives rotenic acid, also obtained by the action of concentrated sulphuric acid on tubaic acid. Rotenic acid contains no asymmetric centre, since the acid regenerated from the pure *brucine* salt, m. p.  $202^\circ$ ,  $[\alpha]_D^{25} + 18^\circ$ , is inactive. Catalytic reduction of rotenic acid with platinum-black in acetic acid (or palladium-black in alcohol) converts it into *dihydrorotenic acid*, m. p.  $168^\circ$ , which is resolved by fractional crystallisation of its *brucine* salt from acetone. The less soluble active *brucine* salt, m. p.  $150^\circ$ ,  $[\alpha]_D^{25} + 10.8^\circ$ , giving an active acid, m. p.  $165.5\text{--}170^\circ$ ,  $[\alpha]_D^{25} - 23.17^\circ$ . Reduction of *isorotenone* and its derivatives occurs much less readily than in the rotenone series, but with hydrogen and platinum-black in acetic acid a substance,  $C_{21}H_{22}O_5$  (?), m. p.  $167^\circ$  (depressing that of dihydrodeoxyrotenone), is obtained. Dehydrogenation of *isorotenone* with iodine in hot alcoholic sodium acetate converts it into *isodehydorotene*, m. p.  $191^\circ$  (*oxime*, m. p.  $163.5^\circ$ ), which is optically inactive and is also obtained by isomerisation of *dehydorotene* with concentrated sulphuric acid, whilst it is reduced by hydrogen and platinum-black in acetic acid to *isodihydrodeoxyrotenone*, m. p.  $160^\circ$ , and converted by boiling alcoholic potassium hydroxide in hydrogen to *isoderisic acid*,  $C_{23}H_{24}O_8$ , m. p.  $149^\circ$  (*oxime*, m. p.  $170^\circ$ ; *acetyl* derivative, m. p.  $136^\circ$ ; *methyl ester*, m. p.  $124^\circ$ ). The latter is also obtained by isomerisation of *derrisic acid*,  $[\alpha]_D^{25} - 57^\circ$  (*loc. cit.*, where it is described as a hydroxy-keto-acid) (*acetyl* derivative, m. p.  $136^\circ$ ), with concentrated sulphuric acid. Thus the isomeric relationship between rotenone and *isorotenone* and their respective derivatives corresponds with that of tubaic and rotenic acids and involves the movement of a double linking in such a manner that an asymmetric centre is destroyed. Subsequent reduction of rotenic to dihydrorotenic acid re-forms the asymmetric centre, since the latter acid is resolvable. Moreover, consideration of the optical character of its various derivatives shows that rotenone must contain two asymmetric centres, the second of which is situated in the unknown portion of the molecule (*i.e.*, not in the rotenic or tubaic acid skeletons), and it is in this portion of the molecule that dehydrogenation occurs. On the basis of these results together with those of Kariyone (J. Pharm. Soc. Japan, 1928, No. 557, 48), Takei and others (A., 1929, 933), and LaForge and Smith (*ibid.*, 1181), the two series types, represented by tubaic and rotenic acids, respectively, are assigned structures I and II.



All that can be stated concerning the second half of the rotenone molecule is that it contains two methoxyl groups, a methylene group readily oxidisable to a carbonyl group, and a group containing an asymmetric centre which readily loses two atoms of hydrogen

with the consequent destruction of the asymmetric centre. Reduction of *derrisic acid* with hydrogen and colloidal palladium in aqueous acetone affords a substance,  $C_{22}H_{32}O_7$  (?), m. p.  $211^\circ$ , not yet investigated. Both *dehydorotene* and *isodehydorotene* condense with maleic anhydride in boiling benzene to yield substances,  $C_{29}H_{26}O_9$  (?), m. p.  $256^\circ$  (decomp.) and  $261^\circ$  (decomp.), respectively. Various m. p. anomalies of rotenone, *isorotenone*, and rotenic acid are discussed and polymorphism is considered to be the explanation of these. J. W. BAKER.

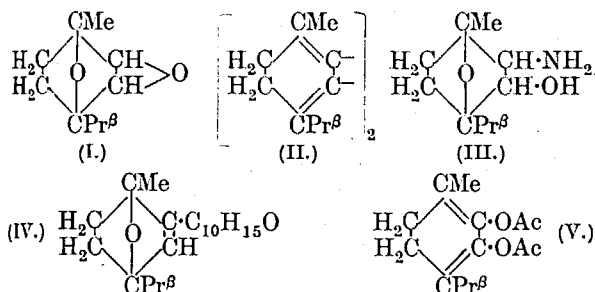
**Effect of heat on *d*- $\alpha$ -pinene.** F. H. THURBER and C. H. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 786—792).—The rate of decrease in optical activity of pinene from Port Orford cedar oil (B., 1927, 733) at  $184\text{--}237^\circ$  is about half of that for pinene from turpentine. The heat of activation (assuming that racemisation occurs) of the latter pinene is approximately 3700 g.-cal. less than that of the former. It is suggested that the pinenes from the two sources differ in structure. When the cedar pinene is heated at  $200^\circ$  in a vacuum high-boiling products are obtained, indicating that the change in rotation is not due to racemisation (cf. Smith, A., 1927, 212), but to some rearrangement of the pinene. H. BURTON.

**Method for distinguishing isomeric, tautomeric, and polymeric, from polymorphic optically active substances.** B. K. SINGH (J. Indian Chem. Soc., 1929, 6, 1007—1011).—Since polymorphism is a function of the solid state, the rotations of solutions of optically active polymorphic substances will be identical (cf. Sidgwick, J.C.S., 1915, 107, 672), whereas isomeric (or tautomeric) substances will give solutions of differing rotatory power. This principle has been applied to three forms of *o*-iodophenylimino-*d*-camphor, m. p.  $87^\circ$  ( $\alpha$ ),  $93^\circ$  ( $\beta$ ), and  $97^\circ$  ( $\gamma$ ), respectively. The  $\alpha$ -modification is obtained by condensing *o*-iodoaniline with *d*-camphorquinone in presence of anhydrous sodium sulphate at  $80\text{--}85^\circ$ ; at  $90\text{--}97^\circ$  the  $\beta$ -form results. When a saturated alcoholic solution of the  $\alpha$ -modification is boiled for a few min., cooled, and then treated with water, the  $\gamma$ -form is precipitated. This variety is also obtained when either the  $\alpha$ - or  $\beta$ -modification is heated at  $79\text{--}80^\circ$  (preferably with a trace of the  $\gamma$ -form). Solutions of the three forms in chloroform, benzene, and methyl alcohol show the same rotatory power and dispersion (for each solvent), indicating that they are polymorphic modifications.

**Ascaridole.** H. THOMS and W. DOBKE (Arch. Pharm., 1930, 268, 128—137).—Investigation of the product of isomerisation of ascaridole leads to the conclusion that it possesses the structure I, with only one ethylene oxide group, rather than the 1:2:3:4-dioxide structure (cf. Wallach, A., 1912, i, 578; Nelson, A., 1911, i, 797; 1913, i, 189).

Isomerisation is carried out in cymene at a temperature not above  $160^\circ$ . A compound,  $C_{20}H_{28}$ , probably II, m. p.  $158^\circ$ , is also formed in 5% yield. When the isomeride is heated with 25% aqueous ammonia at  $125^\circ$  the 3-amino-2-hydroxy-compound (III), m. p.  $141^\circ$ , is obtained in 67% yield, and the analogous 3-methylamino-2-hydroxy-compound, m. p.  $156\text{--}157^\circ$ ,

is formed similarly with methylamine. Secondary amines, or phenylhydrazine, yield no characterisable



products. Interaction with magnesium alkyl or benzyl halides yields no characterisable products, but magnesium phenyl bromide yields the 3-*hydroxy-2-phenyl* compound, m. p. 102.5°, and magnesium camphor bromide yields, with elimination of water, the *compound* IV, m. p. 149°. Interaction with acetic acid gives, in 10% yield, 1 : 2 : 3 : 4-*tetrahydroxy-1-methyl-4-isopropylhexahydrobenzene monoacetate*, m. p. 153°, b. p. 220°/40 mm., from which the tetrahydroxy-compound, m. p. 128°, described by Nelson (*loc. cit.*) is obtained on hydrolysis. Acetylation of ascaridole with acetic anhydride and sodium acetate yields the *glycol diacetate* (V), b. p. 130°/2 mm., *d* 1.063, *n*<sub>D</sub> 1.46828. No additive compounds with phosphoric or arsenic acids can be isolated, and the *compound* with ferrocyanic acid is unstable. None of the reactions investigated is applicable to the determination of ascaridole.

R. K. CALLOW.

R. K. CALLOW.

**Alkylcoumarans and their manufacture.** H. JORDAN etc.—See B., 1930, 135.

**Synthesis of tetrahydroxanthones.** M. SEN (J. Indian Chem. Soc., 1929, 6, 925—930).—When the sodium derivative of *cyclohexanone* is treated with *o*-acetoxybenzoyl chloride in ether and the resulting product hydrolysed with hydrochloric acid, 1:2:3:4-tetrahydroxanthone, m. p. 105°, is obtained. 3-Methyl-1:2:3:4-tetrahydroxanthone, m. p. 130—131°, is prepared from 4-methylcyclohexanone and the above chloride. Using the requisite *cyclohexanone* and acid chloride, the following are also obtained: 6-methyl-, m. p. 113°; 7-methyl-, m. p. 100°; 3:6-dimethyl-, m. p. 137—138°, and 3:7-dimethyl-1:2:3:4-tetrahydroxanthone, m. p. 118—119°. These compounds do not form oxonium salts, and they are hydrolysed by alkali to the *cyclohexanone* and the appropriate *o*-hydroxy-acid. The products formed from *cyclohexanone*-2-carboxylates and phenols (Sen and Basu, A., 1928, 1254) differ from the above, and are, therefore, coumarins. H. BURTON.

H. BURTON.

**Constitution of 5-bromofurylacrylic acid.** H. GLMAN and G. F. WRIGHT (Rec. trav. chim., 1930, 49, 195—196).—Condensation of 5-bromofurfuraldehyde with acetic anhydride and sodium acetate in the presence of a drop of pyridine at 147° gives 5-bromofurylacrylic acid, identical with the acid obtained by the action of zinc on an alcoholic solution of  $\beta$ -bromofuryl- $\alpha$ - $\beta$ -dibromopropionic acid (Gibson and Kahnweiler, A., 1890, 959). The constitution of the bromofurylacrylic acid is thus established.

J. W. BAKER.

**Conversion of furfurylideneacetone into 1-methyl-2-furylcyclopropane.** N. KISHNER (Bull. Soc. chim., 1929, [iv], 45, 767—771).—See A., 1929, 1184.

**Aspects of biochemical synthesis.** P. C. MITTER (17th Indian Sci. Congress, 1930, reprint, also J. Indian Chem. Soc., 1930, 7, 39—57).—A lecture in which the closely related structure of natural anthocyanins, anthraquinone derivatives, flavones, isoflavones, catechins, and related phenolic derivatives is discussed on the basis of biosynthesis from the simple components formaldehyde and its condensation products, sugars, and amino-acids. In discussion of the structural relationships of the terpenes a misquotation of Atterberg's original paper on sylvestrene by Rao and Simonsen (A., 1926, 72, 521) is pointed out, and the author casts doubt on the supposed proof of the absence of sylvestrene in nature, since the irregular union of isoprene units involved in its structure is shared by santene and santonin. The biochemical relationship of sugars to the alkaloids is also discussed. J. W. BAKER.

**Colouring matter of paprika. IV. Rearrangement of capsanthin.** L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1930, 478, 95—111).—Capsanthin (A., 1927, 669; 1928, 1252) reacts with a dilute solution of iodine in carbon disulphide, yielding a *di-iodide*,  $C_{34}H_{48}O_3I_2$ ; with more concentrated solutions, further addition occurs. When treated with bromine in chloroform solution, capsanthin absorbs 7 mols. (two of the original double linkings do not react), whilst with perbenzoic acid in chloroform at 0°, 7 atoms of oxygen per mol. are absorbed. The resulting *heptoxide*,  $C_{34}H_{48}O_{10}$ , softens above 60°, when heated at 150—160° affords a 20—30% yield of impure benzoic acid; it is not clear whether the benzoic acid is formed from the oxide or from combined perbenzoic acid. When treated with dry oxygen, capsanthin absorbs slowly 9 atoms of oxygen per mol.; the almost colourless product is, however, not homogeneous. When capsanthin is heated at 240—300° (bath), 16—25% of its weight of *m*-xylene is produced; similar decomposition of carotene does not give *m*-xylene. The colour reactions of capsanthin with various reagents are given.

[By R. KUHN and F. L'ORSA.]—Determinations of the acetic acid produced during the oxidation of capsanthin by potassium permanganate (Kuhn, Winterstein, and Karlovitz, A., 1929, 425) and chromic acid (unpublished method) show that 5 methyl groups are present in 1 mol. of the coloured compound. H. BURTON.

H. BURTON.

**Catalytic reduction of pyrroles to pyrrolidines.** M. DE JONG and J. P. WIBAUT (Rec. trav. chim., 1930, **49**, 237—246).—Pyrrole and substituted pyrroles are reduced in good yields to the corresponding pyrrolidines with a platinum oxide catalyst; the effect of various substituents and of conditions on the velocity of reduction have been studied. Acetic acid is the best solvent, but absolute methyl or ethyl alcohol or aqueous hydrochloric acid may be used. No reduction occurs in ether, light petroleum, or amyl alcohol. Monoalkyl- or phenyl-substituted pyrroles are reduced more readily than pyrrole itself (2-substituted deriv-

atives more readily than *N*-derivatives) and disubstituted pyrroles more rapidly still. No intermediate reduction products are found and pyrroline (dihydropyrrole) is reduced more rapidly than pyrrole itself. Thus from the appropriate pyrrole derivative are obtained: pyrrolidine (*picrate* B<sub>2</sub>A, m. p. 163–164°, converted into the normal *picrate*, BA, by the action of a second molecule of *picric acid*); 2-methyl-; 1-ethyl-; 2-ethyl-, b. p. 110–120°, *n* 1.4256 (no *picrate*, chloraurate, or chloroplatinate could be obtained); 1-cyclohexyl-, b. p. 214°, *n* 1.4832 (*picrate* BA, m. p. 165°; *picrate* B<sub>2</sub>A, explodes at 315°; chloraurate, m. p. 88°) (by reduction of 1-phenylpyrrole); 2-cyclohexyl-, b. p. 220–230°, *n* 1.5313 (*picrate*, m. p. 153°); 2:4-, *n* 1.4313, and 2:5-dimethyl-, *n* 1.4357 (*picrate*, m. p. 117–118°), and 2:5-dicyclohexyl-, b. p. 312–318°, -pyrrolidine.

J. W. BAKER.

**Synthesis of 1-phenyl- and 1-cyclohexylpyrrolidines.** L. C. CRAIG [with R. M. HIXON] (J. Amer. Chem. Soc., 1930, 52, 804–808).—Pyrrole is best hydrogenated in presence of alcoholic hydrochloric acid and a platinum oxide-platinum-black catalyst (cf. McElvain, A., 1929, 576). A mixture of 2- and 3-methylpyrroles is not reduced (cf. *loc. cit.*). 1-Phenylpyrrole is reduced similarly to 1-cyclohexylpyrrolidine, b. p. 209–211° (*picrate*, m. p. 163–164°), also obtained from pyrrolidine and cyclohexyl bromide. Aniline and tetramethylene chloride at 100° give 1-phenylpyrrolidine [chloroplatinate, m. p. 174–175° (decomp.); *tetroxalate* (+0.5H<sub>2</sub>O), m. p. 156°], which decomposes on distillation; it is also formed in small amount by thermal decomposition of 1-phenylpyrrolidine-2:5-dicarboxylic acid (Le Sueur, J.C.S., 1909, 95, 273) in a vacuum. Bromobenzene and pyrrolidine react at 220° giving a base, b. p. 250–256° (hydrochloride; *picrate*, m. p. 155°), probably formed by fission of the pyrrolidine ring.

H. BURTON.

#### Condensation reactions of cyclic ketones. II. Formation of quinoline derivatives from indigoids.

A. J. HILL, A. S. SCHULTZ, and H. G. LINDWALL (J. Amer. Chem. Soc., 1930, 52, 769–775).—Reduction of hydantoin- $[\Delta^{5:3}]$ -oxindole (A., 1925, i, 305) with tin and alcoholic hydrogen chloride or hydriodic and acetic acids affords *hydantoin-5:3'-oxindole*,  $\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , m. p. 276° (decomp.).

Hydrolysis of this with barium hydroxide and water (1:1) gives 2-keto-1:2-dihydroquinoline-4-carboxylic acid, not melted at 300°, also produced by the action of 10% sodium hydroxide on acetylatisatin, or by condensing isatin with malonic acid. The original oxindole is presumably converted into the acid

$\text{NH} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{CO} \end{smallmatrix} \text{CH} \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , which undergoes

ring fission, dehydrogenation, and subsequent quinoline ring closure. Reduction of the above acid with hydriodic acid and red phosphorus at 140° furnishes 2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylic acid, m. p. 217–218° (the *ethyl ester*, m. p. 155°, is obtained by reduction with tin and alcoholic hydrogen chloride), also formed by similar reduction of hydantoin- $[\Delta^{5:3}]$ -oxindole, *hydantoin- $[\Delta^{5:3}]$ -5':7'-dibromo-oxindole*, and 2:5-diketopiperazine- $[\Delta^{3:6:3:6}]$ -di-

oxindole, m. p. above 300°. The above dibromocompound and *hydantoin- $[\Delta^{5:3}]$ -5'-bromo-oxindole*, both not melted at 300°, are prepared by condensing hydantoin and 5:7-dibromo- and 5-bromo-isatin, respectively, in presence of acetic anhydride and sodium acetate at 150°. 2:5-Diketopiperazine- $[\Delta^{3:6:3:6}]$ -di-5':7'-dibromo-oxindole, and -di-5'-bromo-oxindole, both not melted at 300°, are prepared similarly from diketopiperazine.

The oxindoleacetic acid of Gränacher and Mahal (A., 1923, i, 713) is 2-keto-1:2:3:4-tetrahydroquinoline-4-carboxylic acid (cf. Aeschlimann, A., 1927, 256).

H. BURTON.

**Catalytic perhydrogenation of isoquinoline.** J. RANEDO and A. VIDAL (Anal. Fis. Quím., 1930, 28, 76–78).—By hydrogenation of isoquinoline in acetic acid solution at the ordinary temperature, using platinum oxide as catalyst, tetrahydroisoquinoline is readily obtained. At 100° there results *decahydroisoquinoline*, b. p. 210° (*chloroplatinate*, begins to melt at 129°; mercuric chloride compound, m. p. 205°; *acetyl derivative*, b. p. 180°/30 mm.; *nitrosoamine*).

H. F. GILLBE.

**Manufacture of basic derivatives of substituted quinolinecarboxylic acids.** SOC. CHEM. IND. IN BASLE.—See B., 1930, 167.

**Autoxidation of dialuric acid.** E. S. HILL (J. Biol. Chem., 1930, 85, 713–725).—The autoxidation of dialuric acid to alloxan in presence of atmospheric oxygen at 25° has been studied at various reactions. Over the range  $p_{\text{H}}$  1–7.5 the rate shows maxima at  $p_{\text{H}}$  5.0 and 7.0 (the latter being the greatest) and minima at  $p_{\text{H}}$  6.8 and 7.5; at reactions more alkaline than  $p_{\text{H}}$  7.5 the rate of oxidation increases continuously with the alkalinity. C. R. HARRINGTON.

**Formation of 4-hydroxymethylglyoxaline at low temperatures from lævulose and an ammoniacal solution of copper hydroxide.** P. GIRARD and J. PARROD (Compt. rend., 1930, 190, 328–330).—When an aqueous-ammoniacal solution of lævulose is shaken with copper hydroxide in an atmosphere of oxygen at the ordinary temperature, a green precipitate containing copper is obtained, from which, after treatment with hydrogen sulphide in aqueous suspension, removal of the precipitated copper sulphide, precipitation of the aqueous filtrate with lead acetate, and removal of excess of lead with hydrogen sulphide, a specimen of 4-hydroxymethylglyoxaline, identical with that obtained by Pyman (J.C.S., 1911, 99, 668), is isolated as its *picrate* (cf. Windaus and Ulrich, A., 1914, i, 662).

J. W. BAKER.

**Influence of substituents on the formation and capacity for rearrangement of acylated indazoles.** K. VON AUWERS, A. ERNECKE, and E. WOLTER (Annalen, 1930, 478, 154–175).—5:7-Dimethylindazole is converted by methyl iodide at 100° into 2:5:7-trimethylindazole (*picrate*, m. p. 159–160°), whilst its silver derivative and methyl iodide in ether give the 1:5:7-isomeride (*picrate*, m. p. 161–162°). Methylation with methyl iodide and alcoholic sodium ethoxide affords a mixture of the trimethyl derivatives. Methyl 5:7-dimethylindazole-2-carboxylate, m. p. 118°, eliminates carbon dioxide when heated at the b. p./120–140 mm., furnishing a mixture of the



above trimethyl derivatives. Acetylation of 5:7-dimethylindazole with acetic anhydride or with acetyl chloride and pyridine gives 2-acetyl-5:7-dimethylindazole, m. p. 116—117° (cf. Bamberger, A., 1899, i, 543), which is hydrolysed readily by hydrogen chloride in ether to the original substance. When heated for a short time at the b. p. this acetyl derivative undergoes a partial rearrangement into 1-acetyl-5:7-dimethylindazole, m. p. 72°, which is unaffected by hydrogen chloride in ether. Similarly, 2-benzoyl-5:7-dimethylindazole, m. p. 111—112° (prepared by the pyridine method), is partly converted at the b.p./vac. into the 1-benzoyl derivative, m. p. 98°, which is also obtained directly from the indazole and benzoyl chloride. 5:7-Dibromoindazole (A., 1925, i, 73) (2-ethyl derivative, b. p. 196—204°/15 mm.; the 1-ethyl derivative could not be prepared) is acetylated by acetic anhydride to 5:7-dibromo-2-acetylindazole, m. p. 155—156°, also formed from the silver derivative and acetyl chloride. This is readily hydrolysed by hydrogen chloride in ether, but does not undergo rearrangement when heated. At relatively high temperatures the acetyl group is eliminated. The following substituted 5:7-dibromoindazoles are also described: 2-benzoyl, m. p. 136.5—137° (from the silver derivative and benzoyl chloride); 2-chloroacetyl, m. p. 146—148°; and the ethyl, m. p. 112.5—113°, and amyl, m. p. 57—58°, esters of the 2-carboxylic acid.

An attempt to synthesise 5:7-dibromo-1-acetylindazole by the method previously described (A., 1927, 160) failed, since the oxime, m. p. 186°, of 3:5-dibromo-2-aminobenzaldehyde, on acetylation, affords the O-acetyl derivative, m. p. 129°, only. Energetic acetylation results in the formation of the corresponding nitrile. Bromination of o-acetamidobenzaldehyde in acetic acid gives 5-bromo-2-acetamidobenzaldehyde, m. p. 170—171° (oxime, m. p. 191—192°); further bromination could not be effected. Acetylation of 3:5:7-tribromoindazole with acetic anhydride yields the 1-acetyl derivative, m. p. 140°; the 2-acetyl derivative could not be prepared.

The 2-acetyl derivative, m. p. 85—86°, of 7-methylindazole (picrate, m. p. 158°) is converted by short heating at the b. p./vac. into 75% of the 1-acetyl derivative, m. p. 31—32°. Similarly, 2-chloroacetyl-7-methylindazole, m. p. 125.5—126.5°, furnishes 85% of the 1-chloroacetyl derivative, m. p. 93—94°, and methyl 7-methylindazole-2-carboxylate, m. p. 79—80°, gives methyl 7-methylindazole-1-carboxylate, b. p. 166°/13 mm., m. p. 59.5—60.5°. The ease of rearrangement of the acetyl group from the 2- to the 1-position is diminished by a methyl group, and inhibited by a bromine atom, in the 7-position.

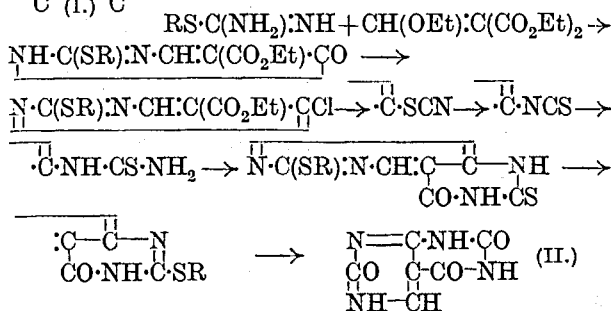
The nitroso-derivative, m. p. 36—37°, of 3:5-dichloro-o-acetotoluidide is converted by Jacobson's method (A., 1908, i, 298) into 5:7-dichloroindazole, m. p. 200°. The 2-acetyl, b. p. 180—184°/12 mm., m. p. 146—147°; 2-chloroacetyl, m. p. 156—157°, and 2-carbethoxy-derivatives, m. p. 100.5—101°, are not transformed into the corresponding 1-acyl derivatives when heated. Spectrochemical data for several of the above indazoles are recorded, which show that 2-acylindazoles have usually a considerably higher exaltation than the 1-acyl derivatives.

H. BURTON.

Formation of derivatives of dihydrobenziminazole and tetrahydroquinoxaline by the action of acetic anhydride and zinc chloride on nitro-derivatives of alkylanilines. P. VAN ROMBURGH and H. W. HUYSER (Rec. trav. chim., 1930, 49, 165—176).—See A., 1928, 428. The 2-chloro-derivatives of 5- and 6-nitro-1-methylbenziminazole have m. p. 202—203° and 186°, respectively. 6-Nitro-3-keto-4-acetyl-1-ethyl-1:2:3:4-tetrahydroquinoxaline (from 2:4-dinitroethylaniline, zinc chloride, and acetic anhydride) has m. p. 166—167°.

Syntheses in the triazine series. M. SEN (J. Indian Chem. Soc., 1929, 6, 1001—1006).—Equimolecular quantities of phenylhydrazine and N-acetyl-N-phenylglycine react in boiling alcohol, forming the feebly basic 6-keto-1:4-diphenyl-3-methyl-1:4:5:6-tetrahydro-1:2:4-triazine, m. p. 163—164°. Similarly, N-acetyl-N-o-tolyl- and N-acetyl-N-α-naphthyl-glycines afford 6-keto-1-phenyl-4-o-tolyl-3-methyl-, m. p. 183—184°, and 6-keto-1-phenyl-4-α-naphthyl-3-methyl-tetrahydrotriazine, m. p. 221°, respectively. Attempts to prepare similar compounds from hippuric acid or N-acetyl-glycine and phenylhydrazine resulted in the formation of mixtures of triazines and glyoxalones. When hippuric acid phenylhydrazone, m. p. 137—138°, is heated at 155—160°, a mixture of triazine and glyoxalone is again obtained. Hippuric acid and α-phenylbenzylhydrazine give 1-benzylanilino-2-phenyl-5-glyoxalone, m. p. 147°. β-Acetylphenylhydrazine and N-phenylglycine (or its ethyl ester) do not react. H. BURTON.

Pyrimidines. CXII. Synthesis of heterocyclic compounds containing condensed pyrimidine rings. T. B. JOHNSON and Y. F. CHU (Rec. trav. chim., 1930, 49, 197—201).—The synthesis of a new type of condensed heterocyclic compound, 1:3:7:9-dipyrimidine (I) (nomenclature based on that of purine derivatives) is effected in accordance with the general scheme:



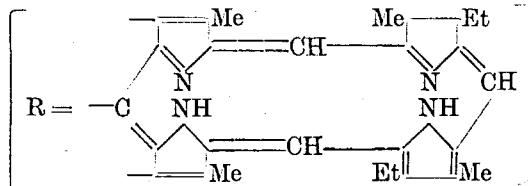
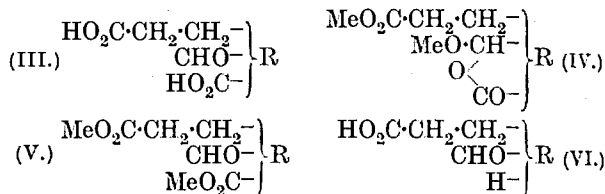
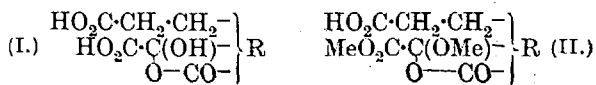
By the action of concentrated aqueous ammonia at the ordinary temperature, ethyl 2-ethylthiol-6-thiocarbonylpyrimidine-5-carboxylate (described in a future publication) is converted into 10-hydroxy-8-thiol-2-ethylthiol-1:3:7:9-dipyrimidine, m. p. 242—243°, in 79% yield. This is converted by sodium ethoxide and ethyl bromide into 10-hydroxy-2:8-diethylthiol-1:3:7:9-dipyrimidine, m. p. 117—119°, which is hydrolysed by boiling hydrochloric acid to 2:8:10-trihydroxy-1:3:7:9-dipyrimidine (II), decomp. above 300°.

which is the cyclic ureide of cytosinecarboxylic acid. Similarly, by the action of concentrated ammonia at 90—100° on 2-ethylthiol-6-phenylthiocarbamylpyrimidine-5-carboxylate (future paper) is obtained 10-hydroxy-8-thiol-2-ethylthiol-9-phenyldipyrimidine, m. p. 220—222°.

J. W. BAKER.

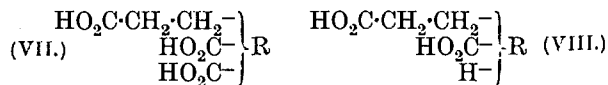
**Chlorophyll. VIII. Chlorin *e* and chloroporphyrins derived from it.** H. FISCHER and O. MOLDENHAUER (Annalen, 1930, 478, 54—94).—The formation of a tripotassium salt by chlorin *e* (I) (Willstätter) is confirmed. Methylation of the salt by methyl sulphate yields the dimethyl ester,  $C_{37}H_{44}O_6N_4$ , m. p. 199°, which, crystallised from ether, yields the dimethyl ester,  $C_{37}H_{46}O_6N_4$ , m. p. 217°, not identical with the trimethyl ester obtained by Treibs and Wiedemann (A., 1929, 941) with diazomethane.

The action of fatty acids alone and with hydriodic acid on chlorin *e* and related compounds has been examined. In general the action of formic acid resembles that of acetic acid with hydriodic acid, whilst propionic and butyric acids cause greater degradation. Chlorin *e* with acetic and hydriodic acids (50°; 8 min.) yields, with the loss of 1 mol. of carbon dioxide, chloroporphyrin  $e_5$  (III),  $C_{32}H_{34}O_5N_4$  or  $C_{33}H_{36}O_5N_4$ . This yields two dimethyl esters, m. p. 272° (IV) and 284° (V) (corr.), with diazomethane and methyl-alcoholic hydrogen chloride, respectively; IV is transformed into V by methyl-alcoholic hydrogen chloride, but the reverse change does not occur. Chloroporphyrin  $e_5$  yields only the diethyl ester with alcoholic hydrogen chloride and hydrogen sulphide. It is converted by heating with formic acid or with methyl-alcoholic potassium hydroxide under pressure into rhodoporphyrin. In the latter reaction only pyrroporphyrin is found as a by-product, in contrast with the behaviour of chlorin *e* (Treibs and Wiedemann). Rhodoporphyrin is not converted into chlorin *e* by the action of hydrogen peroxide and sulphuric acid, an unidentified substance being formed. The iron salt of chloroporphyrin  $e_5$  yields pyrroporphyrin when fused with resorcinol. The ability to yield phylloporphyrin with alkali is restored in chloroporphyrin  $e_5$  dimethyl ester, m. p. 284°, but with formic acid the ester yields only rhodoporphyrin. To conclude that formic acid inhibits the formation of the phylloporphyrin structure is incorrect, for chlorin *e* yields with formic acid chloroporphyrin  $e_3$  (VI),  $C_{33}H_{36}N_4O_3$  [methyl ester with methyl-alcoholic hydrogen chloride, m. p. 238° (corr.); methyl ester with diazomethane, m. p. 232° (corr.); ethyl ester (obtained with alcoholic hydrogen chloride and hydrogen sulphide); iron and copper salts], which resembles phylloporphyrin in properties and probably in structure and is converted by methyl-alcoholic potassium hydroxide under pressure solely into phylloporphyrin, which is also obtained by treatment with acetic acid or fuming sulphuric acid. The formulæ given below are used in a provisional explanation of the results:



Decomposition of chlorin *e* with boiling acetic acid yields phylloporphyrin and a small quantity of a new chlorin. With propionic or butyric acids a porphyrin of phylloporphyrin type, but differing in absorption, and a chlorin are obtained.

The action of acetic and hydriodic acids on either the di- or tri-methyl esters of chlorin *e* yields chloroporphyrin  $e_6$  (VII),  $C_{33}H_{46}O_6N_4$  (trimethyl ester, m. p. 255°, obtained either with methyl-alcoholic hydrogen chloride or diazomethane; iron salt), accompanied by a chlorin which is probably an intermediate product. Decomposition of VII by methyl-alcoholic potassium hydroxide yields rhodo- and pyrroporphyrins, but practically no phylloporphyrin. The ester, under similar conditions, and the iron salt, by fusion with resorcinol, also yield, however, phylloporphyrin. Whilst chloroporphyrin  $e_6$  is obtained by the action of formic acid on chlorin *e* trimethyl ester, repetition of the treatment with formic acid yields chloroporphyrin  $e_4$  (VIII),  $C_{32}H_{34}O_4N_4$  (dimethyl ester, m. p. 252°), which is decomposed by methyl-alcoholic potassium hydroxide to give phylloporphyrin and an unidentified porphyrin. The iron salt of chloroporphyrin  $e_6$  is converted by heating with sodium and amyl alcohol into a perhydro-derivative, which yields two rhodins when oxidised by ferric chloride.



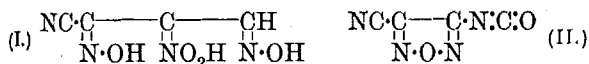
The decarboxylation of porphyrins has been investigated by quantitative methods, and the significance of the comparative ease with which the reaction takes place with different porphyrins when heated alone or with formic or acetic and hydriodic acids is discussed. Chlorin *e* loses 2 mols. of carbon dioxide when heated in nitrogen at 200°, yielding phylloporphyrin and an unidentified chlorin. Chloroporphyrin  $e_5$  loses 1 mol. of carbon dioxide under the same conditions. isoUroporphyrin loses 4 mols. of carbon dioxide with acetic and hydriodic acids, whilst uroporphyrin loses only 1 mol. (cf. A., 1927, 1088).

Spectrographic data are given for the substances described.

R. K. CALLOW.

[Fulminic acids.] X. Constitution of polymerised fulminic acids. H. WIELAND, Z. KITASATO, and S. UTZINO (Annalen, 1930, 478, 43—53).—When pericyanilic acid (I) is refluxed with thionyl

chloride without a solvent the reaction differs from that previously described (A., 1929, 1468), and the product is the intensely smelling *cyanofurazan cyanate* (II), b. p. 60°/12 mm., which is probably formed by a

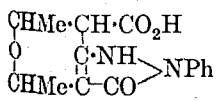


Beckmann change through a nitrile oxide or an acinitro-compound. The constitution of II is deduced from the following reactions. When boiled with water it loses carbon dioxide (1 mol.). Treated with concentrated sulphuric acid at 60° and poured on to ice, it yields by addition of water *cyanofurazancarboxylic acid*,  $\text{NC}\cdot\text{C}_2\text{N}_2\cdot\text{O}\cdot\text{NH}\cdot\text{CO}_2\text{H}$ , m. p. 143° (decomp.), which is decomposed by boiling water to give *aminofurazancarboxylamide* (III),  $\text{NH}_2\cdot\text{C}_2\text{N}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 147—148°, m. p. above 300° after resolidification. Treatment of II with concentrated sulphuric acid at 90—100° yields *aminofurazancarboxylic acid* (IV) (+H<sub>2</sub>O), m. p. 213—214° (barium and copper salts; *N*-benzoyl derivative, m. p. 199—200°), also obtained by partial hydrolysis of III with barium hydroxide. Hydrolysis of II with barium hydroxide solution yields hydroxyfurazancarboxylic acid, m. p. 175—176° (cf. Hantzsch and Urbahn, A., 1895, i, 393) (sparingly soluble copper salt), which is also obtained by complete hydrolysis of III or IV by barium hydroxide. Interaction of II with aniline yields (?) *cyanofurazancarbanilide*,  $\text{NC}\cdot\text{C}_2\text{N}_2\cdot\text{O}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 244°, and a substance,  $\text{C}_{10}\text{H}_5\text{ON}_5$ , m. p. 143—144°, which may be the corresponding carbodi-imide or the compound in which the phenylimino-group has replaced the nuclear oxygen.

The constitution III was assigned by Ulpiani (cf. A., 1912, i, 611) to an intermediate product in the formation of *isofulminuric acid*, the amidine formula for which is now further supported. "*β*-isoFulminuric acid" is most probably not aminofurazancarboxylic acid, as had been suggested by Ulpiani.

R. K. CALLOW.

**Derivatives of a dicyclic system of condensed pyrazole and pyran rings.** C. MANNICH and M. W. MÜCK (Arch. Pharm., 1930, 268, 137—139).—Treatment of ethyl 2:6-dimethyltetrahydropyrene-3:5-dicarboxylate (Petrenko-Kritschenko, A., 1896, i, 471) with phenylhydrazine in methyl alcohol yields the *phenylhydrazone*, m. p. 147—148°, which is then treated with sodamide in toluene. Simultaneous condensation and hydrolysis occur, with formation of the compound (annexed formula), m. p. 200—201°. Methylation in sodium hydroxide solution with methyl sulphate yields the *methyl ester* of the



*N*-methyl derivative, m. p. 153—154°, and the alkali-soluble *N*-methyl derivative, m. p. 186—187°.

R. K. CALLOW.

**Unsaturation and tautomeric mobility of heterocyclic compounds. I. Benzthiazole and dihydrobenzthiazole derivatives.** R. F. HUNTER (J.C.S., 1930, 125—147).—Benzthiazole in chloroform or acetic acid solution with bromine gave *benzthiazole N*-dibromide, m. p. 88—89° (decomp.), or the *N*-tetra-

*bromide*, m. p. 67—68°, although when benzthiazole not previously purified by redistillation over copper was used the bromo-additive compound ( $\text{C}_7\text{H}_5\text{NBr}_3\text{S}$ )<sub>2</sub>, m. p. 100—103° (decomp.), was obtained.

By boiling solutions of any of the preceding bromo-compounds in 70% alcohol, 4:5:6:7-tetrabromobenzthiazole, m. p. 122°, was formed. Bromination of 1-aminobenzthiazole in chloroform solution led to 1-aminobenzthiazole *N*-dibromide, m. p. 265° (decomp. after becoming pale yellow at 160—170°), or, if excess of bromine were used, 1-aminobenzthiazole *tetrabromide*, m. p. 266° (decomp. after sintering with bromine loss at 170°). Similarly, phenylthiocarbamide gave 1-aminobenzthiazole *hydrodibromide*, m. p. 127—128°, decomp. 131°; the same compound was obtained by bromination of 1-aminobenzthiazole. With boiling acetic anhydride it formed 5-bromo-1-acetamidobenzthiazole; thermal decomposition in a vacuum gave 1-aminobenzthiazole *hydrobromide*.

1-Anilino-benzthiazole *tetrabromide* had m. p. 127° (decomp.) (lit. 117°), the *hydrotribromide* had m. p. 130° (decomp.) (lit. 125°); 1-*p*-toluidino-5-methylbenzthiazole *hydrotribromide* and *hydrotribromide* had m. p. 130—132° (decomp., lit. 145°) and 145—147° (lit. 148°), respectively.

The dibromo-base, m. p. 210—211°, obtained from the *hydrohexabromide* of 1-*o*-toluidino-3-methylbenzthiazole was evidently 5:4'-dibromo-1-anilino-3:2'-dimethylbenzthiazole, since it was also obtained by reduction of the bromo-additive compound (decomp. 270° after becoming colourless at 186—190°), formed by heating *s*-di-*p*-bromo-*o*-tolylthiocarbamide with bromine in chloroform.

The mobility of 1-hydroxybenzthiazole was studied as follows: (1) it was prepared in three ways, by heating an alcoholic solution of 1-chlorobenzthiazole with hydrogen chloride, by treatment of *o*-aminophenylmercaptan or its chloroform-ether solution with carbonyl chloride; (2) by the action of methyl sulphate in chloroform solution in the presence of potassium hydroxide 1-keto-2-methyl-1:2-dihydrobenzthiazole was obtained; (3) bromination gave 5-bromo-1-hydroxybenzthiazole, m. p. 225—226°, also prepared (a) from 1-chloro-5-bromobenzthiazole and hot alcoholic hydrogen chloride and (b) from the following sequence: alcoholic *p*-bromophenylthiocarbimide on heating formed *p*-bromophenylthio-urethane, m. p. 106—107°, converted by warm aqueous potassium ferricyanide into 5-bromo-1-ethoxybenzthiazole, m. p. 75—76°. Hydrolysis of this with hydrobromic acid gave 5-bromo-1-hydroxybenzthiazole, m. p. 223°.

1-Thiolbenzthiazole, m. p. 179° (lit. 174°), was obtained either by heating *o*-aminophenyl mercaptan and carbon disulphide in alcohol or by condensation of *o*-aminophenyl mercaptan with thiocarbonyl chloride; with methyl-alcoholic methyl sulphate it gave 1-methylthiolbenzthiazole, m. p. 47—49°, whilst with chloroform and bromine it gave 1-thiolbenzthiazole *tetrabromide*, m. p. 147° (decomp. after previous shrinking). 1-Nitrosoimino-2-ethyl-1:2-dihydrobenzthiazole and phosphorus pentasulphide when heated together formed 1-thiol-2-ethyl-1:2-dihydrobenzthiazole, m. p. 75°.

1-Phenylbenzthiazole gave a *tetrabromide*, m. p.

134—136°, or a *hexabromide*, m. p. 156° (decomp. with effervescence over a range of 40°).

1-Phenylbenzoxazole formed a *hexabromo-additive compound*, m. p. 153—155°, passing in a vacuum (over alkali) into the *hydrotribromide* of 5(?)*-bromo-1-phenylbenzoxazole*, m. p. 154—155° (with previous shrinking). This was reduced by sulphurous acid to 5(?)*-bromo-1-phenylbenzoxazole*, m. p. 106—107°. 1-Phenylbenzelenazole *tetrabromide*, from the selenazole, chloroform, and excess of bromine, had m. p. 148°.

Interaction in chloroform of *as*-phenylmethylthiocarbamide and bromine gave 1-imino-2-methyl-1:2-dihydrobenzthiazole *hydropentabromide*, m. p. 121—122° (decomp.), which, on exposure to air, formed the more stable *hydrodibromide*, m. p. 194—196° (decomp., sintering at 190°). Both compounds gave the base, m. p. 123° (*acetyl* derivative, m. p. 141—142°), by sulphurous acid reduction, but when boiled with alcohol formed 1-imino-2-methyl-1:2-dihydrobenzthiazole *hydrobromide*, m. p. 275° (decomp.). The *hydrotribromide* of 5-bromo-1-imino-2-methyl-1:2-dihydrobenzthiazole lost bromine at 100—110° and remained unmelted at 280°; in boiling alcoholic solution it gave the *hydrobromide*, m. p. above 290°. The 5-bromo-base had m. p. 110° (*acetyl* derivative, m. p. 219—220°).

Bromine and 1-keto-2-methyl-1:2-dihydrobenzthiazole gave a *tetrabromide*, m. p. 120°, passing in a vacuum into the *dibromide*, m. p. 101—103°, of 5-bromo-1-keto-2-methyl-1:2-dihydrobenzthiazole, m. p. 126—127°, which was formed by heating the *nitroso-derivative* (explosion point 161°) of 5-bromo-1-imino-2-methyl-1:2-dihydrobenzthiazole.

1-Thiol-2-methyl-1:2-dihydrobenzthiazole *tetrabromide* had m. p. 124—126° (decomp., after reddening at 115—120°). Bromine and 1-nitrosoimino-2-methyl-1:2-dihydrobenzthiazole gave a *tetrabromide*, m. p. 280° (decomp.).

1-Imino-2-ethyl-1:2-dihydrobenzthiazole *hydrotribromide* (from ethylthiocarbamide and bromine) had m. p. 160—161° (decomp.) (also prepared from the imino-base, hydrogen bromide, acetic acid, and bromine); concentration of its alcoholic solution gave the base *hydrobromide*, m. p. 247—248° (decomp.). 1-Acetimido-2-ethyl-1:2-dihydrobenzthiazole had m. p. 127—128°. Bromination of the previous base gave a *hydrotribromide*, m. p. 182—184° (decomp.) (also obtained from the 5-bromo-base, hydrogen bromide, and bromine in acetic acid), thermal decomposition of which gave 5-bromo-1-imino-2-ethyl-1:2-dihydrobenzthiazole, m. p. 68—70° (*acetyl* derivative, m. p. 187°; *hydrobromide*, m. p. 270—272°). Ethylation of 5-bromo-1-aminobenzthiazole led to the same acetimido-derivative, m. p. 187°.

Nitration of 1-imino-2-ethyl-1:2-dihydrobenzthiazole afforded the 5-nitro-derivative, m. p. 139—140° (*acetyl* derivative, m. p. 242—243°), which with methyl sulphate and alkali gave 5-nitro-1-methyl-1:2-dihydrobenzthiazole, m. p. 154° (also obtained by methylating 1-imino-2-ethyl-1:2-dihydrobenzthiazole to the 1-methylimino-derivative and nitrating this. The last compound was reduced to the 5-amino-base, m. p. 124—125°, which by di-

azotisation etc. gave 5-bromo-1-methylimino-2-ethyl-1:2-dihydrobenzthiazole, m. p. 89°.

Dinitration of the foregoing imino-base or mononitration of the 5-nitro-derivative led to *dinitroiminoethyl*dihydrobenzthiazole, m. p. 242—244°.

Iminoethyl-dihydrobenzthiazole with acetic acid and sodium nitrite gave the 1-nitrosoimino-derivative, explosion point 153°, which when heated in xylene solution formed 1-keto-2-ethyl-1:2-dihydrobenzthiazole (*tetrabromide*, m. p. 80—82°, after turning yellow at 60—70°); the derived 5-bromo-1-keto-2-ethyl-1:2-dihydrobenzthiazole had m. p. 96—97° (also obtained by evaporation of a xylene solution of 5-bromo-1-nitrosoimino-2-ethyl-1:2-dihydrobenzthiazole, explosion pt. 157—158°).

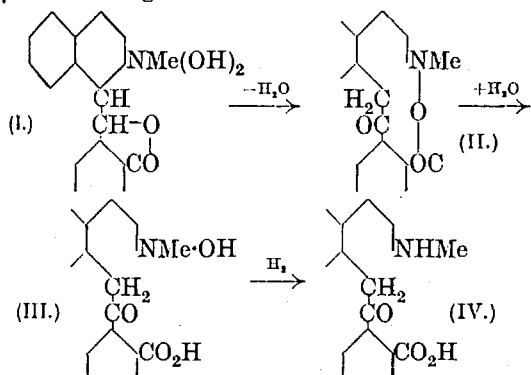
5-Nitro-1-keto-2-ethyl-1:2-dihydrobenzthiazole, m. p. 198°, was obtained (1) by heating the corresponding 5-nitro-1-nitrosoimino-compound, explosion pt. 154°, in xylene solution, and (2) by adding the 1-keto-compound to nitric acid.

Nitration of 1-imino-2-ethyl-1:2-dihydrobenzthiazole *hydrotribromide* gave the 5-nitro-derivative; decomposition of the *hydrotribromide* by sulphuric acid gave, after acetylation, 1-acetimido-2-ethyl-1:2-dihydrobenzthiazole and the 5-bromo-derivative in the proportions of 5:7, respectively. Nitration of iminoethyl-dihydrobenzthiazole *hydrobromide* and its *N*-acetyl derivative gave 5-nitro-derivatives. Nitration of the base in sulphuric acid solution gave impure 5-nitro-base and some dinitro-compound.

5-Bromo-3-nitro-1-imino-2-ethyl-1:2-dihydrobenzthiazole, m. p. 168—169° (*acetyl* derivative, m. p. 252—253°), was prepared similarly. In these nitrations the first action of nitric acid is one of decomposition, possibly with production of nitrosyl bromide which may brominate any base initially escaping nitration.  
R. J. W. LE FÈVRE.

Conversion of a tertiary amine oxide into a dialkylhydroxylamine: *N*-hydroxynornarceine. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1930, 190, 310—312).—Narcotine oxide (I) (A., 1929, 335) in dry chloroform solution is slowly converted into *anhydro-N*-hydroxynornarceine (II), which is insoluble in dilute acids, is not reduced by either sulphur dioxide or zinc and hydrochloric acid, does not react with either acetic anhydride or methyl iodide, but by the action of bromine in dry chloroform is converted into the *hydrobromide* of a *monobromo-derivative*, C<sub>22</sub>H<sub>27</sub>O<sub>3</sub>NBr, m. p. 186°, and is hydrolysed by concentrated hydrochloric acid to the *hydrochloride*, m. p. 213°, of *N*-hydroxynornarceine (III), m. p. 191° (*N*-sulphonic acid, m. p. 175°). By the action of the appropriate alcohol and anhydrous hydrogen chloride on either this product on the original *anhydro*-compound are obtained the *methyl*, m. p. 137°, and *ethyl*, m. p. 151° (*hydrochloride*, m. p. 197°; *N*-sulphonic acid, m. p. 146°), esters of *N*-hydroxynornarceine, which possess the properties of hydroxylamine derivatives (reduction of Fehling's solution, mercuric chloride, and ammoniacal silver nitrate; ready reaction with sulphur dioxide to give *N*-sulphonic acid derivatives). Reduction of *N*-hydroxynornarceine with ferrous sulphate in alkaline solution gives nor-

narceine (IV). These transformations are represented by the following scheme :



and are considered to support the authors' view, regarding tertiary amine oxides as derivatives of hydroxylamine.

J. W. BAKER.

**Pictet and Gams' berberine synthesis.** J. S. BUCK and R. M. DAVIS (J. Amer. Chem. Soc., 1930, 52, 660—664).—Treatment of homoveratroylhomopiperonylamine with phosphoric oxide and reduction of the product formed with tin and hydrochloric acid (cf. Pictet and Gams, A., 1911, i, 807) affords a mixture of 6:7-methylenedioxy-3':4'-dimethoxy-1:2:3:4-tetrahydroprotopapaverine, m. p. 84° (cf. Haworth, Perkin, and Rankine, A., 1924, i, 1098), and 9-keto-6:7-methylenedioxy-3':4'-dimethoxyprotopapaverine (I), m. p. 208°. The last-named compound is identical with Pictet and Gams' veratrylnorhydrograstinine; it does not react with methylal. When 9-keto-6:7-methylenedioxy-3':4'-dimethoxy-3:4-dihydroprotopapaverine is treated with zinc dust and 10% sulphuric acid, I and 9-hydroxy-6:7-methylenedioxy-3':4'-dimethoxy-1:2:3:4-tetrahydroprotopapaverine, m. p. 161—162°, are produced. The last-named substance condenses with formaldehyde in presence of methyl alcohol and sodium hydrogen carbonate forming 13-hydroxy-2:3-methylenedioxy-10:11-dimethoxytetrahydroprotoberberine, m. p. 153°. Catalytic reduction (Adams) of I in acetic acid solution gives 9-hydroxy-6:7-methylenedioxy-3':4'-dimethoxyprotopapaverine, m. p. 161°. H. BURTON.

**5:6:7:8-Tetrahydroquinolines and their derivatives.** V. Hydrogenation under pressure of cinchonine, and 5:6:7:8-tetrahydroquinoline. J. VON BRAUN and G. LEMKE (Annalen, 1930, 478, 176—196).—Reduction of cinchonine with hydrogen in presence of reduced nickel and decahydronaphthalene at about 200°/25 atm., until 6 atoms of hydrogen per mol. are absorbed, gives (A) ether-soluble (secondary-tertiary bases) and (B) ether-insoluble (ditertiary bases) products. Hydrogenation of the pyridine ring (A) and the benzene ring (B) occurs in addition to reduction of the vinyl group. The mixture of bases from A is separated by fractional crystallisation of the hydrochlorides from alcohol into  $\alpha$ - and  $\beta$ -hexahydrodeoxycinchonines (Heidelberger and Jacobs, A., 1922, i, 672), and a hexahydrocinchonine,  $[\alpha]_D^{24} + 7^\circ 36'$  (dihydrochloride, m. p. 265—268°,  $[\alpha]_D^{20} + 62^\circ$ ; diacetyl derivative hydrochloride,

m. p. 270°,  $[\alpha]_D^{20} + 49^\circ$ ; nitroso-derivative, m. p. 159—160°,  $[\alpha]_D^{20} + 139^\circ 30'$ ); a second hexahydrocinchonine,  $[\alpha]_D^{20} + 164^\circ 18'$  (dihydrochloride,  $[\alpha]_D^{20} + 50^\circ 8'$ ; diacetyl derivative hydrochloride, m. p. 240°,  $[\alpha]_D^{20} + 4^\circ 20'$ ), is also isolated by way of its nitroso-derivative, m. p. 161°,  $[\alpha]_D^{20} + 71^\circ 9'$ , from the fraction containing the deoxycinchonines. Heidelberger and Jacobs' hexahydrocinchonine (*loc. cit.*) is probably a mixture of the above isomeric hexahydrocinchonines, both of which differ from that described by Skita and Brunner (A., 1916, i, 835). From B, unchanged cinchonine and the (Bz)-hexahydrocinchonine, m. p. 240°,  $[\alpha]_D^{20} + 170^\circ 12'$  in alcohol (monoacetyl derivative hydrochloride, m. p. 273°; nitrite, of Skita and Brunner (*loc. cit.*) are isolated. The final mother-liquors from A contain a small amount of a ditertiary base,  $C_{16}H_{28}ON_2$ , m. p. 190—195°,  $[\alpha]_D^{25} - 29^\circ 28'$  in alcohol, probably a cinchonidine derivative. Prolonged treatment of the above Bz-hexahydrocinchonine with 8% acetic acid at 130—140° gives the corresponding cinchotoxin [5:6:7:8-tetrahydro-4-quinolyl  $\beta$ -4-piperidinoethyl ketone], the N-benzoyl derivative of which is converted by treatment first with amyl nitrite and alcoholic sodium ethoxide, and then with carbon dioxide, into the corresponding isonitroso-derivative, m. p. 70° (not sharp). Treatment of this with p-toluenesulphonyl chloride in 5% potassium hydroxide solution at 60°, and subsequent hydrolysis of the nitrile formed (cf. Kaufmann, Rothlin, and Brunschweiler, A., 1917, i, 50) with copper sulphate solution containing a small amount of 1% hydrochloric acid, yields the copper salt of 5:6:7:8-tetrahydrocinchononic acid, m. p. 242° (with slight evolution of gas). Slow thermal decomposition of this acid affords 5:6:7:8-tetrahydroquinoline, b. p. 222°,  $d_4^{23} 1.025$  (picrate, m. p. 157°; chloroplatinate, decomp. 210°), which is readily dehydrogenated by distillation over zinc dust in an atmosphere of hydrogen to quinoline. 5:6:7:8-Tetrahydroquinoline is also obtained by treatment of its 2-chloro-derivative, b. p. 270—272°,  $d_4^{23} 1.187$  (picrate, m. p. 129—130°), with zinc dust and hydrochloric acid. The chloro-compound is prepared by the action of a mixture of phosphoric and phosphoryl chlorides at 120—130° on the 2-hydroxy-derivative, which is obtained by decarboxylation of the acid from 2-keto-3-cyano-2:3-dihydroquinoline (Sen-Gupta, J.C.S., 1915, 107, 1347).

It is not possible to obtain pure 5:6:7:8-tetrahydroquinoline by reducing quinoline with red phosphorus and hydriodic acid (*d* 1.9) at 200—210° (cf. Yamaguchi, J. Pharm. Soc. Japan, 1926, No. 553, 53); 1:2:3:4-tetrahydro- and probably decahydro-derivatives are also formed.

Reduction of methyl 2:3-dimethylcinchonate (A., 1923, i, 835) in presence of nickel at 170° affords 24% of methyl 2:3-dimethyl-5:6:7:8-tetrahydrocinchonate, m. p. 62—63°, and 70% of the 1:2:3:4-tetrahydro-ester, isolated as the nitroso-derivative, m. p. 135°. Methyl 2-phenyl-3-methylcinchonate, m. p. 84° (picrate, m. p. 178°), gives similarly 25% of the 1:2:3:4-tetrahydro-derivative (nitroso-derivative, m. p. 69—70°) in addition to methyl 2-phenyl-3-methyl-5:6:7:8-tetrahydrocinchonate, m. p. 88° (free acid, decomp. 315°; picrate, m. p. 190°; hydrochloride;

*methiodide*, m. p. 148°). Ethyl cinchonate yields almost entirely *ethyl 1:2:3:4-tetrahydrocinchonate*, b. p. 176°/13 mm. (oily *nitroso-derivative*), which is reduced by sodium and alcohol to *4-hydroxymethyl-1:2:3:4-tetrahydroquinoline*, b. p. 186—188°/13 mm., m. p. 60° (1-methyl derivative *methiodide*, m. p. 151°). This alcohol is converted by hydrobromic acid at 100° into the *hydrobromide*, m. p. 163°, of *4-bromo-methyl-1:2:3:4-tetrahydroquinoline (picrate)*, m. p. 135°).  
H. BURTON.

**Some compounds of the phenols with quinine and cinchonine.** E. TOMČEK (J. Pharm. Chim., 1930, [viii], 11, 101—106).—The methods of preparation adopted were (1) double decomposition of the potassium phenoxide and the alkaloid sulphate in alcoholic solution, (2) direct combination in alcoholic solution, and (3) combination of an alkaloid salt with a phenol; the compounds obtained by method (3) contain 1 mol. of phenol to 2 mols. of alkaloid, the acid radical, and, usually, 2 mols. of water of crystallisation. The compounds are well-crystallised solids, with a phenolic odour, and easily decomposed. The following are described: *β-Naphthol-quinine sulphate*,  $C_{10}H_8O_2 \cdot 2C_{20}H_{24}O_2N_2 \cdot H_2SO_4 \cdot H_2O$ , m. p. 214° (decomp.); *β-naphthol-quinine (1:1; +H<sub>2</sub>O)*, m. p. 224° (decomp.); *thymol-quinine sulphate*,  $C_{10}H_{14}O_2 \cdot 2C_{20}H_{24}O_2N_2 \cdot H_2SO_4 \cdot 2\frac{1}{2}H_2O$ , m. p. 220° (decomp.); *thymol-quinine (1:1; +2H<sub>2</sub>O)*, m. p. 226° (decomp.); *trichlorophenol-quinine (1:1; +2H<sub>2</sub>O)*, m. p. 103°; *tetrachlorophenol-quinine (1:1; +2H<sub>2</sub>O)*, m. p. 114°; *pentachlorophenol-quinine (1:1; +H<sub>2</sub>O)*, m. p. 174°; *quinine phenolsulphonate*,  $C_{20}H_{24}O_2N_2 \cdot OH \cdot C_6H_4 \cdot SO_3H \cdot H_2O$ , m. p. 145°; *pyrogallol-quinine sulphate*,  $C_6H_6O_3 \cdot 2C_{20}H_{24}O_2N_2 \cdot H_2SO_4 \cdot 1\frac{1}{2}H_2O$ , m. p. 222° (decomp.); *naphthyl salicylate-quinine*,  $OH \cdot C_6H_4 \cdot CO_2C_{10}H_7 \cdot C_{20}H_{24}O_2N_2$ , m. p. 83°; *quinine-salicypyrine*,  $C_{20}H_{24}O_2N_2 \cdot C_{18}H_{15}O_4N_2 \cdot 1\frac{1}{2}H_2O$ , m. p. 192°; *quinine-methyl salicylate (1:1; +2H<sub>2</sub>O)*, m. p. 152°; *guaiacol-quinine (1:1)*, m. p. 160°; *m-xyleneol-quinine (1:1)*, m. p. 163°; *trichlorophenol-quinine (1:1; +2H<sub>2</sub>O)*, m. p. 252° (decomp.); *tetrachlorophenol-cinchonine (1:1; +2H<sub>2</sub>O)*, m. p. 194° (decomp.); *pentachlorophenol-cinchonine (1:1; +2H<sub>2</sub>O)*, m. p. 152°; *p-nitrophenol-cinchonine (1:1)*, m. p. 250° (decomp.); *pyrogallol-cinchonine sulphate*,  $C_6H_6O_3 \cdot 2C_{19}H_{22}ON_2 \cdot H_2SO_4 \cdot 2\frac{1}{2}H_2O$ , m. p. 167°; *β-naphthol-cinchonine (1:1; +H<sub>2</sub>O)*, m. p. 256° (decomp.); *cinchonine-methyl salicylate (1:1; +2H<sub>2</sub>O)*, m. p. 206° (decomp.); *β-naphthol-cinchonine sulphate*,  $C_{10}H_8O_2 \cdot 2C_{19}H_{22}ON_2 \cdot H_2SO_4 \cdot 2\frac{1}{2}H_2O$ , m. p. 147°. The compounds of quinine and cinchonine with pentachlorophenol are exceedingly stable, and may be boiled with sulphuric acid without decomposition; when heated they inflame and give a rose-violet smoke.

S. I. LEVY.

**Microchemical reactions of aconitine.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 165—168).—The most sensitive reaction is that with potassium dichromate, which will detect 2 mg. at a dilution of 1:1000. The reactions with iodine, bromine, sodium perchlorate, and potassium permanganate will detect the same quantity at a dilution of 1:500.

S. I. LEVY.

**Identity of japaconitine and aconitine; two new Aconitum alkaloids.** R. MAJIMA (Proc. Imp. Acad. Tokyo, 1929, 5, 415—417).—See this vol., 228, 229.

**Potentiometric determination of alkaloids by means of potassium mercuri-iodide.** L. MARICQ (Bull. Soc. chim. Belg., 1929, 38, 426—434).—Small quantities (e.g., 20 mg.) of codeine, narcotine, strychnine, brucine, cocaine, and quinine may be determined with a mean error of about 1% by the method previously described for morphine (A., 1929, 1320).  
H. E. F. NORTON.

**Diarsines. II. Tetra-aryldiarsines.** F. F. BLICKE, O. J. WEINKAUFF, and G. W. HARGREAVES (J. Amer. Chem. Soc., 1930, 52, 780—786).—The following tetra-aryldiarsines are obtained from iodo-diarylsarsines and mercury in benzene (cf. A., 1929, 1090): *tetraphenyl-*, m. p. 129—130° (all m. p. are in sealed tubes filled with nitrogen); *tetra-p-tolyl-*, m. p. 165—167°; *tetra-p-anisyl-*, m. p. 172—175°; and *tetra-α-naphthyl-diarsines*, m. p. 249—252°. *5:5'-Bisphenoxarsine*, m. p. 176—177° (lit. 159°) (from 5-iodophenoxarsine, m. p. 145—146°), and *bis-oo'-diphenyllylenearsine*, m. p. 269—273°, are also described. *Chloro-oo'-diphenyllylenearsine (iodo-derivative)*, m. p. 166—167° is prepared from diphenyl, arsenic trichloride, and aluminium chloride at 165—185°. All the above diarsines absorb oxygen, and mol.-wt. determinations by the b.-p. method (in an atmosphere of nitrogen) or the f.-p. method (in solvents saturated with nitrogen) give values indicating that if dissociation does occur, it does not exceed 10% at 80° in benzene.  
H. BURTON.

**Diphenyl series. Arsenic derivatives of diphenyl.** D. E. WORRALL (J. Amer. Chem. Soc., 1930, 52, 664—669).—4-Bromodiphenyl, sodium, and arsenic trichloride in benzene give a small amount of diphenyl and *tri-4-diphenyllylsarsine*, m. p. 182—183° [*dibromide (+CHCl<sub>3</sub>)*, softens above 200°; *sulphide*, m. p. 239—240°]. The *dichloride (+CHCl<sub>3</sub>)*, m. p. 272—273° after softening, of this is hydrolysed by alcoholic ammonia to the *dihydroxide*, m. p. 262—263° after softening. Thermal decomposition of the dichloride gives chlorodiphenyl and impure *chlorodi-4-diphenyllylsarsine*, m. p. 123° after softening at 110° (oxide, softens above 90°; *sulphide*, softens above 110°). *Tri-4-diphenyllylmethylarsonium iodide (iodo-chloride)*, m. p. 86—88°; corresponding *hydroxide*, decomp. 120° after softening, to methyl alcohol and the original tertiary arsine has m. p. 151—152° (decomp.). *Di-4-diphenyllylsarsinic acid*, softens at 95° and melts partly at 110°, is also described. When the tertiary arsine is heated with arsenic trichloride at 300°, and the product hydrolysed, *4-diphenyllylsarsenious oxide*, m. p. 163—165° after softening (*sulphide*, softens above 108°), is obtained. This is oxidised to *4-diphenyllylsarsinic acid*, melts partly at 180—181° after softening.  
H. BURTON.

**[Arsenic] derivatives of pyridine. V. Tautomerism of 2-hydroxypyridine-5-arsinic acid.** A. BINZ, C. RÄTH, and H. MAIER-BODE [with J. HOHENSTEIN] (Annalen, 1930, 478, 22—42).—Different arsenic acids may be obtained from 5-amino-



2-hydroxypyridine by the diazo-reaction (A., 1927, 890) and from 2-pyridone by fusion with arsenic acid. The former appears to be 2-pyridone-5-arsinic acid (I), and the latter (II) to be a mixture of I and 2-hydroxypyridine-5-arsinic acid.

The interaction of 2-pyridone with arsenic acid takes place in two stages. At 130° simple esterification occurs. At 210° further reaction occurs, and after 5 hrs. the chief product obtained by treatment with hypophosphorous acid and then with hydrogen peroxide is I, whilst the mixture II, m. p. 200—230° (mercury salt), separates from the mother-liquors. Transformation of I into II occurs when the reaction mixture is heated for 1—5 days, or when I is heated with 2-pyridone for 1 day. The intermediate arseno-compound previously described (*loc. cit.*) is 5:5'-arseno-2:2'-pyridone, insoluble in acid or alkali, whilst the product obtained in the preparation of II is a mixture, decomp. 227—229°, of this and 2:2'-di-hydroxy-5:5'-arsenopyridine, with amphoteric properties varying in different preparations. Conversion of I and II into the dichloroarsines and treatment in sodium hydroxide solution with mercuric chloride yields 2-pyridone-5-mercurichloride, m. p. 236° (darkens), in 63% and 56% yield, respectively, and 5-iodo-2-pyridone, m. p. 189—191° (Magidson and Menschikoff, A., 1925, i, 301), is obtained from this by the action of iodine in methyl alcohol. The mixed dichloroarsine hydrochlorides, m. p. 110—120° (decomp.), derived from II yield with ammonia a mixture of arsenoxides, m. p. 251° (decomp.). When I and II are reduced by sulphur dioxide in dilute sulphuric acid in presence of potassium iodide and treated with thiophenol, they yield, respectively, di(phenylthiol)-5-pyrid-2-onylarsine, m. p. 153°, and a readily separable mixture of this and di(phenylthiol)-2-hydroxy-5-pyridylarsine,  $\text{OH}\cdot\text{C}_5\text{H}_4\text{N}\cdot\text{As}(\text{SPh})_2$ , m. p. 124°. Conversion of these compounds back into the arsinic acids, either by direct oxidation with methyl-alcoholic iodine solution or by hydrolysis in the cold with hydrochloric acid and oxidation with hydrogen peroxide, yields in the first case I, and in the second the mixture II.

Fusion of *N*-methyl-2-pyridone with arsenic acid yields *N*-methyl-2-pyridone-5-arsinic acid (III), m. p. 254—257°, which yields with bromine *N*-methyl-3:5-dibromo-2-pyridone, m. p. 182°, and is reduced to the arsenoxide, m. p. 102—117°, which reacts with thiophenol to give di(phenylthiol)-5-*N*-methylpyrid-2-onylarsine, m. p. 122°. The corresponding dichloroarsine hydrochloride, m. p. 167°, and arseno-compound, decomp. 215—240°, have been prepared. The converse reaction, methylation of the arsinic acid with methyl iodide or methyl sulphate and alkali, yields in the case of both I and II a mixture, m. p. 217—218°, of III and 2-methoxypyridine-5-arsinic acid, which yields with bromine *N*-methyl-3:5-dibromo-2-pyridone or 3-bromo-*N*-methyl-2-pyridone-5-arsinic acid, and with iodine in potassium iodide, 3:5-di-iodo-*N*-methyl-2-pyridone, m. p. 267—268° (decomp.) (Garthe, Diss., Berlin, 1929). When the methylated mixture is heated, III may be isolated from the product. The mixture yields di(phenylthiol)-2-methoxy-5-pyridylarsine, m. p. 91°. These reactions can be explained only on the assumption that the methyl group wanders freely between nitrogen and oxygen.

A series of higher alkyl derivatives has been prepared, for which the pyridone structure is assumed. The same products are obtained either by heating the alkylpyridones with arsenic acid or by alkylating 2-pyridone-5-arsinic acid. The m. p. falls and the solubility of the arseno-compounds in water increases with increasing length of the alkyl chain. The following are described: *N*-Ethyl-2-pyridone-5-arsinic acid, decomp. 183° (corresponding arsenoxide, m. p. 92—93°; dichloroarsine hydrochloride, m. p. about 132°, and arseno-compound, decomp. 162—164°); *N*-*n*-propyl-2-pyridone-5-arsinic acid, m. p. 197° (arsinoxide, m. p. 74—75°; dichloroarsine hydrochloride, m. p. 124°; arseno-compound, m. p. 121—132°); *N*-*n*-butyl-2-pyridone-5-arsinic acid, m. p. 146—147° (arsinoxide, decomp. 83°; dichloroarsine hydrochloride, m. p. 113—115°; arseno-compound, m. p. about 190°).

R. K. CALLOW.

**Mercuration of coumarins.** R. N. SEN and D. CHAKRAVARTI (J. Indian Chem. Soc., 1929, 6, 847—853).—Treatment of a solution of coumarin in dilute sodium hydroxide with mercuric oxide and subsequent acidification with hydrochloric acid yields 6-chloromercuricoumarin, decomp. 178°, which, when freshly prepared, is soluble in ammonia; with an excess of mercuric oxide 6:8-di(chloromercuri)-coumarin, decomp. 207°, is produced. This dimercurated product gives an additive compound,  $\text{C}_9\text{H}_4\text{O}_2\text{Cl}_2\text{Hg}_2\cdot\text{C}_5\text{H}_5\text{N}$ , m. p. 225°, when treated with pyridine. 4:7-Dimethylcoumarin is mercurated as above to a 6:8-di(chloromercuri)-derivative.

Dissolution of coumarin in sodium hydroxide solution, neutralisation with acetic acid, and subsequent treatment with a solution of mercuric acetate in dilute acetic acid gives 3:5-di(acetoxymercuri)-o-coumaric acid, decomp. 215° (formed also from o-coumaric acid and mercuric oxide in alkaline solution, and subsequent acidification with acetic acid), which is demercurated by boiling with dilute hydrochloric acid to o-coumaric acid. Similar treatment of 4-methylumbelliferone affords 7-hydroxy-4-methyl-6:8-di(acetoxymercuri)coumarin, whilst 4-methyldaphnetin furnishes 7:8-di(acetoxymercurioxy)-4-methylcoumarin. 6-Aminocoumarin is mercurated in acetic acid solution to 6-acetoxymercuriaminocoumarin.

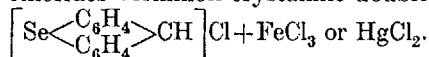
H. BURTON.

**Preparation and purification of magnesium diphenyl.** H. GILMAN and R. E. BROWN (Rec. trav. chim., 1930, 49, 202—204).—An 80—90% yield of pure magnesium diphenyl in benzene-ether solution is obtained by heating a mixture of 1 g.-mol. of pure mercury diphenyl and 0.2 g.-atom of powdered magnesium in a sealed tube (sealed at 3 mm. pressure) at 200—210°. The isolation of the product is effected in an inert atmosphere in a special apparatus, which is fully described, and in which the product is washed free from diphenyl and mercury diphenyl using benzene.

J. W. BAKER.

**Basicity of selenoxanthhydrols.** F. FRANÇOIS (Compt. rend., 1930, 190, 191—193).—Reduction of selenoxanthone by sodium amalgam and alcohol furnishes selenoxanthhydrol, m. p. 115—116°, which with magnesium phenyl bromide yields phenylselenoxanthhydrol, m. p. 105°. Selenoxanthhydrol and

phenylselenoxanthhydrol both dissolve in mineral acids, forming more deeply coloured solutions than the corresponding oxygen and sulphur compounds. A solution of the selenoxanthhydrol in acetic and hydrochloric acids gives with mercuric and ferric chlorides vermilion crystalline double salts,



C. C. N. VASS.

**Chromoproteins of red algæ. II. Scission with pepsin and acids.** Isolation of a pyrrole colouring matter. R. LEMBERG (Annalen, 1930, 477, 195—245).—Further or corrected crystallographic and spectrophotometric data for *Ceramium* and *Nori* phycoeyan (which are not identical) and phycoerythrin are given (cf. A., 1928, 533), and a detailed spectrophotometric examination of these chromoproteins in various aqueous hydrochloric acid solutions and of their fission products with pepsin and hydrochloric acid is described, for details of which the original must be consulted. For the true pigments of phycoeyan and phycoerythrin, obtained by scission with hydrochloric acid at 80—85°, the names phycoeyanobilin and phycoerythrobilin are suggested. These, unlike the parent chromoproteins, form complex zinc salts. The absorption curve obtained with *Nori* phycoeyan in concentrated hydrochloric acid at the ordinary temperature is a composite of that obtained in 0.1N-hydrochloric acid and of that obtained after heating with concentrated hydrochloric acid at 80°, a similar relationship being observed with the spectra of the complex zinc salts. The absorption curve obtained when phycoerythrin is heated with concentrated hydrochloric acid at 85° is a composite of those of the hydrochloride of phycoeyanobilin (85.5%) and unaltered phycoerythrobilin (14.5%), a similar proportion being obtained by examination of the curves of the complex zinc salts. This is explained by the fact that phycoerythrobilin is readily oxidised by atmospheric oxygen to phycoeyanobilin, slowly in concentrated hydrochloric acid at the ordinary temperature, but rapidly and completely with acid ferric chloride. Scission of *Ceramium* phycoeyan with warm concentrated hydrochloric acid gives a chloroform-soluble phycoeyanobilin the absorption spectrum of which is identical with that from *Nori* phycoeyan, but with cold concentrated acid a different absorption spectrum is obtained which, although the position of the maxima corresponds with a mixture of phycoeyano- and erythrobilin, is not due to such a mixture, since warm concentrated hydrochloric acid in the absence of air destroys the band corresponding with phycoerythrobilin, which under these conditions is stable. *Phycoeyanobilin*,  $\text{C}_{34}\text{H}_{44}\text{O}_8\text{N}_4$  (1.46% of the chromoprotein), isolated by extraction with chloroform after scission of *Nori* phycoeyan with warm concentrated hydrochloric acid, may be obtained crystalline under prescribed conditions. It is amphoteric, forming readily hydrolysable salts with strong acids, and yielding an amorphous, unstable, *methyl ester*,  $\text{C}_{34}\text{H}_{44}\text{O}_8\text{N}_4(\text{OMe})_2$ , when esterified with 5% methyl-alcoholic hydrogen chloride. Reduction of phycoeyanobilin with hydrogen iodide in acetic acid gives alkaline products containing pyrrole bases, whilst the

acid fraction gives a strong Ehrlich reaction, but attempts to isolate bilirubin or cryptopyrrolecarboxylic acid were unsuccessful owing to the small quantity of material. Reduction with sodium amalgam in neutral solution in an atmosphere of nitrogen yields a substance which gives an intense urobilin reaction and is rapidly oxidised in air. Isolation of phycoerythrobilin by similar methods fails owing to the sparing solubility of phycoerythrin in concentrated hydrochloric acid and the slight solubility of the erythrobilin in chloroform, but by scission with 20% methyl-alcoholic hydrogen chloride at 80—85° (in nitrogen) the chloroform-soluble phycoerythrobilin *methyl ester* (2.75% of the chromoprotein) is obtained, slightly contaminated with protein matter. The relationship of these pigments to those from bile is discussed and it is suggested that *Nori* phycoeyan is probably identical with the bluish-green phycoeyan isolated by Kylin (A., 1912, i, 289) from *Batrachosperm* and by Boresch (A., 1922, i, 210) from *Schizophyceæ*. The protein components of phycoerythrin and phycoeyan are similar but probably not identical.

J. W. BAKER.

**Biochemistry of sulphur. V. Cystine content of phaseolin.** M. X. SULLIVAN (U.S. Pub. Health Rep. Suppl., 1929, No. 80, 7 pp.).—Hydrolysis of phaseolin, the globulin from *Phaseolus vulgaris*, either with boiling hydrochloric acid ( $d_{20}^{20}$  1.096) alone, which causes considerable precipitation of humin, or with addition of stannous chloride or titanous chloride, which prevents this, gives a hydrolysate which, in agreement with biological evidence, contains no traces of cystine detectable either by the author's colorimetric method (cf. this vol., 199) or the iodometric method of Okuda (A., 1926, 190). This result is confirmed in that it also gives a negative result for cystine with sodium nitroprusside in the presence of a little sodium cyanide, or with the lead sulphide test (boiling with lead acetate and 5N-sodium hydroxide). To the filtrate from hydrolysis, after cleaning with norit, 25% sodium hydroxide is added until  $p_H$  3.5 is obtained. To 5 c.c. of this solution are added 2 c.c. of a 5% sodium cyanide solution, and, after 10 min., 1 c.c. of a 0.5% aqueous solution of 1:2-naphthaquinone and 5 c.c. of a 10% solution of anhydrous sodium sulphite in 0.5N-sodium hydroxide. After 30 min. 1—2 c.c. of a 25% sodium hydroxide solution and 1 c.c. of a 2% sodium hyposulphite solution are added, and the red colour is matched against a standard containing 100—200 parts per million of cystine in 0.1N-hydrochloric acid. A positive reaction with the Folin-Looney method (A., 1922, ii, 539) is given by non-cystine complexes and even by a 1% solution of pyruvic acid or furfuraldehyde.

J. W. BAKER.

**Mol. wt. of casein. II.** T. SVEDBERG, L. M. CARPENTER, and D. C. CARPENTER (J. Amer. Chem. Soc., 1930, 52, 701—710; cf. this vol., 356).—Casein, obtained by the method of Van Slyke and Baker (A., 1918, i, 413), consists of a mixture of proteins. The major part of the product has a mol. wt. between 75,000 and 100,000, as determined by the method of sedimentation velocity in phosphate buffers at  $p_H$  6.8. Different preparations do not give the same

results. When the casein is dissolved in the phosphate buffer at 40°, the mol. wt. is found to be 188,000 by the method of sedimentation equilibrium, indicating that polymerisation or association of all the molecules occurs during the heating. H. BURTON.

**Bjerrum's theory of amphoteric ions and the hydration of proteins.** H. H. WEBER (Biochem. Z., 1930, 218, 1—35).—Further work pointing to the independence of protein hydration and protein ionisation (cf. A., 1929, 395) is described. When hydrogen and hydroxyl ions react with an ampholyte, changes of total volume occur, the size of which (like the corresponding heats of reaction and changes of dissociation constant with dielectric constant of medium) depend predominantly on the kind of group which reacts and only slightly on the kind of molecule carrying this group. By means of these volume changes it is shown that not only aliphatic but also heterocyclic amino-acids and aliphatic dipeptides exist almost quantitatively as amphoteric ions at the isoelectric point. Comparison of gelatin in the normal and deaminised conditions shows that all the free amino-groups are ionised at the isoelectric point, that they dissociate on the alkaline side quantitatively between  $p_H$  9 and 12, and that the last stage of the hydroxyl-ion combination curve over this range depends on the repression of dissociation of the free amino-groups. The changes of dissociation with dielectric constant show that the union with hydrogen ions between  $p_H$  1.5 and 3.5 with all the proteins investigated depends on the repression of the dissociation of carboxyl groups.

P. W. CLUTTERBUCK.

**Determination of the products of protein-hydrolysis.** E. ZUNZ (Ann. Soc. Zymol., 1929, 1, 236; Woch. Brau., 1930, 47, 57—60).—From a review of the literature the following methods are proposed. Decolorisation is effected by barium chloride and silver nitrate. The liquid is neutralised to azolitmin paper, the preparation and standardisation of which are described. Portions are titrated (A) in 80% alcoholic solution with 0.1N-sodium hydroxide to thymolphthalein and (B) in 50% alcohol with 0.1N-alcoholic potassium hydroxide to phenolphthalein ( $p_H$  8.3). The amino-nitrogen (C) is calculated from  $100(A - B)/71 = C$ , and  $A - C$  corresponds with the peptide-nitrogen. The value  $A$  really corresponds with the carboxyl groups, and by titrating the 80% alcoholic portion back with 0.1N-hydrochloric acid to neutral-red a true measure of the total amino-groups is obtained.

F. E. DAY.

**Determination of tyrosine and tryptophan in proteins.** J. TILLMANS, P. HIRSCH, and F. STOPPEL (Biochem. Z., 1930, 217, 422).—The modification of

the authors' original method (A., 1928, 1278) proposed by Bauer and Strauss (A., 1929, 1324) is not allowable. The method is suitable only for proteins soluble in hot dilute nitric acid. K. V. THIMANN.

**Microanalytical determination of carbon and hydrogen.** K. LINDENFELD (Rocz. Chem., 1930, 10, 84—95).—An apparatus is described differing from that of Pregl in the following respects. The products of combustion are absorbed in Blumer tubes, in place of those used by Pregl. A platinum spiral is introduced into the combustion tube immediately past the porcelain boat. Ceria is used as the catalyst. Finally, three burners are used, in place of Pregl's one long one. R. TRUSZKOWSKI.

**Gas-volumetric microdetermination of nitrogen by Pregl's method.** B. FLASCHENTRÄGER (Mikrochem., 1930, 8, 1—3).—A reply to Halla (A., 1929, 899). Pregl's method for nitrogen is held to be perfectly satisfactory. H. F. HARWOOD.

**Test of acetic acid with benzidine.** K. SERKE (Apoth.-Ztg., 1929, 44, 1018—1019; Chem. Zentr., 1929, ii, 1951).—When acetic acid is heated at 60° with benzidine it should remain colourless; a positive reaction indicates the presence of pyroigneous acid, acetaldehyde, paraldehyde, vanillin, sodium sulphite, or formic acid. A. A. ELDRIDGE.

**Microchemical saponification process.** L. ROSENTHALER (Mikrochem., 1930, 8, 72—74).—A drop of the oil to be examined is placed on a slide, and a drop of a saturated alcoholic solution of potassium hydroxide is added; solid fats should be melted before addition of the alkali. The resulting crystals of the potassium salts of the fatty acids are then examined microscopically. H. F. HARWOOD.

**Micro-determination of methylimides.** P. HAAS (Mikrochem., 1930, 8, 89—94).—Polemical against Friedrich (A., 1929, 949). H. F. HARWOOD.

**Micro-determination of methylimides.** A. FRIEDRICH (Mikrochem., 1930, 8, 94—99).—A reply to Haas (see preceding abstract).

H. F. HARWOOD.

**Detection and determination of small quantities of pyridine.** J. V. KULIKOV and T. N. KRESTOVOSDVIGENSKAJA (Z. anal. Chem., 1930, 79, 452—459).—The additive compound of pyridine and cyanogen bromide reacts with aromatic amines to form intensely coloured derivatives of glutaconaldehyde, and this reaction has now been utilised for the colorimetric determination of pyridine. When aniline is used the method will detect 0.025 mg. of pyridine in 1000 c.c. of solution.

H. F. HARWOOD.

## Biochemistry.

**Effects of breathing oxygen at high pressures on tissue gas tensions.** J. A. CAMPBELL (J. Physiol., 1930, 68, Proc., vii).—With high pressures of oxygen the venous blood of rabbits approaches the arterial blood and there is evidence that the animals die of carbon dioxide poisoning. E. BOYLAND.

**Blood pigment. II. Human hæmoglobin.** F. HAUROWITZ (Z. physiol. Chem., 1930, 186, 141—147; cf. A., 1929, 942).—Crystalline human hæmoglobin was prepared in rectangular plates containing C 53.7, H 7.28, N 17.0, Fe 0.37, S 0.44, O 21.2%. The blood of the newly-born child was more resistant

than adult blood to sodium hydroxide. The prosthetic groups are the same in both cases. In the blood of the newly-born the decomposition by sodium hydroxide proceeds quickly during the first 2 min. and then suddenly more slowly. It is supposed that two hæmoglobins are present, 20% of the easily decomposed one, identical with that of adult blood, and 80% of a resistant foetal hæmoglobin.

J. H. BIRKINSHAW.

**Carbon monoxide-hæmoglobin.** A. K. BOOR and A. BACHEM (J. Biol. Chem., 1930, 85, 743—749).—Photographs of the absorption spectra of samples of carbon monoxide-hæmoglobin prepared from different species are given. All preparations are spectroscopically identical. C. R. HARRINGTON.

**"Inactivation" of oxyhæmin.** A. HAMSÍK (Z. physiol. Chem., 1930, 186, 263—270; cf. A., 1929, 1189).—Active hæmin is inactivated not only by drying, but also by boiling with water and by prolonged washing with cold water. Oxy-, carboxy-, and met-hæmoglobin when precipitated with acetone first yield crystals which then decompose, forming cathæmoglobin. These compounds do not lose their power of crystallisation from acetic or formic acid on drying.

J. H. BIRKINSHAW.

**Distribution of amino-acids between plasma and erythrocytes.** B. MESSING (Biochem. Z., 1930, 218, 54—63).—The distribution of amino-nitrogen between the plasma and cells of dog's blood does not depend on the properties of the individual amino-acids, but gives almost the same concentration curve for all the acids used (glycine, leucine, alanine, asparagine). The amino-nitrogen content of freshly-removed corpuscles is always higher than that of the plasma. If the external concentration of amino-nitrogen is artificially increased by adding isotonic solutions of amino-acids to dog's blood *in vitro* the corpuscles absorb amino-nitrogen only slightly if at all up to a certain limit. The initial rise of the concentration curve for the erythrocytes depends not so much on the addition of amino-acid as on the degree of their saturation with amino-acid at the beginning of the experiment or on some such property of the cells themselves.

P. W. CLUTTERBUCK.

**Absence of calcium from the human red blood-corpuscle.** S. L. LEIBOFF (J. Biol. Chem., 1930, 85, 759—764).—The results of previous workers showing the absence of calcium from the red corpuscles of human blood are confirmed.

C. R. HARRINGTON.

**Rate of disappearance of radioactive substances from body fluids. Determination of blood volume.** W. KROPATSCHECK (Biochem. Z., 1930, 218, 191—205).—A method is described for determining the total blood volume in rabbits by injection of thorium-B as indicator substance. Rapid dialysis of thorium-B from aqueous solutions is prevented by addition of gelatin. When added to Ringer's solution 97.46% of the active material is precipitated but to serum only 28%. When thorium-B is added to blood *in vitro*, about 90% is accumulated in the cells. In carrying out a determination of blood volume, 10 c.c. of blood are removed, the serum is separated, mixed with the active material, the pre-

cipitate centrifuged off, and the resulting active solution injected. Samples of about 0.5 c.c. are then removed for activity measurements before fall of activity becomes appreciable. The amount of active substance lost in the urine is extremely small, being equivalent in 2 hrs. only to 1—2 c.c. of blood. The advantages claimed for the method are that the volume of both cells and plasma may be determined, that only small amounts of blood are necessary (0.5 c.c.) and therefore several determinations are possible without serious injury to the animal. The disadvantages are the initial removal of 10 c.c. of blood and the decrease of activity. If the radioactive substance is injected without first combining with a colloidal substance the initial values are reduced to one half to one third, a larger part of the activity disappears from the blood, and in the following 20—30 min. the activity oscillates and finally becomes constant for a considerable time.

P. W. CLUTTERBUCK.

**Menstrual blood.** A. RONA and O. WALDBAUER (Zentr. Gynäkol., 1928, 997—1005; Chem. Zentr., 1929, ii, 2690).—Total and plasma-protein is usually similar in quantity in menstrual and venous blood, but the residual nitrogen is usually higher in the former.

A. A. ELDRIDGE.

**Possibilities of an individual chemical synthesis of serum-protein. II. Sulphur content of human serum-protein.** K. LANG (Arch. exp. Path. Pharm., 1930, 148, 222—231).—The protein-sulphur in the serum of various individuals has been determined as well as the total protein and the amount of albumin and globulin. The figure obtained for total protein-sulphur does not agree in about 50% of the cases with that calculated from the quantity of albumin and globulin present. It is concluded, in agreement with previous work on the tryptophan content of blood-serum (A., 1929, 1476), that the chemical composition of the blood-proteins is not constant, but may vary in different individuals.

W. O. KERMACK.

**Detection and presence in human blood of substances contracting the vessels.** G. KAHLSON and R. VON WERZ (Arch. exp. Path. Pharm., 1930, 148, 173—197).—A biological method for the detection of vaso-constrictor substances in blood-serum is described. The average concentration at which adrenaline can be detected by this method is about 1 in  $10^9$ . In a highly sensitive preparation capable of detecting adrenaline at a concentration of 1 in  $10^{11}$  a negative result was obtained with normal human blood, although a vaso-constrictor substance is found in the serum from cases of toxic thyroid and fevers.

W. O. KERMACK.

**Effect of hæmorrhage on acid-base equilibrium of blood.** C. G. JOHNSTON and D. W. WILSON (J. Biol. Chem., 1930, 85, 727—741).—Hæmorrhage in normal unanæsthetised dogs caused first a rise and then a more marked fall in the  $p_H$  of the blood; the increased acidity was accompanied by accumulation of lactic acid, not, however, in sufficient amounts to account for the whole of the diminution of the alkaline reserve. Subsequent hæmorrhages, in dogs already anæmic, produced similar effects of a more pronounced character.

C. R. HARRINGTON.

**Acid in the blood-serum of children in health and disease.** J. CSAPÓ (Magyar orvosi Arch., 1929, 30, 270—276; Chem. Zentr., 1929, ii, 1950).—A direct method for the determination of organic acid in blood-serum is based on Van Slyke and Palmer's method for urine. In normal children the acid corresponds with 12 c.c. ( $\pm 30\%$ ) of 0.1N-acid per 100 c.c.

A. A. ELDRIDGE.

**Determination of  $p_H$  of blood.** M. TALENTI (Arch. Farm. speriment., 1930, 50, 103—109).—Errors in colorimetric methods applied to plasma are indicated. The application of the hydrogen electrode of Verain (A., 1926, 1067) and the quinhydrone electrode of Mislowitzer (A., 1925, i, 1483) is described.

F. O. HOWITT.

**State of calcium in serum.** W. HERTZ (Biochem. Z., 1930, 217, 337—345).—The amount of serum-calcium which passes the ultra-filter is reduced by parathyroidectomy in dogs; subcutaneous injection of parathyroid extract increases it, although the total calcium is increased still more. K. V. THIMANN.

**Colorimetric determination of small quantities of iron [in blood].** G. DENIGÈS (Bull. Soc. Pharm. Bordeaux, 1929, 67, 81—84; Chem. Zentr., 1929, ii, 2231).—The ash of blood (0.5 c.c.) is dissolved in concentrated hydrochloric acid; the colour is compared with that of hydrochloric acid to which varying quantities of dilute ferric chloride solution have been added.

A. A. ELDRIDGE.

**Mannose and the protein-sugar residue of mammals and birds.** H. BIERRY (Compt. rend., 1930, 190, 404—406).—Hydrolysis of the purified proteins of the plasma of various animals and birds gives *d*-mannose. The effects of insulin hypoglycaemia are counteracted almost equally by dextrose and mannose.

P. G. MARSHALL.

**Restoration of blood-sugar by the liver.** F. RATHERY, R. KURILSKY, and (MLLE.) Y. LAURENT (Compt. rend., 1930, 190, 448—449).—Determination of the blood-sugar in the portal and superior hepatic veins of normal, starving, depancreatized, and starving phloridzinized dogs, shows that in all cases the liver supplies sugar to the blood, independently of the level of the liver-glycogen.

R. K. CALLOW.

**Daily blood-sugar variation in fasting and in non-fasting subjects.** J. S. SWEENEY (Arch. Int. Med., 1930, 45, 257—260).—In fasting normal subjects the blood-sugar varies but little during the 24 hrs. In non-fasting normal subjects a marked rise in the blood-sugar level occurs after the morning meal, a less marked one after the midday meal, and a still smaller one after the evening meal.

W. O. KERMAK.

**Effect of quartz-lamp light on blood-enzymes.** B. M. KOLDAYEV and M. M. ALTSCHULLER (Z. physiol. Chem., 1930, 186, 223—228).—Quartz-lamp irradiation of rabbits produces a transitory decrease in serum-amylase and blood-catalase and an increase in the serum-lipase. There is no direct relationship between these changes and the degree of irradiation. The decrease in the amylase content is not observed in all cases. Periodic irradiation produces similar changes with slower reversion to normality.

J. H. BIRKINSHAW.

**Tyrosinase in crustacean blood.** K. G. PINHEY (J. Exp. Biol., 1930, 7, 19—36).—Crustacean blood blackens in air owing to the formation of melanin. The blood contains an indophenol-oxidase and tyrosinase. The tyrosinase activity is reduced by cyanide, hydrogen sulphide, copper sulphate, ferric chloride, fluorides, or pyrophosphates and by low concentrations of urethane or thymol, but higher concentrations of thymol ( $M/7$ ) increase the action of the tyrosinase.

E. BOYLAND.

**Electrostatic properties of human fibrinogen.** G. VON FARKAS and B. GROÁK (Z. ges. exp. Med., 1929, 66, 596—613; Chem. Zentr., 1929, ii, 1937).—The optimal  $p_H$  for precipitation depends on the method of separation and the buffer mixture used; the double optimum is ascribed to the presence of two proteins both of which are coagulable.

A. A. ELDRIDGE.

**Hæmolytic power of spleen.** S. MARINO and G. DE BONIS (Arch. Farm. speriment., 1929, 50, 1—15).—Physiological saline extracts of spleens of fasting and feeding dogs show no hæmolysis *in vitro* of red corpuscles of the corresponding splenectomized dog or of animals of the same species.

F. O. HOWITT.

**Cholesterol content of blood-forming organs.** K. YOSHINAKA (Okayama Ig. Zasshi, 1928, 40, 2504—2523).—In rabbits receiving cholesterol the cholesterol content of the liver increases, whilst that of the spleen and bone-marrow diminishes before increasing. In experimental anaemia the cholesterol decreases in all the blood-forming organs, then increases largely in the liver and fluctuates in the spleen and bone-marrow. If thyroid substance is given during phenylhydrazine poisoning the cholesterol content of the liver and spleen at first increases and then decreases, whereas that of the bone marrow continuously decreases.

CHEMICAL ABSTRACTS.

**Kidney lipase in the human embryo and the new-born infant.** F. TACHIBANA (Kinki J. Gynecol., 1928, 11, 1308—1314).—Lipase appears in the fourth month, and thereafter increases, particularly in the fifth month.

CHEMICAL ABSTRACTS.

**Localisation of virtual adrenaline.** A. LEULIER and L. REVAL (Compt. rend., 1930, 190, 452—454).—The virtual (combined) adrenaline of the suprarenal capsules (sheep, ox, horse) (cf. Mouriquand and Leulier, A., 1927, 168) appears to be confined to the medullary and to be absent from the cortical zone.

R. K. CALLOW.

**Structure of dental enamel.** H. KLEIN and W. R. AMBERSON (J. Dental Res., 1929, 9, 667—688).—When the enamel of the canine teeth of dogs is used to separate two salt solutions, membrane potentials may be demonstrated. The enamel is penetrable by potassium and chlorine ions; it is penetrable slowly by water and by calcium chloride.

CHEMICAL ABSTRACTS.

**Nitrogen excretion in Selachian ontogeny.** J. NEEDHAM and D. M. NEEDHAM (J. Exp. Biol., 1930, 7, 7—18).—The carbamide content of the dogfish egg increases with development; it remains in the yolk and later in the blood of the animal.

E. BOYLAND.

**Phosphorus compounds of muscle and liver.** C. H. FISKE and Y. SUBBAROW (Science, 1929, 70, 381—382).—The muscle nucleotide, myoadenylic acid, is not a normal constituent of muscle, except possibly in traces, but is a decomposition product of a new substance which is precipitated as the calcium salt from a protein-free muscle filtrate. The new substance contains adenine and carbohydrate as well as 3 mols. of phosphoric acid, two of which are readily removed by hydrolysis with acid. Most of the organic acid-soluble phosphorus of liver can be precipitated from the protein-free filtrate by alcohol after removal of inorganic phosphate. A calcium salt of  $\alpha$ -glycerophosphate finally results after dissolution in water and reprecipitation. L. S. THEOBALD.

**Do the spectrograms of Kahlenberg and Closs demonstrate the presence of aluminium in biological material?** E. V. MCCOLLUM, O. S. RASK, and J. E. BECKER (J. Biol. Chem., 1930, 85, 779—781).—Polemical (cf. A., 1928, 793; Kahlenberg and Closs, A., 1929, 1098). C. R. HARRINGTON.

**Presence of aluminium in animal and plant material.** L. KAHLENBERG and J. O. CLOSS (J. Biol. Chem., 1930, 85, 783—784).—Polemical (cf. preceding abstract). C. R. HARRINGTON.

**Determination of the protein content of intra-ocular fluids with the nephelometer. I.** II. A. FRANCESCHETTI and H. WIELAND (Arch. Augenheilk., 1928, 99, 1—44, 45—62; Chem. Zentr., 1929, ii, 2231).—For the determination of small quantities of protein an accuracy of 0.3% is attained. A micro-apparatus, dealing with 0.2 c.c. (0.002 mg. of protein), is described. The protein content of rabbits' aqueous and vitreous humour, respectively, is 0.05 and 0.012%. In man the aqueous humour contains 0.019—0.034% of protein. The effect of pathological conditions is considered. A. A. ELDRIDGE.

**Coating of the fat-globules of milk.** I. PRIEGER (Biochem. Z., 1930, 217, 331—336).—The cataphoresis of particles of natural milk-fat and of an artificial emulsion prepared by shaking the pure fat with water was observed under the microscope, and the isoelectric point of the artificial particles was found to be  $p_H$  2.94, whilst that of the natural particles of milk-fat was 4.21 and of butter-fat 3.95. This is held to indicate that the particles of natural fat are surrounded with a coating of protein material. K. V. THIMANN.

**Urobilin.** O. BANG (Acta med. Scand., 1929, 29, 1—203; Chem. Zentr., 1929, ii, 2085).—Urobilin is detected by shaking slightly acid urine (10 c.c.) with 95% alcohol (10 c.c.), finely-powdered zinc acetate (1 g.), and 5% tincture of iodine (1—2 drops) and filtering; after 30 min. fluorescence is observed. For determination the Einar-Larsen method and Schlesinger's test are applied. Urinary urobilin is increased after ingestion of food. Immediately after birth the urinary urobilin of the infant is maximal. The relation between excretion of urobilin and pathological conditions is considered. A. A. ELDRIDGE.

**Determination of dextrose in urine.** D. GANASSINI (Arch. Ist. Biochim. Ital., 1930, 2, 31—36).

—The following modification of Causse and Bonnans' method ("Guide pratique pour l'Analyse des Urines," Paris, 210) is recommended. The solutions required are: (1) 35 g. of copper sulphate, made up to 1 litre with water and 5 c.c. of sulphuric acid; (2) 150 g. of Rochelle salt and 90 g. of carbonate-free sodium hydroxide, made up to 1 litre. To prepare a solution which keeps for some time, 0.5 g. of powdered potassium ferrocyanide is added to a mixture of 20 c.c. of (1) with 20 c.c. of (2); the liquid should be stored in a yellow glass bottle and should be made some hours before use. Twenty drops of this solution, heated to boiling, should maintain its colour. The urine is added, one drop at a time, the liquid being heated to boiling after each addition, and the addition continued until a brown precipitate appears. If much sugar is present, the urine will require previous dilution. The reagent is standardised by means of a urine to which a known amount of pure dextrose has been added; 1 c.c. should require 0.0021 g. of dextrose. T. H. POPE.

**Human body-fluids. I. Anasarcous liquid.** O. FLÖSSNER and REHBERG (Z. Biol., 1930, 89, 573—581).—From the anasarcous liquid histidine was isolated, together with small amounts of purine bases, isoamylamine, *p*-hydroxyphenylpropionic acid, fatty acids, and lactic acid. It is concluded that these substances would normally have been involved in further synthesis, and considerable metabolic derangement is indicated. K. V. THIMANN.

**Endocrine glands. V. Adrenals.** C. H. LAWRENCE and A. W. ROWE (Endocrinol., 1929, 13, 1—39).—A chemical study in pathological conditions. Albumin was present in, and urobilinogen absent from, the urine in every case. Adrenal disease is accompanied by a low level of protein metabolism. CHEMICAL ABSTRACTS.

**Water content of blood, of muscular tissue, and of certain organs after the extirpation of suprarenal capsules in the rat.** C. I. PARHON, M. CAHANE, and V. MÄRZA (Bull. Acad. Sci. Roumaine, 1929, 12, 22—25).—The water content of the blood in the muscular tissue and in certain organs of the rat from which the suprarenal capsules have been removed is greater than that in a normal rat. A. I. VOGEL.

**Alcohol and blood-sugar in diabetes.** T. C. HUNT (Lancet, 1930, i, 121—124).—Alcohol stimulates gastric and insulin secretion and thus lowers the blood-sugar. E. BOYLAND.

**"Durener" sickness.** G. B. VAN KAMPEN (Landw. Versuchs-Stat., 1929, 108, 287—303).—Animal disorders following the feeding of soya-bean meal (Stockman, J. Comp. Path. Ther., 1916, 39, 95) are probably not the result of residual trichloroethylene used for oil extraction, but are due to the removal of lipins from the material to an extent which constitutes a deficiency for normal milk production. The decrease in white corpuscles (Stang, Landw. Versuchs-stat., 1927, 105, 79) is a direct result of this. Light petroleum removes much less lipin from soya bean than does trichloroethylene and its use is recommended. A. G. POLLARD.



**Effect of adrenaline on the respiratory metabolism in exophthalmic goitre.** I. SCHILL (Magyar Orvosi Arch., 1929, 30, 202—209; Chem. Zentr., 1929, ii, 1935).

**Glutathione content of blood of psychopathic patients.** E. KING, L. BAUMGARTNER, and I. H. PAGE (Biochem. Z., 1930, 217, 389—394).—The blood is hemolysed, protein precipitated with trichloroacetic acid, iodine added, and its excess titrated, the absorption of iodine being ascribed to the glutathione. Precipitation of protein with tungstic or molybdic acid gives comparable results only if carried out at  $pH$  2. The "glutathione" content of blood is not notably affected by hunger, and is the same in psychopathic as in normal patients. K. V. THIMANN.

**Blood of rabbits with sarcoma.** K. IINO (Sei-i-kwai Med. J., 1929, 48, No. 8, Abstr., 8—9).—Blood-cholesterol, -lecithin, and -fibrin and serum-protein (mainly -globulin) at first increased, and then decreased, as the sarcoma grew. The serum-anti-trypsin was increased, -amylase was unchanged, and -lipase was diminished. CHEMICAL ABSTRACTS.

**Preparation of sarcomelanin from sarcomelanin acid.** O. ADLER (Biochem. Z., 1930, 217, 324—330).—Sarcomelanin was prepared from a melanosisarcoma (horse) and the corresponding melanin acid prepared therefrom by fusion with potassium hydroxide and subsequent precipitation with hydrochloric acid. On heating the sarcomelanin acid for 2 hrs. at  $270^\circ$  a substance apparently identical with natural sarcomelanin was obtained.

K. V. THIMANN.

**Chemical composition of scorbutic bones.** L. STATSMANN (Biochem. Z., 1930, 217, 395—399).—A series of analyses of the bones of normal and scorbutic guinea-pigs is recorded. The principal differences are that the water is lower, and the ash higher, in the scorbutic than in the normal, whilst the calcium and phosphorus, calculated on the total dry substance, are only slightly higher.

K. V. THIMANN.

**Serum-calcium and -inorganic phosphorus following splenectomy.** R. D'AUNOY and A. ZOELLER (Med. J. Record, 1929, 130, 495—496).—The determining factor is probably the carbon dioxide tension; splenectomy itself has no influence on the values in rabbits. CHEMICAL ABSTRACTS.

**Metabolism of insects.** F. TAUCHERT (Z. Biol., 1930, 89, 541—546).—The loss of weight of the pupæ of *Sphinx ligustri* is largely due to the loss of water. The respiration of the caterpillar is more variable than that of the pupa, the respiratory quotient rising to 5. The oxygen consumption of the bee is about ten times the body-volume per min.

K. V. THIMANN.

**Hydrogenation of cholesterol in the organism.** R. SCHÖNHEIMER, H. VON BEHRING, and R. HUMMEL (Naturwiss., 1930, 18, 156).—Cholesterol is eliminated mainly in the faeces as dihydrocholesterol and coprosterol. The determination of the proportion of hydrogenated sterol to cholesterol is based on the fact that cholesterol dibromide, in contrast with the dihydro-isomerides, does not give a precipitate with digitonin. Experiments carried out *in vitro* on

cholesterol and cholesterol-rich organs under widely different conditions of putrefaction provided no evidence of bacterial hydrogenation. It was, however, observed that cholesterol preparations, from whatever organ obtained, showed a definite but small (1—6%) proportion of hydrogenated sterol. A sample from gall-stones contained 1% of dihydrocholesterol, but coprosterol has not been isolated from organs. A hydrogenated sterol is secreted in the intestine.

R. A. MORTON.

**Lecithin.** II. G. ROSENFELD (Biochem. Z., 1930, 218, 48—53).—Lecithin can be synthesised by the animal body providing fatty acids and phosphorus are available, the choline being formed from most proteins but more particularly from substances containing glycine.

P. W. CLUTTERBUCK.

**Normal and alimentary blood-alcohol during exercise.** II. U. CASSINIS and L. BRACALONI (Atti R. Accad. Lincei, 1929, [vi], 10, 382—388).—During fasting or alimentary glycaemia, the blood-alcohol curve is not modified by muscular work. During walking or rowing the alimentary blood-alcohol curve caused by ingestion of a single dose of alcohol remains constantly at a lower level than the curve obtained during resting, whilst as a result of running this curve falls suddenly. With ingestion of the alcohol in several doses, the alcohol curve during walking rises less rapidly and reaches a lower height than during resting; rowing produces no important modifications of the curve. The total quantity of alcohol eliminated by the kidneys during 1—2 hrs. is only a small fraction of the alcohol administered, in spite of the increased secretion of urine.

T. H. PORE.

**Variations in sugar of blood and urine after ingestion of galactose.** V. J. HARDING and F. H. VAN NOSTRAND (J. Biol. Chem., 1930, 85, 765—778).—Ingestion of 20—50 g. of galactose in normal human subjects is invariably followed by some excretion of galactose in the urine; in some cases an increase in the non-fermentable sugar of the blood was also observed and in these the urinary excretion of galactose was considerably greater. No renal threshold for galactose appears to exist. The possibility of a rapid conversion of galactose into dextrose in the organism is suggested by the hyperglycaemia which was occasionally observed to follow ingestion of galactose.

C. R. HARRINGTON.

**Rôle of succinic acid in biology.** L. VAUDIN (J. Pharm. Chim., 1930, [viii], 11, 197—199).—A recapitulation of results already published (A., 1897, ii, 425).

C. W. SHOPPEE.

**Succinic acid in muscle.** III. Glutamic and aspartic acids as precursors. D. M. NEEDHAM (Biochem. J., 1930, 24, 208—227).—When glutamic and aspartic acids, or aspartic acid alone, are added to minced muscle under anaërobic conditions, malic, fumaric, and succinic acids are formed. The addition of glutamic acid gives rise to succinic acid only. There is no increase of ammonia, urea, uric acid, or amide-nitrogen nor is there a change in the total amino-nitrogen of the mixtures, when succinic, fumaric, and malic acids are thus produced. An increased oxygen uptake corresponding with one half or two thirds of the calculated amount for complete oxidation is found

when glutamic or aspartic acid is added to minced muscle. On the other hand, the addition of glycine, alanine, valine, leucine, or tyrosine has an inhibitory effect on the muscle's own respiration. Under aerobic conditions traces of malic and fumaric acids are found on addition of glutamic and aspartic acids. There is no change in the soluble nitrogen fractions. After incubation of aspartic acid with muscle in air or oxygen one half to two thirds of the acid, determined by converting it into malic acid, disappears. S. S. ZILVA.

**Oxygen consumption of the heart in varying, approximately isotonic, work.** L. BAUER (Z. Biol., 1930, 89, 513—522).—Using the method of Eismayer and Quincke (A., 1928, 1397), it is shown that the amount of oxygen used for each contraction of the heart does not increase proportionately with increase in pressure, and therefore in work done, but bears a linear relationship to the initial volume before contraction. K. V. THIMANN.

**Oxygen consumption, carbon dioxide and lactic acid production of the heart under various conditions of work.** G. EISMAYER and H. QUINCKE (Z. Biol., 1930, 89, 523—535).—The oxygen consumption and carbon dioxide production are different in isotonic from those in isometric beating, and also vary, although not directly, with the pressure and with the frequency of the beat, reaching an optimum in the latter case. It is concluded that the time during which the corpuscles remain in metabolic contact with the surface largely determines the oxygen consumption. The oxygen consumption decreases with time, owing to exhaustion of reserve sugar, and it is greater at higher pressure because less lactic acid is produced. K. V. THIMANN.

**Respiration of frog muscle in presence of sugar and hormones.** P. ROTHSCHILD (Biochem. Z., 1930, 217, 365—367).—Addition of 0.2% of dextrose or levulose to muscle of freshly-caught autumn frogs in phosphate solution increases the oxygen consumption by 30—60%. With summer frogs no increase takes place. Insulin, adrenaline, and thyroxine are without effect at  $p_H$  6, 7, or 8, whether in phosphate or in potassium chloride, thus confirming the results of Paasch and Reinwein (A., 1929, 1343), but not those of Ahlgren (Skand. Arch. Physiol., 1926, 47, 271). K. V. THIMANN.

**Muscular contraction.** H. H. WEBER (Biochem. Z., 1930, 217, 430—432).—The theory of Meyer (this vol., 104) assumes complete combination between the myogen of muscle and hydroxyl ions at  $p_H$  7.4. The actual amount of combination is from 5 to 33%, and the contraction deduced from the theory cannot therefore agree with that observed. K. V. THIMANN.

**Muscular contraction.** K. H. MEYER (Biochem. Z., 1930, 217, 433—435).—A reply to Weber (preceding abstract). Combination is complete at  $p_H$  7.4, but it only involves the protein in the contracted portion of the muscle and not that of the whole muscle. K. V. THIMANN.

**Physiological significance of muscle creatine-phosphoric acid.** G. MARTINO (Arch. Farm. speriment., 1929, 50, 31—42).—An interpretation of the formation and behaviour of creatinephosphoric acid ("phosphagen" of Eggleton and Eggleton; A., 1927,

271, 274, 990) is offered. A general explanation of differences in results of direct and indirect faradic stimulation of muscle is given. F. O. HOWITT.

**Significance of adenylic acid for muscle function. VI. Origin of muscle-ammonia.** G. EMBDEN and G. SCHMIDT (Z. physiol. Chem., 1930, 186, 205—211; cf. A., 1929, 346).—The enzymes of fresh frog's muscle were destroyed by acid treatment and the muscle was exposed to an enzyme capable of deaminating only muscle-adenylic acid. The ammonia eliminated by this procedure corresponds with that obtained by exposing the minced muscle for 3—4 hrs. in a slightly alkaline solution. Thus it is shown that the ammonia formed in a short autolysis of frog's muscle is derived exclusively from muscle-adenylic acid. J. H. BIRKINSHAW.

**Influence of training on the mineral substance of muscle.** S. W. FOMIN (Biochem. Z., 1930, 217, 423—429).—The difference in potassium content between trained and untrained muscle (biceps femoris) of the dog depends on the lapse of time between the last training and removal of the muscle. If removed 20 hrs. after, the potassium content is 13% lower than the normal; it reaches a maximum of 25% higher than the normal when removed 3 days after the last training. After 6 days it approximates to the normal value. K. V. THIMANN.

**Protein removal with mercury in neutral or alkaline solution.** K. HINSBERG and D. LASZLO (Biochem. Z., 1930, 217, 354—358).—To avoid acid hydrolysis and consequent destruction of the acid-labile organic phosphates of muscle, mercuric chloride is added in presence of sodium acetate and chloride, the solution neutralised with borax, and the precipitated protein filtered off. High orthophosphate and low phosphagen values were at first obtained, but after keeping 24 hrs. the correct orthophosphate values are approached and catalytic decomposition of the phosphagen is therefore improbable. K. V. THIMANN.

**Ammonia formation in the kidney.** A. BORNSTEIN and G. BUDELMANN (Biochem. Z., 1930, 218, 64—72).—The mean ammonia formation of Starling's surviving kidney preparation of starving dogs is 0.189 mg. of ammonia per g. of kidney per hr. Ammonia formation from glycine occurs both with the surviving kidney and with the kidney of the partly eviscerated dog, the increase of blood-ammonia calculated in respect to the weight of the organ being of the same order as that of the liver. P. W. CLUTTERBUCK.

**Ammonia formation in the retina.** H. RÖSCH (Z. physiol. Chem., 1930, 186, 237—259; cf. A., 1928, 792).—The effect of illumination on ammonia formation in the retina of the opened eyes of frogs kept in the dark is least in spring and early summer, but is much increased at this period if the frogs previous to death are exposed to diffused daylight. The same effect was observed with living frogs even in June, the period of greatest reversibility. The normal ammonia content of the retina of frogs kept in diffused light is always greater than for those kept in darkness. In autumn the effect was produced with reduced illumination, but reversibility could not be shown in the isolated eye.

A quartz lamp produced the same effect as the metal-filament lamp originally used; ultra-violet rays, 365–366 m $\mu$ , were inactive. Hard X-rays were much less efficient than soft rays. Minced retina deaminates muscle-adenosinephosphoric acid and particularly adenosine, adenine is scarcely attacked, and yeast-adenosinephosphoric acid only slightly.

J. H. BIRKINSHAW.

**Creatine and creatinine. II. Influence of organ extracts, bacteria, and  $p_{H}$  on creatine and creatinine. III. Amount of creatine and creatinine in pathological tissues of female genital organs. IV. Fate of creatine and creatinine in the incubated hen's egg.** N. SATO (Sei-i-kwai Med. J., 1929, 48, No. 8, Abstr. 12, 12–13, 13).—II. Creatine or creatinine is not destroyed in 72 hrs. at 37° by *Bacillus coli communis* or extracts of organs, muscles, or the digestive tract; at  $p_{H}$  7.3 creatine is unaffected, whilst at  $p_{H}$  5.3, 6.0, 7.1, and 7.7 it is partly converted into creatinine.

III. Placental tissue contains more creatine than the umbilical cord; ovary and ovarian cyst differed little. The body of the uterus contained more than the neck, the latter value being similar to that in carcinoma. Creatine values were higher in a myoma of the uterus than in the uterus itself.

IV. The newly laid hen's egg contains a small quantity of creatinine and traces of creatine. Increases during incubation were followed.

#### CHEMICAL ABSTRACTS.

**Benzoylated amino-acids in the animal organism. V. Synthesis of glycine and of hippuric acid in rats.** W. H. GRIFFITH (J. Biol. Chem., 1930, 85, 751–758).—In the experiments previously described (A., 1929, 843) poor growth was obtained owing to deficiency of vitamin-B. Increased supply of this vitamin resulted in increase in the intake of food and in growth. The tolerance for sodium benzoate was not much raised, however, and under the best conditions not more than 5% of the nitrogen ingested was excreted as hippuric acid. The previous conclusion, that the ability of the rat to synthesise glycine is limited, is therefore confirmed.

C. R. HARRINGTON.

**Protein metabolism of children on diets extremely low in carbohydrates.** I. McQUARRIE and R. T. SHEAHAN (J. Nutrition, 1929, 2, 31–47).—The protein allowance normally employed is too low. Ketosis, by taxing the protein molecule for its ketolytic fraction, is chiefly responsible for the excessive demand on the protein. When the diet contains sufficient base to neutralise the acid produced by its acid-forming constituents the rate of excretion of nitrogen is decreased. The epileptic convulsion itself exerts little direct influence on the total urinary nitrogen.

#### CHEMICAL ABSTRACTS.

**New function of lymphocytes in the intestinal wall, especially in the intestinal follicles.** R. OHNO (Biochem. Z., 1930, 218, 206–246).—In men and animals, an enormous number of leucocytes (chiefly lymphocytes) migrate through the intestinal wall into the intestinal canal, especially after food. These are in a state of degeneration. The lymphocytes in the lymphatic glands and in the intestinal follicles can activate powerfully the digestion of protein, starch,

and fat by pancreatic juice and can assist the action of bile and enterokinase. The process is of considerable importance in intestinal digestion.

P. W. CLUTTERBUCK.

**Digestibility of crude fibre by hens.** H. T. HENNING (Landw. Versuchs-Stat., 1929, 108, 253–286).—The relative digestibility of the crude fibre of fresh cabbage is more than double that of cereals. The amounts utilised by hens are sufficient to justify the inclusion of crude fibre in calculations of the nutrient value of foodstuffs. The crude fibre of barley is as little digestible as filter-paper. Comminution of cereals has no influence on the digestibility of their crude fibre. The digestibility of the crude fibre of cabbage is considerably reduced by cooking and that of peas entirely destroyed. A second feeding of ejected fibre shows that maximum digestion occurs during a single passage through the digestive organs. The digestion of crude fibre takes place almost exclusively in the cæcum.

A. G. POLLARD.

**Utilisation of calcium by the growing chick.** F. E. MUSSEHL, R. S. HILL, M. J. BLISH, and C. W. ACKERSON (J. Agric. Res., 1930, 40, 191–199).—Growing chickens can adjust themselves to wide ranges of acidity and alkalinity in the diet when vitamin-D and ultra-violet radiation are provided. This toleration extends beyond likely variations in ordinary rations. In experiments calcium was more effectively furnished as calcium phosphate than as the carbonate, lactate, sulphate, or chloride. Addition of 0.5% of magnesium to the diet had little influence on growth, but magnesium carbonate caused rickets.

E. HOLMES.

**Iodine metabolism of milch goats.** S. WEISER and A. ZAITSCHEK (Biochem. Z., 1930, 217, 359–364).—Potassium iodide (38 mg.) was added to the daily diet of healthy goats and the iodine determined in the urine, faeces, and milk daily for 8 days, corrections being made for the iodine absorbed in the food and water; 18–30% of the iodine was found in the milk and 31–42% retained in the animal. The animals were in equilibrium as regards nitrogen, and considerable retrogression of the thyroid was the only observable change.

K. V. THIMANN.

**Effect of ozone on guinea-pigs.** H. B. McDONNELL (J. Assoc. Off. Agric. Chem., 1930, 13, 19–34).—The presence of about 1 mg. of ozone per litre of air considerably shortens the life of normal and tuberculous guinea-pigs, largely by inducing pneumonia.

K. V. THIMANN.

**Effect of certain drugs on the oxidation processes of mammalian nerve-tissue.** M. A. F. SHERIF (J. Pharm. Exp. Ther., 1930, 38, 11–29).—The effect of certain local anaesthetics and other compounds on the oxygen consumption of nerve-tissue has been examined. Cocaine hydrochloride, novocaine borate, and urethane decrease the rate of oxygen consumption, the first-named being the most and the last the least active. Caffeine citrate increases oxidation at concentrations less than 0.5%, but above this concentration oxidation is decreased. The decrease of oxygen consumption within 3 hrs. is prevented by the presence of galactose but not by dextrose.

W. O. KERMACK.

**Ionic changes and the oxygen consumption of the frog's auricle.** A. J. CLARK and A. C. WHITE (J. Physiol., 1930, 68, 433—440).—Ethyl urethane, acid, excess of potassium, or lack of calcium decreased the oxygen consumption and energy production in proportionate amounts. E. BOYLAND.

**Effect of irradiation on oxidation. Effect of X-rays on the carbon and oxidation quotients of urine.** H. KUBO (Strahlenther., 1929, 33, 70—88; Chem. Zentr., 1929, ii, 1938).—On irradiation of rabbits with X-rays the quotients are similarly affected (depression, followed by a gradual rise to normal) but not to exactly the same degree. There is a difference between the effect of X-rays and that of ultra-violet light, radiothorium, or radium bromide.

A. A. ELDRIDGE.

**Hyperthermia induced by high-frequency electric current.** F. BISCHOFF, H. J. ULLMANN, E. HILL, and M. L. LONG (J. Biol. Chem., 1930, 85, 675—686).—Hyperthermia of relatively slow onset (0.01—0.015° rise in the oral temperature per min.) was induced by high-frequency electric current. The main effect observed was a rise in the  $p_H$  of the blood due to loss of carbon dioxide; as a result a larger proportion of the total base was bound by the proteins, and the venous blood remained more fully oxygenated than under normal conditions. In some cases the inorganic phosphorus of the blood, and to a still greater extent that of the urine, was diminished. The results are similar to those obtained by other workers following the external application of heat to the body.

C. R. HARINGTON.

**Mechanism of ammonium chloride acidosis.** A. FÖLLING (Acta med. Scand., 1929, 71, 221—279; Chem. Zentr., 1929, ii, 2339).—On administration of ammonium chloride the  $p_H$  of arterial blood falls from 7.22 to 7.16, since the ammonia is converted into urea. Neutralisation is effected by sodium hydrogen carbonate. Urinary excretion takes place chiefly (80—90%) as ammonium chloride. Production of ammonia takes place in the kidneys; the ammonium content of the blood remains constant.

A. A. ELDRIDGE.

**Lowering of viscosity of water, blood-serum *in vitro*, and blood *in vivo* by certain anions.** I. SIMON (Arch. Farm. sperim., 1929, 50, 64—66).—Anions such as chlorides, bromides, and iodides lower the viscosity of distilled water, blood-serum *in vitro*, and, in the living animal, that of the blood. High concentrations tend to have the opposite effect.

F. O. HOWITT.

**Effect of sodium salicylate on the viscosity of blood in the living animal.** L. SALAZAR (Arch. Farm. sperim., 1929, 50, 67—71).—Small amounts of sodium salicylate lower the viscosity of water and of blood-serum. Subcutaneous administration in dogs of aqueous solutions lowers the viscosity of the blood.

F. O. HOWITT.

**Distribution of matter between the cell and its surroundings.** G. WATZADSE (Pflüger's Archiv, 1929, 222, 640—648; Chem. Zentr., 1929, ii, 2053).—Many substances to which cells are permeable despite low solubility in ether are markedly soluble in olive oil and other physiological solvents, hence supporting the lipid theory of distribution. Adsorption

experiments with organic non-electrolytes show, however, that the chemical nature of the interface plays a more important part in the elucidation of physiological distribution processes than the original lipid- and adsorption-theories admit.

A. A. ELDRIDGE.

**Gas-liquid surface tension and liquid-liquid interfacial tension. Theories of narcosis and permeability.** J. TRAUBE, L. J. WEBER, and C. GUIRINI (Biochem. Z., 1930, 217, 400—404).—The surface tension of aqueous solutions of a series of organic substances of increasing mol. wt. from acetonitrile to *isoamyl* alcohol has been determined by the stalagmometric method. The surface tension aqueous solution-air decreases with increasing mol. wt., parallel with the interfacial tensions aqueous solution-paraffin and aqueous solution-oleic acid. The significance of this relationship for the permeability theory of cell narcosis is discussed.

K. V. THIMANN.

**Polarity of the molecule, interfacial activity, and the theory of narcosis.** N. V. LAZAREV, J. N. LAVROV, and A. P. MATVEJEV (Biochem. Z., 1930, 217, 454—464).—Stalagmometric measurements were made of the effect of narcotic substances on the interfacial tension water-benzene and water-olive oil. Hydrocarbons, saturated chloro-substitution compounds, and ethyl ether have no effect, whilst alcohols and fatty acids considerably lower the tension. Surface activity is not, therefore, a general property of the simple narcotic substances, but depends on the polar activity of the molecule.

K. V. THIMANN.

**Influence of calcium and potassium on the effect of narcotics.** M. OGAWA (Folia pharmacol. japon., 1928, 8, 1—11).—Administration of an almost inactive dose of calcium into mice decreases the action of chloral hydrate, urethane, paraldehyde, or sodium luminal on mice, whilst a non-injurious dose of potassium has no noteworthy influence.

CHEMICAL ABSTRACTS.

**Accelerated production of specific urinary pigments by drug administration. I. Effect of phenyldimethylpyrazolone on urobilin formation.** F. G. GERMUTH (J. Amer. Pharm. Assoc., 1930, 19, 132—135).—Continued employment of phenyldimethylpyrazolone (1 g. per day) over a period of 10 days promotes the disintegration of erythrocytes, which results in the appearance of an increased amount of urobilin in the urine. In normal urine the average of 10 samples was 43 mg. per litre and in pathological samples, 112 mg. per litre.

E. H. SHARPLES.

**Does antipyrin change the composition of serum-protein?** E. OHLSSON (Arch. exp. Path. Pharm., 1930, 148, 164—172).—The administration of antipyrin to rabbits or dogs does not significantly alter the albumin-globulin ratio of the serum.

W. O. KERMACK.

**Liberation of formaldehyde in the aqueous humour of the eye after administration of hexamethylenetetramine.** M. A. F. SHERIF (J. Pharm. Exp. Ther., 1930, 38, 231—239).—Both the aqueous humour of the eye and the cerebrospinal fluid were studied, rabbits being the experimental animals and formaldehyde being detected by the phloroglucinol reagent. Determinations of  $p_H$  were made simul-

taneously with the formaldehyde test. The aqueous humour shows a rapid change in  $p_H$  on exposure to air or by injection of sodium dihydrogen phosphate. Injection of hexamethylenetetramine alone does not give rise to formaldehyde, and the limiting factor is the  $p_H$  value, which is varied by the amount of acid sodium phosphate injected. With a constant dose of hexamethylenetetramine, no formaldehyde is produced if the amount of acid phosphate given is less than 0.25 g. per kg.

P. G. MARSHALL.

**Effect of quinine on blood-sugar.** T. IMAHAST (Okayama Ig. Zasshi, 1928, 40, 2291—2302).—Quinine is hypoglycaemic (rabbit, dog) in doses of 10—50 mg. per kg., and hyperglycaemic in larger doses. Small doses of quinine suppress the hyperglycaemia of adrenaline, diuretin, dextrose (intravenous), and pancreas extirpation and increase insulin hypoglycaemia.

CHEMICAL ABSTRACTS.

**Action of quinine on blood-catalase.** A. SABATINI (Arch. Farm. sperim., 1929, 50, 72—97).—Catalase activity in blood taken from young rabbits with and without subcutaneous injection of quinine dihydrochloride is followed manometrically. No profound modification of activity is shown. Variations of alkaloid concentration have no influence on the final catalase value. These findings are somewhat contrary to those of Laqueur (A., 1906, ii, 870).

F. O. HOWITT.

**Determination of strychnine in biological material.** J. T. PRIESTLEY (J. Pharm. Exp. Ther., 1930, 38, 241—246).—Blood, diluted with 4 vols. of distilled water, is kept for 10 min., and 0.1 c.c. of 10% acetic acid added for each 25 c.c.; after heating at 100° for 10 min. it is centrifuged and an aliquot portion evaporated with warm air. The residue is transferred with hot distilled water (just acidified with 0.1N-sulphuric acid) to a centrifuge tube; after centrifuging, the strychnine is present in the clear supernatant fluid. The effect of injection of an aliquot portion of this into the dorsal lymph sac of a frog is compared with that produced by a known amount of strychnine. The average error of the method, which by suitable modification of the preliminary stages can be applied to liver and muscle, is 10%.

P. G. MARSHALL.

**Ergotamine.** I. **Effect of ergotamine on the blood-sugar and adrenaline hyperglycaemia in trained unanæsthetised dogs.** J. B. YOUNG and W. H. TREMBLE (J. Pharm. Exp. Ther., 1930, 38, 121—132).—The intravenous administration to trained unanæsthetised dogs of ergotamine tartrate in doses up to 0.5 mg. per animal did not alter the blood-sugar level in a constant direction nor did it prevent the rise in blood-sugar following administration of adrenaline.

W. O. KERMACK.

**Jesaconitine.** A. BERNI (Arch. Farm. sperim., 1930, 50, 110—124).—The reactions of jesaconitine (m. p. 101—102°) with alkaloid reagents are given. The pharmacological behaviour, which is similar to that of the two japaconitines (Benigni, Arch. intern. Pharm. Ther., 1930), is described. F. O. HOWITT.

**Pharmacological properties of  $\beta$ -naphthoquinoline and some of its derivatives.** B. KINDT and H. VOLLMER (Arch. exp. Path. Pharm., 1930,

148, 198—210).—The pharmacological actions of the following compounds have been investigated in frogs, guinea-pigs, and rabbits:  $\beta$ -naphthoquinoline, its mono- and di-nitro- and -amino- and nitroamino-derivatives and  $p$ -phenanthroline. These compounds exhibit central paralytic action and other toxic effects. The following have been prepared: *amino- $\beta$ -naphthoquinoline*, m. p. 173° (by reduction of nitro- $\beta$ -naphthoquinoline with stannous chloride and hydrochloric acid); *nitroamino- $\beta$ -naphthoquinoline*, m. p. 249° (from dinitro- $\beta$ -naphthoquinoline by partial reduction with sodium hyposulphite); *diamino- $\beta$ -naphthoquinoline*, m. p. 249° (from dinitro- $\beta$ -naphthoquinoline by reduction with stannous chloride and hydrochloric acid); by methylation of amino- $\beta$ -naphthoquinoline, *dimethylamino- $\beta$ -naphthoquinoline* was obtained as the *hydrochloride*, which decomposed above 200°.

W. O. KERMACK.

**Absorption of the ethyl ester of 6-methylphenylcinchoninic acid (tolysin) and its fate in metabolism.** I. **Absorption of tolysin from the intestinal tract.** II. **Fate of tolysin in metabolism and its toxicity.** O. FÜRTH and E. KUHN (J. Pharm. Exp. Ther., 1930, 38, 57—69, 71—84).—I. Methods are described for the determination of cinchophen (2-phenylquinoline-4-carboxylic acid) and of tolysin (ethyl 2-phenyl-6-methylquinoline-4-carboxylate) in intestinal contents. The absorption of these compounds administered by mouth to rabbits, dogs, or men is in all cases considerable, and in the case of man is approximately 100%.

II. Experiments which have been made on the antipyretic and toxic action of cinchophen and tolysin show that the latter compound is rapidly absorbed from the intestine, although only slowly from the subcutaneous tissues. From the urine of rabbits to which tolysin was administered, an *acid*,  $C_{17}H_{13}O_4N$ , decomp. 292—297°, has been isolated, which is apparently a dihydroxy-derivative of 2-phenyl-6-methylquinoline-4-carboxylic acid.

W. O. KERMACK.

**Paralysis- and convulsion-causing poisons in *Sinomenium acutum*, Rehd. and Wiels.** K. ISHIKAWA (Fukuoda Ik. Zasshi, 1928, 21, 2121—2161).—The active constituent is an amorphous substance having a paralytic effect. An *alkaloid*,  $C_{36}H_{45}O_8N$  or  $C_{36}H_{45}O_9N$ , caused convulsions. Of two other substances prepared one caused maximal pupillary dilation in the frog and the other produced clonic convulsions.

CHEMICAL ABSTRACTS.

**Differential analysis of heart poisons.** VII. **Calcium and strontium paradox.** VIII. **Action of bivalent cations on the contractility of the frog ventricle.** B. KISCH (Arch. exp. Path. Pharm., 1930, 148, 140—149, 150—163).—VII. A frog's heart which has been kept for a considerable time on a calcium-free Ringer solution is first inhibited when perfused with a solution poor in potassium, and then begins to beat at its normal rate. Other similar anomalous effects are also described.

VIII. The contractility of the ventricle of the frog's heart is increased by bivalent cations in the order  $Mg < Sr < Ca < Ba$ . The presence of potassium or of sodium antagonises the effect of the bivalent cations.

W. O. KERMACK.

**Effect of arsenic on gas metabolism of insects.**

J. A. PARFENTJEV and W. DEVRIENT (Biochem. Z., 1930, **217**, 368—377).—Injection of the minimal lethal dose of arsenic trioxide into the cockroach *Periplaneta americana* does not greatly lower the oxygen consumption, and the respiratory quotient is raised by about 10%. After death from potassium cyanide poisoning or by mechanical killing the gas metabolism continues almost unchanged for several hours.

K. V. THIMANN.

**Cobalt as vaso-dilator.**

J. M. LE GOFF (J. Pharm. Exp. Ther., 1930, **38**, 1—8).—Injection of 0.04—0.05 g. of cobalt chloride produces marked vasodilatation with marked redness of the face and fall in blood-pressure.

W. O. KERMAK.

**Effect of hydrochloric acid on the fluctuations of phosphorus and calcium metabolism in experimental lead poisoning.** A. CARNI and E. ISRAÏLEVIE (Trudy mat. Ukrain. gosud. Inst. pat., 1928, **6**, 237—249).—With dogs the blood-calcium was raised and in certain periods the elimination of calcium was increased; the hydrochloric acid has a therapeutic effect.

CHEMICAL ABSTRACTS.

**Effect of hydrochloric acid on the variation of the intermediary nitrogen metabolism in experimental lead poisoning.** F. M. SUPONITZKA (Trudy mat. Ukrain. gosud. Inst. pat., 1928, **6**, 250—261).—In dogs with lead poisoning the blood-nitrogen showed intermediate changes although the total nitrogen was unchanged. The increase in urea was diminished by administration of hydrochloric acid.

CHEMICAL ABSTRACTS.

**Toxicity of lead compounds.**

J. S. BUCK and D. M. KUMRO (J. Pharm. Exp. Ther., 1930, **38**, 161—172).—The toxicity of six groups of lead compounds has been tested by intravenous and intraperitoneal injection in rats, the types of compound varying from ionised bivalent lead compounds to non-ionised compounds containing quadrivalent lead in organic combination. The lead trialkyl salts are extremely toxic, as are most of the lead tetra-alkyl compounds with the exception of lead tetramethyl. Lead trimethyl chloride and its homologues produce a watery discharge from the eyes and nose together with retarded respiration, the effect increasing with the larger radical. Lead nitrate is tolerated in doses of 330 mg. per kg. for several weeks when injected subcutaneously, but it produces parenchymatous nephritis. Lead tetramethyl produces a lowering of temperature with few cerebral symptoms as a result of intraperitoneal injection in olive oil solution, and its minimum lethal dose is 70—100 mg. per kg. Stippling cannot be used as a criterion of "plumbism" in rats, and urobilin tests are of doubtful value.

P. G. MARSHALL.

**Biochemistry of mercury compounds. I. Effect of acids, bases, salts, and blood-serum on diffusion of mercury compounds *in vitro*.**

F. H. L. TAYLOR and A. G. YOUNG (J. Pharm. Exp. Ther., 1930, **38**, 217—229).—Collodion membranes were used for dialysis of mercury compounds in 0.01N-hydrochloric acid or sodium hydroxide; 10% solutions of potassium iodide, calcium chloride, and ammonium chloride were also used as diffusion media, controls being made in each case with distilled water.

The compounds tested were mercuric and mercurous chlorides, potassium mercury tetraiodide, mercuric succinimide, "mercurochrome," "novasurol," and "salyrgan." Increase of  $c_H$  produced an increased diffusion of inorganic mercury salts except potassium mercury tetraiodide, but excess of hydroxyl ions had no effect. Excess of alkali increased the diffusion of the organic compounds to a greater extent than acid. Potassium iodide greatly increased the diffusion of both types of compound. Calcium chloride exerted an effect analogous to, although less than, hydrochloric acid. Ammonium chloride affected inorganic salts and "mercurochrome" similarly to hydrochloric acid, but on "novasurol" and "salyrgan" its effect resembled that of potassium iodide. Metallic mercury did not diffuse into the electrolytes used, with the exception of potassium iodide, but horse serum was found to contain 11.20 mg. per 100 c.c. after 48 hrs. dialysis. Only traces of the organic compounds diffused into horse serum, and mercuric succinimide occupied an intermediate position between organic and inorganic compounds.

P. G. MARSHALL.

**Chemical nature of enzymes.**

E. R. MILLER (Science, 1929, **70**, 356—357).—An aqueous extract from a mushroom showed enzymic activity towards 3:4-dihydroxyphenylalanine. Tyrosinase is not colloidal and this appears to invalidate a general application of Willstätter's conception.

L. S. THEOBALD.

**Blood-catalase.** N. SHINDOH (Okayama Ig. Zasshi, 1928, **40**, 230—250).—Determinations of the blood-catalase and the catalase index in various pathological conditions have been made.

CHEMICAL ABSTRACTS.

**Determination of catalase in plant material.**

H. VON EULER, K. MYRBÄCK, and S. MYRBÄCK (Z. physiol. Chem., 1930, **186**, 212—222).—The catalase present in aqueous extracts or suspensions of barley shoots undergoes rapid destruction on keeping. Inhibitors do not seem to be present. The optimum  $p_H$  for catalase action is 7—8. The reaction constant is independent of substrate concentration. The greater part of the catalase is present in the top of the shoot, the amount reaching a maximum after 6—8 days' germination.

J. H. BIRKINSHAW.

**Dehydrogenation processes in muscle.**

A. HAHN and W. HAARMANN (Z. Biol., 1930, **89**, 563—572).—Dehydrogenation of lactic acid to pyruvic acid occurs in muscle without the necessity for the addition of a hydrogen acceptor (A., 1929, 1489), to the extent of 50—60% of that produced with methylene-blue as hydrogen acceptor. More than 25% of the lactic acid originally in the muscle may be so converted. Malic, fumaric, and citric acids are also dehydrogenated as shown by the production of carbon dioxide on digestion with muscle in a vacuum. It is concluded that muscular tissue contains unknown substances which act as hydrogen acceptors.

K. V. THIMANN.

**Liver dehydrogenase. XXII. Mechanism of oxidative processes.** H. WIELAND and K. FRAGE (Z. physiol. Chem., 1930, **186**, 195—204).—The oxidising power of liver enzymes on alcohol and acetaldehyde was studied. The auto-respiration of



minced liver does not diminish on keeping, but the power of alcohol oxidation falls to about one half in 3 days. The carbon dioxide evolution is completed in the first half hour with alcohol and sodium acetate, but continues in presence of acetaldehyde, which also produces the greatest oxygen uptake. Greater auto-respiration is shown by the washed tissue than by the untreated tissue or the aqueous extract. In presence of alcohol and acetaldehyde the greatest activity is shown by the untreated tissue. An active enzyme preparation was obtained from the extract by treatment with acetone, also by extracting minced tissue with 0.067*M*-phosphate buffer of  $p_H$  6.2. Methylene-blue acts as hydrogen acceptor; when the enzyme system loses its power of accelerating aldehyde oxidation, methylene-blue is no longer decolorised.

J. H. BIRKINSHAW.

**Effect of lipins, particularly of phospholipin, on the action of enzymes.** Y. SUEYOSHI and K. AOKI (Sei-i-kwai Med. J., 1929, 48, No. 8, Abstr. 13—14).—Colloidal lecithin, cholesterol, or olein inhibited the action of amylase, protease, and lipase.

CHEMICAL ABSTRACTS.

**Specificity and mechanism of action of the sugar-splitting enzymes.** R. WEIDENHAGEN (Fermentforsch., 1930, 11, 155—163).—The hypothesis is advanced that the hydrolytic action of enzymes on the polysaccharides and glucosides is decided by the nature of the linkings in the component monosaccharides.  $\alpha$ -Dextrose, whether linked with another hexose or with an aglucone, is always hydrolysed by  $\alpha$ -glucosidase. Thus sucrose is split by  $\alpha$ -glucosidase or  $\beta$ -*h*-fructosidase. Melezitose is completely hydrolysed by  $\alpha$ -glucosidase, raffinose requires  $\alpha$ -glucosidase and  $\beta$ -*h*-fructosidase.

J. H. BIRKINSHAW.

**Use of the Zeiss immersion refractometer for measurement of invertase action.** G. GORBACH (Biochem. Z., 1930, 217, 440—453).—The hydrolysis of sucrose can be followed with the immersion refractometer, but with somewhat less precision than with the polarimeter. As only three scale divisions are involved, the method is not suitable for enzyme purification experiments, but it is very rapid in use. Enzymes present in very small amount can be determined by the use of the supplementary prism. The reaction velocity shown by the instrument is modified by the presence of dextrose and of substances associated with the enzyme in the tissue.

K. V. THIMANN.

**Effect of ethylene on the activity of diastase and invertase.** D. T. ENGLIS and C. D. ZANNIS (J. Amer. Chem. Soc., 1930, 52, 797—802).—Ethylene has no influence on the hydrolysis of soluble starch by taka-diastase or by diastase from alfalfa meal, or on the hydrolysis of maize starch by diastase from maize meal. The inversion of sucrose by invertase is also unaffected by ethylene. The effect of ethylene in the ripening of fruits appears to be primarily concerned with colour change (cf. Chace and Church, B., 1927, 890).

H. BURTON.

**Isolation of methylglyoxal as intermediate substance in glycolysis.** M. VOGT (Klin. Woch., 1929, 8, 793—794; Chem. Zentr., 1929, ii, 2212—2213).—Isolation of methylglyoxal was effected by

employing minced kidneys and liver of the pig or rabbit (after extraction with alcohol and ether), and as substrate hexosediphosphate. A. A. ELDRIDGE.

**System of biological heavy metal reagents.** F. EICHHOLTZ (Arch. exp. Path. Pharm., 1930, 148, 369—376).—A list is given of a series of reagents which form complex salts with the heavy metals and so inhibit the catalytic actions and reduce or remove their toxic effects on the animal organism. By means of these reagents it is possible to determine which heavy metal is responsible for any particular catalysed reaction in a biological system. It has thus been shown that the glycolysis of carcinomatous tissue is brought about by copper, whilst the Pasteur reaction is catalysed by iron.

W. O. KERMAK.

**Asymmetric hydrolysis of esters by enzymes.** III. R. WILLSTÄTTER, R. KUHN, and E. BAMANN. **Influence of optically active, foreign substances on the configuration-specificity of the liver-esterase of various animals.** E. BAMANN and P. LAEVERENZ (Ber., 1930, 63, [B], 394—404; cf. A., 1928, 755; 1929, 957).—The sign of rotation of the mandelic acid obtained by the hydrolysis of ethyl *r*-mandelate by the esterase of pig's liver is found to be independent of the mode of preparation of the enzyme and of the temperature. Addition of strychnine, quinidine, quinine, brucine, codeine, or atoxyl under varied conditions does not influence the optical choice of the enzyme, although the rate of fission of the racemate is more or less considerably depressed. With the liver esterases of man and rabbit, addition of alkaloids to the enzyme or reaction solution changes the relationship of the proportions of the antipodic components of the racemate which enter into reaction; in many cases the influence is so pronounced that a change of sign is observed in the product. It is not essential that the phenomenon should be accompanied by an alteration in the rate of fission of the racemate, but acceleration or retardation is frequently observed.

H. WREN.

**Lipases. IV. Organ-lipases and their inhibition by poisons.** K. GYOTOKU. **V. Lipases and proteins.** VI. **Separation of lipase into two inactive constituents.** K. GYOTOKU and S. TERASHIMA (Biochem. Z., 1930, 217, 279—291, 292—305, 306—319).—IV. The sensitivity to atoxyl poisoning of serum- and liver-lipase, or stomach-lipase of the guinea-pig, is reduced or abolished on purification by Willstätter's method. The reason for the varying behaviour of these lipases is therefore to be sought for in the accompanying substances rather than in the enzyme itself, which is probably insensitive. When lipases of which the activity is normally inhibited by sodium fluoride are purified, their sensitivity to this poison is reduced; on the other hand, those which are not normally inhibited by sodium fluoride are rendered sensitive on purification. In this case it is considered that the lipase is sensitive to the poison, but the accompanying substances modify the sensitivity. The inhibition curves take the form of an adsorption isotherm and not of dissociation curves of a weak acid (cf. Rona and Haas, A., 1923, i, 1258). The sensitivity of various lipases to cocaine and strychnine is also reduced on purification.

V. Amylase, tryptase, and lipase show differences in behaviour with Chamberland filters. Amylase passes filters L1 and L2 completely, tryptase L1 and partly through L2, and lipase only partly through L1. This is held to indicate that lipase is bound to larger protein molecules than amylase. On the other hand, amylase is largely precipitated from serum, with the globulin, by 33% saturation with ammonium sulphate, whilst lipase is not precipitated until 60% saturation is reached. Serum-, pancreas-, and stomach-lipase extracts give the same results. At 40–50% saturation, when the proteins are separated into two fractions, the sum of the lipase contents of precipitate and filtrate is reduced by about one third. The same phenomenon occurs at slightly lower saturation with lipase of the stomach or pancreas of the dog.

VI. By the addition of quinine to a lipase preparation, two fractions are obtained, one of which is entirely inactive and the other only slightly active; on remixing the fractions in the same proportions the activity of the original lipase is immediately regained. There is no time factor in the return of activity and the relation between the fractions is therefore different from that between trypsinogen and enterokinase. Heat treatment of either fraction separately reduces the activity of the resultant mixture. The separated fractions keep better than the mixture, and after 40 days the activity rises again to a value in some cases higher than the original. The sensitivity or insensitivity to inhibition by quinine, atoxyl, or sodium fluoride is a specific property of the filtrate fraction, which is considered to be the true enzyme. The mixture of the filtrate fraction of one lipase with the precipitate fraction of another lipase shows the same  $pH$  optimum as of that from which the filtrate was derived. The authors therefore consider the precipitate fraction in the light of an activator.

K. V. THIMANN.

**Decomposition of oils by fat-decomposing enzymes.** K. EZOL (J. Exp. Digest. Dis., Japan, 1929, 28, 190–194).—Oils are decomposed by the splenic fat-decomposing enzyme in the following order of diminishing ease: olive, sesame, rape-seed, arachis, linseed, palm, whale, lard, castor, cod-liver, sardine, walnut, tripalmitin, silkworm-chrysalis. There is no definite relation between the quantity of fat decomposed and the iodine value (Wijs). If change in properties of the silkworm-chrysalis oil is prevented, the ease of decomposition approaches that of olive oil.

CHEMICAL ABSTRACTS.

**Natural activators and inhibitors of proteolytic enzymes.** W. GRASSMANN, H. DYCKERHOFF, and O. VON SCHOENEBECK (Z. physiol. Chem., 1930, 186, 183–194).—Cysteine activates papain, proteinase of yeast, and  $\beta$ -proteinase of kidney and inhibits the dipeptidase and polypeptidase of yeast; in these respects it resembles hydrogen sulphide and hydrocyanic acid. Pyrophosphate is inactive towards the proteinases of papaw, yeast, and kidney, and inhibits the action of yeast di- and poly-peptidase. Pancreas trypsin resembles the polypeptidases. It is only inhibited by small amounts of cysteine or pyrophosphate when insufficiently provided with enterokinase; cysteine on the other hand activates pancreas-trypsin in the same way as kinase. J. H. BIRKINSHAW.

**Digestion of edestin by pepsin in presence of quinine hydrochloride.** J. SMORODINCEV and K. GLAGOLEV (Russ. Z. trop. Med., 1928, 6, 293–295).—The digestion of edestin by pepsin was inhibited by quinine hydrochloride when the pepsin solution ( $pH$  1.54) was diluted with water, but not when hydrochloric acid was added.

CHEMICAL ABSTRACTS.

**Degradation of caseinogen by pancreatin and pancreatic juice, also by trypsin-kinase and erepsin.** E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1930, 11, 127–142).—The completeness of the digestion of solutions of caseinogen at varying concentrations with trypsin-kinase and erepsin was tested by a subsequent digestion with pancreatic juice or pancreatin. In every case there was considerable further hydrolysis. Erepsin following pancreatin also produces further hydrolysis, indicating that pancreatin contains insufficient amounts of erepsin. In all cases the amount of hydrolysis increased with decreasing concentrations of caseinogen. J. H. BIRKINSHAW.

**Influence of "foreign" components in polypeptides on their capability for hydrolysis by enzymes.** E. ABDERHALDEN and H. MAYER (Fermentforsch., 1930, 11, 143–154).—The following polypeptides were prepared: *glycyl-d-leucylglycine*, m. p. 215° (becomes brown); *phenylcarbamyl-d-leucylglycyl-l-leucine*, m. p. 125°; *d- $\alpha$ -bromoisohexoyl-glycyl-l-leucine*,  $[\alpha]_D^{20}$   $-54^\circ$ ; *d- $\alpha$ -bromoisohexoyl-glycyl-d-leucine*, m. p. 167° (corr.),  $[\alpha]_D^{20}$   $+53.2^\circ$ , giving *l-leucylglycyl-d-leucine*, m. p. 245° (corr.),  $[\alpha]_D^{20}$   $+26^\circ$ ; *chloroacetyl-l-leucylglycyl-d-leucine*, m. p. 104°, giving *glycyl-l-leucylglycyl-d-leucine*, m. p. 245° (corr.),  $[\alpha]_D^{20}$   $-15.8^\circ$ ; *l- $\alpha$ -bromoisohexoyl-glycyl-l-leucylglycyl-d-leucine*, m. p. 101°,  $[\alpha]_D^{20}$   $-21.4^\circ$ , giving *d-leucylglycyl-l-leucylglycyl-d-leucine*, m. p. 160° (frothing),  $[\alpha]_D^{20}$   $-12^\circ$ ; *d- $\alpha$ -bromoisohexoyl-glycyl-d-leucylglycyl-l-leucine*, m. p. 105°,  $[\alpha]_D^{20}$   $+20.8^\circ$ , giving *l-leucylglycyl-d-leucylglycyl-l-leucine*, m. p. 180° (frothing),  $[\alpha]_D^{20}$   $+17^\circ$ . Only *glycyl-l-leucylglycyl-d-leucine* was hydrolysed by erepsin. Trypsin-kinase hydrolysed *glycyl-d-leucylglycyl-l-leucine*, *l-leucylglycyl-d-leucylglycyl-l-leucine* and *phenylcarbamyl-d-leucylglycyl-l-leucine*. Enzymes which attack the tetrapeptide *glycyl-l-leucylglycyl-d-leucine* in no case hydrolyse the tripeptide *l-leucylglycyl-d-leucine*. Polypeptides are thus hydrolysed by trypsin-kinase when the component carries a carboxyl group which is an "unnatural" one. J. H. BIRKINSHAW.

**Behaviour of polypeptides containing thyroxine in their structure towards enzymes and examination of their biological behaviour.** E. ABDERHALDEN and E. SCHWAB (Fermentforsch., 1930, 11, 164–169).—The action of hydrolytic enzymes on the following peptides was examined: *dl-leucylthyroxine*, m. p. 215° (darkens and decomp.), prepared from *dl- $\alpha$ -bromoisohexoyl-dl-thyroxine*, m. p. 162° (decomp.); *N-methyl-dl-leucyl-dl-thyroxine*, m. p. above 150°; *di-dl-leucyl-dl-thyroxine*, m. p. 155–158° (decomp.). The bromoisohexoyl derivative was hydrolysed by trypsin-kinase, the leucyl derivative by erepsin and thyroid extract, but not by trypsin-kinase. The *N*-methyl-leucyl derivative was not hydrolysed by erepsin or trypsin-kinase. The dileucyl compound

was hydrolysed by pepsin hydrochloride and by gastric juice. This is the first example of fission of a peptide-like compound by pepsin hydrochloride.

J. H. BIRKINSHAW.

**Nature of enzyme actions carried out with enzymes of the polypeptidase group.** E. ABDERHALDEN and W. ZEISSET (Fermentforsch., 1930, **11**, 183—223).—The action of erepsin and trypsin-kinase on a number of polypeptides consisting of *dl*-norvaline in combination with glycine, *d*-alanine, and *dl*-norleucine and a few compounds of valine was examined. The enzymic hydrolysis was compared with that produced by *N*-sodium hydroxide. Erepsin quickly hydrolysed most of the polypeptides, although the rate varied with the preparation of the enzyme. This effect was also noted with trypsin-kinase. The action of an enzyme prepared by adsorption and elution from erepsin-free pancreas-trypsin on various  $\alpha$ -halogenoacyl derivatives of  $\alpha$ -amino-acids and polypeptides is tabulated. The following were prepared: *dl*- $\alpha$ -bromoisovaleryl-*dl*-norvaline, m. p. 128—129°, giving *dl*-valyl-*dl*-norvaline, m. p. 270—271° (decomp.); *dl*- $\alpha$ -bromo-*n*-valeryl-*dl*-valine, m. p. 162—164° (decomp.), giving *dl*-norvalyl-*dl*-valine, m. p. 265—267° (decomp.); *dl*- $\alpha$ -bromo-*n*-valeryl-*d*-alanine, m. p. 74—76°, decomp. 171—173°, giving *dl*-norvalyl-*d*-alanine, m. p. 220—223° (decomp.),  $[\alpha]_D^{25}$  -32.35°; *dl*- $\alpha$ -bromo-*n*-valerylglycine, m. p. 122°, giving *dl*-norvalylglycine, m. p. 229—232° (decomp.); *dl*- $\alpha$ -bromo-*n*-valerylglycylglycine, m. p. 135°, giving *dl*-norvalylglycylglycine, m. p. 225—227° (decomp.); chloroacetylglycyl-*dl*-norvaline, m. p. 154—155°, giving glycylglycyl-*dl*-norvaline, m. p. 227—230° (decomp.); *dl*- $\alpha$ -bromo-*n*-valerylglycyl-*dl*-norvaline, m. p. about 110°, giving *dl*-norvalylglycyl-*dl*-norvaline, m. p. 230—232° (decomp.); *dl*- $\alpha$ -bromo-*n*-valerylglycyl-*dl*-valine, m. p. 140°, giving *dl*-norvalylglycyl-*dl*-valine, m. p. 238—240° (decomp.); *dl*- $\alpha$ -bromo-*n*-valerylglycyl-*dl*-norleucine, m. p. 125—126°, giving *dl*-norvalylglycyl-*dl*-norleucine, m. p. 247—249° (decomp.); *dl*- $\alpha$ -bromo-*n*-hexoylglycyl-*dl*-norvaline, m. p. 118—120°, giving *dl*-norleucylglycyl-*dl*-norvaline, m. p. 243—246° (decomp.); *dl*- $\alpha$ -bromoisovalerylglycyl-*dl*-norvaline, m. p. 157—158° (decomp.), giving *dl*-valylglycyl-*dl*-norvaline, m. p. 230—232° (decomp.); chloroacetyldiglycyl-*dl*-norvaline, m. p. 216—217° (decomp.), giving glycyl-*dl*-norvaline, m. p. 218—219° (decomp.); *dl*- $\alpha$ -bromo-*n*-valeryldiglycylglycine, m. p. 181° (decomp.), giving *dl*-norvalyldiglycylglycine, m. p. 203—205° (decomp.). All temperatures are uncorrected.

J. H. BIRKINSHAW.

**Relations between enzyme and substrate. Behaviour of erepsin and trypsin-kinase towards polypeptides in which the free amino- or carboxyl group is protected, or in which both these groups are substituted.** E. ABDERHALDEN and H. BROCKMANN (Fermentforsch., 1930, **11**, 251—266).—The previously observed difference in the behaviour of amino-acids when crystallised from water and when crystallised from alcohol was studied using *dl*- $\alpha$ -bromoisohexoyldiglycylglycine. The alcohol-crystallised substance alone could be chlorinated with phosphorus pentachloride and acetyl chloride; this form contains half a molecule of alcohol. It is suggested that the alcohol is situated between two mole-

cules of the bromo-derivative linked by subsidiary valencies to the carboxyl group. The acyl chloride was converted by means of methylamine in ethereal solution into *dl*- $\alpha$ -bromoisohexoyltriglycylmethylamine, m. p. 232—233° (corr.). Methylamine gave *N*-methyl-*dl*-leucyltriglycylmethylamine, m. p. 197—200° (corr.). A new method of preparing such compounds was found. *dl*- $\alpha$ -Bromopropionyl-*dl*-alanyl-*dl*-norvaline, m. p. 183—184° (corr.), gave a methyl ester, m. p. 131—132°. The action of methylamine gave the *N*-methyl derivative of the methyl-substituted amide, *N*-methyl-*dl*-alanyl-*dl*-alanyl-*dl*-norvalylmethylamine, m. p. 213—214° (corr.). *dl*-Alanyl-*dl*-alanyl-*dl*-norvaline, m. p. 233—234° (corr., decomp.), and *N*-methyl-*dl*-alanyl-*dl*-alanyl-*dl*-norvaline, m. p. 264—265° (corr., decomp.), were also prepared.

Erepsin hydrolysed *dl*-alanyl-*dl*-alanyl-*dl*-norvaline and left unattacked all the *N*-methyl derivatives of the polypeptides examined. Trypsin-kinase hydrolysed the simple polypeptides and the *N*-methyl derivatives. *N*-Methyl-*dl*-alanyl-*dl*-alanyl-*dl*-norvalylmethylamine and *N*-methyl-*dl*-leucyltriglycylmethylamine were unattacked by trypsin-kinase, yeast maceration juice, and gastric juice. The free amino-group of the substrate is thus necessary to the action of certain enzymes and the free carboxyl group is essential for others.

J. H. BIRKINSHAW.

**Attempts to separate from organ press-juices by fractional precipitation with acetone polypeptidases with specific action.** E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1930, **11**, 267—269).—By fractional precipitation of kidney press-juice with acetone, six fractions were obtained, some of which hydrolysed *dl*-leucylglycine but not chloroacetyl-*dl*-leucine, whilst others showed the reverse behaviour.

J. H. BIRKINSHAW.

**Higher alcohols of fermentation.** J. SWENARTON (Science, 1929, **70**, 554—555).—Crude fusel oil from industrial fermentation contains in addition to *n*-propyl, isobutyl, *sec*-butyl alcohol, and isobutylcarbinol, alcohols of the hexyl, heptyl, octyl, nonyl, and decyl series. *n*-Heptyl alcohol is definitely present. These higher alcohols are probably produced by the vital activity of the yeast-cells.

L. S. THEOBALD.

**Detection of pyruvic acid in yeast fermentation.** S. KOSTYTSHEV (Biochem. Z., 1930, **217**, 421).—The method of Klein and Fuchs (A., 1929, 1491) for the detection of pyruvic acid by addition of *p*-nitrophenylhydrazine is impossible because the *p*-nitrophenylhydrazone is not produced at the concentrations concerned.

K. V. THIMANN.

**Difference of biological action produced in yeasts by various radiations.** A. LACASSAGNE (Compt. rend., 1930, **190**, 524—526).—Three states are recognised as resulting from the irradiation of *Saccharomyces ellipsoideus* with ultra-violet, X-, and  $\alpha$ -rays: (a) absence of cellular division, (b) accomplishment of a single division, (c) accomplishment of several divisions. The proportion of the three groups varies with the dose and also with time. The smallest exposures to ultra-violet rays lead to (a), but in many cases this is only apparent and division ultimately occurs; (b) is not observed, and sterilis-

ation is due to the real occurrence of (a). The action of X-rays is characterised by the absence of (a) for doses which lead increasingly to (b). The process of sterilisation by (b) (death during the course of the first cellular division) is even more distinct in the case of  $\alpha$ -rays than for X-rays. C. W. SHOPPEE.

**Metabolism of the yeast- and mycelium-forms of *Mucor Guilliermondii*.** H. LÜERS, R. KÜHLES, and H. FINK (Biochem. Z., 1930, 217, 253—278).—The conditions under which *Mucor Guilliermondii* gives rise to yeast-like cells instead of the normal mycelium (Fuchs, Zentr. Bakt., 1925–1926, 66, 490) have been studied. The respiratory quotient of the yeast form is more than double that of the pure mycelium, both grown on sugar-phosphate medium, and conditions favouring rapid growth and high metabolism therefore produce the former type, which is still further favoured by anaërobic conditions. The increased metabolism of the yeast form is correlated with the enzyme content, which in the case of maltase and oxidoreductase is double, in the case of zymase and carboxylase treble, that of the pure mycelium. The cells of the yeast form have a higher glycogen and protein content than those of the mycelium. K. V. THIMANN.

**Microbic metabolism of carbohydrates. I. Mechanism of fermentation.** S. YOSHIDA (Sci-i Kwai Med. J., 1929, 48, No. 8, Abstr. 9—12).—When suspended in levulose solution (0.01%), washed yeast (30 min. at 18–20°) or bacteria (1 hr. at 5–8°) adsorbed the sugar without decomposing it; mannitol, which is not utilised, was not adsorbed, neither was sugar adsorbed by dead organisms. Adsorption of utilisable sugar is the first step in fermentation.

#### CHEMICAL ABSTRACTS.

**Oxidation-reduction phenomena in fungi.** F. LABROUSSE and (MLLE.) S. PHILIPPON (Compt. rend., 1930, 190, 403—404).—Some species oxidise guaiacol and have therefore an oxidation-reduction potential greater than that of water (i.e., +1.23 volt). Others reduce cresyl-blue and methylene-blue and have an oxidation-reduction potential of less than 1.23 volt. Simultaneous oxidation of guaiacol and reduction of methylene-blue cannot occur. P. G. MARSHALL.

**Oxalic acid in mould cultures.** T. CHRZASZCZ and D. TRUKOV (Biochem. Z., 1930, 218, 73—85).—The amount and velocity of oxalic acid formation depend on the kind and the amount of amino-compounds in the medium. Increase of amino-compounds up to a certain limit increases the amount of oxalic acid, but to such an extent that the acid must be derived from sugar. At the limiting concentration the growth of a mould is inhibited. The smaller the number of carbon atoms per nitrogen atom in the amino-compound, the more readily oxalic acid accumulates and the smaller is the amount of amino-compound necessary at the beginning to cause its accumulation. P. W. CLUTTERBUCK.

**Growth and acid production of *Aspergillus niger* under water.** H. AMELUNG (Chem.-Ztg., 1930, 54, 118).—*A. niger* has been cultivated in a medium containing sucrose (10%), ammonium sulphate (0.5%), potassium dihydrogen phosphate (0.25%),

and magnesium sulphate (0.12%), through which air was constantly bubbled. The growth and acid production of the fungus which was growing below the medium and not at the surface were followed during 30 days and were both reduced when the temperature was lowered from 35° to 17–20°. Addition of calcium carbonate had little effect, but neutralisation of the acid with sodium carbonate retarded growth and acid production. The acid formed was chiefly citric acid. W. O. KERMAK.

**Utilisation of micro-organisms for human food materials. XI. Sterols of the mycelium of *Aspergillus oryzae*. XII. XIII. Culture of *A. oryzae*. I. Relation between the growth of mycelium and bios substances. II. Relation between the growth of mycelium and buffer strength of the medium.** R. TAKATA (J. Soc. Chem. Ind. Japan, 1929, 32, 268—269B, 269—270B, 270—271B).—The mycelium of *A. oryzae* contains a sterol, m. p. 147—148° (acetyl derivative, m. p. 187—188°). The biological properties of the irradiated sterol resemble those of Tanret's fungisterol.

XII. *A. oryzae* grows well on a pure synthetic medium containing dextrose as the only source of organic matter. Addition of bios, up to a certain amount, favours the growth, but a greater concentration of bios is toxic. *Saccharomyces saké* grows the better the more bios is present. *A. oryzae* synthesises bios during its growth.

XIII. In media in which the supply of nitrogen is from physiologically acid substances (e.g., ammonium salts) the transition velocity of  $p_H$  value is high and consequently the buffer strength of the medium has considerable influence on the growth of the mycelium. In the case of media in which the nitrogen is derived from physiologically alkaline substances (e.g., urea or nitrate) the transition velocity of  $p_H$  is small and accordingly the buffer strength of the medium has little influence on the growth of mycelium.

A. A. GOLDBERG.

**Soil *Actinomyces*. III. Standardisation of a plate method of counting soil *Actinomyces*.** M. G. RAO and V. SUBRAHMANYAN (J. Indian Inst. Sci., 1929, 12A, 253—273).—Improved culture media are described in which maximum numbers of colonies of *Actinomyces* are obtained with certainty and the development of other organisms is minimised. A minimum of mineral salts is used, calcium chloride is substituted for the more usual carbonate, ammonium sulphate is replaced by a mixture of asparagine and sodium nitrate, and "soluble starch" is included. During incubation  $p_H$  7.4 is maintained in the medium.

A. G. POLLARD.

**Physiology of nutrition of the diphtheria bacillus.** I. H. BRAUN and F. MÜNDEL (Zentr. Bakt. Par., 1929, I, 112, 347—354; Chem. Zentr., 1929, ii, 1805).—In a synthetic medium containing sodium aspartate, cystine, potassium phosphate, and sodium acetate, diphtheria bacilli grow without loss of vitality or toxin formation. A. A. ELDRIDGE.

**Influence of constituents of the culture medium on bacteria. I. Variability of the resistance and its relation to morphology and chemical composition.** G. MURAKAWA (Fukuoka Ik. Zasshi,

1928, 21, 83—84).—Fission of added carbohydrate increases the carbohydrate, fat, lipin, and residual nitrogen content of the plasma. Addition of protein, fat, lipins, or non-splitting carbohydrates is ineffective.

#### CHEMICAL ABSTRACTS.

#### Urea solutions as culture media for microbes.

II. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1930, 12, 18—22; cf. A., 1929, 1109).—The decomposition of urea in solution in presence of phosphoric and other acids, and of the three sodium and potassium orthophosphates, has been examined by determinations of hydrogen-ion concentrations and of liberated ammonia. S. I. LEVY.

**Physico-chemical alteration of the blood by intravenous bacterial toxins and non-specific protein.** L. YUH (Fukuoka Ig. Zasshi, 1928, 21, 69—70).—Injection of large doses of coli, typhus, pyocyanus, staphylococcus, and streptococcus toxins into rabbits caused the following changes in the blood: prolongation of coagulation time; diminution of fibrin enzyme, viscosity, plasma-carbon dioxide, serum-calcium, oxygen saturation, serum-globulin, and total serum-protein; increase of residual nitrogen and sugar (transitorily); decrease followed by increase of sedimentation time, and serum-albumin.

#### CHEMICAL ABSTRACTS.

**Relation between hormones and bacterial toxins, especially the influence of follicle liquid on tetanus toxin in relation to the uterine hormone.** T. IMAMURA (Acta Med. Keijo, 1929, 12, 249—285).—Resistance of mice to tetanus toxin is increased by injection of the follicle liquid (cow). Injection of emulsions of corpus luteum or testicle, or of cow's milk, also somewhat increases the resistance to tetanus toxin, whilst protein-free ovarian hormone does not. Hysterectomised mice show no increase in resistance, whilst male mice, whether castrated or not, show less increase in resistance than the female. Thyroidectomy has little effect. Injection of the follicle liquid also increases the amount of antibody produced on administration of the anatoxin of tetanus toxin. The phenomena are ascribed to endocrine disturbance, particularly to abnormal secretion of uterine hormone, stimulated by the protein and hormone of the follicle liquid.

#### K. V. THIMANN.

**Production of typhoid antitoxic substance and its relation with hormones.** H. KATABUCHI (Acta Med. Keijo, 1929, 12, 105—146).—Injection of suprarenal cortex extract into rabbits leads to production in the blood of a specific typhoid antitoxin. The antitoxin is not produced after thyroid- or parathyroid-ectomy. Injection of other gland extracts produces the antitoxin, but in smaller amount.

#### K. V. THIMANN.

**[Attempted] production of antitoxin from diphtheria toxin under the influence of trypsin.** L. KIMMELSTIEL (Z. Immunität., 1929, 62, 245—251; Chem. Zentr., 1929, ii, 1810).—Diphtheria toxin is decomposed by trypsin, but the product has no antitoxic action.

#### A. A. ELDRIDGE.

**Disinfecting properties of chloropicrin.** A. SMORODINCEV (Z. Desinfekt., 1929, 21, 169—172; Chem. Zentr., 1929, ii, 1805).—Chloropicrin has a

high penetrating power for porous materials. Its disinfecting power at 38° is double that at 4°. Spore-forming bacteria are very resistant.

#### A. A. ELDRIDGE.

**Effect of hydrogen-ion concentration on the bactericidal action of mercurochrome-220, soluble, on *B. coli*.** R. I. HILLER and A. E. STAMLER (J. Urol., 1929, 22, 699—704).—Low concentrations have no effect at  $p_H$  7.0—7.5, but inhibit growth in more acid media, except between  $p_H$  5.9 and 6.3.

#### CHEMICAL ABSTRACTS.

**Oligodynamic action.** N. LEITNER (Zentr. Bakt. Par., 1929, I, 112, 368—375; Chem. Zentr., 1929, ii, 1804—1805).—The oligodynamic action of water activated by copper is affected by addition of sodium, potassium, calcium, or aluminium chloride, the inhibiting action at first increasing and then diminishing with increasing concentration.

#### A. A. ELDRIDGE.

**Change of sensitivity of animals with diet. I.** S. LEE (Biochem. Z., 1930, 217, 320—323).—Subcutaneous administration of adrenaline to dogs fed on oats produced a rise in the blood-sugar to double the original value; the rise is only half as great in dogs on a soya-bean diet and almost nil in those fed on greenstuff. Ephedrine produces a considerable rise in the blood-sugar of the greenstuff-fed dogs and a slight rise in that of the dogs on soya-bean diet. In those on oat diet a slight hypoglycaemia was produced.

#### K. V. THIMANN.

**Effect of ephedrine on adrenaline hyperglycaemia.** O. HAINZT (Magyar orvosi Arch., 1929, 30, 277—280; Chem. Zentr., 1929, ii, 1936).—Slight diminution of the hyperglycaemia probably occurs.

#### A. A. ELDRIDGE.

**Activity of the anterior lobe of the pituitary gland.** E. A. SPAUL (J. Exp. Biol., 1930, 7, 49—87).—The metamorphic activity is estimated by its action on axolotl. Its action is specific and distinct from that of thyroxine. Pituitary extracts lose their activity on treatment with pepsin or trypsin and to a smaller extent even with hydrochloric acid.

#### E. BOYLAND.

**Rate of thermal decomposition at 100° of the oxytocic principle of the posterior lobe of the pituitary gland. I. Effect of hydrogen-ion concentration.** T. D. GERLOUGH (J. Amer. Chem. Soc., 1930, 52, 824—834).—Extraction of the active posterior lobe powder with varying concentrations of acetic acid, acetic acid and sodium chloride solution, and hydrochloric acid gives solutions with the same oxytocic value when the  $p_H$  of the extracts are  $3.2 \pm 0.2$  and  $4.4 \pm 0.2$ , regardless of the solvent used. The best conditions for extraction are with acetic acid and  $p_H$   $4.4 \pm 0.2$  at 96—98°, when maximum coagulation of inert protein is found. The rate of decomposition of the oxytocic principle at 100° and  $p_H$  2.0—5.1 conforms to that calculated for a first order reaction. The solutions adjusted to  $p_H$  3.0—3.4 at 25° are found to be the most stable at 100°.

#### H. BURTON.

**Quantity and distribution of insulin in blood.** H. BRUGSCH and H. HORSTERS (Arch. exp. Path. Pharm., 1930, 148, 295—308).—The insulin contained

in blood may be determined by injecting it into the peritoneal cavities of white mice and ascertaining the quantity required to lower the blood-sugar level and bring about convulsions. In the normal and diabetic fasting subject, the blood contains less than six units of insulin per 100 c.c. After intravenous injection of insulin into rabbits or dogs, it remains in the circulating blood for about 90 min. before beginning to disappear. In the case both of man and of animals the insulin is in the plasma and not in the corpuscles. W. O. KERMACK.

**Insulin in urine.** H. BRUGSCH and H. HORSTERS (Arch. exp. Path. Pharm., 1930, 148, 309—329).—Normal human urine contains only small quantities (about 0.5—1.0 unit per 100 c.c.) of insulin as measured by its effects when injected intraperitoneally into white mice, whilst diabetic urine contains rather less. There is no significant increase after administration of dextrose, laevulose, or clear soup. After administration of clinical doses of insulin into normal adults, a small percentage appears in the urine; in diabetics the excretion is delayed.

W. O. KERMACK.

**Substances producing hyperglycaemia and hypoglycaemia occurring in blood of dogs.** E. MORACCI (Arch. Farm. sperim., 1929, 50, 43—63).—Blood (9—15 c.c.) is taken 2 hrs. after a meat meal from the jugular vein of starving and normal animals. Active protein (0.0162—0.5334 g.) is obtained by treatment with alcoholic sulphuric acid etc. Rabbit tests on this material show that normal feeding animals give a substance capable of lowering the blood-sugar, whilst animals fed after a starvation period of 72 hrs. generally give a substance which raises the blood-sugar, an effect neutralised or reversed by ligation of the pancreatic duct. Adsorption of substances producing hyperglycaemia takes place in the intestinal lumen during digestion.

F. O. HOWITT.

**Passage of insulin from the foetus to the mother.** J. OLOW (Biochem. Z., 1930, 217, 475—481).—Insulin injected into the foetus of pregnant dogs produces a slight fall in the blood-sugar of the mother, but considerably less than that produced by direct subcutaneous injection. The effects of the laparotomy probably invalidate the result.

K. V. THIMANN.

**Effect of insulin on gaseous metabolism.** C. HOLTEN (Acta med. Scand., 1929, 71, 285—300; Chem. Zentr., 1929, ii, 2338).—Administration of insulin increases the respiratory quotient in diabetes from 0.769 to 0.811, and in normal persons from 0.843 to 0.92; the decrease in blood-sugar is 53% and 20%, respectively. The heat production is reduced only in diabetes. It is suggested that in diabetes insulin causes the conversion of carbohydrate into fat.

A. A. ELDRIDGE.

**Effect of oral administration of insulin and of various diets on the blood-sugar.** F. SCHELLONG (Verh. Deut. Kong. inn. Med., 1928, 236—238; Chem. Zentr., 1929, ii, 2215).—Administration of insulin affects not only the islets but also the general regulation of blood-sugar.

A. A. ELDRIDGE.

**Effect of hormones on the distribution of sugar and cell permeability in the animal organism.** R. SIEGEL (Klin. Woch., 1929, 8, 1655—1660; Chem. Zentr., 1929, ii, 1934).—In normal fasting mice the quotient blood-sugar/muscle-sugar is 1.3; after injection of insulin (0.06 unit per 100 g.) the muscle-sugar is unchanged, and the quotient falls to 0.7. The cell permeability is affected by insulin so that sugar can pass into the musculature, whilst lack of insulin diminishes the power of the tissues to take up sugar; extirpation of the pancreas scarcely affected the muscle-sugar, but the quotient rose to 1.55. Injection of thyroxine has no effect on the value; injection of adrenaline raised the blood-, but not the muscle-, sugar. On the other hand adrenaline, like insulin, has a glycogen-fixing action in liver cells. The action of adrenaline is thus dictated by its concentration in the blood.

A. A. ELDRIDGE.

**Action of thymus-gland extract on yeast-cells.** M. HELLER and G. FESCHTSCHENKO (Biochem. Z., 1930, 217, 465—472).—Thymus preparations increase the rate of fermentation of *S. cerevisiae*. The activity of the powder is reduced by about one third on heating. Muscle extract also increases the amount of fermentation, but to a smaller extent. Slight morphological changes in the yeast-cells, and an increase in weight due solely to carbohydrate, were observed to accompany the increased activity.

K. V. THIMANN.

**Thyroxine and the oxygen consumption of spermatozoa.** G. S. CARTER (J. Exp. Biol., 1930, 7, 41—48).—The addition of thyroxine to spermatozoa of *Echinus miliaris* causes the original high oxygen consumption to be maintained. The secretions of eggs of the same species produce the same effect to a greater extent.

E. BOYLAND.

**Thyroxine and allied substances. II. Effects on the oxygen consumption of rats.** J. H. GADDUM (J. Physiol., 1930, 68, 383—405).—The naturally occurring *l*-thyroxine produces a greater increase in oxygen consumption than does the *d*-form. Given orally, iodine as thyroglobulin was more effective than thyroxine, owing to the difficulty with which the latter is absorbed. *N*-Acetylthyroxine and diacetylthyroxine produced a large increase in oxygen consumption on subcutaneous injection. Thyronine was inactive, tetrabromothyronine slightly active, and di-iodothyronine active. Thyroxamine, di-iodotyrosine, and  $\beta$ -di-(3:5-di-iodo-4-hydroxyphenyl)-alanine had no effect.

E. BOYLAND.

**Effect of thyroid on the fowl.** F. B. HURT (J. Exp. Biol., 1930, 7, 1—6).—Daily doses of 2 mg. of thyroid-iodine per kg. body-weight were lethal to fowls and doses of half this amount caused marked loss in weight. Small doses caused increased pigmentation, but doses above 1 mg. per kg. caused depigmentation.

E. BOYLAND.

**Chemical assay of thyroid gland.** C. R. HARRINGTON and S. S. RANDALL (Quart. J. Pharm., 1929, 2, 501—506).—The thyroxine-iodine in preparations of thyroid glands (found by determining the iodine before and after precipitating the acid-insoluble thyroxine from the alkaline hydrolysate) does not bear



any constant ratio to the total iodine. In 8 commercial samples, the thyroxine-iodine varied from 0.03 to 0.19% of the dried gland and varied from 28% to 60.5% of the total organic iodine. It is suggested that dried thyroid be standardised to contain  $0.09 \pm 0.01\%$  of thyroxine-iodine. W. O. KERMACK.

**Determination of iodine in thyroid gland, thyroxine, and other organic compounds.** G. MIDDLETON (Quart. J. Pharm., 1929, 2, 536—538).—The method consists in destroying the organic matter by heating in presence of sodium carbonate, oxidising the iodine to iodate, and titrating, after addition of iodide, with thiosulphate. W. O. KERMACK.

**Influence of the parathyroid hormone on liver function.** M. H. KIM (Acta Med. Keijo, 1929, 12, 203—248).—Azorubin appears in the bile duct of normal dogs about 2 min. after its intravenous injection; within 2 hrs. an average of 82% of the dye can be recovered therefrom, and 9% from the urine. After parathyroidectomy its first appearance in the bile is later and the total amount in 2 hrs. is less. The amount in the urine is, however, greater, indicating partial substitution of the liver's functions by the kidney. Transplantation of parathyroid gland restores normal conditions. After parathyroidectomy protein appears in the bile, although normally absent. There is also at first a hyperglycemia, followed by a hypoglycemia. If sugar is intravenously injected after parathyroidectomy it appears in the bile during the hypoglycemic stage, but the increase in the blood is not different from the increase in the blood of normal animals. The calcium content of the bile and of the blood of parathyroidectomised dogs is not normal, and after injection of calcium the additional calcium appears to a smaller extent in the bile than in the normal case. K. V. THIMANN.

**Stimulating effect of testicular substance on sugar metabolism.** D. J. VERDA, W. E. BURGE, and F. C. GREEN (Endocrinol., 1929, 13, 46—48).—Testicular and ovarian substances stimulate the rate of sugar metabolism of goldfish in proportion to the quantity used. CHEMICAL ABSTRACTS.

**Follicular hormone: preparation in crystallised, water-soluble form; determination.** B. FRATTINI and M. M. MAINO (Arch. Ist. Biochim. Ital., 1930, 2, 3—30).—This hormone may be obtained crystalline as follows. Ovaries are triturated and macerated for some hours with 3 vols. of 1% acetic acid solution, the mixture being then kept at 90° for an hour to remove protein. After filtration, the residue is subjected again to the same treatment. From the united filtrates the hormone is precipitated by addition of 1% of copper sulphate, the precipitate being filtered off, washed thoroughly with water, and treated, in suspension in water, with hydrogen sulphide. After filtration, the clear brown liquid is heated on a water-bath and the hydrogen sulphide eliminated by a current of air. Extraction of the liquid with ether gives an ethereal solution from which the hormone may be obtained in crystalline form. The hormone is soluble in neutral or faintly alkaline water, the iso-electric point being  $p_H$  4. It is slightly soluble in absolute alcohol and may be dialysed through animal

membranes and adsorbed by precipitates formed in its solutions. It withstands sterilisation at 110° for 15 min. and resists well the action of acids, but is destroyed by a trace of alkali at 110°. It is resistant to reducing and oxidising agents and does not give the biuret, xanthoproteic, Millon's, and Lassaigne's reactions. It is precipitated by neutral salts, heavy metal salts, or tannic or benzoic acid, and may be freed in this way from polypeptides and amino-acids. A standard technique for its determination is suggested. T. H. POPE.

**Relation between quantity and action of female sexual hormone.** A. LIPSCHÜTZ (Biochem. Z., 1930, 218, 247—248).—A correction (cf. this vol., 118). P. W. CLUTTERBUCK.

**Vitamin-A and carotene.** E. M. HUME and I. S. MACLEAN (Lancet, 1930, i, 290—292).—The presence or absence of fat does not affect the biological activity of carotene, but it would appear that ethyl oleate is an unsuitable solvent for its biological administration. E. BOYLAND.

**Vitamin-A and carotene.** N. BEZSSONOFF (Compt. rend., 1930, 190, 529—532).—Feeding experiments on rats show that the addition of a daily dose of a vegetable lipid preparation (Rev. path. végét., 1927, 9, 568), estimated colorimetrically to contain 0.0021 mg. of carotene, to a vitamin-A-free diet produces a greater effect than that furnished by a daily dose of 9 mg. of cod-liver oil in controls deprived of vitamin-A. Various objections are quoted against the identity of vitamin-A and carotene, and the possible relationship of these substances is discussed. C. W. SHOPPEE.

**Permanence of vitamin-A in cod-liver oil as shown by the colour test.** N. EVERS (Quart. J. Pharm., 1929, 2, 556—565).—The vitamin-A potency of cod-liver oil estimated by the antimony trichloride colour reaction does not deteriorate rapidly when the oil is properly stored and protected from light and air, but may be markedly affected when exposed to light and oxidation. Sunlight appears to destroy the vitamin-A activity more rapidly than ultra-violet radiation from a mercury-vapour lamp. W. O. KERMACK.

**Variations in the results obtained by different observers with the antimony trichloride colour test for cod-liver oil.** N. EVERS (Quart. J. Pharm., 1929, 2, 566—569).—Different observers may employ different techniques in carrying out the antimony trichloride colour reaction and so obtain inconsistent results. W. O. KERMACK.

**Vitamins in bile.** H. MAKIMURA (Acta Med. Keijo, 1929, 12, 147—191).—Avitaminosis-A in rats is temporarily relieved by the administration of ox-bile, but the toxic effects of the bile rapidly counteract the relief. Addition of bile-powder to pigeons on a vitamin-B-deficient diet postpones the onset of avitaminosis-B, and in a dose of 0.07—0.1 g. per 100 g. body-weight is definitely curative. A dose of 0.018—0.027 g. per 100 g. body-weight is similarly curative of avitaminosis-C in guinea-pigs. In both these cases larger doses produce toxic effects. In animals on normal diet, the venous blood from the caecum and

colon is the richest in vitamins, whilst in those on avitaminous diet with added bile the venous blood from the jejunum and ileum is richest in vitamins. It is concluded that vitamins flow through the intestinal and portal veins to the liver, where they are stored, and whence they enter the bile to some extent.

K. V. THIMANN.

**Determination of antineuritic vitamin-B.** H. M. EVANS and S. LEPKOVSKY (J. Nutrition, 1929, 2, 1—5).—Growth of rats in the absence of antineuritic vitamin-B depends largely on the composition of the basal diet used. A sucrose-protein diet is most sensitive for the determination of the vitamin.

CHEMICAL ABSTRACTS.

**Determination of vitamin-D.** V. G. HELLER and C. CASKEY (J. Nutrition, 1929, 2, 59—65).—The  $p_{H}$  of the faeces increases as the animal body becomes depleted of vitamin-D. The results are erratic and depend on the nature of the basic ration and supplements. They indicate, however, the proper time of application of the X-ray method.

CHEMICAL ABSTRACTS.

**Effect of vitamin-D and of reaction of diet on response to parathyroid extract.** A. F. MORGAN and E. A. GARRISON (J. Biol. Chem., 1930, 85, 687—711).—Young dogs on a rachitic diet show little or no response to dosage with parathyroid extract, whether active rickets be present or not. After administration of vitamin-D, however, such dogs show an exaggerated response to parathyroid extract, again independently of the presence of rickets. Administration of 0.5 g. of sodium carbonate per kg. of body-weight *per diem* caused exaggeration of the effects of parathyroid in all animals, regardless of diet, whilst ammonium chloride had no such effect. C. R. HARRINGTON.

**Toxicity of large doses of irradiated ergosterol to laboratory animals.** H. SIMONNET and G. TANRET (Compt. rend., 1930, 190, 400—402).—Ergosterol, irradiated to 30% or practically complete transformation, and administered *per os* to rabbits in doses of 40 mg. per day, causes death in 58—175 days or 10—15 days, respectively. Toxicity is not lost after heating to 150°. Calcification of the arteries and kidneys is observed. The toxicities and antirachitic activities of the isolated amorphous products do not vary with the time of irradiation employed. Subcutaneous injection causes death more slowly. Calcification is observed at the point of injection. Irradiated ergosterol is little toxic to mice, guinea-pigs, rats, or dogs. Rats receiving large doses give litters which are unaffected by a rachitic diet after weaning. Irradiation of cholesterol yields non-toxic products, and irradiation of ergosterol peroxide yields inactive and non-toxic products. R. K. CALLOW.

**Influence of diets on the formation of biliary and renal calculi.** I. Diet deficient in fat-soluble vitamin. K. USUKI (Japan. J. Gastroenterol., 1929, 1, 18—28).—The formation of calculi is closely related to vitamin-D. The gallstones consisted chiefly of bilirubin, cholesterol, and calcium, whilst the nephroliths contained calcium, oxalates, and phosphates.

CHEMICAL ABSTRACTS.

**Determination of carbon dioxide assimilation.** W. TSCHESNOKOV and K. BAZYRINA (Ber. deut. bot.

Ges., 1930, 47, 600—602).—Experiments are described showing that the claims made for the accuracy of the apparatus for the determination of carbon dioxide assimilation in field work described by Krasnosselski-Maximov (*ibid.*, 313) are unfounded.

E. A. LUNT.

**Determination of lignin.** H. PRINGSHEIM (Biochem. Z., 1930, 217, 473—474).—A reply to the criticisms of Paloheimo (A., 1929, 1498).

K. V. THIMANN.

**Effect of acid and alkaline hydrolysis on the determination of hemicellulose and associated groups in young apple wood.** F. GERHARDT (Plant Physiol., 1929, 4, 373—383).—Extraction with hot water and digestion with saliva removed 23% of the tissue. The ammonium oxalate extract (7%) contained approx. 25% of the pentosans and 50% of the "uronic" acids. Hydrolysis with dilute acid removed 21% of the residue (after extraction with ammonium oxalate), 10% of the lignin, and 50% of the remaining pentosans. Sodium hydroxide (4%) at the ordinary temperature removed about half of the total lignin. After purification the hemicellulose fraction of a 1-year-old apple tree gave lignin 15, pentoses 70, ash 5, moisture 5%. No hexoses were found; *d*-xylose and *l*-arabinose (7:1 mols.) were present. Of the total reducing sugars in this fraction, 88% was *d*-xylose and 12% *l*-arabinose.

CHEMICAL ABSTRACTS.

**Changes in the wood of pine stumps in the ground after felling.** G. DUPONT and M. SOUM (Bull. Inst. Pin, 1928, 313—323; Chem. Zentr., 1929, ii, 1804).—A fossil pine stump showed a composition similar to that of fresh wood. The cellulose content was unaltered, much lignin was present, and the lignin showed the colour reactions of fresh wood. The resinous materials were converted into neutral products containing much resin. The stump of a 65-year-old pine tree suffered in 14 yrs. changes which are attributed to a hypothetical enzyme supposed to be formed by a mould. Cellulose disappeared, lignin is unchanged quantitatively, but no longer shows colour reactions and approaches humic acids in its properties; resin acids are increased.

A. A. ELDRIDGE.

**Relationship between anthocyanin formation and growth in *Abutilon avicennae*.** H. KOSAKA (J. Dept. Agric. Kyushu, 1929, 2, 207—240).—The appearance of reddish-violet colouring matters related to the anthocyanins has been investigated in relation to the stage of growth in two varieties of *A. avicennae*. The colour formation changes inversely as the growth velocity measured by change in dry weight. Intensity of colour formation is increased by solar radiation.

E. A. LUNT.

**Pigment of the ripe berries of *Tamus communis*.** L. ZECHMEISTER and L. VON CHOLNOKY (Ber., 1930, 63, [B], 422—427).—The fresh berries are crushed and dehydrated with methyl or ethyl alcohol and the residue is dried at 35°. The powder is percolated with carbon disulphide. Addition of anhydrous alcohol to the solution thus obtained precipitates lycopene,  $C_{40}H_{56}$ , m. p. 168—170° (corr.) [individual, apparently homogeneous specimens have m. p. 164° (corr.)], identical with the substance obtained

by Willstätter and Escher (A., 1910, i, 330) from tomatoes. Colorimetric determinations indicate the presence of 0.34 g. of lycopene in 1 kg. of fresh fruit; of this, 66% is isolatable in the crystalline form. Other pigments can be present only in subsidiary amount.

Lycopene is determined colorimetrically by dissolution in the smallest possible quantity of carbon disulphide, dilution of the solution with light petroleum, and comparison with 0.2% potassium dichromate solution (cf. Connell, A., 1925, i, 214). H. WREN.

**Ethereal oil and crystalline ester from the heart wood of *Vouacapoua americana*, Aubl.** D. B. SPOELSTRA (Rec. trav. chim., 1930, 49, 226—236).—Exhaustive extraction of the heart wood of *V. americana*, Aubl., with boiling benzene and fractional distillation of the product yields a crude ethereal oil fraction, b. p. 140—170°/20 mm. (1.5%), and a higher fraction, b. p. 180—220°/0.5 mm. (4.5—5%). Refractionation of the ethereal oil gives a mixture of bicyclic sesquiterpene hydrocarbons, b. p. 130—138°/18 mm.,  $d_{40}^{25}$  0.9105,  $n_D^{25}$  1.4993,  $[\alpha]_D^{25} +2.4^\circ$ , containing cadinene (isolated as its dihydrochloride and dehydrogenated by sulphur to cadalene), and a sesquiterpene alcohol (or mixture), b. p. 160—170°/20 mm.,  $d_{40}^{25}$  0.9759,  $n_D^{25}$  1.5087,  $[\alpha]_D^{25} -31.5^\circ$ . From the high-boiling fraction is isolated the methyl ester, b. p. 185°/0.5 mm., m. p. 105° (corr.),  $[\alpha]_D^{25} +100.6$ —101.4° (in carbon tetrachloride) of vouacapenic acid,  $C_{26}H_{42}O_3$ , m. p. 226—229° (sinters 215°),  $[\alpha]_D^{25} +107$ —108° (in carbon tetrachloride), which is obtained by hydrolysis of the ester with 0.5N-alcoholic potassium hydroxide. The ester contains one methoxyl group and no free hydroxyl group or carbonyl group. Vouacapenic acid is not esterified with alcoholic sulphuric acid, but diazomethane converts it into the original methyl ester. By the action of methyl iodide on the silver salt of the acid a substance,  $C_{22}H_{32}O_3$ , m. p. 167.5—168.5°, is obtained, which is probably a C-methyl derivative of the original methyl ester, since it contains only one methoxyl group. The third oxygen atom in vouacapenic acid is probably in the form of a bridged ether linking, a view which is confirmed by the results of catalytic reduction (see below). Titration of the acid and its ester with perbenzoic acid indicates the presence of two double linkings. Catalytic reduction of methyl vouacapenate with hydrogen and a platinum oxide catalyst in glacial acetic acid yields a tetrahydro-derivative,  $C_{22}H_{34}O_3$ , m. p. 129—131.5°,  $[\alpha]_D^{25} +44.9^\circ$  (in carbon tetrachloride), which contains no hydroxyl group, together with a hexahydro-derivative,  $C_{22}H_{36}O_3$ , b. p. 190°/0.8 mm., which contains one hydroxyl group, probably formed by fission of the bridged oxygen linking. Reduction with a platinum-black catalyst in ethyl acetate proceeds much more slowly, the sole product being the tetrahydro-compound. Vouacapenic acid therefore contains a reduced tricyclic skeleton containing two double linkings. Catalytic dehydrogenation of the methyl ester with selenium gives a mixture of two substances not yet investigated. J. W. BAKER.

***Gleditsia triacanthos*, Linné. Chemistry of the fruit.** L. E. HARRIS (J. Amer. Pharm. Assoc.,

1930, 19, 117—119).—Alcoholic extraction of the ground seeds of *G. triacanthos* yielded 9.25% of extract, from which was isolated an oil (3.19% of the seed) having  $d_{40}^{25}$  0.9336,  $n_D^{25}$  1.4685, saponification value 155.2, iodine value (Hanus) 93.9, and containing the glycerides of oleic, palmitic, and stearic acids.

E. H. SHARPLES.

**Hydrocyanic acid in vetches. Its distribution in the various organs of the *Leguminosae-Papilionaceae* as a cyanogenetic glucoside.** P. GUÉRIN (Compt. rend., 1930, 190, 512—514).—The present and previous observations (A., 1929, 362; this vol., 260) show that in hydrocyanic acid-containing *Leguminosae*, the cyanogenetic glucoside may be localised in various entirely different organs, and occasionally in one organ only. In the vetches it occurs only in the seeds; in *Lotus* it is absent from the seeds, but appears after germination in the leaf-like cotyledons, and is present in the leaf-stalk, the root, and the flower. In *Tetragonolobus*, *Dorycnium*, and *Bonjeania* the glucoside is absent from the seeds, and does not appear in the leaf-like cotyledons after germination; it is also completely absent from the leaf-stalks. On the other hand, the cyanogenetic glucoside is present at the same time in both the seeds and the leaf-stalks of *Phaseolus lunatus*.

C. W. SHOPPEE.

**Assimilation of nitrate by asparagus in absence of light.** G. T. NIGHTINGALE and L. G. SCHERMERHORN (New Jersey Agric. Exp. Sta. Bull., 1928, No. 476, 1—24).—Nitrate was reduced in the roots to nitrite and ammonia; an increase in asparagine and amino-acids followed. Assimilation of nitrate in darkness was accompanied by a loss of carbohydrate in excess of that in plants having no external supply of nitrogen. In darkness, absorption of nitrate continued to exhaustion of available carbohydrate and death; death did not ensue in the absence of external supplies of nitrogen. Below 10° transformation of nitrate to organic nitrogen was slow or absent; at 20° it was rapid. Translocation of nitrogen occurs below 10°. CHEMICAL ABSTRACTS.

**Transport of nitrogenous substances in the cotton plant. III. Relation between longitudinal movement and concentration gradients in the bark.** E. J. MASKELL and T. G. MASON (Ann. Bot., 1930, 44, 1—29; cf. this vol., 260).—When the transport of nitrogen in the cotton plant is arrested by ringing the stem near the base and removing the leaves, the negative nitrogen gradient exhibited in respect of protein-nitrogen and crystalloid nitrogen in the bark increases. When the transport of nitrogen is reversed, the negative gradient increases, especially in the inner half of the bark. The normal negative gradient consists of a static negative component dependent on stored nitrogen, and a smaller dynamic positive component which governs the transport of nitrogen. This latter dynamic component becomes zero when transport is stopped, and is reversed when transport is reversed.

W. O. KERMACK.

**Composition of plants containing methyl salicylate glucosides.** P. PICARD (Schweiz. Apoth.-Ztg., 1929, 67, 341; Chem. Zentr., 1929, ii, 2210).—

Invertin indicates the presence of sucrose in *Viola cornuta*, L., and various polyoses in *Viola gracilis*, L., and *Polygala vulgaris*, L. *Viola cornuta*, L., contains *violuloside*,  $C_{19}H_{26}O_{12}$ , m. p. 168.5°, affording on hydrolysis methyl salicylate and probably (from the rotation) an equimolecular mixture of dextrose and arabinose.

A. A. ELDRIDGE.

**Pyrethrum flowers.** II. Relation between maturity and pyrethrin content. III. Pyrethrin content of different commercial varieties. C. B. GNADINGER and C. S. CORL (J. Amer. Chem. Soc., 1930, 52, 680—684, 684—688).—II. Determinations of the pyrethrin content of the flowers of American *P. roseum* at various stages of maturity by the method previously described (B., 1929, 996) show that the content increases as the flowers mature. The roots, stems, and leaves contain no pyrethrins before the flower buds are formed. The fully open flowers of Japanese and Dalmatian *P. cinerariaefolium* contain 18—61% more pyrethrins than the closed flowers. The distribution of the active principles in the Japanese variety is: achenes (92.4%), receptacles (3.5%), scales (2.0%), disc and ray florets (traces).

III. The average pyrethrin content of various grades of Japanese and Dalmatian *P. cinerariaefolium* is 0.853 and 0.449%, respectively. American *P. roseum* contains 0.63% of pyrethrins. H. BURTON.

**Occurrence of *d*-norisoephedrine in *Catha edulis*.** O. WOLFES (Arch. Pharm., 1930, 268, 81—83).—Extraction of the alkaloids from the leaves and shoots of *C. edulis* by treating an alkaline mixture with benzene yields a mixture of cathine, cathidine, and cathinine, which were incompletely characterised by Stockman (A., 1913, i, 84). Cathine has been separated from the water-soluble fraction and found to be identical with *d*-norisoephedrine (Nagai and Kanao, A., 1929, 807).

R. K. CALLOW.

**Biological significance of alkaloids in plants.** B. LONGO and C. PADERI (Atti R. Accad. Lincei, 1929, [vi], 10, 322—324).—Alkaloids act as excitants on seeds and plants containing them, the action being non-specific with the seeds and specific with the plants.

T. H. POPE.

**Melanins.** H. SCHMALFUSS and H. BARTHEMEYER [with H. BRANDES] (Z. indukt. Abstamm.-Vererbungslehre, 1928, 47, 261—269; Chem. Zentr., 1929, ii, 2211).—Experiments with pods of *Vicia faba*, L., showed that change in enzyme concentration, but not that of oxygen, hydrogen ion, or chromogen, has considerable effect on melanin formation. Physiological processes arrest the oxidation of the (probably respiratory-functioning) chromogen to melanin. Treatment with ammonia, chloroform or ether, bruising, or suitable drying accelerates the formation of melanin.

A. A. ELDRIDGE.

**Physiological importance of the mineral elements in plants.** I. Relation of potassium to the properties and functions of the leaf. W. O. JAMES (Ann. Bot., 1930, 44, 173—198).—The effect of the application of potassium manures to the soil

in which potato plants are growing, on the number, area, weight, and water content of the leaves and on the rates of starch formation, translocation, and senescence has been investigated. Potassium sulphate and "potash manure salts," but not potassium chloride, decrease the number of leaves. Potassium chloride and "potash manure salts" but not potassium sulphate bring about an increase in the size of a selected leaf. The water content and dry weight of the leaf appear to be unaffected by the application of "potash manures." Starch formation per unit leaf area increases significantly in response to potassium and it is probable that there is also an increase in the rate of starch transportation. Senescence as indicated by the yellowing of the leaves may be delayed by the application of potassium sulphate. "Coppering" of young leaves is shown to be related to potassium deficiency.

W. O. KERMACK.

**Presence and distribution of titanium in Phanerogams.** G. BERTRAND and V. SPIRT (Ann. Inst. Pasteur, 1930, 44, 185—194).—The titanium content has been determined of various parts of a large number of mono- and di-cotyledonous plants. This element appears to be widely distributed and failed to be detected only in certain special cases such as polished rice or the edible part of the fruit of the banana. The highest contents were found in the leaves and branches of maté (150 mg. per kg.), the whole seeds of cacao (48.0 mg. per kg.), and in rice polishings (24.0 mg. per kg.).

W. O. KERMACK.

**Inorganic constituents of *Echinacea*.** S. H. CULTER (J. Amer. Pharm. Assoc., 1930, 19, 120—121).—The following analyses are given: total ash (on crude drug) 7.74%; water-soluble ash 1.85% (K 16.97%,  $SO_4$  13.26%,  $CO_3$  38.39%, Cl 4.10%); water-insoluble ash 5.89% (Ca 13.19%, Mg 2%,  $SiO_2$  26.2%,  $Fe^{+++}$  0.827%, Al 2.19%); acid-insoluble ash 3.16%, and acid-soluble ash 4.58%.

E. H. SHARPLES.

**Micro-determination of lipins.** E. BACKLIN (Biochem. Z., 1930, 217, 482—491).—The lipin solution is oxidised by a solution of silver dichromate in sulphuric acid, and the evolved carbon dioxide is absorbed by 5% sodium hydroxide in the burette of a micro-Van Slyke apparatus. Acid is then run in and the volume of the carbon dioxide measured in the same burette. Corrections are made for aqueous vapour tension and for re-absorption of carbon dioxide by the liquid. Using 0.1—0.5 mg. of lipin or fat the error varies from 1.3 to 4.3%. The method is well adapted for the determination of lipins from blood.

K. V. THIMANN.

**Specific colour reaction for histamine.** W. ZIMMERMANN (Z. physiol. Chem., 1930, 186, 260—262).—Dilute solutions of histamine salts with small amounts of cobalt nitrate, on addition of alkali give a violet precipitate or coloration. The mixture is decolorised by oxidation (e.g., atmospheric oxygen) or reduction. The reaction is specific for histamine and may be used to follow the putrefactive decomposition of a histidine solution.

J. H. BIRKINSHAW.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

MAY, 1930.

### General, Physical, and Inorganic Chemistry.

**Spectrographic investigation of the continuous hydrogen spectrum.** Y. HUKUMOTO (Sci. Rep. Tôhoku, 1929, 18, 581—584).—Examination of the spectra from the wide and narrow portions of a hydrogen discharge tube shows the dependence of the intensity of the Balmer and continuous spectra on the current density in the tube. O. J. WALKER.

**Energy distribution in the continuous hydrogen spectrum.** Y. HUKUMOTO (Sci. Rep. Tôhoku, 1929, 18, 585—595).—The energy distribution in the continuous hydrogen spectrum from an electrodeless discharge tube is compared with the known energy distribution in the continuous spectrum from tungsten electrodes sparking under water. The energy intensity of the hydrogen spectrum rapidly increases towards the ultra-violet and probably has a maximum value at 2500 Å. The under-water spectrum is independent of the nature of the electrodes, and extends in the short wave-lengths to at least 1850 Å.

O. J. WALKER.

**Spectrographic investigation of hydrogen discharge tubes.** Y. HUKUMOTO (Sci. Rep. Tôhoku, 1929, 18, 597—600).—A preliminary note on the investigation of the discharge spectrum of hydrogen in a special form of discharge tube having a hole either in the neighbourhood of one of the electrodes or in the middle of the tube. The intensities of the Balmer lines and of the secondary and continuous spectra of the portion of the discharge which breaks out through the hole are compared.

O. J. WALKER.

**Variations in the continuous spectrum of the hydrogen molecule with the conditions of excitation.** D. CHALONGE and N. T. ZÉ (Compt. rend., 1930, 190, 632—634).—The experiments of Chalonge and Lambrey (A., 1929, 616) have been extended for pressures of 2—91 mm. of mercury and discharge currents of 10—300 milliamp. Comparison of the photomicrometric curves of the spectra obtained for varying conditions of excitation in polished and unpolished glass tubes showed differences attributed to the catalytic influence of the latter (cf. Wood, A., 1922, ii, 759). Apparent contradictions to the results of Bay and Steiner (Z. Physik, 1929—1930, 59, 48) are explained. J. GRANT.

**Moment of inertia of hydrogen from band spectra.** H. H. HYMAN and C. R. JEPPESEN (Nature, 1930, 125, 462; cf. Hyman and Birge, A., 1929, 235).—Using all available data it is found that  $B_v = 60.587 - 2.7938(v + 0.5) + 1.0500 \times 10^{-2}(v + 0.5)^2 - 24.058 \times 10^{-4}(v + 0.5)^3$ , the actual vibrational

energy levels being given by  $v = 0, 1, 2$ , etc. This gives  $B_0 = 59.192 \text{ cm.}^{-1}$  and using Birge's new conversion factor  $(27.66 \pm 0.04) \times 10^{-40}$ ,  $I_0 = 0.4673 \times 10^{-40} \text{ g.-cm.}^2$  and  $r_0 = 0.7500 \times 10^{-8} \text{ cm.}$  It is shown by Birge and Jeppesen, however (cf. following abstract), that  $B_0$  is perturbed and the above value is incorrect. Hori's data (A., 1927, 1005) are not in agreement with his published values for  $B_v$  and  $D_v$ .

L. S. THEOBALD.

**Moment of inertia of hydrogen from Raman effect.** R. T. BIRGE and C. R. JEPPESEN (Nature, 1930, 125, 463).—Rasetti's data (A., 1929, 1127) have been critically analysed and give  $B_0 = 59.354 \text{ cm.}^{-1}$  and  $B_1 = 56.4035 \text{ cm.}^{-1}$  as compared with the values  $59.40 \pm 0.03$  and  $56.47$  published by Rasetti. The equation for  $B_v$  derived by Hyman and Jeppesen (cf. preceding abstract) gives  $B_1 = 56.4115 \text{ cm.}^{-1}$ . The value of  $B_0$  from the Raman effect, however, is 0.27% greater than the extrapolated value from band spectra and it is concluded that there is a perturbation in the moment of inertia of the lowest vibrational state of hydrogen. The value of  $B_0$  derived from the Raman effect is to be regarded as essentially correct and the true value of  $I_0$  for hydrogen is  $0.46602 \times 10^{-40} \text{ g.-cm.}^2$  and of  $r_0$ ,  $0.74891 \times 10^{-8} \text{ cm.}$  L. S. THEOBALD.

**Zeeman effect in the band spectrum of helium.** II. A. HARVEY (Proc. Roy. Soc., 1930, A, 126, 583—591; cf. Curtis and Jevons, A., 1928, 1066).—Estimates are given of the magnitudes of the Zeeman patterns in  $\text{He}_2$  bands of the type  $3D \rightarrow 2P^3\Pi$ . Resolution into components has not been effected. In the region photographed by Curtis and Jevons (*loc. cit.*) all the three possible sub-types occur:  $D\Sigma \rightarrow P\Pi$ ,  $D\Pi \rightarrow P\Pi$ , and  $D\Delta \rightarrow P\Pi$ . The effects in these are widely different and appear to be intimately related to the phenomenon of uncoupling of the electronic orbital angular momentum  $L$  from the internuclear axis. When the coupling is tight the effects fall off rapidly with increasing rotational quantum number  $K$ , whilst with complete uncoupling the effects, which are comparatively large, are independent of  $K$ . The correspondence between the two phenomena appears to be so close that the Zeeman effect can be taken as a measure of the uncoupling. The results of observations of the Zeeman effect for the few bands of the  $p\text{He}_2$  (singlet) system which appear on the plates are in general agreement with those for the triplet system. The only bands in the secondary hydrogen spectrum for which Zeeman effects have been recorded ( $3D^1\Sigma \rightarrow 2P^1\Sigma$ ) are closely related to those showing the

largest effect in  $\text{He}_2$ , and as in  $\text{He}$ , these also show very pronounced uncoupling. L. L. BIRCUMSHAW.

**Second genus orbits for the helium atom.** D. BUCHANAN (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 227—245).—Mathematical. A discussion of the restricted problem of three bodies in which there is a central nucleus of finite mass attracting two mutually repellent "electrons" of infinitesimal mass. With certain proportionality factors this represents the helium atom. The construction of the "second genus" orbits of two dimensions in the vicinity of the arc orbits is discussed. The forces of attraction and repulsion are assumed to vary according to the inverse square law, and the method of treatment is that of classical mechanics. J. W. SMITH.

**Nuclear moment of lithium.** S. GOUDSMIT and L. A. YOUNG (Nature, 1930, 125, 461—462).—The nuclear magnetic moment of lithium is not large and the wide hyperfine structure results from the presence of a single  $1s$  electron. L. S. THEOBALD.

**Bands of lithium hydride and lithium.** W. WEIZEL (Z. Physik, 1930, 60, 599—602).—Nakamura's (this vol., 124) upper term in the lithium hydride bands is regarded as a  $pc^1\Sigma$ -term. Striking anomalies are explained by  $l$ -decoupling. R. A. MORTON.

**Band system with diatomic carbon vapour.** H. KOPFERMANN and H. SCHWEITZER (Z. Physik, 1930, 61, 87—94).—The band system previously observed by Deslandres and D'Azambuja has been obtained with greater intensity by using a vacuum carbon arc. The fine structure of the spectrum was investigated, and a table of the frequencies of the lines observed is given. The spectrum corresponds with a  $^1\Pi$ — $^1\Pi$  transition of the diatomic carbon molecule. A. J. MEE.

**Sodium and magnesium spark lines in the far ultra-violet, and the quantitative application of the irregular doublet law to isoelectronic sequences.** J. E. MACK and R. A. SAWYER (Physical Rev., 1930, [ii], 35, 299—308).—The lines of sodium and magnesium, including new levels in  $\text{Na III}$ ,  $\text{Mg IV}$ , and  $\text{Mg V}$ , identified through the transition  $2s \leftarrow 2p$ , and the relativistic screening numbers for oxygen-like and fluorine-like systems are tabulated. The relativistic screening number  $\sigma_2$  ( $L_{21}L_{22}$ ) is 3.19 for  $Z=10, 11$ ; the difference from the value 3.49 for heavier atoms is probably due to outer screening. Wentzel's result for the first order screening number  $\sigma_1$  in  $X$ -rays is applied instead of the usual qualitative form of the irregular doublet law to determine the rate of dependence of the transition energy  $2s^22p^5 \leftarrow 2s2p^6$  on  $Z$  in the fluorine-like isoelectronic sequence; the high result  $49 \times 10^3 \text{ cm.}^{-1}$  is verified by the new  $\text{Na III}$  and  $\text{Mg IV}$  data. N. M. BLIGH.

**Structure of resonance line groups of sulphur vapour.** P. SWINGS (Bull. Acad. Polonaise, 1929, A, 616—620; cf. this vol., 124).—The doublet series previously reported were examined with high dispersion and shown to be simple rotation doublets. Several groups of luminescence lines, doublets, and multiplets were examined with high dispersion, and weak lines in addition to the intense lines were found. Intensity variations between components of a group

were observed in the resonance spectrum at different temperatures and pressures. N. M. BLIGH.

**Absorption of light by chlorine, bromine, and their gaseous mixtures.** L. T. M. GRAY and D. W. G. STYLL (Proc. Roy. Soc., 1930, A, 126, 603—612).—Statements made by Allmand (cf. A., 1925, ii, 1074) and by Weigert and Brodmann (*ibid.*, 1075) to the effect that the absorption of chlorine is dependent on the incident intensity and on the nature of the source of light have been tested and are not confirmed. It is concluded that the extinction coefficients of von Halban and Siedentopf (A., 1923, ii, 48, 105) can be applied to pure chlorine over a reasonable pressure range. The extinction coefficients of bromine vapour, for wave-lengths from 240 to  $580 \mu\mu$ , have been obtained by means of a quartz monochromator, thermopile, and Paschen galvanometer, using a mercury arc as the source of light. Measurements of the transmission of chlorine-bromine light-filters, containing an excess of liquid bromine, demonstrate the existence of bromine chloride in mixtures of gaseous bromine and chlorine. The results suggest that the differences between the transmission of chlorine-bromine mixtures as measured by the photographic and galvanometric methods are probably due to varying degrees of photodecomposition of bromine chloride, the variations being due to differences in light intensity. The extinction coefficients of the compound have been estimated for the chief mercury arc lines below  $300 \mu\mu$ . The equilibrium constant is estimated as about 0.03.

L. L. BIRCUMSHAW.  
**Absorption spectrum of bromine vapour between 6117 and 6309 Å.** (Miss) M. B. HAYS (J. Franklin Inst., 1929, 208, 363—369).—The first and second order spectra given by a 14-ft. Rowland grating were used. Band heads given by Nakamura (cf. A., 1929, 625) at 6200 and 6211 Å. are shown to be branches of the band at 6150 Å. Individual lines are resolved except near the band heads. A. B. D. CASSIE.

**Nuclear moment of bromine.** T. L. DE BRUIN (Naturwiss., 1930, 18, 265, and Nature, 1930, 125, 414).—The strong lines at 6632, 6560, 6351, and 6149 Å. in the arc spectrum of bromine are combinations of a  $^4P_{5/2}$  ground level and appear as quadruplets with decreasing frequency differences and intensities. Taking the values  $3/2$  and  $5/2$  for  $i$  and  $j$ , respectively, the separations in the four levels are obtained. The observed ratio of  $4:2.7:1.7$  is in fair agreement with the theoretical value,  $4:3:2$ . It would appear that  $i$ , the nuclear momentum, has the value  $3/2$ . W. R. ANGUS.

**Absorption of electrically excited cadmium, zinc, and thallium vapours.** G. HOFFMANN (Z. Physik, 1930, 60, 457—463).—Cadmium and zinc triplet lines, due to absorption from the metastable  $2^3P_0$  and  $2^3P_2$  levels, appear, and at  $408^\circ$ , absorption from the labile level,  $2^3P_1$ , is almost equally intense. Thus the labile level  $2^3P_1$  has a comparatively long life, as Prokofiev (A., 1928, 1309) inferred for light atoms from dispersion measurements. Thallium absorbs from the  $2^2P_{3/2}$  metastable level. Absorption by metastable cadmium atoms is greatest with an inert



gas in the tube, less with nitrogen, and zero with hydrogen.

A. B. D. CASSIE.

**New resonance series of selenium.** (MLLE.) H. GRÜNBAUM (Bull. Acad. Polonaise, 1929, A, 611—615).—Two new resonance series excited by the calcium lines  $\lambda$  3934 and 3969 Å. were found; they are in agreement with Rosen's frequency relation (cf. A., 1927, 608). Intensities and calculated and observed frequencies are tabulated. The absorption of the exciting radiation corresponds with transitions from the normal state of the molecule  $n=8$  to the excited states  $n'=5$  and 4 for the radiations  $\lambda$  3934 and 3969 Å., respectively.

N. M. BLIGH.

**Second spectrum of xenon in the spectral interval 9000—6000 Å.** G. DÉJARDIN (Compt. rend., 1930, 190, 580—582).—Excitation by means of an electrodeless oscillating discharge (Bloch, Bloch, and Déjardin, A., 1924, ii, 286), which enables spark and arc lines to be differentiated, has been applied to xenon. With the exception of  $\lambda$  6370 and 6238 Å. the lines obtained belong to the X II spectrum and fall into two groups  $\lambda$  5900—7000 and 7000—9000 Å. obtained on plates sensitised with pinacyanol and dicyanine, respectively.

J. GRANT.

**New lines of samarium in the arc spectrum at normal pressure between  $\lambda$  3100 and 2200 X.** S. PIÑA DE RUBIES (Anal. Fis. Quím., 1930, 28, 212—222).—See A., 1929, 479, 617.

**Spectral emission of mercury arcs in quartz.** A. ANDANT and J. LECOMTE (J. Phys. Radium, 1930, [vii], 1, 65—76).—The relative intensities of the principal lines emitted by mercury-vapour lamps of various designs and functioning under different conditions were found. With determinations from the yellow doublet up to 2536 Å. it was found that for the same arc the intensity of radiation emitted changes greatly with the arrangement of apparatus, especially with the voltage at the terminals. For two different arcs and for the same spectral line an identical variation in each lamp does not produce the same effect on the emission.

A. J. MEE.

**First spark spectrum of mercury Hg II.** G. DÉJARDIN and R. RICARD (Compt. rend., 1930, 190, 634—635).—The combinations suggested by Naudé (A., 1929, 1352) are not sufficiently justified, since they include a number of lines which according to the electrodeless discharge method (this vol., 389) probably belong to the Hg III and Hg IV spectra.

J. GRANT.

**Excitation of mercury by means of collisions with slower sodium ions.** B. KIRCHSTEIN (Z. Physik, 1930, 60, 184—195).—Excitation of the mercury line 2537 Å. can be detected as a result of collisions of mercury atoms with sodium ions of voltages down to 35. Quantitative experiments indicate that for 50-volt ions one collision out of  $10^6$  causes excitation.

R. A. MORTON.

**Theoretical interpretation of the hyperfine structure in singly-ionised thallium, Tl II.** H. E. WHITE (Proc. Nat. Acad. Sci., 1930, 16, 68—71).—Practically all the observed terms in Tl II have  $^2S_{1/2}6s$  as a limit and therefore in series all of the fine structures must approach in width the  $^2S_{1/2}$

separation. The large fine-structure separations are due primarily to the 6s electron. F. G. TRYHORN.

**Structure of the Pb IV spectrum.** A. S. RAO and A. L. NARAYAN (Z. Physik, 1930, 61, 149—150).—A table showing the regular doublet terms in the Pb IV spectrum is given.

A. J. MEE.

**Excitation of the spectrum.** L. S. ORNSTEIN (J. Franklin Inst., 1929, 208, 589—594).—An account of work published elsewhere (cf. A., 1929, 4; Peteri and Elenbaas, *ibid.*, 732).

C. A. SILBERRAD.

**Method of horizontal comparison in the location of spectra of elements. II.** K. MAJUMDAR (Indian J. Physics, 1930, 4, 359—365).—The linear relation previously found (cf. A., 1928, 1296) between the frequency of the corresponding multiplets of the successive elements for the  $L_2M_2 \rightarrow L_2M_1$  and  $M_2N_2 \rightarrow M_2N_1$  transitions is not found to hold exactly for the more complex case of the  $L_2M_3 \rightarrow L_2M_2$  and  $M_2N_3 \rightarrow M_2N_2$  transitions; also the multiplets in the latter case for some elements are found to be more irregularly distributed about the mean than in the first case. The successful use in the location of spectra of the curves obtained is mentioned, and the predicted positions of some unclassified spectra are shown.

H. A. JAHN.

**Early stages of electric sparks.** E. O. LAWRENCE and F. G. DUNNINGTON (Physical Rev., 1930, [ii], 35, 396—407).—With the Kerr-cell electro-optical shutter adapted by Beams (cf. A., 1926, 1069) which allows exposure times as short as  $4 \times 10^{-8}$  sec. the early stages of sparks between electrodes of zinc, cadmium, and magnesium were investigated. During  $50 \times 10^{-8}$  sec. after the beginning of the sparks, the spark doublet lines  $3d_{1,2} - 4f_{1,2}$  had widths of 45 Å. for zinc and 30 Å. for cadmium and magnesium; the luminosity of the metallic vapours spreads from the electrodes with respective speeds  $\times 10^5$  of 2.1, 1.5, and 1.2 cm./sec., and the discharge is confined to a filament having a cross-section at the anode of  $5 \times 10^{-4}$  cm.<sup>2</sup>, broadening to four times this size at the cathode. The discharge current density is estimated to reach the value  $1.7 \times 10^6$  amp./cm.<sup>2</sup> Assuming broadening due to the Stark effect of inter-ionic fields, the inter-ionic field was calculated as  $10^6$  volts/cm.; the average separation of the ions is  $3.8 \times 10^{-7}$  cm., corresponding with ionisation of one third of the molecules in the discharge path, in agreement with one half of the discharge current being carried by the positive ions moving towards the cathode with the observed velocity of  $2.1 \times 10^5$  cm./sec. Temperature estimations of the early periods of the spark by four methods lead to values of the order  $10,000^\circ$  Abs., indicating thermal ionisation as an important feature of the discharges.

N. M. BLIGH.

**Duration of metastable states.** J. M. ANDERSON (Canad. J. Res., 1930, 2, 13—25; cf. Meissner and Graffunder, A., 1928, 212; Zemansky, A., 1929, 1122).—Mathematical. Assumptions as to the efficiency of collisions and the interaction of two metastable states are specified and the half-value time of absorption from metastable electronic atomic states is calculated on the hypothesis that the whole

decay is due to collision phenomena. The probability of an exchange is shown to depend on the absolute value of the energy difference between the states concerned. Results for helium, neon, and argon at normal and very low temperatures show fair agreement with experimental values. The energy tolerance of a quantum transition is estimated at from  $2 \times 10^{-7}$  to  $2 \times 10^{-5}$  volt. N. M. BLIGH.

**Axiality of light emission and atomic structure.** IV. Dissymmetry of light emission from the effect of an electric field. V. Dissymmetry of light emission in the axial effect of canal rays. J. STARK (Ann. Physik, 1930, [v], 4, 607—664, 665—684).—IV. Dissymmetry is indicated by the displacement of components and their relative intensities in parallel and perpendicular electric fields. For all the series lines of hydrogen investigated up to the present, and for the components of the Balmer hydrogen lines, the intensity of the component displaced towards the red is less than that of the component displaced towards the violet, when the emission is in the direction of the electric field. When the emission is perpendicular to the field the opposite is the case, the intensity of the component displaced towards the red being greater than that of the component displaced towards the violet. According to this, the intensity of emission of a hydrogen series line displaced towards the red in the field is smaller in the direction of the field than perpendicular to it, and inversely for the violet component. For the greater number of hydrogen series lines investigated the intensity ratio of two symmetrical components in the perpendicular emission has a value greater than 1, and approximately equal to the reciprocal of the ratio in the parallel emission. There are, however, special cases. In the case of helium very similar results were obtained.

V. The connexion between the effects in the electric field and for canal rays is investigated, and the accuracy of previous methods is examined. Observations were made with hydrogen lines, and with helium lines of which the intensity for perpendicular fields is greater than for parallel fields, and for the converse lines. It was found, also, that the mercury 4359 line was displaced towards the violet by an electric field in a similar way to the helium lines. The results of former determinations are collected, and it is shown that there is general agreement between the sign of the dissymmetry in the axial effect of canal rays, and also in the effect of the electric field. A. J. MEE.

**Spectral intensity and groove form of the diffraction grating.** (MISS) J. E. ROSENTHAL (J. Opt. Soc. Amer., 1930, 20, 87—96).—A general expression is deduced for the intensity of light of any wave-length diffracted by a triangular groove. C. W. GIBBY.

**Impeded glow discharge.** A. GÜNTHER-SCHULZE (Z. Physik, 1930, 61, 1—14).—The anomalous fall of potential at the cathode in the case of a glow discharge when a plane larger than the anode is placed at a small distance from it, and parallel to it, so that the discharge was impeded, was investigated. It was found that with hydrogen, oxygen, and helium, the

potential drop at the cathode decreases first, reaches a minimum, and then rapidly rises as the anode distance increases. As long as the potential drop falls, the edge of the glow approaches the anode, and as soon as it rises, the glow recedes. For neon, the cathode drop increases with approaching anode at the start. Nitrogen and argon occupy an intermediate position. According to the size of the cathode drop there is an initial increase or decrease. For all the gases it is possible by approaching the anode sufficiently closely to extinguish the glow altogether. For large gas pressures the glow disappears in the neighbourhood of a cathode drop of 600 volts. A. J. MEE.

**New phenomena in the annular spark.** N. SIRACUSANO (Atti R. Accad. Lincei, 1930, [vi], 11, 64—69).—A study has been made of the annular discharge produced with a copper spiral under low pressure, by means of an intermittent high tension. With very low gas pressure the discharge consisted of two annular glows lying in planes parallel to the plane of the spiral. The distance between the two glows increased with increase in the intensity of excitation. The spark disappeared on short-circuiting the spiral. The nature of the discharge changes suddenly when the explosive gap in the oscillating circuit was reduced below 2 mm. The most remarkable observation was that as the intensity of excitation was reduced the globe containing the spiral became filled with a pale green luminosity which persisted for periods up to 15 min. after the excitation had ceased. F. G. TRYHORN.

**Reflexion of long wave-length X-rays at a plane mirror.** J. THIBAUD (J. Phys. Radium, 1930, [vii], 1, 37—48).—The reflexion of the  $K\alpha$ -rays of carbon at a glass mirror has been investigated by Dershem (Physical Rev., 1929, 34, 1015), and this work is here corrected. Using a glass mirror, and radiation of wave-length 44.9 Å., the Kallmann-Mark dispersion formula leads to the result  $\delta = 1 - n = 5.73 \times 10^{-3}$ , where  $n$  is the refractive index of the medium. This takes into account discontinuities in the absorption of the dispersion medium. The above result is of the same order as that obtained by using the simplified formula of Drude and Lorentz. The intensity of reflexion was calculated as a function of the angle of incidence, taking absorption into account. A series of curves is drawn for different values of the coefficient of extinction,  $K$ , and  $\delta$ . It is possible to determine with accuracy the limiting angle  $\theta_m = \sqrt{2\delta}$  from the experimental reflexion curves. A. J. MEE.

**Critical potentials for the excitation of soft X-rays from iron.** (MISS) A. C. DAVIES, F. HORTON, and (MISS) E. BLUNDELL (Proc. Roy. Soc., 1930, A, 126, 661—674).—It is suggested that the complexity of the critical potentials for soft X-rays and the difficulties of correlating them with atomic levels might be due to the surface arrangement of atoms, with the underlying idea that the close packing of the atoms in a solid might influence the orbits of the less deeply-seated electrons within the atoms. A study has been made of the critical potential curves for the photo-electric effect of soft X-radiation over the region 0—220 volts, using an iron target

maintained at various temperatures (cf. A., 1926, 214). The nature of the break locating a definite critical potential on different curves of the same range is not always the same, even although the existence of the break is obvious and is shown at the same voltage on the curve (cf. Thomas, A., 1926, 104). A number of new critical points are found between 112 and 165 volts; these first appeared when the target was bombarded while red hot, and most of them persist in the curves taken under various conditions of the target subsequent to the bombardment during heating. The only critical potential for which the evidence suggests a dependence on the target being hot for its appearance is one occurring at about 201 volts. Except for the point at 201 volts, there is no evidence for any connexion between the critical potentials and the magnetic condition of the target, or between the critical potentials and the temperature as such.

L. L. BIRCUMSHAW.

**New weak lines in the *K*-series of the elements from vanadium to yttrium.** H. BEUTHE (Z. Physik, 1930, 60, 603—616).—Two hitherto unknown lines in the *K*-series of the elements from vanadium to yttrium have been observed, one line lying on the short-wave side of the corresponding absorption edge for the elements nickel to vanadium. The  $\lambda$ -values for these lines depend then on the type of chemical linking. These and all other "forbidden" lines of the X-ray spectrum can be regarded as the sum or difference of two known lines, e.g., the two observed *K*-lines as  $K\alpha_1 + L\alpha_1$  or  $K\alpha_1 + L\beta$ . It is assumed that the appearance of these lines is connected with the lack of two and more electrons in different levels of the same atom.

R. A. MORTON.

**Influence of chemical linking on the *K*-X-ray emission spectrum of sulphur.** O. LUNDQUIST (Z. Physik, 1930, 60, 642—651).—Free sulphur is characterised by the intensity maxima in the *K*-series:  $\beta_1$  5020.9,  $\beta_x$  5013.2;  $\alpha_1$  5361.02,  $\alpha_2$  5363.99 X. In order to determine the rôle of chemical linking a large number of sulphides and sulphates has been studied under high dispersion, the plates being measured by means of a registering photometer. The majority of the sulphides exhibit the  $\beta_1\beta_x$  lines with unchanged wave-length, but those of chromium, zinc, cadmium, lead, strontium, and barium show a more or less marked loss of definition, the two maxima being replaced by a single one near 5017—5018. The  $\alpha_1\alpha_2$  lines are shown by all the sulphides studied, the wave-lengths being unchanged. The sulphates fall into two groups, in one of which the  $\beta_1\beta_x$  lines are unchanged and in the other the  $\beta_1$  line is unchanged but  $\beta_x$  is shifted to 5014.3—5014.8. For the  $\alpha_1\alpha_2$  lines the sulphates vary considerably in intensity but not in position; the  $\text{SO}_4$   $\alpha_1$  and  $\alpha_2$  lines also appear.

R. A. MORTON.

**Relativistic *L*-doublet in the X-ray region.** J. ZAHRADNÍČEK (Z. Physik, 1930, 60, 712—715).—The screening factor  $s$  used for the relativistic *L*-doublet in the formula for the wave numbers of hydrogen-like spectra has been calculated. The results indicate that  $s$  is a function of the atomic number.

R. A. MORTON.

**Theory of the Zeeman effect for salts of the rare earths.** H. BETHE (Z. Physik, 1930, 60, 218—233).—Quantum mechanical methods enable certain special assumptions to be eliminated without loss of complete qualitative agreement with experimental data.

R. A. MORTON.

**Zeeman effect of the green auroral line.** A. RUBINOWICZ (Naturwiss., 1930, 18, 227).—Polemical against McLennan and Sommer. No possible decision can be reached by longitudinal observation. By transverse observation lines corresponding with  $\Delta m = \pm 1, \pm 2$  changes are observed. The lines corresponding with  $\Delta m = 0$  are missing, but appear in oblique observation. The green auroral line is attributed to a quadrupole moment and it is possible to work out a  $\pi$  doublet with normal and a  $\sigma$  doublet with two-fold splitting.

J. FARQUHARSON.

**Quantitative spectral analysis of the sun's atmosphere.** V. AMBARZUMIAN (Z. Physik, 1930, 60, 255—268).—Mathematical.

R. A. MORTON.

**Theory of absorption lines in stellar atmospheres.** V. AMBARZUMIAN (Z. Physik, 1930, 61, 151—152).—A relationship between the intensity within a spectral line and other physical quantities in stellar atmospheres is given.

A. J. MEE.

**Electrical breakdown of gases.** W. ROGOWSKI (Naturwiss., 1930, 18, 246—247).—The mechanism of the breakdown of gases under high potentials is discussed.

A. J. MEE.

**Electrostatic electron emission on illumination of metal surfaces.** L. ROSENKEWITSCH (Naturwiss., 1930, 18, 226).—Theoretical. An equation is deduced for the intensity of the stream of electrons emitted from a metal surface in an applied electric field, when there is insufficient illumination for other photo-effects. By means of this equation conditions were so chosen that the effect could be investigated.

J. FARQUHARSON.

**Energy losses of electrons in mercury vapour.** D. C. ROSE (Nature, 1930, 125, 460—461).—The effects of collisions with mercury atoms of electrons of energies of 8, 18.4, 34.6, and 49 volts have been investigated. Inelastic peaks have been identified at energy losses of 4.9, 6.7, 9.2, 10.4, 11.5, and 13.5—14 volts. Their significance is discussed.

L. S. THEOBALD.

**Mechanism of electron liberation at the cathode of a glow discharge.** M. STEENBECK (Wiss. Veröff. Siemens-Konz., 1929, 8, [2], 94—96).—The possibility of the electron emissions being due to a strong electric field between the cathode surface and an adsorbed layer of positive ions has been investigated. Such a field would affect the surface tension of a drop of mercury used as the cathode. The decrease is calculated and it is photographically shown that such a decrease in surface tension does not take place. As a corollary it follows that the discharge of a positive ion at the cathode must take place in less than  $10^{-4}$  sec.

W. E. DOWNEY.

**Spatial distribution of photo-electrons.** S. E. SZCZENIEWSKI (Physical Rev., 1930, [ii], 35, 347—374).—Mathematical. The perturbation of a hydrogen-like atom by a plane polarised electro-

magnetic wave is considered on Dirac's equation, and perturbed wave functions are obtained, leading to a formula for the spatial distribution of the photo-electrons (cf. Carrelli, A., 1929, 1121).

N. M. BLIGH.

**Determination of atom factors by means of electrons.** H. MARK and R. WIERL (Z. Physik, 1930, 60, 741—753).—Wave mechanics shows reflexion of electrons by crystal planes to be similar to reflexion of X-rays. Relative values of the intensity of reflexion of electrons from crystal faces in thin metal films were measured photographically for aluminium, silver, and gold. The corresponding atom factors were calculated. Agreement with Bethe's theoretical calculations (A., 1928, 1303) is satisfactory.

A. B. D. CASSIE.

**Quantum theory of electrons.** H. MANDEL (Z. Physik, 1930, 60, 782—794).—Mathematical.

A. B. D. CASSIE.

**Number of dispersion electrons in sodium and lithium vapours.** B. TRUMPY (Z. Physik, 1930, 61, 54—60).—The intensities of the series lines of sodium and lithium can be calculated. The calculation is taken up to the fifth member of the principal series of these elements. The theoretical  $f$ -value is in agreement with earlier observations.

A. J. MEE.

**Elementary processes of ionic and electronic collisions.** H. KALLMANN and B. ROSEN (Z. Physik, 1930, 61, 61—86).—The recombination of ions in different gases was investigated. The ions used were  $\text{He}^+$ ,  $\text{Ne}^+$ ,  $\text{A}^+$ ,  $\text{N}_2^+$ ,  $\text{N}^+$ ,  $\text{O}_2^+$ ,  $\text{O}^+$ ,  $\text{C}^+$ ,  $\text{CO}^+$ ,  $\text{CO}_2^+$ , in helium, argon, nitrogen, carbon monoxide, carbon dioxide, ammonia, and mercury vapour. There is good recombination if the neutralisation energy of the ions is in approximate agreement with the ionisation energy of the gases.

A. J. MEE.

**Electron waves.** C. J. DAVISSON (J. Franklin Inst., 1929, 208, 595—604).—An account of recent work on the diffraction of electrons by crystals is given. When a stream of electrons of velocity 130 volts is directed against a nickel crystal at an angle of  $44^\circ$ , the distribution of the electrons scattered in the plane of incidence shows three maxima, one being the analogue of the Bragg X-ray beam, the other two in full agreement with the hypothesis that the beam of electrons suffers "refraction" on entering and leaving the metal.

C. A. SILBERRAD.

**Electron and positive-ion emission from tungsten, molybdenum, and tantalum incandescent filaments in potassium vapour.** (FRL.) E. MEYER (Ann. Physik, 1930, [v], 4, 357—386).—The electron and positive-ion emission for different potassium vapour pressures has been studied as a function of temperature, using tungsten, molybdenum, and tantalum filaments. The curves are of the same type as those already recorded for tungsten in potassium, rubidium, and caesium vapours. The electron emission reaches a maximum which occurs at the same filament temperature under different potassium vapour pressures. Using different metals, the electron emission from potassium films varies greatly with the nature of the supporting material. This effect is not, as Langmuir has assumed, determined by the

difference between the ionisation potential of the alkali metal and the work of escape of the support metal. It depends on the surface properties of the material used. The potassium vapour pressure calculated from the ion emission is not in agreement with that deduced from the temperature of the discharge tube. Owing to the nature of the surface of the wire it would seem that not all the potassium atoms acted on are ionised. The adsorbed layer is probably a few atoms thick.

R. A. MORTON.

**Reflexion of hydrogen atoms from crystals: velocity selection in the specular beam.** T. H. JOHNSON (J. Franklin Inst., 1929, 207, 639—643).—An attempt is made to determine whether there is any velocity selection in the specular reflexion of hydrogen atoms from a rock-salt crystal. The reflected beam was made to fall at the same incident angle on a second crystal. If there is velocity selection it would be reflected with greater intensity than a beam containing the same number of atoms distributed according to the Maxwellian law. The difference found was less than sufficient to increase the probability of specular reflexion by more than a factor of five.

C. J. SMITHELLS.

**Reflexion of hydrogen atoms from crystals: intensity measurements of the specularly reflected beam.** T. H. JOHNSON (J. Franklin Inst., 1929, 207, 629—637).—Quantitative results on the intensity of specularly reflected beams of hydrogen atoms from the surface of a rock-salt crystal have been obtained, the darkening produced on films of molybdic oxide being measured with a densitometer. The intensity of the reflected beam is greatest for grazing incidence, and falls rapidly between  $30^\circ$  and  $40^\circ$  from grazing, the value at  $60^\circ$  being one fifth the value of grazing incidence. The intensity at any angle is greater at low temperatures than at high temperatures of the crystal, and the effect of the angle of incidence is greater at low temperatures.

C. J. SMITHELLS.

**Theory of recombination of gaseous ions.** L. B. LOEB and L. C. MARSHALL (J. Franklin Inst., 1929, 208, 371—388).—The bearing of the recent results of Marshall (cf. A., 1929, 1210) on the theory of recombination of gaseous ions is discussed. These results indicate that the motion of ions relative to one another is largely one of random diffusion, i.e., Thomson's theory is correct, and not Langevin's. The success of any theoretical treatment is limited by lack of data on the mass of an ion.

A. B. D. CASSIE.

**Emission of positive ions from tungsten and molybdenum.** L. P. SMITH (Physical Rev., 1930, [ii], 35, 381—395).—The mass spectrum for tungsten and molybdenum filaments at temperatures from  $1700^\circ$  to  $2000^\circ$  Abs. showed that the emitted ions consist of sodium, the two isotopes of potassium, and aluminium; these impurities disappear at high temperatures, when the filaments yield positive ions of their own metal. The temperature variation of the positive-ion current at high temperatures yields values of 6.55 and 6.09 volts, as against 10.88 and 9.26 volts calculated from a simple cyclic process involving the thermionic work function, ionising

potential, and latent heat of evaporation of the metal, for the positive-ion work function of tungsten and molybdenum, respectively. The ions are probably formed as a by-product of an irreversible recrystallisation of the metal. It is shown theoretically that the ions are emitted from the metal and are not formed after a neutral atom evaporates. N. M. BLIGH.

**Reflexion of beams of the alkali metals from crystals.** J. B. TAYLOR (Physical Rev., 1930, [ii], 35, 375—380).—Using a method previously described (cf. A., 1929, 1212), and a detector depending on positive-ion emission, beams of lithium, potassium, and caesium, incident at angles from  $2^\circ$  to  $60^\circ$ , were reflected from crystals of sodium chloride and lithium fluoride in order to study the wave nature of these atoms. With a sensitivity of 0.01% of specular reflexion, no reflexion or diffraction was found. The measured angular distribution of reflected atoms followed closely the cosine law. N. M. BLIGH.

**Concentration of positive ions in the mercury-neon low-voltage arc.** W. DE GROOT (Z. Physik, 1930, 60, 617—623).—The concentration of positive mercury ions inside an oxide spiral in a low-voltage arc in a mixture of neon and mercury vapour has been determined by photographic and photo-electric methods. Both lead to values of the same order, namely,  $1-2 \times 10^{12}$  ions per c.c. It is emphasised that since the fine structure of the resonance line  $1942 \text{ \AA. } (2^2P_{1/2}-1^2S_{1/2}, \text{Hg II})$  is unknown the optically determined concentrations are minimal values.

R. A. MORTON.

**Efficiency of quenching collisions and radius of the excited mercury atom.** S. MROZOWSKI (Z. Physik, 1930, 60, 716—717).—A correction to Gaviola's work (cf. this vol., 125) is suggested.

R. A. MORTON.

**Diffraction of molecular radiation.** I. ESTERMANN and O. STERN (Z. Physik, 1930, 61, 95—125).—When a ray of helium or hydrogen molecules falls on a crystal face of lithium fluoride, split along the cleavage plane, the ray becomes diffracted just as at a grating. The different order spectra were found, and the effects of altering the angle of incidence and orientation of the crystal determined. The de Broglie wave-length is altered by changing the temperature (thus altering the velocity,  $v$ ), and by changing the gas (thus altering the mass of the molecules,  $m$ ). The results appear to be general, holding, not only for the gases and crystal used in the experiment, but for all substances under similar conditions. The wave-length can be calculated if the grating space is taken as the distance between like ions in the crystal by the formula  $\lambda = h/mv$ ,  $h$  being the grating space.

A. J. MEE.

**Effective cross-section and molecular structure in the hydrocarbon series: methane, ethane, propane, butane.** E. BRÜCHE (Ann. Physik, 1930, [v], 4, 387—408).—A new Ramsauer cell is described. The effective cross-section curves for methane, ethane, propane, and butane have been determined. Between 1 and 7 volt $\frac{1}{2}$  the curves are all of the same type, the maximum occurring at 2.6 volt $\frac{1}{2}$  in all cases; the heights, however, increase in order as the series is ascended. On the assumption that the

molecules of the higher hydrocarbons exhibit a rod-like structure, the cross-section being of the methane type, it is possible to calculate the effective cross-section curves from the methane curve with a high degree of agreement with experiment. The separation of carbon nuclei in the molecules is calculated on the above basis to be 2.4  $\text{\AA.}$ , in satisfactory agreement with data from widely different studies.

R. A. MORTON.

**Constitution of oxygen and its employment as the basis of the at. wt. system.** E. MOLES (Anal. Fis. Quím., 1930, 28, 127—136).—Study of the absorption spectra of air appears to show that oxygen is present as a mixture of isotopes, those of at. wt. 18 and 17 being present to the extent of 1 in 1250 and 1 in  $10^4$ , respectively, of the quantity of oxygen of at. wt. 16. The smallness of these proportions no doubt accounts for these isotopes not having been previously discovered, and, further, does not introduce appreciable inaccuracy when oxygen is taken as the basis of the at. wt. system.

H. F. GILLBE.

**At. wt. of the oxygen isotope  $O^{18}$ .** R. MECKE and K. WURM (Z. Physik, 1930, 61, 37—45).—By determining the frequency difference of band spectra lines it is possible to determine the at. wts. of isotopes, or, rather, the ratio of the masses of two isotopes. The method is here applied to oxygen, the atmospheric oxygen bands,  $A$  and  $A'$  groups, of wave-length 7600  $\text{\AA.}$  being used. Assuming the standard at. wt. of oxygen to be 16, that of the isotope  $O^{18}$  is  $17.991 \pm 0.010$ . The accuracy of the method is estimated at 1 in 10,000.

A. J. MEE.

**Elements unidentified or doubtful in the sun.** C. E. ST. JOHN (Astrophys. J., 1930, 70, 160—174; cf. A., 1929, 1419).—From a discussion of available data it is concluded that the presence of the following elements in the sun is not yet definitely established: argon, krypton, neon, radon, xenon, actinium, arsenic, gold, bismuth, fluorine, chlorine, bromine, iodine, mercury, masurium, osmium, phosphorus, protoactinium, radium, polonium, rhenium, tantalum, iridium, selenium, tellurium, thorium, uranium, and the rare earths holmium, illinium, lutecium, terbium, and thulium.

L. S. THEOBALD.

**Radioactivity hypothesis for the "Serono effect" in irradiated phosphatides.** N. GENTILE (Rass. Clin. Terap. Sci. Aff., 1928, 27, 451—457; Chem. Zentr., 1929, ii, 1259).—The rays emitted by phosphatides irradiated with ultra-violet light are similar to radioactive rays but have a smaller penetrating power than X-rays or  $\gamma$ -rays (cf. Serono and Cruto, Boll. Chim. Farm., 1929, 68, 99).

A. A. ELDRIDGE.

**Actinium problem and the at. wt. of protoactinium.** A. VON GROSSE (Z. anorg. Chem., 1930, 186, 38—40).—Polemical against Elsen (A., 1929, 737). It is pointed out that the carrier of element 91 (protoactinium) in the residues from radium refining is zirconium phosphate and not tantalum pentoxide.

A. R. POWELL.

**Scattering of  $\alpha$ -particles by light atoms.** C. MÖLLER (Nature, 1930, 125, 459).—Theoretical.

L. S. THEOBALD.

**Scattering of electrons and  $\alpha$ -particles.** G. BECK (*Nature*, 1930, **125**, 458).—The anomalies which occur in the scattering of  $\alpha$ -particles and in that of electrons by atoms can both be treated similarly by wave-mechanical considerations.

L. S. THEOBALD.

**Anomalous scattering of  $\alpha$ -rays by light atoms.** T. SEXL (*Naturwiss.*, 1930, **18**, 247—248).—The problem is treated on the basis of wave mechanics assuming that the anomalous scattering is due to a polarisation of the nucleus.

A. J. MEE.

**Supernormal  $\alpha$ -particle range for thorium-C.** E. STAHEL (*Z. Physik*, 1930, **60**, 595—598).—It is shown that the  $\alpha$ -particles of abnormally high range are certainly not emitted from thorium-C'', but arise from either thorium-C or thorium-C'.

R. A. MORTON.

**Expulsion of  $\alpha$ -particles by radioactive nuclei.** II. G. I. POKROWSKI (*Z. Physik*, 1930, **60**, 845—849; cf. this vol., 393).—It is assumed that long-range  $\alpha$ -particles are emitted after absorption of  $\gamma$ -radiation. This gives a close relation between the energy of these particles and the distribution of energy represented by the  $\gamma$ -ray spectrum.

A. B. D. CASSIE.

**Unobservable electrons and  $\beta$ -rays.** V. AMBARZUMIAN and D. IVANENKO (*Compt. rend.*, 1930, **190**, 582—584).—The analogy between the emission of  $\beta$ -particles from radioactive nuclei and that of light quanta by atoms is the basis of a theory of  $\beta$ -particles analogous to Dirac's theory of light quanta. The  $\beta$ -emission is due to transition of an electron from a negative ("unobservable") energy level to an ordinary positive level, the diffuse portion of the resulting spectrum being due to expulsion from numerous different negative levels. The probability of emission therefore increases with increase in the energy of intranuclear transition, since electrons are then removed from deeper levels. Difficulties are encountered in explaining the mass of the proton produced simultaneously with the  $\beta$ -particle and in applying Fermi statistics to continuous spectra.

J. GRANT.

**Absolute determination of the energy of the primary  $\beta$ -rays from radium-E.** (FRL.) L. MEITNER and W. ORTHMANN (*Z. Physik*, 1930, **60**, 143—155).—The mean absolute energy of a primary  $\beta$ -particle from radium-E has been determined from calorimetric data, the number of radium-E particles decomposing per second being ascertained from standard preparations calibrated in radium equivalents. The most probable value, 337,000 volts  $\pm$  6%, is in good agreement with the value, 344,000 volts  $\pm$  10%, obtained by Ellis and Wooster (*A.*, 1928, 103). Since the magnetic spectrum of the  $\beta$ -rays extends over the energy range 2— $10 \times 10^5$  volts and the energy obtained by heat measurements corresponds not with the maximum energy but with a very much smaller velocity, the primary  $\beta$ -radiation must leave the atomic nucleus with a continuous energy distribution. This confirms Ellis' assumption that the  $\beta$ -decomposition is not characterised by a defined  $\beta$ -radiation energy. Radium-E does not emit a continuous  $\gamma$ -ray spectrum capable of compensating inhomogeneity of the energy set free by the  $\beta$ -decom-

position. From the calorimetric data on two standardised polonium preparations the mean number of atoms disintegrating per sec. per g. of radium is  $3.68 \times 10^{10}$ .

R. A. MORTON.

**Wave-mechanical character of the  $\beta$ -decomposition.** II—IV. J. KUDAR (*Z. Physik*, 1930, **60**, 168—175, 176—180, 686—689).—II. An explanation of radioactive  $\beta$ -radiation is advanced. The  $\beta$ -particles expelled from radioactive nuclei have high azimuthal quantum numbers. The binding of  $\beta$ -electrons with positive energy occurs in such a way that the repelling action of centrifugal force is annulled by a nuclear attraction which cannot be described more precisely. This suggests a basis for the continuity of primary  $\beta$ -spectra. Since the disintegration on this theory is a radiationless process, the difficulty that no  $\gamma$ -radiation occurs to correspond with the continuous primary  $\beta$ -spectrum appears to be disposed of.

III. The general formula for the disintegration constant has been deduced in relation to the azimuthal quantum number. The  $\beta$ -constants are of the correct order if the azimuthal quantum number  $n = 4$ . For radium-E, radium-D, and uranium- $X_1$  (for which the range of the primary  $\beta$ -spectrum is known) a closer comparison with experiment lends support to the ideas used in the theoretical treatment.

IV. Earlier work is modified and extended.

R. A. MORTON.

**Scattering and absorption of electrons by lead in the superconducting state.** J. C. McLENNAN, J. H. McLEOD, and J. O. WILHELM (*Trans. Roy. Soc. Canada*, 1929, [iii], **23**, III, 269—277).—In an attempt to reconcile the phenomenon of superconductivity with modern views of electrical conductivity, measurements have been made of the coefficient of absorption of a thin film of lead for  $\beta$ -rays from mesothorium (speeds 0.37—0.66 that of light) at a temperature just above the critical superconductivity temperature (7.2° Abs.) and at a temperature 3° below the latter, but no differences were observed. This may be compared with Keesom's observation of diffraction patterns using X-rays with lead both above and below 7.2° Abs., and the absence of change in the lead lattice when the temperature is lowered below this value (4th Int. Cong. Refrig., 1924, 7, 125).

J. W. SMITH.

**Experiments on influencing radioactive disintegration.** F. BÉHOUNEK (*Physikal. Z.*, 1930, **31**, 215—224).—The experiments of Maracineanu (*A.*, 1926, 879; 1927, 710, 807; 1928, 455) on the exposure to sunlight of uranic trioxide ( $UO_3$ ) and pitchblende ( $U_3O_8$ ) and also of lead, copper, and zinc have been repeated. The irradiation did not affect the activity of uranium oxides and no activation of the exposed metals could be detected. Three polonium preparations were studied after exposure at 1332 and 200 m. above and 1350 m. below the sea level. No change in the period could be detected although from the work of Bogoiavlenski (*A.*, 1929, 1358) such a change might be expected.

An experiment on uranium- $X_1$  ( $\beta$ -emission) failed to record any effect of cosmic rays on the disintegration, although the experimental arrangement was unusually sensitive.

R. A. MORTON.



**Standardisation of radium-*E* preparations in "radium equivalents."** E. WALLING (*Z. physikal. Chem.*, 1930, **B**, 7, 74—79).—The activity of the amount of radium-*E* in radioactive equilibrium with radium has been determined by separating radium-*D* (lead) quantitatively from a uranium mineral, allowing sufficient time for the equilibrium quantity of radium-*E* to accumulate, and measuring the activity in a suitably screened  $\beta$ -ray electroscope. M. S. BURR.

**Measurements of atomic disintegration with aluminium, beryllium, iron, and carbon by the recoil method.** H. POSE (*Z. Physik*, 1930, **60**, 156—167).—The yield of atomic disintegrations using aluminium, beryllium, iron, and carbon with polonium as the source of  $\alpha$ -particles has been studied by means of the recoil method. For the three metals a small number of *H*-particles occur in proportions of the order  $5 \times 10^{-8}$  *H*-particles per  $\alpha$ -particle when the angle between primary and secondary radiation is  $135^\circ$  and the absorption 43.3 mm. of air. R. A. MORTON.

**Actinium.** (MME.) P. CURIE (*J. Chim. phys.*, 1930, **27**, 1—8).—A detailed account of the methods employed to obtain preparations of actinium of the greatest possible concentration is given. The methods used for determining the actinium are also described.

F. J. WILKINS.

**[Radioactivity of lead exposed to solar radiation.]** A. SMITS and (MLLE.) C. H. MACGILLAVRY (*Compt. rend.*, 1930, **190**, 635—637).—The actual measurements of Maracineanu (*A.*, 1927, 710) have been confirmed, but her conclusion that the radioactivity of solarised lead is due to the sun is considered unproved. Spark and arc spectrum methods cannot be used with certainty for the spectroscopic detection of small traces of mercury in lead on account of the volatility of the former metal, and a method is described in which the gases and volatile matter are expelled from the lead in a vacuum by heat and cooled to  $-190^\circ$  to separate gases such as helium and nitrogen. Mercury lines were always found in lead spectra unless the metal had been subjected to a special process of purification (*A.*, 1928, 933).

J. GRANT.

**[Radioactivity of lead exposed to solar radiation.]** H. DESLANDRES (*Compt. rend.*, 1930, **190**, 637—639).—Comments on the work noted in the preceding abstract and that of Boutaric and Roy (*this vol.*, 393).

J. GRANT.

**Radioactivity acquired by materials exposed to the action of atmospheric agents.** A. LEPAPE and M. GESLIN (*Compt. rend.*, 1930, **190**, 676—678).—A plate and disc of lead (1.5 mm. thick), zinc, a slate, and atmospheric dust collected from a gutter were examined electroscopically, and all were shown to possess an  $\alpha$ -radiation absorbed by 0.05 mm. of aluminium, that of the lead (inner face), the tile, and the zinc (outer face) being equal, whilst that of the outer face of the lead (exposed to the sun) was about four times as great (*cf.* Smits and Macgillavry, above). The dust had the least activity. Examination of scrapings from the specimens showed that the seat of activity was on a surface layer 0.1 mm. thick, and the phenomena are due probably to the presence in this layer, as impurities, of radio-elements removed

from the atmosphere as dust or by the action of rain or the electric field of the atmosphere. J. GRANT.

**Cosmic radiation and radioactivity.** L. R. MAXWELL (*J. Franklin Inst.*, 1929, **207**, 619—628).—The radioactivity of a plate carrying an active deposit of polonium was measured at a depth of 1150 ft. at the bottom of a zinc mine, and at the surface. The rock was mainly willemite, and its absorption for cosmic radiation was equivalent to 3200 ft. of water. The rate of disintegration of the polonium remained constant to within 1% and it is concluded that cosmic radiation has no effect. It is also shown mathematically that if each cosmic ray striking the plate were to cause the disintegration of 1 atom of polonium, this could produce only 0.1% of the observed disintegration. C. J. SMITHELLS.

**Variation of the residual ionisation with pressure at different altitudes, and its relation to cosmic radiation.** W. F. G. SWANN (*J. Franklin Inst.*, 1930, **209**, 151—200).—The residual ionisation in air under pressures (*P*) up to 1000 lb./in.<sup>2</sup> has been determined at (i) Pike's Peak (14,000 ft.), (ii) Colorado Springs (6000 ft.), and (iii) New Haven (sea level), in a spherical iron vessel, walls 2.5 cm. thick, shielded by 2 in. of lead, placed in similar chambers at each place. The ionisation (*I*) at 100 and 1000 lb. was at (i) 38.5 and 127.0, respectively, at (ii) 17.4 and 57.3, and at (iii) 11.4 and 39.5, whilst  $dI/dP$  decreased at (i) from 0.2780 under 100 lb. pressure to 0.0303 under 1000 lb., at (ii) from 0.101 to 0.0145, and at (iii) from 0.0664 to 0.0109. The results are discussed, and shown to be definitely inconsistent with cosmical radiation of one frequency, but consistent with an infinite number of different pairs of frequencies, or of two definite frequencies combined with an infinite number of possibilities as regards a third. C. A. SILBERRAD.

**History of cosmic rays.** R. A. MILLIKAN (*Physikal. Z.*, 1930, **31**, 241—247).—A discussion of the priority of discoveries in the history of cosmic rays.

W. E. DOWNEY.

**Radiometer forces and out-gassing.** T. BRINGS (*Z. Physik*, 1930, **60**, 759—775).—The dependence of radiometer action on the external conductivity of the illuminated and dark faces of a vane was investigated. When the dark side has greater conductivity, the diminution in radiometer action, compared with that of a vane of equal surface conductivities, increases with decreasing pressure, in agreement with Stern's theoretical results (*ibid.*, 1926, **39**, 341). When the direction of illumination is reversed, the radiometer action shows an increase, which does not disappear with increasing pressure. This is not in agreement with theory, but implies that gas adsorbed on the surface may change its external conductivity.

A. B. D. CASSIE.

**Electron affinities of the elements.** J. H. BARTLETT, jun. (*Nature*, 1930, **125**, 459—460).—An approximate extrapolation method to determine which elements have a positive electron affinity and to predict the approximate position of any lines of the electron affinity spectrum is outlined. Using this method, the electron affinity of hydrogen is 1.4 volts, that of helium is negative, indicating that He-

is unstable. For lithium it may be positive, decreasing to beryllium, increasing to carbon, decreasing to nitrogen, and increasing to about 3.5 volts for fluorine. No discrete electron affinity spectrum for  $H^-$  or  $Cl^-$  appears to be possible. L. S. THEOBALD.

**Electron affinity of the hydrogen atom according to wave mechanics.** E. A. HYLLERAAS (Z. Physik, 1930, 60, 624—630).—Methods applicable to the calculation of ionisation potentials of helium,  $Li^+$ ,  $Be^{++}$ , etc. also suffice for calculating the electron affinity of the hydrogen atom, i.e., the energy of formation of a  $H^-$  ion from a hydrogen atom and an electron. The value  $0.700 \pm 0.015$  volt or 16 kg.-cal. per mol. is arrived at. R. A. MORTON.

**Mass defect curve and nuclear constitution.** G. GAMOW (Proc. Roy. Soc., 1930, A, 126, 632—644).—Certain conclusions are deduced from a model of a nucleus built up from  $\alpha$ -particles in a manner similar to a water drop held together by surface tension. Attractive forces which overcome at short distances the forces of repulsion between the  $\alpha$ -particles are assumed, and the mutual potential energy of two  $\alpha$ -particles at a distance  $r$  apart is written  $U(r) = +4e^2/r - f(r)$ , the function  $f(r)$  decreasing very rapidly with distance. The potential energy of a particle inside a space in which the others are distributed almost uniformly is given by the integral  $u = -\int_a^\infty f(r) \cdot 4\pi r^2 \rho dr$ , where  $\rho$  is the density of the particles and  $d$  the smallest distance between them. This need be taken only up to a distance  $r^*$ , which corresponds with the sphere of molecular action in the theory of capillarity, and such an assemblage of  $\alpha$ -particles will be like a drop of water where the inside pressure due to the kinetic energy of quantised motion is in equilibrium with the forces of surface tension which tend to diminish the radius of the drop. All the  $\alpha$ -particles in the nucleus are in the same state with quantum number unity, and it is shown that the increase of drop radius with the number of  $\alpha$ -particles is given by

$r_0 \sim (Am/h^2)^{1/(n-3)} N_\alpha^{(n-1)/3(n-3)} \sim R_0 \cdot N_\alpha^{(n-1)/3(n-3)}$ , where  $r_0$  is the radius of a nucleus consisting of  $N_\alpha$   $\alpha$ -particles. This is in accordance with the observations on anomalous  $\alpha$ -scattering for light elements and the rate of  $\alpha$ -disintegration for heavy ones. By taking into account the coulomb repulsive forces, which are important for heavy nuclei, an expression is obtained for the whole nuclear energy, and a theoretical curve for the mass defect is compared with that obtained experimentally by Aston. Agreement is found in the region of light elements, but the curve rises too soon to the zero axis with increasing nuclear mass. These results are discussed with special reference to the possible radioactive properties of the elements. The theory suggests the formation of a number of radioactive elements of at. wt. between 120 and 200, and the failure to detect these experimentally is considered to be due to the fact that radioactive elements in this region have necessarily a very short life. L. L. BIRCUMSHAW.

**Continuous absorption.** J. A. GAUNT (Proc. Roy. Soc., 1930, A, 126, 654—660).—Mathematical. Stellar opacities, calculated by applying an adaptation

of Kramers' classical theory of X-ray emission, are very much smaller than Eddington's estimates from astronomical observations. The present paper summarises an attempt to discover whether the quantum theory yields a value nearer to that of Eddington. The results show that the classical theory cannot be far wrong in cases of importance in astrophysics. L. L. BIRCUMSHAW.

**Interaction of electric charges.** A. S. EDDINGTON (Proc. Roy. Soc., 1930, A, 126, 696—728).—The corrected value of the constant  $hc/2\pi e^2$ , previously predicted as 136 (A., 1929, 231), is now found to be 137. The 136 symmetrical degrees of freedom are a generalisation of rotations in space and are relative to the frame of reference employed, whilst the odd degree of freedom represents alteration of an absolute quantity, viz., the distance between a pair of electrons. The distinction between time and space is traced to the transformation properties of matrices of Dirac's type. It appears probable that when a number of electric charges form a perfectly rigid system, 1/137 of their mass is lost. The ratio 136/137 agrees approximately with the reduction of mass of the proton when it enters into a nucleus, and 137/136 is, in fact, intermediate between the at. wt. of hydrogen expressed in terms of  $He=4$  and of  $O=16$ .

L. L. BIRCUMSHAW.

**New regularity in the list of existing nuclei.** H. A. BARTON (Physical Rev., 1930, [ii], 35, 408—414; cf. Beck, A., 1928, 1301).—For elements below atomic number 61 a new regularity is observed in which most of the known nuclei fall into three clusters, each characterised by a two-dimensional symmetry. Plotting the nuclei as points with ordinates  $P$  and abscissæ  $E$  indicating the number of protons and electrons respectively in the nucleus, there exists for each cluster a centre  $(P, E)$  such that if there is a nuclear type  $(P-X, E-Y)$  there is, in general, also a symmetrical type  $(P+X, E+Y)$ . From this rule undiscovered isotopes are predicted, and a possible physical interpretation of the regularity is suggested. N. M. BLIGH.

**Absorption spectrum of carbon disulphide in the near ultra-violet.** F. A. JENKINS (Astrophys. J., 1929, 70, 191—193).—The absorption bands of carbon disulphide are very complex and difficult to analyse. A number of weaker bands with sharp heads and shaded toward the violet has been observed; they appear to correspond with the  $P$ - and  $R$ -branches of a band in the spectrum of a diatomic molecule with the source at a low temperature. A strong sequence with heads  $\nu=29,336.7, 29,081.3, 28,815.9, 28,543.5, 28,270.6$ , and  $27,986.9$   $cm^{-1}$  is particularly prominent. Wilson's analysis of carbon disulphide bands (A., 1929, 1214) is considered incorrect. L. S. THEOBALD.

**Absorption of ultra-violet light by methoxybenzoic acids.** A. BORYNIEC and L. MARCHLEWSKI (Bull. Acad. Polonaise, 1929, A, 630—635; cf. A., 1929, 1362).—The absorption spectra of carefully purified  $o$ - and  $p$ -methoxybenzoic acid in aqueous and alcoholic solution respectively were examined. Beer's law holds for each solution. Lines are tabulated and molecular extinction curves are given, showing

band maxima at 2850 and 2300 for the *o*- and at 2535 Å. for the *p*-compound. The curves are compared with those of salicylic and *m*- and *p*-hydroxybenzoic acids. N. M. BUGH.

**Ultra-violet absorption spectrum of aniline vapour.** J. SAVARD (Compt. rend., 1930, 190, 678—681).—The spectrum includes 185 lines and bands between  $\lambda$  2980 and 2632 Å., more intense lines beyond  $\lambda$  2813 Å., and a continuous absorption zone from  $\lambda$  2632 Å., the positions of which may be calculated from the equations given. The deformability and characteristic constants of the aniline molecule are comparable with those of other benzene derivatives, but the amino-group is responsible for lower energies of excitation of the bands  $\nu_1$  34,330 and  $\nu_2$  34,821, whilst the spectrum is also unique in that there is a continuous absorption zone corresponding with dissociation or ionisation of the molecule. The ratios of the variations in molecular vibrational energy ( $\alpha_0 + \beta_0$ ) of benzene, toluene, phenol, and aniline to the heats of combustion are constant (1.42—1.48). J. GRANT.

**Absorption spectra of salt solutions. I. Absorption spectra due to the halogens and some metallic ions.** S. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 12, 230—250).—Cations can be divided into two groups according as they do, or do not, show absorption in the visible and ultra-violet regions. The former group have variable valencies and are unstable in solution. The spectra correspond with the next to the lowest terms of the line spectra given by the gaseous ions of the corresponding elements. Spectra due to non-hydrated ions have been observed in an aqueous solution of the salts which undergo hydrolysis strongly; in the acid solutions of the same salts, "affinity spectra" (i.e., halogen anion absorption spectra) due to the solvated ions have been observed.

W. E. DOWNEY.

**Automatic recording of extinction curves of absorption spectra.** R. BRDIČKA and M. PAVLÍK (Coll. Czech. Chem. Comm., 1930, 2, 120—128).—A mechanical device is described and illustrated for setting in continuous vertical motion the inner tube of Baly's absorption vessel in such a manner that the thickness of the absorbing layer varies exponentially with the time and for continuously photographing the absorption spectra on a uniformly moving plate driven by a synchronous electric motor. The photographs obtained represent typical extinction curves and the apparatus can also be used for the determination of molecular extraction coefficients. A. R. POWELL.

**Colours of inorganic salts.** C. P. SNOW and F. I. G. RAWLINS (Nature, 1930, 125, 349—350).—The suggestion of Saha (this vol., 272) concerning colour in organic compounds receives support from work now being done on the spectra of crystals of chromium salts. The somewhat narrow bands in the red and blue for a number of hydrated and complex salts are due to  $\text{Cr}^{+++}$ , but the broad, structureless region of absorption from the green to the orange occurring in the spectra of all hydrated chromic salts appears to be due to co-ordination electrons, and is

similar in position to the only band given by the  $\text{CrO}_4$  and  $\text{Cr}_2\text{O}_7$  ions. Until the rôle of the co-ordinating electrons is elucidated the colour of the compounds of the transitional elements cannot be fully explained. The first cause predicted by Saha can usually be predicted, but the second, due to the formation of complex ions, is unknown.

L. S. THEOBALD.

**Peculiar luminous reaction of sulphuric acid.** A. BALANDIN (Z. anorg. Chem., 1930, 187, 398—400).—If a vessel filled with water and wetted with sulphuric acid on the outside is held in the hot part of a Bunsen flame, a bluish-violet luminescence is observed. It is suggested that the phenomenon is due to the reduction of the sulphuric acid to elementary sulphur by atomic hydrogen in the flame and subsequent oxidation of the sulphur. A "cold-warm" wall appears to be necessary, although the inside cold temperature may be as high as 290°. A similar, but less marked, phenomenon was observed with phosphoric acid, the luminescence being greenish-yellow. Sulphurous acid behaves similarly to sulphuric acid, and ammonium sulphide gives first a yellow luminescence and then the same blue as the two sulphur acids. The yellow luminescence is attributed to negatively-charged and the blue to positively-charged sulphur. M. S. BURR.

**Ozone in luminescence.** E. L. NICHOLS and F. G. WICK (Proc. Nat. Acad. Sci., 1930, 16, 32—36).—The effect of ozone on substances rendered thermoluminescent by X-rays has been determined. In all cases (calcium sulphate with a trace of manganese as activator, cadmium phosphate, various calcites and fluorides, zinc sulphide, calcium sulphide, and sodium chloride) the thermoluminescence was reduced by the ozone. The effect in the first three cases was much more pronounced than in the others. The result is due probably to oxidation by the ozone of the reduction product formed by the action of the X-rays. The slow oxidation of this product by ordinary oxygen produces the normal thermoluminescence. Similar effects have been found with substances rendered thermoluminescent by cathode-ray bombardment. F. G. TRYHORN.

**Photodichroism and photoanisotropy. VI. Colour selectivity (?) of visual purple.** F. WEIGERT and M. NAKASHIMA (Z. physikal. Chem., 1930, B, 7, 25—69).—Gelatin layers containing the visual purple of frogs, and thus forming an artificial retina, have been investigated by methods previously described (A., 1929, 1248). Photodichroic effects similar to those observed in photochloride and dye systems have been obtained. The dichromatic colour selectivity is extraordinarily sharp, but the form of the curve gradually changes as a result both of increasing excitation of the artificial retina by light and of keeping in the dark until, in the latter case, it corresponds finally with the absorption spectrum of visual purple. These results refer to the visual purple of summer frogs. Anomalous results were obtained with the visual purple of winter frogs and of fish. The results are discussed in relation to the known properties of visual purple and also in relation to colour vision. M. S. BURR.

**Heat radiation or resonance radiation of carbonic acid?** W. GERLACH (Ann. Physik, 1930, [v], 4, 571—574).—An experiment is described which proves that radiation absorbed by carbon dioxide is not transformed into resonance radiation but into heat energy. A bolometer method was used. A. J. MEE.

**Extinction of sodium fluorescence by means of foreign gas.** J. G. WINANS (Z. Physik, 1930, 60, 631—641).—Sodium iodide and sodium bromide vapours have been irradiated with ultra-violet light and the intensity of the sodium fluorescence has been studied in relation to the pressure of added gases (bromine, carbon dioxide, nitrogen, hydrogen, argon, and neon-helium mixtures). The intensity is markedly reduced by means of bromine and carbon dioxide, which react with sodium vapour, whilst hydrogen and nitrogen, which are not reactive towards sodium vapour, had little effect on the intensity. If it be assumed that every collision between an excited sodium atom and a molecule reduces the intensity, the sum of the effective radii ( $\sigma$ ) for sodium ions colliding with different gas molecules can be deduced. Within the limits of error,  $\sigma$  with molecular hydrogen is independent of the velocity of the sodium ions. When the added gas is bromine  $\sigma$  is greater for lower velocities than for higher velocities. The values for  $\sigma$  using hydrogen and nitrogen are much smaller than those given by Mannkopf (A., 1926, 557).

R. A. MORTON.

**Thermoluminescence of glass exposed to light.** R. E. NYSWANDER and B. E. COHN (J. Opt. Soc. Amer., 1930, 20, 131—136).—Some kinds of glass which have been turned violet by prolonged exposure to bright sunlight are thermoluminescent if heated to above 100°. Glass freshly exposed to sunlight shows luminescence before colour is produced. This effect has been investigated in pure zinc borate glasses containing traces of barium, calcium, strontium, magnesium, manganese, aluminium, nickel, cobalt, chromium, silver, cerium, thallium, and thorium; the most intensely luminescent were those containing thorium, cerium, silver, chromium, cobalt, and manganese. The rate of increase of luminescence with time of irradiation, both with sunlight and a carbon arc, decay after excitation, and effect of concentration have been investigated.

C. W. GIBBY.

**Reversible oxidation in luminescence.** E. L. NICHOLS (J. Opt. Soc. Amer., 1930, 20, 106—114).—Evidence is adduced in support of the hypothesis that luminescence is always an oxidation process.

C. W. GIBBY.

**Activators in cando-luminescence.** E. L. NICHOLS and L. J. BOARDMAN (J. Opt. Soc. Amer., 1930, 20, 115—130).—The cando-luminescence of thorium oxide on heating with a hydrogen flame has been investigated. It is subject to fatigue, the substance gradually yielding less readily to alternate oxidation and reductions. Traces of the oxides of copper, manganese, chromium, and the rare earths, which enhance the fluorescence of certain solids, also increase the luminescence of incandescent oxides. The activator must be in solid solution, and its effect passes through a maximum at a characteristic temperature.

C. W. GIBBY.

**Gas space luminescence in a heterogeneous reaction.** L. FROMMER and M. POLANYI (Z. physikal. Chem., 1930, B, 6, 371—381).—The action of chlorine on aluminium in the presence of copper gives rise to a luminescence in the space surrounding the metal. The band spectrum of the light emitted was identified with that of cuprous chloride. The action of chlorine on aluminium gives rise to an active substance, which in the presence of chlorine excites the luminescence of cuprous chloride. Under certain conditions the luminescence may appear at a considerable distance from the metal. The active substance is probably a subchloride of aluminium ( $\text{AlCl}_2$ ).

J. A. V. BUTLER.

**The two normal states of the NO molecule.** M. LAMBREY (Compt. rend., 1930, 190, 670—672).—The fact that the optical densities of a layer of nitric oxide of constant thickness for the  $\beta$ - and  $\gamma$ -bands are proportional to the pressure,  $p$  (cf. this vol., 272), and to  $p^{1/31}$ , respectively, is considered the first spectroscopic verification of the existence of two normal  $^2P$  states of the nitric oxide molecule (cf. Pogány and Schmid, A., 1929, 740). The former state is characteristic of the molecule itself, whilst the latter is due to collision of NO molecules with one another or with other molecules, and has a mean life of  $1.5 \times 10^{-9}$  sec.

J. GRANT.

**New measurements in the fourth positive CO bands.** R. S. ESTEY (Physical Rev., 1930, [ii], 35, 309—314; cf. Birge, A., 1927, 184).—The part of the fourth positive system of carbon monoxide between 1970 and 2800 Å. was remeasured and tabulated, with 16 newly-observed bands. The equation deduced for the band heads gives  $D' = 12.00$  and  $D'' = 11.17$  volts for the heat of dissociation. Intensities are tabulated and intensity distribution curves calculated, using Morse's function (cf. A., 1929, 975). Agreement with Snow and Rideal's value (cf. *ibid.*, 1363) for the moment of inertia for the normal state  $I = 15.0 \times 10^{-40}$  g.-cm.<sup>2</sup> is obtained. The quantum assignment of Asundi's infra-red electronic bands is revised (cf. *ibid.*, 865).

N. M. BLIGH.

**Fine structure of the beryllium fluoride bands.** F. A. JENKINS (Physical Rev., 1930, [ii], 35, 315—335; cf. A., 1927, 916).—Using a cored carbon arc at atmospheric pressure new wave-length measurements were made of the rotational lines of the BeF bands in the regions  $\lambda\lambda$  3009.5—3026.3, 2908.9—2927.8, and 3126.1—3140.8, which include all the stronger lines of the (0,0), (1,0), and (0,1) bands. Wave-numbers and visual intensity estimates are tabulated for the lines in the six branches of each band. Rotational terms are analysed, and the structure is found to be that characteristic of a  $^2\Pi \rightarrow ^2\Sigma$  electronic transition. Equations to represent all the lines of a band, and values for the molecular constants, are deduced.

N. M. BLIGH.

**Infra-red emission bands under high dispersion.** M. NEUNHOEFFER (Ann. Physik, 1930 [v], 4, 352—356).—The intensity curve for the water band (hydrogen flame) at  $1.8\mu$  has been determined in emission, using a reflexion grating. The fine structure is similar to that already recorded for the  $2.7\mu$  band

(A., 1929, 975). Hettner's analysis does not account satisfactorily for the results. R. A. MORTON.

**Vibration spectrum of the ammonia molecule.** J. W. ELLIS (J. Franklin Inst., 1929, 208, 507—519).—Measurement of the infra-red absorption spectrum of ammonia in carbon tetrachloride and aqueous solutions shows that the absorption bands due to the ammonia in such solutions are quite analogous to those observed with the gas, but that the positions of certain bands are modified by the solvent. The whole of the near infra-red and visible absorption spectrum is interpreted on the basis of three fundamental vibrations of the molecule, viz., the 10.55, 6.132, and 2.916  $\mu$  bands. The band near 3  $\mu$  is double and is supposed to consist of this third fundamental and the first overtone of the 6.132  $\mu$  fundamental, with the centre of its  $Q$  branch near 2.998  $\mu$ . The bands at 1.51, 1.035, 0.795, 0.652, and 0.556  $\mu$  appear to represent overtones of the 2.916  $\mu$  band. They are expressed by the equation  $\nu_n = 97 + 3400n - 70n^2$  cm.<sup>-1</sup>, and are believed to arise from the anharmonic vibrations within the NH linking, because the energy of this oscillator (5.1 equivalent volts) is of the same order as that calculated chemically for the NH linking (3.99 equivalent volts) and also because this series of bands persists through the spectra of primary and secondary amines with only systematic minor shifts. The constant term 97 cm.<sup>-1</sup> is attributed to a change in the potential energy of the molecule due to slight internuclear rearrangement before or while absorption by vibration takes place. There is no evidence of overtones of the 10.55  $\mu$  band. The frequencies of the overtones of the 6.132  $\mu$  fundamental are slightly greater than even multiples of the fundamental frequency. This fundamental is also associated with the NH linking, since it persists in the spectra of many organic ammonia derivatives. There is one possible difference band at 4.02  $\mu$ , due to a positive change in the 10.55  $\mu$  vibration and a simultaneous negative change in the 2.196  $\mu$  vibration. This is consistent with observations on the Raman effect. J. W. SMITH.

**Search for new bands in the near infra-red spectra of CN, N<sub>2</sub><sup>+</sup>, and BeF.** R. K. ASUNDI (Indian J. Physics, 1930, 4, 367—384).—On the basis of Mulliken's classification of the molecules CN, N<sub>2</sub><sup>+</sup>, and BeF as similar one-valency electron emitters an unsuccessful attempt was made to discover, in the near infra-red, band systems corresponding for BeF with the transition 2<sup>2</sup>S → 1<sup>2</sup>S (known for all the other molecules of this class), for N<sub>2</sub> with the transition 2<sup>2</sup>P → 1<sup>2</sup>S (also known for the other molecules), and for CN, N<sub>2</sub><sup>+</sup>, and BeF with the transition 2<sup>2</sup>S → 2<sup>2</sup>P (known for BO). Some new bands were obtained with BeF, but with the dispersion used they were too close together to be measured. The values obtained for the known red CN bands are tabulated and a reason is given for selecting the 10,938.0 cm.<sup>-1</sup> band as the real 0—0 band instead of the hitherto accepted 14,433.1 band. In explanation of the negative results it is mentioned that Mulliken's later work shows that the molecular levels of CO<sup>+</sup> and BO are to be distinguished from those of N<sub>2</sub><sup>+</sup> and CN. H. A. JAHN.

**Black bodies in the extreme infra-red.** C. H. CARTWRIGHT (Physical Rev., 1930, [ii], 35, 415—420).—Using hot glass in conjunction with a cold thin glass shutter the absorbing power of 25 materials painted on the receiver of a thermocouple was tested for radiation of wave-lengths near 4  $\mu$  and greater than 50  $\mu$ . White lead, litharge, red phosphorus, powdered glass, copper sulphide, and celestite were found to be the best absorbers. N. M. BLIGH.

**Improved technique for excitation of the Raman effect with special reference to gases.** R. W. WOOD (J. Franklin Inst., 1929, 208, 617—626).—An account of work already published (cf. A., 1929, 627, 741). C. A. SILBERRAD.

**Raman lines of mercury in arc improbable.** R. W. WOOD (Nature, 1930, 125, 464).—No relative enhancement of the lines of the spectrum of the mercury arc could be detected (cf. Venkatesachar and Sibaiya, this vol., 14). L. S. THEOBALD.

**Raman effect in liquid  $\alpha$ - and  $\beta$ -hydrogen.** J. C. McLENNAN, H. D. SMITH, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 247—253).—In addition to the three Raman lines observed previously (McLennan and McLeod, A., 1929, 378), three other lines have been observed in the Raman spectrum of liquid hydrogen, viz., 4106 and 4146 Å., excited by the mercury 4047 line, and 4293 Å., excited by the 4358 line. The 4427 and 4472 Å. lines correspond with the 0 → 2 rotational transition in  $\alpha$ -hydrogen and the 1 → 3 rotational transition in  $\beta$ -hydrogen, respectively, and the ratio of the intensities of these lines has been employed to determine the ratio of the amounts of  $\alpha$ - and  $\beta$ -hydrogen present. As the liquid hydrogen was kept, the percentage of the  $\alpha$ -modification gradually increased. The six Raman lines observed with liquid hydrogen correspond with five different transitions, all of which have been observed with gaseous hydrogen (Rasetti, A., 1929, 1127). Only one is an anti-Stokes line. J. W. SMITH.

**Raman effect for solutions of sulphur dioxide.** W. D. HARKINS, D. M. GANS, and H. E. BOWERS (Nature, 1930, 125, 464).—Modified lines characteristic of the sulphur dioxide molecule appear in the scattering of solutions of this gas in water, benzene, and carbon tetrachloride. The most prominent lines are at 4588 and 4238 Å. excited by 4358 and 4047 Å., respectively, of the mercury arc. The shift indicates an infra-red wave-length of 8.8  $\mu$ . L. S. THEOBALD.

**Raman effect in liquefied gases.** J. B. AUSTIN (Nature, 1930, 125, 464).—The significance of the two new lines (displacements 321 and 338 mm.<sup>-1</sup>) found by Daure (this vol., 14) in the spectrum of liquid ammonia is discussed. It is suggested that the outer lines represent a scattering of the light which gives the central line (displacement 330 mm.<sup>-1</sup>) by complex or associated molecules; a secondary Raman effect in the liquid may thus occur. L. S. THEOBALD.

**Raman effect of water.** P. PRINGSHEIM and S. SCHLIVITCH (Z. Physik, 1930, 60, 581—585).—By subjecting water to the light from a mercury arc three double Raman bands occur in the visible and

a constant frequency difference of  $\Delta\nu \sim 3400 \text{ cm.}^{-1}$  indicates that they are excited by the three mercury lines 3655, 4047, and 4358 Å. The relative intensity distribution of the three Raman bands is unaffected by rise of temperature or by the introduction of soluble salts (cf. Dadiou and Kohlrausch, A., 1929, 976; Meyer, *Physikal. Z.*, 1929, 30, 170).

R. A. MORTON.

**Raman effect. V. Raman spectrum of organic substances (C:O and C:C double linkings; halogen derivatives).** A. DADIEU and K. W. F. KOHLRAUSCH (*Monatsh.*, 1930, 55, 58—84).—The Raman spectra of ethyl alcohol, ethyl ether, propaldehyde, formamide, acetamide, ethyl cyanoacetate, sodium and ammonium acetates, chloroform, methylene and butyl chlorides, hexachloroethane, tetrachloro- and tetrabromo-ethane, dichloro- and dibromo-ethane, ethyl and propyl chlorides and bromides, di-, tri-, and tetra-chloroethylene, allyl chloride, bromide, and thiocyanate have been determined and the results tabulated. The effect of constitutional factors on the characteristic frequency is discussed and the results for different types of linking, including  $\text{X-CH}_2\text{-X}$ ,  $\text{CH}_2\text{-C}$ ,  $\text{H-CX}_3$ ,  $\text{CH}_2\text{:C}$ ,  $\text{H-C}_6\text{H}_5$ ,  $\text{C:CHX}$ ,  $\text{C:C}$ ,  $\text{C:O}$ , and  $\text{C:N}$ , are given.

A. I. VOGEL.

**Raman spectra of some organic liquids.** J. ÔKUBU and H. HAMADA (*Sci. Rep. Tôhoku*, 1929, 18, 601—608).—The Raman spectra of pyridine, anisole, hexane, and picoline have been measured. There is a close similarity between the spectra of pyridine and picoline, of anisole and toluene, and of hexane and pentane.

O. J. WALKER.

**Raman effect and infra-red spectrum for carbon tetrachloride and silicon tetrachloride.** C. SCHAEFFER (*Z. Physik*, 1930, 60, 586—594).—Marvin's interpretation (A., 1929, 974) of the infra-red absorption and Raman spectra of carbon tetrachloride and silicon tetrachloride as based on six characteristic frequencies in each case is rejected and replaced by a classification based on four bands, viz., for carbon tetrachloride at 46.07, 31.74, 21.83, and 13.21, 12.61  $\mu$  (doublet) and for silicon tetrachloride at 65.78, 47.62, 23.47, and 16.67  $\mu$ . Combinations of these account for the infra-red absorption maxima and the Raman lines with considerable accuracy. The spectra of titanium tetrachloride and stannic chloride seem to agree with analogous classifications.

R. A. MORTON.

**Raman effect with liquid methane.** J. C. McLENNAN, H. D. SMITH, and J. O. WILHELM (*Trans. Roy. Soc. Canada*, 1929, [iii], 23, III, 279—282).—In addition to the lines observed by Daure (A., 1929, 865), another line has been observed in the Raman spectrum of liquid methane, of wave-length 4621 Å. and excited by the mercury line 4047 Å., thus representing a frequency shift of 3071  $\text{cm.}^{-1}$  in the direction of longer wave-lengths. A Raman band, also excited by the 4047 Å. line, was also observed between 4596 and 4616 Å. On analysis this appeared to consist of four components, corresponding with frequency shifts of 2953, 2999, 3023, and 3047  $\text{cm.}^{-1}$ , respectively.

J. W. SMITH.

**Raman effect in some crystals.** H. NISI (*Proc. Imp. Acad. Tokyo*, 1929, 5, 407—410).—The Raman

spectra of beryl and tourmaline exhibit several lines nearly coincident with those of quartz; tourmaline, in common with beryl, probably contains the  $\text{SiO}_4$  group. Only one Raman line has been observed with dauburite on account of its powerful luminescence, and two new quartz lines have been discovered. Gypsum exhibits two strong lines, corresponding with the water of crystallisation and the sulphate group, but the latter does not coincide with the corresponding line in aqueous solutions of sulphates, whereas with barytes the lines coincide. Both crystals exhibit two other lines which are found also in the spectra of sulphate solutions. The variations of intensity of the Raman lines of sulphates follow a course parallel with that of the corresponding infra-red reflexion maxima.

H. F. GILLBE.

**Raman spectra of crystalline powders.** P. KRISHNAMURTI (*Nature*, 1930, 125, 463).—The difficulty of a continuous background overpowering all but the strongest Raman lines (cf. Bär, A., 1929, 1361) has been avoided by running the mercury arc at a lower temperature and by interposing a light filter (a concentrated solution of didymium chloride) between the arc and the illuminated solid. Some of the Raman lines change position when benzophenone is fused. Results for 18 inorganic nitrates are summarised. With nitrate crystals belonging to the cubic system the frequency shift is about the same as for nitric acid. The Raman line corresponding with a remote infra-red frequency appeared prominently in lithium and mercurous nitrates, and could be detected with sodium, calcium, barium, zinc, silver, and mercuric nitrates.

L. S. THEOBALD.

**Relation between intensity and scattering angle for molecular light scattering.** G. I. POKROWSKI (*Z. Physik*, 1930, 60, 850—855).—It is shown that scattering by a great depth of molecules should give an unsymmetrical distribution of scattered light about the primary beam. This theoretical result is verified by data on light scattered by the earth's atmosphere.

A. B. D. CASSIE.

**Grimm's law and the ionisation potentials of water and ammonia molecules.** R. GRINFELD (*Physikal. Z.*, 1930, 31, 247—252).—The ionisation potentials of water and ammonia by Lenard's method are  $18.0 \pm 0.5$  volts and  $16.1 \pm 0.5$  volts, respectively. These values are in good agreement with those for neon and methane and thereby confirm Grimm's law, according to which water, ammonia, and methane are "pseudo-neon atoms." Using Franck and Hertz' method, the following excitation potentials were found for water, viz., 6.4, 19.6, and 25.5 volts and probably 14.0 and 20.1 volts. It is concluded that 6.4 volts is the resonance potential of the water molecule.

W. E. DOWNEY.

**Electrical properties of molecules.** A. H. W. ATEN (*Chem. Weekblad*, 1930, 27, 98—101).—Association in organic liquids cannot be regarded as analogous to compound formation, but resembles rather a kind of steric hindrance caused by limitation of the freedom of orientation of the molecules; the conditions obtaining resemble those prevailing in concentrated solutions of strong electrolytes.



An ionising solvent is one wherein the dipoles are situated on or near the surface of the molecules in such a manner that both poles are able to exert their influence on the solute ions; this hypothesis is in accordance with the observed fact that compounds having a simple molecular structure, such as ammonia and water, usually form the best ionising solvents.

H. F. GILLBE.

**Dielectric constants of water at various temperatures.** A. C. CUTHBERTSON and O. MAASS (J. Amer. Chem. Soc., 1930, **52**, 483—489).—An adaptation of the method of Williams and Krehma (A., 1926, 1000) for dielectric constant measurements is described, involving the use of a dielectric cell constructed on the principle of a variable condenser, lead and end effects being thereby eliminated. The following values have been obtained for dielectric constants at 25° on the basis air=1: chloroform, 5.61; nitrobenzene, 35.20; ether, 4.02; benzene, 2.28. The dielectric constant of water was studied over the temperature range 0—75°. From 25° to 75° the dielectric constant decreases linearly with the temperature, the temperature coefficient being -0.258. Below 25° it decreases more rapidly with temperature. The value at 0° is 84.4, at 25° 75.4, and at 75° 62.9. At 18°, the observed dielectric constant (77.0) is lower than the value generally accepted. The wave-length used in these measurements is 200 metres. The molecular polarisability at various temperatures is calculated. The Debye equation has no significance for a substance of this kind.

J. W. SMITH.

**Hydrogen peroxide. VII. Dielectric constants, refractive indices, and ionising power of hydrogen peroxide and its aqueous solutions.** A. C. CUTHBERTSON and O. MAASS (J. Amer. Chem. Soc., 1930, **52**, 489—499).—The dielectric constants of hydrogen peroxide solutions have been determined at 0° for solutions containing 0—99.45% H<sub>2</sub>O<sub>2</sub>, using the variable dielectric cell method (cf. preceding abstract). A maximum occurs at a concentration of about 35%. The dielectric constant of pure hydrogen peroxide is determined by extrapolation as 89.2 at 0°. The refractive indices of the solutions have been determined by the goniometer method (cf. A., 1921, ii, 106) for three hydrogen lines. These show no abnormalities such as are observed in the dielectric constants. The value of the molecular refractive power of pure hydrogen peroxide is too large for the molecule to be represented by two hydroxyl groups. The dispersive power points in the same direction. It is suggested that the co-ordinate oxygen linking given by Sugden's parachor has a definite atomic refractive power of 2.1. The polarisability as calculated from the refractive indices increases continuously with the peroxide concentration. A method for measuring electrical conductivities in hydrogen peroxide solutions is developed and is applied to potassium chloride and acetic acid solutions. In the former the dissociation is about the same as in aqueous solution, but acetic acid solutions have much smaller conductivities than in water. The specific conductivity of pure hydrogen peroxide is  $2 \times 10^{-6}$ , so it can be only very slightly dissociated.

J. W. SMITH.

**Determination of dipole moments in polar solvents.** O. HASSEL and A. H. UHL (Naturwiss., 1930, **18**, 247).—The objections which can be brought against the method of determining dipole moments in dilute solutions are of greater importance when the determination is carried out in polar solvents. Experiments made with mixtures of two molecular polar types in benzene solution indicate that it is possible even in the case of a polar solvent to obtain approximately correct values for dipole moments. A series of substances of which the moments were measured in benzene solution were then dissolved in various polar liquids, and the change of the dielectric constant caused by the dissolution of the substance, and also the change in refractive index, were measured. The total atomic and orientation polarisation was calculated by means of a formula. Large deviations from the  $\mu$  values in benzene solution occurred only in the case of nitrobenzene, and for solutions of chloroform in ether and of ether in chloroform. In the last two there is a special molecular combination.

A. J. MEE.

**Dipole moments of some organic molecules.** K. L. WOLF (Physikal. Z., 1930, **31**, 227—229; cf. A., 1929, 243, 244).—The infra-red term of the molecular polarisation is usually neglected, but the moments obtained in this way are a little too high. The term is regarded as equal to 15% of the molecular refraction. In the following data the figures in parentheses represent the uncorrected values and those given first include the effect of the infra-red term: menthone 2.82 (2.88), camphor 2.94 (2.99), fenchone 2.90 (2.95), acetylacetone 2.78 (2.85); formic 1.19 (1.21), acetic 0.74 (0.80), propionic 0.63 (0.72), butyric 0.68 (0.78), and isovaleric acid 0.63 (0.76); ethyl diazoacetate 2.03 (2.07); benzophenone 2.95 (3.02), dianisylmethane 1.61 (1.75), dianisyl ketone 3.90 (3.84), dianisyl thioketone 4.44 (4.84).

R. A. MORTON.

**Molecular volumes and cohesive forces of some geometrical- and position-isomeric compounds.** A. WASSERMANN (Ber., 1930, **63**, [B], 559—565).—Examples are cited to show that in the comparison of the mol. volumes of isomeric compounds interatomic and intermolecular distances must equally be taken into account. As measure of cohesive forces, a comparison of m. p. and solubility in the case of solids and of b. p. in the case of liquids is adopted. Two cases are distinguished: (1) cohesive forces and densities alter in the same sense whereby it is possible that the space demand of isomeric molecules is different but not determinable solely from density, and (2) change of cohesive force causes no alteration or an opposite change in density, indicating that a measurable effect on the mol. volume has been produced. Under (1) the following examples are cited. The *para*-compounds with higher m. p. and smaller solubilities have greater density than the *ortho*-substances; thus the m. p., solubility (millimol. per litre in water at 25°), and  $d_4^{25}$  for the fluorobenzoic acids are: *o*-, 126°, 51.6, 1.460; *m*-, 123°, 10.7, 1.474; *p*-, 186°, 8.7, 1.479. Liquid *ortho*-compounds have frequently higher b. p. and density than the *meta*- or *para*-substances. The behaviour of solid methyl maleate and fumarate, of *cis*- and *trans*-oxidoethylene-

dicarboxylic acid, and of *cis*- and *trans*-hexahydrophthalic acid resembles that of maleic and fumaric acids. The b. p. and density of derivatives of *trans*-cinnamic acid are generally greater than those of the corresponding *cis*-compounds. On the other hand, many *cis*-compounds have higher b. p. and density than the *trans*-substances, for example the  $\alpha\beta$ -dichloro- and -dibromo-ethylenes and the liquid methyl maleate and fumarate.

Under (2) the following examples are cited, the figures recording m. p., solubility in water at 25°, and density: chlorobenzoic acids, *o*-, 139°, 13.3, 1.544; *m*-, 154°, 2.6, 1.496; *p*-, 236°, 0.49, 1.541: bromobenzoic acids, *o*-, 148°, 9.24, 1.929; *m*-, 156°, 2.00, 1.845; *p*-, 251°, 0.28, 1.894: iodobenzoic acids; *o*-, 162°, 3.84, 2.249; *m*-, 186°, 0.47, 2.171; *p*-, 266°, 0.14, 2.184; phthalic acid, 193°, 0.54, 1.593; terephthalic acid, >333°, 0.0014, 1.510.

When the *trans*-compound has a higher m. p. or b. p. than the *cis*-substance and a smaller or not larger density, it is assumed that the smaller space demand of the *cis*-molecule is of more influence on the mol. volume than the small intermolecular distances of the *trans*-derivatives.

H. WREN.

**Magnetic birefringence of *p*-azoxyanisole at temperatures above the point of disappearance of the mesomorphic state.** (MLE.) J. ZADOCK.

KAHN (Compt. rend., 1930, 190, 672—674).—The positive magnetic birefringence of *p*-azoxyanisole in the isotropic state is considerably greater than that of ordinary liquids, and varies rapidly with temperature, especially in the neighbourhood of the nematic state, the temperature curve being hyperbolic. These results were anticipated by Foëx (this vol., 141) from his analogy between the nematics and the ferromagnetics which indicated that above the clarification point (comparable with the Curie point) there is a molecular field favourable to molecular orientation.

J. GRANT.

**Active nitrogen and hydrogen; the two forms of hydrogen.** H. CORAUX (Chim. et Ind., 1930, 23, 267—272).—The production and properties of active nitrogen and hydrogen are described, and theories as to their nature are discussed. The prediction of and experimental evidence for the existence of ortho- and para-hydrogen are summarised briefly.

N. M. BLIGH.

**Active nitrogen. VII. Decay of the nitrogen afterglow.** E. J. B. WILLEY (J.C.S., 1930, 336—349; cf. A., 1929, 403, 1117).—The afterglow decay was investigated by an improved method, the glow being measured by a photo-cell. The decay is partly homogeneous or heterogeneous, according to experimental conditions. If the walls of the vessel are not poisoned by gaseous impurities the recombination process is a non-luminous surface reaction; for an increase in impurity up to 0.1% the wall reaction diminishes and the homogeneous decay increases (cf. Lewis, A., 1929, 624; Herzberg, A., 1928, 457), the order of the process being determined by the state of the walls; when the surface reaction is minimised the effects of pressure and addition of other gases are in agreement with the three-body recombination theory. The afterglow probably originates in a

reaction  $N + N' \longrightarrow N'_2$ ;  $N'_2 + N_2 \longrightarrow 2N_2$ , where  $N'$  is a 2.3-volt metastable, chemically active atom (cf. Compton and Boyce, A., 1929, 365). No changes in the order of the decay nor in the spectral characteristics of the glow between 5900 and 4000 Å. were observed.

N. M. BLIGH.

**Attempt to produce pure para-nitrogen.** E. JUSTI (Naturwiss., 1930, 18, 227—228).—Considerations of the intensity relationships in the band and Raman spectra of nitrogen have led to the suggestion that ordinary nitrogen consists of two parts of para-nitrogen with rotation quantum numbers 0, 2, 4, 6 . . . and one part of ortho-nitrogen having the quantum numbers 1, 3, 5, 7 . . . Attempts to prepare the para-form by the method of Bonhoeffer and Harteck (cf. A., 1929, 479) were unsuccessful. By causing the condensation of nitrogen near the triple point a new modification has been produced and is being examined.

W. R. ANGUS.

**Structural principles of compounds of boron and hydrogen.** E. WIBERG (Z. anorg. Chem., 1930, 187, 362—368).—Polemical against Hellriegel (this vol., 137). The conception of a special "boron linking" to explain the existence of the different boron hydrides is unnecessary. From its position in the periodic table it is reasonable to regard boron as quinquivalent towards hydrogen. As proof that Grimm's hydride law may be applied to boron the similarity between the properties of diborane,  $B_2H_6$ , and ethylene is pointed out. This indicates that boron is quinquivalent in this compound, the two boron atoms being joined by a double linking.

M. S. BURR.

**Boron hydrides and sodium triphenylboride.** F. FALTIS (Z. anorg. Chem., 1930, 187, 369—378).—Theoretical. On the basis of the experimental work of Stock and others (A., 1929, 279) a theory of the structure of boron hydrides has been put forward. It resembles Hellriegel's theory (this vol., 137) in so far as it is based on the conception of a tervalent boron, but it involves the formation of cyclic structures to build up the higher members of the series. In the additive compounds with sodium and ammonium the presence of double linkings to form, for instance, the anion  $BH_2 \cdot BH_2$  (cf. Wiberg, A., 1928, 936) must be admitted. The triphenyl or trimethyl borides show no tendency to form double molecules but combine with sodium or ammonium. The formation of these compounds is not the result of the completion of the electron octet by addition or subtraction of electrons, but of an endeavour to bind a single valency electron in the fourth co-ordination position.

M. S. BURR.

**Intermolecular affinity of fumaric and maleic acids and their dimethyl esters, and of  $\alpha$ - and meso-tartaric acids and their methyl and ethyl esters.** A. WASSERMANN (Z. physikal. Chem., 1930, 146, 418—445, 446—461).—The molecular heats of the dimethyl esters of maleic and fumaric acids have been measured. They are, respectively, (62.3—0.025*t*) kg.-cal. and (41.5+0.242*t*) kg.-cal. The heat of fusion of the maleic ester is 3.52 kg.-cal./g.-mol. From the data and that of other investigators the heats of combustion of the solid, liquid, and gaseous

esters may be calculated. In the gaseous states the heats of combustion of the stereoisomeric esters agree within the limits of experimental error. In the solid state the heat of combustion of the maleic ester is approximately 3 kg.-cal./g.-mol. greater than for the fumaric ester. This indicates that the attraction between the molecules in the solid state is greater for the fumaric than for the maleic ester, a conclusion which is confirmed by determinations of the density;  $d_4^{25}$  is 1.34 for the former and 1.22 for the latter. M. p. and solubilities give further confirmation. The heats of dissolution and the first and second heats of ionisation of maleic and fumaric acids have been determined, and, with the help of these data and also of the calculated values for the heat of hydration of the primary and secondary anions, heats of formation of the isomeric molecules and ions have been calculated and compared. The intermolecular affinity of fumaric acid thus appears to be more than 2.5 kg.-cal. per mol. greater than that of maleic acid. This conclusion is supported by the fact that there are 3 molecules in the unit cell of the crystal lattice of fumaric acid and only 2 molecules in that of maleic acid. Fumaric acid is more strongly adsorbed by charcoal than is maleic acid, which also seems to indicate that the former has the greater cohesive power.

Determinations have been made of the specific heat, heat of fusion, and heat of dissolution of the diethyl esters of *d*- and meso-tartaric acids. The heats of hydration of the two esters have been calculated and are found to agree within the limits of experimental error. The densities have also been determined. Heats of dissolution and ionisation of *d*- and meso-tartaric acids and of racemic acid have been obtained. From these and other data it is shown that, in the gaseous state, *d*- and meso-tartaric acids and their diethyl and dimethyl esters have, in each case, the same energy content. The heat of combustion of solid racemic acid differs from that of the other two, indicating a different intermolecular affinity. Observations on crystal structure, molecular volume, m. p., etc. confirm these conclusions.

M. S. BURR.

**Structure of the water molecule and its relation to Werner's co-ordination law in general and to the crystal structure of water in particular.** R. REINICKE (Z. anorg. Chem., 1930, 187, 49—59).—The theory previously developed is applied to the structure of the water molecule. It is considered that it is not a straight-line molecule, but that the angle between the hydrogen-oxygen linkings is  $97^\circ$ , and the crystal structure of ice is discussed on this basis. The views are also applied to the structure of salt hydrates and of co-ordination compounds in general.

J. W. SMITH.

**Measurements with bi- and quadri-valent compounds of the rare earths. IV. Classification of the rare earths.** W. KLEMM (Z. anorg. Chem., 1930, 187, 29—32).—The classification of the trivalent ions of the rare earths suggested previously (this vol., 177) is discussed from the point of view of the modern theory of the structures of these ions.

J. W. SMITH.

**Quantum theory of double linkings.** E. HÜCKEL (Z. Physik, 1930, 60, 423—456).—Chemical

evidence for resistance to rotation of the parts of a molecule about C:C and C:N double linkings is summarised. Lennard-Jones' method (cf. A., 1929, 1360) is applied to the electronic configuration of the oxygen, acetylene, and ethylene molecules. Oxygen is a straightforward example of the method, the actual binding of the two valency electrons being an "Impulsvalenz" due to opposed orbital angular, but parallel spin momenta of the two electrons. It has, therefore, a  $^3\Sigma$  paramagnetic ground term. The double linking in formaldehyde and ethylenes is no longer cylindrically symmetrical, and  $\sigma$  and  $\pi$  values have, therefore, no real meaning. Each  $\pi$  term, ordinarily degenerate, splits into two. A notation is given to specify these and their possible combinations. The electronic configuration of the ground state of the molecule is deduced from its magnetic properties. A qualitative estimate of the energy values of these terms shows that *cis*- and *trans*-isomerides alone are stable; i.e., quantum mechanics predicts resistance to rotation about the double linking.

A. B. D. CASSIE.

**Relation of van der Waals forces to homopolar binding forces.** R. EISENSCHITZ and F. LONDON (Z. Physik, 1930, 60, 491—527).—A systematic perturbation method is developed, which combines in one the homopolar and van der Waals forces, and contains earlier calculations on chemical linking as first approximations. The method is applied to derive the van der Waals constant of atomic hydrogen.

A. B. D. CASSIE.

**Magnetism.** P. WEISS (Anal. Fis. Quím., 1930, 28, 146—159).—The magnetic properties of various materials are discussed in relationship to atomic and molecular structure.

H. F. GILLBE.

**Quantum-mechanical theory of the homopolar linking.** W. HEITLER (Physikal. Z., 1930, 31, 185—204).—A full summary.

R. A. MORTON.

**Stable states of molecules.** M. DUNKEL (Z. physikal. Chem., 1930, B, 7, 81—107).—Theoretical. A systematic classification of di- and poly-atomic molecules formed by the elements of the first horizontal series has been carried out by the free use of the physical conceptions previously applied to diatomic molecules. The electronic structure of the possible compounds of the elements named is given and their chemical behaviour correlated with it. The constitution of certain compounds of doubtful structure is discussed, and reasons are given for the non-existence of certain other molecules.

F. L. USHER.

**Valency of sulphur in dithionates.** O. STELLING (Z. physikal. Chem., 1930, B, 7, 157—159).—The inference regarding the valency of sulphur in dithionates drawn by Winger and Yost (A., 1929, 983) from the results of experiments on its X-ray absorption spectrum is criticised. The latter depends, not only on the valency of the sulphur, but also on the nature of the atoms to which it is directly bound. The wave-length of the *K*-absorption edge for sulphur in sodium thiosulphate agrees closely with that for sulphur in potassium dithionate. It is therefore considered that the latter contains two similar sexavalent sulphur atoms as expressed in the Blomstrand-Mendeleév formula.

F. L. USHER.

**Solution volume and ionic radii of alkali halides.** W. HERZ (Z. anorg. Chem., 1930, **187**, 382—384).—The volumes of the alkali halide molecules in solution, calculated from density determinations, have been compared with the volumes calculated from the ionic radii (cf. this vol., 534). At higher concentrations  $V_m$  is always greater than  $V_i$ , whilst at lower concentrations the converse holds. In most cases there is equality at a normality between 0.2 and 0.1. On comparing the same halide of different alkali metals, or different salts of the same alkali metal, the ratio  $V_m$  to  $V_i$  increases, in general, with the mol. wt., but there are exceptions.

M. S. BURR.

**Dissociation work of oxygen and sulphur.** V. KONDRATEEV (Z. physikal. Chem., 1930, **B**, **7**, 70—73).—The dissociation work of the oxygen molecule, recalculated from spectral data relating to nitrogen peroxide and to ozone, has a mean value of 120 kg.-cal. This necessitates the adoption of a revised value for sulphur of 101 kg.-cal. The values for the dissociation work of selenium and tellurium are less than 84 and 65 kg.-cal., respectively.

M. S. BURR.

**Cosine law of reflexion as a consequence of the second law of thermodynamics.** P. CLAUSING (Ann. Physik, 1930, [v], **4**, 533—566).—The second law of thermodynamics requires as a consequence the cosine law for the directional distribution of molecules leaving a wall of a vessel. The principle of detailed balancing, which states that for each elementary process in a system in equilibrium the frequency of the forward process is equal to that of the opposing one, requires that for each direction, and for each velocity, the number of molecules which are allowed to leave must equal the number absorbed. By the application of this principle and the second law it is shown that so long as the latter can be regarded as true the cosine law must follow.

A. J. MEE.

**Formula for molecular streaming according to Smoluchowski and to Gaede.** P. CLAUSING (Ann. Physik, 1930, [v], **4**, 567—570).—Mathematical. A new proof of the formula of Smoluchowski and of Gaede which was used in the previous work (cf. preceding abstract) is given.

A. J. MEE.

**Fluctuation of rotation energy of polyatomic gases.** K. SZELL (Z. Physik, 1930, **60**, 210—217).—Theoretical.

R. A. MORTON.

**Dynamic actions in slow rotational motions in viscous liquids.** B. FINZI (Atti R. Accad. Lincei, 1930, [vi], **11**, 59—63).—Equations have been derived for the resultant and moment of dynamic action acting on and about a line within the liquid due to the viscosity in slow rotational movement in a viscous liquid.

F. G. TRYHORN.

**Glancing angle of reflexion from calcite for silver ( $K\alpha_1$ ) X-rays.** C. D. COOKSEY and D. COOKSEY (Nature, 1930, **125**, 461).—The weighted mean value of 14 observations of the first order glancing angle at which the  $K\alpha_1$  line of silver is reflected from the cleavage planes of calcite, obtained by a new method, is  $5^\circ 17' 13.81'' \pm 0.06''$  reduced to  $18^\circ$ . The corresponding wave-length is  $0.558238 \text{ \AA.} \pm 0.000002 \text{ \AA.}$

using  $3.02904 \text{ \AA.}$  for the effective grating space of calcite.

L. S. THEOBALD.

**Diffraction of X-rays by vitreous solids and its bearing on their constitution.** J. T. RANDALL, H. P. ROOKSBY, and B. S. COOPER (Nature, 1930, **125**, 458).—The constitution of glasses has been studied by examining the diffraction effects produced by passing copper  $K\alpha$  radiation through silica, wollastonite, sodium and potassium borates, boric oxide, selenium, potash and soda feldspars, dextrose, and sucrose, in the glassy state. Silica glass corresponds with either cristobalite or tridymite crystallites of average size  $1.5\text{--}2.0 \times 10^{-7} \text{ cm.}$  with evidence much in favour of the former. Wollastonite corresponds with crystalline pseudo-wollastonite, and in the case of potash feldspar the crystallites are mainly silica, and probably cristobalite. Potash feldspar devitrifies to cristobalite, whilst wollastonite glass, which is more stable, devitrifies to crystalline wollastonite at  $900^\circ$ . The observations of Parmelee and co-workers on the position and number of bands obtained with fused silica and feldspar glass are not confirmed; only one band, at  $4.33 \text{ \AA.}$ , has been found with fused silica.

L. S. THEOBALD.

**Soft X-rays and secondary electrons.** E. RUBBERG (K. Svenska Vet. Akad. Handl., 1929, **7**, [1], 153 pp.).—The interaction between electrons and soft X-rays in solids was investigated. The velocity distribution of the photo-electrons excited by the rays was measured by electric and magnetic methods; the curves obtained afford information on the nature of the process occurring in the photo-electric substance and on the frequency of the radiation; the efficiency of soft X-ray production was calculated from photo-electric measurements and a study of the absorption of the X-rays. A stopping potential and magnetic method of velocity analysis are described, and, applied to the photo-electric emission, lead to the same results; the former gives a value of 265 volts for the carbon  $K\alpha$  quantum. The emission was found to consist of a small number of fast- and a large group of slow-moving electrons which were proved by absorption measurements with a fluorite window not to be produced by radiation of the corresponding frequency; their velocity distribution is identical with that of the low-energy emission due to electron bombardment. The fast electrons probably constitute the secondary emission produced by fast primary photo-electrons. For the same radiation heavy elements give a greater number of fast electrons than light elements. Evidence was found of absorption of carbon  $K\alpha$  radiation by the  $K$  electrons of boron. The calculated term value is, boron  $K$ ,  $189 \pm 5$  volts. Using different anodes the values obtained for the characteristic soft X-ray quanta emitted were: carbon  $K\alpha$ ,  $277 \pm 10$ ; boron  $K\alpha$ ,  $183 \pm 10$ ; beryllium ( $K$ ),  $100 \pm 10$ ; aluminium ( $L$ )  $64 \pm 5$  volts. The absorption coefficient of gold leaf for the carbon radiation was  $2.9 \times 10^5 \text{ cm.}^{-1}$ . The yield of soft X-ray energy when solids are bombarded by 300-volt electrons is of the order  $10^{-5}$ ; the cause of this low efficiency is discussed. Velocity distribution curves for the emission from solids due to electron bombardment were obtained with a

magnetic focussing apparatus; measurements for aluminium, carbon, boron, beryllium, and lithium showed no characteristic velocity groups related to the excitation of soft X-ray levels. True electron reflexion was established for all voltages in the region 0—1000 volts. For all cold targets the energy most frequently lost by a bombarding electron on collision had a characteristic value of about 25 volts; this is due to an adsorbed surface layer which is removed at incandescence temperature but re-established on cooling in a vacuum. Incandescent platinum and carbon targets show no sign of excitation of soft X-ray levels; new maxima found indicating characteristic amounts of energy transferred on collision were  $9.0 \pm 0.4$  volts for platinum, and  $7.0 \pm 0.5$  volts for carbon. It is concluded that in conducting targets under electron bombardment, for higher voltages a small fraction of the primary electrons is reflected without loss of energy and a greater fraction is scattered, the lost energy being largely utilised for the production of secondary electrons in the target. Inelastic collisions also occur, involving the ionisation of low energy levels of atoms in the target. Excitation of soft X-ray levels occurs only with vanishingly small probability, in conflict with the usual interpretation of secondary emission critical potentials. Experimental evidence indicates that the energy of the excited atoms connected with the maxima for hot targets is not dissipated in radiation of the corresponding frequency.

N. M. BLIGH.

**Grating constants of gold-silver mixed crystals.** G. SACHS and J. WEERTS (*Z. Physik*, 1930, 60, 481—490).—A new arrangement to give precision measurements of grating constants is described. The possible experimental error is calculated, and corresponds with an error in wave-length of  $0.0002 \text{ \AA}$ . The grating constants are measured for varying proportions of gold and silver, and the deviations from the additive law are discussed.

A. B. D. CASSIE.

**New wave-length standard for X-rays.** A. H. COMPTON (*J. Franklin Inst.*, 1929, 208, 605—616).—The discrepancy between the wave-lengths of X-rays as deduced from crystal and from grating measurements (cf. Bearden, A., 1929, 984), and the resultant discrepancies in the values of constants deducible therefrom, are discussed. The discrepancies vary, but are largely (up to over ten times) in excess of probable experimental error. No explanation is arrived at, but it is pointed out that the new values of  $e$  and  $h$  give 136.45 as the value of  $1/\alpha$ , a figure nearer to Eddington's 136 (A., 1929, 231; cf. this vol., 518) than figures accepted hitherto.

C. A. SILBERRAD.

**Secondary phenomena in X-ray spectra.** F. K. RICHTMEYER (*J. Franklin Inst.*, 1929, 208, 325—361).—A summary of earlier measurements on X-rays. Modern refinements show: (i) a deviation from the  $\lambda^3$  absorption law; (ii) absorption discontinuities are not sharp; (iii) the wave-length of absorption discontinuities varies slightly with chemical combination; (iv) emission lines are accompanied by satellites; (iii) and (iv) are discussed. The  $M$  electrons around phosphorus in phosphates may be regarded as removed. The difference in energy required to

remove a  $K$  electron from the neutral phosphorus atom, and from that with no  $M$  electrons, is calculable; it is much greater than the corresponding difference in frequency between the  $K$ -absorption edges of phosphorus and of phosphates. This discrepancy gives, however, a measure of the screening effect of surrounding atoms, and so a new approach to valency problems. Emission satellites appear in numbers varying with the element, and seem accompanied by a continuous spectrum on their short-wave side. Wentzel suggests that the  $K$  satellites are due to double ionisation of the  $K$  ring. The resulting frequency relations are supported by experiment, but the observed intensity of the satellites is too great. The excitation potential of the satellites is also inexplicable. Richtmeyer shows that if  $\Delta\nu$  be the frequency difference between a satellite and its parent line,  $(\Delta\nu)^{1/2}$  is proportional to the at. number of the element. He suggests that satellites are due to simultaneous electron jumps, one between inner orbits and the other between outer orbits. This explains his frequency relation and other experimental results.

A. B. D. CASSIE.

**X-Ray diffraction in organic liquids. I. Cyclic compounds. II. Chain compounds.** M. ISHINO, S. TANAKA, and A. TSUJI (*Mem. Coll. Sci. Kyōtō*, 1930, A, 13, 1—16, 17—26).—I. The diffraction of X-rays by various cyclic organic compounds in the liquid state has been investigated by the Debye-Scherrer method. Since the diffraction halo of a mixture of liquids is characteristic of the mixture and the haloes of the constituents are suppressed, it is concluded that the dimensions of such haloes are determined, not by the molecular structure, but by the intermolecular distance, values of which have been calculated for the substances examined. With some liquids a single sharply-defined halo is obtained, probably indicating that the molecules are spherical. Cylindrical or disc-shaped molecules are supposed to be responsible for haloes with two distinct maxima, corresponding with the two principal dimensions of the molecules. In cases where the halo shows one distinct maximum with a marked scattering to one side of it, it is inferred that regularity of orientation is more pronounced in respect of one dimension than in respect of the other, whilst if there are equal deviations from regularity in respect of both the halo has no distinct maximum. The ordinary structural formula seems to be no index to the actual form of the molecule.

II. The diffraction haloes of various open-chain compounds have been examined. Hydrocarbon haloes have a single sharp maximum, the size of which is practically independent of the number of carbon atoms. All the other compounds examined give two maxima, the inner being taken to correspond with the length of the molecule, and the outer, apparently the counterpart of the hydrocarbon maximum, with its cross-sectional diameter.

R. CUTHILL.

**X-Ray diffraction in liquids. I. Aqueous and non-aqueous solutions.** S. TANAKA and A. TSUJI (*Mem. Coll. Sci. Kyōtō*, 1930, A, 13, 27—33).—Investigation of the diffraction of X-rays by aqueous solutions has given results similar to those obtained

by Krishnamurti (A., 1928, 1079). Dilute non-aqueous solutions, however, show only a single halo. Increase in concentration reduces its diameter and at the same time the outer scattering increases until in some cases it develops into a halo of large diameter.

R. CUTHILL.

**Crystal structure of xenon.** G. NATTA and A. G. NASINI (Nature, 1930, 125, 457).—The crystal structure of xenon has been determined by applying the powder method to a thin layer (0.004 cm., approx.) of the gas condensed on the surface of a quartz capillary. Xenon, like argon, shows a face-centred cubic structure. The elementary cell of four atoms has  $a\ 6.18 \pm 0.01\ \text{\AA}$ , the volume is  $236.03 \times 10^{-24}\ \text{c.c.}$ ;  $d_{\text{calc}}\ 3.64\ \text{g./c.c.}$  The atomic radius is calculated to be  $2.18\ \text{\AA}$ .

L. S. THEOBALD.

**Structure of strontium chloride hexahydrate.** Z. HERRMANN (Z. anorg. Chem., 1930, 187, 231—236).—The orthohexagonal unit cell contains 2 mols., and has  $a\ 7.906$ ,  $b\ 13.68$ ,  $c\ 4.07\ \text{\AA}$ . The space-group is  $C_{2h}^2$ .

F. L. USHER.

**Crystal structure of native copper.** (Sir) H. C. H. CARPENTER and M. S. FISHER (Bull. Inst. Min. Met., 1930, 27—32; cf. Carpenter and Tamura, A., 1928, 503).—The microstructures of twenty typical specimens of native copper are described. It is concluded that they were all formed at low temperatures, probably by the interaction of aqueous solutions of meteoric origin. Oolitic markings are characteristic of formation by rhythmic precipitation; zonal and herring-bone markings, and irregular striations of formation by replacement. Columnar crystals with multiple twinning and irregular markings denote formation by aqueous action, and annealing twins and blurred striations thermal metamorphism. Heat treatment showed that none of the specimens was originally homogeneous, and had therefore never been near its m. p. The temperature of four specimens had reached about  $400^\circ$  and of four about  $500^\circ$ .

C. W. GIBBY.

**X-Ray examination of the system iron-arsenic.** G. HÄGG (Z. Krist., 1929, 74, 134—135; Chem. Zentr., 1929, ii, 1889).—Arsenic, up to 5%, is soluble in  $\alpha$ -iron at the ordinary temperature; the phase poorest in arsenic,  $\text{Fe}_3\text{As}$ , tetragonal, has  $a\ 3.627$ ,  $c\ 5.973\ \text{\AA}$ , the unit cell containing 2 mols. The phase  $\text{FeAs}$ , rhombic, has  $a\ 3.366$ ,  $b\ 6.016$ ,  $c\ 5.428\ \text{\AA}$ . ( $a:b:c = 0.5595:1:0.9023$ ); the unit cell contains 4 mols. The space-group is  $V_h^{10}$ .

A. A. ELDRIDGE.

**Structure of staurolite.** S. NÁRAY-SZABÓ (Z. Krist., 1929, 74, 103—116; Chem. Zentr., 1929, ii, 1910).—The orthorhombic unit cell contains 4 mols. of  $\text{H}_2\text{FeAl}_4\text{Si}_2\text{O}_{12}$ ;  $a\ 7.82$ ,  $b\ 16.52$ ,  $c\ 5.63\ \text{\AA}$ .

A. A. ELDRIDGE.

**Structure of cyanite.** S. NÁRAY-SZABÓ, W. H. TAYLOR, and W. W. JACKSON (Z. Krist., 1929, 74, 117—130; Chem. Zentr., 1929, ii, 1910).—A structure is proposed for cyanite and compared with that of staurolite (cf. preceding abstract). A. A. ELDRIDGE.

**Eudidymite and epididymite.** G. GOSSNER and O. KRAUS (Zentr. Min. Geol., 1929, A, 257—266; Chem. Zentr., 1929, ii, 1910).—Eudidymite,

$\text{BeSi}_2\text{O}_5 \cdot \text{NaHSiO}_3$ , is pseudohexagonal,  $a:b:c = 1.730:1:1.909$ ; the unit cell,  $a\ 12.70$ ,  $b\ 7.34$ ,  $c\ 14.01\ \text{\AA}$ ,  $\beta\ 102^\circ 34'$ , contains 8 mols.; space-group probably  $C_{2h}^2$ . Dimorphism with epididymite is indicated.

A. A. ELDRIDGE.

**X-Ray study of tetramethylammonium perchlorate and permanganate.** K. HERRMANN and W. ILGE (Z. Krist., 1929, 74, 47—63; Chem. Zentr., 1929, ii, 1890).—In both compounds the unit cell contains 2 mols., and the space-group is  $D_{2h}^{10}$ . The values of the ratio  $a:c$  are in each case,  $1:0.708$ , whilst values of  $J_a$  are  $8.290$ ,  $8.439\ \text{\AA}$ . and  $J_c\ 6.006$ ,  $6.019\ \text{\AA}$ , respectively.

A. A. ELDRIDGE.

**Structure of naphthalene and anthracene.** K. BANERJEE (Nature, 1930, 125, 456).—Robertson's conclusions concerning the crystal structure of naphthalene and anthracene (A., 1929, 1367) are at variance with those of other workers for related compounds. Further, they do not explain the intensities of reflexion from many of the crystal planes. The results of an X-ray investigation of naphthalene and anthracene now show that these intensities are best explained by supposing that all the carbon atoms in one molecule are arranged in one plane with the planes of the molecules inclined to the cell faces. The correct positions of the molecules are obtained by first placing them along the  $bc$  planes, rotating through  $25^\circ$  about the  $c$  axis, and then rotating them about  $b$  axes through  $12^\circ$  and  $9^\circ$  for naphthalene and anthracene, respectively.

L. S. THEOBALD.

**Structure of naphthalene and anthracene.** J. M. ROBERTSON (Nature, 1930, 125, 456—457).—Banerjee's structure (cf. preceding abstract) is considered to be essentially correct. Measurements of the intensities of the reflexions from a number of anthracene planes made by Bragg lead to a similar structure.

L. S. THEOBALD.

**Crystal structures of some derivatives of diphenyl.** G. L. CLARK and L. W. PICKETT (Proc. Nat. Acad. Sci., 1930, 16, 20—27).—An X-ray analysis has been made by the Laue method of some diphenyl derivatives, the dimensions of the unit cells being measured from rotation photographs about each of the three axes of the crystals. Identification of the reflexions corresponding with each set of planes was made with certainty from sets of oscillating photographs, each covering a range of  $15^\circ$ . The crystal unit of diphenyl was found to be monoclinic with the dimensions  $a\ 8.11$ ,  $b\ 5.67$ ,  $c\ 9.57\ \text{\AA}$ ,  $\beta\ 94.5^\circ$ . The crystal is assigned to the monoclinic prismatic class with the space-group  $C_{2h}^2$ , based on the simple monoclinic lattice. There are two molecules in the unit cell and conditions of symmetry demand that the molecule should have a centre of symmetry only, and hence a staggered ring is probable. The unit cell of dimesityl is monoclinic prismatic, with the dimensions  $a\ 8.21$ ,  $b\ 8.58$ ,  $c\ 22.55\ \text{\AA}$ ,  $\beta\ 96.5^\circ$ . The space-group based on the simple monoclinic lattice  $\Gamma_m$  is  $C_{2h}^2$  and the unit cell contains four asymmetric molecules. The unit cell of  $o$ -tolidine is orthorhombic, contains four molecules, and has the dimensions  $a\ 6.50$ ,  $b\ 7.48$ ,  $c\ 23.62\ \text{\AA}$ . Diphenic acid has an orthorhombic cell with the dimensions  $a\ 14.12$ ,  $b\ 11.90$ ,  $c\ 13.75\ \text{\AA}$ , containing eight molecules. The



arrangement in this compound is quite different from that of the other diphenyl derivatives, as the unit cell is approximately half as long in one dimension and twice as wide in the other two. F. G. TRYHORN.

**Possible influence of the surrounding medium on the symmetry of certain minerals.** L. ROYER (Compt. rend., 1930, 190, 503—505; cf. this vol., 21).—The (111) face of a crystal of sulphur, etched by crude petroleum (from Gabian, Herault), shows figures indicating bisphenoidal symmetry in accordance with the usual classification of sulphur; another portion of the same face, etched with carbon disulphide, indicates holohedral symmetry. The same petroleum etches calcite in the same way as an active acid (A., 1929, 631). It is concluded that sulphur is really holohedral and that its hemihedrism is solely due to activity of the medium in which the crystals were formed. Brown peat water is also an active medium.

C. A. SILBERRAD.

**Gibbs-Ewald reciprocal lattice.** A. L. PATERSON (Nature, 1930, 125, 447).—A correction (cf. this vol., 272).

L. S. THEOBALD.

**Problem of the two Curie points.** R. FORRER (J. Phys. Radium, 1930, [vii], 1, 49—64).—The reasons for the existence of two Curie points for all ferromagnetic metals is discussed. They represent two different properties, and it will therefore be expected that there will be two mechanisms to explain them. One can be attributed to spontaneous orientation of the elementary magnets, and the other to hysteresis. Three temperature regions can be distinguished for ferromagnetic metals. In the first, at low temperatures, spontaneous orientation and hysteresis occur together. In the second, between the two Curie points, only one of these conditions is met with. In the normal case it is hysteresis (nickel, iron, cobalt, etc.), otherwise it is spontaneous orientation (e.g., the ferro-cobalts). In the third region neither of these properties is found. For ferro-magnetic magnetisation the two properties are necessary. A. J. MEE.

**Influence of size of grain on residual magnetism of soft iron.** O. VON AUWERS and G. J. SIZOO (Z. Physik, 1930, 60, 576—580).—The disagreement between the previous results of the authors (Auwers, Z. tech. Physik, 1928, 9, 475; Sizoo, A., 1929, 246) as to the influence of grain size on the residual magnetism of soft iron is shown to be due to an unavoidable uncertainty of the value for the shearing of the hysteresis curve. In any case grain size has a much smaller influence on the true (sheared) residual magnetism than on the coercive force and area of the hysteresis curve.

H. A. JAHN.

**Theory of the metallic change of resistance in a magnetic field.** N. H. FRANK (Z. Physik, 1930, 60, 682—685).—The influence of electron spin on the change of resistance of a metal in a magnetic field is much smaller than the effect due to the Lorentz force. No satisfactory explanation is yet available either for Kapitza's measurements with high fields or for the normal effect with small fields.

R. A. MORTON.

**Peltier and Thomson effects for bismuth crystals.** H. D. FAGAN and T. R. D. COLLINS

(Physical Rev., 1930, [ii], 35, 421—427; cf. Bridgman, A., 1929, 1136; Boydston, A., 1928, 114).—The Peltier *E.M.F.* against copper, and the Thomson coefficient were measured in single-crystal rods for an orientation range of 16—90°. The data obtained are not in agreement with the Voigt-Thomson symmetry relation.

N. M. BLIGH.

**Absolute cohesion in metals. Disruptive negative pressures and chemical disruptive volumes.** P. F. MEHL (J. Amer. Chem. Soc., 1930, 52, 534—540).—The negative pressures necessary for the disruption of metal lattices and the critical volumes at which this should occur may be calculated from the equation of state developed by Richards (A., 1927, 103). Using Born's exponents for the sodium chloride crystal with suitable transformation a value is calculated for the disruptive negative pressure for this lattice in close agreement with the value obtained by Joffe ("The Physics of Crystals," New York, 1928) from Born's potential energy equation. The disruptive negative pressures and critical disruptive volumes of the twelve cubic lattice metals for which Richards gave constants in his equation of state are calculated. These may be taken as a measure of absolute cohesion. Corrected tensile strength data are much lower than the calculated disruptive negative pressures. This is probably due to the presence of very fine cracks inducing stress concentration. Hence the tensile strengths of metals and alloys have by no means reached their maximum possible values.

J. W. SMITH.

**Elasticity of Pintsch crystals of tungsten.** S. J. WRIGHT (Proc. Roy. Soc., 1930, A, 126, 613—629).—With the main object of testing Bridgman's conclusion that tungsten crystals are very nearly isotropic and that any variation of elastic properties with orientation should be small (Proc. Amer. Acad. Arts Sci., 1925, 60, 305), the elastic constants of single crystals of tungsten have been studied by dynamical methods. The method employed was to observe the periodic times of oscillation in torsion and in bending of wires of various orientations, and thus to determine values of the torsional modulus of rigidity ( $n$ ) and the longitudinal Young's modulus ( $E$ ) for each wire. Bridgman's results are confirmed, and the following values are calculated:  $E = 3.886 \times 10^{12}$  dynes/cm.<sup>2</sup>,  $n = 1.514 \times 10^{12}$  dynes/cm.<sup>2</sup>;  $\sigma = 0.284$ .

L. L. BIRCUMSHAW.

**Fracture of [plastic] deformed cadmium crystals.** W. BOAS and E. SCHMID (Naturwiss., 1930, 18, 227).—The tension of cadmium crystals has been studied throughout the temperature range 85—473° Abs. At 473° Abs. the recrystallisation departs from its ordinary simple form. There is a definite temperature at which the crystal splits into non-crystallographic granular films. The slip energy of the crystal is discussed.

W. R. ANGUS.

**Dependence of breaking strain and elastic limit for rock-salt crystals on the conditions of crystallisation.** A. SMEKAL (Physikal. Z., 1930, 31, 229—232; cf. A., 1929, 753, 871, 1370).—In continuation of earlier work on the differences in physical properties between crystals of salt after fusion, and natural rock salt, the breaking stress and

elastic limits of various samples have been measured. Various samples of rock salt were heated for from 2 to 6 hrs. at temperatures up to 800°, and the breaking stresses of the "tempered" materials obtained. In all cases the magnitude falls considerably as the heating temperature rises from 0° to 600°, but rises from 600° onwards. The variations in breaking stress are least noticeable for the finest crystals of purest material. The fused material exhibits a relatively high cohesion. Very small quantities of impurities seem to affect the stability of the crystal aggregate.

R. A. MORTON.

**Melting, mechanical working, and some physical properties of rhodium.** W. H. SWANGER (Bur. Stand. J. Res., 1929, 3, 1029—1040).—Pure rhodium absorbs large quantities of oxygen when melted in an oxy-hydrogen oxidising flame or in the induction furnace in air and the metal then "spits" violently on solidification. When the metal is melted in thoria crucibles in a vacuum induction furnace it solidifies to a smooth silver-white ingot having an exceedingly coarse crystal structure; this metal is frequently too brittle to forge, but that melted on lime with the oxy-hydrogen flame can always be forged at a red heat if it is allowed to solidify slowly in a slightly reducing flame. When melted in a graphite crucible rhodium takes up 1.8% C. Forged ingots can be swaged at 1000° down to wire of 1 mm. diameter and this can be drawn finer first at a red heat through tungsten carbide dies and finally at the ordinary temperature through diamond dies. Rhodium has  $d$  12.41 and melts at  $1985^\circ \pm 10^\circ$ , the resistivity of a 1 mm. wire, annealed at 1200°, is 4.93 microhm-cm. at 20°, its *E.M.F.* against pure platinum is 1.61 millivolts at 200°, 3.92 at 400°, 6.77 at 600°, 10.16 at 800°, and 14.05 at 1000°, and its temperature coefficient of electrical resistance is 0.00436 between 0° and 100°. The linear coefficient of thermal expansion varies from  $8.1 \times 10^{-6}$  to  $9.6 \times 10^{-6}$  between 20° and 500° and the Brinell hardness is 101.

A. R. POWELL.

**Recrystallisation of metals.** G. TAMMANN and W. CRONE (Z. anorg. Chem., 1930, 187, 289—312).—From theoretical considerations, variations in the size of crystallites in cast metals ought to follow a curve of the form of the Gauss probability curve of errors, whilst the variations in recrystallised metals should be in accordance with Maxwell's distribution law. These conclusions have been confirmed by measurements on aluminium and cadmium. At constant temperature, the number of crystallites in a recrystallised metal diminishes with time at a rate depending on temperature, amount of deformation, degree of purity, and the nature of the metal concerned. The curve of dependence on time is an unsymmetrical hyperbola, as also is the curve showing rate of change of boundaries of particles with time. On deformation by rolling the rate of change of size of crystallites diminishes with increasing degree of deformation, and, for the same degree, increases with rise of temperature. With increasing deformation the number of crystallites increases if the metal is heated at the same temperature for the same time. The effect of the presence of a foreign metal has been

examined in the case of zinc containing 0.05, 0.1, and 1% Sn, respectively. In the first two mixtures the velocity of change of the crystallite boundaries is practically the same as for pure zinc, but it is diminished when the solubility of tin in zinc is exceeded. When a wire is heated by an electric current, changes in electrical conductivity and tensile strength are usually observed before changes in structure. The crystallites formed by the primary recrystallisation of a metal increase in size as the rate of cooling of the original melt is increased. If the recrystallised metal then undergoes a slight deformation and is reheated the secondary recrystallisation results usually in larger crystallites than the primary one, but the size depends on the nature and degree of the deformation, the temperature to which the deformed metal has been raised, and the conditions under which the primary recrystallisation has taken place. The causes of the various phenomena observed are discussed.

M. S. BURR.

**Kinetics of recrystallisation of metals.** R. KARNOP and G. SACHS (Z. Physik, 1930, 60, 464—480).—The relation between the degree of stretching and the time for the commencement of recrystallisation of stretched and slightly conical copper rods is investigated at definite temperatures. By stretching a conical specimen the resulting decrease in cross-section, and therefore the degree of stretching, varies along its length, and when it is kept at a certain temperature recrystallisation starts at the most deformed end first and spreads later down the length of the rod. It is shown that even at low temperatures and with small degrees of stretching recrystallisation would occur after a sufficient lapse of time. The rates of undistorted growth of single aluminium crystals in the process of recrystallisation are measured and found to be linear with the time, and by extrapolation the times of the formation of the nuclei are deduced. The number of nuclei and the velocity of growth for copper at different temperatures and degrees of stretching are calculated from the results of the first experiments.

H. A. JAHN.

**Volume change of manganese during solidification.** Y. MATUYAMA (Sci. Rep. Tōhoku, 1929, 18, 733—736).—By means of a thermo-balance it has been found that the contraction in volume of metallic manganese during solidification is 1.7%.

O. J. WALKER.

**Density of molten metals and alloys.** Y. MATUYAMA (Sci. Rep. Tōhoku, 1929, 18, 737—744; cf. A., 1929, 993).—The densities of molten antimony and silver in the temperature ranges 630—930° and 961—1061°, respectively, have been measured. In both cases the relation between temperature and density is linear, and the values of  $d$  at the m. p. are: antimony 6.504, silver 9.301. The densities of molten zinc-antimony alloys have also been measured and the existence of the binary compounds SbZn and Sb<sub>2</sub>Zn<sub>3</sub> in the liquid state has been confirmed.

O. J. WALKER.

**Modification of Barger's method of mol. wt. determination.** E. BERL and O. HEFTER [with F. RAU, G. S. DJANG, and UMSTÄTTER] (Annalen, 1930, 478, 235—246).—Barger's method is modified by

using a capillary in the form of a  $\cap$  with a tube inserted at the bend for displacement of air when the solutions are introduced into the limbs. The openings are finally sealed and readings of the movement of the menisci made for three weeks. Determinations are repeated with reference to solutions of different concentrations until the concentration at which no distillation would occur can be interpolated. Using acetone solutions, with azobenzene in one limb, a mean error of about 2%, maximum 6.5%, is obtained.

Determinations of the mol. wts. of nitrates of carbohydrates have been made. Cellobiose nitrates and maltose nitrate give normal mol. wts. Raffinose nitrate is partly, and sucrose nitrate is almost wholly split up into monosaccharide compounds. Inulin is also degraded during nitration. Nitrated starch ( $\text{NO}_2 : \text{C}_6 = 2.57 : 1$ ) has a mol. wt. corresponding with  $6-7\text{C}_6\text{H}_{10}\text{O}_5$ . Figures are also given for lubricating oils.

R. K. CALLOW.

**Highly polymerised compounds. XXXIV. Modification of Barger's method of mol. wt. determination.** R. SIGNER (Annalen, 1930, 478, 246—266).—The apparatus employed consists of a U-tube with sealed, graduated limbs at right angles to the bend. The junctions of the limbs and the bend are expanded to bulbs carrying side-tubes for filling purposes. Solutions of known concentration are kept in the bulbs and measured at intervals by tilting the apparatus so that they run into the limbs. Distillation is hastened by evacuating the apparatus and using temperatures higher than normal. When distillation ceases the volume of each solution can be read off and the mol. wt. calculated. An accuracy of 2% is obtained.

Mol. wt. determinations of some highly polymerised substances are recorded, as follows: *cyclocaoutchouc* in benzene, 6300—6700; *caoutchouc* in menthol, 4600—5603; *balata* fractions in pentatriacontane, 12,000 and 21,000.

R. K. CALLOW.

**Dual theory of metallic conduction.** E. H. HALL (Proc. Nat. Acad. Sci., 1930, 16, 45—55).—A review of progress since 1921, with a list of the revised characteristic constants of the metals used in the application of the theory. F. G. TRYHORN.

**Electrical properties and structures of metallic films obtained by thermal and cathodic sputtering.** F. JOLIOT (Compt. rend., 1930, 190, 627—630).—Films of platinum formed by thermal evaporation or by cathodic sputtering are produced in an unstable crystalline state and the influence of heat in both cases increases the rate of change to a stabler crystalline state. The effect is accompanied by a decrease in electrical resistance with rise in temperature, and is slowed down in the case of cathodically produced films by occluded air. J. GRANT.

**Conduction of electricity in metals, and allied phenomena.** T. E. STERN (Proc. Roy. Soc., 1930, A, 126, 570—582).—On the classical theory of conduction in metals many of the properties of electrical circuits could be investigated either by special transport theories or by more general theories about matter in equilibrium, with identical results; this is no longer the case on the new statistics. It is shown

that there exist in general two classes of phenomena associated with electricity in metals: (1) phenomena associated with the flow of electricity in closed circuits, which may be investigated only by making use of transport theories, and (2) those associated with insulated conductors, which may be investigated by general theories of equilibrium. The consequences of this difference are investigated, with special reference to the Thomson effect, the latent heat of evaporation of electrons, and the Peltier effect. Electrical phenomena in crystalline media are also discussed.

L. L. BIRCUMSHAW.

**Change of resistance of gold crystals at very low temperatures in a magnetic field and superconductivity.** P. KAPITZA (Proc. Roy. Soc., 1930, A, 126, 683—695; cf. A., 1929, 632).—The recent work of Meissner and Scheffers (this vol., 142) on the change of resistance of gold crystals in a magnetic field at the temperatures of liquid nitrogen, liquid hydrogen, and liquid helium is discussed. The formula used to interpret the curves was different from that proposed by the author (*loc. cit.*), Meissner and Scheffers assuming that the change of resistance follows a hyperbolic, instead of a linear, law. If, however, the results of their experiments are interpreted with the original formulæ, a full confirmation of the author's theoretical assumptions is obtained. Values of  $\Delta R_0/R_0$  calculated for different temperatures are found to be fairly constant if the linear formula is used, but show a marked variation with temperature if the hyperbolic formula is employed. The "additional" resistance  $\Delta R_0/R_0$  is found to be identical with the residual resistance  $R_r/R_0$  for the same sample of wire as measured by Meissner and Scheffers at the temperature of liquid helium. Meissner and Scheffers' criticisms of the author's suggestion as to the origin of superconductivity is considered, and a curve is constructed, showing the change of the ideal resistance of lead near 0° Abs., which demonstrates that from a purely experimental point of view it is impossible to deny that the ideal resistance may reach the very small values actually observed in the superconductive state.

L. L. BIRCUMSHAW.

**Measurements with the aid of liquid helium. VI. Transition curve for the superconductivity of titanium.** W. MEISSNER (Z. Physik, 1930, 60, 181—183).—Unicrystalline titanium (0.2% zirconium, 0.03% lead) has resistance  $R_0$  at 273.2° Abs.,  $4.47 \times 10^{-3}\Omega$ ; at 4.21°  $r$  ( $=R/R_0$ ) is 0.215; at 1.16°, 0.052; and at 1.13°, 0.0015. A sample obtained from fused titanium likewise showed a very sudden decrease in  $r$  near 1.15—1.16°. Although  $r$  falls to less than 1% of its value at 4° Abs. true superconductivity is not reached, but the shape of the transition curve indicates that a small further fall in temperature would bring about its appearance. Many, if not all, metals seem likely to exhibit superconductivity if the temperature is low enough. R. A. MORTON.

**Electrical conductivity of certain metals at low temperatures.** J. C. MCLENNAN, L. E. HOWLETT, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 287—306).—A study has been made of the changes with temperature of the electrical conductivities of a number of metals and alloys from

the ordinary temperature to  $2.2^{\circ}$  Abs. Molybdenum, hafnium, uranium, titanium, tungsten, magnesium, and zirconium all yield normal temperature-resistance curves, with residual resistances at very low temperatures. Mischmetal shows a normal resistance curve for a mixture of elements, and there is no indication of any of its components becoming superconducting down to  $2.3^{\circ}$  Abs. Niobium gives strong indications of becoming superconducting, but it is considered probable that its rapid decrease in resistance at very low temperatures is attributable to the presence of tantalum and carbon as impurities. Even at  $2.4^{\circ}$  Abs. the resistance is quite considerable, however. Tantalum becomes superconducting at  $4.2$  Abs. (cf. Meissner, A., 1929, 250). A very thin film of lead prepared by cathodic sputtering on zinc became superconducting at the same temperature as pure lead. The alloy of the composition  $\text{Na}_3\text{Pb}_5$  also becomes superconducting at the same temperature as lead. The resistance of the alloy decreases with time for a considerable period after preparation, and also shows a characteristic ageing effect with cooling. The eutectic alloy of cadmium and antimony is not superconducting. Its resistance is minimal at  $165^{\circ}$  Abs. and then rises rapidly with fall of temperature to  $2.4^{\circ}$  Abs.

J. W. SMITH.

**Electrical conductivity of ruthenium.** J. C. McLENNAN, J. F. ALLEN, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 283—286).—The electrical resistance of ruthenium remains quite high from the ordinary temperature down to the temperature of liquid helium. Between  $4.2^{\circ}$  and  $2.3^{\circ}$  Abs., however, the conductivity rises sharply, increasing about 100-fold over this short temperature range. Below  $2.3^{\circ}$  the resistance decreases only slightly as the temperature is lowered, but at  $2.04^{\circ}$  Abs. the resistance suddenly disappears completely and the metal becomes superconducting. Previously observed examples of superconducting metals and alloys are tabulated.

J. W. SMITH.

**Heat capacity of saturated liquid ethane from the b. p. to the critical temperature, and heat of fusion of the solid.** R. WIEBE, K. H. HUBBARD, and M. J. BREVOORT (J. Amer. Chem. Soc., 1930, 52, 611—622).—Two forms of calorimeter suitable for determination of heat capacities are described, one made of steel and designed for use at pressures above 1 atm., and the other of copper for low pressures. The heat capacities of saturated ethane vapour and of saturated liquid ethane have been determined over the temperature range  $67.46$ — $305.2^{\circ}$  Abs. In contradiction to the results of Eucken and Hauck (A., 1928, 826) the heat capacity is found not to rise linearly with the temperature. From the data obtained the entropies and heat contents of the liquid and vapour over this temperature range have been calculated. The heat of fusion of ethane is  $667.5 \pm 3$  g.-cal./mol., and the m. p.  $-183.65 \pm 0.10^{\circ}$ .

J. W. SMITH.

**Heat capacity of saturated liquid nitrogen and methane from the b. p. to the critical temperature.** R. WIEBE and M. J. BREVOORT (J. Amer. Chem. Soc., 1930, 52, 622—633).—The specific heats of liquid nitrogen and methane have been measured

from their b. p. to their critical temperatures, and the results compared with those of previous investigators. From the data obtained the heat contents and the entropies of the saturated liquids and vapours at different temperatures over this range have been calculated and are given in tabular and graphical form.

J. W. SMITH.

**Magnetic susceptibilities of single metallic crystals.** J. C. McLENNAN and (Miss) E. COHEN (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 159—168).—The magnetic susceptibilities of single crystals of tellurium and tin have been determined as  $-0.308 \times 10^{-6}$  and  $0.024 \times 10^{-6}$ , respectively, and show no detectable change in susceptibility with change of orientation, although the electrical conductivity, elastic constants, and thermal expansion of these crystals depend on the direction in which the measurements are made (Bridgman, A., 1925, ii, 1136). On the other hand, the magnetic susceptibilities of single crystals of bismuth and antimony, like those of zinc and cadmium (cf. A., 1929, 19), depend on the position of the crystallographic axes with respect to the direction of measurement, showing a minimum value in a direction parallel to the trigonal axis and a maximum value in a direction perpendicular to this axis. The diamagnetic susceptibility of bismuth increases with fall of temperature, the maximum and minimum values increasing from 1.50 and 1.16, respectively, at the ordinary temperature to 1.89 and 1.42 at liquid air temperature. The mean value at the latter temperature is in good agreement with that given by Owen (Ann. Physik, 1912, 37, 657). Unlike other crystals, in the case of antimony the curves obtained when the pull produced by the crystal is plotted against the angle of rotation are not  $\sin^2$  curves, but are flattened at the minimum. This is contrary to theory, but no explanation is advanced to account for the observation. Single crystals of antimony behave like an isotropic aggregate and do not change in susceptibility with temperature between the ordinary temperature and that of liquid air, the values being, maximum  $-1.13 \times 10^{-6}$ , minimum  $-0.63 \times 10^{-6}$ , and mean  $-0.80 \times 10^{-6}$ . Attempts to prepare large single crystals of selenium were unsuccessful. Measurements of the susceptibilities of non-metallic selenium and powdered metallic selenium both yield the value  $-0.29 \times 10^{-6}$ .

J. W. SMITH.

**Heat capacity and entropy of potassium perchlorate from  $12^{\circ}$  to  $298^{\circ}$  Abs. Heat of dissolution of potassium perchlorate. Entropy and free energy of perchlorate ion.** W. M. LATIMER and J. E. AHLBERG (J. Amer. Chem. Soc., 1930, 52, 549—553).—Measurements have been made of the heat capacity of potassium perchlorate from  $12^{\circ}$  to  $298^{\circ}$  Abs. and of the heat of dissolution of potassium perchlorate at  $298.1^{\circ}$  Abs., and the values used to calculate the entropy of potassium perchlorate and the entropy and free energy of the perchlorate ion. The entropy of potassium perchlorate at  $298.1^{\circ}$  Abs. is  $36.1 \pm 0.3$  g.-cal./degree, and its heat of dissolution (1 mol. in 1800 mols. of water)  $12,115 \pm 50$  g.-cal. The entropy of the perchlorate ion at the same temperature is 46.2 entropy units and its free energy  $-10,937$  g.-cal.

J. W. SMITH.

Heat capacities of organic compounds at low temperatures. II. Low-temperature thermostat. Thousandth degree copper-constantan thermocouple reference tables from 85° to 310° Abs. J. C. SOUTHARD and D. H. ANDREWS (J. Franklin Inst., 1929, 207, 323—339).—A low-temperature thermostat is described which is capable of being maintained constant to 0.001° for an indefinite length of time provided that proper stirring is employed. It may be cooled rapidly to liquid air temperatures and requires only a short time to establish equilibrium after a temperature change. No vacuum pumps are needed and only small quantities of liquid air are used in its maintenance. The pentane is encased in a copper container, thus eliminating the possibility of breakage producing an explosive mixture of pentane and liquid air.

The *E.M.F.* produced by copper-constantan thermocouples have been measured accurately over the temperature range 90—311° Abs. and fit approximately the equation  $E = E_0 - 0.447T^{1.699}$ . Tables are given whereby the temperature can be read to 0.001° from the measured *E.M.F.* over this range. The temperature gradient per unit length between the "hot" and "cold" junctions of the thermocouple does not affect the *E.M.F.* noticeably provided that the wire is homogeneous. J. W. SMITH.

Thermodynamic properties of ammonia. II. Joule-Thomson effect and heat capacity at constant pressure. J. A. BEATTIE (J. Math. Phys. Mass. Inst. Tech., 1930, 9, 11—21).—On the basis of the Beattie-Bridgeman equation of state (cf. A., 1927, 819) expressions for  $c_p$  and the Joule-Thomson coefficient ( $\mu$ ) have been obtained, and the results calculated thereby compared with recent experimental determinations. Agreement is satisfactory for  $c_p$  for temperatures between 100° and 150°, and for  $\mu$  between 30° and 150°. Causes of deviation are discussed.

C. A. SILBERRAD.

Measurement of the specific heats of gases. S. CHAPMAN (Proc. Roy. Soc., 1930, A, 126, 675—682).—A more convenient and accurate application of the principle used by Blackett, Henry, and Rideal in their continuous-flow method of comparing the specific heats of gases (this vol., 282) is suggested. The approximate formula  $\theta_c = \alpha \theta_0 / 4$  is deduced, where  $\theta_c$  is the rise of temperature due to the flow of gas at a point midway along a uniform tube of length  $l$ ,  $\theta_0$  is the difference in temperature between the two ends of the tube (maintained at the constant temperatures  $\theta_a$  and  $\theta_b$ ), and  $\alpha = \sigma q / 2KA$ .  $K$  and  $A$  denote the thermal conductivity and sectional area of the tube walls,  $q$  is the rate of flow of gas along the tube, and  $\sigma$  is the specific heat of the gas per unit volume. This formula is applied to an apparatus consisting of two similar tubes connecting the same two constant-temperature chambers at  $\theta_a$  and  $\theta_b$ , and surrounded by the same outer casings. The two gases, the specific heats of which it is desired to compare, are passed through the tubes at rates adjusted so that the central temperatures of the tubes remain equal in spite of the flow. The method is thus a balance method in which temperature differences are annulled, the only measurement being that of a

flow ratio. The advantages of this method, as compared with that of Blackett, Henry, and Rideal, are discussed. L. L. BIRCUMSHAW.

Fusion curves of hydrogen, neon, nitrogen, and argon. F. SIMON, M. RUHEMANN, and W. A. M. EDWARDS (Z. physikal. Chem., 1930, B, 7, 80).—A correction (cf. this vol., 403). Data accidentally omitted from a diagram in the original communication are given. M. S. BURR.

Differential calorimeter for the absolute measurement of very small quantities of heat. W. ORTHMANN (Z. Physik, 1930, 60, 137—142).—An apparatus which is capable of the absolute measurement of a heat evolution of  $5 \times 10^{-3}$  g.-cal. per hour with an error of not more than 4% is described. For relative measurements the error is smaller.

R. A. MORTON.

Relation between heat of vaporisation and temperature of liquids. V. A. KIREEV (J. Russ. Phys. Chem. Soc., 1929, 61, 2331—2344).—The expression  $L/RT = K = K_s(1.10 - \tau)/(1.10 - \tau_s)$ , where  $L$  is the molecular heat of evaporation of a liquid at some given absolute temperature  $T$ ,  $K$  is a constant, the value of which is  $K_s$  at the b. p. of the liquid, and  $\tau$  and  $\tau_s$  are respectively the reduced absolute temperature and the reduced b. p., is deduced and experimentally verified for a number of liquids for the range  $\tau_s < \tau < 0.90$ . The only individual parameters entering into this expression are the molecular heat of evaporation at the b. p., the absolute b. p., and the absolute critical temperature. An analogous expression,  $\lambda/RT = B = B_s(1.07 - \tau)/(1.07 - \tau_s)$ , is also derived, in which  $\lambda$  represents the latent mol. heat of vaporisation. R. TRUSZKOWSKI.

B. p. of hydrocarbons. B. V. NEKRASSOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2027—2036).—An empirical formula,  $T = K(M - \Sigma)/\sqrt{\Sigma}$ , is given, where  $T$  is the b. p. of a hydrocarbon,  $K$  is a constant (about 29 in most cases),  $M$  is the mol. wt., and  $\Sigma$  is the sum of certain numerical equivalents, for each carbon and hydrogen atom, for double linkings, for cyclic structures, for tertiary and quaternary carbon atoms, methylene groups, etc. Where the structural formula of a given hydrocarbon is known, the b. p. can thus be calculated with an accuracy of  $\pm 5^\circ$ .

R. TRUSZKOWSKI.

Thermal expansion of zinc and cadmium crystals and the crystal structure of erbium and niobium. J. C. McLENNAN and R. J. MONKMAN (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 255—267).—By examination of the X-ray spectrograms obtained with mixtures of cadmium and zinc powders with copper powder, a comparison has been obtained between the spacings in the crystals of cadmium and zinc and those in copper at the ordinary temperature and at liquid air temperature. The coefficient of expansion of copper over this temperature range being known accurately, the coefficients of expansion of the other metals can be deduced. Comparison with data obtained at the ordinary temperature shows that the coefficients of expansion are lower at lower temperatures, but that the ratios between the coefficients for the different axes remain constant. The spacings found in crystals of erbium agree very

well with those which would be produced by a close-packed hexagonal structure with the side of the basal triangle  $a_0 = 3.74 \times 10^{-8}$  cm. and an axial ratio of 1.63. A specimen of niobium containing tantalum gave a body-centred cubic structure with  $a = 3.91$  Å., which is the same as that found for pure tantalum. A second sample gave no body-centred structure, but a number of lines which have not yet been analysed. It is concluded that either niobium does not give the body-centred structure which would be expected from its position in the periodic table, or else its structure is identical with that of tantalum.

J. W. SMITH.

**Energy content of oxidoethylenedicarboxylic acid and its ions.** A. WASSERMANN (Z. physikal. Chem., 1930, 146, 462—469).—The molecular heat of formation of *cis*-oxidoethylenedicarboxylic acid is 300.1 kg.-cal. and of the *trans*-acid 299.4 kg.-cal. This indicates that the cohesive force between the molecules of the latter is greater than that of the former. Adsorption experiments with animal charcoal, fibrous alumina, and metastannic acid confirm this, since, in all cases, the *trans*-acid is more readily adsorbed than the *cis*-acid. Density, m.p., and solubility data are also in agreement with this conclusion. Determinations have been made of the sum of the heats of dissolution and of primary ionisation and also of the sum of the heats of dissolution and of primary and secondary ionisation. The ions of both acids have evidently the same energy content in dilute aqueous solutions. From dissociation data it may also be concluded that the primary ions of the two acids have similar heats of hydration. Thus, in the gaseous state, there can be no difference in energy content between the two acids.

M. S. BURR.

**Relation between the ionic radii and entropy and between the ionic radii and vibration frequency of alkali halides.** W. HERZ (Z. anorg. Chem., 1930, 186, 251—252).—If  $V_i$  is the sum of the atomic volumes of the ions assuming them to be spheres,  $S$  the entropy, and  $\nu$  the vibration frequency of the alkali halides it is shown that  $S/V_i^{1/3}$  is approximately a constant which varies between  $6 \times 10^8$  and  $7 \times 10^8$  and that  $\nu V_i$  is also approximately constant, the individual figures varying between  $1.5 \times 10^{-10}$  and  $2.0 \times 10^{-10}$ . In both cases lithium salts show the widest deviations from the mean value.

A. R. POWELL.

**Properties of metal hydrides. II.** A. SIEVERTS and A. GOTTA [with S. HALBERSTADT] (Z. anorg. Chem., 1930, 187, 155—164; cf. A., 1928, 712).—The densities of zirconium hydride and tantalum hydride, prepared by saturating the metals with hydrogen at atmospheric pressure, are 5.67 and 15.10, respectively, considerably lower than those of the corresponding metals. The following heats of formation are given:  $\text{ZrO}_2$ , 255 kg.-cal.;  $\text{Ta}_2\text{O}_5$ , 479 kg.-cal.;  $\text{ZrH}_2$ , 40.5 kg.-cal.;  $\text{TaH}$  probably slightly positive.

F. L. USHER.

**Temperature coefficients of density and viscosity.** W. HERZ (Z. anorg. Chem., 1930, 187, 379—381).—The temperature coefficients of the viscosity and density of a number of organic compounds have been compared, in some cases between temperatures  $7/12$  and  $8/12 T_k$ , where  $T_k$  is the absolute critical

temperature, and in other cases between temperatures  $5^\circ$  above and  $5^\circ$  below  $7/12 T_k$ . The viscosity temperature coefficient averages seven or eight times the density temperature coefficient for non-associated liquids. For associated liquids, however, e.g., water, acetic acid, and the alcohols, the value of the ratio is much larger still.

M. S. BURR.

**Fluidities and densities of the octyl alcohols. Association of liquids.** E. C. BINGHAM and L. B. DARRALL (J. Rheology, 1930, 1, 174—203).—The fluidities and specific volumes of 23 octyl alcohols have been determined from  $0^\circ$  to  $100^\circ$ . New atomic temperature constants of fluidity have been calculated on the assumption that the constitution of chemical compounds may not affect the fluidity except so far as it affects the degree of association. The association of each alcohol has been calculated at two different fluidities (100 and 200 rhes) and a temperature coefficient of association obtained. The association decreases regularly as the substituted side-chain is moved from the end of the carbon chain towards the centre. The association decreases also as the hydroxyl group is moved from the terminal carbon atom towards the centre, but the effect is irregular beyond the third carbon atom. A formula has been evolved by means of which the degree of association of any alcohol up to the nonyl alcohols can be predicted, the average deviation from the available data being 1.2%.

E. S. HEDGES.

**Relation of fluidity of liquids to temperature.** S. E. SHEPPARD (J. Rheology, 1930, 1, 208—210).—In the shearing over unit area defining viscous resistance, it may be supposed that at any moment there is an equilibrium between undeformed and deformed molecules, to which the Boltzmann distribution function applies. This leads to an expression relating fluidity to temperature of the form  $\log \phi = -k/T + C$ , where  $T$  is the absolute temperature and  $k$  and  $C$  are constants. Although the expression can only be a first approximation, it has been found valid for every liquid so far tested over a wide range of temperature. Deviations become considerable as the f. p. is approached. It is concluded that the expression specific heat  $\times (M\theta)^{2/3}/k$ , where  $\theta$  is the density and  $M$  the formula weight, should be a constant  $K$  for all normal liquids, whilst a relative indication of molecular association should be obtained as  $\alpha = (K/K')^{3/2}$  for deviating liquids. The data available give good confirmation of this relation.

E. S. HEDGES.

**Vapour pressure of mercury at low temperatures.** A. STOCK and W. ZIMMERMANN (Monatsh., 1930, 55, 1—2).—The vapour pressure of mercury, determined by the streaming method, is  $5.8 \times 10^{-6}$  mm. at  $-40^\circ$ . The results at  $-40^\circ$  and  $-60^\circ$  (cf. A., 1929, 1373) are not in agreement with those calculated from the Nernst formula.

A. I. VOGEL.

**Equation of state for fluids. IV. Equation expressing the volume as an explicit function of the pressure and temperature.** J. A. BEATTIE (Proc. Nat. Acad. Sci., 1930, 16, 14—19).—An equation of state of the virial form  $V = nRT/p + n\beta/RT + n\gamma p/R^2 T^2 + n\delta p^2/R^3 T^3$ , where  $\beta$ ,  $\gamma$ , and  $\delta$  are the functions of the equation of state constants in the



Beattie-Bridgeman equation (A., 1927, 819), is derived. It gives a good representation of the volume for all gases which are above their critical temperature. The agreement is not so good for gases below their critical temperature and especially in the region which is near the critical temperature and the saturation line.

F. G. TRYHORN.

**Heat conductivity of atmospheric nitrogen up to 500°.** T. WILNER and G. BORELIUS (Ann. Physik, 1930, [v], 4, 316—322).—Using Schleiermacher's cylinder method the following values for the specific heat conductivity in g.-cal./cm. deg. sec. have been obtained: dry, carbon dioxide-free air at 24°,  $60 \pm 1.4 \times 10^{-6}$ ; atmospheric nitrogen,  $96 \pm 5 \times 10^{-6}$  and  $112 \pm 4 \times 10^{-6}$  at 325° and 500°, respectively. In conjunction with other data, these results indicate no serious difference between nitrogen and air, and the equation  $10^6 \lambda = -28.5 + 5.15 \times T^{1/2}$  g.-cal./cm. deg. sec. agrees well with experiment. It is calculated that  $k$  in the equation  $\lambda = k c_v \eta$  is  $1.84 \pm 0.1$  at 325° and  $1.85 \pm 0.06$  at 500°.

R. A. MORTON.

**Vapour density of zirconium tetrachloride.** J. A. N. FRIEND, A. T. W. COLLEY, and R. S. HAYES (J.C.S., 1930, 494—497).—The preparation of pure zirconium tetrachloride is described. Zirconia was purified from hafnium by precipitation as citrate, and tested for cerium by a borax bead method. The equivalent of the metal was determined from the ratio  $\text{Zr}(\text{SO}_4)_2 : \text{ZrO}_2$  as 22.02. The heated oxide, obtained from the citrate by ignition, was converted into tetrachloride by a current of dry chlorine laden with carbon tetrachloride vapour. The lowest temperature of this reaction was found to be 355°. The vapour density of the tetrachloride was determined in chlorine at 400°, 445°, 500°, and 700°; there was no evidence of association. The vapour density falls with rise of temperature; the reactions are apparently very complex, some trichloride being formed.

N. M. BLIGH.

**Thermodynamic theory of heat conduction.** W. JAZYNA (Physikal. Z., 1930, 31, 253—264).—Mathematical. The conception of matter being equivalent to energy is applied to Fourier's theory of heat conduction.

W. E. DOWNEY.

**Compressibility at 0° and below one atmosphere and the deviation from the law of Avogadro of several gases.** V. Nitrogen, ammonia, and hydrogen sulphide. S. MAVERICK. VI. Carbon monoxide, nitric oxide, and hydrogen chloride. C. SCHLATTER (J. Chim. phys., 1930, 27, 36—43, 44—53).—The deviation from Avogadro's law for more or less easily liquefied gases was determined. The values of  $1 + \lambda$  are: nitrogen 1.00040, ammonia 1.01515, hydrogen sulphide 1.01035, carbon monoxide 1.00048, nitric oxide 1.00119, and hydrogen chloride 1.00737.

F. J. WILKINS.

**Determination of contraction of a glass bulb as a result of differences in pressure.** W. MUND and J. VANDAMME (Bull. Soc. chim. Belg., 1929, 38, 422—425).—The contraction of a glass bulb when the external pressure is increased may be conveniently measured by filling the bulb with water and fitting it with the neck projecting and open to the air into

a closed vessel of water in communication with a source of pressure. The movement of the meniscus in the neck of the bulb indicates the contraction.

R. CUTHILL.

**Viscosity of liquids.** E. N. DA C. ANDRADE (Nature, 1930, 125, 309—310).—The formula  $\eta = Ae^{b/T}$ , where  $A$  and  $b$  are constants, holds over a wide range of temperature for many substances. Data for butyl alcohol and octane between 0° and 120° are quoted in illustration.

L. S. THEOBALD.

**Viscosity of gases.** S. S. KISTLER (J. Franklin Inst., 1929, 207, 389—395).—An error in reasoning usually adopted to calculate the viscosity of gases according to the kinetic theory is pointed out. Although the correct result is attained, the mechanism of the transfer of momentum tacitly implies inelastic collisions, which are contrary to the fundamental assumptions of the kinetic theory. A more correct method of deduction is indicated.

J. W. SMITH.

**Derivation of equation of state of a mixture of substances from the equations of state of the constituents.** R. D. KLEEMAN (J. Franklin Inst., 1930, 209, 229—236; cf. A., 1929, 1373).—The equation of state of a mixture of three substances is  $p = \phi(T) \times \psi[(A_1 M_a + B_1 M_b + C_1 M_c)/v, (A_2 M_a + B_2 M_b + C_2 M_c)/v, \dots]$ , where  $p = \phi(T) \times \psi(A_1 M_a/v, A_2 M_a/v, \dots)$ , etc. are the equations of state for, and  $M_a, M_b, M_c$  the masses of, the substances  $a, b$ , and  $c$ , and  $A_1, A_2, \dots, B_1, B_2, \dots$  and  $C_1, C_2, \dots$  are functions of  $T$  independent of each other.  $\phi, \psi$ , and  $A_1$ , etc. must be functions complying with the conditions that (i) when the masses are all zero the pressure is zero; (ii) pressure is independent of total mass; and (iii) the form of  $\phi, \psi$ , and  $A_1$ , etc. do not change when one or more of the masses is zero.

C. A. SILBERRAD.

**Comparison of the Kleeman and Beattie-Bridgeman equations of state for gas mixtures.** W. E. DEMING and (MISS) L. E. SHUPE (J. Franklin Inst., 1930, 208, 389—395).—The pressures of mixtures of nitrogen and methane are calculated by Kleeman's method of combination of coefficients (A., 1929, 1373), and compared with the experimental and calculated figures of Beattie (*ibid.*, 253). It is shown that the Beattie-Bridgeman method of combination of parameters gives the better results except at low temperatures and high pressures. A more general form of Kleeman's equation is developed, and Kleeman's own form is criticised.

H. A. JAHN.

**Determination of the diffusion index of ammonia against air.** E. WINTERGERST (Ann. Physik, 1930, [v], 4, 323—351).—Quantitative methods for studying diffusion are reviewed and the possibilities of error in the Loschmidt method considered in detail. In the ammonia-air system the principal disturbances arise from absorption of ammonia on the walls of the iron tube. The diffusion index for the combination ammonia-air for 760 mm. and 0° is 0.071 m.<sup>2</sup>/hr. or 0.198 cm.<sup>2</sup>/sec. Formulae for the calculation of diffusion constants and the influence of alterations in mixture ratios, temperature, and pressure are considered.

R. A. MORTON.

**Influence of molecular attractive forces on the viscosity of gaseous mixtures.** G. JUNG and H. SCHMICK (Z. physikal. Chem., 1930, B, 7, 130—147; cf. A., 1928, 1180).—The influence of the mass and of the attractive forces of molecules on the form of the viscosity-composition curves of binary gaseous mixtures is theoretically discussed. By choosing gases the molecules of which have nearly equal masses the influence of the persistence factor is largely eliminated, and the course of the viscosity curve is determined mainly by the attractive forces. Viscosity-composition curves have been determined for the following mixtures: hydrogen chloride-air, hydrogen chloride-carbon dioxide, ammonia-air, carbon dioxide-air, hydrogen sulphide-air, methane-ammonia, and carbon dioxide-sulphur dioxide. The results confirm the theoretical conclusion that the mean free path in the case of mixtures of molecules of different electric symmetry is greater than would be given by a linear relationship between mean free path and composition. F. L. USHER.

**Theory of concentrated solutions. VIII. Composition of liquid-vapour phases in equilibrium in binary systems.** J. LEWIN (Bull. Soc. chim. Belg., 1930, 39, 91—99; cf. this vol., 147).—The method of Calingaert and Hitchcock (A., 1927, 417), even with experimental refinements, is found to be applicable only in special cases. A new static method is described for determining, with an accuracy of 1%, the composition of the vapour phase in equilibrium with a binary liquid mixture; the vapour is isolated and condensed by liquid air or solid carbon dioxide, and the composition of the resulting liquid mixture is determined by observations with the Pulfrich refractometer. Experimental results are given for graduated mixtures of carbon disulphide with acetone, ether, cyclohexane, isobutyl chloride, and isopentane, at temperatures varying between 20° and 35°. The results are in agreement with those of previous workers. The systems carbon disulphide-acetone and carbon disulphide-ether give azeotropes, the first containing 66.1 mol.-% and the second 13.6 mol.-% of carbon disulphide.

J. R. I. HEPBURN.

**Separation of azeotropes.** M. LECAT (J. Chim. phys., 1930, 27, 75—88).—A list of ninety-two positive normal azeotropic mixtures is given. C. W. GIBBY.

**Distillation of a binary mixture and the form of the (*p*-*t*) curves of its constituents.** M. LECAT (Ann. Soc. Sci. Bruxelles, 1929, 49, 261—333).—Tabulated data for 1018 binary systems are given showing the co-ordinates of the point of intersection of the saturated vapour tension curves of the constituents, and also the type of azeotropism exhibited by the system. The application of Bancroft's rule to such systems is discussed, and it is shown that on the whole azeotropism is more frequent in those systems without a point of intersection of the vapour-pressure curves of the constituents. A comparison of Bancroft's method of predicting azeotropism with the method suggested by the author indicates that the latter is the more trustworthy. F. G. TRYHORN.

**Azeotropic mixtures containing several components.** W. SWIENTOSLAWSKI (Rocz. Chem., 1930,

10, 97—114).—A systematisation of the phenomena associated with the distillation of azeotropic mixtures is given, together with a theoretical consideration of the problems connected with this subject.

R. TRUSZKOWSKI.

**Diffusion of zinc in copper crystals.** C. F. ELAM (Inst. Metals, Mar. 1930. Advance copy, 15 pp.).—When a copper crystal rod is heated in contact with zinc at 450° the end nearest the zinc becomes slowly converted into white  $\gamma$ -brass; further along a layer of bright yellow  $\beta$ -brass, sharply separated from the  $\gamma$ , is formed and, at the remote end of the rod, a dull yellow layer of  $\alpha$ -brass is produced, but there are no regions of ( $\alpha$ + $\beta$ ) or ( $\beta$ + $\gamma$ ) such as are obtained by melting. No penetration of zinc occurs along crystal boundaries and there is no preferential penetration along certain crystallographic directions. At 750° more rapid diffusion takes place so that no  $\gamma$  is formed in the presence of an excess of copper and the order of the phases is: copper,  $\alpha$ , ( $\alpha$ + $\beta$ ),  $\beta$ ; zinc definitely penetrates into the copper lattice at this temperature, forming a layer of  $\alpha$  having the same orientation as the original crystal. When a crystal of copper is heated in intimate contact with  $\alpha$ -brass no change occurs in 6 hrs. at 900°, but after scratching the surface with a file and again heating, the section recrystallises with the formation of uniform  $\alpha$  which penetrates only as far as recrystallisation has taken place. By heating a crystal of  $\beta$ -brass in contact with zinc,  $\gamma$ -crystals having a twinned relationship to the  $\beta$  may be obtained. Pure copper may be obtained by heating any of the brasses in a vacuum, evolution of zinc commencing at 550° in the case of  $\beta$ -brass, showing that zinc diffuses in or out of brass according to the temperature and vapour pressure. A. R. POWELL.

**Ternary silver alloys. II. System silver-aluminium-zinc.** S. UENO (Mem. Coll. Sci. Kyōtō, 1930, A, 13, 91—100; cf. this vol., 284).—Alloys of silver, zinc, and aluminium in which the ratio of silver to zinc is not less than 1 have been investigated, and from the results an equilibrium diagram has been constructed. R. CUTHILL.

**X-Ray analysis of iron-vanadium alloys.** A. ŌSAWA and S. ŌYA (Sci. Rep. Tōhoku, 1929, 18, 727—731).—The relation between lattice constant and concentration does not obey Vegard's law, but may be represented by an empirical expression of the second order with respect to the vanadium concentration. By extrapolation a value of 3.044 Å. is obtained for the lattice constant of pure vanadium. O. J. WALKER.

**Abnormal change in volume of the ternary system of bismuth, lead, and tin.** T. ISIHARA (Sci. Rep. Tōhoku, 1929, 18, 715—725).—Dilatometric measurements show that the abrupt change in volume in the above system takes place at 81° during heating and at 71° during cooling. The reversible change point is therefore about 76°. The change in volume is due to the formation of a ternary compound of the composition Bi<sub>2</sub>SnPb by a reaction in the solid phase. This compound is stable below 76° and decomposes into three solid solutions above this temperature. It has a greater expansion coefficient

than any of the coexisting phases and does not dissolve them.

O. J. WALKER.

**Composition of eutectics.** D. STOCKDALE (Inst. Metals, Mar. 1930. Advance copy, 19 pp.).—In an attempt to prove that the atoms of the two elements in a binary eutectic are present in a simple ratio the author has redetermined the composition of six binary eutectics by means of a very sensitive apparatus for the taking of cooling curves. A new graphical method of determining the liquidus from these curves is described in detail. The compositions of the eutectics examined were as follows, the nearest atomic ratio of the constituents being given in parentheses: cadmium-tin, 32.25% Cd (Cd:Sn, 1:2); cadmium-zinc, 82.60% Cd (Cd:Zn, 11:4); lead-tin, 38.14% Pb (Pb:Sn, 6:17); silver-copper, 71.94% Ag (Ag:Cu, 3:2); silver-antimony, 56.00% Ag (Ag:Sb, 10:7); aluminium-copper, 66.85% Al (Al:Cu, 19:4). The deviations of the observed compositions from those required by the above ratios varied from 0.01 to 0.13%, but the author considers that the existence of a simple rule governing the composition of eutectics is improbable.

A. R. POWELL.

**Mixed crystal series calcium fluoride-strontium fluoride.** E. RUMPF (Z. physikal. Chem., 1930, B, 7, 148—154).—Debye-Scherrer diagrams of mixtures of calcium and strontium fluorides prepared (a) by fusion, (b) by precipitation, and (c) by continued grinding of the components show that a complete series of mixed crystals is formed, for which the Vegard additivity rule is valid.

F. L. USHER.

**Photomicrographic methods applied to two-component salt mixtures.** W. M. MADGIN (J.C.S., 1930, 458—463).—The structures of solidified mixtures of lead nitrate and potassium nitrate have been investigated by taking photomicrographs of specimens which had been polished and etched with 96% alcohol, or treated with hydrogen sulphide. Mixtures containing more than 65% of lead nitrate cannot be investigated on account of thermal decomposition. In mixtures containing less than 65% the solids are completely immiscible (cf. Guthrie, A., 1885, 329).

C. W. GIBBY.

**Solubility of lead sulphate in water and in sodium sulphate solutions.** M. HUYBRECHTS and N. A. DE LANGERON (Bull. Soc. chim. Belg., 1930, 39, 43—57).—Anomalies indicated at 18° and 30° in the solubility of lead sulphate in aqueous solutions of sodium sulphate (cf. Huybrechts and Ramelot, A., 1927, 536) are studied in greater detail. The lead sulphate employed was prepared from lead nitrate, and was specially purified by prolonged washing; free nitric acid was completely removed only after 3 months' treatment. The purity of the product was controlled by the phenolsulphonic acid test for nitric acid, and by  $p_H$  measurements. The lead content of the saturated solutions was determined colorimetrically as lead sulphide. The solubility of lead sulphate in aqueous solutions of sodium sulphate at 15°, 20°, 25°, and 30° attains a minimum value of 3—5 mg. per litre, in solutions containing 5—7 g. of anhydrous sodium sulphate per litre; an interpolation formula is given for the variation of solubility with concentration of

sodium sulphate. The authors conclude that the anomalies previously observed are non-existent, and that the solvent action of sodium sulphate cannot be correlated, as formerly supposed, with variation in the concentrations of the hydrated and anhydrous sodium sulphate in equilibrium in the solution. From a comparison of all the experimental values, the mean solubility of lead sulphate in water is given as  $41.6 \pm 0.5$  mg. per litre at 20°.

J. R. I. HEPBURN.

**Solubility of soluble electrolytes. II. Solubility of the alkali and alkaline-earth bromides in hydrobromic acid.** A. F. SCOTT and E. J. DURHAM (J. Physical Chem., 1930, 34, 531—537; cf. A., 1927, 405).—Solubility data for the bromides of lithium, sodium, potassium, ammonium, calcium, strontium, barium, and magnesium, in water and in solutions of hydrobromic acid at 25° are recorded. On addition of hydrobromic acid, saturated solutions of lithium, calcium, strontium, and magnesium bromides develop a pink coloration which is not due to the liberation of bromine; these acid solutions also fume strongly.

L. S. THEOBALD.

**Phosphoric acid. II. Compound formation between orthophosphoric acid and certain organic acids.** J. H. WALTON and R. J. KEPFER (J. Physical Chem., 1930, 34, 543—548; cf. this vol., 426).—The solubilities of phenol, and of citric, malic, oxalic, succinic, and isovaleric acids in orthophosphoric acid solutions of various concentrations have been determined. The formation of additive compounds with phosphoric acid is indicated and the general rule advanced by Kendall (A., 1922, ii, 34) is supported. Phosphoric acid forms these compounds somewhat less readily than does sulphuric acid.

**Solubility products of inorganic salts in liquid ammonia compared with those of the same salts in other solvents with especial reference to their dielectric constants.** K. FREDENHAGEN [in part] with K. KRIEGHOFF and B. VON FREYTAG-LORINGHOFFEN (Z. anorg. Chem., 1930, 186, 1—37).—The solubility of various alkali, ammonium, and silver halides, nitrates, and hydroxides in liquid ammonia has been determined by conductivity measurements of the saturated solutions and by concentration cell measurements. The ionic concentration of saturated solutions of nitrates is the same in water as in ammonia and of iodides much greater in ammonia than in water; the solubility of silver iodide in ammonia is  $10^8$  times as great as that in water, whereas the solubility of silver fluoride is  $10^{15}$  times as great in water as in ammonia. Potassium, ammonium, and lithium fluorides have no detectable solubility in ammonia, potassium hydroxide is also insoluble, and water, although miscible with liquid ammonia, does not increase its conductivity and hence is not directly, or even indirectly as  $\text{NH}_4\text{OH}$ , ionised. The conductivity of liquid ammonia at  $-73.5^\circ$  is about  $1.6 \times 10^{-8}$  by direct measurement and  $1.6 \times 10^{-9}$  by calculation based on the *P.D.* in the cell:  $\text{H}_2 | 0.1N\text{-NH}_4\text{NO}_3 | 0.1N\text{-KNH}_2 | \text{H}_2$ . The electrostatic theory of electrolytic dissociation, according to which the ionic saturation concentrations of salts in different solvents is dependent on the dielectric constants of the solvents, is shown to be not even a first

approximation to the experimental facts. Thus, in spite of the high dielectric constants of hydrogen cyanide, acetonitrile, and hydrogen fluoride, these liquids are very poor solvents for most of the salts which dissolve readily in water. In hydrogen fluoride only fluorides dissolve in the same manner as in water, namely, forming a metal cation and fluorine anion; most other salts are decomposed, sometimes into new types of cation, but always into fluorine anion. The author puts forward a theory according to which the affinity of the elements for the anodic constituent of the solvent determines their electrolytic solution potentials against the solvent, and this theory is shown to explain the fact that for solvents which are chemically analogous to one another there is an approximate relation between their dissolving and dissociating powers and their dielectric constants.

A. R. POWELL.

**Solubility of phytosterol in ethyl and methyl alcohols.** B. REWALD (Biochem. Z., 1930, 218, 485—486).—The ethyl alcohol solution contains 0.38 g. per 100 at 0° and 13.15 g. at 78.8°. The methyl alcohol solution contains 0.10 g. per 100 at 0° and 1.68 g. at 64.9° (cf. Erlandsen, A., 1926, 898).

W. MCCARTNEY.

**Adsorption processes. II.** V. N. KRESTIN-SKAJA (J. Russ. Phys. Chem. Soc., 1929, 61, 2111—2132).—Adsorption of crystal-violet and of benzoic and acetic acids on wood charcoal is an exceedingly slow process, which does not attain equilibrium after the lapse of 3 days. The velocity of adsorption is conditioned by the velocity of diffusion of the adsorbed substance into the pores of the adsorbent. As a result, the influence of variable factors, such as mass of adsorbent taken, volume of solution, and time, on the value of  $x/m$  depends on changes in the velocity of diffusion. Benzoic acid is irreversibly adsorbed on wood charcoal, so that adsorption equilibrium is not attained for such systems; ethyl alcohol provokes only partial elution of adsorbed acid. Equimolecular quantities of acetic acid and of benzoic acid are adsorbed at limiting saturation of the adsorbent.

R. TRUSZKOWSKI.

**Adsorption and the permeability of membranes. I. Copper ferrocyanide as a semipermeable membrane.** H. B. WEISER (J. Physical Chem., 1930, 34, 335—351).—The adsorption of sodium and potassium ferrocyanides, hydroferrocyanic acid, cupric chloride, and potassium sulphate by copper ferrocyanide gel has been determined. The ferrocyanides are strongly adsorbed. Adsorption in the case of potassium ferrocyanide is so strong that it is practically irreversible between 0 and 0.4 g.-mol. of adsorbed ferrocyanide per g.-mol. of copper ferrocyanide. The order of adsorption is potassium ferrocyanide > sodium ferrocyanide > hydroferrocyanic acid. Potassium sulphate and cupric chloride are relatively weakly adsorbed and adsorption in these cases is reversible. Copper ferrocyanide gel is impermeable to alkali ferrocyanides and only slightly permeable, if at all, to the acid. This is not due to negative adsorption by the membrane. Copper ferrocyanide is permeable to potassium sulphate and copper chloride as well as to the large molecules of sodium phosphomolybdate and phosphomolybdic

acid, hence impermeability to the ferrocyanide ion is not due to a sieve-like action. Walden's contention (A., 1893, ii, 203) that copper ferrocyanide is in general permeable to acids, but not to their sodium salts, is erroneous. It is inferred that a porous membrane will be permeable to a solvent and not to the solute if it shows sufficient negative adsorption to the pore walls with a film of solvent and if the pores are fine enough to be filled by the adsorbed film (cf. Bancroft, A., 1917, ii, 444). Thus a copper ferrocyanide membrane is permeable to water but not to sucrose owing to strong negative adsorption. Complete semipermeability of a porous membrane such as copper ferrocyanide occurs when this condition obtains or when the positive adsorption of the solute is large enough to saturate the solution in the pores within the range that the adsorption is practically reversible. This second condition explains the impermeability of copper ferrocyanide to ferrocyanides.

L. S. THEOBALD.

**Adsorption of salts from non-aqueous solutions by artificial silk (cellulose hydrate).** W. HELLAT (Kolloid-Z., 1930, 50, 265—269).—The adsorption of salts from non-aqueous solutions by artificial silk is greatly affected by the presence of moisture, even small amounts of water increasing the amount of salt adsorbed. No generally applicable rule for adsorption was found in these experiments. From solutions in methyl or ethyl alcohol, sodium iodide is taken up in accordance with Henry's law, lithium chloride is negatively adsorbed between the concentrations 1.5 and 5%, but at greater concentrations is adsorbed in accordance with Henry's law. Potassium iodide and calcium chloride give normal adsorption curves. From a mixture of iodine and ethyl alcohol only the alcohol is adsorbed. Lithium chloride is adsorbed negatively from pyridine solution. The swelling of artificial silk for the solvents used falls in the following order: water > methyl alcohol > ethyl alcohol > butyl alcohol.

E. S. HEDGES.

**Colour reaction of Japanese acid clay towards leucomalachite-green hydrochloride.** N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1929, 32, 214—216B).—Non-acidic reagents (e.g., aqueous benzidine) colour the clay homogeneously, whilst acidic reagents, such as leucomalachite-green hydrochloride, colour the clay heterogeneously. The substance which oxidises benzidine is homogeneously distributed throughout the clay; that which oxidises leucomalachite-green is distributed in small discrete particles ( $d < 2.9$ ) containing iron.

A. A. GOLDBERG.

**Thickness of [adsorption] layers.** L. I. WEBER and G. LEWIN (Kolloid-Z., 1930, 50, 197—199).—When liquids are allowed to flow out of a capillary tube the thickness of the layer adhering to the walls of the tube is always of the order of  $10^{-4}$  cm. This value agrees with that obtained by other investigators using different methods. The molecular range of surface forces is discussed.

E. S. HEDGES.

**Surface tensions [of sugar solutions].** K. ŠANDRA and R. SIGMUND (Z. Zuckerind. Čechoslov., 1930, 54, 317—323).—The change of the surface tension of solutions of various grades of sugar on the

addition of small quantities of hydrochloric acid, gelatin, and of various fats and oils has been determined by stalagmometric measurements. Small quantities of these substances have marked effects on the surface tension, and the effect increases with the concentration of the sugar solution.

J. A. V. BUTLER.

**Brownian movement in surface films.** H. A. McTAGGART (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 153—158; cf. A., 1928, 232).—Qualitative experiments have been made to compare the conditions associated with the formation of small droplets on a flat surface (an oil film on water) with those which obtain in the formation of small bubbles. The Brownian motion of these droplets is apparently two-dimensional. It is unusually animated and is probably due to the greater kinetic activity at the surface. When the area of films of olive oil and of oil of almonds (both containing large proportions of olein and palmitin) is reduced gradually the first small droplets with Brownian motion appear just before the break in the area-tension curve.

J. W. SMITH.

**Unimolecular films.** C. G. LYONS and E. K. RIDEAL (Nature, 1930, 125, 455—456).—A recapitulation of previous conclusions (Lyons and Rideal, A., 1929, 875) as a reply to the criticisms of Adam (this vol., 408).

L. S. THEOBALD.

**Unimolecular films of batyl alcohol.** B. C. J. G. KNIGHT (Nature, 1930, 125, 351).—The cross-section of the head group of batyl alcohol is 26 sq. Å. This indicates that batyl and chimyl alcohols have the unsymmetrical  $\alpha$ -structure.

L. S. THEOBALD.

**Sphingomyelin, phrenosin, and kersin in films one molecule thick on water.** K. TURNER and M. M. WATSON (Biochem. J., 1930, 24, 113—118).—For each of the above substances the area occupied by the molecule in a closely-packed surface film can be compressed to about 42 sq. Å. This is in good agreement with what would be expected from the configurations of the molecules as deduced from their chemical behaviour on the supposition that the limiting value is the area occupied by the paraffin chains set side by side vertically to the water.

S. S. ZILVA.

**Solutions of diphenylcarbamide in nitrocellulose.** DESMAROUX and MATHIEU (Compt. rend., 1930, 190, 752—753).—The Röntgen diagram of a film of nitrocellulose, obtained by evaporation of an ethereal-alcoholic solution on a glass plate, shows only one diffraction circle. The films obtained from solutions of *s*-diphenyldiethylcarbamide in the nitrocellulose solution show two circles, the smaller of which is due to the carbamide. The intensity, but not the diameter, increases with the amount of the carbamide present.

H. BURTON.

**Are black soap films birefringent?** K. S. KRISHNAN (Indian J. Physics, 1930, 4, 385—404).—The unpublished results of work by C. V. Raman on the behaviour of soap bubbles of various thicknesses when placed in monochromatic light between crossed Nicols (one acting as polariser, the other as analyser) are discussed. The optical behaviour of thin films is very different from that of thick ones. The edge of

the black (thin) soap film is luminous and the inner portions are dark, whereas the reverse is the effect with thick bubbles. Slight rotation of the analysing Nicol in the case of black films completely destroys the cross except near the luminous edges, whilst with thick bubbles the dark cross assumes the form of hyperbolic isogyres. The structure of soap films and their thickness are discussed from the points of view of reflexion and X-ray diffraction. When a thick soap bubble is placed between crossed Nicols in polarised light it shows a dark cross, the arms of which are parallel to the planes of polarisation of the Nicols, and also a number of rings depending on the thickness and uniformity of the film. The appearance of the hyperbolic isogyres and interference rings is explained. As a thin film drains a black spot appears at the top and extends downwards, covering anything up to three quarters of the entire surface. Photographs of these effects are reproduced. Transmission by an isotropic spherical shell and the effect of rotating the analysing Nicol are considered theoretically. The results give no information on the optical anisotropy of thin bubbles.

W. R. ANGUS.

**Passive state and adhesion.** (MISS) M. NOTTAGE (Proc. Roy. Soc., 1930, A, 126, 630—631).—The surface of a copper plate which has been treated with boiling absolute alcohol and cooled in dilute nitric acid is found to assume a uniform dull red tint, and survives conditions under which a normal copper surface would rapidly tarnish. Measurements of the tensile strength of joints formed by thin films of palmitic acid between a passive copper surface, formed by this method, and normal copper and steel yield evidence of a remarkable increase in the intensity of the attraction field caused by a surface film of extreme tenuity.

L. L. BIRCUMSHAW.

**Collodion membranes.** V. Specific permeability of collodion membranes for molecular solutions. E. MANEGOLD and R. HOFMANN (Kolloid-Z., 1930, 50, 207—217).—Collodion membranes undergo a reversible contraction in solutions of both electrolytes and non-electrolytes and the magnitude of this effect increases linearly with the concentration. The specific permeability of the membranes is greater in dilute solutions of electrolytes than in pure water; for potassium and sodium chlorides the specific permeability increases with the concentration; for calcium and strontium chlorides and hydrochloric acid the value decreases with increasing concentration, passes through a maximum, and again rises. In solutions of sodium acetate and sulphate the specific permeability is at certain concentrations less than in pure water, and in solutions of sucrose over a wide concentration range the value is equal to that in water. The difference between the specific permeabilities of the membranes to pure water and *N*-hydrochloric acid becomes smaller with decreasing water content of the membrane. The specific permeability for hydrochloric acid decreases with increasing hydrostatic pressure of filtration, but does not fall below the value for pure water. The variation of the specific permeability with electrolyte concentration is attributed to an alteration of the electrokinetic potential, reduction in the value of which

would decrease the polarisation of the water dipoles and raise the specific permeability. The observation that the specific permeability in concentrated solutions is less than in pure water is explained in terms of the adsorption of ions, the rise of the electrokinetic potential, and the blocking effect of the dissolved molecules.

E. S. HEDGES.

**Attempt to determine the osmotic pressures of very dilute solutions.** E. W. R. STEACIE and O. MAASS (*Trans. Roy. Soc. Canada*, 1929, [iii], 23, III, 203—207).—An attempt has been made to measure very small osmotic pressures by using the vapour phase as a semi-permeable membrane and measuring the heating or cooling effect produced at the surface by raising or lowering the solvent. The desired effect was masked, however, by the distillation of the solvent to the walls of the vessel, owing, presumably, to the presence there of traces of impurities which went into solution and tended to be continually diluted by the condensation of water until the vapour-pressure equilibrium was reached. J. W. SMITH.

**Anomalous dispersion of polar solutions.** R. GOLDAMMER and H. SACK (*Physikal. Z.*, 1930, 31, 224—227).—The dielectric constants of isobutyl alcohol in paraffin oil (concentration 8.8, 13.2, and 17.8%) have been determined for wave-lengths 52.8, 77.5, and 139.0 cm. over the temperature range 3—50°, and viscosities over the same range have also been evaluated. The results afford evidence of anomalous dispersion in a region distinct from optical dispersion. The viscosity data exhibit a parallelism with the dielectric constants consistent with Debye's dipole theory (cf. Mizushima, A., 1928, 934; Kitchen and Müller, A., 1929, 242).

R. A. MORTON.

**Apparent hydration of ions. IV. Densities and viscosities of saturated solutions of silver nitrate in nitric acid.** J. W. INGHAM (*J.C.S.*, 1930, 542—552; cf. A., 1928, 948, 1184; 1929, 1233).—The densities and viscosities of saturated solutions of silver nitrate in nitric acid up to 12*N*, and of nitric acid alone over the same range, have been determined. The solution volumes of silver nitrate, nitric acid, and water are calculated (cf. Jablczyński, *Rocz. Chem.*, 1923, 3, 362; Bragg, A., 1920, ii, 537). The silver ion has an apparent radius less than that calculated from lattice measurements, and hydration factors of 1.4—0.90 are found for it.

C. W. GIBBY.

**Relation between particle distribution and space in loose-grained products.** A. H. M. ANDREASEN (*Kolloid-Z.*, 1930, 50, 217—228).—A theoretical investigation of the packing of particles of different sizes in space.

E. S. HEDGES.

**Problems of present-day colloid chemistry. III. Electrical double layer.** H. R. KRUYT (*Chem. Weekblad*, 1930, 27, 101—103).—The properties of the electrical double layer surrounding a colloidal particle are discussed on the assumption that certain factors affect the thermodynamic *P.D.*, whilst others affect the capillary-electric *P.D.*

H. F. GILLBE.

**Colloidal ice in frozen sugar solutions.** N. VON WEIMARN (*Kolloid-Z.*, 1930, 50, 241—247).—Sugar solutions of concentrations between 20 and

70% were chilled in a bath at  $-80^{\circ}$  and the following observations were made. With solutions containing 50—65.5% of sugar, colloidal ice was produced. With 50—55% solutions the colloidal state lasted only for a few seconds, but with solutions near the eutectic composition (62.4%), which set to a glass, the colloidal ice was stable for at least 24 hrs. With more concentrated solutions the appearance of the colloidal state was delayed, and glasses containing 66—70% of sugar remained quite clear during the time of observation (24 hrs.). These results are discussed in the light of P. P. von Weimarn's theory.

E. S. HEDGES.

**Nephelometry of cellulose acetate solutions.** S. IWASAKI and S. MASUDA (*J. Soc. Chem. Ind. Japan*, 1930, 33, 43B).—The opacity of solutions of cellulose acetate in acetone and in other solvents has been investigated nephelometrically. In acetone and also in acetone-methyl alcohol solutions the transparency decreases linearly with the concentration. In acetone-benzene (up to 20% acetone) and in acetone-water (up to 10% acetone) there is no change in opacity although in the former case the viscosity increases. Acetone-ethyl alcohol solutions decrease in opacity with increasing alcohol content; the viscosity simultaneously decreases to a smaller degree. An explanation of these results is advanced.

A. I. VOGEL.

**Effect of ions on the sedimentation of colloidal particles by centrifuge.** H. M. EVANS and R. E. CORNISH (*J. Amer. Chem. Soc.*, 1930, 52, 1009—1012).—Very slow sedimentation is not necessarily due to convection currents. It is shown that the addition of suitable salts to proteins greatly facilitates sedimentation in ionising solvents.

J. G. A. GRIFFITHS.

**Stability and coagulation of mists and clouds.** A. WIGAND and E. FRANKENBERGER (*Physikal. Z.*, 1930, 31, 204—215).—Stability of a mist is due largely to the fact that the droplets carry electrical charges of the same sign; the mist tends to become homogeneous as regards both the size and charge of the droplets. An attempt is made to calculate the charge necessary for stability, taking into account the thermal motion of the droplets and streaming effects. Comparison with measurements carried out under different weather conditions confirm the electrostatic theory of stability. The mechanism of coagulation of a mist is considered in a similar manner.

R. A. MORTON.

**Coagulation of colloids by emulsions formed by temperature changes.** I. A. JANEK and A. SCHMIDT (*Kolloid-Z.*, 1930, 50, 263—265).—When a sol is treated with an equal volume of a mixture consisting of 1 vol. of chloroform, 3 vols. of water, and 4 vols. of ethyl alcohol, or a mixture of 3 vols. of benzene, 1 vol. of water, and 6 vols. of ethyl alcohol, a fine emulsion is produced and after a time coalescence to two liquid layers ensues. The solid disperse phase of the original sol is then found to accumulate at the liquid-liquid interface, often in the form of a thin film. Alternatively, the coagulating emulsion may be formed by temperature alteration, such as by adding another liquid which is sufficiently miscible with water at the ordinary temperature and



then cooling. Details of experiments carried out by this means are given. E. S. HEDGES.

**Effect of ions of similar charge in the coagulation of colloids by electrolytes.** W. PAULI and M. WITTENBERGER (*Kolloid-Z.*, 1930, 50, 228—241).—Experiments on the coagulation of ferric hydroxide sol by a number of salts having the same anion and different cations show that the order of effectiveness of the cations in preventing the coagulating effect of the anion is as follows:  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{NH}_4 < \text{Ag} < \text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{La}$ . Salts having the same cation and different anions gave the following order for coagulation by the anion:  $\text{Fe}(\text{CN})_6''' > \text{Fe}(\text{CN})_6''' > \text{oxalate} > \text{SO}_4 > \text{F} > \text{acetate} > \text{CNS} > \text{Cl} > \text{Br} > \text{NO}_3 > \text{ClO}_3 > \text{I}$ . These results are discussed from the point of view of the valency and the mobility of the ions. It is inferred that the activity and not the concentration of the ions is the important factor in coagulation and that the effect of the ions for which the sign of the charge is the same as that of the colloid is to influence the activity of the oppositely charged ion.

E. S. HEDGES.

**Determination of the charge on a colloid and the mechanism of its coagulation.** M. N. CHAKRAVARTI, S. GHOSH, and N. R. DHAR (*J. Physical Chem.*, 1930, 34, 326—334).—Mainly theoretical. The electric charge on a colloidal particle originates in the preferential adsorption of ions from an electrolyte present in the medium. The thickness of the double layer surrounding the particles is at least of the order  $10^{-7}$  cm., and the electric charge on a particle is not greater than  $10^{-6}$  e.s.u. A relationship between the coagulating powers of uni-, bi-, and ter-valent ions is deduced.

L. S. THEOBALD.

**Liquid sheaths and clearing.** H. WERNER (*Kolloid-Z.*, 1930, 50, 247—262).—Suspensions settle more rapidly after the addition of electrolytes. In the presence of electrolytes the clearing can be followed by observing the rate of fall of the sharply-defined boundary. The time curve consists of two portions, the lower portion indicating when all the particles of the suspension are loosely in contact. For a given suspension the mean degree of packing of the particles corresponding with the point where the curve indicates that they first make contact is independent of the nature and concentration of the electrolyte. From the position of this point on the curve and from measurements of the final volume of sediment it is possible to calculate the density of the liquid sheaths of the particles. The force binding together the individual particles into aggregates depends in the first place on a definite force of attraction between the particles, which is opposed by the resistance of the liquid sheath to deformation; the total effect therefore depends on the size, nature, and concentration of the dispersed particles, the concentration of the electrolyte, the nature of the dispersion medium, and the temperature. A method has also been devised for determining the attractive force between the particles and the dispersion medium.

E. S. HEDGES.

**Problems of present-day colloid chemistry.**  
**V. Kinetics of coagulation.** H. R. KRUYT (*Chem. Weekblad*, 1930, 27, 129—131).—The work of von

Smoluchowski and of Müller and the theoretical developments connected therewith are reviewed, consideration being given to the efforts to adapt the conclusions reached to partly stabilised systems. The lack of a general knowledge of the electrical double layer and of its distribution over the particle makes any quantitative consideration of coagulation phenomena very difficult.

S. I. LEVY.

**Action of salts of polynuclear bases on colloidal suspensions and on the electro-capillary curve.** J. A. V. BUTLER and W. O. KERMACK (*Proc. Roy. Soc. Edin.*, 1929, 49, 300—312).—Salts of 5:6-benz-4-carboline and its derivatives (A., 1928, 302, 650) precipitate colloidal gum benzoin and other negatively-charged lyophobic sols at comparatively low concentrations, but at considerably higher concentrations they do not bring about flocculation of these colloids, but confer a positive charge on the previously negatively-charged colloidal particles. From observations on the effect of the simultaneous presence of benzcarboline salts and of gelatin of  $p_H$  4.6 and 7.0, evidence has been obtained that the presence of gelatin decreases the adsorption of benzcarboline ions. The effect of various benzcarboline salts on the electro-capillary curve of mercury has been determined. In presence of small concentrations (0.00005*M*) of the salts, the maximum of the electro-capillary curve occurs to the right of that of the primitive (negative polarisation of the mercury), and the greatest fall in surface tension occurs to the left of the maximum of the primitive (positive polarisation of the mercury). These results indicate high adsorption of benzcarboline ions even on a positively-charged surface. The possible cause of this unexpected result is discussed.

W. O. KERMACK.

**Structure of gelatin sols and gels. I. Viscosity of gelatin solutions.** S. E. SHEPPARD and R. C. HOUCK (*J. Physical Chem.*, 1930, 34, 273—298).—The change in viscosity of gelatin solutions (7%) with time over a wide  $p_H$  range and at different temperatures has been studied. Comparable results are possible only with gelatin sols of definite  $p_H$  of the same age at constant temperature. No definite temperature exists at which viscosity is independent of time. Sols of the same  $p_H$  when kept below a certain temperature zone show a steady increase of apparent viscosity with time; a steady fall of  $\eta$  with time occurs at temperatures above this zone. The shape of the  $\eta$ - $p_H$  curve is determined mainly by the age of the solution. The curves obtained by plotting the rate of change of fluidity,  $\phi_k = \Delta\phi/\Delta t$ , against  $p_H$  consist of inclined straight lines which would meet on extrapolation at  $p_H$  6, but are intercepted by a horizontal portion between  $p_H$  5 and 8. The rate of change of fluidity is related to the hydrolysis coefficient  $k$  by the expression  $\phi_k = a \log k + b$ , where  $a$  and  $b$  are constants. The relation of gelatin to collagen is also discussed.

L. S. THEOBALD.

**Direct determination of volume contraction.** P. STAMBERGER and C. M. BLOW (*Kolloid-Z.*, 1930, 50, 269—271).—An apparatus in which the total diminution in volume of the system gel+swelling liquid can be measured directly is described. A

known weight of the gel is put into an evacuated flask fitted with a pipette and a capillary tube. A known volume of the swelling liquid is then allowed to flow from the pipette so as to fill the flask and part of the capillary tube. Subsequent changes in volume are followed by taking readings of the height of the meniscus in the capillary tube. The apparatus has been used for observing the swelling of caoutchouc in toluene; the mean result indicates a contraction in the total system of about 0.006 c.c. per g. of caoutchouc.

E. S. HEDGES.

**Swelling work and heat of swelling.** R. FRICKE and J. LUKE (*Naturwiss.*, 1930, **18**, 307).—For agar-agar, casein, and maiden-hair hydrogels, the differences between the heat and work contents associated with the swelling of two gels within a specific range of concentration are approximately equal, although the former are much greater than the latter. The methods employed for determining the values of the changes in the heat and work content are outlined.

W. R. ANGUS.

**Equation occurring in the kinetic theory of gases.** A. RAJCHMAN (*Compt. rend.*, 1930, **190**, 729—730; cf. Frobenius, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1908, 471).—A simpler proof of an equation is given.

C. A. SILBERRAD.

**Solution of certain cases of the general equation of diffusion.** R. L. PEEK, jun. (*Physical Rev.*, 1930, [ii], **35**, 554—561).—Mathematical.

N. M. BLYTH.

**Equilibrium in synthesis and decomposition of methyl alcohol.** B. S. LACY, R. G. DUNNING, and H. H. STORCH (*J. Amer. Chem. Soc.*, 1930, **52**, 926—938; cf. Newitt and others, *A.*, 1929, 508).—From determinations of the equilibria  $2\text{H}_2 + \text{H} \cdot \text{CO}_2\text{Me} = 2\text{MeOH}$  (copper catalyst) and  $\text{MeOH} + \text{CO} = \text{H} \cdot \text{CO}_2\text{Me}$  (sodium methoxide catalyst, static method) and including the data of Christiansen (*A.*, 1926, 358), the equilibrium constant,  $K_p = (p_{\text{MeOH}}(\text{atm.})/[p_{\text{CO}}][p_{\text{H}}]^2)$ , is computed to be  $3 \times 10^{-2}$ ,  $3 \times 10^{-3}$ , and  $5 \times 10^{-4}$  at 200°, 250°, and 300°, respectively.

By direct synthesis and decomposition of methyl alcohol at 50 atm. total pressure with a flow method and a reduced copper-uranium-thorium catalyst, the equilibrium constant ( $K_p$ ) is  $1.9 \times 10^{-4}$  and  $1.25 \times 10^{-3}$  at 300° and 250°, respectively, and  $3.0 \times 10^{-2}$  at 200° by synthesis only; at 20 atm. and 250°, the constant is  $1.8 \times 10^{-3}$ , by synthesis. The discrepancy between these results and that of Smith and Branting (*A.*, 1929, 265) is discussed.

J. G. A. GRIFFITHS.

**Dissociation constant of water from an equilibrium involving mercuric oxide and mercurous bromide.** R. F. NEWTON and M. G. BOLINGER (*J. Amer. Chem. Soc.*, 1930, **52**, 921—925).—The composition of potassium bromide solutions in equilibrium with mercuric oxide, mercurous bromide, and mercury has been investigated at 25°. The free energy change is  $\frac{1}{2}\text{HgO}(s) + \frac{1}{2}\text{Hg}(l) + \frac{1}{2}\text{H}_2\text{O}(l) + \text{Br}' = \frac{1}{2}\text{Hg}_2\text{Br}_2(s) + \text{OH}' + 943 \text{ g.-cal. at } 25^\circ$ . This result is not affected by very slow compound formation between mercuric oxide and mercurous bromide (cf. Fischer and von Wartenburg, *A.*, 1905, ii, 456).

The dissociation constant of water at 25° ( $K_w = 1.02 \times 10^{-14}$ ) is calculated from the above determin-

ation and existing data (Ming Chow, *A.*, 1920, ii, 281; Gerke and Geddes, *A.*, 1927, 734).

J. G. A. GRIFFITHS.

**Dissociation constants and heats of ionisation of simple amino-acids and peptides.** G. E. K. BRANCH and S. MIYAMOTO (*J. Amer. Chem. Soc.*, 1930, **52**, 863—868).—Acidic ( $K_a$ ) and basic ( $K_b$ ) dissociation constants of glycine,  $\alpha$ -alanine, glycylglycine, and glycylalanine have been determined in aqueous solution at 20° and 0° by electrometric titration. Dissociation constants and heats of dissociation at 25° are calculated: glycine,  $K_a = 2.54 \times 10^{-10}$ ;  $\Delta H_a = 10,700 \text{ g.-cal.}$ ;  $K_b = 2.21 \times 10^{-12}$ ;  $\Delta H_b = 14,600$ ;  $\alpha$ -alanine,  $2.06 \times 10^{-10}$ ; 11,450;  $2.21 \times 10^{-12}$ ; 14,600; glycylglycine,  $7.41 \times 10^{-9}$ ; 9830;  $1.15 \times 10^{-11}$ ; 14,800; glycylalanine,  $6.025 \times 10^{-9}$ ; 11,100;  $1.15 \times 10^{-11}$ ; 14,800. The influence of constitution on these quantities is discussed.

J. G. A. GRIFFITHS.

**Ethyl acetate equilibrium. II. [Salt effect.]** R. C. CANTELO and R. D. BILLINGER (*J. Amer. Chem. Soc.*, 1930, **52**, 869—875).—An extension of previous work (*A.*, 1929, 139) includes the effects of the bromide, acetate, and nitrite of sodium on the equilibrium constant,  $K = [\text{ester}][\text{water}]/[\text{acid}][\text{alcohol}]$ , which in all cases increases with rising concentration of salt, although values of  $K$  are depressed below 3.7 for the last two salts.

The velocity of esterification at 78° is catalysed by the six salts (0.1—0.4*N*) named in order of decreasing effect: sodium bromide, chloride, iodide, thiocyanate, acetate, and nitrite. The last two retard the reaction. The acetate is believed to have a secondary salt effect. The changes of the velocity and of the equilibrium constant are attributed to alterations of the activity coefficients of the reactants in the presence of salts. The Debye-McAuley relation for the activity of non-electrolytes (*A.*, 1925, ii, 172) is verified.

J. G. A. GRIFFITHS.

**Neutral salt action. Relative influence of cations and anions on the equilibrium**  $2\text{Fe}(\text{CN})_6''' + 3\text{I}' = 2\text{Fe}(\text{CN})_6'''' + \text{I}_3'$ . V. K. LAMER and H. B. FRIEDMAN (*J. Amer. Chem. Soc.*, 1930, **52**, 876—885).—In a continuation of previous work (*A.*, 1928, 1325) it is shown that 1—3*M*-concentrations of potassium, sodium, chloride, nitrate, and sulphate ions have marked specific effects on the above equilibrium. The equilibrium constant is larger in the presence of potassium than of sodium ions, and of chloride than of nitrate ions. When these cations or anions are interchanged, the free energy differences of the reaction are almost linear functions of the concentration of the neutral salt added. The principle of specific interaction does not apply.

Evidence is adduced for the existence of  $\text{I}_3'$  ions, since the equilibrium constant for a given thermodynamic environment drifts with change of iodide concentration if the formation of  $\text{I}_3'$  ions is neglected.

J. G. A. GRIFFITHS.

**Equilibrium between bivalent and quadrivalent palladium and chlorine in hydrochloric acid solutions.** H. B. WELLMAN (*J. Amer. Chem. Soc.*, 1930, **52**, 985—999).—Measurements of the solubility of potassium chloropalladate have been made in *N*-hydrochloric acid containing potassium

chloride and saturated with chlorine at 740 mm. at 25°. The solubility product,  $[K']^2[PdCl_6'']$ , is constant and equal to  $5.97 \times 10^{-6}$  (concentrations: molal). The oxidation equilibrium  $PdCl_4'' + Cl_2 = PdCl_6''$  has been investigated by passing chlorine largely diluted with nitrogen through solutions of potassium chloropalladate in hydrochloric acid. Little, if any, trivalent palladium is present, since the concentration of  $PdCl_6''$  in *N*-hydrochloric acid in contact with solid potassium chloropalladate is nearly equal to that calculated from the solubility product. The values of  $[PdCl_6'']/[PdCl_4''] [Cl_2]$  in *N*- and 0.3*N*-hydrochloric acid and 0.3*N*-hydrochloric acid and 0.7*N*-sodium chloride solutions support the assumption that the palladium is present largely in the form of the above ions and not as hydrolysed or non-ionised acids. The reduction potential of the reaction  $PdCl_4'' + 2Cl' = PdCl_6'' + 2e$  at 25° is computed to be -1.288 volt. J. G. A. GRIFFITHS.

**Nitric acid. V. Action of nitric oxide on nitric acid.** (a) The system up to *N*-nitric acid concentration in aqueous solution. A. KLEMENC and E. HAYEK (Z. anorg. Chem., 1930, **186**, 181–224; cf. A., 1929, 655).—The equilibria of the system  $3HNO_2(sol.) \rightleftharpoons HNO_3(sol.) + 2NO(gas) + H_2O$  have been determined at 12.5° and 30° in solutions between 0.02*N* and *N* with respect to nitric acid and the values of the constant *K* have been extrapolated to infinite dilution. At 12.5°  $K_0 = 13.2 \pm 0.2$  and at 30°  $K_0 = 39.6 \pm 0.4$ , whence the activity coefficient of nitrous acid is 1.00–1.05, according to the concentration of the nitric acid in the solution. The equilibrium potential of the system has been measured and the results agree with those found in the literature except for solutions more concentrated than 0.5*N*-nitric acid at 12.5°, where the deviations noted indicate the presence of other molecules. A table of the activity coefficients of nitric acid at 12.5° and 30° is given for concentrations between 0.01*N* and 0.1*N*. The values of the heat of formation of nitrous acid found by Thomsen and Berthelot are 1800 and 1400 g.-cal. too high, respectively, the true value being close to 28,910 g.-cal., which agrees with that of Swientoslawski (Z. physikal. Chem., 1910, **72**, 60).

A. R. POWELL.

**The acid-base function.** J. N. BRÖNSTED (Z. anorg. Chem., 1930, **43**, 229–233).—A review of recent conceptions of the nature of acids and bases.

J. A. V. BUTLER.

**Contamination by dust particles and intensive desiccation.** A. W. C. MENZIES (Nature, 1930, **125**, 445–446).—The importance of the removal or fixation of dust particles in work on intensive drying is emphasised. Salt hydrate systems show a period of induction both in the process of dehydration and of rehydration and deliquescence when dust particles are absent.

L. S. THEOBALD.

**Compound formation in system naphthalene-*m*-dinitrobenzene.** E. L. SKAU (J. Amer. Chem. Soc., 1930, **52**, 945–950).—F.-p. data for the system naphthalene-*m*-dinitrobenzene indicate eutectics at 50.8° and 49.7° with 46.3 and 59.5% of naphthalene, respectively. A compound (m. p. 51.2°) is formed (cf. Olivari, Rend. soc. chim. ital., 1911, [ii], **3**, 90; Kre-

mann, A., 1905, ii, 77). Pushin's conclusions (A., 1926, 1208) are criticised. J. G. A. GRIFFITHS.

**Tensimetric analysis of the systems  $ZnSO_4-H_2O$  and  $(NH_4)_3Cr(C_2O_4)_3-H_2O$ .** A. P. PALKIN (J. Russ. Phys. Chem. Soc., 1929, **61**, 2133–2137).—A study of the vapour pressure of water over crystals of zinc heptahydrate shows that these lose water to form hexahydrate, which then undergoes conversion into stable monohydrate. Rosenheim's salt,  $(NH_4)_3Cr(C_2O_4)_3 \cdot 3H_2O$ , has a continuous water vapour-pressure curve, with, however, a halt at 2.5*H*<sub>2</sub>O.

R. TRUSZKOWSKI.

**Hydrated oxides. XX. System aluminium oxide-water.** G. F. HÜTTIG and O. KOSTELITZ. **XXI. System cobaltous oxide-water. XXII. Catalytic activity of metallic cobalt prepared from different hydrated cobalt oxides.** G. F. HÜTTIG and R. KASSLER (Z. anorg. Chem., 1930, **187**, 1–15, 16–23, 24–28).—I. The isobaric dehydration of specimens of hydrated aluminium oxide prepared in different ways has been studied, the number of molecules of water associated with each molecule of aluminium oxide while in equilibrium with a water vapour pressure of 10 mm. being followed over the temperature range 12–500°. The X-ray spectra of the different preparations have also been investigated. The X-ray examination shows that the freshly-precipitated compound is amorphous; it contains only about 1 mol. of water of combination. On continuous heating it loses its colloid character, giving up a part of its water readily but retaining the remainder up to high temperatures. At the ordinary temperature this form passes into the stable crystalline hydrate  $Al_2O_3 \cdot 3H_2O$ . It is concluded, however, that a series of intermediate hydrates exists between the mono- and tri-hydrate.

II. Isobaric dehydration curves at a water-vapour pressure of 10 mm. have been followed for specimens of hydrated cobaltous oxide prepared in different ways. With the freshly-precipitated material the water content at first falls rapidly with rise of temperature until it contains about 1.5 mols.  $H_2O$  to each mol. of cobaltous oxide, after which it decreases slowly with rise of temperature up to 168°, when it has the composition  $CoO \cdot H_2O$  (approx.). At this temperature there is considerable loss of water at constant temperature, the composition changing to about  $CoO \cdot 0.4H_2O$ , which again loses water steadily with rise in temperature. At 300° 0.1 mol. of water is still held by the cobaltous oxide. The difference between the rose and blue forms of hydrated cobaltous oxide is one of fineness of division only; the blue form is the more finely divided. The two forms have identical X-ray spectra, distinct from that of anhydrous cobaltous oxide. On heating either form with water a more stable product, containing less water and showing the above phenomena to a much less marked extent, is formed. This stabilisation is more rapid with the blue than with the rose form.

III. The catalytic activities of specimens of metallic cobalt produced by reduction of oxides and hydrated oxides prepared in different ways have been compared. The reaction used was the decomposition of formic acid into carbon dioxide and hydrogen. The cata-

lytic activity is conditioned by the temperature of reduction of the oxide, but so long as this temperature is between 300° and 550° the difference is negligible. Raising the reduction temperature to 1000° or 1200°, however, considerably decreases the activity of the preparation. The metal obtained from oxides produced by precipitation was in all cases more active than that from oxides prepared by heating the nitrates, but the differences were not considerable enough to allow generalisations to be made. J. W. SMITH.

**System sodium iodate-sodium sulphate-water.** H. W. FOOTE and J. E. VANCE (Amer. J. Sci., 1930, [v], 19, 203—213).—The equilibrium relations at 25°, 29.5°, and 50° afford evidence for the formation of the double salts  $\text{NaIO}_3 \cdot 3\text{Na}_2\text{SO}_4$  and  $\text{NaIO}_3 \cdot 4\text{Na}_2\text{SO}_4$ . The following invariant points (transition points) are indicated:  $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and  $\text{NaIO}_3 \cdot 3\text{Na}_2\text{SO}_4$  26.95°;  $\text{NaIO}_3 \cdot 3\text{Na}_2\text{SO}_4$ ,  $\text{NaIO}_3 \cdot 4\text{Na}_2\text{SO}_4$ , and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  30°;  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{NaIO}_3 \cdot 4\text{Na}_2\text{SO}_4$  32.33°;  $\text{NaIO}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{NaIO}_3 \cdot \text{H}_2\text{O}$ , and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  16.7°. The ternary eutectic temperature is -1.27°.

C. W. GIBBY.

**Polythermic region of crystallisation of Glauber salt in the system:  $2\text{NaCl} + \text{MgSO}_4 \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ .** V. P. ILJINSKI and A. F. SAGAIDATSHNI (J. Russ. Phys. Chem. Soc., 1929, 61, 1953—1974).—The equilibrium relations have been reinvestigated over the range limited by the transition temperature of Glauber's salt and the eutectic temperatures. R. TRUSZKOWSKI.

**Deviations from the law of Neumann, Joule, and Kopp and the apparent mol. heat of water in solid compounds.** N. DE KOLOSOVSKI and I. SKOULSKI (Bull. Soc. chim., 1930, [iv], 47, 136—147).—The mean heat capacities of silica, ferric oxide, aluminium oxide, lime, cyanite, kaolinite, china clay, white and red bauxite have been determined over ranges from 15—150° to 15—350°. The heat capacities of the last five are invariably smaller than the values calculated from their composition, assuming additivity. The apparent mol. heat of water in ferric hydroxide, hydrated china clay, white hydrated French bauxite, red hydrated bauxite from Tikhvine, and kaolinite from Podolsk have been determined. In bauxites and china clay it is equal to that of water of crystallisation of crystalline hydrates, in ferric hydroxide it approaches that of free water, whilst in kaolinite it is much smaller. Water has a greater heat capacity in substances from which it is easily removed by heating. J. A. V. BUTLER.

**Energy of polymerisation of water.** R. WILDT (Z. anorg. Chem., 1930, 187, 127—128).—The energy of polymerisation of water into the form of ice I is given by the equation  $P = E_1 + E_2 - E_3 - E_4$ , where  $E_1$  is the latent heat of ice I,  $E_2$  the heat change associated with the change  $(\text{H}_2\text{O})_{x(\text{water})} \rightarrow x\text{H}_2\text{O}_{\text{vapour}}$  at 0°,  $E_3$  is the latent heat of vaporisation of water in the unimolecular state at 0°, and  $E_4$  the latent heat of freezing of unimolecular water at 0°. The first three are calculated from existing data, and the last from analogy with hydrogen sulphide, yielding

a value of  $P = 1.43 + 10.7 - 4.0 - 0.4 = 7.7$  kg.-cal./per mol. This value is thought to be correct to  $\pm 0.5$  kg.-cal. It is noted that the energy of polymerisation of ice is much greater than the heat of formation of the easily decomposable hydrates of chlorine, carbon dioxide, and nitrous oxide with 5 or 6 mols. of water.

J. W. SMITH.

**Thermochemistry of compounds in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . III. Heat of hydration of calcium oxide.** T. THORVALDSON, W. G. BROWN, and C. R. PEAKER (J. Amer. Chem. Soc., 1930, 52, 910—915).—The heat of hydration of calcium oxide at 20° is 276.3 g.-cal. per g. by direct determination. The value calculated from earlier data is 278.9 g.-cal. per g. at 20°. This discrepancy is attributed to slow physical changes in the particles (cf. von Glasenapp, A., 1922, ii, 848). J. G. A. GRIFFITHS.

**Heats of combustion of camphor, azobenzene, and hydrazobenzene.** W. SWIENTOSLAWSKI and J. BOBINSKA (Bull. Acad. Polonaise, 1929, A, 621—630).—See this vol., 295.

**Heats of combustion and mol. volumes of organic compounds.** W. HERZ (Z. Elektrochem., 1930, 36, 99—101).—The heat of combustion divided by the mol. refraction is for the paraffins and olefines constant; the aliphatic alcohols yield a similar although smaller constant. The significance of these results, and of those derived for the fatty acids, aldehydes, ketones, and esters, is discussed.

H. F. GILLBE.

**Interatomic binding forces of some isomeric carboxylic acids and their esters.** A. WASSERMANN (Helv. Chim. Acta, 1930, 13, 113—119).—It has been shown (cf. this vol., 534) that both the *cis*- and *trans*-forms of certain carboxylic acids and their esters have the same heat of combustion in the gaseous state. This means that the average atomic binding force in the two isomerides is the same. Since this may not necessarily mean that the effective binding force (cf. Ebel and Bretscher, A., 1929, 744) is also the same, the evidence of comparative data with reference to the behaviour of the isomerides has been examined. The degree of dissociation of maleic acid in the first stage is greater than that of fumaric acid, indicating a difference in the effective binding force of the hydrogen ion. In acid solution maleic acid is esterified more readily than fumaric acid, whilst in alkaline solution the dimethyl ester of maleic acid is hydrolysed more readily than the fumaric ester. This indicates that the effective binding force of the alkyl radical is greater in the maleic than in the fumaric ester. Reactions involving the ethylene linking indicate a similar difference in the effective binding force. Similar conclusions may also be reached with regard to the other isomerides considered. M. S. BURR.

**Measurement of resistance of electrolytes.** O. SCARPA (Gazzetta, 1930, 60, 96—104).—A modification of the Kohlrausch method is described which permits of the use of polarisable electrodes. A cell containing similar electrodes and electrolyte to those of the cell the resistance of which is to be measured is inserted in series with the fixed resistance in the balancing arm of the bridge. O. J. WALKER.

Electrical conductivities of solutions of tetraethylammonium iodide in benzonitrile. A. R. MARTIN (J.C.S., 1930, 530—535; cf. Walden, A., 1906, ii, 149, 335).—Measurements have been made at 0°, 25°, 50°, and 70° for  $\nu = 100$ —10,000. The conductivities at infinite dilution derived by the method of Ferguson and Vogel (A., 1925, ii, 1163) are found to be very closely proportional to the fluidity of the solvent. The mobilities in benzonitrile of the ions  $\text{NEt}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Ag}^+$ ,  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$  are calculated. Taking into account the interionic force effects, the values of the dissociation constant for tetraethylammonium iodide have been calculated for each of the four temperatures. From these values the heat of dissociation is approximately 1 kg.-cal. per g.-mol.

C. W. GIBBY.

Conductivity of uni-univalent salts in cyclohexanol. O. E. FRIVOLD (J. Franklin Inst., 1929, 208, 627—642).—The conductivities of lithium chloride, bromide, and perchlorate, and of guanidine nitrate, in cyclohexanol at concentrations between  $10^{-5}$  and  $10^{-3}M$  have been determined at 25°. The values of  $\Lambda_\infty$  for the four salts are respectively 1.09, 0.79, 1.42, and 1.03. The  $\Lambda - \sqrt{c}$  curves afford no evidence of linear relationships excepting possibly the data for guanidine nitrate at low concentrations, and the directions of the limiting tangents indicate complete disagreement with Onsager's modification of the Debye-Hückel theory. The viscosity of cyclohexanol is 0.596 at 25°, 0.424 at 30°.

C. A. SILBERRAD.

Carbonium electrolytes. K. ZIEGLER and H. WOLLSCHITT (Annalen, 1930, 479, 90—110).—An apparatus for measuring the conductivity of dilute solutions of triarylmethyl halides and perchlorates in sulphur dioxide is described. These measurements have been made to ascertain if the isomerisation (ionisation) of triarylmethyl halides can be regarded as a characteristic of the electrochemical state of the triarylmethyl residue. The conductivity of solutions of triarylmethyl chlorides rises with increased dilution; a limiting value is sometimes reached. The greater is the tendency for rearrangement of the chloride, the higher is the initial conductivity. When the ratio  $\lambda_p/\lambda_\infty$  is plotted against  $\log \nu$  for four triarylmethyl perchlorates, the curves obtained are almost identical irrespective of the groups (Me, OMe) in the benzene nuclei. Triarylmethyl perchlorates are strong electrolytes for which  $K = 1.2$ — $1.3 \times 10^{-2}$  at  $\nu = 100$ . Triphenylmethyl chloride has  $K = 1.1 \times 10^{-4}$ . The limiting conductivities ( $\lambda_\infty$ ) for the triarylmethyl chlorides are about 20 units higher than for the corresponding perchlorates. In more concentrated solutions, however,  $\lambda_p$  is lower for the chloride. The value of  $\lambda_\infty$  for the chlorides is diminished by the introduction of groups; the lowest values are found with large substituents. The increase in the tendency for isomerisation of a series of chlorides  $\text{CRPh}_2\text{Cl}$ , is in the following order ( $R =$ ):  $\text{Ph}$ ,  $\beta\text{-C}_{10}\text{H}_7$ ,  $\text{Ph}\cdot\text{C}_6\text{H}_4$ ,  $\alpha\text{-C}_{10}\text{H}_7$ ,  $\text{C}_6\text{H}_4\text{Me}(p)$ ,  $\text{C}_6\text{H}_4\cdot\text{OMe}(o)$ ,  $\text{C}_6\text{H}_4\cdot\text{OMe}(p)$ . The triarylmethyls with small tendency for association have considerably ionised chlorides. 9-Chloro-9-phenylfluorene ( $K = 6 \times 10^{-9}$ ), 1-bromo-1:2:3-triphenylindene ( $K = 3 \times 10^{-8}$ ), and bromopentaphenylcyclopentadiene ( $K = 3 \times 10^{-8}$ ) are weak electrolytes. H. BURTON.

Influence of temperature on polarisation capacity and resistance. E. E. ZIMMERMAN (Physical Rev., 1930, [ii], 35, 543—553).—The temperature coefficients of polarisation capacity and resistance have been determined for gold and platinum electrodes in 0.63, 1.5, and 2.42*N*-solutions of sulphuric acid, and at different frequencies for a 1.46*N*-solution. The electrodes were reduced by thermal treatment to a condition of minimum capacity, during which process the value of the polarisation capacity decreased to one half and the resistance increased to a few times the original value. The temperature coefficient of capacity is about twice as great for platinum as for gold, and is apparently independent of the concentration; it increases with frequency for platinum but decreases for gold. The absolute values of the slopes of the capacity-temperature and resistance-temperature curves decrease with increasing frequency.

N. M. BLIGH.

Measurement of small continuous *E.M.F.* without considerable consumption [of current]. M. COURTINES and J. GELOSO (J. Chim. phys., 1930, 27, 54—59).—Details are given of the application of a triode to the measurement of *E.M.F.* of the order of 1 volt with an accuracy of 0.01 volt.

F. J. WILKINS.

Electromotive behaviour of single zinc crystals. Equilibrium potential. P. A. ANDERSON (J. Amer. Chem. Soc., 1930, 52, 1000—1008).—The electromotive behaviour of the primary cleavage face of single zinc crystals, prepared in three different ways, has been investigated in air-free cells of the type  $\text{Zn}, \text{ZnCl}_2\text{aq.}(0.4496M), \text{HgCl}, \text{Hg}$ . The metal yields reversible electrodes of constant and reproducible potential (1.078 volts at 25°) which is almost identical with that of electrolytically-prepared matrix electrodes. The equilibrium potential is independent of minute traces of impurities, crystal edges, and planes additional to the primary cleavage plane, and is attained more rapidly by etching the plane surface. The equilibrium potential is identified with the step-wise growth or disintegration of the crystal and the potentials of the different faces must be measured by the low initial non-equilibrium values.

J. G. A. GRIFFITHS.

Electrode potential [of platinum] in solutions of mixtures of ter- and bi-valent manganese salts. J. CHLOUPEK (Coll. Czech. Chem. Comm., 1930, 2, 129—133).—The potential of a platinum electrode immersed in solutions of ortho-, pyro-, and metaphosphoric acids and arsenic acid containing mixtures of manganous and manganic oxides has been measured against the mercurous sulphate electrode in 2*N*-sulphuric acid. The value varied between +0.98 and +1.18 volt and increased slowly with the time at first, then decreased owing to instability of the solutions.

A. R. POWELL.

Electrochemical properties of the ion of mercurous oxide. A. I. BRODSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 2205—2215).—The activity coefficients of  $\text{Hg}_2^{2+}$  in aqueous solutions of mercurous nitrate at various concentrations have been determined from *E.M.F.* measurements for the chains  $\text{Hg}|\text{Hg}_2(\text{NO}_3)_2|\text{KNO}_3|\text{Hg}_2(\text{NO}_3)_2, \text{Cl}_2$  or  $\text{Br}_2|\text{Hg}$ . The

coefficients found are in good agreement with the saturation law and with Debye's second approximation; the factor preceding  $\sqrt{c}$  is, however,  $\sqrt{2}$  times less than the theoretical value. The normal potential of the electrodic process  $2\text{Hg} \rightarrow \text{Hg}_2^{++}$  is 0.7966 at 10.8°, 0.8014 at 14.9°, 0.8040 at 19.2°, and 0.8080 volt at 26.5°, as compared with the normal hydrogen electrode at 18°. The solubilities of mercurous chloride, bromide, and iodide at 25° are respectively  $11.5 \times 10^{-19}$ ,  $5.5 \times 10^{-23}$ , and  $49.5 \times 10^{-30}$ ; the solubilities of a number of other sparingly soluble salts of mercury are calculated from the experimental data of other authors. R. TRUSZKOWSKI.

Polarographic studies with the dropping mercury cathode. IX. Deposition of zinc and cadmium from ammoniacal solutions. M. DOBRYSZYCKI (Coll. Czech. Chem. Comm., 1930, 2, 134—144).—Deposition of cadmium or zinc from ammoniacal sulphate solutions proceeds reversibly at the dropping mercury cathode for all concentrations of ammonia. The deposition potential of cadmium in *N*-ammonia is shifted by about 0.2 volt and that of zinc by about 0.3 volt. The results indicate that the co-ordination number of zinc and cadmium in ammoniacal solution is 4, but that this is merely a mean value. A. R. POWELL.

Electrokinetic potential of metals and the *E.M.F.* of movement. S. PROCORIU (J. Chim. phys., 1930, 27, 29—35).—The movement of a metallic electrode with respect to the surrounding electrolyte sets up an *E.M.F.* of movement which appears to be similar in character to the electrokinetic potential. In the case of metallic electrodes in pure water these two potentials are of the same sign and also of the same order of magnitude. F. J. WILKINS.

Temperature measurements at working electrodes. III. B. BRUŽS (Z. physikal. Chem., 1930, 146, 356—362; cf. this vol., 185).—The heat effects for various current densities have been investigated at electrodes of copper, zinc, and cadmium in sulphate solutions and silver, lead, and bismuth in nitrate solutions. The heat effects are proportional to the temperature coefficients of the electrodes as determined by Ostwald, and to the calculated differences between the entropy of the metal and that of metal ions in solution. It is considered that the method may be used to determine the entropies of metal ions in solution. J. A. V. BUTLER.

Photo-electric phenomena of solutions of potassium ferrocyanide. A. BLANC (Compt. rend., 1930, 190, 674—676; cf. A., 1928, 808).—The small photo-electric current which is produced when solutions of potassium ferrocyanide are exposed to the mercury arc has a negligible fatigue effect, a nearly constant value being obtained after 10 min. exposure. The slope of the current-electric field curve is the same as that obtained with metals, except when the latter show the fatigue effect. For a given field the current intensities are proportional to the ferrocyanide concentration. J. GRANT.

Quantum theory of the kinetics of homogeneous and heterogeneous reactions. S. ROGIN-

SKY and L. ROSENKEWITSCH (Nature, 1930, 125, 347—348).—Assuming that a spontaneous disintegration of the molecule is possible, a formula for the velocity coefficient of a reaction has been obtained on the basis of quantum mechanics. L. S. THEOBALD.

Gaseous combustion. W. T. DAVID (Nature, 1930, 125, 409—410).—A reply to Bone (this vol., 424). L. S. THEOBALD.

Persistence of velocity and the theory of second order gas reactions. L. S. KASSEL (Physical Rev., 1930, [ii], 35, 261—263).—Theoretical. For second order gas reactions, if reaction occurs whenever two reactant molecules collide with sufficient velocity, the molecular velocities do not deviate appreciably from the predictions of Maxwell's distribution law, provided the molecular masses are nearly equal, in contrast to Fowler's conclusions. Fowler's correction becomes appreciable if the molecular masses are widely different. N. M. BLIGH.

Calculation of energy of activation in bimolecular reactions. H. EYRING (Z. physikal. Chem., 1930, B, 7, 244—245).—The following rule is given for the calculation of energy of activation in bimolecular gas reactions. In the reaction  $A+B \rightarrow C+D+W$ , where *W* has always a positive sign and is the heat of reaction, compounds are decomposed of which the heats of dissociation may be given as  $y_1 > y_2 > y_3 \dots$ , and compounds are formed of which the heats of dissociation are, similarly,  $x_1 > x_2 > x_3 \dots$ . The activation energy *E* is then equal to  $Z/2$ , where *Z* is either  $y_1$  or  $x_1 - W$ , whichever value is the greater. Calculated values of *E* have been compared with experimental values for a number of reactions. M. S. BURR.

Inflammability of hydrogen. VIII. Energy required to ignite hydrogen-air mixtures and the effect of explosion inhibitors. IX. Inflammability of hydrogen-nitrogen and of hydrogen-carbon dioxide mixtures, and the effect of explosion inhibitors. X. Prevention of flame propagation in hydrogen-air mixtures. Y. TANAKA and Y. NAGAI (Proc. Imp. Acad. Tokyo, 1929, 5, 418—421, 422—425, 426—429; cf. A., 1929, 654).—VIII. The condensed spark discharge energy required to ignite mixtures of air and hydrogen in various proportions has been determined, together with the influence of ethyl bromide, tin tetramethyl, diethyl selenide, and benzene when present in mol. percentages up to about 3. With mixtures containing less than 20% of hydrogen the ignition energy at first increases with the quantity of the third component added, becomes constant, and finally increases rapidly; with richer mixtures the flat portion of the curve vanishes, since the upper limit of inflammability is reached at a low concentration of the added substance. The ignition energy is a minimum in mixtures containing about 20% of hydrogen, indicative of the sensitivity of the combustion to an excess of oxygen.

IX. The influence of tin tetramethyl on the inflammability limits of hydrogen-carbon dioxide and hydrogen-nitrogen mixtures in air has been determined. The minimum hydrogen content for sustained combustion is about 22% in mixtures



containing 1% of tin tetramethyl, and is slightly lower at higher and lower concentrations.

X. The largest mesh copper gauze which will prevent the propagation of flame through a hydrogen-air mixture containing tin tetramethyl, lead tetramethyl, benzene, or tin tetramethyl and carbon tetrachloride has been determined. The results show clearly the influence of these additions, which is due to the rise of temperature necessary for propagation of the flame. H. F. GILLBE.

Homogeneous isothermal reaction  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$  in the presence of water vapour. B. TORLEY (Nature, 1930, 125, 560-561).—A summary of the results obtained in the oxidation of carbon monoxide in silica vessels. A homogeneous reaction occurs between  $530^\circ$  and  $730^\circ$  in a mixture of carbon monoxide, oxygen, and water (0.13% and above) at pressures above 70 mm. The presence of water vapour appears to be essential and the velocity of reaction is approximately proportional to the concentration of water vapour. At a given concentration of water vapour, the rate of reaction is approximately proportional to the concentration of carbon monoxide when oxygen is in excess, and to a power of the concentration of oxygen when carbon monoxide is in excess. The reaction has a chain mechanism with stable chains at pressures exceeding a certain limit; in this region, the reaction is accompanied by a violet glow. Induction periods prior to explosion have been occasionally observed.

L. S. THEOBALD.

Ignition of carbon monoxide detonating mixture by decomposition products of water. L. FARKAS, P. GOLDFINGER, and F. HABER (Naturwiss., 1930, 18, 266; cf. A., 1929, 1148).—Jets of water were used as electrodes so that all probability of the results being vitiated by traces of metal from metal electrodes was eliminated. The acceleration of the reaction is considered. W. R. ANGUS.

Decomposition of nitrogen pentoxide at very low pressures. H. C. RAMSPERGER and R. C. TOLMAN (Proc. Nat. Acad. Sci., 1930, 16, 6-13; cf. A., 1929, 1016).—The determination of the rate of decomposition of nitrogen pentoxide at low pressures showed that in accordance with earlier work there is no diminution in the specific rate of decomposition down to pressures of about 0.2 mm., but that a diminution becomes evident at pressures of about 0.04 mm. and increases in magnitude down to the lowest pressures investigated, namely, about 0.0006 mm. At this lowest pressure the specific rate of decomposition had fallen to about 0.67 of its high-pressure value. The rate of homogeneous decomposition is essentially of the first order over the whole pressure range. The discrepancy between these results and those of earlier workers is attributed to the fact that in the present work the wall effect has been eliminated as far as is possible by the use of reaction vessels of 45 litres capacity. The results agree qualitatively although not quantitatively with the theory of chemical activation by collision.

F. G. TRYHORN.

Explosive combustion of ammonia in admixture with air. O. SCHLEPHAKE, A. VON NAGEL,

and J. SCHEMEL (Z. angew. Chem., 1930, 43, 302-308).—An initiated combustion freely proceeds explosively only within sharply-defined, narrow concentration limits, which, with rise of temperature, widen somewhat in the absence of moisture, and in the presence of moisture approach one another until they coincide at  $40-45^\circ$ . Liability to explosive ignition depends also on the size and shape of the containing vessel and the type of ignition; in large vessels a gas flame, or even a match, will produce ignition, whereas in small or narrow vessels a spark is essential. Incandescent metal wire will not initiate combustion unless the wire is coated with a catalyst capable of accelerating the decomposition of ammonia into its elements (platinum-black, iron sponge), and a stoichiometrical gas mixture is employed. The explosion velocity in illuminating gas-air mixtures exceeds ten times that in ammonia-air or power gas-air mixtures, although addition of other explosive gases raises the explosion velocity of the latter. Analogously, ammonia-air mixtures require much longer time to attain maximum explosion pressures than mixtures of air with illuminating gas, or hydrogen. An expression is deduced for the shattering power of a gaseous explosion which agrees qualitatively with the experimental results. The shattering power is diminished by increase in the size of the containing vessel and also if the walls of the vessel are heat-insulating; it also depends on the locality of the ignition (particularly in the case of ammonia-air mixtures). These results were confirmed by explosions carried out in protected glass flasks and in iron vessels provided with a sheet lead lid which is deformed more or less, or rent, according to the force of the explosion. S. K. TWEEDY.

Thermal decomposition of hydrazine. P. J. ASKEY (J. Amer. Chem. Soc., 1930, 52, 970-974).—Hydrazine at  $22-154$  mm. decomposes on quartz at  $270-310^\circ$  according to the equation  $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$ . The decomposition of hydrazine at  $7-11$  mm. pressure on platinum wire at  $173-530^\circ$  and on tungsten wire at  $360-500^\circ$  is represented by the equation  $2\text{N}_2\text{H}_4 = 2\text{NH}_3 + \text{N}_2 + \text{H}_2$ . The reactions are of approximately first order. Hydrogen retards the decomposition on platinum, but not on tungsten.

J. G. A. GRIFFITHS.

Oxidation of benzaldehyde and formaldehyde in the gaseous phase. P. J. ASKEY (J. Amer. Chem. Soc., 1930, 52, 974-980).—The relative velocities of gas-phase oxidation with oxygen of benzaldehyde at  $198-242^\circ$  and formaldehyde at  $321-400^\circ$  were determined by the pressure changes. The oxidations are chain reactions, since "packing" the bulbs decreased the velocities. Excess of oxygen retards the oxidation of benzaldehyde, but more carbon dioxide is produced if the initial pressure of oxygen is less.

J. G. A. GRIFFITHS.

Theory of periodic reactions in homogeneous systems. A. SKRABAL (Z. physikal. Chem., 1930, B, 6, 382-422).—Theoretical. The conditions under which the simultaneous transformations of three tautomerides can give rise to a periodic reaction have been investigated. If the principle of microscopic reversibility holds, the reaction is necessarily aperiodic.

When the individual reactions give rise to "unilateral equilibrium," or are micro-heterogeneous in character, strongly damped periodic changes may occur.

J. A. V. BUTLER.

**Velocity of reaction in mixed solvents. I. Velocity of reaction between potassium persulphate and potassium iodide in organic solvents-water mixtures.** M. PRASAD, C. L. MANKODI, and R. D. GODBOLE (J. Indian Chem. Soc., 1930, 7, 59—65; cf. Kiss and Hatz, A., 1929, 271).—The rate of reaction between potassium persulphate and potassium iodide in water and binary mixtures of water and up to 50 vol.-% of methyl, ethyl, and propyl alcohols, glycol, glycerol, and pyridine at 25° has been determined. With decrease in the proportion of water in the solvent medium the velocity coefficient decreases continuously, although with propyl alcohol-water mixtures it ultimately passes through a minimum and rises again at higher alcohol concentrations. The retarding effect of the organic substance, which is the less marked the more hydroxyl groups there are in the molecule, appears to bear no relationship to either the viscosity or the dielectric constant of the solvent.

R. CUTHILL.

**Kinetics of nitric acid. Oxidation of arsenious acid.** E. ABEL, H. SCHMID, and J. WEISS (Z. physikal. Chem., 1930, 147, 69—86).—The oxidation of arsenious acid by nitric acid at 25° has been investigated. The rate of the reaction is the rate of the relatively slow intermediate reaction  $2\text{HNO}_2 + \text{H}_3\text{AsO}_3 = \text{H}_3\text{AsO}_4 + 2\text{NO} + \text{H}_2\text{O}$ . Nitrous anhydride is the immediate oxidising agent, and the oxidation involves the following two concurrent series of reactions, which represent the general mechanism of oxidation by nitric acid (R= substance undergoing oxidation):  $\text{HNO}_2 + \text{HNO}_3 \rightarrow \text{N}_2\text{O}_4 + \text{H}_2\text{O}$ ,  $\text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O} \rightarrow 4\text{HNO}_2$ , and  $2\text{HNO}_2 \rightarrow \text{N}_2\text{O}_3 + \text{H}_2\text{O}$ ,  $\text{N}_2\text{O}_3 + \text{R} \rightarrow \text{RO} + 2\text{NO}$ .

R. CUTHILL.

**Hydrogen peroxide as an oxidising agent in acid solution.** X. W. H. HATCHER and A. C. HILL (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 213—224).—The action of hydrogen peroxide at 100° on propionic and *n*- and *iso*-butyric acids and the effects of concentration of reactants, of addition of sodium ion, and of addition of hydrochloric acid on these reactions have been investigated. Combining the observations with previous results (cf. A., 1928, 256) it is concluded that the longer is the carbon chain in the fatty acid series the less is the susceptibility to oxidation. The sodium salts are only slightly oxidised, since at 100° and in the presence of sodium ions the peroxide is decomposed rapidly. Only with sodium butyrate is the reaction more rapid than with the acid. When undissociated, hydrochloric acid retards the reaction by decomposing the hydrogen peroxide, but when almost completely dissociated it accelerates the reaction, this effect being most marked with the butyric acids. This may be due to the intermediate formation of acetone. In each case an early step in the mechanism of oxidation is the production of a per-acid, followed by hydroxylation at the  $\alpha$ -carbon atom, yielding aldehydes and ketones which are further oxidised. There is no evidence of the formation of oxalic acid, but in any case it would

readily be oxidised further. *n*-Butyric acid is the only one giving evidence of  $\beta$ -oxidation and therefore formation of a keto-acid. The analogy between the oxidation by hydrogen peroxide and by potassium permanganate in acid solution is discussed.

J. W. SMITH.

**Reaction of the solvent alcohol on dissolved esters in presence of the sodium alkoxide.** A. S. TOWNSHEND (Trans. Roy. Soc. Canada, 1929, [iii], 23, III, 225—226).—The reaction between phenyl benzoate and alcohols in the presence of the sodium alkoxide has been investigated. The rate of this reaction increases with increasing alkalinity of the solution and with rise of temperature. The addition of small quantities of water to the alcohol decreases the rate of reaction and increases the rate of saponification, whereas dilution of the alcohol with benzene (up to 85% of benzene) increases the rate of reaction. The addition of phenol to the solution decreases the rate of the reaction, but eventually it proceeds to completion, and all attempts to reverse the reaction by using concentrated solutions of phenol were unsuccessful. The rate of conversion of phenyl benzoate with ethyl alcohol and with *n*-butyl alcohol is almost the same, but it is somewhat faster with *iso*amyl alcohol and benzyl alcohol and much faster with methyl alcohol. Using secondary alcohols there is a considerable amount of saponification, but nevertheless the rate with *sec*-butyl alcohol is much faster, and that with *isopropyl* alcohol much slower than with ethyl alcohol. The reaction is more rapid with phenyl acetate than with phenyl benzoate, but less rapid with phenyl phthalate.

J. W. SMITH.

**Variation of the velocity coefficient of a bimolecular reaction with temperature.** J. A. CRANSTON and J. G. LAIRD (J. Roy. Tech. Coll. Glasgow, 1930, 2, 187—190).—The change of the rate of saponification of ethyl acetate has been measured between 0° and 44° by determining the decrease in conductivity of the solution as the sodium hydroxide became converted into sodium acetate. The variation of the velocity coefficient (*K*) with temperature is given by the equation  $K_1 = K_0 e^{(u/2)(T_1 - T_0)/T_1 T_0}$ , in which the constant *u* has a mean value of 11,300.

C. A. KING.

**Kinetics, statics, and energetics of the thermal reaction  $\text{CH}_2\text{I}-\text{CH}_2\text{I} = \text{CH}_2 + \text{CH}_2 + \text{I}_2$  in carbon tetrachloride solutions.** M. J. POLISSAR (J. Amer. Chem. Soc., 1930, 52, 956—969).—The thermal decomposition of ethylene iodide in carbon tetrachloride between 40° and 152° has been investigated in the presence of  $1.5 \times 10^{-5}$ —0.1 equiv. per kg. of iodine, which catalyses the reaction. The velocity is directly proportional to the concentration of ethylene iodide (0.011—0.19 equiv. per kg.) and to the square root of that of iodine, but a slow uncatalysed decomposition also occurs. The decomposition of solid ethylene iodide is catalysed by iodine.

It is suggested that an ethylene iodide molecule can decompose only after collision with an iodine atom, whence the heat of activation of the iodide calculated from the velocity coefficients ( $Q=13,000$  g.-cal.) and the kinetic theory ( $Q=11,250$ ) is approximately equal to the heat of dissociation ( $Q=11,300$ ) com-

puted from the equilibrium constants. Analogous calculations are applied to other reactions (Bodenstein and Plaut, A., 1925, ii, 135; Slaton, J.C.S., 1904, 85, 1697). J. G. A. GRIFFITHS.

**Relative rates of absorption of gaseous olefines into sulphuric acid at 25°.** H. S. DAVIS and R. SCHULER (J. Amer. Chem. Soc., 1930, 52, 721—738).—The rates of absorption with varying amounts of sulphuric acid (60—97.8%) have been determined at 25° in a constant-volume apparatus. Since the acid is used in relatively large excess, the data given apply to the initial stage of reaction only. The amount of olefine absorbed per sec. is proportional to its partial pressure. Slow rotation of the absorption chamber causes an increase in the absorption rate due to increasing the surface area; the rate is not affected greatly by changes in the speed of rotation. A specific absorption coefficient ( $C$  = the average number of c.c. of gas absorbed by 1 cm.<sup>2</sup> of acid surface in 1 sec. at constant pressure) is calculated for each olefine in order to compare the rates when different surface areas are employed. The data for the reaction between ethylene and concentrated sulphuric acid show that (i) the acid film on the glass vessel absorbs as efficiently as the acid surface, (ii) the absorption rate is not changed greatly by renewal of the surfaces or by agitation caused in the acid by rotation, and (iii) the rate is not appreciably affected by a nine-fold change in the volume of the acid. The reaction takes place, therefore, in a thin film at the surface of the liquid.

The rate of absorption of propylene is about 300 times that of ethylene for 80—97.8% sulphuric acid; the absolute values of the rates of both gases change almost 200 times over the same range of concentration. Propylene is absorbed by 87% acid at the same rate in absence or presence of oxygen or ethylene. Propylene and  $\Delta^{\alpha}$ -butene dissolve at about the same rate in acid of the same concentration, and the ratio  $\Delta^{\beta}$  :  $\Delta^{\alpha}$ -butene is constant (1.7 : 2.6) for 70—87% acid. *iso*Butene is absorbed more rapidly than  $\Delta^{\beta}$ -butene, and trimethylethylene more rapidly than *isobutene*.

The work of Michael and Brunel (A., 1909, i, 197) and of Dobrjanski (B., 1926, 394) is criticised.

H. BURTON.

**Kinetics of crystallisation of supersaturated solutions.** E. N. GAPON (J. Russ. Phys. Chem. Soc., 1929, 61, 2319—2326).—The curve representing the velocity of crystallisation of supersaturated solutions is similar to that for an autocatalysed reaction. In the presence of indifferent salts the induction period is greatly shortened, the velocity of reaction is increased, and the point of maximum velocity is attained sooner than in their absence. Non-electrolytes and colloids are without influence on the velocity of crystallisation.

R. TRUSZKOWSKI.

**Hydration of ions and molecules.** E. N. GAPON (J. Russ. Phys. Chem. Soc., 1929, 61, 2327—2330).—The velocity of crystallisation of sodium picrate from solutions containing 0—50% of ethyl alcohol increases as the alcohol content rises. The expression  $(\log k_x - \log k_0)/x^2 = \text{constant}$ , where  $x$  is the molecular concentration of ethyl alcohol, and  $k_0$

and  $k_x$  are respectively the velocity coefficients in pure water and in aqueous alcohol, is derived from theoretical considerations, and is verified experimentally. R. TRUSZKOWSKI.

**Velocity of dissolution of metals in aqueous salt solution. II.** E. BEKIER and A. BASIŃSKI (Rocz. Chem., 1930, 10, 71—83).—The process of dissolution of tin in stannic chloride solution is primarily of a chemical nature; diffusion plays only a subordinate rôle in this process, as is shown by the negligible effect on the velocity of reaction of stirring, and by the temperature coefficient of the reaction (2.0). The addition of hydrochloric acid or of chlorides accelerates dissolution, as a result of inhibition of hydrolysis of stannic chloride. The velocity coefficient of the reaction increases rapidly with increase in concentration of ammonium and hydrogen chlorides, whence it is concluded that the concentration of the ion  $\text{SnCl}_6^{--}$ , formed from hydrogen or ammonium chlorostannate, determines the velocity of reaction. R. TRUSZKOWSKI.

**Action of nitric acid on some metals.** E. S. HEDGES (J.C.S., 1930, 561—569).—The rate of dissolution of copper and silver in nitric acid is decreased almost to zero by sufficiently rapid rotation of the metal, but is increased again almost to its normal value by the addition of nitrous acid. In concentrated nitric acid copper rotated at 2000 r.p.m. dissolves relatively slowly and becomes coated with a film of cupric oxide; this film causes the copper to dissolve only slowly in dilute nitric acid at rest. The inhibiting effect of carbamide on the dissolution of copper in nitric acid is reduced by raising the temperature or increasing the concentration of the acid. In 25% nitric acid at 30° a rotating copper anode corrodes more slowly than a stationary anode and is positive to the latter by 0.16 volt. These results indicate that the primary action of nitric acid on copper affords cupric oxide and nitrous acid which then combine to yield cupric nitrite; this is then decomposed by nitric acid with the formation of copper nitrate and oxides of nitrogen. Thus nitric acid appears to oxidise copper superficially and causes it to become passive, whereas nitrous acid activates the metal by removing the film. Tin, zinc, and magnesium dissolve more readily when rotated than when stationary in dilute nitric acid, and nitrous acid has no accelerating effect on the action; in these cases therefore the initial product of the reaction is, probably, hydrogen. A. R. POWELL.

**Measurement of the corrosion of metals.** G. GOLLNOW.—See B., 1930, 379.

**Thermodynamics of catalysis.** A. BERTHOUD (J. Chim. phys., 1930, 27, 112—113).—A reply to Dubrisay (this vol., 41; cf. Cohen and Miyake, A., 1926, 466). C. W. GIBBY.

**Oxidation of *n*-hexane; reaction in presence of antioxidants.** M. BRUNNER (Helv. Chim. Acta, 1930, 13, 197—207).—The changes in pressure and in the concentration of acid and "active oxygen" (peroxides) in *n*-hexane-oxygen mixtures containing 0.3% or 1.0% of aniline at 200° or 210° have been followed. The reaction shows an induction period

which increases with increasing concentration of the inhibitor; oxidation proceeds at the end of this period at the normal rate. The non-formation of water during the induction period shows that the inhibition extends to the primary reaction (dehydrogenation). The concentration of the aniline remains unchanged until just before the onset of the main reaction, when it falls rapidly to zero.

H. E. F. NOTTON.

**Kinetics of the catalytic oxidation of arsenious acid with ferric chloride in presence of potassium iodide.** J. C. SARMA (J. Indian Chem. Soc., 1930, 7, 31—37; cf. Jellinek and Vinogradov, A., 1924, ii, 836).—The rate of reaction between ferric chloride and arsenious acid in aqueous solution has been measured at 50° and 60° in presence of potassium iodide as catalyst, and using the ceric sulphate method for the determination of ferrous salt (Willard and Young, A., 1928, 725). The reaction is bimolecular in respect of the ferric salt and unimolecular in respect of the arsenious acid, and probably consists of two consecutive reactions:  $2\text{Fe}^{3+} + 2\text{I}^- \rightleftharpoons 2\text{Fe}^{2+} + \text{I}_2$ , followed by  $\text{I}_2 + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} = 2\text{HI} + \text{H}_3\text{AsO}_4$ , the latter being the relatively slow reaction. From the velocity coefficients the heat of reaction per g.-mol. of arsenious acid is calculated to be +13,600 g.-cal. The velocity is proportional to some power of the catalyst concentration higher than the first.

R. CUTHILL.

**Polarity of the carbon-halogen linking. III. Inhibitory effect of water on acid hydrolysis of halogenonaphthols.** J. R. SANNEY (J. Amer. Chem. Soc., 1930, 52, 93—95).—The dehalogenation of 1-iodo- $\beta$ -naphthol (cf. A., 1928, 57) in acid alcoholic solutions is retarded by water. If the alcohol is replaced by acetic acid, this effect is more pronounced, but irregularities occur with low concentrations of water. The addition of alkali halides and stannic chloride accelerates the reaction.

J. G. A. GRIFFITHS.

**Autocatalysis in oxidation. II. Action of catalysts on the autoxidation of abiatic acid.** G. DUPONT and J. LÉVY (Bull. Soc. chim., 1930, [iv], 47, 147—156).—The influence of catalysts on the autoxidation of abiatic acid has been studied by determining their influence on the relation between the velocity of absorption of oxygen at constant volume and the mean and initial pressure of oxygen previously observed in the absence of a catalyst (A., 1929, 811; this vol., 42, 86). In xylene solution quinol, pyrogallol, and resorcinol have a strong antioxygenic action. Phenol has only a slight action, but thymol is a pronounced antioxygen. Picric acid, salicylic acid, and iodine are without antioxygenic action, but rubber is a powerful antioxygen, probably owing to the presence of sulphur derivatives. Sulphur is without effect, hydrogen sulphide exerts a slight action, and sulphur dioxide a pronounced initial effect which does not persist. Sulphuric acid is a powerful antioxygen, but hydrochloric, acetic, and benzoic acids are without action. Cadmium, zinc, copper, magnesium, and sodium abietates and copper and lead acetates show a more or less pronounced antioxygenic action at the start, the effect then disappearing. These observations afford an

explanation of inconsistent or contradictory results obtained in determining oxidation velocities. Metallic mercury, nickel, manganese, and iron abietates, and especially cobalt abietate, are positive catalysts and accelerate the oxidation, manganese abietate having an initial antioxygenic effect. In the presence of alcohol the autocatalysis is masked, and cobalt oxide acts initially (60 hrs.) as an antioxygen. Acetic acid yields essentially the same results as xylene, but in carbon tetrachloride the catalytic activity of cobalt abietate is destroyed.

R. BRIGHTMAN.

**Slow and induced oxidation of glycogen, lecithin, cholesterol, formate, oleate, stearate, and some food materials.** C. C. PALIT and N. R. DHAR (J. Physical Chem., 1930, 34, 711—723).—An aqueous solution of sodium formate and a suspension of glycogen are oxidised by air at 25° in the presence of sodium hydroxide or sodium hydrogen carbonate or different metallic hydroxides. The oxidation of glycogen is retarded by fats and by nitrogenous substances, whilst that of carbohydrates by hydrogen peroxide and ferric sulphate is retarded by glycine and potassium stearate and oleate. The induced oxidation of these last two substances by air is retarded by carbohydrates and to a greater extent by a mixture of carbohydrate and carbamide. Dextrose, glycine, potassium oleate, lecithin, cholesterol, milk, egg-yellow, and egg-white are oxidised by air at 25° in the presence of inductors chiefly to carbon dioxide and not to any intermediate product. Comparative experiments on the induced oxidation of fats, carbohydrates, and nitrogenous substances show that in neutral solution with cerous hydroxide as inductor the order in which oxidation occurs is egg-white > egg-yellow > starch > dextrose > butter.

L. S. THEOBALD.

**Geometrical inversion. I. Resonance reactions.** P. NEOGI and S. K. MITRA (J. Indian Chem. Soc., 1929, 6, 970—973).—Like maleic acid, methyl and ethyl maleates and citraconic acid undergo rapid inversion by the united action of manganese dioxide and sulphur dioxide. Manganese sulphate, manganese sulphate and sulphur dioxide, manganese dithionate, and dithionic acid do not produce any such effect. Inversion does not occur in the cases of erucic and oleic acids. The reactions are analogous to Skraup's experiment on the transformation of maleic acid in presence of the combined action of hydrogen sulphide and sulphur dioxide. The conclusion is reached that these reactions belong to a new type, distinct from "induced reactions," since they are brought about through the presence of another entirely independent chemical change in the system. The term "resonance reaction" is suggested for this type of change, and such a reaction is defined as one which takes place in the midst of another chemical reaction, but not in the presence of any of the reactants singly, nor in the presence of the products of the latter reaction. The explanation put forward is that the energy liberated by specific exothermic reactions causes geometrical inversion by activation of the labile isomeride.

J. W. SMITH.

**Reactions at the surface of hot metallic filaments. I. The reaction  $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$**

on platinum. II. The reaction  $\text{H}_2 + \text{CO}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$  on platinum-iridium alloys. III. The reaction  $\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$  on platinum coated with barium oxide. B. S. SRIKANTAN (J. Indian Chem. Soc., 1929, 6, 931—947, 949—958, 959—967).—I. With the object of accounting for the imperfect reproducibility of the results of Prichard and Hinshelwood (A., 1925, ii, 564), the reaction between carbon monoxide and hydrogen at the surface of a hot platinum wire has been reinvestigated, using better temperature control and testing the drift in the activity of the wire. The reaction starts with a high velocity, but this falls rapidly to a low and steady value, owing to the poisoning of the more active centres on the surface by the carbon monoxide formed thereon. Heating the wire in a vacuum for a long time almost eliminates the initial fall in reaction velocity, but the wire is very considerably deactivated. The granular parts of the surface, containing the active centres, are probably sintered during this process, leaving a less active surface. Comparative experiments with platinum wire scratched with emery show that a rough surface is more active than a smooth or sintered one. Nitrogen acts merely as an inert diluent, and does not affect the reaction rate. The velocity coefficient of the reaction rises by about 2.5 times for a rise of temperature of  $80^\circ$  at about  $1000^\circ$ , indicating a heat of activation of about 38,000 g.-cal.

II. A platinum-iridium alloy containing 30% Ir is the most catalytically active of these alloys for the carbon dioxide-hydrogen reaction, but the activity cannot be correlated with the composition of the alloys because a 5% alloy is more active than either a 10% or 15% alloy. The heat of activation is 36,000 g.-cal. with a 5% alloy between  $870^\circ$  and  $930^\circ$ , whilst with a 15% alloy it is 83,000 g.-cal. over the range  $895$ — $935^\circ$  and 43,000 g.-cal. between  $935^\circ$  and  $975^\circ$ . As in the case of platinum wires, after prolonged high-temperature treatment the alloy wires become sintered and lose their activity considerably. With higher proportions of iridium (25 and 30%) there is superimposed on this effect a strong and irreversible adsorption of the carbon monoxide on the surface; with a 20% alloy this can be partly expelled from the surface by heating in a vacuum.

III. The active catalyst in the reaction between carbon dioxide and hydrogen on a platinum wire coated with barium oxide is a complex of barium carbonate and barium oxide. The temperature coefficient of the reaction is 1.18 over the temperature range  $612$ — $769^\circ$ , and 1.08 over the range  $769$ — $826^\circ$ , the corresponding energies of activation being 27,000 g.-cal. and 15,000 g.-cal., respectively. The reaction is unimolecular. Carbon dioxide is readily adsorbed by the surface, and the rate of reaction rises with the carbon dioxide present up to a partial pressure of 300 mm., whereas excess hydrogen diminishes the rate of reaction. With either gas in excess the velocity of reaction increases gradually to a certain point, after which constant velocity coefficients are obtained. No explanation is offered for this circumstance.

J. W. SMITH.

Possible relationship between heats of activation and activity of contact catalysis. II. G. M.

SCHWAB (Z. physikal. Chem., 1929, B, 5, 406—412).—On the assumption that when prepared at a definite temperature the surface particles of certain catalysts attain a state of stable energy partition, and of a certain relationship between the activation heat and the surplus energy of the active centres, an equation is derived relating the activity and heat of activation with the temperature of preparation of the catalyst. The equation is of the same form as that obtained empirically by Cremer (this vol., 44) for the catalytic decomposition of ethyl alcohol by metallic oxides and for the decomposition of ethyl chloride by various metallic halides. The calculated temperatures of preparation of the catalyst agree satisfactorily with the temperatures actually employed. H. F. GILLBE.

Catalytic reduction of carbon monoxide at ordinary pressure. I. Investigation of the catalysts by means of heating curves. II. Investigation of the influence of substances on the catalytic action of cobalt by means of heating curves. S. KODAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 12, 193—204, 205—210).—I. Reduced copper is incapable of causing reduction of carbon monoxide in presence of hydrogen (cf. Hoover and others, A., 1927, 440). A nickel catalyst causes reduction, which reaches a maximum at about  $280^\circ$ ; this temperature, as well as the temperature at which the reaction initiates, however, is somewhat dependent on the reduction temperature of the nickel, although the activity of the nickel is independent of this latter temperature. The carbon monoxide is reduced only, and not decomposed. In the case of a cobalt catalyst the carbon monoxide is both reduced and decomposed, the initial reaction temperature increasing with the reduction temperature of the catalyst. Cobalt reduced at  $310^\circ$  catalyses the reduction better than the decomposition; the reverse holds for cobalt reduced at  $350^\circ$ . Metal carbide is not formed with either catalyst. Iron is oxidised by the carbon monoxide, and the latter is decomposed by the iron oxide formed.

II. Addition of potassium carbonate to the cobalt catalyst hinders the reduction and promotes the decomposition of the carbon monoxide. Thoria, or a 30% addition of copper, not only completely prevents the decomposition of the monoxide but, particularly the former, also promotes the reduction. A large excess of copper, aluminium oxide, or manganese oxide is detrimental to the cobalt catalyst.

S. K. TWEEDY.

Catalytic reduction of carbon monoxide at ordinary pressure. III. Production of liquid hydrocarbons with cobalt-copper-thoria catalyst. S. KODAMA.—See B., 1930, 271.

Catalytic reduction of carbon monoxide at ordinary pressure. IV. Influence of beryllium oxide, magnesium oxide, zinc oxide, and cadmium on the cobalt-copper catalyst. S. KODAMA (J. Soc. Chem. Ind. Japan, 1930, 33, 60B).—Magnesium oxide is the most efficient promoter; beryllium oxide is a poor promoter, and zinc oxide poorer still. Cadmium acts as a poison. S. K. TWEEDY.

Change of bromoethylamine into dimethyleneimine hydrobromide and the reverse reaction

in the presence of charcoal. H. FREUNDLICH and F. JULIUSBURGER (*Z. physikal. Chem.*, 1930, **146**, 321—355).—In order to test J. J. Thomson's principle that "if surface tension increases as the chemical action goes on, the capillarity will tend to stop the action," the reaction: (1)  $\text{CH}_3\text{Br}\cdot\text{CH}_2\cdot\text{NH}_2$  (I)  $\rightleftharpoons$   $\text{CH}_2=\text{CH}_2$  > NH (II) + HBr in neutral and alkaline solution, and the reverse reaction: (2)  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (III) +  $\text{HBr}=\text{CH}_3\text{Br}\cdot\text{CH}_2\cdot\text{NH}_2$  (IV) in hydrobromic acid solution, have been investigated. The adsorption isotherms of the four substances have been determined and it is found that the quantities adsorbed, and therefore the surface tension lowerings, are in the order I > II > III > IV.

In accordance with Thomson's principle, the presence of charcoal retards reaction (1). In the presence of a constant concentration of sodium hydroxide it is found that a constant velocity coefficient is given by the equation  $dx/dt = k \cdot m(a-x/m)^{3/2}$ , where  $a$  is the initial amount of I,  $x$  the amount which has undergone change at a time  $t$ , and  $m$  the quantity of charcoal present. From determinations at different temperatures, the heats of activation have been found to be 12,480 g.-cal. in the homogeneous reaction and 10,220 g.-cal. in the presence of charcoal.

In accordance with Thomson's principle, since IV causes a greater surface tension lowering than III, it was found that reaction (2) is accelerated by the presence of charcoal. The reaction is of the second order in both cases.

The equilibrium between bromoethylamine and dimethylencimine hydrobromide cannot be estimated in neutral solution with certainty, owing to side reactions, but whilst in the presence of charcoal the amount of II remained constant at 63%, in homogeneous solution the reaction proceeded to 90% in 22 hrs. In the reverse reaction the amount of I present after a considerable time was 36% at charcoal and 10% in homogeneous solution.

J. A. V. BUTLER.

**Hydrogenation over metallic caesium.** D. G. HILL and G. B. KISTIAKOWSKY (*J. Amer. Chem. Soc.*, 1930, **52**, 892—894).—Ethylene combines with hydrogen at the surface of caesium at 25° and more rapidly at 200°, but reaction is retarded by formation of metallic hydride. Sodium hydride alone was produced when the caesium was replaced by sodium. Ammonia was not formed from nitrogen and hydrogen in the presence of caesium. J. G. A. GRIFFITHS.

**X-Ray investigation of the structure of copper-zinc oxide catalysts.** R. H. ABORN and R. L. DAVIDSON (*J. Physical Chem.*, 1930, **34**, 522—530).—The catalysts previously used in the decomposition of methyl alcohol (Frolich, Fenske, and Quiggle, *A.*, 1928, 1112) have been subjected to X-ray analysis. They are essentially crystalline and are of the same lattice type as the principal components in their normal conditions. The edge of the cubic cell of the copper lattice expands with an increase in percentage of zinc oxide in the catalyst. This is attributed to the formation of  $\alpha$ -brass. The vertical and horizontal dimensions of the unit hexagonal cell of the zinc oxide lattice vary in the same way with a change

in composition. This consists of a change from contraction at high concentrations of zinc oxide to an expansion at a high concentration of copper. This may be due to a partial reduction of the oxide or to a solid solution of copper in the oxide. The axial ratio of zinc oxide, however, remains practically constant. No diffraction lines due to zinc have been observed; a few extra lines are best ascribed to  $\gamma$ -brass. Comparison of these results with catalytic activity indicates an important relationship between inter-atomic spacings in a catalyst and its specific activity. In the decomposition of methyl alcohol (cf. Frolich, Davidson, and Fenske, *A.*, 1929, 406) the essential feature is not the effect of the catalysts on the total decomposition but their selectivity.

L. S. THEOBALD.

**Platinum-black catalysts.** I. Physical properties and catalytic activity. II. Heats of adsorption. G. B. TAYLOR, G. B. KISTIAKOWSKY, and J. H. PERRY (*J. Physical Chem.*, 1930, **34**, 748—752, 799—820).—I. The particle size and catalytic activity in simple gas reactions of three samples of platinum-black prepared by different methods have been compared. The first sample prepared by heating precipitated ammonium chloroplatinate in hydrogen at 200° and then in nitrogen at 250—300° consisted of a relatively coarse crystalline powder; the second, prepared by reduction of platonic chloride in hot hydrazine solution, consisted mainly of aggregates of submicroscopic crystallites, whilst the third, prepared by pouring an aqueous solution of platonic chloride and formaldehyde into a boiling solution of sodium hydroxide, consisted of very minute crystallites showing much less aggregation. These last two samples showed the greater catalytic activity, the third being superior in oxidation reactions and the second in reductions.

II. The differential heats of adsorption of the samples of platinum-black prepared as described above for hydrogen, oxygen, carbon monoxide, and sulphur dioxide have been determined by the method of Taylor and Kistiakovsky (*A.*, 1927, 426). The heats of adsorption are large, being of the order of  $3 \times 10^4$  g.-cal. for hydrogen, sulphur dioxide, and carbon monoxide and  $10^5$  g.-cal. for oxygen. Catalytic activity runs parallel to the adsorption characteristics of these samples of platinum-black. The reversibility of adsorption, the effect of heat treatment on adsorption, and the effect of the method of preparation on the adsorption characteristics of the catalysts are discussed. Thermal data for the adsorption of one gas by the catalyst coated with another are also recorded.

L. S. THEOBALD.

**Relations between the activity of catalysts for the synthesis of methyl alcohol and their chemical and crystalline structure.** I. G. NATTA (*Giorn. Chim. Ind. Appl.*, 1930, **12**, 13—23).—The action of certain metallic oxides in promoting the catalytic activity of zinc oxide for the synthesis of methyl alcohol from carbon monoxide and hydrogen has been examined with regard to their effect on the structure of the zinc oxide. The most active form of zinc oxide is that obtained from the basic carbonate at temperatures below 350°. The oxides which act



as promoters are of two kinds: (1) Certain bivalent oxides (magnesium, nickel, copper, cobalt, iron, and manganese) with ionic diameters varying between 0.60 and 0.90 Å. These pass into solid solution in the zinc oxide lattice, and their activity is the greater the more they deform the lattice. (2) Oxides which remain in a finely-divided amorphous or colloidal state and prevent the growth of the zinc oxide granules, e.g., aluminium and chromium oxides. Above 400° and 500°, respectively, these oxides form aluminate and chromite with a spinel structure, and the catalytic activity decreases. O. J. WALKER.

**Electro-deposition of nickel. I. Effect of  $p_{H_2}$  and of various buffering agents; presence of oxygen in the deposits.** J. B. O'SULLIVAN.—See B., 1930, 287.

**Preparation of pure electrolytic nickel. I. Elimination of copper from nickel-copper electrolytes.** C. G. FINK and F. A. ROHRMAN.—See B., 1930, 377.

**Electrolytic production of Turkey-red iron oxide pigment.** W. H. BRUCKNER.—See B., 1930, 383.

**Reduction of phenol.** W. D. BANCROFT and A. B. GEORGE (Amer. Electrochem. Soc., May, 1930. Advance copy, 7 pp.).—The percentage yield of cyclohexanol obtained by passing a stream of hydrogen containing phenol vapour over platinised asbestos at 185° is somewhat higher than that obtained by passage over nickel under identical conditions. Since nickel is more effective than platinum in most catalytic hydrogenations and therefore may be presumed to activate hydrogen to a greater extent, the observed result is taken as evidence that platinum is more effective than nickel in activating phenol, and an attempt is made to correlate this with the observation of Fichter and Stocker (A., 1914, i, 946) that phenol can be electrolytically reduced to cyclohexanol fairly readily at a platinised platinum cathode but not at all at a lead cathode, although the hydrogen overvoltage at the former is very small, whilst at the latter it is large. H. J. T. ELLINGHAM.

**Preparation of salicylaldehyde by electrolytic reduction of sodium salicylate.** G. KAWADA and J. YOSIDA (Bull. Hyg. Res. Inst. Japan, 1929, 35, 261—274).—Optimal results (yield 80%) were obtained by using 20% sodium sulphate solution containing boric acid and borax for dissolving the sodium salicylate and sodium hydrogen sulphate, employing a mercury cathode and lead anode (surrounded by parchment paper) and electrolysing at 8—13° at 2 amp. per cm.<sup>2</sup> CHEMICAL ABSTRACTS.

**Electrolytic deposits on aluminium and its alloys.** BALLAY.—See B., 1930, 287.

**Chemical action in the glow discharge. III. Synthesis of nitrogen dioxide.** J. W. WESTHAYER and A. K. BREWER (J. Physical Chem., 1930, 34, 554—562; cf. this vol., 304).—The synthesis of nitrogen dioxide in the glow discharge has been investigated by means of the apparatus and methods previously employed (*loc. cit.*). Owing to the formation of ozone in the positive column, however,

results have been confined to the negative glow. The effects of excess of nitrogen or oxygen, different discharge currents, and the addition of helium or argon are analogous to those obtained in the ammonia synthesis. The rate of reaction is directly proportional to the discharge current and a maximum yield of 1 mol. of NO<sub>2</sub> per electron flowing in the outer circuit is obtained. As in the case of ammonia, the synthesis is initiated principally by N<sub>2</sub><sup>+</sup> ions, and a yield of 2 mols. of NO<sub>2</sub> per N<sub>2</sub><sup>+</sup> ion is indicated. A suggested mechanism is discussed.

L. S. THEOBALD.

**Temperature coefficient of the photochemical formation of hydrogen chloride.** O. R. WULF (Proc. Nat. Acad. Sci., 1930, 16, 27—32).—The variation of the photochemical temperature coefficient of the hydrogen-chlorine reaction has been calculated on the assumptions that chlorine is the only photochemically active constituent, and that the primary photochemical act is the dissociation of the chlorine molecule. The temperature coefficients calculated for the chlorine quantum level  $n''$  0—6 vary from 0.994 to 1.68, for 10° intervals. This corresponds with a wave-length range from 4659 to 5492 Å. The photochemical combination of hydrogen and chlorine over the longer of the wave-lengths to which it is sensitive appears to illustrate Tolman's theory in its simplest form, the influence of temperature being in large part due to its effect on the absorption of light by the chlorine. F. G. TRYHORN.

**Reactions of gases with dissolved substances or liquids during exposure to light of short wave-length. I—II.** F. KRAUSS and E. BRUCHHAUS (Z. anorg. Chem., 1930, 189, 53—63, 64—71).—I. If oxygen is passed through an aqueous potassium iodide solution exposed to light of wave-lengths down to about 253 mμ from a Uviol lamp, iodine is liberated. The proportion of iodide oxidised increases with increase in the time of exposure and in the acidity of the solution, but decreases with increase in the iodide concentration. This reaction occurs only if the reactants are exposed together in the same homogeneous system, and the maximum amount of reaction corresponds only with the amount of oxygen actually in solution; it is impossible to activate either reactant by exposing it separately. Potassium oxalate in acid solution is oxidised under similar conditions only in presence of manganous sulphate as catalyst, the amount of reaction increasing with rise in temperature and with increase in the amount of catalyst, the time of exposure, and the acidity of the solution, but decreasing with the oxalate concentration. Sodium tungstate and ammonium molybdate in aqueous solution are reduced by hydrogen.

II. A solution of ruthenium hydroxide in hydrochloric acid may similarly be reduced with hydrogen. The resulting solution, which contains bivalent ruthenium, gives *caesium aquopentachlororuthenoate*, Cs<sub>3</sub>(RuCl<sub>5</sub>.H<sub>2</sub>O) (orange), on addition of caesium chloride. From solutions of this compound hydrogen sulphide precipitates the ruthenium quantitatively, and alkali hydroxides form a white precipitate, probably the hydroxide of bivalent ruthenium.

R. CUTHILL.

**Photolysis of organic iodides; utilisation of light.** G. EMSCHWILLER (Compt. rend., 1930, 190, 741—744; cf. A., 1924, i, 929; ii, 719).—Contrary to the conclusions previously reached that the photochemical decomposition of organic iodo-compounds is in accordance with Einstein's relation, it is now found that the coefficient of utilisation of light ( $C$ ) depends on (i) temperature, (ii) nature of the iodo-compound, and, apparently, (iii) quality of radiation. When these conditions are kept constant and oxygen is excluded, the rate of decomposition still steadily decreases. This is shown to be due to the liberated iodine acting as an absorbent screen; allowance for this gives a constant value for  $C$ . The values of  $C$  (in arbitrary units) for ethyl iodide, iodobenzene, and methyl iodide are respectively 17, 4, and less than 1, this last corresponding with the greater thermal stability of methyl iodide (cf. Kahan, J.C.S., 1908, 93, 132). C. A. SILBERRAD.

**Reactions of photochemically excited oxygen.** A. KLEMENC and F. PATAT (Naturwiss., 1930, 18, 281).—It was suspected that an oxidation of hydrocarbons under the action of ultra-violet light previously observed (A., 1929, 892) was due to excited or atomic oxygen, and not to any reaction in which mercury is involved. Experiments have, therefore, been carried out with rigid exclusion of mercury vapour and water vapour. Under these conditions oxygen and carbon monoxide readily form carbon dioxide at normal pressure under the action of ultra-violet light. Similarly, hydrogen and oxygen react to form water. No reaction, however, takes place between carbon monoxide and hydrogen in the absence of mercury vapour. This indicates that carbon monoxide has not been activated by the wave-length 1820 Å. for which it has a feeble absorption. The possibility of oxygen activation, however, is supported by Granath's observation (A., 1929, 1350) that oxygen shows a strong selective absorption in the region round 1950 Å. which is present in the ultra-violet radiation employed. M. S. BURR.

**Photochemical sensitisation of the combustion of hydrogen and carbon monoxide.** L. FARKAS, F. HABER, and P. HARTECK (Naturwiss., 1930, 18, 266—268).—Very small amounts of ammonia were added to hydrogen-oxygen and carbon monoxide-oxygen explosive mixtures and the increased reaction velocity was studied at various temperatures between 120° and 420° with and without irradiation by a zinc spark. Tables and a graph illustrating the results are given. The chain reaction induced by hydrogen atoms is considered for both cases. W. R. ANGUS.

**Photo-decomposition of molecules having diffuse band spectra.** H. S. TAYLOR and J. R. BATES (Nature, 1930, 125, 599).—The formation of atomic hydrogen by dissociation of ammonia is indicated by the production of marked amounts of formaldehyde and a white deposit (possibly of hexamethylene-tetramine) when mixtures of ammonia, hydrogen, and carbon monoxide are passed through a quartz tube illuminated by the mercury arc.

L. S. THEOBALD.

**Photolysis of diazo-compounds.** W. SCHRÖTER (Z. wiss. Phot., 1930, 28, 1—29).—The quantum

yield  $\phi$  (number of molecules transformed/number of quanta absorbed) in the photolysis of diazo-compounds has been measured by determining the light energy absorbed by a diazo-solution and the transformation thus produced in the latter by a "fading" method, A, in which concentration change is determined by comparison with standards, and a "nitrogen" method, B, in which the nitrogen evolved is determined. Both methods applied to 2-amino- $\alpha$ -naphthol-4-sulphonic acid (I) and *p*-aminodiphenylamine (II) reveal that  $\phi$  is independent of the intensity and wave-length of the light, and of concentration and temperature of solution over a wide range. For aqueous solutions of I,  $\phi=0.40\pm0.06$  by A, and  $0.35\pm0.03$  by B; for II,  $\phi=0.52\pm0.05$  by A, and  $0.20\pm0.02$  by B. The lower values obtained by B are attributed to side reactions inhibiting the complete evolution of the nitrogen set free. On adding acid  $\phi$  for I is unchanged, whilst for II,  $\phi=0.35$ ; on adding alkali  $\phi$  for I=0.15 and for II precipitation occurs.  $\phi$  increases to 0.5—0.6 for both substances when ethyl or methyl alcohol is used as solvent. The deviation of these values from unity may be due to thermal transformation of part of the absorbed light or to side reactions rendering the measurements inaccurate, and the higher values obtained in alcoholic solvents may be due to formation of a soluble diazo-molecule-alcohol complex favouring reaction. X. Irradiation of I causes noticeable changes but no evolution of nitrogen, but with II nitrogen is readily evolved. Method B applied to diazobenzenesulphonic acid gives values of  $\phi=0.07$ —0.1. H. I. DOWNES.

**Photochemical oxidation of formaldehyde by hydrogen peroxide in acid medium with tungstic acid sol as photo-catalyst.** J. C. GHOSH and S. K. NANDY (J. Indian Chem. Soc., 1929, 6, 975—986).—The photo-oxidation of formaldehyde by hydrogen peroxide in acid solution has been investigated in a similar manner to the oxidation of dextrose (Ghosh and Mukherjee, A., 1929, 777), conditions of experiment being so arranged that the tungstic acid sol behaved as a pure photo-catalyst. Neither of the reactants nor a mixture in the absence of tungstic acid sol shows any decomposition in ultra-violet light. The velocity of reaction with respect to hydrogen peroxide is unimolecular at low concentrations, but tends to become zero-molecular at higher initial concentrations. The velocity coefficient diminishes slowly with increasing concentration of hydrogen peroxide until the concentration is almost equal to that of the tungstic acid, when it diminishes very rapidly, after which it again diminishes slowly. The velocity coefficient is inversely proportional to the hydrogen-ion concentration and increases slightly with the concentration of formaldehyde. If the concentration of peroxide is equal to or greater than that of the tungstic acid the velocity coefficient diminishes with increasing concentration of tungstic acid. For lower concentrations of free hydrochloric acid the velocity coefficient varies as the square root of the intensity of the incident radiation, but the variation of velocity with intensity is much less at higher acid concentration. The quantum efficiency of the reaction is 2—7. The temperature coefficient of the reaction velocity is

small. It is suggested that the tungstic acid molecules combine with the hydrogen peroxide to form a peroxide which remains dissolved in true solution, but that only the sol of tungstic acid presents a photo-sensitive surface.  
J. W. SMITH.

**Photochemical decomposition of acetaldehyde solution.** J. C. GHOSH and S. K. NANDY (J. Indian Chem. Soc., 1929, 6, 911—914).—The photochemical decomposition of dilute aqueous acetaldehyde solutions in ultra-violet radiation is unimolecular, and the velocity coefficient is independent of the initial concentration of the solution. The quantum efficiency of the reaction is 1.34, and it is assumed that a reaction chain is set up; this is supported by the small but definite temperature coefficient of the velocity of reaction. The molecular extinction coefficients of acetaldehyde in the region 2800—2300 Å. are very large, so it is assumed that all the incident effective radiation is absorbed even by dilute solutions of acetaldehyde, and that the amount of energy absorbed does not vary with the concentration.

J. W. SMITH.

**Temperature coefficients, quantum efficiency, and the relation between intensity and velocity of the hydrolysis of sucrose in visible and infra-red radiations.** A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1929, 6, 879—884).—The rate of hydrolysis of acid sucrose solutions in radiations of the visible and near infra-red regions has been investigated. The quantum efficiency is very high and increases with the temperature and concentration of the reacting system and with the frequency of the incident radiation. The temperature coefficients of the hydrolysis between 35° and 45° are 3.18 at 4725 Å., 3.32 at 5650 Å., and 3.7 at 7304 Å., compared with 3.85 for the dark reaction, i.e., the greater is the acceleration due to the radiation the smaller is the temperature coefficient. From the temperature coefficient of the thermal reaction, the wavelength of radiation which should accelerate the change, according to the radiation theory, is 11,900 Å. This is regarded as a threshold limit, radiation of longer wave-length being inactive. Extinction coefficient measurements show that there is appreciable absorption of radiations over the range 4400—7000 Å., and that the light absorption is proportional to the intensity of the incident radiation. The relation between the absorption of light and the velocity of the hydrolysis of sucrose varies from 1 to 1.5, depending on the velocities of the thermal and photochemical reactions, and the quantum yield increases with decrease in intensity of illumination.

J. W. SMITH.

**Photochemical reduction of ferric salts by mandelic, lactic, and tartaric acids.** J. C. GHOSH and R. M. PURAKAYASTHA (J. Indian Chem. Soc., 1929, 6, 827—837).—In the presence of tartaric, lactic, or mandelic acids as oxygen acceptor, the photochemical reduction of ferric chloride is zero-molecular. Hydrochloric acid has no effect on the velocity of the reaction except in so far as it diminishes the extinction coefficient of the ferric chloride solutions for light of longer wave-lengths. With both mandelic and lactic acids the life period of the excited ferric

ion is of the order of  $10^{-9}$  sec. With tartaric acid the reaction is complicated by the circumstance that the immediate product of photo-oxidation of the acid is also able to react with ferric salts under the influence of light. In the case of mandelic acid, the quantum efficiency is 1 at 4880 Å., but becomes nearly 1.4 at 3900 Å.; with tartaric acid and lactic acid it is nearly 0.5 at 4880 Å. and 0.8 at 3900 Å.  
J. W. SMITH.

**Photochemical reduction of silver salts by pinachrome.** A. STEIGMANN (Z. wiss. Phot., 1929, 27, 113—116).—Silver nitrate and ammoniacal silver oxide are reduced photochemically by pinachrome.

R. CUTHILL.

**Constitution of ultramarines.** J. HOFFMANN (Z. anorg. Chem., 1930, 189, 91—100).—The effect of the  $\alpha$ - and  $\beta$ -radiation from radium on various ultramarines and ultramarine substrates has been investigated. The ultramarine substrates change in colour, apparently as a result of the discharge of metal ions. White, green, and violet, but not blue, red, and yellow ultramarines also change in colour, which is in harmony with the view that in the latter group the colour is due to colloiddally dispersed sulphur. It appears that sodalite has a resistant constituent,  $\text{Na}_4\text{Al}_4\text{Si}_6\text{O}_{24}$ , and that the ionisable chlorine is combined with sodium.

R. CUTHILL.

**Chemical elements and compounds.** (SIR) P. C. RÂY (J. Indian Chem. Soc., 1930, 7, 1—9).—A lecture.

R. CUTHILL.

**Hydrogen atoms as oxidation and reduction agents.** J. P. ETHER and F. HABER (Naturwiss., 1930, 18, 266).—When ordinary hydrogen, containing atomic hydrogen, was passed through aqueous solutions of silver nitrate, copper sulphate, or copper chloride, only in certain conditions was the metal deposited. Bubbling hydrogen through a colourless acid solution of copper oxide gave rise to blue cupric ions, whereas metallic copper was obtained when the gas was bubbled through a colourless ammoniacal copper oxide solution. Experiments were carried out at 100 and 760 mm. pressure. The concentration of hydrogen ions in the aqueous salt solution decided the course of the reaction.

W. R. ANGUS.

**Concentration of hydrogen peroxide solutions.** C. D. HURD and M. P. PUTERBAUGH (J. Amer. Chem. Soc., 1930, 52, 950—953).—A residue of 30% hydrogen peroxide was obtained by distilling a 3% aqueous solution with xylene. Concentration to 90% hydrogen peroxide was effected by distillation at 25—30 mm. with *p*-cymene. Decomposition was small below 57°.

J. G. A. GRIFFITHS.

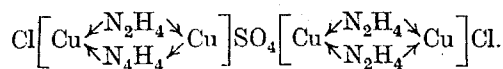
**Production of hydrogen peroxide from barium peroxide by means of carbonic acid.** P. ASKENASY and R. ROSE (Z. anorg. Chem., 1930, 189, 10—35).—In the production of hydrogen peroxide by the action of carbon dioxide on aqueous barium peroxide suspensions, the best yield (about 90%) is obtained by passing the gas under a pressure of 25 atm. for 7 min. through a suspension corresponding in composition with a 2.5% hydrogen peroxide solution at 0—15°. Addition of 1% of acetic or hydrochloric acid or the corresponding barium salts to the mixture before reaction enables equally good yields of 5—6% peroxide

solutions to be obtained, and the mixture is also more readily filtered after reaction. By adding fresh barium peroxide to the resulting solution and repeating the carbon dioxide treatment still more concentrated peroxide solutions can be prepared, but the yield in the second stage is not as good as in the first. If dilute carbon dioxide is used instead of the pure gas, the pressure should be such that the partial pressure of the carbon dioxide is 20–25 atm. The dilute peroxide solutions can be distilled under reduced pressure without appreciable decomposition, and by further distillation solutions of 20–30% concentration can be obtained. It is suggested that the above process is suitable for the manufacture of hydrogen peroxide, the barium peroxide being regenerated from the carbonate (cf. below). R. CUTHILL.

**Mechanism of autoxidation processes, and the formation of and part played by hydrogen peroxide in such processes.** P. N. RAIKOV (Z. anorg. Chem., 1930, 189, 36–52).—Theoretical. It is suggested that in autoxidation processes the water combines with molecular oxygen to form an oxonium compound, hydrogen ozonide,  $=O=O=O\text{<}\overset{H}{\text{H}}$ , which undergoes tautomeric change to a pseudo-ozonide,  $>O=O\text{<}\overset{H}{\text{OH}}$ , in which the oxygen atom held only by secondary valencies is active. Loss of this active atom leads to the formation of hydrogen pseudo-peroxide, which changes, largely under the influence of the inductor, into the true peroxide (cf. A., 1928, 256), and this in its turn loses oxygen by acting as an oxidising agent, the original water thus being re-formed. By means of this theory it is possible to explain the phenomena of autoxidation without it being necessary to postulate the temporary existence of nascent hydrogen, a theory which in any case seems to involve insuperable difficulties.

R. CUTHILL.

**Reaction between cupric chloride and hydrazine sulphate.** T. IREDALE and (MISS) C. E. MALLIN (J.C.S., 1930, 395–397).—Slow addition of cupric chloride solution to a solution of hydrazine sulphate containing sufficient alkali hydroxide to liberate the base results in the separation of brown glistening crystals of the compound,  $2\text{CuCl}\cdot\text{Cu}_2\text{SO}_4\cdot 4\text{N}_2\text{H}_4$ . The substance decomposes in hot water, yielding cuprous oxide, hydrazine chloride, and hydrazine sulphate; it dissolves in formamide, pyridine, and concentrated aqueous ammonia, but is insoluble in alcohol. Sulphuric and nitric acids decompose it with the deposition of copper. The following constitutional formula is suggested:



A. R. POWELL.

**Reaction between hydrogen sulphide and silver.** S. LILLENFELD and C. E. WHITE (J. Amer. Chem. Soc., 1930, 52, 885–892).—Both oxygen and moisture are necessary for the blackening of silver by hydrogen sulphide (cf. Hahn, A., 1917, ii, 371). No hydrogen is liberated during this reaction at the ordinary temperature or at 210°. The interaction of

dry air-free hydrogen sulphide and silver at 190° yields hydrogen. Silver is blackened by sulphur. It is suggested that hydrogen sulphide is oxidised by oxygen at the surface of silver and the sulphur atoms produced combine with the metal.

J. G. A. GRIFFITHS.

**[Preparation and properties of] caesium bismuth iodide.** C. C. MELOCHE and P. V. CLARK (J. Amer. Chem. Soc., 1930, 52, 907–910).—The addition of hydrogen bismuth iodide to caesium nitrate gives a red crystalline precipitate of  $\text{Cs}_3\text{Bi}_2\text{I}_9$  (Wells and Foote, A., 1897, ii, 551), which is hydrolysed in water, but not in dilute hydriodic acid at 25°. The solubility in absolute alcohol at 25° is less than 0.8 mg. per 100 c.c. The compound is stable in air up to 210°. Beyond 230°, part of the iodine is replaced slowly by oxygen and a white substance of the approximate composition  $\text{Bi}_2\text{O}_3\cdot 3\text{CsI}$  is ultimately produced. J. G. A. GRIFFITHS.

**Beryllium salicylate.** F. E. JONES, W. E. HAMER, C. W. DAVIES, and C. R. BURY (J. Physical Chem., 1930, 34, 563–569).—*Beryllium salicylate dihydrate* has been prepared in the form of monoclinic, hemihedral crystals,  $a:b:c = 0.7409:1:0.5828$ ,  $\beta 107^\circ 17'$ ;  $d_4^{25} 1.534$ ; water is retained at 100°, but at somewhat higher temperatures, decomposition occurs. The electrical conductivity and  $p_H$  of aqueous solutions have been determined; in common with the malonate and oxalate, the conductivity is small and changes but slowly with concentration. A structure for this compound is suggested, and the behaviour of beryllium salts in aqueous solution is discussed. L. S. THEOBALD.

**Optimum concentration of phosphorogen and flux in [phosphorescent] zinc sulphide and the variation with temperature.** R. COUSTAL and F. PREVET (Compt. rend., 1930, 190, 739–741).—The relation between the optimum quantities of flux (a mixture of alkali salts), phosphorogen, and temperature has been examined by preparing phosphorescent zinc sulphide by the calcination method at 800°, 1200°, and 1400°, and by the explosion method (cf. A., 1929, 524) at an estimated temperature of 3000°. The optimum percentages of flux, and of copper as phosphorogen, and duration of heating are respectively: (800°)  $>2$ ,  $10^{-4}$ , 2 hrs.; (1200°) 1,  $0.7 \times 10^{-4}$ , 20 min.; (1400°) 0.1,  $0.3 \times 10^{-4}$ , 5 min.; (3000°) 0,  $10^{-6}$  (i.e., the amount of copper present in the purest obtainable zinc), a few seconds. With manganese as phosphorogen the optimum percentage (about  $10^{-3}$ ) seems almost independent of temperature. C. A. SILBERRAD.

**Production of barium oxide from barium carbonate.** P. ASKENASY and R. ROSE (Z. anorg. Chem., 1930, 189, 1–9).—A loosely granular form of barium oxide, with a purity of about 90% and particularly suitable for making barium peroxide to be used as a source of hydrogen peroxide, is produced by heating a mixture of the carbonate with 25–30% of carbon, preferably petroleum coke, at 1200–1300°. The excess of carbon, which serves to prevent the mass sintering together, is subsequently removed by heating in a current of air or steam at about 1300°.

R. CUTHILL.

**Action of ammonia on  $\text{HgCl}_2 \cdot 2\text{NH}_3$ .** M. FRANÇOIS (Compt. rend., 1930, 190, 744—745; cf. this vol., 307). The course of this reaction is similar to that between ammonia and  $\text{HgBr}_2 \cdot 2\text{NH}_3$ . The reaction  $\text{HgCl}_2 \cdot 2\text{NH}_3 \rightleftharpoons \text{NH}_2\text{HgCl} + \text{NH}_4\text{Cl}$  continues until the ammonia solution contains 17.07 g. of ammonium chloride per litre; the further reaction yielding dimercuriammonium chloride stops when 1.61 g. of ammonium chloride per litre is present. Dimercuriammonium chloride always occurs in the hydrated state,  $\text{NH}_2\text{Hg}_2\text{Cl} \cdot \text{H}_2\text{O}$ , the bromine and iodine analogues being anhydrous. C. A. SILBERRAD.

**Formation of monomercurammonium bromide and dimercurammonium bromide.** M. FRANÇOIS (Bull. Soc. chim., 1930, [iv], 47, 165—173).—Monomercurammonium bromide ( $\text{NH}_2\text{HgBr}$ ) and dimercurammonium bromide ( $\text{NH}_2\text{Hg}_2\text{Br}$ ) are formed by the action of concentrated ammonia solutions on diamminomercuric bromide ( $\text{HgBr}_2 \cdot 2\text{NH}_3$ ), according to the reactions  $\text{HgBr}_2 \cdot 2\text{NH}_3 = \text{HgH}_2\text{NBr} + \text{NH}_4\text{Br}$ ,  $2\text{HgH}_2\text{NBr} = \text{Hg}_2\text{NBr} + \text{NH}_4\text{Br}$ . As the quantity of the ammonia solution reacting with a constant amount of the diammine increases, the concentrations of mercury and bromine in the solution increase stepwise with two constant regions marking the occurrence of the reactions. The reversibility of the reactions has been established.

J. A. V. BUTLER.

**Formation of azide of samarium [and of other metals].** G. KOMPPA and J. WUORINEN (Suomen. Kem., 1929, 2, 60—62).—The possibilities of forming azides of samarium, of other rare earths, and of aluminium were investigated. Samarium is quantitatively precipitated as hydroxide by boiling its neutral solutions with excess of alkali azide. Hydrogen sulphide reacts with samarium oxide at  $350^\circ$  to form an *oxysulphide* ( $?\text{Sm}_3\text{O}_4\text{S}_2$ ). S. K. TWEEDY.

**Detection of pure para-nitrogen.** P. HARTECK and H. W. SCHMIDT (Naturwiss., 1930, 18, 282—283).—An attempt has been made with a sample of very pure nitrogen to repeat Justi's experiment (this vol., 524) and prepare para-nitrogen by freezing, but without success. M. S. BURR.

**Parallelism in the decomposition of ammonium, hydrazine, and hydroxylamine nitrites. Hyponitrous acid as a hydroxyaminonitrous acid.** L. F. AUDRIETH (J. Physical Chem., 1930, 34, 538—542).—Mainly theoretical. The decomposition of hydroxylamine nitrite may be regarded as involving initial solvolytic action of hydroxylamine on nitrous acid with the intermediate formation of hyponitrous acid. Similar mechanisms are postulated for the decomposition of ammonium and hydrazine nitrites, but in these cases the intermediate products are too unstable to be isolated. L. S. THEOBALD.

**Action of gaseous ammonia on phosphoric oxide.** A. SANFOURCHE, A. HERNETTE, and M. FAU (Bull. Soc. chim., 1930, [iv], 47, 273—279).—The reaction has been investigated by passing ammonia diluted with dry air over the solid oxide, by allowing the gas to react with phosphoric oxide suspended in carbon tetrachloride, and by passing ammonia into a vessel in which phosphoric oxide is being produced

by the combustion of red phosphorus in a mixture of air and nitrogen. The product in all cases is diammonium amidopyrophosphate. The triammonium salt can be obtained by the further action of ammonia or by increasing the proportion of ammonia in the reacting gas. Variations in humidity affect only the yield, and not the composition, of the product. C. W. GIBBY.

**Action of bromine on phosphorus trichloride.** T. MŁOBEDEZKI and S. KRAKOWIECKI (Rocz. Chem., 1930, 10, 158—196).—Brownish-red crystals,  $\text{PCl}_{1.671-1.779}\text{Br}_{5.337-5.781}$ , separate on the walls of a vessel containing bromine vapour, on connexion with another vessel containing phosphorus trichloride vapour, on the walls of which yellow crystals, of a limiting composition  $\text{PCl}_4\text{Br}$ , deposit. Using phosphorus pentachloride in place of trichloride, ruby-red crystals, of a composition varying from  $\text{PCl}_{2.443}\text{Br}_{4.624}$  to  $\text{PCl}_{3.094}\text{Br}_{5.761}$ , appear. If liquid bromine and phosphorus trichloride are allowed to interact at  $25^\circ$ , various products are obtained according to the relative proportions of substrates taken. In mixtures containing from 0.0833 to 0.333 atom of bromine per mol. of trichloride two phases form: a red, liquid phase, varying in composition from  $\text{PCl}_{2.952}\text{Br}_{0.154}$  to  $\text{PCl}_{2.705}\text{Br}_{0.461}$ , and yellow crystals, in which the ratio Cl:Br per atom of phosphorus varies from 4.240:0.732 to 4.185:0.815. When 0.333—1.0 atom of bromine is used, two liquid and two solid phases appear; the upper liquid phase has a composition lying within the same limits as before, whilst in the lower one the ratio Cl:Br has a limiting value of 3.439:4.677. The two solid phases are yellow crystals, Cl:Br from 4.199:0.890 to 4.230:0.835, and ruby-red crystals,  $\text{PCl}_{1.920}\text{Br}_{5.081}$ . When from 1 to 5 atoms of bromine are used, the composition of the upper liquid phase is as above, that of the lower one varies from  $\text{PCl}_{3.439}\text{Br}_{4.677}$  to  $\text{PCl}_3\text{Br}_5$ , the yellow crystals do not appear, and the composition of the red ones is the same as before. When 5—7 atoms of bromine are used, only one liquid and one solid phase appear; the former varies in composition from  $\text{PCl}_3\text{Br}_5$  to  $\text{PCl}_3\text{Br}_7$ , whilst the latter consists of the above-mentioned ruby-red crystals. Finally, with 7—20 atoms of bromine, only one liquid phase exists, varying in composition from  $\text{PCl}_3\text{Br}_7$  to  $\text{PCl}_3\text{Br}_{20}$ . All the above systems on evaporation yield yellow crystals of varying composition. The lower liquid phase, containing chlorine and bromine in the proportions 3.439:4.677 to 3:18, completely solidifies on cooling to  $0^\circ$  and seeding with the ruby-red crystals, whilst that in which Cl:Br=3:20 leaves a small quantity of liquid residue under these conditions. It is supposed that the products described above are solutions of yellow crystals,  $\text{PCl}_4\text{Br}$ , ruby-red crystals,  $\text{PCl}_2\text{Br}_5$ , and of bromine, in various proportions; thus the phase of composition  $\text{PCl}_3\text{Br}_5$  is regarded as  $\text{P}_2\text{Cl}_6\text{Br}_{10} = \text{PCl}_4\text{Br} + \text{PCl}_2\text{Br}_5 + 2\text{Br}_2$ . The yellow crystals are best prepared by acting on a solidified mixture of composition  $\text{PCl}_3:5\text{Br}$  with phosphorus trichloride. A mixture of four parts of phosphorus pentachloride to one part of pentabromide, which possesses the same empirical composition as the yellow crystals, has physical properties quite different

from those of these crystals, pointing to their being a definite chemical compound, and not a solid solution. Chlorides and bromides of phosphorus interact when mixed, with the production of various solid and liquid phases; a more detailed description of these products is not, however, given. R. TRUSZKOWSKI.

**Pyroarsenic acid and pyroarsenates.** A. ROSENHEIM and H. ANTELMANN (Z. anorg. Chem., 1930, 187, 385—397).—Contrary to the conclusions of Simon and Thaler (A., 1927, 511), the hydrated arsenic oxide,  $\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , *pyroarsenic acid*, mentioned by Kopp, has been shown to exist. It is obtained in the form of hard, microscopic, prismatic crystals by evaporating a concentrated aqueous solution of pure arsenic acid in an open dish until a temperature of 170—180° is reached. The weight remains constant even when the substance is heated at 155°. By the direct action of dry gaseous ammonia, liquid ammonia, methylamine, and ethylamine the following *pyroarsenates* have been obtained:  $(\text{NH}_4)_2\text{H}_2\text{As}_2\text{O}_7$ ,  $(\text{NH}_4)_4\text{As}_2\text{O}_7$ ,  $(\text{NH}_3\text{Me})_4\text{As}_2\text{O}_7$ , and  $(\text{NH}_3\text{Et})_4\text{As}_2\text{O}_7$ , respectively. From approximately 50% arsenic acid solutions at 180° the following complex metallic *pyroarsenates* have been prepared:  $\text{BaCuAs}_2\text{O}_7$ ,  $\text{SrCuAs}_2\text{O}_7$ ,  $\text{CaCuAs}_2\text{O}_7$ ,  $\text{BaHgAs}_2\text{O}_7$ ,  $\text{H}_2\text{O}$ , and  $\text{SrHgAs}_2\text{O}_7$ , indicating that pyroarsenic acid is present in solution in equilibrium with the ortho-acid. It may be concluded that pyroarsenic acid is hydrolysed to the ortho-acid much more rapidly than the corresponding pyrophosphoric acid.

M. S. BURR.

**Allotropic modifications of sulphur. III. Behaviour of iodine towards sulphur and selenium.** C. R. PLATZMANN (Bull. Chem. Soc. Japan, 1930, 5, 79—86).—Cryoscopic measurements with solutions of selenium in sulphur show that mixed crystal formation occurs between the isomorphous forms of monoclinic sulphur ( $\text{S}_8$ ) and selenium ( $\text{Se}_8$ ). Normal cryoscopic constants are obtained for solutions of both diphenyl and iodine in sulphur solutions containing selenium. Consequently the cryoscopic relations of these compounds are uninfluenced by the presence of selenium, and it is suggested that the selenium and iodine combine, or that dissociation of the selenium molecule occurs in sulphur solution. The small degree of complexity of selenium in iodine solution in the absence of sulphur ( $\text{Se}_1$ — $\text{Se}_2$ ) and its complexity ( $\text{Se}_8$ ) in sulphur solution are remarkable, since only slight dissociation is to be expected in view of the close agreement between the m. p. and dielectric constants of iodine and selenium. F. G. TRYHORN.

**Precipitation of metallic sulphides due to the diffusion of salt mixtures.** M. WATANABE (The Earth, Japan, 1927, 8, 407—418).—A discussion in relation to the formation of ore deposits.

CHEMICAL ABSTRACTS.

**Partial reduction compounds of molybdates.** G. CANNERI (Gazzetta, 1930, 60, 113—125).—In a current of hydrogen alkali dimolybdates are reduced according to the equation  $\text{R}_2\text{Mo}_2\text{O}_7 + \text{H}_2 = \text{R}_2\text{MoO}_4 + \text{MoO}_3 + \text{H}_2\text{O}$ . Reduction by means of metallic tin produces a complex reaction in which molybdenum-blue is formed probably through the formation of quinquevalent molybdenum, which reacts with the

unchanged acid molybdate in the presence of water. Electrolytic reduction under suitable conditions gives rise to definite compounds similar in appearance and properties to the tungsten bronzes. The compounds  $\text{Na}_2\text{O} \cdot 4\text{MoO}_3$ ,  $\text{MoO}_2$ ,  $\text{Na}_2\text{O} \cdot 5\text{MoO}_3$ ,  $\text{MoO}_2$ ,  $\text{K}_2\text{O} \cdot 5\text{MoO}_3$ ,  $\text{MoO}_2$ ,  $\text{Li}_2\text{O} \cdot 4\text{MoO}_3$ ,  $\text{MoO}_2$  were isolated, and a study of their properties, and in particular their behaviour with hydrogen chloride at temperatures near 600°, leads to formulæ of the type  $\text{O} \cdot \text{Mo}[\text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{MoO}_2 \cdot \text{O} \cdot \text{R}']_2$ , ( $\text{R}' = \text{Na}, \text{Li}$ ), and  $\text{O} \cdot \text{Mo}(\text{OR}')[\text{O} \cdot (\text{MoO}_2 \cdot \text{O})_5 \cdot \text{R}']$ , ( $\text{R}' = \text{Na}, \text{K}$ ).

F. G. TRYHORN.

**Existence and behaviour of complex polyiodides.** G. JONES (J. Physical Chem., 1930, 34, 673—691).—A summary and discussion of the results of previous investigators. The view that iodine and iodides react in aqueous solution to form a negative tri-iodide ion is supported by much evidence of a varied nature. Arguments against this view based on the alleged non-existence of solid potassium tri-iodide at 25°, the rise in f. p. occurring when iodine is added to solutions of potassium iodide, and on diffusion experiments are considered to be fallacious. Evidence for the formation of a more complex polyiodide, possibly  $\text{I}_{14}^{--}$ , is pointed out.

L. S. THEOBALD.

**New type of fluoride of tervalent manganese.** F. OLSSON (Z. anorg. Chem., 1930, 187, 313—320).—By the action of hydrogen fluoride on manganic acetate along with the fluoride of an organic base, two series of double salts, of the general formulæ  $\text{MMnF}_4 \cdot n\text{H}_2\text{O}$  and  $\text{M}_2\text{MnF}_5$ , have been obtained. The former represents a new type, whilst the latter is analogous with the alkali manganifluorides. The following *tetrafluoromanganates* have been prepared: *pyridine*,  $\text{C}_5\text{H}_5\text{NHMnF}_4 \cdot \text{H}_2\text{O}$ ; *quinoline*,  $\text{C}_9\text{H}_7\text{NHMnF}_4 \cdot 3\text{H}_2\text{O}$ ; *tetramethylammonium*,  $\text{NM}_4\text{MnF}_4 \cdot 2\text{H}_2\text{O}$ ; *guanidine*,  $\text{NH}_2\text{C}(\text{NH}_2)_2\text{HMnF}_4 \cdot 3\text{H}_2\text{O}$ ; *dimethylamine*,  $\text{NH}_2\text{Me}_2\text{MnF}_4 \cdot 2\text{H}_2\text{O}$ ; *diethylamine*,  $\text{NH}_2\text{Et}_2\text{MnF}_4 \cdot 2\text{H}_2\text{O}$ ; *ethylamine*,  $\text{NH}_3\text{EtMnF}_4$ ; *propylamine*,  $\text{NH}_3\text{PrMnF}_4 \cdot \text{H}_2\text{O}$ ; and the *pentafluoromanganates*: *ethylenediamine*,  $\text{en}_2\text{H}_2\text{MnF}_5$ ; *guanidine*,  $[\text{NH}_2\text{C}(\text{NH}_2)_2\text{H}]_2\text{MnF}_5$ ; *ethylamine*,  $(\text{NH}_3\text{Et})_2\text{MnF}_5$ . The compounds are relatively stable in air, the ethylenediamine and guanidine compounds being considerably more stable than the others. In water a reddish-brown solution is formed and is gradually decomposed. In alcohol or acetic acid stable reddish-violet solutions are formed and the solubilities of some of the salts in these solvents are given. They are insoluble in ether. M. S. BURR.

**Complexes of the cyanide of quadrivalent manganese.** A. YAKIMACH (Compt. rend., 1930, 190, 681—683; cf. A., 1928, 1200).—*Potassium manganicyanide*,  $\text{K}_4\text{Mn}(\text{CN})_8$ , may be prepared by the addition of a saturated solution of potassium permanganate to an 80% solution of potassium cyanide until red needle-shaped crystals are produced. After several days the precipitate is filtered off and the limpid filtrate, which should be free from colloidal manganic hydrate, kept for 3 weeks, when it deposits large, brilliant red crystals. The compound is decomposed by water into hydrogen cyanide and brown



manganese hydroxide, by concentrated acids, and by alcohols (except 75% methyl alcohol) after prolonged contact. It decomposes at 230° without melting.

J. GRANT.

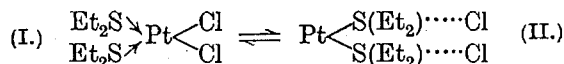
**Action of mercuric oxide on manganous chloride and of manganous oxide on mercuric chloride.** H. PÉLABON and (Mlle.) DELWAULLE (Bull. Soc. chim., 1930, [iv], 47, 156—164).—When small quantities of mercuric oxide are shaken with manganous chloride solutions the reaction  $3\text{MnCl}_2 + 4\text{HgO} = \text{Mn}_3\text{O}_4 + 2\text{HgCl}_2 + 2\text{HgCl}$  takes place; with larger quantities  $\text{Mn}_2\text{O}_3$  or  $\text{MnO}_2$  is formed according to the equations:  $2\text{MnCl}_2 + 3\text{HgO} = \text{Mn}_2\text{O}_3 + \text{HgCl}_2 + 2\text{HgCl}$ ;  $2\text{HgO} + \text{MnCl}_2 = \text{MnO}_2 + 2\text{HgCl}$ . The last reaction causes a reduction in the amount of mercuric chloride found in the solution. The action of manganous oxide on mercuric chloride solutions has also been investigated. According to the relative amounts of oxide and solution, the oxides  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ , or  $\text{Mn}_3\text{O}_4$  are formed. Similar results are obtained by the action of mercuric oxide on ferrous chloride solution, ferric oxide being formed. With larger additions of mercuric oxide, the concentration of mercuric chloride diminishes owing to the formation of the basic salt  $2\text{HgO} \cdot \text{HgCl}_2$ . J. A. V. BUTLER.

**Hydrates of ferric oxide of definite composition.** P. A. THIESSEN and R. KÖPPEN (Z. anorg. Chem., 1930, 189, 113—136).—Experiments on the isobaric and isothermal dehydration of hydrated ferric oxide prepared by hydrolysis of ferric ethoxide have revealed the existence of the following hydrates:  $\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ ,  $2\text{Fe}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $2\text{Fe}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ ,  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and  $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and have also given indications of the hydrates  $2\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Fe}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . The rate of dehydration is considerably influenced by the size of the particles. The hydrates do not take up water when placed under water, even under a pressure of 3000 atm. A method for preparing any given hydrate in a pure state is outlined. The isothermal dehydration curve of goethite indicates the formation of the hydrate  $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , but dehydration of a sample of limonite gave a continuous curve, suggesting the presence of a hydrate, presumably goethite, with adsorbed water. R. CUTHILL.

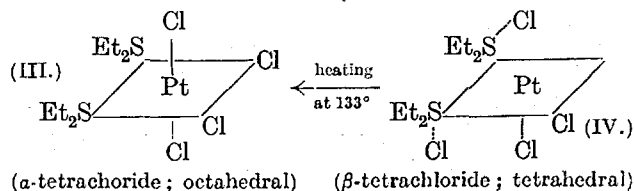
**Reactions between ferric oxide and silica.** J. A. HEDVALL and P. SJÖMAN (Svensk Kem. Tidskr., 1930, 42, 40—42).—Ferric oxide prepared from ferrous oxalate was mixed with quartz and heated electrically in oxygen at temperatures varying from 550° to 1350°. A reaction commences at 575°, probably in connexion with the  $\alpha$ - $\beta$  change of quartz, and continues up to 900°. In mixtures in which the ratio of ferric oxide to quartz was 1:1, 15% of the silica entered into combination. In mixtures with excess of silica a second reaction commences at 900° in connexion with the conversion of quartz into cristobalite, a product resembling rose quartz being formed to the extent of 7%. No definite compounds could be isolated, but proof of combination was established by X-ray photographs. The results are regarded as confirming the author's rule that the degree of activity of solid mixtures is considerably increased at the point where a change of phase takes place. H. F. HARWOOD.

**Alkali metal bromides of rhodium.** P. POULENC (Compt. rend., 1930, 190, 639—641).—The following compounds have been prepared by the interaction of solutions of alkali metal bromides and rhodium bromide:  $\text{Na}_3[\text{RhBr}_6] \cdot 12\text{H}_2\text{O}$ , red, water-soluble crystals non-isomorphous with the corresponding chlorine compound;  $(\text{NH}_4)_3[\text{Rh}_2\text{Br}_9]$ , green hexagonal crystals, isomorphous with the corresponding potassium, rubidium, and caesium salts. The latter salts form in solution equilibrium mixtures of the three complexes  $\text{M}_3[\text{Rh}_2\text{Br}_9]$ ,  $\text{M}_4[\text{Rh}_2\text{Br}_{10}] \cdot 6\text{H}_2\text{O}$ , and  $\text{M}_5[\text{Rh}_2\text{Br}_{11}] \cdot 6\text{H}_2\text{O}$ , in proportions which depend on the reaction of the medium. The complexes  $\text{K}_3[\text{RhCl}_4 \cdot 5\text{Br}_{1.5}] \cdot \text{H}_2\text{O}$  and  $\text{K}_5[\text{Rh}_2\text{Cl}_{1.5}\text{Br}_{9.5}] \cdot 6\text{H}_2\text{O}$  were also prepared. The fact that the stability of the complex decreases with increase in number of the bromine atoms, so that the type  $\text{M}_3[\text{RhX}_6]$  is seldom obtainable as in the case of the chlorine compounds, is explained by the Kossel-Magnus theory that the larger radius of the bromine atom compared with the chlorine atom keeps it at a greater distance from the central atom. J. GRANT.

**Interpretation of the isomerism amongst co-ordination compounds of platinum.** F. G. ANGELL, H. D. K. DREW, and W. WARDLAW (J.C.S., 1930, 349—369).—The isomerism of the  $\alpha$ - and  $\beta$ -dichlorides obtained by treating platinous chloride with ethyl sulphide has been reinvestigated and shown to be due to structural difference. In the  $\alpha$ -compounds the sulphur atoms are linked to the platinum by Sidgwick co-ordination linkings (I), whereas the  $\beta$ -compounds are of the sulphonium type, in which the chlorine is united to the sulphur atoms (II) and is



potentially ionised. The  $\alpha$ -salts are non-polar and the  $\beta$ -salts are electrolytes in aqueous solution; the former react slowly with moist silver oxide, yielding ethyl sulphide, silver chloride, and platinous oxide, whereas the latter rapidly reacts to produce a strong base, *platinumbisdiethylsulphonium hydroxide*, two hydroxyl groups replacing the chlorine atoms in II. Neutralisation of solutions of the base with acids produces pure  $\beta$ -salts, of which the *oxalate* (m. p. about 60°), *dibromide* (m. p. 93—95°), and *dichromate* (m. p. 140°) are described. When the dichlorides are treated with chlorine the corresponding *tetrachlorides* (III and



IV) are obtained; the  $\alpha$ - has m. p. 198° and the  $\beta$ -salt melts between 120° and 130° and rapidly changes to the  $\alpha$ -salt. The *tetrabromides* are even more labile. The same  $\alpha$ -*dichlorodibromide* is obtained by addition of bromine to the  $\alpha$ -dichloride as is obtained by passing chlorine through a solution of the  $\alpha$ -dibromide. The corresponding additions to the  $\beta$ -dihalides yield labile

$\beta$ -tetrahalides, which are converted into the  $\alpha$ -mixed halide readily on warming. These transformations can be explained only by assuming that platinum in the quadrivalent compounds is tetrahedral and that conversion into the octahedral form takes place solely by *cis*-addition of two further groupings. The six valency electrons of platinum have the same fixed spatial directions whether one, two, or three pairs are saturated and saturation occurs only in pairs occupying respectively the three *cis*-positions of the developed octahedron. It follows that the skew tetrahedron shown in I should occasion molecular asymmetry; this possibility is being investigated.

A. R. POWELL.

**Derivatives of tetramminoplatinous chloride.** N. S. KURNAKOV and I. A. ANDRÉEVSKI (Z. anorg. Chem., 1930, 189, 137—144).—Crystallisation of a mixed solution of tetramminoplatinous chloride and the chloride of Reiset's second base yields a double salt,  $\text{PtCl}_2 \cdot 2\text{NH}_3 \cdot 4(\text{PtCl}_2 \cdot 4\text{NH}_3)$  (brownish-yellow), which is capable of forming solid solutions in the first-named salt. The yellowish-brown colour of tetramminoplatinous chloride prepared by the action of ammonia on potassium chloroplatinite thus receives an explanation.

R. CUTHILL.

**Quantitative analysis by X-rays.** T. H. LABY and C. E. EDDY (Nature, 1930, 125, 524—525).—A discussion of the method of X-ray analysis and a criticism of certain points of Hevesy's communication (*ibid.*, 1929, 124, 841).

L. S. THEOBALD.

**Quantitative spectrographic analysis as a general microchemical method.** H. LUNDEGÅRDH (Svensk Kem. Tidskr., 1930, 42, 51—65).—The general methods in use are briefly discussed, and a process devised by the author is described. The flame spectrum of the substance is photographed, using an acetylene flame and a special form of sprayer to inject the solution, and the intensity of the lines is measured by means of a thermoelectric photometer, the results being compared with a standard curve obtained from known quantities of the element under examination. Of 40 elements tested it was found possible to determine 25 by this method, the amount detectable in the 3 c.c. of solution required by the apparatus varying from 0.0001 mg. for lithium to 1.0 mg. for lead. The degree of accuracy attainable is about  $\pm 5\%$ . The spark spectra may be employed in the case of elements for which the above method is unsuitable; it is advisable in this case to use simultaneously a definite amount of a comparison substance such as beryllium, barium, or cadmium in order to eliminate errors due to variations in the intensity of the spectrum. The method is particularly well adapted for cases where a large number of analyses of similar type have to be carried out on small amounts of material, as in agricultural analysis, and the results afford curves of similar character to those obtained by ordinary chemical analysis carried out on considerably larger quantities of substance.

H. F. HARWOOD.

**Use of the antimony electrode for differential titration in aqueous or alcoholic solutions.** I. I. SHUKOV and V. M. GORTIKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2055—2072).—See this vol., 50.

**Quinhydrone electrode.** A. I. BRODSKY and F. I. TRACHTENBERG (J. Russ. Phys. Chem. Soc., 1929, 61, 2189—2204).—See A., 1929, 1240.

**Determination of equilibrium constants of chemical reactions by potentiometric titration.** F. L. HAHN and R. KLOCKMANN (Z. physikal. Chem., 1930, 146, 373—403; cf. following abstract).—A method of finding equilibrium constants by potentiometric titration, based on determining  $\Delta\epsilon/\Delta v$ , where  $\Delta\epsilon$  is the maximum value of the change of potential produced by an addition of volume  $\Delta v$  of the reagent, is described. In the titration of a weak acid with a strong base, the concentration of hydrogen ions and hence the dissociation constant of the acid can be calculated from this quantity. The method is suitable for accurate determinations of dissociation constants of weak acids and bases, and of the solubility products of slightly soluble salts. Values are given of the dissociation constants of pyridine, quinoline, aniline, boric acid, and phenol and of the solubility product of silver chloride.

J. A. V. BUTLER.

**Determination of end-points in potentiometric titrations. IV. Influence of errors of measurement and disturbances on the end-point error.** F. L. HAHN (Z. physikal. Chem., 1930, 146, 363—372).—A discussion of the influence on the end-point error of the quantity of reagent added between successive readings. When the magnitude of each addition is progressively reduced, the precision with which the end-point can be found first increases to a point of greatest exactness and afterwards diminishes.

J. A. V. BUTLER.

**Problem of dilution in colorimetric hydrogen-ion measurements. II. Use of isohydric indicators and superpure water for accurate measurements of hydrogen-ion concentrations and salt errors.** S. F. ACREE and E. H. FAWCETT (Ind. Eng. Chem. [Anal.], 1930, 2, 78—85).—Accurate  $p_H$  determinations in dilute or weakly buffered solutions can be obtained colorimetrically only by (a) the adjustment of the  $p_H$  value of the standard indicator solutions, (b) the use of the isohydric indicator methods, (c) the use of pure water ( $p_H$  7.0), and (d) correction for salt and protein errors; the necessary details with respect to the above are described. Tables and curves are given to show the errors in  $p_H$  caused by dilution of the buffer solutions with ordinary ( $p_H$  5.0) distilled water or with air-carbon dioxide equilibrium water ( $p_H$  5.7), and the relation between the dilution of buffer solutions and the salt and protein errors of the indicators used is shown.

H. F. HARWOOD.

**Modified methyl-red and sodium alizarin-sulphonate indicators.** A. H. JOHNSON and J. R. GREEN (Ind. Eng. Chem. [Anal.], 1930, 2, 2—4).—The presence of a blue or greenish-blue dye increases the sensitiveness of the indicator. Results with a large number of indicator-dye mixtures are given.

S. I. LEVY.

**Determination of the water content [of substances] by means of calcium hydride.** O. NOTEVART (Z. anal. Chem., 1930, 80, 21—56).—The method of Dupré (A., 1906, ii, 626) for determining water in explosives etc. has been modified by the substitution of calcium hydride for calcium carbide.

The material under investigation is weighed out in a special type of flask which permits the subsequent formation of a layer of calcium hydride on a perforated plate above the substance. The flask is connected by capillary tubing with a Lunge volumeter in which the evolved hydrogen is measured; ethylene glycol being employed as confining liquid. Since technical calcium hydride always contains nitride, the amount of water corresponding with each c.c. of hydrogen evolved must be ascertained by a blank experiment. Each determination occupies from 24 hrs. to several days, dependent on the hygroscopic nature of the material. The method cannot be used with substances the vapour pressure of which at 20° exceeds 25 mm. or with substances containing volatile alcohols. Fatty substances and viscous tars and oils are best dissolved in anhydrous *s*-tetrachloroethane before introduction into the apparatus. A series of dehydration curves obtained from a number of different substances is given.

H. F. HARWOOD.

**Determination of halogen in insoluble inorganic halides.** R. H. KLEIN (Analyst, 1930, 55, 192–193).—The halide (0.5 g.) is triturated with 20 c.c. of water and 1 g. of zinc dust, and after 10 min. the supernatant liquid is decanted, the washings of the insoluble material are added, and the whole is titrated with 0.1*N*-silver nitrate solution. Good results were obtained with mercuric iodide, lead chloride, and silver iodide, but not with mercurous chloride.

D. H. HEWER.

**Direct determination of bromide in presence of chloride.** G. G. LONGINESCU and T. I. PIRTEA (Bull. Acad. Sci. Roumaine, 1929, 12, No. 7–10, 57–59; cf. Longinescu and Badescu, A., 1927, 124).—Twenty-five to 30 c.c. of the solution are placed in a 200-c.c. flask fitted with a funnel and an exit tube (both fused through the glass stopper) connected with a wide glass tube containing lumps of calcium oxide. Ten c.c. of concentrated sulphuric acid and 1 c.c. of 30% hydrogen peroxide are introduced, and the flask is heated to 80° while a current of air is aspirated through it, and maintained at this temperature until the liquid has become colourless (0.5–1.5 hrs.). After cooling, the lime is rinsed out into water containing 1–2 g. of sodium sulphite; dilute nitric acid is added until dissolution is complete, and the bromide determined gravimetrically as usual. The residual chloride in the flask may be determined either gravimetrically or volumetrically; in the latter case the excess of hydrogen peroxide is first removed by addition of ferrous sulphate and boiling, followed by treatment with dilute nitric acid.

H. F. HARWOOD.

**Use of the iodine monochloride end-point in volumetric analysis.** I. Titration of iodide. E. H. SWIFT. II. Titration of arsenious acid with permanganate and with ceric sulphate. E. H. SWIFT and C. H. GREGORY (J. Amer. Chem. Soc., 1930, 52, 894–900, 901–906).—I. Potassium iodide in 3.5–4.5*M*-hydrochloric acid may be titrated accurately with potassium iodate, potassium permanganate, and ceric sulphate. The end-point is attained very slowly at lower acidities. Potassium dichromate requires 8.0*M*-hydrochloric acid. The iodine first liberated is oxidised,  $I_2 + 2HCl + O =$

$2ICl + H_2O$ , and the end-point determined by the disappearance of iodine from 5 c.c. of carbon tetrachloride which have been added; 0.03 mg. of iodine in 50 c.c. acid solution may be detected.

II. Sodium arsenite in 4*M*-hydrochloric acid, to which carbon tetrachloride and 5 c.c. of 0.017*M*-iodine monochloride have been added as indicator, is determined accurately by potassium permanganate and ceric sulphate; the end-point is determined as above. In the electrometric titration of arsenious acid with ceric sulphate the hydrochloric acid should be 4*M* (cf. Willard and Young, A., 1928, 725).

J. G. A. GRIFFITHS.

**Microscopical examination of precipitates as an aid to precise analysis.** I. Determination of sulphates as barium sulphate. S. POPOV and E. W. NEUMAN (Ind. Eng. Chem. [Anal.], 1930, 2, 45–54).—The precipitation of barium sulphate under varying conditions has been studied and the precipitates so formed have been examined microscopically. The addition of the sulphate solution to barium chloride gives better results in the determination of sulphates than those obtained by the usual methods; the contamination of the precipitate by chlorine is greater in the reverse method, but this is offset by the solubility of the barium sulphate. The customary methods tend to give low results, and this is ascribed to the preferential adsorption of sulphate ion rather than of chloride ion. No method yields satisfactory results in the presence of potassium nitrate. The microscopic crystals of barium sulphate formed by the reverse method of precipitation are much more uniform in character in almost all cases than those obtained by other methods; a number of photomicrographs of barium sulphate precipitates formed under different conditions are given. The conclusion is also reached that barium sulphate suffers a progressive loss of weight when heated at 950°. The following procedure for the determination of sulphates is recommended. To a nearly boiling solution containing 4–8 c.c. of 3*N*-hydrochloric acid and 5 c.c. excess of barium chloride (about 0.1*M*) the sulphate solution is added drop by drop with continual stirring, about 4 min. being taken for the addition. Conditions should be such that the weight of barium sulphate formed is about 0.8 g., and the final volume of the liquid 350 c.c. The whole is digested for 1 hr. near the b. p., the precipitate filtered, washed with hot water, and ignited for 1 hr. at 800°. If iron is present in the solution it is advisable to collect the barium sulphate shortly after precipitation.

H. F. HARWOOD.

**Reduction potentiometry.** I. Determination of selenium, tellurium, and gold. K. SOMEYA (Z. anorg. Chem., 1930, 187, 337–361).—The use of weak reducing agents in potentiometric titrations has been investigated with the object of simplifying the process by making it unnecessary to exclude air. Selenium in selenious acid, tellurium in tellurous acid, and gold in the trichloride may be successfully titrated with potassium iodide. The titration of selenium is unaffected, or only slightly affected, by the presence of tellurium, copper, or iron, but gold must not be present. The presence of selenium, copper, or iron

makes the titration of tellurium impossible. In solutions containing gold and tellurium both elements may be titrated potentiometrically, but the results for gold are not quite so accurate as for tellurium. Selenious acid may be titrated with sodium thio-sulphate without exclusion of air and between wide limits of acidity. The titer is unaffected by the presence of tellurium or alkali halides, and becomes too large in the presence of gold. Selenious acid may also be titrated with alkali, using a quinhydrone electrode.

M. S. BURR.

**Determination of phosphoric acids.** K. HINSBERG and D. LASZLO (*Biochem. Z.*, 1930, 217, 346—353).—The mixture of ortho- and pyro-phosphate is precipitated as calcium salt, washed with 70% alcoholic ammonia, and determined colorimetrically by Lohmann's modification (*A.*, 1928, 665, 1054) of the method of Fiske and Subbarow. The orthophosphate is precipitated with magnesia mixture and determined in the same way or by titration. Using about 1 mg. of each phosphate, errors averaging 1—2% were obtained.

K. V. THIMANN.

**Oxidimetric determination of phosphate ion.** L. BRESTAK and O. A. DAFERT (*Z. angew. Chem.*, 1930, 43, 216).—The phosphate solution (5 c.c.) is treated in succession with 30 c.c. of a saturated solution of recently recrystallised sodium sulphite, 40 c.c. of a 3% ammonium molybdate solution, and 62 c.c. of 20% sulphuric acid; the mixture is heated slowly to boiling and boiled gently until all odour of sulphur dioxide disappears, and, after cooling, the blue solution is titrated with 0.01*N*-potassium permanganate solution (1 c.c. = 0.003552 g.  $P_2O_5$ ). For accurate results at least 1.5 g. of sodium sulphite must be used for every 0.01 g. of phosphoric anhydride present; under these conditions the phosphomolybdic acid formed is reduced to the compound  $H_3PO_3 \cdot 11MoO_3 \cdot 3MoO_2$ , whereas the excess of molybdate used is unaffected by the sulphite. Iron and arsenic interfere.

A. R. POWELL.

**Accuracy of the Gutzeit method for the determination of minute quantities of arsenic.** J. W. BARNES and C. W. MURRAY (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 29—31).—The determination of arsenic in organic materials by the Gutzeit method under ordinary laboratory conditions is liable to a probable error of  $\pm 0.0039$  mg. for quantities of arsenic up to 30  $\mu$ g.; the error can be reduced to  $\pm 0.0023$  mg. by using as reference a graph prepared from a large number of determinations carried out on aliquot parts of one and the same solution. If the total arsenic present exceeds 4 mg. the calomel method of determination should be used. Experiments showed that no loss of arsenic is to be feared during the destruction of the organic material of the sample by the Kjeldahl method, even although considerable charring takes place.

H. F. HARWOOD.

**Determination of silica in phosphate rock.** W. L. HILL and K. D. JACOB.—See B., 1930, 372.

**Drop method of qualitative analysis for anions containing the cyanogen group.** A. SCHAPOVALENKO (*J. Russ. Phys. Chem. Soc.*, 1929, 61, 2101—2110).—The usual methods employed for the

analysis of anions containing the cyanogen group can also be applied as drop methods. A drop of ferric or ferrous iron solution is placed on filter-paper, and a capillary tube containing the solution under examination is drawn across the spot, which is then moistened with 1—2*N*-acid; the production of Prussian or Turnbull's blue, or of a red coloration, shows the presence respectively of not less than 0.001*N*-ferrocyanide, 0.00001*N*-ferricyanide, or 0.001*N*-thiocyanate. The presence of cyanide ion can be demonstrated by applying a drop of cupric sulphate to a drop of solution on filter-paper, and then adding a drop of a solution of benzidine in acetic acid, when a blue coloration appears at concentrations of cyanide above 0.00001*N*. When ferrocyanide, ferricyanide and thiocyanate are present together in concentrations not below 0.001*N* the following procedure is adopted. A drop of saturated lead nitrate solution is placed on filter-paper and the solution under examination is placed on this. A small quantity of water is placed at the centre of the spot, when insoluble lead ferrocyanide remains at the centre, whilst ferricyanide and thiocyanate are displaced to the peripheries of the spot. On passing a capillary containing ferric iron across the spot, and a second capillary with ferrous iron at right angles to the first line, a blue coloration at the peripheries indicates ferricyanide, and at the centre ferrocyanide, whilst a red coloration at the peripheries indicates thiocyanate. The sensitivity of these reactions diminishes with increasing concentration of other ions.

R. TRUSZKOWSKI.

**Determination of sodium hyposulphite.** M. FRANÇOIS and (MLLE.) L. SEGUIN.—See B., 1930, 371.

**Picric acid test for potassium.** E. R. CALEY (*J. Amer. Chem. Soc.*, 1930, 52, 953—956).—Optimal conditions for the detection of potassium as the picrate have been determined. The addition of 7—8 vols. of saturated alcoholic picric acid to 1 vol. of solution containing 1 part of potassium (preferably chloride) in 1250 parts yields a precipitate in 30 min. Strong acidity reduces the sensitivity. Ammonia and more than 0.004 g. per c.c. of sodium interfere. Magnesium and lithium do not interfere.

J. G. A. GRIFFITHS.

**Potentiometric determination of barium, lead, and sulphate.** S. MUKAI (*Bull. Tech. Coll. Kyushu Imp. Univ.*, 1929, 4, 17—21).—A platinum wire is used as the indicator electrode and a calomel half-cell as the other electrode. 0.1*M*-Potassium chromate solution is added to the barium solution at 30°; the error is 0.6%. For lead, 0.1*M*-lead nitrate is employed; irregular results are obtained with the acetate. For sulphate, 0.1*M*-potassium sulphate is precipitated with an excess of lead nitrate, the lead remaining in the filtrate being determined. The error is 0.55%.

CHEMICAL ABSTRACTS.

**Use of protective colloids in colorimetric determination of certain metals as lakes of dyes.** W. E. THRUN.—See B., 1930, 383.

**Micro-determination of magnesium.** H. VON EULER, H. HELLSTRÖM, and D. RUNEHJELM (*Z. physiol. Chem.*, 1930, 187, 127—132).—A spectrophotometric and a colorimetric method (blue colour

with 1 : 2 : 5 : 8-tetrahydroxyanthraquinone) for the micro-determination of magnesium gave errors of 36% and 6%, respectively, for a concentration of 0.01 mg. of magnesium per c.c. J. H. BIRKINSHAW.

**Quantitative separation of zinc from magnesium.** H. L. PIOTROWSKI (*Przemysł Chem.*, 1930, **14**, 105—111).—Zinc is precipitated as carbonate from solutions containing magnesium and not more than about 0.2 g. of zinc by adding 10% sodium carbonate solution until most of the zinc is precipitated, boiling, adding phenolphthalein, and then adding more carbonate until the solution becomes pink. Potassium dichromate solution (3%) is then added until the colour of the solution changes sharply from pink to yellow. The object of this operation is to dissolve any magnesium carbonate also precipitated, zinc carbonate being practically insoluble in these conditions. The well-washed precipitate is dissolved in hot dilute hydrochloric acid, and sodium carbonate solution is added until most of the zinc is precipitated, when the suspension is filtered and the residue washed with hot water. The filtrate and washings are treated as before with slight excess of sodium carbonate and then with dichromate, the residue is redissolved in hydrochloric acid, excess of carbonate is added, and the precipitate is filtered and washed. The two filter-papers containing zinc carbonate are then dried and ignited, and the residue is weighed as zinc oxide. This method involves a mean error of  $\pm 0.04\%$ . R. TRUSZKOWSKI.

**Colour reaction for zinc, and the composition of the precipitate obtained by the action of potassium ferrocyanide on zinc salts in the presence of cobalt.** A. SCHACHKELDIAN (*J. Russ. Phys. Chem. Soc.* 1929, **61**, 2217—2220).—Zinc and cobalt are precipitated together as a bulky, bluish-green, amorphous precipitate on the addition of potassium ferrocyanide; this precipitate has a composition corresponding with the formula  $\text{Zn}_3\text{Co}[\text{Fe}(\text{CN})_6]_3$ .

R. TRUSZKOWSKI.

**Nephelometric determination of zinc.** L. T. FAIRHALL and J. R. RICHARDSON (*J. Amer. Chem. Soc.*, 1930, **52**, 938—944).—The separation and determination of zinc in ash of biological origin are described. Zinc and copper are precipitated quantitatively, between  $C_H$   $10^{-2.5}$  and  $10^{-4}$ , as sulphides uncontaminated with iron. The copper is separated. The nephelometric determination of 1.4—0.5 mg. of zinc as ferrocyanide is accurate to  $\pm 0.06$  mg. only within narrow limits of acidity and salt concentration; suitable values are  $C_H$   $10^{-2.3}$  and 0.0268*M* with respect to potassium chloride. Maximum opalescence is attained in 10 min. Accuracy of comparison is greatest with standards containing 0.20—0.25 mg. Zn in 50 c.c. J. G. A. GRIFFITHS.

**Reaction of lead.** LIGOR BEY and M. FAILLEBIN (*Bull. Soc. chim.*, 1930, [iv], **47**, 225—226).—The lead compound is added to 5 c.c. of ammonia (5 c.c. of concentrated ammonia solution to 100 c.c. of water) and shaken for several minutes, when 5 c.c. of a 5% aqueous solution of resorcinol are added. In the presence of lead a blue colour is developed; 0.03 g. per litre can be detected, but in very dilute solutions the colour does not appear for a considerable time.

The test is limited by the fact that ammoniacal solutions of resorcinol themselves become yellow and finally blue in the presence of air; 0.1% of lead sulphate in barium sulphate can be detected.

J. A. V. BUTLER.

**Secondary precipitation processes during the mutual action of lead chloride and sulphuric acid.** Z. KARAOGLANOV (*Ber.*, 1930, **63**, [B], 597—603).—When lead chloride in boiling aqueous solution is rapidly precipitated by sulphuric acid, the amount of chlorine in the precipitate diminishes with increasing dilution, increases with the amount of hydrochloric acid present, and, under like conditions, with the quantity of precipitated lead sulphate. The presence of nitric acid in addition to hydrochloric acid increases the amount of chlorine, which depends also on the amount of precipitant. Hydrogen, sodium, ammonium, and potassium chlorides are decreasingly causative of the presence of chlorine in the precipitate. If the sulphuric acid is added slowly, the precipitate contains rather more chlorine than with rapid addition; the effect of addenda is almost unchanged. If precipitation is effected at the ordinary temperature more chlorine is present in the lead sulphate; it is immaterial whether precipitation is effected rapidly or slowly. If boiling sulphuric acid is rapidly precipitated with lead chloride, the precipitate contains much more chlorine than when the reverse order is used. It increases with increase in the amount of hydrochloric acid, of precipitant, and of nitric acid. Sodium, ammonium, and potassium chlorides do not occasion the presence of so much chlorine in the precipitate as does hydrochloric acid. Slow precipitation of boiling sulphuric acid with lead chloride yields a product with less chlorine than when the action is rapid; the amount of halogen is particularly high when both nitric and hydrochloric acids are present. Precipitation at the ordinary temperature gives closely similar results except in the presence of nitric acid. The chlorine is not present in the precipitate as a compound volatile when heated. Pre-formed lead sulphate does not adsorb chlorine from solutions of hydrochloric acid or lead chloride. The observations are explained on the basis of a main change,  $\text{Pb}^{2+} + \text{SO}_4^{2-} = \text{PbSO}_4$ , and a secondary process,  $2\text{PbCl} + \text{SO}_4^{2-} = (\text{PbCl})_2\text{SO}_4$ .

H. WREN.

**Gravimetric determination of thallium in mouse poisons.** W. LEPPER.—See B., 1930, 304.

**Determination of small amounts of copper in the presence of iron.** L. J. CHALK (*Analyst*, 1930, **55**, 187—191).—Copper may be determined in a biological solution (35 c.c.) containing up to 0.1 mg. Cu by rendering slightly alkaline with sodium hydroxide, adding sufficient *N*-sulphuric acid to dissolve the ferric hydroxide in the cold, followed by 1 c.c. of 10% tartaric acid solution, 0.5 c.c. of pyridine, and 5 c.c. of chloroform. The whole is made up to 50 c.c., shaken, the chloroform layer poured into a Nessler glass, and the liquid compared colorimetrically with a standard prepared in a similar manner. This method is not applicable in the presence of more than 1 mg. of ferrous iron, and if iron is present in the original solution the analysis should be completed within a short time of adding the tartaric acid and

the amount of pyridine limited to 5 c.c. Acetates must be absent. Cobalt, nickel, and silver cause interference, and in the presence of lead and barium hydrochloric acid should be substituted for sulphuric. Mercurous and ferrous salts must be oxidised before the determination is made. The method is slightly less sensitive than that of Callan and Henderson (cf. this vol., 53).  
D. G. HEWER.

**Determination of copper in organic matter.** E. CHERBULIEZ and S. ANSBACHER (Helv. Chim. Acta, 1930, 13, 187—194).—Minute quantities of copper present in organic matter may be determined by destroying the latter with sulphuric and perchloric acids in presence of nitric acid (cf. A., 1929, 898), precipitating copper as sulphide from the sulphuric acid solution obtained, redissolving in nitric acid, and titrating with nitroso-chromotropic acid (cf. Brenner, A., 1920, ii, 194). Quantities of 20  $\gamma$  may be titrated in this way with an accuracy of 0.5  $\gamma$  ( $\gamma=10^{-6}$  g.). The influence of the presence of other metals has been determined. Silver, arsenic, antimony, and bismuth have no influence on the titration. Mercury, lead, cadmium, and tin affect the result only slightly when present in amount equal to that of the copper. When, however, their concentration is ten times that of the copper, mercury and lead cause an error of 10%, cadmium 6.5%, and tin -2.2%. The method is suitable for use in biological investigations.  
M. S. BURR.

**Potentiometric determination of copper without the use of a calomel electrode, and the solubility product of copper hydroxide.** R. TOMIL, E. OKABE, and S. TAKEDA (Bull. Dept. Appl. Chem. Waseda Univ., Japan, 1929, 9, 6—12).—In the titration of copper sulphate with sodium hydroxide a capillary tube containing a thin copper wire and a glass tube around which a copper wire is wound are employed as electrodes. The use of gelatin in the capillary tube ensures a smooth titration curve. The solubility product of cupric hydroxide is  $3.72 \times 10^{-10}$ .

#### CHEMICAL ABSTRACTS.

**Determination of aluminium by means of hydrazine carbonate in the presence of manganese.** J. LUKAS and A. JÍLEK (Coll. Czech. Chem. Comm., 1930, 2, 113—119).—The solution is neutralised with ammonia, avoiding a precipitate, diluted to 200 c.c., and treated with 1 g. of ammonium nitrate and 2 c.c. of hydrazine carbonate solution. After 4 hrs. the precipitate is collected, washed with hot water, and redissolved in 1:1-hydrochloric acid. Reprecipitation of the alumina is effected as before and the second precipitate is ignited and weighed. Manganese is precipitated from the combined filtrates as manganese ammonium phosphate. A. R. POWELL.

**Dehydration of analytical precipitates by ignition.** W. MIEHR, P. KOCH, and J. KRATZERT (Z. angew. Chem., 1930, 43, 250—254).—The dehydration of aluminium hydroxide on heating, with formation of crystalline corundum, has been investigated, the progress of the reaction being followed by (a) weighing, (b) determination of the hygroscopic nature of the ignited precipitate, (c) formation of lake with alizarin, (d) Debye-Scherrer X-ray diagrams. Alumina ignited at temperatures between 900° and 1150° still

contains water, and is markedly hygroscopic; ignition at 1200° yields an oxide which is still hygroscopic, but the results obtained are adequate for analytical purposes. After ignition at 1300—1350° the resulting alumina is anhydrous and non-hygroscopic. The authors consider that failure to comply with the above conditions for the ignition temperature are liable to cause a positive error of 0.8—3.0% in the determination of alumina. In the determination of aluminium as the phosphate, the precipitate must be ignited to constant weight at 1200—1300°; higher temperatures must not be employed, as loss results through volatilisation of phosphoric acid. A good blowpipe is adequate to effect the dehydration of silica precipitates, and the ignited silica is not markedly hygroscopic.  
H. F. HARWOOD.

**Determination and separation of rare earths from other metals. XVIII. Determination of indium and its separation from monoxides and sesquioxides.** L. MOSER and F. SIEGMANN (Monatsh., 1930, 55, 14—24).—Contrary to the experience of Meyer (Annalen, 1869, 150, 153),  $\text{In}(\text{OH})_3$  is quantitatively precipitated from hot solution by ammonia in the presence of ammonium chloride and on heating is quantitatively converted into the sesquioxide, which is not hygroscopic (cf. Thiel and Luckmann, A., 1928, 852). Indium is quantitatively precipitated from solutions of its salts by hexamethylenetetramine and also by 10% potassium cyanate solution (added until alkaline to methyl-orange) in the presence of ammonium salts as  $\text{In}(\text{OH})_3$ . It is also precipitated in 0.03—0.05N-hydrochloric acid solution by hydrogen sulphide as  $\text{In}_2\text{S}_3$ , which is weighed after heating at 350—400° and then allowing to cool in a current of hydrogen sulphide. The separation of indium from other metals, present in varying proportions, is described. It is separated from zinc and from nickel by precipitation with potassium cyanate in slightly acid solution in the presence of ammonium chloride (if the ratio of zinc to indium exceeds 10 this process must be repeated); from cobalt, by adding potassium cyanide to the neutral solution until the precipitate has dissolved, then a little 10% potassium cyanate solution and heating to boiling, when  $\text{In}(\text{OH})_3$  is thrown down (precipitation must be repeated if the ratio of cobalt to indium is greater than 10); from manganese, by passing hydrogen sulphide into the boiling solution containing ammonia and acetic acid and weighing as  $\text{In}_2\text{S}_3$ ; from aluminium, by adding sulphosalicylic acid followed by ammonium carbonate until neutral (methyl-orange) and a little acetic acid, and precipitating with hydrogen sulphide; from iron (ferric), by treating the 0.03—0.05N-hydrochloric acid solution with hydrogen sulphide at 70° during 2 hrs.; and from chromium, by precipitation as  $\text{In}(\text{OH})_3$  with potassium cyanide in slightly alkaline solution (methyl-orange).  
A. I. VOGEL.

**Separation and determination of gallium. I.** S. Ato (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 12, 225—229).—The solution of the chloride or nitrate is evaporated to dryness to remove acid, and the residue is dissolved in 10 c.c. of 6N-acetic acid and 100 c.c. of water. Ten c.c. of a 10% solution of camphoric acid in alcohol or acetone are added, and



the whole is heated for 10 min. at 100°. The resulting precipitate is filtered, washed with 0.6*N*-acetic acid, ignited, and weighed as  $\text{Ga}_2\text{O}_3$ . If gallium alone is present in the solution under examination the precipitation can preferably take place in an aqueous solution without previous addition of acetic acid, as filtration is more easily carried out under these conditions. The method affords a separation of gallium from numerous other metals, but indium, iron, and a few other elements are also quantitatively precipitated by camphoric acid. H. F. HARWOOD.

**Comparison of certain hydrogen-ion indicator electrodes in the presence of ferric iron.** L. W. ELDER, jun. (Amer. Electrochem. Soc., May, 1930. Advance copy, 11 pp.).—A comparative study has been made of the behaviour of platinum-hydrogen, platinum-air, antimony, and glass electrodes in the titration of acid solutions of ferric chloride, of ferrous chloride, and of mixtures of these two salts with sodium hydroxide solution. When only ferrous iron is present all the electrodes except the air electrode give practically congruent titration curves. When ferric iron is present the only electrode which gives potentials corresponding with the hydrogen-ion concentration throughout the titration is the glass electrode. The antimony electrode exhibits more positive potentials, especially in the earlier stages of the titration, probably owing to the presence of quinquevalent antimony in the solution. With the gas electrodes the potential during the earlier stages is highly positive, the hydrogen electrode clearly acting as an oxidation-reduction electrode under these conditions. Nevertheless, all the electrodes except the air electrode give closely similar potentials just before the first point of inflexion, which corresponds with the precipitation of ferric iron. Whichever electrode is used, this point of inflexion occurs slightly too late, but this error is least with the hydrogen electrode. Small errors are also observed in the position of the second point of inflexion, which corresponds with the precipitation of ferrous iron. These errors are attributed to the adsorption of alkali by the precipitates and to the oxidation of ferrous hydroxide during the first stages of its precipitation. From the titration data the solubility products of ferrous and ferric hydroxide are calculated to be  $4.8 \times 10^{-16}$  and  $3 \times 10^{-38}$  to  $4 \times 10^{-38}$ , respectively.

H. J. T. ELLINGHAM.

**Colorimetric determination of cobalt alone and in presence of nickel.** E. S. TOMULA (Suomen Kem., 1929, 2, 72–80).—Deep blue alkali cobaltotetrathiocyanate is employed for purposes of colorimetric comparison with a standard. The influence of methyl or ethyl alcohol and of acetone on the colour intensity was observed (cf. Ditz, A., 1901, ii, 284), and the conditions necessary for maximum intensity were ascertained. The solution for analysis must have a cobalt concentration not exceeding 0.02 mol. per litre; 100 c.c. of this solution should contain 5 g. of ammonium thiocyanate and 50 c.c. of acetone, and the standard must contain the same. The content of nickel must not exceed that of the cobalt except in very dilute solutions.

S. K. TWEEDY.

**Phyto-microchemical detection of nickel, and its occurrence in plants.** A. MARTINI (Mikrochem., 1930, 8, 41–45).—The author claims to have detected the presence of nickel microchemically in a large number of plants by means of the reaction with caesium chloride and sodium selenite, crystals of the compound  $\text{Cs}_2[\text{Ni}(\text{SeO}_3)_2]$  being formed.

H. F. HARWOOD.

**Rapid iodometric determination of chromium as chromate in presence of organic substances.** F. FEIGL, K. KLANFER, and L. WEIDENFELD (Z. anal. Chem., 1930, 80, 5–12; cf. B., 1930, 159).—The removal by boiling of the excess of hydrogen peroxide from chromate solutions which have been oxidised by hydrogen peroxide and alkali is practically impossible in the presence of certain organic substances, such as gelatin. The method of Kubelka and Wagner (B., 1926, 683), whilst yielding good results, is tedious, and a simpler and more rapid process has now been devised. After oxidation of the chromium, 5 c.c. of a 5% solution of nickel nitrate are added, the liquid is boiled for 3 min., cooled, and potassium iodide added; after acidification with hydrochloric acid the liberated iodine is titrated as usual. Quite small amounts of nickel salts (5–8 mg.) are sufficient to effect complete decomposition on boiling of large quantities of hydrogen peroxide, even in the presence of organic matter. If bromine and alkali have been employed to convert the chromium salt into chromate the excess of the oxidising agent may be easily removed by the addition of potassium thiocyanate solution, cyanate, sulphate, and bromide being formed. The cooled solution is then titrated as usual after addition of potassium iodide and acidification with 2*N*-sulphuric acid.

H. F. HARWOOD.

**Analysis of chromite and determination of chromium.** I. MAJDEL.—Sec B., 1930, 330.

**Gravimetric determination of tungsten in the presence of vanadium.** A. JÍLEK and J. LUKAS (Chem. Listy, 1930, 24, 73–83).—The solution containing tungstate and vanadate is neutralised with hydrochloric acid, 1 c.c. of which is then added together with 0.5 g. of hydroxylamine hydrochloride. The solution is now diluted to 100 c.c., and boiled until a blue coloration appears. One c.c. of hydrochloric acid is added, the solution is again diluted to 200 c.c., 10 c.c. of 2% arsenic acid are added, and the solution is brought to boiling, when 20 c.c. of 2% quinine hydrochloride solution are rapidly added with shaking. The solution is left for 10–12 hrs. with occasional agitation, when the precipitate, having the approximate composition  $(\text{C}_{29}\text{H}_{24}\text{O}_2\text{N}_2)_3\text{AsO}_4 \cdot 12\text{WO}_3$ , is collected, and washed first with 200 c.c. of a solution containing 2 c.c. of hydrochloric acid, 2 c.c. of 2% arsenic acid, and 4 c.c. of 2% quinine hydrochloride, and then with 200 c.c. of a similar solution without arsenic acid. The dry precipitate is ignited together with the filter-paper, the residue is moistened with nitric acid, and ignition is continued to constant weight, when the residue is assumed to be  $\text{WO}_3$ . This method gives good results for quantities of not more than 0.2 g. of  $\text{WO}_3$  and of  $\text{V}_2\text{O}_5$ . Where the quantity of either oxide exceeds 0.1 g. double precipitation is recommended in order to ensure absence of adsorbed

vanadium from the quinine precipitate. Vanadium in the filtrate is determined in the following way: the filtrate is evaporated to dryness, 10 c.c. of concentrated sulphuric acid are added to the residue, which is further heated at 100° in the presence of copper sulphate. The acid solution is diluted, and vanadium is reduced by boiling with sulphurous acid. Copper and arsenic are now removed by means of hydrogen sulphide, excess of which is removed by boiling. The solution is then rendered slightly alkaline, and vanadium is converted into vanadate by boiling with hydrogen peroxide, excess of which is destroyed at 100°. Vanadium is then precipitated with mercuric nitrate, and the precipitate is ignited and weighed as  $V_2O_5$ .

R. TRUSZKOWSKI.

**Separation of uranium from zirconium, tantalum, niobium, titanium, iron, manganese, lead, tin, copper, nickel, and chromium.** D. GUIMARÃES (Ann. Acad. Brasil. Sci., 1929, 1, 198—200).—The need for a complete separation of uranium from admixtures with other elements when employing the uranium content as the basis of calculation of the age of a mineral is emphasised, and a new method of separation is described. The metals are precipitated by ammonia solution, and the uranium is redissolved by addition of bromine water, dilute ammonium nitrate solution being used for washing the precipitate. After boiling off the excess of bromine, lead, tin, etc. are precipitated by hydrogen sulphide, and a slight excess of sodium carbonate solution is added to remove traces of iron, manganese, and aluminium. The filtrate is then acidified and boiled to remove carbon dioxide, and the uranium is reprecipitated with ammonia. This final precipitation may be repeated several times to remove traces of the alkali metals, and the precipitate is ultimately ignited and weighed.

H. F. GILLBE.

**Use of phenolic acids in the detection, separation, and determination of metals. IV. Colorimetric detection of titanium.** P. N. DAS-GUPTA (J. Indian Chem. Soc., 1929, 6, 855—863).—The actions of tannic, gallic, and resorcylic acids on titanium salt solutions, followed by the addition of sodium acetate, have been studied. Of these only gallic acid is suited for the determination of titanium. Using gallic acid or gallic acid and sodium acetate, an absolute amount of  $3 \times 10^{-6}$  g. of titanium can be detected by a pale yellow or pale greenish-yellow coloration in a volume not exceeding 4—5 c.c., even in the presence of other metals. In presence of vanadium, sulphurous acid must be added before the reagent, with uranium present dilute ammonium acetate or acetic acid is added after the sodium acetate, and in presence of tungsten hydrogen peroxide is added before the test, changing the colour to pale violet. Gallic acid in sulphuric acid may be used to detect titanium in presence of molybdenum. In each case other coloured ions, with the exception of nickel, cobalt, and small quantities of chromium, interfere with the test. In the presence of ferrous iron, syrupy ammonium acetate is poured into the bottom of the solution. A small yellow layer at the junction enables  $6 \times 10^{-6}$  g. of titanium to be detected. Alkali phosphates reduce the sensitivity to one half, and excess of ammonium chloride causes turbidity

on keeping. Fluoride should not be present during the test.

J. W. SMITH.

**Determination of small amounts of titanium in alloy steels.** H. MATHESIUS.—See B., 1930, 330.

**Selenious acid as a specific reagent for the determination and separation of bismuth and titanium.** R. BERG and M. TEITELBAUM (Z. anorg. Chem., 1930, 189, 101—112).—If an approximately 5% solution of selenious acid is added slowly to a 0.25—0.33*N*-bismuth nitrate solution with warming until in excess and the whole is then boiled, the bismuth is precipitated quantitatively as the selenate, and can be weighed either as the anhydrous selenate after drying at 100—105°, or as bismuth oxide after ignition, or may be determined volumetrically (A., 1928, 383). Under these conditions zinc, cadmium, copper, cobalt, nickel, manganese, aluminium, magnesium, calcium, and beryllium remain in solution, and by double precipitation a satisfactory separation from lead is also obtained. Large quantities of sulphate ions should be absent. Titanium can be quantitatively precipitated in the cold from a hydrochloric acid solution not more than 0.2*N* in respect of acid, the precipitate being converted into the dioxide by ignition and weighed as such. Titanium can be satisfactorily separated in this way from even large amounts of aluminium, and also from manganese, nickel, cobalt, magnesium, calcium, and beryllium, but uranium and chromium are strongly adsorbed and zirconium and thorium are precipitated at the same time. If zinc is present, precipitation should be carried out very slowly, and ferric iron must be reduced with hyposulphite prior to the addition of selenious acid, otherwise ferric selenate is precipitated.

R. CUTHILL.

**Apparatus for making single-crystal wire.** S. SUNAGA (J. Study Metals, Japan, 1929, 6, 117—123).—A needle dipping into the molten metal is raised with uniform speed. Requirements regarding material and velocity are recorded. A circular section is obtained by the use of a die. Single crystals of bismuth, tin, and cadmium, and of bismuth-lead and mercury-cadmium alloys have been thus prepared.

CHEMICAL ABSTRACTS.

**Modification of adiabatic micro-calorimetry.** W. SWIENTOSLAWSKI (J. Chim. phys., 1930, 27, 96—97).—An account is given of modifications in the construction of a micro-calorimeter already described (Swientoslawski and Dorabalska, A., 1927, 1163).

C. W. GIBBY.

**Isothermal determination of small positive heat effects.** A. WASSERMANN (Z. physikal. Chem., 1930, 146, 409—417).—A calorimeter is described for determining small positive heat effects by von Wartenberg's isothermal method (A., 1926, 909), using the negative heat of dilution of concentrated ammonium nitrate solution as compensator. The calibration of the calorimeter by the heat of dissolution of lithium chloride is also described. The accuracy of the method increases with the amount of heat to be measured.

M. S. BURR.

**Sodium peroxide as a fusion medium.** S. W. PARR (Ind. Eng. Chem. [Anal.], 1930, 2, 10—12).—The use of sodium peroxide in calorimetric determin-

ations is discussed, and an improved type of jacket for the fusion cup is described; lead gaskets are preferable to rubber ones in the apparatus, as the latter may give rise to explosions. It is recommended to employ potassium perchlorate of a standardised degree of fineness as an accelerator with the peroxide, and the necessary correction factors for this are indicated. The need for using a thermometer of proved accuracy in the determinations is also emphasised.

H. F. HARWOOD.

**Small gas-fired laboratory furnace.** F. H. NORTON and C. L. NORTON, jun. (J. Amer. Ceram. Soc., 1930, 13, 161—166).—The construction of a small furnace which is heated by an ordinary Meker burner is described. High temperatures can be attained rapidly and maintained steadily. The performance of the furnace is largely due to the use of a pure kaolin refractory, which is made highly porous to act as an insulator as well as a refractory. The properties of this material are given. F. SALT.

**Mounting media for microscopic work.** J. M. PRESTON (Nature, 1930, 125, 563).—A medium giving  $n=1.42$  when liquid and  $n=1.47$  and suitable for unstained cellulose materials is obtained from cellulose nitrate 25%, triacetin 25%, and methyl ethyl ketone 50%. Cellulose acetate can replace the nitrate, giving lower values for  $n$ . L. S. THEOBALD.

**Continuous automatic purification of mercury.** J. CORBIÈRE (Bull. Soc. chim., 1930, [iv], 47, 331—332).—The mercury is lifted by suction and falls through a column of dilute nitric acid. It collects in a reservoir, whence it is drawn up into an electrically-heated still-head, the current being cut off automatically if the level in the reservoir falls too low.

C. W. GIBBY.

**Self-balancing potentiometer.** F. MOORE (Rev. Sci. Instr., 1930, 1, 125—139).—The design of a self-balancing potentiometer is described in detail.

C. W. GIBBY.

**Calibration of conductivity apparatus.** I. W. WARK (J. Physical Chem., 1930, 34, 885—886).—A short method of calibrating the bridge used in conductivity apparatus is described and is compared with the standard method. L. S. THEOBALD.

**Low-pressure tensimeter.** K. C. D. HICKMAN (J. Physical Chem., 1930, 34, 627—636).—An apparatus for the determination of vapour pressures between 0.05 mm. and 1 atm. is described. Vapour pressure-temperature curves for numerous substances, especially the phthalic esters, are reproduced. The apparatus is well suited for use with gasolines or with heavy lubricating oils. L. S. THEOBALD.

**Purification, properties, and uses of certain high-boiling organic liquids.** K. C. D. HICKMAN and C. R. SANFORD (J. Physical Chem., 1930, 34, 637—653).—Apparatus and methods for the vacuum distillation of high-boiling liquids are described. Butyl phthalate and butyl benzyl phthalate can replace mercury in the Langmuir condensation pump and a laboratory type of pump utilising these liquids is described. A number of lubricants which prevent the adhesion of mercury to glass is described and an explanation of such adhesion is advanced.

L. S. THEOBALD.

**Automatic pipette filler.** H. JAMES (Chemist-Analyst, 1930, 19, No. 1, 20—21).—A rubber bulb is attached to the arm of a distillation flask which carries a cork bored to allow free insertion of the pipette up to the bulb, the liquid being contained in the bulb of the flask. CHEMICAL ABSTRACTS.

**Filtration pipette for spot indicator tests.** E. R. CALEY (Ind. Eng. Chem. [Anal.], 1930, 2, 77).—A device for the simultaneous filtration and withdrawal of a few drops of liquid from a solution containing a precipitate in suspension is described.

H. F. HARWOOD.

**Weight burette.** H. B. FRIEDMAN and V. K. LAMER (Ind. Eng. Chem. [Anal.], 1930, 2, 54).—A modified form of the Ripper weight burette, which possesses several advantages over the usual type, is described.

H. F. HARWOOD.

**Receiver for vacuum distillation.** G. A. R. KON (J.C.S., 1930, 182—183).—A compact receiver having only two taps is described and figured.

S. K. TWEEDY.

**Absolute micromanometer depending on electrostatic compensation.** P. BRICOUT (Compt. rend., 1930, 190, 733—735).—The micromanometer is based on the fact, already made use of by Knudsen (A., 1911, ii, 188), that a light metal plate placed between two parallel plates maintained at temperatures  $T_1$ ,  $T_2$  in a gas at pressure  $p$  and temperature  $T$  is subjected to a force per cm.<sup>2</sup> of  $p(T_2 - T_1)/2T$ . This force is balanced electrostatically. The instrument is fully described, and is sensitive to pressures of from  $10^{-2}$  to  $10^{-3}$  baryes.

C. A. SILBERRAD.

**Laboratory labour-saving devices.** H. WEBER (Chem. Fabr., 1930, 69—71).—Ingenious devices for cooling, for supplying liquid continuously to a relatively small evaporating vessel, for continuously supplying liquid for washing slimy and troublesome precipitates, and for automatically filling pipettes and burettes are described.

S. I. LEVY.

**Edelhauser's extraction apparatus.** ANON. (Chem.-Ztg., 1930, 54, 156).—A simpler form of the Twisselmann apparatus, by means of which the solvent after extraction is completed is distilled without loss and without dismounting the condenser into a separate receiver, is described.

S. I. LEVY.

**Concentrating dialyser.** H. S. SIMMS (J. Exp. Med., 1930, 51, 319—326).—Collodion bags are surrounded by flowing water under reduced pressure. A litre of fluid can be concentrated to a few c.c. in this way in 3—4 hrs.

E. BOYLAND.

**Laboratory fractionation column.** J. CLEMENS (Chem. Fabr., 1930, 95—96).—The apparatus consists of (1) a preliminary expansion tube packed with glass rods, (2) a vertical 6-bulb column with condenser jacket, the cooling water flowing downwards, (3) a siphon tube returning condensate to the distillation and leading the vapour to a second 6-bulb column similar to the first. The counter-current cooling is claimed to give very sharp fractionation.

C. IRWIN.

**Development and application of laboratory apparatus for the extraction of solid and liquid materials.** P. H. PRAUSNITZ (Arch. Pharm., 1930,

268, 170—184).—A review of published methods, with special reference to improvements involving the use of sintered glass filter-plates. H. E. F. NOTTON.

**Condensation pumps.** K. C. D. HICKMAN and C. R. SANFORD (Rev. Sci. Instr., 1930, 1, 140—163).—The construction of mercury condensation pumps is reviewed historically. Experiments are described dealing with the use of organic liquids of high b. p. instead of mercury, in pumps of various designs. Only higher hydrocarbons and esters of phthalic acid were found satisfactory. The phthalates, particularly butyl benzyl and di-*n*-butyl phthalate, are more satisfactory than hydrocarbons, since the latter give lower speeds and decompose on continuous usage. Phthalates tend to give phthalic anhydride on starting up, and attack metal on prolonged boiling. C. W. GIBBY.

**Automatic recording of the infra-red at high resolution.** F. S. BRACKETT and E. D. MCALISTER (Rec. Sci. Instr., 1930, 1, 181—193).—The construction of a spectrometer of the Littrow type with photographic recording is described. Stability is obtained by placing the hot junction of the thermocouple in a hollow enclosure the temperature of which is that of the cold junction. The most satisfactory thermocouples were of bismuth and bismuth-tin alloy; the method of constructing them is described. C. W. GIBBY.

**Polarising microscope in organic chemistry.** H. C. BENEDICT (Ind. Eng. Chem. [Anal.], 1930, 2, 91—93).—A selection of cases in which small quantities of materials, reaction products, etc. have been quickly identified is recorded. S. I. LEVY.

**Macro-apparatus for cataphoresis.** F. O. HOWITT and E. B. R. PRIDEAUX (J. Sci. Instr., 1930, 7, 89—94).—An apparatus for measuring the velocity of electrophoresis by direct observation of an interface made visible by a highly dispersed gold sol is described. C. W. GIBBY.

**Projection model to illustrate the passage of an  $\alpha$ -particle in the neighbourhood of an atomic nucleus.** E. N. DA C. ANDRADE (J. Sci. Instr., 1930, 7, 94—96).—A small apparatus suitable for projection is described. A glass sphere rolls on a glass plate the surface of which is so shaped that the path traversed is a parabola. C. W. GIBBY.

**Apparatus for determining the specific heat of a material in powder form.** J. H. AWBERY and E. GRIFFITHS (Proc. Physical Soc., 1930, 42, 71—74).—A calorimeter utilising electrical heating, and suitable for work on heavy powders such as dry clay, is described. A helicoidal blade stirrer carries the hot junctions of a thermocouple for measuring temperature. N. M. BLIGH.

**Apparatus for measurement of change in gas volume at constant pressure.** V. MAJER (Chem. Fabr., 1930, 85—86).—A measuring burette is connected to a levelling tube and also to a glass cylinder of water having connexions to pressure, vacuum, and to a small water reservoir. The actual pressure in the burette may be varied by altering a water seal in the cylinder. The levelling tube is provided with a mechanical arrangement for raising or lowering and the observer need watch only one scale during measurements. The apparatus is intended especially for

measuring the absorption of carbon dioxide in sugar solutions. C. IRWIN.

**Anhydrous magnesium perchlorate as a drying agent.** S. LENHER and G. B. TAYLOR (Ind. Eng. Chem. [Anal.], 1930, 2, 58).—Magnesium perchlorate trihydrate ("dehydrite") can be readily dehydrated without fusion occurring if the salt is slowly heated to 250° under a pressure of less than 0.1 mm. The resulting product is much more efficient than the original material as a desiccating agent for gases. H. F. HARWOOD.

**Barium oxide as a desiccant.** H. S. BOOTH and L. H. MCINTYRE (Ind. Eng. Chem. [Anal.], 1930, 2, 12—15).—The use of anhydrous barium oxide as a desiccating agent is advocated. Tests, using a specially constructed apparatus, showed that the amount of water vapour remaining in a gas after passage through a tube filled with this material is only 1 mg. in 10,000 litres. The porous oxide prepared by the low-temperature reduction of barium carbonate with carbon is well adapted for use as a desiccant; on account of its expansion on hydration it should be used in tubes in conjunction with glass wool, or else in the form of lumps from 7 to 10 mm. in diameter. Owing to the granular nature of the oxide somewhat larger tubes are necessary in order to effect the same drying rate than when phosphorus pentoxide is employed, but the efficiency is approximately the same. The desiccating action of barium oxide remains undiminished up to high temperatures, and its use as a general drying agent for laboratory purposes and as a substitute for calcium chloride in desiccators for analytical work is strongly recommended. H. F. HARWOOD.

**Laboratory shaker.** H. E. BENT (Ind. Eng. Chem. [Anal.], 1930, 2, 106).—A form of laboratory shaker which is practically noiseless in action and permits of a wide range of speed and amplitude is described. H. F. HARWOOD.

**Reductor apparatus for detecting tin.** J. H. REEDY (Ind. Eng. Chem. [Anal.], 1930, 2, 117—118).—The solution to be tested is treated with hydrochloric acid until the acid concentration is 0.6*N*, heated to boiling, and filtered into mercuric chloride solution through a 10 cm. column of powdered lead ("test lead") contained in a glass tube 1—2 cm. in diameter; the liquid remaining in the column is washed through with very dilute hydrochloric acid. Under these conditions 0.0002 g. of tin in 10 c.c. will give a definite turbidity due to mercurous chloride. The presence of other metals (except chromium and nickel) does not prevent the reaction, but many anions interfere and must be previously removed by evaporation of the solution with an excess of hydrochloric acid. H. F. HARWOOD.

**Apparatus for detecting oxygen in gaseous mixtures.** T. HONDA (Mazda, Japan, 1928, 3, 329—341).—The gas is passed over yellow phosphorus, the oxide smoke causing fluctuations of the current in a photo-cell circuit and thereby operating an alarm bell through a relay. CHEMICAL ABSTRACTS.

**Determination of substances which evolve chlorine.** F. L. HAHN (Ber., 1930, 63, [B], 579—582).—An apparatus for the determination of sub-

stances which evolve chlorine is figured and described. It embodies the following features: use of a small quantity of concentrated hydrochloric acid, and of carbon tetrachloride to assist in the removal of chlorine, minimum contact of the vapours with air, and prevention of regurgitation. H. WREN.

**Titration table.** J. W. STILLMAN and T. L. BARTLESON (Ind. Eng. Chem. [Anal.], 1930, 2, 108—109).—The bottles containing the volumetric solutions

are placed below the working bench, the solution being sucked up into the burette through a three-way tap. A special hollow rod clamped to the bench and connected above with the top of the burette and below with the source of vacuum serves both as a support for the burette and a means of conveying the suction. The arrangement possesses the advantage over that usually employed that if a leak develops in the system the whole of the standard solution does not thereby run to waste. H. F. HARWOOD.

## Geochemistry.

**Ionic ratios in the waters of the North Pacific Ocean.** T. G. THOMPSON and C. C. WRIGHT (J. Amer. Chem. Soc., 1930, 52, 915—921).—The most accurate determinations of calcium and magnesium in sea-water are obtained by the gravimetric calcium oxalate method and Epperson's modified magnesium ammonium phosphate method (A., 1928, 386), respectively. Three precipitations are essential in both cases. In the North Pacific Ocean, the ionic ratios are constant: Ca/Mg,  $0.3212 \pm 0.0016$ ; Ca/Cl,  $0.02150$ ; Mg/Cl,  $0.06694$ . The results are compared with analyses of other seas. J. G. A. GRIFFITHS.

**Water of the Vena d'Oro well.** R. NASINI and E. BOVALINI (Annali Chim. Appl., 1930, 20, 56—66).—This well, about 6 kilometres from Belluno and on the opposite bank of the Piave, yields water with  $p_H$  7.45 and osmotic concentration 5.48 millimols. per kg. The solid residue is 0.2375 g. (at  $110^\circ$ ) per litre, consisting mainly of calcium, sodium, and magnesium carbonates and calcium sulphate. Ammonia and nitrites are absent and the amount of dissolved gases (oxygen, carbon dioxide, nitrogen, and rare gases) is relatively high. T. H. POPE.

**Chemical changes in pools containing vegetable remains infected with sulphur bacteria.** D. ELLIS and J. H. STODDART (J. Roy. Tech. Coll. Glasgow, 1930, 2, 336—346).—An isolated pool of sea-water in which *Thioporphyrta volutans* was developing was examined over a period of 10 weeks. In agreement with other investigations, it was found that an initial increase in hydrogen sulphide content was followed by a loss as the sulphur bacteria developed, and the oxygen diminished as a result of their respiration. Variation in calcium and magnesium content had no significance, and determinations of sulphate gave inconclusive results. The value of  $p_H$  (7.2—7.6) was of the same order as that at which other sulphur bacteria grow, and its variation depended on the variation in hydrogen sulphide content and the activity of saprophytic bacteria. The five-fold increase in the number of the latter and the consequent increase in dissolved organic matter did not inhibit the growth of the sulphur bacteria.

R. K. CALLOW.

**Petrological study of sulpharsenites from the Binnental.** D. GRUSCA (Bull. Acad. Sci. Roumaine, 1929, 12, No. 7—10, 44—49).—Grains of the minerals sartorite, jordanite, rathite, baumhauerite, and hutchinsonite were embedded in plaster of Paris and subsequently polished; the results of the microscopical

examination of the polished surfaces in ordinary and polarised light are given. The identity of the minerals was established by spectrographic analysis and sp. gr. determinations. Jordanite has  $d$  6.24, baumhauerite  $d$  5.28, and sartorite  $d$  5.05. Photomicrographs accompany the paper. H. F. HARWOOD.

**Geology of the fire-clays of southern Saskatchewan.** G. M. HUTT (J. Amer. Ceram. Soc., 1930, 13, 174—181).—The clay deposits described extend S.E. to S.W. of Moose Jaw to the Alberta and U.S. boundaries. They belong to the Whitemud formation of late Cretaceous age. They occur largely in outcrops, but vary considerably in character. The clays in the eastern portion are more refractory than those in the west, having fusion points up to cone 33.

F. SALT.

**Kaolin minerals.** C. S. ROSS and P. F. KERR (J. Amer. Ceram. Soc., 1930, 13, 151—160).—Chemical, optical, X-ray, and thermal methods were used in a study of the clay minerals. Kaolin consists of at least three distinct minerals, with definite optical, X-ray, and thermal properties: kaolinite, which predominates in most kaolin and china-clay deposits; dickite, the suggested name for the mineral first described by A. B. Dick from Anglesey; and nacrite, which is rare. The optical and other properties of the three minerals are compared and contrasted. Each shows a distinct dehydration curve, breaking down by loss of water at different temperatures. Dickite, nacrite, and most samples of kaolinite conform to the formula  $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ ; kaolinite, however, sometimes varies from it, and may belong to an isomorphous series. F. SALT.

**Formation of Japanese gold.** C. IWASAKI (Tech. Rep. Tôhoku, 1930, 9, 149—174).—An examination of minerals from Japanese gold mines is reported. The history of the formation of the various deposits is discussed in light of the results obtained.

S. K. TWEEDY.

**Triassic bentonite of the painted desert.** V. T. ALLEN (Amer. J. Sci., 1930, [v], 19, 283—288).—An analysis of a bentonite from the Blue Forest, Arizona, is given. The dominant clay mineral is montmorillonite. The bentonite was probably formed from volcanic ash which fell into water. C. W. GIBBY.

**Scawtite, a new mineral from Scawt Hill, Co. Antrim.** C. E. TILLEY [with M. H. HEY] (Min. Mag., 1930, 22, 222—224).—Scawtite was found as minute plates in vesicles in a hybrid rock formed by the

assimilation of chalk in a dolerite intrusion. It is monoclinic with perfect cleavage (001) and a second cleavage (010); optically positive  $2V$   $74^\circ$ ,  $\alpha$  1.597,  $\beta$  1.606,  $\gamma$  1.621;  $d$  2.77,  $H$   $4\frac{1}{2}$ —5. The mineral is readily decomposed by dilute hydrochloric acid. Analysis gave  $\text{CaO}$  46.4,  $\text{SiO}_2$  34.2,  $\text{CO}_2$  18.0, total 98.6. The formula is  $6\text{CaO}\cdot 4\text{SiO}_2\cdot 3\text{CO}_2$  or perhaps  $4\text{CaO}\cdot 3\text{SiO}_2\cdot 2\text{CO}_2$ . The allied mineral spurrite ( $2\text{Ca}_2\text{SiO}_4\cdot \text{CaCO}_3$ ) has different physical and optical properties.

L. J. SPENCER.

**New occurrence of zunyite near Postmasburg, South Africa.** L. T. NEL [with L. J. SPENCER] (Min. Mag., 1930, 22, 207—220).—Zunyite, previously known only from Colorado, has been found in some abundance as small (1—2 mm.) tetrahedra embedded in altered highly aluminous shales of the Waterberg System (pre-Cambrian). Analyses are given of the shales, which contain also diasporite, kaolin, and leverrierite. Analyses I—III of the zunyite by J. McCRAE and H. G. WEALL agree with the formula  $\text{Al}_8(\text{OH}, \text{F}, \text{Cl})_{12}(\text{SiO}_4)_3$ .

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$
I	29.1	54.25	0.5	trace	trace	trace
II	24.25	56.75	1.3	0.4	0.35	1.65
III	24.1	56.85	1.45	0.3	0.2	1.45
	Cl.	F.	$\text{P}_2\text{O}_5$	$\text{H}_2\text{O}+$	$\text{H}_2\text{O}-$	Total.
I	2.45	0.8	0.15	13.45	0.9	101.60
II	3.5	0.5	0.25	11.4	0.4	100.75
III	4.8	0.4	0.25	11.65	0.35	101.80

Also traces of  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ .

The crystals are sometimes twinned about a triad axis with interpenetration;  $d$  2.884, 2.873,  $H$   $7\frac{1}{4}$ ,  $n_x$  1.5996.

L. J. SPENCER.

**Pericline and acline-A twins in the acid plagioclases.** F. C. PHILLIPS (Min. Mag., 1930, 22, 225—230).—Some discrepancies in the statement of these twinned crystals are pointed out. A curve shows the relation in the isomorphous series between the chemical composition and the angle of the trace of the composition-plane on (010).

L. J. SPENCER.

**Potassium nitrate in Central Australia.** D. MAWSON (Min. Mag., 1930, 22, 231—237).—Potassium nitrate was found in small caverns near Goyder's Pass in the McDonnell Ranges. It impregnates the rock and forms an efflorescence on the surface, and has no doubt been derived from bat guano. A picked sample of the white salt gave 99% of potassium and sodium nitrates, of which 95% is the potassium salt. Some other occurrences of mineral nitrates in Australia are noted.

L. J. SPENCER.

**Chromite.** L. W. FISHER (Amer. Min., 1929, 14, 341—357).—Chromite, as pure  $\text{FeO}\cdot \text{Cr}_2\text{O}_3$ , occurs only in meteorites; there is wide variation in the amounts of oxides entering into the composition of both acid and base of terrestrial chromite. Mineralogically, chromite is not a definite mineral. The chemical composition is indicated approximately by the colour in thin section.

CHEMICAL ABSTRACTS.

**Probertite.** A. S. EAKLE (Amer. Min., 1929, 14, 427—430).—Probertite, from Kramer district, Kern Co., California,  $d$  1.91,  $H$  3—4, monoclinic,  $n_a$  1.515,  $n_\beta$  1.520,  $n_\gamma$  1.538, contained  $\text{Na}_2\text{O}$  14.03,  $\text{CaO}$  12.76,

$\text{B}_2\text{O}_3$  47.80,  $\text{H}_2\text{O}$  24.83%, corresponding with the formula  $\text{Na}_2\text{CaB}_6\text{O}_{11}\cdot 6\text{H}_2\text{O}$ .

CHEMICAL ABSTRACTS.

**Copper pitch ore.** F. N. GUILD (Amer. Min., 1929, 14, 313—318).—The composition is variable; the principal constituents are: silica, ferric oxide, cupric oxide, manganous oxide, water, and carbon dioxide. The material may be classified in five groups according to its composition.

CHEMICAL ABSTRACTS.

**Gillespite.** W. T. SCHALLER (Amer. Min., 1929, 14, 319—322).—Gillespite,  $\text{Fe}^{II}\text{BaSi}_4\text{O}_{12}$ , tetragonal, affords on treatment with hydrochloric acid silica scales, of the same shape as the original material, and containing  $\text{SiO}_2$  83.7,  $\text{H}_2\text{O}$  15.9%. The composition and properties of associated celsian and hedenbergite are recorded.

CHEMICAL ABSTRACTS.

**Adularia.** K. SETO (J. Petr. Min. Ore Deposits, Japan, 1929, 1, 278—280).—A specimen from Takatama mine, Fukushima, contained  $\text{SiO}_2$  65.02,  $\text{Al}_2\text{O}_3$  17.95,  $\text{MgO}$  0.01,  $\text{CaO}$  0.61,  $\text{Na}_2\text{O}$  0.052,  $\text{K}_2\text{O}$  16.34%.

CHEMICAL ABSTRACTS.

**Kaolinite.** K. SETO (J. Petr. Min. Ore Deposits, Japan, 1929, 1, 179—181).—Analyses of kaolinite from Korea and Japan are recorded.

CHEMICAL ABSTRACTS.

**Chrysotile asbestos deposits of Shabani, S. Rhodesia.** F. E. KEEF (Third Empire Min. Congr., April, 1930, 43 pp.).—Descriptions of the geology of these deposits and of the mines are given, together with a note on the methods of working.

C. W. GIBBY.

**Torbanites of S. Africa.** C. H. C. CRAIG (Third Empire Min. Congr., April, 1930, 8 pp.).—A description of the geology of torbanites in the Transvaal, with a note on the methods of retorting.

C. W. GIBBY.

**Unique occurrence of lechatelierite, or silica glass.** A. F. ROGERS (Amer. J. Sci., 1930, [v], 19, 195—202).—A description of lechatelierite found at Meteor Crater, Winslow, Arizona, is given. It has probably been formed by fusion of Coconino sandstone.

C. W. GIBBY.

**Process of degradation of the rocks of Alto Rio Branco.** D. GUIMARÃES (Ann. Acad. Brasil. Sci., 1929, 1, 191—195).—The mechanism of the breakdown of basaltic minerals is discussed, the influence of the hydroxyl ion being especially emphasised.

H. F. GILLBE.

**Phycological examination of fossil red salt from three localities in the southern States.** J. E. TILDEN (Amer. J. Sci., 1930, [v], 19, 297—304).—The red colour of a fossil red salt found in well borings in Texas, Kansas, and Oklahoma is due to the presence of iron associated with organic remains.

C. W. GIBBY.

**Lignin theory [of the origin of coal].** H. BODE (Brennstoff-Chem., 1930, 11, 81—86).—Examination from the chemical point of view of theories of the origin of coal leads to no definite conclusion, whereas a number of biological and geological considerations controvert the lignin theory due to Fischer and Schrader (cf. B., 1924, 584; 1926, 393). The principal



facts not in accord with the theory are (a) the bactericidal action of the humic acids, which would inhibit the decomposition of the cellulose, and (b) the survival in the coal of plant structures which must originally have consisted principally of cellulose. It is concluded that both the lignin and the cellulose of the original plants have contributed to the formation of coal.

A. B. MANNING.

**Lignin theory of the origin of coal from the biological point of view.** R. LIESKE (Brennstoff-Chem., 1930, 11, 86—90; cf. preceding abstract).—Polemical; a reply to Bode. Recent experimental work has shown that bacterial activity is possible in the presence of humic acids. The mechanism whereby plant structures are preserved in coal is discussed.

A. B. MANNING.

**Origin and nature of bituminous coals.** G. L. STADNIKOV (Proc. II Int. Conf. Bit. Coal, 1928, 1, 608—624).—A discussion. The difficulties of Engler's theory of the production of cyclic hydrocarbons from fatty acids are examined. The characteristics of bog-

head coals, tars, and by-products, and their chemical treatment are tabulated. CHEMICAL ABSTRACTS.

**Age of iron meteorites.** F. PANETH, W. D. URRY, and W. KOECK (Nature, 1930, 125, 490—491).—An improved method enables the helium and radium contents to be determined on the same sample of meteorite. The calculated ages of 27 iron meteorites based on these determinations are tabulated. The results agree with the view that the iron meteorites originated in the solar system. Previous determinations of age by the helium method are too low when the meteorite has been heated and not brought into solution, as only a small percentage of the total helium is then evolved. L. S. THEOBALD.

**Presence of germanium in meteorite from Cranbourne.** V. M. GOLDSCHMIDT (Z. physikal. Chem., 1930, 146, 404—405).—A meteorite from Cranbourne was found by chemical and X-ray spectral analysis to contain at least 0.1% of germanium. J. A. V. BUTLER.

## Organic Chemistry.

**Primary and associated results of replacement of hydrogen directly attached to 4-co-ordinated carbon.** W. COCKER, A. LAPWORTH, and A. WALTON (J.C.S., 1930, 440—455).—The conjunction of Lewis' electronic displacement theory with the idea of incipient ionisation in the systems  $X\text{-CHR}^n$ , where  $X$  is a  $m$ -directing substituent, e.g.,  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{COR}$ , etc., has shown that these substituents have a restraining effect on the electrons of 4-co-ordinated (saturated) carbon, facilitating the removal of a hydrogen atom as proton by suitable acceptors. Conversely, the more powerful  $op$ -directing substituents in similar systems have the opposite effect, so that if the 4-co-ordinated carbon atom is associated with an atom or a group which alone, or in conjunction with a suitable acceptor, can act as an anion a state of incipient ionisation ensues in an opposite sense. In the series,  $\ominus\text{O}$ ,  $\text{NAlk}_2$ ,  $\text{OH}$ , and  $\text{OMe}$  the effect decreases in the order given, which is also the descending order of  $op$ -substitution. Thus the substitution of a hydrogen atom in methyl chloride by the methoxyl group tends to ionisation of the chlorine atom; the product, chlorodimethyl ether, is decomposed by water, reacts readily with alcohols to yield  $\alpha$ -alkoxyethers, and instantaneously with tertiary amines to form quaternary salts. In the presence of excess of the base these quaternary salts are able to react with alcohols to form the  $\alpha$ -alkoxy-ether:  $\text{OMe}\cdot\text{CH}_2\text{Cl} + \text{NR}_3 \rightarrow \text{OMe}\cdot\text{CH}_2\cdot\overset{+}{\text{N}}\text{R}_3\overset{-}{\text{Cl}}$  (i);  $\text{NR}_3 +$

$\text{OMe}\cdot\text{CH}_2\cdot\overset{+}{\text{N}}\text{R}_3\overset{-}{\text{Cl}} + \text{R}'\text{OH} \rightarrow \text{NR}_3 + \text{NR}_3\overset{+}{\text{H}}\overset{-}{\text{Cl}} + \text{OR}'\cdot\text{CH}_2\cdot\text{OMe}$  (ii). This reaction proceeds best when the necessary reagents are slowly mixed, but at best is inferior to Einhorn's method for the acylation of alcohols (A., 1898, i, 577) which seems to be identical in principle. Further, in contrast with the general stability of  $C$ -cyano-compounds (even in the cyano-hydrins which are quite stable in presence of acids and

only partly resolved into their components in alkaline solution; J.C.S., 1901, 79, 1268; 1906, 89, 948), the  $\alpha$ -aminonitriles (e.g.,  $\alpha$ -diethylaminopropionitrile; Klages, A., 1902, i, 354) are decomposed by water at the ordinary temperature. The nitrile may be synthesised by reversing this decomposition, i.e., by mixing diethylamine, acetaldehyde, and hydrogen cyanide, or in smaller yield by extracting a mixture of equimolecular proportions of diethylamine and acetaldehyde, dissolved in concentrated aqueous potassium cyanide, with much ether. Neither methoxyacetone nitrile nor methoxypropionitrile, on the other hand, yields detectable traces of hydrogen cyanide or metallic cyanide when heated alone, with aqueous or anhydrous alkalis, with potassium in boiling toluene, or with silver nitrate and dilute nitric acid.

Methoxymethylpyridinium chloride with benzyl alcohol yields *methoxymethyl benzyl ether*, b. p. 208—211°. By warming the requisite alcohol with a mixture of chlorodimethyl ether and pyridine for several hours were obtained: *methoxymethyl cyclohexyl ether*, b. p. 190—210° (in poor yield with a substance, b. p. 255—274°), *methoxymethyl sec.-octyl ether*, b. p. 188—190°, and a crude ether from technical amyl alcohol. Phenol did not react. H. A. PIGGOTT.

**Highly-polymerised compounds. XXXVI. Viscosity of solutions of paraffin.** H. STAUDINGER and R. NODZU (Ber., 1930, 63, [B], 721—724).—A sample of paraffin, m. p. 58—64°, is separated by distillation in a high vacuum into fractions of m. p. 48—50°, 54—62°, 63—71°, and 73—78°, the average mol. wts. of which in boiling benzene are 336, 435, 521, and 744. Determinations of the viscosities of their solutions in carbon tetrachloride and of dotriacontane and pentatriacontane under similar conditions shows that the expression  $\eta_{sp}/cM$  is constant. It is therefore established that the mol. wt. of a dis-

solved molecular colloid can be determined from measurements of viscosity in the case of thread molecules of strictly homopolar character.

H. WREN.

**Action of chlorine on ethylene.** H. BAHR and H. ZIELER (Z. angew. Chem., 1930, 43, 233—236).—In the absence of catalysts, ethylene chloride is formed from ethylene and chlorine in 90% yield at  $-20^{\circ}$  to  $-30^{\circ}$ , but the yield decreases as the temperature rises. Trichloroethane is formed to an increasing extent as the temperature rises, and at the ordinary temperature is the main product. The amount of tetrachloroethane is always small, but increases with rise of temperature. The higher chlorination products are not formed by subsequent action of chlorine on ethylene dichloride, but by direct action of chlorine on ethylene. The course of the change depends on the temperature and not on the relative proportions of the reactants.

J. A. V. BUTLER.

**Polymerisation. XII. Polymetric forms of isobutylene.** S. V. LEBEDEV and G. G. KOBLIANSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 2175—2187).—See this vol., 316.

**Properties of conjugated compounds. VIII. Addition of bromine to  $\alpha\delta$ -,  $\alpha\gamma$ -, and  $\beta\gamma$ -dimethylbutadienes.** E. H. FARMER, C. D. LAWRENCE, and W. D. SCOTT (J.C.S., 1930, 510—521).—Dibromides of the hydrocarbons are prepared and their constitutions studied by oxidation with permanganate and ozone. Physical data are used as evidences of isomerisation.  $\Delta^{85}$ -Hexadiene ( $\alpha\delta$ -dimethylbutadiene) yields on dibromination  $\beta\epsilon$ -dibromo- $\Delta^7$ -hexene, b. p.  $85^{\circ}/11$  mm.,  $d_4^{20}$  1.622,  $n_D^{20}$  1.534 (Duden and Lemme, A., 1902, i, 337), unmixed with other products. It shows no tendency to isomerisation. Oxidation with permanganate yields  $\beta\epsilon$ -dibromohexane- $\gamma\delta$ -diol, m. p.  $95^{\circ}$  (prepared but not characterised by Duden and Lemme), and a syrupy product, possibly a stereoisomeride. Further oxidation gives  $\alpha$ -bromopropionic, lactic, and pyruvic acids. No evidence of the presence of an  $\alpha\beta$ -dibromide was obtained.  $\delta$ -Methyl- $\Delta^{85}$ -penta-diene on bromination gives  $\beta\epsilon$ -dibromo- $\delta$ -methyl- $\Delta^8$ -pentene, b. p.  $101$ — $103^{\circ}/22$  mm. (decomp.),  $d_4^{20}$  1.624 (undistilled). This decomposes partly to a monobromo-compound, b. p.  $60$ — $62^{\circ}/22$  mm., when distilled, and on ozonisation yields bromoacetone and  $\alpha$ -bromopropaldehyde, but no fission products of an  $\alpha\beta$ - or a  $\gamma\delta$ -dibromide. Neutral permanganate oxidises it to  $\beta\epsilon$ -dibromo- $\delta$ -methylpentane- $\gamma\delta$ -diol, m. p.  $94$ — $95^{\circ}$ .  $\beta\gamma$ -Dimethylbutadiene yields mainly  $\alpha\beta$ -dibromo- $\beta\gamma$ -dimethyl- $\Delta^8$ -butene, m. p.  $47^{\circ}$  (cf. Kondakov, A., 1901, i, 62; Macallum and Whitby, *ibid.*, 1928, 614), but in addition a little liquid product which could not be purified completely, and when heated to  $100^{\circ}$  is partly converted into the solid dibromide. This change is reversible, the solid dibromide passing partly into the liquid on heating. Oxidation of the liquid dibromide with permanganate yields  $\alpha\delta$ -dibromo- $\beta\gamma$ -dihydroxy- $\beta\gamma$ -dimethylbutane, b. p.  $148^{\circ}/16$  mm., m. p.  $93^{\circ}$ , and further oxidation gives bromoacetone and unidentified products.

H. A. PIGGOTT.

**Compounds of phosphorus pentachloride and pentabromide with carbon tetrachloride.** S.

KRAKOWIECKI (Rocz. Chem., 1930, 10, 197—198).—Saturated solutions of phosphorus pentachloride in boiling carbon tetrachloride deposit on cooling crystals of a double compound,  $2\text{PCl}_5 \cdot \text{CCl}_4$ ; the corresponding product with the pentabromide is  $\text{PBr}_5 \cdot 2\text{CCl}_4$ .

R. TRUSZKOWSKI.

**Propylene bromo-chlorides.** A. DEWAELE (Bull. Soc. chim. Belg., 1930, 39, 87—90).— $\alpha$ -Chloropropan- $\beta$ -ol, b. p.  $126$ — $128^{\circ}$ , is converted by red phosphorus and bromine and treatment of the product with phosphoric oxide to remove unchanged chlorohydrin into  $\alpha$ -chloro- $\beta$ -bromopropane, b. p.  $117.5$ — $118^{\circ}/756$  mm.,  $d_4^{20}$  1.537,  $n_D^{20}$  1.47447. Similarly,  $\beta$ -chloropropan- $\alpha$ -ol affords  $\beta$ -chloro- $\alpha$ -bromopropane, b. p.  $117.5$ — $117.8^{\circ}/756$  mm.,  $d_4^{20}$  1.531,  $n_D^{20}$  1.47449, together with a high-boiling product, probably the chlorohydrin phosphite, which decomposes on distillation at about  $210^{\circ}$ , giving  $\beta$ -chloropropylene.  $\beta$ -Chloro- $\alpha$ -bromopropane is not formed by heating the chlorohydrin with fuming hydrobromic acid at  $100^{\circ}$  under pressure; the main product being  $\alpha$ -bromo- $\Delta^2$ -propene (cf. Baudrenghien, A., 1929, 801).

In addition to  $\gamma$ -chlorobutyronitrile, the action of alcoholic potassium cyanide on trimethylene bromochloride furnishes glutarodinitrile,  $\alpha$ -chloro- $\beta$ -bromopropane, and trimethylene dichloride. The production of the last-named compound is due to the isomerisation  $2\text{CH}_2\text{Cl} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br} \rightarrow \text{CH}_2(\text{CH}_2\text{Cl})_2 + \text{CH}_2(\text{CH}_2\text{Br})_2$ , which can be realised by heating under reflux trimethylene bromochloride with an equal weight of alcohol. Refluxed alone, trimethylene bromochloride is unchanged.

C. W. SHOPPEE.

**$\alpha$ -Bromo- $\alpha$ -nitrohydrocarbons. I.  $\alpha$ -Bromo- $\alpha$ -nitro- $\Delta^2$ -butene and -pentene.** J. LOEVENICH, J. KOCH, and U. PUCKNAT (Ber., 1930, 63, [B], 636—646).—Olefines in which strongly negative groups are attached to the  $\alpha$ -carbon atom have little tendency to add negative atoms or groups, whereas union with positive atoms or groups is facilitated.

$\alpha$ -Nitrobutan- $\beta$ -ol, prepared from nitromethane and propaldehyde, is converted by the action of bromine on its sodium salt in ether into  $\alpha$ -bromo- $\alpha$ -nitrobutan- $\beta$ -ol, b. p.  $111$ — $112^{\circ}/12$  mm., which, with acetyl chloride in chloroform, affords the corresponding acetate, b. p.  $118^{\circ}/12$  mm., transformed by anhydrous sodium carbonate into  $\alpha$ -bromo- $\alpha$ -nitro- $\Delta^2$ -butene, b. p.  $74$ — $75^{\circ}/12$  mm. Cold methyl alcohol in presence of methyl-alcoholic potassium hydroxide converts the last-named compound into  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -methoxybutane, b. p.  $88$ — $89^{\circ}/12$  mm., whereas with boiling sodium methoxide the unstable  $\alpha$ -dinitro- $\beta$ -methoxybutane is produced, analysed as the sodium salt,  $\text{C}_5\text{H}_9\text{O}_5\text{N}_2\text{Na}$ .  $\alpha$ -Bromo- $\alpha$ -nitro- $\beta$ -ethoxybutane has b. p.  $98^{\circ}/12$  mm. Treatment of  $\alpha$ -bromo- $\alpha$ -nitro- $\Delta^2$ -butene with ammonia in well-cooled ether gives  $\alpha$ -bromo- $\beta$ -nitro- $\alpha$ -aminobutane (potassium salt; hydrochloride), which decomposes with separation of ammonium bromide when preserved.  $\alpha$ -Bromo- $\alpha$ -nitro- $\alpha$ -piperidinobutane could not be isolated as the free base, but yields a hydrochloride, m. p.  $131^{\circ}$ , and hydrobromide, m. p.  $121^{\circ}$ .  $\alpha$ -Bromo- $\alpha$ -nitro- $\beta$ -anilino-butane is even more unstable and is isolated as the hydrochloride, which rapidly becomes oily. Treatment of  $\alpha$ -bromo- $\alpha$ -nitro- $\Delta^2$ -butene with methylamine

in alcohol gives methylamine hydrobromide and  $\alpha$ -nitro- $\Delta^2$ -butinene, a mobile liquid which cannot be distilled without explosion and speedily undergoes polymerisation.

$\alpha$ -Bromo- $\alpha$ -nitropentane- $\beta$ -ol, b. p. 119—120°/13 mm., is converted through the acetate, b. p. 125—126°/13 mm., into  $\alpha$ -bromo- $\alpha$ -nitro- $\Delta^2$ -pentene, b. p. 97—98°/14 mm. The following additive compounds are described:  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -methoxypentane, b. p. 102—103°/12 mm.; the sodium salt of  $\alpha$ -dinitro- $\beta$ -methoxypentane;  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -ethoxypentane, b. p. 115°/14 mm.;  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -aminopentane, m. p. 74° (hydrochloride, m. p. 138°);  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -piperidinopentane hydrochloride and hydrobromide, m. p. 120°;  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -anilinopentane hydrochloride.  $\alpha$ -Nitro- $\Delta^2$ -pentinene is obtained from  $\alpha$ -bromo- $\alpha$ -nitro- $\Delta^2$ -pentene and diethylamine.

H. WREN.

**Behaviour of alkoxide solutions towards nitric oxide.** II. H. WIELAND and F. N. KERR (Ber., 1930, 63, [B], 570—579; cf. A., 1929, 46).—Sodium is dissolved in an excess of the alcohol and the solution is shaken with nitric oxide. Frequently it is advantageous to prepare the alkoxide in benzene suspension; under these conditions, hyponitrite, as reduction product of nitric oxide, remains in solution, whereas from the alcoholic solution nitrous oxide is almost quantitatively evolved. Methyl alcohol, in contrast to all other monohydric alcohols, does not react with nitric oxide. The gas reacts with sodium ethoxide, but not with ethyl alcohol, since absorption of nitric oxide diminishes in proportion as water is added to the absolute ethyl-alcoholic solution and ceases when 2 mols. are present. Primary alcohols with branched chains react more readily than normal alcohols and the neighbourhood of unsaturated groups accelerates the change. Secondary alcohols usually react more readily than the primary compounds. *n*-Propyl, *n*-butyl, isobutyl, isoamyl, *n*-hexyl, and benzyl alcohols yield primarily the aldehydes  $R\cdot CH_2\cdot ONa + 2NO \rightarrow R\cdot CHO + N_2O + NaOH$ . This is followed rapidly by the Traube change, in all cases in which hydrogen is attached to carbon vicinal to the carbonyl group. The final products are formate and the sodium salt of the diisonitroamine containing one fewer carbon atom than the alcohol. The compounds  $CHMeO_2N_2Pb$  and  $CHEt(O_2N_2Ag)_2$  are described. *iso*Propyl alcohol and phenylmethylcarbinol are transformed through acetone or acetophenone into acetate or benzoate and the sodium salt of methylene-diisonitroamine. Analogously, cyclohexanol gives cyclohexanone and thence the trisodium salt of  $\epsilon$ -diisonitroamino-*n*-hexoic acid (corresponding silver salt, decomp. 127—128°). Benzhydrol affords benzophenone and sodium hyponitrite, giving an excellent method for the preparation of the latter compound. Borneol and menthol react rapidly. The presence of a second oxygen atom in the molecule appears to inhibit the reaction, since ethylene glycol, hydrobenzoin, glycerol, trimethylene glycol,  $\beta$ -methoxy- and  $\beta$ -phenoxy-ethyl alcohols do not react.

Cinnamyl alcohol in presence of methyl alcohol yields formate and the sodium salt of  $\alpha$ -methoxy- $\alpha$ -phenylethylidenediisonitroamine, decomp. 225—226°

q q

(corresponding silver salt; dimethyl ester, m. p. 134°). Cinnamaldehyde affords the same products, whereas phenyl styryl ketone yields the sodium salt and benzoate. In presence of ethyl alcohol, cinnamyl alcohol gives the sodium salt of  $\alpha$ -ethoxy- $\alpha$ -phenylethylidenediisonitroamine, decomp. 252—255° (corresponding dimethyl ester, m. p. 89—90°), also derived from cinnamaldehyde and phenyl styryl ketone. Cinnamic acid and styrene do not react. Allyl alcohol appears to afford the sodium salt  $OMe\cdot CH_2\cdot CH(N_2O_2Na)_2$ .

H. WREN.

**Syntheses by means of magnesium alkyl halides.** W. C. DAVIES, R. S. DIXON, and W. J. JONES (J.C.S., 1930, 468—473).—In general, the interaction of magnesium *n*-amyl and *dl*- $\beta$ -methylbutyl bromides with aldehydes and ketones leads to the corresponding carbinol, with *n*-decane or *dl*- $\gamma$ -dimethyloctane, respectively. In some cases the carbinols lose water during the reaction and yield unsaturated hydrocarbons; but, even if capable of isolation, the carbinols are readily dehydrated. From *n*-amyl bromide and the requisite aldehyde or ketone may be prepared: phenyl-*n*-amylcarbinol, b. p. 170°/50 mm.,  $d_4^{25}$  0.9477,  $n_D^{25}$  1.5042, oxidised to phenyl *n*-amyl ketone (Schroeter, A., 1907, i, 530); *p*-anisyl-*n*-amylcarbinol, b. p. 207—210°/50 mm. (much anisaldehyde is recovered unchanged), partly dehydrated by redistillation at low pressures (cf. Stedman and Stedman, A., 1929, 692), yielding a distillate, which, saturated with hydrogen chloride and then boiled with excess of pyridine and finally treated with water, gives  $\alpha$ -*p*-anisyl- $\Delta^2$ -hexene, b. p. 187—188°/50 mm.,  $d_4^{25}$  0.9594,  $n_D^{25}$  1.5356. Methyl-*n*-amylcarbinol, b. p. 97.5°/50 mm.,  $d_4^{25}$  0.8108,  $n_D^{25}$  1.4527; methyl-*n*-amyl-*n*-nonylcarbinol, b. p. 199—200°/50 mm.,  $d_4^{25}$  0.8316,  $n_D^{25}$  1.4446, and phenylmethyl-*n*-amylcarbinol (unsaturated hydrocarbon simultaneously formed), b. p. 169°/50 mm.,  $d_4^{25}$  0.9389,  $n_D^{25}$  1.5028, are described.

From *dl*- $\beta$ -methylbutyl bromide are derived: methyl  $\beta$ -methylbutyl ketone, b. p. 68°/50 mm.,  $d_4^{25}$  0.8085,  $n_D^{25}$  1.4050 (semicarbazone, m. p. 120—121°) [by oxidation of carbinol from acetaldehyde]; phenyl- $\beta$ -methylbutylcarbinol, b. p. 163°/50 mm.,  $d_4^{25}$  0.9523,  $n_D^{25}$  1.5059, which on dehydration, but not on distillation, yields hexenylbenzene, but this hydrocarbon is not produced during the reaction (cf. Klages and Sautter, A., 1904, i, 302); phenyl  $\beta$ -methylbutyl ketone, b. p. 163°/50 mm.,  $d_4^{25}$  0.9610,  $n_D^{25}$  1.5093 (semicarbazone, m. p. 160°). An attempt to prepare *p*-anisyl  $\beta$ -methylbutyl ketone failed. Methyl-( $\beta$ -methylbutyl)-*n*-nonylcarbinol, not satisfactorily purified, has b. p. 198—200°/50 mm.,  $d_4^{25}$  0.8301,  $n_D^{25}$  1.4438,  $[R_L]_D$  77.50. A substance, b. p. 255—265°/50 mm.,  $d_4^{25}$  0.8433,  $n_D^{25}$  1.4582,  $[R_L]_D$  103.5, simultaneously produced seems to be  $CMe(C_5H_{11})(C_9H_{19})\cdot O\cdot C_5H_{11}$ . Methyl-ethyl-( $\beta$ -methylbutyl)carbinol has b. p. 95—97°/50 mm.,  $d_4^{25}$  0.8177,  $n_D^{25}$  1.4521. Phenylmethyl-( $\beta$ -methylbutyl)carbinol, b. p. 163.5°/50 mm.,  $d_4^{25}$  0.9388,  $n_D^{25}$  1.5027, on dehydration yields  $\beta$ -phenyl- $\delta$ -methyl- $\Delta^2$ -hexene, b. p. 142°/50 mm.,  $d_4^{25}$  0.8839,  $n_D^{25}$  1.5117.

H. A. PIGGOTT.

**Refractive power of certain acetylenic and saturated  $\alpha$ -glycols in solution.** V. KRESTINSKI and N. PERSIANSHEVA (J. Russ. Phys. Chem. Soc., 1929, 61, 2073—2088).—See this vol., 319.

**Dehydration of two stereoisomeric  $\gamma$ -ethylenic glycols in presence of hydrogen ions in water. Determination of their spatial configuration.** BOURGUEL and R. RAMBAUD (Bull. Soc. chim., 1930, [iv], 47, 173—194).—*cis*- $\beta$ - $\epsilon$ -Dimethyl- $\Delta^{\gamma}$ -hexene- $\beta$ -diol, m. p. 70.5—70.7°, in dilute aqueous hydrochloric, sulphuric, phosphoric, acetic, and tartaric acids at 15° yields the  $\gamma$ -oxide, m. p. 102°,  $d^{20}_4$  0.812,  $n^{20}_D$  1.409, the dehydration being catalysed by the hydrogen ions. The reaction is unimolecular and complete, the oxide being the only product. In 0.1N-hydrochloric acid at 38° the velocity coefficient is 0.00187, and at 50°, 0.01085, the temperature coefficient thus being high. Comparison with measurements in 0.1N-sulphuric and 0.102N-tartaric acid indicates that the velocity of catalysis is only approximately proportional to the hydrogen-ion concentration, increasing more rapidly than the latter. In weakly acid medium,  $p_H$  6.3, at 89°, the velocity is constant, the acidity being unaffected by addition of the ditertiary glycol. In 0.285N-hydrochloric acid at 30° and at 38°, the velocity coefficient decreases slightly but regularly as the concentration of the glycol increases, a result which may be due to the presence of undissociated oxonium salt.

Dehydration of the  $\alpha$ -isomeride, m. p. 74—76.5°, is not complete in the presence of hydrogen ions. A kinetic study of the reaction indicates that the material is a compound or solid solution of 4 parts of the *cis*-glycol with 1 part of the *trans*-isomeride, m. p. 101°. The latter is obtained from the  $\alpha$ -isomeride by fractional crystallisation from water. In presence of hydrogen ions it is slowly dehydrated, yielding not a  $\gamma$ -oxide, but a triolefine, probably  $\beta$ - $\epsilon$ -dimethyl- $\Delta^{\gamma\gamma\epsilon}$ -hexatriene, b. p. 124—126°,  $d^{20}_4$  0.778,  $n^{20}_D$  1.483, and a fraction, b. p. 145—160°, which probably contains  $\beta$ - $\epsilon$ -dimethyl- $\Delta^{\gamma\gamma}$ -hexadien- $\epsilon$ -ol (cf. Salkind, A., 1923, i, 176).  
R. BRIGHTMAN.

**Action of hydrogen bromide and bromine on glycols of the ethylene series.** J. S. SALKIND and S. A. SABOJEV (J. Russ. Phys. Chem. Soc., 1929, 61, 2139—2150).—See A., 1929, 1267.

**Action of phosphorus halides and halogen acids on the acetylenic  $\gamma$ -glycols. II.** V. N. KRESTINSKI and L. J. BASHENOVA-KOSLOVSKAIA (J. Russ. Phys. Chem. Soc., 1929, 61, 1691—1711; cf. A., 1926, 1121).—The complex mixture obtained by the action of phosphorus tribromide on tetramethylbutinenediol (*loc. cit.*) was examined, and the properties of the various products were investigated. The mixture, on fractionation and freezing out, was found to contain two solid and one liquid isomeric dibromides,  $C_8H_{12}Br_2$ . The solids had m. p. 46—48° and 39°. The first of these when heated at 100° in a sealed tube darkened, and deposited on cooling crystals of the second. On treatment with potassium carbonate, it yielded the original glycol, and on oxidation, acetic, hydroxyisobutyric, and possibly traces of oxalic acid. The second dibromide is obtained almost exclusively by the action of hydrobromic acid on the original glycol, and is the more stable product, since the first isomerises into it on moderate heating and by the action of acid reagents. The formulae suggested are  $CMe_2Br \cdot C \equiv C \cdot CMe_2Br$  and  $CMe_2 \cdot CBr \cdot CBr \cdot CMe_2$ , re-

spectively. The liquid dibromide, b. p. 112—118°/13 mm.,  $n^{20}_D$  1.5505, does not lose both bromine atoms with equal ease, which suggests an unsymmetrical structure. It can be reduced to a hydrocarbon, b. p. 126—127°, and on oxidation yields acetone, acetic and hydroxyisobutyric acids, and the  $\beta$ -lactone acid, trimethylmalic acid, m. p. 118—120°. The dibromide is considered to possess a cyclic structure, and three formulae are suggested, of which the most likely is concluded to be  $CMe_2 \cdot CBr \cdot CBr \cdot CMe_2$ .

M. ZVEGINTZOV.

**Formation of geometrical isomerides by the hydrogenation of the acetylenic  $\gamma$ -glycols. Tetraphenylbutinenediols.** J. S. SALKIND and V. K. TETERIN (J. Russ. Phys. Chem. Soc., 1929, 61, 1751—1757; cf. A., 1927, 643).—By hydrogenating tetraphenylbutinenediol in the presence of colloidal palladium, two geometrical isomerides of the ethylenic  $\gamma$ -glycol, the  $\alpha$  and  $\beta$ , are obtained, the latter only in very small quantities. The  $\beta$ -isomeride, m. p. 195—196°, is very difficult to distinguish by physical methods from a mixture of the original acetylenic glycol and the corresponding saturated glycol. Bromination of the acetylenic glycol gave 3:4-dibromo-2:2:5:5-tetraphenyldihydrofuran, m. p. 198°, whilst the saturated glycol yielded, in the cold, the  $\gamma$ -oxide of tetraphenylbutanediol, m. p. 182°, and on warming tetraphenylbutadiene, m. p. 192—193°. Of the ethylenic glycols, the  $\alpha$ -isomeride reacted very slowly with bromine, giving 2:2:5:5-tetraphenyldihydrofuran, m. p. 185°, together with small amounts of the dibromide, m. p. 192°. The  $\beta$ -isomeride reacted much more readily, the above-mentioned dibromide being obtained. Both oxidation and reduction of each of the isomerides yielded identical products.  
M. ZVEGINTZOV.

**Partial esterification of polyhydric alcohols. X. Discovery of the first true  $\beta$ -glyceride and untrustworthiness of supposed structures of certain diglycerides.** A. FAIRBOURNE (J.C.S., 1930, 369—382).—A further study of the constitution of a number of supposed  $\beta$ -monoglycerides supports the general conclusion (A., 1927, 131) that previous cases of isolation of such are mistaken; exception is made, however, of the  $\beta$ -benzoate of Helferich and Sieber (A., 1928, 44), whose claim of the isolation of the first true  $\beta$ -glyceride is upheld. Similarly, the assumption of  $\alpha\beta$ - and  $\alpha\gamma$ -isomerism in diglycerides is shown by further cases to be based very often on insufficient evidence (cf. A., 1929, 292). A list of apparently trustworthy methods for the preparation of  $\alpha$ -,  $\beta$ -,  $\alpha\beta$ -,  $\alpha\gamma$ - and  $\alpha\beta\gamma$ -esters and ethers is given.

Direct esterification of  $\alpha\gamma$ -di-iodohydrin (A., 1927, 131) yields  $\alpha\gamma$ -di-iodohydrin  $\beta$ -laurate, m. p. 34°: a crude liquid material isolated by Thieme (A., 1912, i, 333), and used in the synthesis of " $\beta$ -monolaurin," is now found to yield on hydrolysis  $\alpha$ -monolaurin, as does also the crystalline di-iodohydrin.  $\alpha$ -Monolaurin  $\beta\gamma$ -diphenylurethane, m. p. 90°, is identical with the phenylurethane of the " $\beta$ -monolaurin" of Grün and Skopnik (A., 1909, i, 874). " $\alpha\beta$ -Dilaurin" (Thieme, *loc. cit.*) and " $\alpha\gamma$ -dilaurin" (Grün, A., 1913, i, 157) are identical.

*α-Monomyristin*, m. p. 68°, prepared by the general method of Fischer and collaborators (A., 1920, i, 805, 807, 808) is identical with the "β-monomyristin" of Grün, Schreyer, and Weyrauch (A., 1913, i, 159). "αβ-" and "αγ-dimyristin," prepared by the methods of Grün and Theimer (A., 1907, i, 464), are identical, m. p. 64–65°, as also are the "αβ-" and "αγ-dipalmitins" of Guth (A., 1903, i, 225), m. p. 69°. αγ-Dichlorohydrin β-stearate, m. p. 39°, obtained from epichlorohydrin and stearyl chloride by Whitby (A., 1926, 819), may be prepared from αγ-dichlorohydrin and stearyl chloride in quinoline; attempts to hydrolyse it or to replace the chlorine using potassium phthalimide failed. "αβ-Distearin" from αβ-dibromohydrin (Guth, *loc. cit.*; Renshaw, A., 1914, i, 477) and by the synthesis of Grün and Theimer is identical with the "αγ-distearin" also prepared by Guth from αγ-dichlorohydrin.

H. A. PIGGOTT.

**Chloromethyl carbonate.** D. MAROTTA (Gazzetta, 1929, 59, 955–961).—The trichloromethyl carbonate,  $(\text{CCl}_3)_2\text{CO}_2$ , obtained by Counceler (A., 1881, 251) by the action of dry chlorine on methyl carbonate is considered to be a polymeride of carbonyl chloride. Structurally it can be represented as the chloro-derivative of trioxymethylene.

O. J. WALKER.

**β-Chloroethyl esters of carbonic and sulphuric acids.** V. V. NEKRASSOV and I. F. KOMISSAROV (J. Russ. Phys. Chem. Soc., 1929, 61, 1933–1939).—The preparation and properties of β-chloroethyl carbonate and sulphate are described. Ethylene chlorohydrin and carbonyl chloride react at 0° giving β-chloroethyl hydrogen carbonate, b. p. 152–153°/752 mm.,  $d_4^{20}$  1.3825,  $n_D^{20}$  1.4465. If this ester is heated under reflux with further quantities of ethylene chlorohydrin at 130–150°, di-β-chloroethyl carbonate, m. p. 8.5°, b. p. 240–241°,  $d_4^{20}$  1.3506,  $n_D^{20}$  1.4610, is obtained. The di-ester is also formed by heating ethylene chlorohydrin with trichloromethyl chloro-carbonate, or with β-chloroethyl nitrite in small quantities.

With sulphuryl chloride, ethylene chlorohydrin yields, when heated at 165°, β-chloroethyl sulphate, m. p. 11°, b. p. 154–154.5°/8 mm.,  $d_4^{20}$  1.4801,  $n_D^{20}$  1.4622. The same product is obtained if β-chloroethyl nitrite is used instead of ethylene chlorohydrin. Both β-chloroethyl carbonate and sulphate are very stable.

M. ZVEGINTZOV.

**Action of chloropicrin on mercaptans.** V. V. NEKRASSOV and N. N. MELNIKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2049–2054).—See A., 1929, 1269.

**Action of zinc dust and zinc oxide on halogen derivatives of aliphatic sulphides.** A. E. KRETOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2345–2384).—The principal products of the action of zinc dust on ββ'-dichlorodiethyl sulphide in presence of primary or secondary aliphatic alcohols or primary fatty-aromatic alcohols are thio-ethers,  $\text{S}(\text{CH}_2\text{CH}_2\text{OR})_2$  and  $(\text{CH}_2\text{S}\cdot\text{CH}_2\text{CH}_2\text{OR})_2$ . Thio-ethers are also obtained when phenols are used instead of alcohols, but their composition has not been established. When alcohols are employed, mono-ethers of di-ββ'-hydroxydiethyl sul-

phide,  $\text{OH}\cdot[\text{CH}_2]_2\text{S}\cdot[\text{CH}_2]_2\text{OR}$ , di-ββ'-hydroxydiethyl sulphide, diethylene sulphide, vinyl ethyl sulphide, dithioethane, vinyl hydroxyethyl sulphide, ethylene, hydrogen sulphide, hydrogen, hydrogen chloride, etc. are formed as secondary products. The formation of di-ββ'-hydroxydiethyl sulphide and its ethers proceeds mainly by loss of hydrogen chloride from ββ'-dichlorodiethyl sulphide, with formation of divinyl sulphide, which then combines with water or alcohol; it occurs more rapidly and more completely in presence of oxides of zinc or other heavy metals, by a process of hydrolysis. The formation of ethers of ethylenedi-β-hydroxyethyl sulphide and its analogues depends on the action of metals and their chlorides (not oxides) and takes place by intramolecular rearrangement. The ββ'-dichlorodiethyl sulphide molecule is unstable and, under the influence of finely-divided metals and oxides, decomposes with formation of a relatively large proportion of gaseous products. The ethers of di-ββ'-hydroxydiethyl sulphide and ethylenedi-β-hydroxyethyl sulphide are stable and form characteristic compounds with mercuric chloride, but do not give crystalline compounds with methyl and ethyl iodides. Oxidation of ethers of di-ββ'-hydroxydiethyl sulphide by hydrogen peroxide in acetic acid solution yields sulfoxides, whilst that of ethylenedi-β-hydroxyethyl sulphide gives a series of crystalline products of progressive oxidation (sulfoxides and sulphones).

The action of zinc dust on ββ'-dichlorodiethyl sulphide in presence of ethyl alcohol yields: ethylene; sometimes ethane in small proportion; diethyl sulphide; vinyl β-hydroxyethyl sulphide, b. p. 150–165°/747 mm.,  $d_4^{20}$  1.1040, which combines with mercuric chloride to form the compound  $\text{C}_4\text{H}_8\text{OS}\cdot\text{HgCl}_2$ , m. p. 170°, with bromine to give the compound  $\text{C}_4\text{H}_8\text{OSBr}_2$ , and with hydriodic acid gives vinyl β-iodoethyl sulphide, which was not obtained quite pure; ββ'-diethoxydiethyl sulphide, b. p. 225–226.5°/746 mm.,  $d_4^{20}$  0.9672,  $n_D^{20}$  1.4585, which forms a mercuric chloride compound (+1HgCl<sub>2</sub>), m. p. 93–93.5°, is only slowly decomposed by alkali or acid, and undergoes rapid catalytic decomposition, with formation of unsaturated hydrocarbons and ether when its vapour is passed over oxides of heavy metals; β-hydroxyethyl β'-ethoxyethyl sulphide, b. p. 238–246°/746 mm.,  $d_4^{20}$  1.0474,  $n_D^{20}$  1.4798, which gives ββ'-di-iododiethyl sulphide, m. p. 68–70°, when treated in the cold with concentrated hydriodic acid, and yields the sulfoxide, b. p. 170–180°/19 mm., and 1:4-sulphone-thiozan,  $\text{SO}_2\langle\text{CH}_2\text{CH}_2\rangle\text{O}$ , m. p. 130°, when oxidised

by means of hydrogen peroxide in acetic acid solution; ethylene di-β-ethoxyethyl sulphide,  $(\text{CH}_2\text{S}\cdot\text{CH}_2\text{CH}_2\text{OEt})_2$ , b. p. 175–190°/20 mm.,  $d_4^{20}$  1.0450,  $n_D^{20}$  1.5020; the compound  $(\text{OEt}\cdot\text{CH}_2\text{CH}_2\text{S}\cdot\text{CH}_2\text{CH}_2)_2\text{O}$ , b. p. 200–220°/17–22 mm.,  $d_4^{20}$  1.0525, which is formed from 2 mols. of β-hydroxyethyl β'-ethoxyethyl sulphide under the influence of the zinc chloride formed.

Oxidation of di-ββ'-ethoxydiethyl sulphide with hydrogen peroxide or dilute nitric acid yields the sulfoxide, b. p. 176–180°/15 mm.,  $d_4^{20}$  1.1160, whilst oxidation with alkaline permanganate gives ethylsulphonic acid. Treatment of this diethyl ether with concentrated hydriodic acid converts it into ββ'-di-

iododiethyl sulphide, b. p. 71—72°,  $d_{20}^{20}$  1.9332, whilst with bromine it gives the dibromide,  $\text{SBr}_2(\text{CH}_2\text{CH}_2\text{OEt})_2$ . Careful chlorination of the diethyl ether, with rapid removal of the resulting hydrogen chloride by a current of air, gives a mixture of a monochloro-derivative,  $\text{C}_8\text{H}_{17}\text{O}_2\text{SCl}$ , b. p. 140—150°/20 mm., with a dichloro-derivative,  $\text{C}_8\text{H}_{16}\text{O}_2\text{S}_2\text{Cl}_2$ , b. p. 155—170°/20 mm. (decomp.). Treatment of the diethyl ether with anhydrous aluminium chloride yields  $\beta\beta'$ -dichlorodiethyl sulphide, *s*-dichloroethane, together with partly hydrolysed ethers of di- $\beta\beta'$ -hydroxydiethyl sulphide, sulphides of unknown composition, and sulphur-free compounds. Anhydrous ferric chloride acts similarly, but less energetically. In a sealed tube at 150—160°, di- $\beta\beta'$ -ethoxydiethyl sulphide unites with ethyl (or methyl) iodide (1 mol.), giving the compound  $\text{C}_{10}\text{H}_{23}\text{O}_2\text{IS}$ ; with higher alkyl iodides the reaction proceeds thus:  $\text{S}(\text{CH}_2\text{CH}_2\text{OR})_2 + \text{R}'\text{I} = \text{SR}'\text{I}(\text{CH}_2\text{CH}_2\text{OR})_2 = \text{OR}\cdot\text{CH}_2\text{CH}_2\cdot\text{S}\cdot\text{CH}_2\text{CH}_2\cdot\text{OR}' + \text{RI}$ . With phenylcarbamide, the ethers give complex condensation products of very high m. p.

$\beta$ -Hydroxyethyl  $\beta'$ -ethoxyethyl sulphide gives  $\beta$ -chloro- $\beta'$ -ethoxydiethyl sulphide, b. p. 122°/25 mm.,  $d_{20}^{20}$  1.075, when treated with phosphorus trichloride, and  $\beta$ -chloro- $\beta'$ -bromodiethyl sulphide, m. p. 24°, b. p. 125—132°/18 mm., with hydrobromic acid saturated at 0°.

When treated with concentrated hydriodic or hydrobromic acid, ethylene di- $\beta$ -ethoxyethyl sulphide gives ethylene di- $\beta$ -iodoethyl sulphide,  $(\text{CH}_2\text{S}\cdot\text{CH}_2\text{CH}_2\text{I})_2$ , m. p. 85° (decomp.), or the corresponding bromo-derivative. The analogous chloro-compound gives the compound  $\text{C}_{10}\text{H}_{22}\text{O}_2\text{S}_2\cdot 2\text{HgCl}_2$ , m. p. 83°. Oxidation with nitric acid or dichromate and sulphuric acid results in profound decomposition, but hydrogen peroxide gives: the monosulphoxide, not obtained pure, the disulphoxide, m. p. 156°, and the sulphoxide-sulphone,  $\text{C}_{10}\text{H}_{22}\text{O}_5\text{S}_2$ , m. p. 112°, and the disulphone, m. p. 105°; the action of concentrated hydriodic acid on the disulphone in a current of carbon dioxide gives ethylene di- $\beta\beta'$ -iodoethyl sulphone,  $(\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{I})_2$ .

The action of zinc oxide on  $\beta\beta'$ -dichlorodiethyl sulphide in presence of water gives di- $\beta\beta'$ -hydroxydiethyl sulphide, whilst in presence of alcohol it yields mono- and di-ethyl ethers; other heavy metal oxides act similarly.

The action of zinc dust on  $\beta\beta'$ -dichlorodiethyl sulphide in presence of methyl alcohol gives: di- $\beta\beta'$ -methoxydiethyl sulphide, b. p. 201—203.5°/746 mm.,  $d_{20}^{20}$  1.0058,  $n_D^{20}$  1.4625, which forms the compound  $\text{C}_6\text{H}_{14}\text{O}_2\text{S}\cdot\text{HgCl}_2$ , m. p. 80°, and yields the sulphoxide,  $\text{C}_6\text{H}_{14}\text{O}_3\text{S}$ , m. p. 39.5—40°, b. p. 164—170°/15 mm.,  $d_{20}^{20}$  1.1250, on oxidation with hydrogen peroxide; the corresponding monomethyl ether, b. p. 230—236°,  $d_{20}^{20}$  1.076; ethylene di- $\beta$ -methoxyethyl sulphide, b. p. 160—175°/18 mm.,  $d_{20}^{20}$  1.0840,  $n_D^{20}$  1.5063, which, on oxidation with hydrogen peroxide in acetic acid solution, gives compounds of m. p. 130° and 110° together with the disulphone,  $\text{C}_8\text{H}_{18}\text{O}_6\text{S}_6$ .

Di- $\beta\beta'$ -propoxydiethyl sulphide, b. p. 243—247°,  $d_{20}^{20}$  0.9439,  $n_D^{20}$  1.4573, forms a mercuric chloride compound, m. p. 71°, and gives the sulphoxide,  $d_{20}^{20}$  1.0068, on oxidation with hydrogen peroxide. The corresponding

disulphide,  $\text{C}_{12}\text{H}_{26}\text{O}_2\text{S}_2$ , b. p. 185—205°/20 mm., gives, on oxidation, the disulphone, m. p. 89°, which forms a mercuric chloride compound (+2HgCl<sub>2</sub>).

Di- $\beta\beta'$ -isobutoxydiethyl sulphide, b. p. 268—272°/732 mm.,  $d_{20}^{20}$  0.9216,  $n_D^{20}$  1.4580, forms the compound  $\text{C}_{12}\text{H}_{26}\text{O}_2\text{S}\cdot\text{HgCl}_2$ , m. p. 71°. The corresponding disulphide,  $\text{C}_{14}\text{H}_{30}\text{O}_2\text{S}_2$ , b. p. 200—214°/18—22 mm., forms the compound  $\text{C}_{16}\text{H}_{30}\text{O}_2\text{S}_2\cdot 2\text{HgCl}_2$ , and gives the disulphone  $\text{C}_{14}\text{H}_{30}\text{O}_6\text{S}_2$  on oxidation. Di- $\beta\beta'$ -isomethoxydiethyl sulphide, b. p. 191—192°/33 mm., ethylene di- $\beta$ -hydroxyethyl sulphide isoamyl ether,  $\text{C}_{16}\text{H}_{34}\text{O}_2\text{S}_2$ , b. p. 210—230°/33 mm.,  $d_{20}^{20}$  0.9631, and the corresponding disulphone,  $\text{C}_{16}\text{H}_{34}\text{O}_6\text{S}_2$ , m. p. 74—75°, were prepared.

The action of zinc dust on  $\beta\beta'$ -dichlorodiethyl sulphide in presence of (1) benzyl alcohol gives di- $\beta\beta'$ -benzyloxydiethyl sulphide, b. p. 225—250°,  $d_{20}^{20}$  1.0962 (approx.); the disulphoxide was prepared; (2) phenol gives a mixture of di- $\beta\beta'$ -phenoxydiethyl sulphide and ethylene di- $\beta$ -hydroxyethyl sulphide diphenyl ether, which could not be separated by distillation; (3) isopropyl alcohol gives di- $\beta\beta'$ -isopropoxydiethyl sulphide, b. p. 231.5—234.5°,  $d_{20}^{20}$  0.9356, which gives a mercuric chloride compound (+2HgCl<sub>2</sub>), m. p. 90°, and the corresponding disulphide.

The action of various finely-divided metals or their oxides on  $\beta\beta'$ -dichlorodiethyl sulphide in presence of inert solvents yields various sulphur compounds.

T. H. POPE.

Diphenylcyanomethyl sulphide, phenylcyanomethyl mercaptan, phenylcyanomethyl thiocyanate, and certain of their derivatives. A. KRETOV and A. PANTSCHENKO (J. Russ. Phys. Chem. Soc., 1929, 61, 1975—1993).—Diphenylcyanomethyl sulphide,  $(\text{CN}\cdot\text{CHPh})_2\text{S}$ , m. p. 150°, obtained, together with dicyanostilbene and phenylcyanomethyl mercaptan, when phenylbromoacetonitrile is treated in alcoholic solution with sodium sulphide and sulphur, is converted by treatment with alkali hydroxide first into dicyanostilbene, m. p. 240°, and then into diphenylmaleic acid. Reduction of the sulphide by means of zinc dust and acetic acid gives dicyanostilbene, m. p. 240°, whilst its reduction with hydriodic acid in acetic acid solution yields the dicyanostilbene with m. p. 160°. By stannous chloride the sulphide is reduced to dicyanostilbene, m. p. 160°, and hydrogen sulphide. Neither sulphoxide nor sulphone is obtained by treating the sulphide with oxidising agents, the molecule undergoing decomposition with formation of sulphuric acid.

Treatment of the sulphide with hydroxylamine gives, not the diamino-oxime, but the monoamino-oxime, which is unstable and at once decomposes, forming cyanostilbenecarboxylamide,  $\text{CN}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 246° (decomp.); this is converted into diphenylmaleic anhydride when heated with sodium hydroxide. Free cyanostilbenecarboxylic acid could not be obtained.

Phenylcyanomethyl mercaptan,  $(\text{CN}\cdot\text{CHPh}\cdot\text{SH})_2$ , m. p. 101°, is obtained either by heating phenylbromoacetonitrile with sodium thiosulphate and decomposing the resulting compound,  $\text{CN}\cdot\text{CHPh}\cdot\text{S}_2\text{O}_3\text{Na}$ , with acid, or by treating phenylchloroacetonitrile with sodium hydrogen sulphide. When heated with alcohol potassium hydroxide, the mercaptan gives hydrogen sulphide, ammonia, and diphenylmaleic anhydride,



whilst its reduction with hydriodic acid leads to the formation of dicyanostilbene, m. p. 158°.

*Phenylcyanomethyl thiocyanate*,  $\text{CN}\cdot\text{CHPh}\cdot\text{CNS}$ , m. p. 64—65°, gives first dicyanostilbene, m. p. 243°, and then diphenylmaleic anhydride when treated with potassium hydroxide, and forms dicyanostilbene when reduced with hydriodic acid. T. H. POPE.

**Analogy between the action of esters of inorganic acids and of the acids themselves.** M. JANCZAK (Rocz. Chem., 1930, 10, 115—157).—The reactions between sodium ethoxide and diethyl and triethyl phosphite, diethyl ethylphosphite, ethyl phosphate, metaphosphate, sulphate, sulphite, iodide, nitrate, and nitrite, triethylamine, ethyl formate, carbonate, acetate, and borate, triethyl and tetraethyl orthocarbonate, ethyl sulphide, and tetraethyl orthosilicate have been studied in non-aqueous solvents, as well as the reactions between anhydrous sodium hydroxide and ethyl sulphate, sulphite, nitrate, or phosphite, and between ethyl sulphate and diethyl sodium phosphite and phosphate. The reactions in these cases are completely analogous to the reactions between inorganic acids and bases in aqueous solution, the products for the above three groups of reactions being alkyl sodium salts of the respective acids, together with, in the first group, ethyl alcohol, in the second ethyl ether, and in the third triethyl esters. Only the esters of those inorganic acids the central atom of which (S, P, or C) possesses a complete octet, no electron of which is shared with oxygen atoms, exhibit the above behaviour. The action of esters of acids which are, in aqueous solution, regarded as being weak acids is different; such esters are more sensitive to the action of hydrogen than of hydroxyl ions, and do not react with sodium ethoxide. R. TRUSZKOWSKI.

**Transformation of fatty acids into hydrocarbons under high pressures.** A. D. PETROV (J. Russ. Phys. Chem. Soc., 1929, 61, 1849—1859).—See this vol., 322.

**Manufacture of ethyl acetate free from alcohol.** F. SCHEUERMANN.—See B., 1930, 275.

**Action of atomic hydrogen on organic compounds [oleic acid].** W. NAGEL and E. TIEDEMANN (Wiss. Veröff. Siemens-Konz., 1929, 8, [2], 187—198).—An apparatus for the study of the action of atomic hydrogen from a Geissler tube on organic compounds is described. Treatment of oleic acid in the apparatus resulted in the production from 3 mols. of acid of 1 mol. of stearic acid and 2 mols. of a polymeride, b. p. above 250°/1 mm. No compounds of lower mol. wt. could be detected. Ethyl phthalate yielded under the same conditions ethyl hexahydrophthalate with polymerised products.

A. R. POWELL.

**Structure of isooleic acid produced during hydrogenation of oleic acid.** S. UENO and N. KUSEI (J. Soc. Chem. Ind. Japan, 1930, 33, 62B).—Ozonisation of isooleic acid, m. p. 50—52.5°, iodine value 41.3°, acid value 198.3°, obtained from the product of the hydrogenation of the fatty acids from Tsubaki oil indicates that it is a mixture of solid  $\Delta^1$ -oleic acid ( $\Delta^1$ -elaidic acid?) and traces of other solid oleic acids ( $\Delta^2$ -,  $\Delta^3$ -oleic acid?), and that the double

linking of ordinary oleic acid migrates to a certain extent during hydrogenation (cf. A., 1929, 423).

C. W. SHOPPEE.

**Polymerisation of the methyl esters of the higher unsaturated acids of train oil.** K. KINO (J. Soc. Chem. Ind. Japan, 1930, 33, 56—57B).—The variation of chemical and physical properties produced by heating in a current of hydrogen has been investigated. During 15½ hrs.' treatment at 220—230° the viscosity increases five-fold, with increasing density and mol. wt. (345—440); the saponification value remains nearly constant, whilst the iodine value falls; the yield of ether-insoluble bromide decreases from 100 to 11%. The polymerisation process is more rapid at 270—280°, and after 6 hrs.' treatment the viscosity shows a fifty-two-fold increase; the mol. wt. rises from 345 to 687, whilst the saponification value, the iodine value, and the yield of ether-insoluble bromide decrease, the latter becoming zero after 5 hrs. The characteristic odour of the methyl esters does not disappear completely.

The iodine value of the product indicates that in addition to intermolecular polymerisation, intramolecular polymerisation with ring-formation occurs.

C. W. SHOPPEE.

**Preparation of  $\alpha$ -ketonic acids.** V. V. TSCHELINCEV and W. N. SCHMIDT (J. Russ. Phys. Chem. Soc., 1929, 61, 1995—2000).—See A., 1929, 1272.

**Manufacture of ketonic acid esters.** DR. A. WACKER GES. F. ELEKTRO-CHEM. IND.—See B., 1930, 275.

**Condensation of pyruvic acid with aliphatic aldehydes.** A. KIRRMANN (Compt. rend., 1930, 190, 750—752).—Pyruvic acid condenses with acetaldehyde, butaldehyde, and heptaldehyde in presence of acetic anhydride (cf. Wohl and Maag, A., 1911, i, 13) forming  $\alpha$ -keto- $\gamma$ -acetoxyvaleric, b. p. 98°/11 mm.,  $d^{20}_4$  1.152,  $n^{20}_D$  1.4222 (semicarbazone, m. p. 178°; acid chloride, b. p. 55°/12 mm.,  $d^{21}_4$  1.215,  $n^{21}_D$  1.4334),  $\alpha$ -keto- $\gamma$ -acetoxyheptonic, b. p. 114°/10 mm.,  $d^{21}_4$  1.0946,  $n^{21}_D$  1.4250 (semicarbazone, m. p. 132°), and  $\alpha$ -keto- $\gamma$ -acetoxydecanoic acids, b. p. 145°/10 mm.,  $d^{21}_4$  1.0291,  $n^{21}_D$  1.4324 (semicarbazone, m. p. 75°), respectively. The above acids are decomposed by boiling with water to pyruvic acid, probably through the intermediate  $\gamma$ -hydroxy-acid; decomposition is accelerated at the ordinary temperature by alkali. Attempts to prepare metallic salts gave pyruvates; boiling with alcohol affords ethyl pyruvate. H. BURTON.

[Active molecule of oxalic acid.] F. KRAUSS and K. BERGE (Ber., 1930, 63, [B], 568—569; cf. Oberhauser and others, A., 1928, 505; 1929, 793; Krauss and Bruchhaus, A., 1929, 541).—Formic acid is produced during the action of potassium permanganate or ammonium persulphate on oxalic acid and is causative of the formation of calomel from mercuric chloride. The "activation" of oxalic acid by treatment with ferric chloride and hydrogen peroxide is accompanied by production of formic acid, but the reduction of mercuric to mercurous chloride occurs in neutral solution in absence of oxalic acid. Mercuric chloride and ammonium oxalate in boiling solution afford mercurous chloride without the aid

of the "activating" electric current; formic acid is produced. H. WREN.

**Nitration of ethyl malonate.** J. B. MENKE (Rec. trav. Chim., 1930, 49, 381—382).—Good yields of ethyl nitromalonate are obtained by dropping 5 c.c. of ethyl malonate into a mixture of 7 parts of manganous nitrate with 25 parts of acetic anhydride during 5 min. at 55°. When acetic acid is used the temperature of nitration is higher; e.g., with copper nitrate and acetic acid the nitration temperature is 65°. Nitration of ethyl malonate with much nitric acid and acetic anhydride at 30—35° gives mainly ethyl dinitroacetate. R. J. W. LE FÈVRE.

**Properties of conjugated compounds. IX. Formation of bimolecular reduction products of butadiene acids.** C. M. CAWLEY, J. T. EVANS, and E. H. FARMER (J.C.S., 1930, 522—530).—Reduction of ethyl crotylidene malonate with aluminium amalgam leads to a mixture of solid and liquid products (with minute quantities of unimolecular products) regarded as geometrical isomerides of the structure:

$$\begin{array}{l} \text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2 \\ \text{CHMe}\cdot\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2 \end{array}$$

*Ethyl 1:2-dimethyldicyclohexane-4:5-dimalonate* (solid form, m. p. 61.5°, liquid form, b. p. 235—240°/14 mm.) is reduced slowly by hydrogen and colloidal palladium to isomeric forms of *ethyl 1:2-dimethylcyclohexane-4:5-dimalonate*, b. p. 225—230°/7 mm. and 217—233°/13 mm., respectively. The solid dicyclic ester on hydrolysis yields a solid acid, probably *1:2-dimethyl-Δ<sup>5</sup>-cyclohexene-4:5-dimalonic acid*, m. p. 175° (decomp.), together with a syrupy, partly decarboxylated mixture of acids. Attempts at decarboxylation of the solid or liquid products do not yield well-defined compounds. Bromination of the solid ester with 4 atoms of bromine per mol. yields an oily tribromo-derivative, and with 6 atoms an oily tetrabromo-derivative, neither of which gives definite products on oxidation. By hydrolysis of the reduced ester and decarboxylation of the product, or by catalytic reduction of the hydrolysis product of the solid dicyclic ester, followed by esterification of the acid produced, *ethyl 1:2-dimethylcyclohexane-4:5-diacetate*, b. p. 179°/9 mm., is obtained. The reduced derivative of the solid ester yields on bromination *ethyl 1:2-dimethylcyclohexane-4:5-dibromodimalonate* as a yellow oil. Crotonaldehyde condenses with ethyl cyanoacetate to yield *ethyl crotylidene cyanoacetate*, solid form, m. p. 57—58°, liquid, b. p. 122°/9 mm. H. A. PIGGOTT.

**Methyl sebacate.** A. KARVONEN (Suomen Kem., 1929, 2, 101—103).—The vacuum-distilled ester has m. p. 26.4°, b. p. 293°/754 mm. S. K. TWEEDY.

**Stereochemistry of allene compounds.** F. FALTIS, J. PIRSCH, and L. BERMANN (Ber., 1930, 63, [B], 691—702; cf. A., 1927, 856).—It is suggested that in considering the double linking it may be more correct to disregard the tetrahedral conception and to characterise the peculiarities as dependent on the participation of the four valency electrons in the union of the two carbon atoms and to regard the quadrivalent group, >C:C< or >C:C:C<, as a fresh unit to be compared with the quadrivalent

>C< atom. The tetrahedral conception suffices for the explanation of the behaviour of compounds CR<sub>4</sub> and may be considered as based on the tendency of the substituents to arrange themselves in a system with the greatest degree of symmetry. This principle, applied to compounds CR<sub>2</sub>:CR<sub>2</sub>, involves the regular, plane distribution of the four substituents. The same arrangement applies to allene derivatives, for which it is thus opposed to van 't Hoff's conception. A consequence of this assumption is that allene derivatives can yield geometrical isomerides but not optical antipodes. (The resolution of 1-methylcyclohexylidene-4-acetic acid is regarded simply as a consequence of inhibition of the free rotation of the doubly-linked carbon atoms.) Experimental examination of the problem is sought in the production of diethyl di-*l*-menthyl allenetetracarboxylate, in which, according to van 't Hoff's conception, it is considered that a type of asymmetric synthesis may be involved, possibly leading to the production of diastereoisomerides in unequal amount. If, however, only *cis-trans*-isomerism is possible, the product must have a specific rotation approximately predictable for the *l*-menthyl ester of an inactive acid, the activity differing little for the *cis*- or *trans*-form.

The action of *l*-menthol on ethyl malonate at 173° affords unchanged ester and menthene, *ethyl l-menthyl malonate*, b. p. 161—164°/11 mm., [ $\alpha$ ]<sub>D</sub> —59.7° in alcohol, —61.7° in chloroform, and di-*l*-menthyl malonate, m. p. 60—61°, [ $\alpha$ ]<sub>D</sub> —71.3° in alcohol, —76.5° in chloroform. The di-*l*-menthyl ester is stable towards boiling alcohol. In benzene, under the influence of sodium and ethyl alcohol, it suffers alkyl replacement largely with formation of ethyl malonate. Under somewhat similar conditions, ethyl *l*-menthyl malonate gives a mixture of ethyl alcohol, ethyl malonate, ethyl *l*-menthyl and *l*-menthyl malonates. Ethyl *l*-menthyl malonate does not condense with chloroform in toluene in presence of sodium methoxide. If, however, 2 mols. of ethyl *l*-menthyl ester, 4 mols. of alcohol-free sodium ethoxide, 1 mol. of chloroform, and 2 mols. of *l*-menthol in benzene are used, the sodium salt of di-*l*-menthyl dicarbethoxyglutaconate is obtained in 20% yield, accompanied by an apparently homogeneous mixture of this salt with that of the tetraethyl ester. Bromination of the salt in ether and subsequent debromination of the product with silver oxide in boiling acetone affords *diethyl di-l-menthyl allenetetracarboxylate*, m. p. (indef.) 51—54°. The product is divided by light petroleum into four fractions of concordant optical activity ([ $\alpha$ ]<sub>D</sub> —66.1° to —66.5° in acetone), corresponding with that predicted for the menthyl ester of a dicarboxylic acid doubly unsaturated in the  $\alpha\beta$ -position, but containing no conjugation. Activation of the allene complex, as expected from van 't Hoff's theory, does not appear to have been accomplished and the product appears to be a difficultly separable mixture of geometrical isomerides without marked difference in optical activity. Attempts to remove the menthyl groups from the ester by means of methyl and cetyl alcohol and thus to isolate the allene complex without the active menthyl group were unsuccessful.

Ethyl allenetetracarboxylate is hydrolysed by

2 mols. of sodium hydroxide and the sodium ethyl salt is treated with brucine sulphate in aqueous acetone. The brucine salt is separated into five fractions, each of which gives an optically inactive ethyl hydrogen allenetetracarboxylate. H. WREN.

**Oxidation of xanthates and some new dialkyl sulphur- and disulphur-dicarbothionates.** A. CAMBRON and G. S. WHITBY (Canad. J. Res., 1930, 2, 144—152).—The best oxidising agents for the conversion of xanthates  $\text{OR}\cdot\text{CS}_2\text{Na}$  into dialkyl disulphurdicarbothionates,  $(\text{OR}\cdot\text{CS})_2\text{S}_2$ , are (1) a freshly-prepared sodium tetrathionate solution and (2) cyanogen bromide. The latter reagent must be used in aqueous (in which the product is insoluble), benzene, or ethereal (in which the alkali cyanide formed is insoluble) solution, since in alcohol the reaction proceeds smoothly to the formation of the dialkyl sulphurdicarbothionate,  $(\text{OR}\cdot\text{CS})_2\text{S}$ , by interaction of the products of the initial reaction:  $2\text{OR}\cdot\text{CS}_2\text{K} + \text{CNBr} \rightarrow (\text{OR}\cdot\text{CS})_2\text{S}_2 + \text{KCN} + \text{KBr}$ ;  $(\text{OR}\cdot\text{CS})_2\text{S}_2 + \text{KCN} \rightarrow (\text{OR}\cdot\text{CS})_2\text{S} + \text{KSCN}$ . The following oxidising agents are less satisfactory, but are useful in certain cases: (3) nitrous acid; (4) nitrosyl chloride; (5) "chloramine-T," and (6) benzenesulphonyl chloride. By these methods the following are prepared, classification being according to the oxidising agent used: (1) dimethyl, m. p. 23—23.5° (Whitby and Greenburg, this vol., 320), dibenzyl, m. p. 54—54.5° (Ragg, A., 1910, i, 154, describes it as a liquid), *di-β-ethoxyethyl*,  $n_D^{25}$  1.5751 (converted by alcoholic potassium cyanide into *di-β-ethoxyethyl sulphurdicarbothionate*,  $n_D^{25}$  1.5561), *disulphurdicarbothionates*; and dithiobenzoyl and dithionaphthoyl disulphides; (2) *di-n-hexyl*, b. p. 170—175°/3 mm. (slight decomp.),  $n_D^{25}$  1.5569; *di-β-phenylethyl*, m. p. 49.5—50° (converted by distillation under ordinary pressure into styrene, and by the action of alcoholic ammonia into *β-phenylethylxanthogenamide*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{NH}_2$ , m. p. 73—74°); *diisopropyl* (Whitby and Greenburg, *loc. cit.*; also using oxidising agents 3, 4, and 5) *disulphurdicarbothionate*; *dibenzyl*, m. p. 82.5—83°; *di-n-hexyl*,  $n_D^{25}$  1.5410; *diethyl*, m. p. 52.5°, *sulphurdicarbothionates*; (3) *diethyl* (also by 6) and *di-n-butyl disulphurdicarbothionates*, and *tetraethylthiuram disulphide* (Braun and Stechele, A., 1903, i, 618).

J. W. BAKER.

**Highly-polymerised compounds. XVIII. Constitution of polyoxymethylenes.** H. STAUDINGER, R. SIGNER, H. JOHNER, M. LÜTHY, W. KERN, D. RUSSIDIS, and O. SCHWEITZER (Annalen, 1929, 474, 145—275).—In part, a re-statement of the authors' view that the structure of highly-polymerised compounds can be interpreted by normal valency formulae. The differences between the polyoxymethylene modifications are due to characteristic groups at the end of the long chains; the  $\alpha$ -compounds are dihydrates,  $\text{OR}\cdot[\text{CH}_2\cdot\text{O}]_n\cdot\text{CH}_2\cdot\text{OR}$  ( $\text{R}=\text{H}$ ,  $n=2$  to  $>100$ ), the  $\gamma$ -derivatives are the corresponding dimethyl ethers, whereas the  $\delta$ -substances are dimethyl ethers in the molecule of which C-C linkings have been developed by isomerisation of formaldehyde molecules. They are polymeric uniform. The terminal groups influence greatly the degradation and oxidation of the complete molecule (oxidation of the simpler dihydrates by ammoniacal silver solution and susceptibility of

the more complex dehydrates to alkali sulphite and hydroxide; relative stability of the dimethyl ethers to these reagents and intermediate position of the diacetates). The physical properties, particularly those of the more complex products, depend on the length of the chain and are little influenced by the terminal groups. Provided that the material is uniformly polymeric-homologous, the mean mol. wt. can be found by determination of the terminal groups. In polymeric-homologous series, the minimum mol. wt. can be determined from that of the less complex, soluble members or from comparison of the densities. Röntgenometric methods determine the mutual distances and not the molecular lengths of the chains. The non-volatility and insolubility of polyoxymethylenes of moderate complexity establishes the formation of the more complex derivatives by addition of single formaldehyde molecules to crystal nuclei in such a manner that covalent union occurs during addition to the crystal lattice; polymerisation and crystal growth are simultaneous processes. Conversely, degradation takes place by loss of individual formaldehyde molecules from the macromolecules.

Re-examination of the interaction of paraformaldehyde with acetic anhydride (cf. A., 1920, i, 517) indicates that the polyoxymethylene diacetates are degradation products derived from longer chains and not produced by addition. The most favourable conditions for the formation of compounds with 5—20 units are found in heating the reactants (5 mols. : 1 mol.) at 160—170° for 1 hr. After repeated fractional distillation or crystallisation, well-defined individuals are obtained, the molecular refraction of which indicates a normal valency structure. The physical properties (m. p., viscosity, and  $d$ ) of the members of the series vary in a regular manner. The compounds are hydrolysed by acid or alkali, but the fundamental polyoxymethylene dihydrates are unstable under the experimental conditions and immediately become converted into monomeric formaldehyde or its hydrate. The only marked differences exhibited by the individuals lie in the stabilities towards heat. The following new or revised data are recorded for the -oxymethylene diacetates: mono-, m. p. -23°, b. p. 39—40°/0.1 mm.,  $d^{24}$  1.128,  $n_D^{24}$  1.4025; di-, m. p. -13°, b. p. 60—62°/0.1 mm.,  $d^{24}$  1.158,  $n_D^{24}$  1.4124; tri-, m. p. -3°, b. p. 84°/0.1 mm.,  $d^{24}$  1.179,  $n_D^{24}$  1.4185; tetra-, m. p. +7°, b. p. 102—104°/0.1 mm.,  $d^{24}$  1.195,  $n_D^{24}$  1.4233; penta-, m. p. 17°, b. p. 124—126°/0.1 mm.,  $d^{24}$  1.204,  $n_D^{24}$  1.4258; octa-, m. p. 32—34°,  $d^{26}$  1.216; nona-, m. p. 40—43°,  $d^{28}$  1.353; deca-, m. p. 52—53.5°; undeca-, m. p. 65.5—67°; dodeca-, m. p. 73—75°; tetradeca-, m. p. 84—86°; pentadeca-, m. p. 90.5—92°,  $d^{30}$  1.364; hexadeca-, m. p. 93—95°; heptadeca-, m. p. 98.5—99.5°,  $d^{32}$  1.370; nonadeca-, m. p. 107—109°,  $d^{34}$  1.390; eicosa-, m. p. 111—112°; dieicosa-, m. p. 116—118°.

The residue remaining after removal of the volatile and soluble diacetates consists of a mixture of at least fifty polymeric homologues (23—70 units), the integrity of which is established by the results obtained by fractional extraction with water. The mean mol. wt. can therefore be deduced from the acetyl content. Boiling xylene causes loss of formaldehyde and production of a polymeride with about

30 units; at 200°, a less highly polymerised product results.

Treatment of polyoxymethylenes with methyl alcohol affords partly methylated, unstable compounds soluble in sodium sulphite or hydroxide. The dimethyl ethers are obtained from polyoxymethylene and methyl alcohol (6 : 1) in presence of sulphuric acid or hydrogen chloride at 150–160°. The yields are relatively small, so that the isolation of individuals has not been effected, but a sequence of volatile and soluble polymeric homologues is described closely similar in properties to the corresponding acetates. The ethers are hydrolysed by acids but not by alkalis. Compounds with 30–40 units are contained in the products of the action of an insufficiency of methyl alcohol and acids on  $\alpha$ -polyoxymethylenes.  $\gamma$ -Polyoxymethylenes (dimethyl ethers with more than 100 units), mixed with the  $\beta$ -compounds, are obtained by the action of methyl alcohol on paraformaldehyde in presence of sulphuric acid and purified by treatment with hot or cold sodium sulphite on sodium hydroxide. The properties vary somewhat with the mode of purification; the highest observed temperature of decomposition is 190–210°. A method for the determination of the methyl groups is described and the conception of the compounds as dimethyl ethers is strengthened by the preparation of analogous diethyl and dipropyl compounds.

$\delta$ -Polyoxymethylene is prepared by the prolonged action of boiling water on the  $\gamma$ - or mixture of  $\beta$ - and  $\gamma$ -compounds; it has m. p. 150–170° with loss of formaldehyde. The presence of C-C linkings is established by the production of the acetates of glycollaldehyde and higher carbohydrates when the material is boiled with acetic anhydride.

The polyoxymethylene dihydrates form a polymeric-homologous series but are too unstable to permit the isolation of individuals. The lower members (1–8 units) may be obtained by extraction of 30% formaldehyde solution. Paraformaldehyde, when evaporated, gives a minutely crystalline product of dihydrates with 8–50 units, whereas  $\alpha$ -polyoxymethylenes (mean degree of polymerisation more than 100) are derived from 38% formaldehyde solution by treatment with one tenth of its volume of concentrated sulphuric acid.  $\beta$ -Polyoxymethylene, obtained similarly to the  $\alpha$ -compounds except that a larger proportion of sulphuric acid is used, owes its characteristic properties to the presence of small amounts of acid in a state as yet undefined.

The views of Hess ("Chemie der Cellulose," Leipzig, 1928) and of Bergmann (A., 1927, 166) on the constitution of cellulose are discussed.

The close analogues between the polyoxymethylene hydrates and the silicic acids leads to the hypothesis that the latter substances are eucolloids.

H. WREN.

**Electrolytic reduction of aldehydes. VII. Crotonaldehyde.** G. SHIMA (Mem. Coll. Sci. Kyoto, 1930, 13, 85–90).—Electrolytic reduction of crotonaldehyde in dilute sulphuric acid under Law's conditions (J.C.S., 1912, 101, 1016) does not give the high yield of *n*-butyl alcohol claimed by this author. Fractional distillation of the product separates the following compounds: butaldehyde and croton-

aldehyde; *n*-butyl alcohol (mixed with some unsaturated alcohol, probably crotyl alcohol) and octane- $\delta$ -diol, b. p. 123–125°/5 mm. (Bouveault and Locquin, A., 1905, i, 572) (erroneously stated to be a dimethylcyclopentenealdehyde by Hibbert and Read, A., 1924, i, 613), the proportion of these products when reduction is effected at the following temperatures being, respectively, at 0–5°, 30, 8, 50%; at 10–15°, 21, 5, 55%; at 20–25°, 20, 3, 45%. Steam-distillation of the octanediol with dilute sulphuric acid converts it into *n*-propyl *n*-butyl ketone (Bouveault and Locquin, *loc. cit.*) (*semi-carbazone*, m. p. 185–186°). The yield of *n*-butyl alcohol can be increased to a maximum of 50% if electrolytic reduction is carried out in 20% sulphuric (or acetic) acid, without addition of alcohol, at 0–5° with a lead cathode, the aldehyde being added in small successive portions to the cathode solution during electrolysis. Similarly, if reduction is carried out with a mercury cathode (50 cm.<sup>2</sup>), a platinum anode, 10% sodium hydroxide as the anode solution, and crotonaldehyde (21 g.), 50% alcohol (100 c.c.), glacial acetic acid (5 c.c.), and sodium acetate (10 g.) in the cathode compartment, with a current of 4 amp. at 30–40°, fractional distillation of the product yields a fraction, b. p. below 120°/5 mm., which consists of *n*-butyl alcohol (contaminated with an unsaturated alcohol) and  $\Delta^8$ -octadiene- $\delta$ -diol, b. p. 120–125°/10 mm., and a fraction, b. p. 120–130°/5 mm., from which the above octanediol was isolated.

J. W. BAKER.

$\Delta^8$ -Decenaldehyde, the principal constituent of essential oil of *Achasma Walang Val*. P. VAN ROMBURGH.—See B., 1930, 302.

**Reduction of acetone by magnesium in presence of anhydrous aluminium chloride.** M. I. USCHAKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2089–2100).—See A., 1929, 1276.

**Ketals of hydroxyketones.** V. V. EVLAMPYEV (J. Russ. Phys. Chem. Soc., 1929, 61, 2017–2025).—The action of acetol on ethyl orthoformate in presence of hydrochloric acid under the conditions used for preparing acetals from ketones (A., 1923, i, 1061) yields crystalline acetol ethyl-lactolide (acetol ethylcycloacetal) (cf. Bergmann and Gierth, A., 1926, 728) of the composition C<sub>10</sub>H<sub>20</sub>O<sub>4</sub>. If sulphuric acid is used as catalyst instead of hydrochloric acid, a liquid product of the same composition as this lactolide is obtained, but mol. wt. determinations give no clear indication of the molecular complexity of the compound. *Bromoacetone diethylacetal*, b. p. 60.5–61.5°/15 mm., *d*<sub>4</sub><sup>20</sup> 1.1075, was obtained by treating bromoacetone with ethyl orthoformate in absolute alcohol in presence of sulphuric acid. *Iodoacetone diethylacetal* has b. p. 69°/7 mm., *d*<sub>4</sub><sup>20</sup> 1.4761. Various attempts to replace the halogen in chloro-, bromo-, and iodo-acetone diethylacetal by hydroxyl were unsuccessful, but the preparation of acetals of hydroxyketones was accomplished in another way.

The action of ethyl orthoformate on acetol formate in absolute alcoholic solution in presence of sulphuric acid yields acetol ethylcycloacetal, but with acetol acetate this reaction gives *acetoxyacetone diethyl-*

acetal, b. p. 78.5–79.5°/8 mm.,  $d_4^{25}$  0.9990,  $d_{25}^{25}$  0.9774, which on hydrolysis by means of lime yields *hydroxyacetone diethylacetal*,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}(\text{OEt})_2$ , b. p. 68–68.5°/9 mm.,  $d_4^{25}$  0.9828,  $d_{25}^{25}$  0.9637. Acetylation of this gives acetoxyacetone diethylacetal again. Hydrolysis of the acetal by acid is an endothermic reaction (cf. Arbusov, A., 1926, 805). T. H. POPE.

**Dioximes. LXI.** G. PONZIO (Gazzetta, 1930, 60, 49–96).—The isomerism of the glyoximes is discussed at length, and it is shown that many cases of such isomerism are explainable without the aid of the Hantzsch–Werner theory, the inability of which to interpret the formation of peroxides of glyoximes is confirmed by further experimental data. The new experimental results obtained are as follows. Trioximinopropane (mesoxalaldehydetrioxime) gives the complex nickel salt  $\text{Ni}(\text{C}_3\text{H}_4\text{O}_3\text{N}_3)_2$ , undergoing change at about 280°, by the action of nickel or nickel acetate. Acetylmethylglyoxime forms a *dibenzoyl* derivative, m. p. 131°, when treated, in pyridine solution cooled in ice, with benzoyl chloride.  $\beta$ -Phenylglyoxime forms the additive compound,  $\text{C}_8\text{H}_8\text{O}_2\text{N}_2\cdot\text{CuCl}_2$ .  $\beta$ -Phenylmethylglyoxime gives (1) oximinoethyl phenyl ketone when heated with dilute sulphuric acid, (2) phenylmethylfuran when heated with 20% sodium hydroxide solution, (3) the additive compound  $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_2\cdot\text{CuCl}_2$ , (4) a mixture of 4-phenyl-5-methyl-1:2:3:6-dioxdiazine (20%) and phenylmethylfuroxan (80%) when treated in glacial acetic acid with sodium nitrite. *p*-Methoxyphenyl- $\beta$ -methylglyoxime gives *p*-methoxyphenylmethylfuran when heated with 20% sodium hydroxide solution, and forms the crystalline additive compound,  $\text{C}_{10}\text{H}_{12}\text{O}_3\text{N}_2\cdot\text{CuCl}_2$ . Benzoyl- $\beta$ -methylglyoxime forms the compound  $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2\cdot\text{CuCl}_2$ . The m. p. of the two benzildioximes are higher than the values usually accepted, the  $\alpha$ - and  $\beta$ -forms having m. p. 247–248° and 211–212°, respectively. The action of heat on  $\alpha$ -benzildioxime yields diphenylfuran as well as the  $\beta$ -oxime (cf. Meisenheimer and Theilecker, A., 1929, 566), so that the reaction is not merely a simple isomerisation limited by the inverse reaction.

When heated at 170°,  $\gamma$ -benzildioxime yields the  $\beta$ -isomeride, together with about 15% of the  $\alpha$ -isomeride; Auwers and Meyer (A., 1889, 713) and Beckmann and Köster (A., 1893, i, 474) stated that only traces of the  $\alpha$ -compound were formed in this way. When aqueous-alcoholic  $\gamma$ -benzildioxime solution containing acetic acid and nickel acetate is heated on a water-bath, the nickel compound of the  $\alpha$ -isomeride is formed in 40–70% yield. An attempt to decide between the furoxan formula, the dioxdiazine formula, and Green and Rowe's *o*-quinonedioxime formula (J.C.S., 1913, 103, 897) for the products of the dehydrogenation of the symmetrical diarylglyoximes by means of their behaviour towards nitric acid gave inconclusive results. Di-*p*-nitrodiphenylfuran, for which Dodge (A., 1891, 1237) gave m. p. 218–220°, has m. p. 223–224°. *p*-Nitrodiphenylglyoxime peroxide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{N}_2\text{O}_2\cdot\text{Ph}$ , m. p. 114–115°, and dinitrodi-*p*-methoxyphenylglyoxime peroxide,  $\text{C}_2\text{N}_2\text{O}_2[\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{OMe}]_2$ , m. p. 180–181°, are described. The existence of three *p*-methoxybenzildioximes is confirmed, the  $\alpha$ - and  $\beta$ -forms having m. p.

223° and 185°, respectively; the  $\gamma$ -form, m. p. 89–91° (impure), has not been obtained free from the  $\beta$ -isomeride. The compound, m. p. 95–97°, described by Meisenheimer, Lange, and Lamparter (A., 1925, i, 1075) as  $\beta$ -phenylamisyfuroxan is a eutectic mixture of the two peroxides of this dioxime. Replies are made to various criticisms by Meisenheimer and Theilecker (A., 1929, 566) of the work of the author and his collaborators. T. H. POPE.

**Saccharinose and saccharinohexoses. E.** VOTOČEK (Coll. Czech. Chem. Comm., 1930, 2, 158–160).—Reduction of Pélégot's saccharine,  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CMe}(\text{OH})\cdot\text{CO}$  by sodium amalgam and dilute sulphuric acid gives a 2-methylpentose, which, through the cyanohydrin synthesis, generates the corresponding "saccharinohexose," a 3-methylhexose. R. J. W. LE FÈVRE.

**Optical rotation and ring structure in the sugar group.** Optical rotation of the various asymmetric carbon atoms in the hexose and pentose sugars. H. S. ISBELL (Bur. Stand. J. Res., 1929, 3, 1041–1052).—The values for the optical rotatory power of the various asymmetric carbon atoms in both the hexose and pentose series have been calculated from the optical rotations of the methylglucosides and from those of the sugars. The former are slightly higher but of the same order as the values obtained from the corresponding sugars, indicating that the normal forms of *d*-dextrose, *d*-galactose,  $\alpha$ -d-mannose, and  $\alpha$ -d-gulose have the 1:5-ring structure similar to the corresponding glucosides and that replacement of a hydroxyl by a methoxyl group alters the rotation of all the asymmetric carbon atoms. The specific rotations of the unknown forms of *d*-allose, *d*-altrose, *d*-idose, and *d*-talose are predicted from the results obtained. The following new values are recorded:  $[\alpha]_D^{25}$  for  $\alpha$ -*d*-gulose +62.6°,  $\alpha$ -methyl-*d*-guloside +106°, and  $\beta$ -methyl-*d*-guloside –83°;  $[M]_D^{25}$  +11,100, +20,600, and –16,100, respectively.

A. R. POWELL.

**Objective physical method for the determination of sugars in solution.** J. W. MEIJER (Rev. Sci. Instr., 1930, 2, 69–75).—The smallest concentration of dextrose that can be detected with a Laurent polarimeter is 0.0625%, and with a Lippich instrument 0.032%. A photographic method is described, by means of which 0.009% of *l*ævulose and 0.0125% of dextrose can be determined accurately. The construction of the special polarimeter which is required is described.

C. W. GIBBY.

**Comparative experiments on the ring-stability of derivatives of pyranoid and furanoid sugars.** I. H. OHLE and V. MARECEK (Ber., 1930, 63, [B], 612–636).—The most suitable material appears to be sugar derivatives in which the hydroxyl group of the C-1 atom of aldoses is protected by etherification or esterification. Treatment of such compounds with hydrogen bromide in glacial acetic acid results, in the simplest cases, in the breaking of all acetal linkings followed by the acetylation of original or developed hydroxyl groups except the group attached to C-1, which is replaced by bromine. A further

advantage is found in the non-existence of the  $\beta$ -forms of the bromo-derivatives in the presence of mineral acid, so that each ring isomeride can occur only in the  $\alpha$ -form. Difficulties arising from the sensitiveness of the 1-bromo-derivatives to dilute, aqueous acids are avoided by neutralising the latter with ethereal magnesium ethyl bromide. In this manner penta-acetylglucose is very smoothly transformed into acetobromoglucose and 3-*p*-toluenesulphonyldiisopropylideneglucose (cf. Freudenberg and Ivers, A, 1922, i, 523), which does not give the colour reaction described previously with the mixture of acids, into 3-*p*-toluenesulphonyl-2:4:6- $\alpha$ -glucosyl 1-bromide in 75% yield. From 3-*p*-toluenesulphonyl-5:6-diacetylisopropylideneglucose 3-*p*-toluenesulphonyl-2:5:6-triacetyl- $\alpha$ -glucosyl 1-bromide is obtained in more than 90% yield. With 6-*p*-toluenesulphonyl-isopropylideneglucose, -3:5-diacetylisopropylideneglucose, -isodisopropylideneglucose, and -1:2:3:4-tetra-acetyl- $\beta$ -glucose reaction follows a more complicated course and does not yield crystalline products. Determination of loosely and firmly combined bromine (treatment with methyl alcohol and silver carbonate followed by Carius' method applied to the residue) shows that the course of bromination depends greatly on the nature of the material. Attempts to apply a correction for the amount of bromine utilised by the eliminated acetone are not completely successful, since the data can be applied to the derivatives of diisopropylideneglucose, but not to the conversion of tri-*p*-toluenesulphonyl-isopropylideneglucose into 3:5:6-tri-*p*-toluenesulphonyl-2-acetylglucosyl 1-bromide. Blank experiments show that acetone does not yield compounds with firmly combined bromine, so that the latter is contained solely in the sugar residue. The most probable assumption is that the firmly combined bromine is attached to the C-4 carbon atom and enters the molecule through fission of the lactol ring. The extent to which the reaction occurs depends on the constitution of the furanoid glucose derivative and can be used to a limited degree in judging the ring stability of these compounds provided that simple displacement of the oxygen bridge is rendered impossible by substitution of the OH-5 group. A complication, however, arises with those substances which yield intense colorations with hydrogen bromide in glacial acetic acid, since the halochromic effect can be attributed only to products derived from the open-chain aldehyde. The separation of the brominated products in these complex mixtures appears impossible, and attempts have therefore been made to replace the labile bromine by other groups, thus stabilising the most variable component. In this connexion re-examination of the compound described by Ohle and Spenker (A., 1926, 1126) has established its identity with the 6-*p*-toluenesulphonyl-2:3:4-triacetyl- $\beta$ -methylglucoside of Helferich and others (A., 1927, 1174). For the conversion of the bromo-compounds into acetyl derivatives lead tetra-acetate is found very advantageous, liberated bromine being removed with the acetic acid during the reaction. "Firmly-combined" bromine is not removed from acetodibromoglucose under these conditions. 6-*p*-Toluenesulphonylisopropylideneglucose affords a

mixture of the isomeric  $\beta$ -forms of 6-*p*-toluenesulphonyltetra-acetylglucose which cannot be separated into its components by crystallisation. A similar mixture is derived from 6-*p*-toluenesulphonyl-3:5-diacetylisopropylideneglucose and 6-*p*-toluenesulphonylisodisopropylideneglucose, but the quantitative relationship of yield to firmly-bound bromine is not satisfactory. The reason is found in the greater ease of direct replacement of the bromine atom of 1-bromo-compounds in the furanoid series by other substituents than in the pyranoid series. Thus 3-*p*-toluenesulphonyl-2:5:6-triacetyl-2-glucosyl 1-bromide and lead tetra-acetate give only small amounts of 3-*p*-toluenesulphonyl-1:2:5:6-tetra-acetyl- $\beta$ -glucose and much bromine-free syrup containing preponderatingly the corresponding  $\alpha$ -form. Attempts to prepare the homogeneous 6-*p*-toluenesulphonyl-2:3:4-triacetyl- $\alpha$ -glucosyl 1-bromide or -chloride from Helferich's tetra-acetate by hydrogen bromide and glacial acetic acid, titanium tetrachloride or tetrabromide were unsuccessful.

Applicaton of these observations to the free 6-*p*-toluenesulphonylglucose leads to the expectation of a displacement of the equilibrium towards the furanoid form and a distinct loosening of both ring structures, thus necessitating re-examination of the product regarded as 6-*p*-toluenesulphonyl-1:2:3:4-tetra-acetyl- $\alpha$ -glucose (Ohle and Vargha, A., 1929, 1278). The constitution assigned to it is confirmed by the similarity of its behaviour and that of the  $\beta$ -acetate towards stannic chloride by which similar but undoubtedly furanoid mixtures become humified and by comparison with the compound from Helferich's 6-triphenylmethyltetra-acetyl- $\alpha$ -glucopyranose. In pyridine solution, 6-*p*-toluenesulphonylglucose appears present mainly in the pyranoid modifications, but this does not necessarily apply to the product as syrup or in aqueous solution. The introduction of the *p*-toluenesulphonyl group in position 6 appears generally to weaken the cyclic structure and hence it is not surprising that the compound rapidly gives the magenta-sulphurous acid reaction under conditions in which dextrose is inactive. Further, the occurrence of the free aldehydic form involves the possibility of ketonisation under conditions milder than those required for free dextrose; hence 6-*p*-toluenesulphonylglucose cannot be quantitatively titrated according to Willstätter and Schudel. A further effect of the loosening of the ring system is the gradual diminution of the aldose content of the syrup, due, apparently, to the production of polysaccharides.

By reason of the poor yields, treatment of bromo-compounds with tertiary bases does not appear a suitable method for the differentiation and separation; the conversion of 3-*p*-toluenesulphonyl-2:4:6-triacetyl- $\alpha$ -*d*-glucosyl 1-bromide into 3-*p*-toluenesulphonyl-2:4:6-triacetyl- $\beta$ -*d*-glucosido-1-pyridinium *p*-toluenesulphonate, *m. p.* 160°,  $[\alpha]_D^{25}$  -21.31° in chloroform, and 3-*p*-toluenesulphonyl-2:4:6-triacetyl- $\beta$ -1-glucosidophenyltrimethylammonium bromide, *m. p.* 181°,  $[\alpha]_D^{25}$  +19.51° in chloroform, is described.

H. WREN.

**Salep mannan.** O. ROUTALA and E. HEMMILÄ (Suomen Kem., 1929, 2, 96-101).—The behaviour



of the triacetate and tribenzoate of the mannan when heated in glycerol was observed. From the former *mannosan triacetate*, sparingly soluble in glacial acetic acid, was obtained; when hydrolysed this product yields a white soluble substance,  $C_6H_{10}O_5$ , which is also obtained when the mannan is heated in glycerol. The substance is apparently a de-association product of the mannan and is readily converted into the latter (cf. Pringsheim and Liss, A., 1928, 1016).

S. K. TWEEDY.

**Significance of ferric and ferrous complexes of carbohydrates and polyhydric alcohols for the mechanism of Fenton's reaction.** A. T. KÜCHLIN and J. BÖESEKEN (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 1218—1234).—The amount of hydrogen peroxide present at various times has been determined by titration with iodine after addition of stannous chloride in solutions containing glycerol, ferrous sulphate, water, hydrogen peroxide, and sulphuric acid. Provided sufficient hydrogen peroxide is present originally, the concentration decreases during the first few minutes, then increases again, and this may be followed after about 12 min. when the solution has become turbid by a further decrease. The results are interpreted on the view that a complex compound is formed between the glycerol and the ferrous ion, which can add hydrogen peroxide. Similar observations have been made with mixtures containing lævulose instead of glycerol and from the kinetics of the reaction evidence has been obtained of the existence of molecular complexes containing lævulose and ferrous iron, capable of adding hydrogen peroxide. The stability of these molecular compounds is dependent on the hydrogen-ion concentration. Evidence is adduced from spectrophotometric measurements of the existence of a compound of lævulose with ferric chloride, consisting probably of 2 mols. of the former and 1 mol. of the latter. The presence of ferrous or zinc ions influences the rate of mutarotation of lævulose.

W. O. KERMACK.

**Sugar group. I. Derivatives of lævulose and lactose.** N. FRÖSCHL, J. ZELLNER, and H. ZAK (Monatsh., 1930, 55, 25—47).—Acetochlorofructose reacts with phenylhydrazine to give glucosazone, m. p. 206°, and with magnesium ethyl iodide in ether to form the compound  $C_{14}H_{19}O_5Cl_2 \cdot 2MgEtI$ . The compounds  $C_{14}H_{20}O_{10} \cdot 2MgEtI$  and  $C_{16}H_{22}O_{11} \cdot 2MgEtI$  were similarly obtained from tetra-acetylfructose, prepared in 36—40% yield from lævulose and acetic anhydride in pyridine at  $-10^\circ$ , and penta-acetylfructose, respectively.

Hepta-acetylbromolactose (I), from octa-acetyl-lactose (best prepared from lactose, anhydrous sodium acetate, and acetic anhydride at  $110^\circ$ ), condenses with *l*-menthol in dry chloroform in the presence of silver carbonate to give *hepta-acetylmenthyl-lactoside*, m. p.  $92^\circ$ ,  $[\alpha]_D^{20} -34.84^\circ$  in alcohol, in 32% yield; this is hydrolysed by boiling alcoholic barium hydroxide to *menthyl-lactoside* ( $+1.5H_2O$ ), m. p.  $182^\circ$ ,  $[\alpha]_D^{20} +28.04^\circ$  in water. Under similar conditions ethylene glycol yields the *lactoside*,  $C_{28}H_{40}O_{19}$ , m. p.  $64-65^\circ$ ,  $[\alpha]_D^{20} -6.31^\circ$  in alcohol (35% yield); butyl glycollate, geraniol, and thymol afforded tetradeca-acetyltetra-saccharide, m. p.  $75^\circ$ . Hepta-acetylbromolactose

and silver theophylline in dry xylene at  $100^\circ$  give *hepta-acetyltheophyllinelactoside*, m. p.  $104-105^\circ$  (decomp.),  $[\alpha]_D^{20} -10.44^\circ$  in ethyl acetate: *hepta-acetylthiocyanolactoside*, m. p.  $170^\circ$ ,  $[\alpha]_D^{20} +14.27^\circ$  in methyl alcohol, from silver thiocyanate; *hepta-acetylcyanolactoside*, m. p.  $187^\circ$ ,  $[\alpha]_D^{20} +28.71^\circ$  in alcohol, from silver cyanide; *hepta-acetylsuccinimidolactoside*, m. p.  $191^\circ$ ,  $[\alpha]_D^{20} -9.97^\circ$  in chloroform, from silver succinimide, were similarly prepared. Magnesium methyl iodide reacts with hepta-acetylbromo- and with octa-acetyl-lactose to give the compounds  $C_{26}H_{35}O_{17} \cdot Br \cdot 2MgMeI$  and  $C_{28}H_{38}O_{20} \cdot 2MgMeI$ , respectively.

A. I. VOGEL.

**Synthesis of sucrose.** A. PICTET (Helv. Chim. Acta, 1930, 13, 173).—The author is reinvestigating the previously described synthesis of sucrose (A., 1928, 510, 741; 1929, 913) in view of the various unsuccessful attempts published by other workers.

H. BURTON.

[Configuration of digitoxose.] F. MICHEEL (Ber., 1930, 63, [B], 755).—Acetobromo-*d*-glucos-methyl-ose has  $[\alpha]_D^{20} +228.4^\circ$  in chloroform instead of  $+28.4^\circ$  as erroneously printed (this vol., 455). It is therefore an  $\alpha$ -derivative.

H. WREN.

**Synthesis of  $\beta$ -phenylglucoside.** N. M. CARTER (Ber., 1930, 63, [B], 586).—Tetra-acetyl- $\beta$ -phenylglucoside, m. p.  $126^\circ$ ,  $[\alpha]_D^{20} -29.8^\circ$  in benzene, is prepared in 43% yield by the action of silver carbonate on a solution of acetobromoglucose and phenol in benzene. *p*-Cresol and eugenol do not appear to react similarly.

H. WREN.

**Digoxin, a new *Digitalis* glucoside.** S. SMITH (J.C.S., 1930, 508—510).—The mixed glucosides of *D. lanata* on crystallisation from acetone deposit a fraction rich in a new glucoside which may readily be purified by taking advantage of its sparing solubility in 80% alcohol, chloroform, and ethyl acetate. The colourless, crystalline product, *digoxin*,  $C_{41}H_{64}O_{14}$ , m. p.  $265^\circ$  (decomp.) when rapidly heated,  $[\alpha]_D^{20} +13.3^\circ$  in pyridine, gives an olive-brown colour in the Keller reaction (distinction from gitoxin). Hydrolysis readily yields digitoxose and *digoxigenin*,  $C_{23}H_{34}O_5$ , m. p.  $222^\circ$  (corr.),  $[\alpha]_D^{20} +27.0^\circ$  in methyl alcohol, Keller reaction greenish-yellow.

H. A. PIGGOTT.

**Influence of neutral salts on the hydrolysis of starch in the presence of inorganic acids.** E. ANGELESCU and O. MANOLESCU (Bul. Soc. Chim. România, 1929, 11, 99—102).—A study of the influence of neutral salts on the amount of reducing sugar produced by the hydrolysis of starch in the presence of mineral acids has shown that the anions alone have a marked influence, that of the cations being much less. Sodium and magnesium sulphates at concentration greater than  $0.5N$  completely suppress hydrolysis, whilst at  $0.02N$  it is reduced to half. The differences between the values for the two sulphates are slight and are regarded as due to the influence of the cations. Chlorides in general, and magnesium chloride in particular, increase the rate of hydrolysis, whilst nitrates have a similar although less marked effect. In the absence of salts, whilst hydrochloric and nitric acids hydrolyse the same quantity of starch, sulphuric acid is less active, al-

though at the concentration used it has almost the same dissociation constant, consequently this effect is regarded as due to undissociated sulphate molecules. The retarding action of neutral sulphates is considered to be due to their tendency to coagulate the starch, and thus to reverse the swelling and solubilisation processes that precede hydrolysis. Conversely, salts with a dispersing action on starch, e.g., magnesium chloride, accelerate hydrolysis.

H. A. PIGGOTT.

**Influence of temperature on the blue coloration given by iodine in the presence of starch.** E. ANGELESCU and J. MIRCESCU (Bul. Soc. Chim. România, 1929, 11, 81—98).—In the absence of potassium iodide and for iodine concentrations below about 0.001%, the temperature of disappearance of colour produced by a fixed amount of iodine increases to a maximum and then diminishes as the concentration of starch in the solution rises; above this figure the temperature rises steadily. On cooling, the blue colour reappears at a lower temperature than that of disappearance, and on reheating, the temperature of disappearance is lower than at first, but still considerably higher than that of reappearance. This is regarded as being due either to the loss of iodine or to irreversible transformations of the starch, or a combination of these. In starch solutions of constant concentration, increased amounts of iodine increase the temperature of decolorisation, the increase being more marked with the smaller amounts of iodine. In the presence of potassium iodide, the temperature of decolorisation is raised and the effect is particularly noticeable with low concentrations of iodine, more iodine being absorbed by the starch than in the absence of iodide. In addition, the relations are much more regular and the differences between the temperatures of disappearance and reappearance are considerably less; nevertheless, on reheating, the second decolorisation still occurs at a slightly lower temperature than the first.

The colour changes from blue to violet and reddish-brown before it disappears. This can be attributed either to the liberation of free iodine or to the increase in degree of dispersion of the starch. Then the hysteresis effect on cooling may be due to slow coagulation of the starch granules, and the marked effect of potassium iodide on the change in shade to its known dispersing action.

H. A. PIGGOTT.

**Oxidative decomposition of starch by bromine in alkaline solution.** M. HÖNIG and W. RUZICKA (Biochem. Z., 1930, 218, 397—401).—When cold 1% solutions of soluble starch, mixed with barium hypobromite and sufficient barium hydroxide to neutralise acid oxidation products, were irradiated, maltobionic acid was obtained if the oxygen equivalent of the hypobromite used sufficed for either two or three dextrose residues. Gluconic acid was also obtained when higher oxygen equivalents were employed. Maltobionic acid was also obtained from potato starch.

W. MCCARTNEY.

**Micellar theory of the starches and physico-chemical properties of starch substances.** M. SAMEC (Biochem. Z., 1930, 218, 249—268).—A consideration of the properties of starches with special

reference to the state of combination of the phosphorus, silica, and other mineral matter which they contain shows that the theories of Malfitano and of K. H. Meyer receive considerable support from experimental results.

W. MCCARTNEY.

**Structural matter of varieties of cabbage.** III. H. PRINGSHEIM and H. BORCHARDT (Ber., 1930, 63, [B], 664—670; cf. A., 1928, 1227; B., 1929, 468).—The stems of broccoli require more energetic treatment with sodium hydroxide and chlorine dioxide than other varieties of cabbage for the isolation of the structural matter, but, after acetylation, an acetate of very small optical activity is obtained. This is not due to the somewhat more drastic treatment, since cellulose under like conditions affords an acetate with considerable but not full activity. All the usual methods fail when applied to the hydrolysis of the cabbage polysaccharide to sugars, and modified methods of acetolysis do not lead to degradation products soluble in water. If, however, the initial treatment of the cabbage with 6% sodium hydroxide is omitted, the action of zinc chloride and 41% hydrochloric acid affords a clear solution containing xylan in addition to fermentable sugars. The latter substances give a distinct coloration for lævulose (van der Haar's method) and the difference between the titration values according to Bertrand and to Willstätter and Schudel discloses the presence of 10% of a ketone which can only be lævulose, since it is fermentable. Dextrose is present, but galactose or mannose could not be detected. It is therefore established that the cabbage polysaccharide differs characteristically from the structural matters previously investigated and it is suggested that true cellulose is not necessarily the main component of the structural matter of green plants.

H. WREN.

**Integral relationship between the cellulose and the sparingly soluble xylan in the structural element of red beech (*Fagus sylvatica*).** II. E. SCHMIDT, W. JANDEBEUR, and K. MEINEL (Cellulosechem., 1930, 11, 73—79; cf. this vol., 457).—Treatment of beech-wood meal with a 0.25% aqueous solution of chlorine dioxide oxidises the lignin, yielding degradation products not completely soluble in water which may be removed by treatment of the wood with sufficient aqueous solution of salts possessing an alkaline reaction to bring the  $p_H$  of the mixture to 6.8. A greater degree of alkalinity tends to the attack of the structural polysaccharides. The salts employed are sodium sulphite, sodium carbonate, disodium hydrogen phosphate, and potassium xanthate. Dissolution is also effected by sulphur dioxide, in the form of sodium hydrogen sulphite, and by solutions of certain organic compounds as resorcinol and pyridine. Repeated treatment with chlorine dioxide and these reagents alternately removes completely the lignin from the cell constituents. The polysaccharide element of the cell wall is not attacked by this treatment. The relationship previously reported (*loc. cit.*), 3 mols. of cellulose to 1 mol. of sparingly soluble xylan, is confirmed in all cases for the delignified material.

T. H. MORTON.

**Phenylcarbimide derivative of aminoglucose.** A. A. SCHMUK (J. Russ. Phys. Chem. Soc., 1929, 61, 1759—1763).—A *phenylcarbimide* derivative, m. p. 207—208° (decomp.), of aminoglucose is precipitated when an ice-cold solution of aminoglucose in dilute sodium hydroxide is treated with phenylcarbimide. It is somewhat unstable, and decomposes when heated with acetic acid, giving diphenylcarbamide. If phenylthiocarbimide is used, a *thiocarbimide*, m. p. 121°, is obtained, which is moderately soluble in hot water or alcohol and readily reduces ammoniacal silver nitrate and Fehling's solution. Both derivatives differ from the corresponding derivatives of glucosamine. M. ZVEGINTZOV.

**Pyrogenic decomposition of betaine under reduced pressure in the presence of calcium oxide.** G. DECHAMPS (Bull. Soc. chim. Belg., 1930, 39, 67—86).—The products of distillation at 300—350°/15 mm. were collected successively in a cooled receiver (a), 2*N*-sulphuric acid (b), and sodium hydrogen sulphite solution (c). The portion of the distillate (a) non-volatile in steam consists of betaine carried over mechanically; the steam-distillable products are separated by means of their different basicities, the feebly basic part consisting of pyrrole and the strongly basic part being added to (b). The basic products (b) are separated by successive steam-distillations from alkaline solution into more and less volatile fractions; the constituents of the former are separated by the methods of Bertheaume (A., 1910, i, 365; ii, 663) and of François (A., 1907, i, 391; ii, 503), and consist of trimethylamine (73.96%), dimethylamine (18.40%), monomethylamine (3.82%), and ammonia (3.82%); the principal constituent of the latter is *tetramethylethylenediamine* [*chloroplatinate*, m. p. 251° (decomp.)], accompanied by traces of condensation products derived from mono- and di-methylamine and formaldehyde. By treatment with sodium hydroxide and steam, the sodium hydrogen sulphite solution (c) furnishes methyl alcohol, acetone, and *cyclopropanone* (*p*-nitrophenylhydrazones, m. p. 116—117°); a mixture of the *p*-nitrophenylhydrazones of acetone and *cyclopropanone* (4:1) has m. p. 142—143°. Schemes explanatory of the formation of pyrrole, tetramethylethylenediamine, and *cyclopropanone* from betaine are discussed, in the last case involving the intermediate formation of calcium succinate which, when distilled at 300—350°/15 mm., affords acetone and *cyclopropanone*.

The gaseous products consist mainly of carbon dioxide, together with hydrogen, methane, and traces of unsaturated products.

When betaine is fused and immediately cooled again, sufficient formaldehyde is formed by pyrogenic decomposition to be readily detected; on this basis, the author proposes a simple qualitative test for betaine. C. W. SHOPPEE.

**Peptide-like substances. XXXI. Synthesis of a peptide and other derivatives of  $\alpha$ -aminoacrylic acid (dehydroalanine) from pyruvic acid. XXXII. Compounds of pyruvic acid with amino-acids. XXXIII. Peptide linking.** M. BERGMANN and K. GRAFE (Z. physiol. Chem., 1930,

187, 187—195, 196—202, 183—186).—XXXI. Acetamide heated with pyruvic acid gives  $\alpha$ -*diacetamidopropionic acid*, m. p. 189—190° (corr.), which with diazomethane yields the *methyl ester*, m. p. 186° (corr.). For comparison,  $\alpha$ -*diacetamidopropionic acid*, m. p. 181—182° (corr.) after softening at 178°, was prepared from  $\alpha$ -*tribromopropionic acid* by the action of ammonia and subsequent acetylation. Acetamide and pyruvic acid also yield  $\alpha$ -*acetamidopropionic acid*, m. p. 198—200° (corr., decomp.), which may also be obtained by heating  $\alpha$ -*diacetamidopropionic acid* with acetic acid. Hydrogenation in presence of palladium gives *acetyl-dl-alanine*. The constitution is determined by the action of diazomethane, which yields *methyl 3-acetamidopyrazoline-3-carboxylate*,  $C_7H_{11}O_3N_2$ , m. p. 67—68°, which at 70° loses nitrogen, forming a compound,  $C_7H_{11}O_3N$ , m. p. 86.5—87°. Pyruvic acid and chloroacetamide yield  $\alpha$ -*chloroacetamidopropionic acid*, m. p. 163—165° (corr.), catalytically reduced to *chloroacetyl-dl-alanine*, m. p. 127° (corr.), and  $\alpha$ -*di(chloroacetamido)propionic acid*, m. p. 199° (corr.). Chloroacetamidopropionic acid with ammonia forms *glycyldehydroalanine*, m. p. 192—193° (decomp.), which is hydrolysed by pancreatin (Merck).

XXXII.  $\alpha$ -*Diacetamidopropionic acid* with acetic anhydride gives an azlactone, 2:4-*dimethyl-4-acetamido-oxazolin-5-one*,  $C_7H_{10}O_3N_2$ , m. p. 152° (corr.), yielding *diacetamidopropionamide*, decomp. 222°, with methyl-alcoholic ammonia. The azlactone may be used for the synthesis of pyruvylamino-acids. With glycine it yields *diacetamidopropionylglycine* (+EtOH), decomp. 215° (corr.) [*ethyl ester*, m. p. 179° (corr.)]. The latter acid or ester on acid hydrolysis yields pyruvylglycine. The azlactone combines with *dl*-phenylalanine (as sodium salt) to form  $\alpha$ -(*diacetamidopropionyl*)-*dl*-phenylalanine, m. p. 219—220° (corr., decomp.) [*methyl ester*, m. p. 196° (corr.)], which on acid hydrolysis yields *pyruvyl-dl-phenylalanine*, m. p. 94° [*phenylhydrazone*, m. p. 115—118° (corr.)]. The pyruvylamino-acids show characteristic colour reactions.

XXXIII. A case of substitutional activation of the acid amide group such as is present in peptides is furnished by the azlactone of  $\alpha$ -*diacetamidopropionic acid*, which is sensitive to the action of alcohol (methyl, ethyl, or butyl) and yields  $\alpha$ -*amino- $\alpha$ -acetamidopropionic acid*, m. p. 163—165° (corr., decomp.). The latter with mineral acids yields pyruvic acid, ammonium salt, and acetic acid. Acetylation by means of keten yields  $\alpha$ -*diacetamidopropionic acid*. Benzoyl chloride gives  $\alpha$ -*acetamido- $\alpha$ -benzamidopropionic acid*, decomp. 186—187°.

J. H. BIRKINSHAW.

**Hydroxyamino-compounds which show the biuret reaction. V. Synthesis of isoseryl-glycine.** M. TOMITA and J. KARASHIMA (Z. physiol. Chem., 1930, 187, 238—240; cf. A., 1928, 1363).— $\beta$ -Chlorolactyl chloride, prepared by the action of thionyl chloride on chlorolactic acid, combines with glycine to form  $\beta$ -*chlorolactylglycine*, m. p. 105°. Treatment of the latter with aqueous ammonia followed by silver oxide yields *isoseryl-glycine*, m. p. 224° (decomp.), which gives the biuret reaction.

J. H. BIRKINSHAW.

**Selenium derivatives of aliphatic acids.** A. FREDGA (Svensk Kem. Tidskr., 1930, 42, 66—71).— $\alpha$ -Selenocyanoisovaleric acid, m. p. 109—110°,  $k^{25}_{25} 2.59 \times 10^{-3}$ , prepared by the method previously described (A., 1929, 426, 1285) from  $\alpha$ -bromoisovaleric acid, is converted by prolonged treatment with dilute mineral acid into diselenodi- $\alpha$ -isovaleric acid, m. p. 122—123°. Oxidation of this with hydrogen peroxide in presence of barium carbonate and subsequent removal of barium with sulphuric acid afford  $\alpha$ -selenoisovaleric acid, m. p. 111° (decomp.).  $\beta$ -Seleninopropionic acid, m. p. 108° (decomp.) (silver salt), is prepared by oxidation of diselenodi- $\beta$ -propionic acid (*loc. cit.*) with hydrogen peroxide in an acetone solution. H. BURTON.

**Manufacture of carbamide and substitution products thereof.** I. G. FARBEIND. A.-G.—See B., 1930, 275.

**Complex cyanides. IV. Compounds of heavy metals with chromicyanic acid.** H. REIHLEN and F. KRAUT (Annalen, 1930, 478, 219—234).—The behaviour of chromicyanic acid with heavy metals is analogous to that of ferri- and cobalti-cyanic acids (cf. A., 1929, 432, 1430); the only difference is that in chromicyanides the stability of the polynuclear complexes is less, *i.e.*, the tendency to form true salts is greater. Combination of the ion of a heavy metal and a metal hexacyanide ion leads in general to the formation of a compound such as  $[\text{Fe}^{\text{III}}(\text{CN})_6\text{Zn}^{\text{II}}]\text{K}_2$  which contains a polynuclear complex or "individual group." Interaction of such a compound in hot solution with a zinc salt yields, not a zinc salt of the complex ion, but a compound,  $\text{K}_2\{[\text{Zn}(\text{CN})_6\text{Fe}^{\text{III}}_2\text{Zn}]\}$ , a new complex being formed. This ability to add on atoms to the complex is illustrated by the preparation

of the compound  $[\text{Fe}^{\text{III}}(\text{CN})_6\text{Fe}^{\text{III}}_2\text{Fe}^{\text{O}}\text{SCN}]\cdot 30\text{H}_2\text{O}$  from sodium ferricyanide and ferric thiocyanate, in which addition occurs to the non-ionised compound,  $[\text{Fe}^{\text{III}}(\text{CN})_6\text{Fe}^{\text{III}}]$ . The constitution of compounds containing polynuclear complexes is deduced from their behaviour with ammonia, when the number of ammine-forming heavy metal atoms united by ionised linkings is equal to or less than the number of ammonia molecules added, divided by the co-ordination number of the heavy metal. The compound  $[\text{Cr}(\text{CN})_6\text{Cd}]_2[\text{Cd}(\text{NH}_3)_6]\cdot 12\text{H}_2\text{O}$  is an example of the type of compound formed. It is produced by the interaction of ammonium chromicyanide with a cadmium salt in presence of ammonia and ammonium salts, and is converted into the tetrammine salt when dried over sulphuric acid. The corresponding nickel compound,  $[\text{Cr}(\text{CN})_6\text{Ni}]_2[\text{Ni}(\text{NH}_3)_6]\cdot 12\text{H}_2\text{O}$ , is obtained similarly, and likewise yields a tetrammine salt. The chromicyanide compounds differ particularly in their behaviour when the ammonia and hydroxyl-ion concentrations are increased; when cadmium chromicyanide is treated with 12.5*N*-ammonia solution the individual group of the above cadmium hexammine salt is attacked with the formation of the compound  $[\text{Cr}(\text{CN})_6]_2[\text{Cd}(\text{NH}_3)_4]_3\cdot \text{H}_2\text{O}$ . "True" chromicyanides such as this are, however, unstable, and it loses ammonia over sulphuric acid to yield the tetrammine salt of the binuclear com-

plex. Attempted preparation of the hexammine chromicyanide by treating cadmium chromicyanide with ammonia solution saturated at  $-15^\circ$  yields mixed crystals of the composition 3(hexammine salt), 2(tetrammine salt),  $12\text{H}_2\text{O}$ , and mixed crystals of the composition 3(tetrammine salt), (hexammine salt),  $8\text{H}_2\text{O}$  are obtained by decomposition of cadmium chromicyanide with 3—4*N*-ammonia solution and ammonium sulphate solution. The ability of the chromicyanide group to add more than one cadmium atom by non-ionised linkings has been shown by the preparation of a basic cadmium compound of the composition  $\{\text{Cr}(\text{CN})_6\}_3\text{Cd}_7(\text{OH})_5\cdot 12\text{NH}_3\cdot \text{H}_2\text{O}$  by the action of excess of a cadmium salt on potassium chromicyanide ( $\text{Cr}:\text{Cd}=1:2$ ) in 1.25—2.5*N*-ammonium hydroxide solution. The presence of  $12\text{NH}_3$  indicates that there are three  $[\text{Cd}(\text{NH}_3)_4]^+$  ions, and consequently the compound is formulated with a sexavalent anion:

$\{[(\text{OH})_2\text{Cd}(\text{CN})_6\text{Cr}]_3\text{Cd}\{[\text{Cr}(\text{CN})_6\text{CdOH}\cdot \text{H}_2\text{O}]\}[\text{Cd}(\text{NH}_3)_4]_3\}$ . If the ratio  $\text{Cr}:\text{Cd}$  is decreased to 1:1.5 the compound  $\{[(\text{OH})_2\text{Cd}(\text{CN})_6\text{Cr}]_3\text{Cd}\}[\text{Cd}(\text{NH}_3)_4]_2(\text{NH}_4)_3\cdot 2\text{H}_2\text{O}$ , with a septavalent anion, is formed as a consequence of the higher hydroxyl-ion concentration. An analogous basic zinc compound,  $[\text{HO}\cdot \text{H}_2\text{O}\cdot \text{Zn}(\text{CN})_6\text{Cr}]\text{Zn}\{[\text{Cr}(\text{CN})_6\text{Zn}(\text{OH})_2]_2[\text{Zn}(\text{NH}_3)_4]_2(\text{NH}_4)_3\}$ , with a sexavalent anion is formed when "ordinary" zinc chromicyanide is dissolved in dilute ammonia and most of the excess of ammonia removed over sulphuric acid. The "ordinary" chromicyanides obtained in non-ammoniacal neutral or acid solutions probably contain anions which are of this type or more complex, but with aquo-groups replacing the hydroxyl groups. Both potassium and cadmium salts, which differ little in solubility, are formed simultaneously. The potassium salt,  $\{[\text{Cd}(\text{CN})_6\text{Cr}]_3\text{Cd}\}\text{K}\cdot 19\text{H}_2\text{O}$ , is obtained pure by precipitation from hot solutions in which  $\text{Cr}:\text{Cd}=2:3$ , the resultant proportion of cadmium to potassium ions being 1:16. The cadmium salt,  $\{[\text{Cd}(\text{CN})_6\text{Cr}]_3\text{Cd}\}_2\text{Cd}\cdot 72\text{H}_2\text{O}$ , is prepared by digesting the precipitate obtained in the cold with cadmium sulphate solution. Precipitation of chromicyanides in the cold gives mixtures of the potassium and cadmium salts of both the bimolecular complex anions and the multivalent anions. R. K. CALLOW.

#### Constitution of aliphatic diazo-compounds.

H. LINDEMANN, A. WOLTER, and R. GROGER (Ber., 1930, 63, [B], 702—715; cf. A., 1928, 937).—An attempt is made by means of the parachor to decide between the constitutions  $\text{R}_2\text{C} < \text{N} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$ ,  $\text{R}_2\text{C} - \text{N}^+ \equiv \text{N}^-$ , and

$\text{R}_2\text{C} = \text{N} = \text{N}$  for aliphatic diazo-compounds; the structure  $\text{R}_2\text{C}:\text{N}:\text{N}$  is regarded as incompatible with the octet theory. The following data are recorded: diazoacetone,  $d_4^{20}$  1.068,  $\gamma$  35.4; methyl diazoacetate,  $d_4^{24}$  1.158,  $\gamma$  33.3; ethyl diazoacetate,  $d_4^{21}$  1.088,  $\gamma$  31.5; *n*-butyl diazoacetate, b. p.  $73^\circ/14$  mm.,  $54^\circ/1.5$  mm.,  $d_4^{20.5}$  1.023,  $\gamma$  30.3; ethyl diazosuccinate,  $d_4^{18}$  1.127,  $\gamma$  33.9; methyl diazoacetoacetate, b. p.  $64^\circ/0.2$  mm.,  $d_4^{22.5}$  1.177,  $\gamma$  35.7; ethyl diazoacetoacetate,  $d_4^{19}$  1.136,  $\gamma$  33.4; diazoacetylacetone, b. p.  $61^\circ/0.7$  mm.,  $d_4^{21}$  1.145,  $\gamma$  38.9; methyl diazomalonate, b. p.  $98^\circ/11$  mm.,  $63^\circ/1$  mm.,  $d_4^{20.5}$  1.287,  $\gamma$  38.2; ethyl diazomalonate,  $d_4^{19}$  1.172,  $\gamma$  33.4.

The theoretical values of the parachor are calculated as in the case of the azides (*loc. cit.*). The differences between the calculated values for the cyclic and open structures are not great and individual determinations fall between the two groups, but for the ten compounds the cyclic structure is most closely in harmony with the observed data (cf. Sidgwick, A., 1929, 805). This conclusion is not compatible with the existence of optically active diazosuccinic esters, since the cyclic structure possesses no centre of symmetry. Repetition of the work of Levene and Mikeska (A., 1921, i, 233; 1922, i, 818; 1923, i, 663) and of Kendall and Noyes (A., 1926, 1134) yields a more highly dextrorotatory compound than any obtained previously. The presence of ethyl malate in amount sufficient to account for the activity is excluded by the analytical data. Since agitation with hydrochloric acid does not influence the rotation, it cannot be due to ethyl aminosuccinate or a 4-piperidone-2:3:6-tricarboxylic ester. The conclusion is therefore reached that the aliphatic diazo-compounds are equilibrium mixtures of much cyclic and little open forms. Determination of refractive index shows all these compounds to exhibit marked exaltations due, in part, to the complex  $\text{>C} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$ , but in some cases

(diazoacetone, diazoacetylacetone) so considerable as to be understandable only on the hypothesis of the presence of an open form with normal conjugations.

The observed value of the parachor for the diazomalonates is considerably less than that calculated for a three-membered ring structure. On account of their comparatively slight reactivity, the structure

$\text{OR} \cdot \text{C} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} \text{N} \text{ has been proposed for them, but a comparison of the absorption curves of ethyl diazo-succinate and diazomalonate in alcohol lends no support to this formulation.}$   
H. WREN.

**Interaction between alkyl Grignard reagents and antimony trichloride.** W. J. C. DYKE, W. C. DAVIES, and W. J. JONES (J.C.S., 1930, 463—467).—The interaction of alkyl Grignard reagents with antimony trichloride yields as principal product the trialkylstibine in a 60—70% yield, some hydrocarbon produced by action of magnesium on the alkyl halide, a little trialkylstibine oxide in spite of precautions to exclude air, and metallic antimony from the reduction of antimony trichloride by the stibine. The trialkylstibines combine vigorously with oxygen and are liable to ignite spontaneously in the air. With the halogens they combine quantitatively to dihalides, but with alkyl halides reaction is slow; coloured compounds are not produced with carbon disulphide. *Tri-n-propylstibine*, b. p. 100°/25 mm.,  $d_4^{25}$  1.241; *tri-n-butylstibine* (prepared but not characterised by Morgan and Yarsley, A., 1925, i, 378), b. p. 131°/12 mm.,  $d_4^{25}$  1.191; *triisobutylstibine*, yellow, b. p. 135°/31 mm.,  $d_4^{25}$  1.323; *tri-n-amylstibine*, b. p. 168°/16 mm.,  $d_4^{25}$  1.136; *tri-dl-β-methylbutylstibine*, b. p. 150°/14 mm.,  $d_4^{25}$  1.242; *triisocamylstibine*, yellow, b. p. 149°/14 mm.,  $d_4^{25}$  1.227; *tri-n-hexylstibine*, b. p. 190°/10 mm. (decomp.).  
H. A. PIGGOTT.

**Methyltetramethylene and its transformations.** N. A. ROZANOV (J. Russ. Phys. Chem. Soc., 1929, 61,

2291—2302).—The action of fuming hydrobromic acid on methyltetramethylene yields principally β-bromopentane, which is converted into Δ<sup>2</sup>-pentene by treatment with alcoholic potassium hydroxide. The action of fuming hydriodic acid on the hydrocarbon gives a compound which was not obtained pure, but is apparently β-iodopentane, and that of bromine yields αδ-dibromopentane. The action of sulphuric acid on methyltetramethylene gives mainly pentan-β-ol and possibly small proportions of β- and γ-methylbutan-δ-ols; polymerised non-alcoholic compounds are also formed. Nitric acid gives succinic acid, whilst reduction of the hydrocarbon by hydrogen in presence of freshly-reduced nickel yields β-methylbutane.

When passed over alumina at 400°, the hydrocarbon undergoes isomerisation and polymerisation, the principal product being γ-methyl-Δ<sup>2</sup>-butene, which is formed by way of β-methylbutan-δ-ol (cf. Dojarenko, A., 1927, 138, 871); Δ<sup>2</sup>-pentene and β-methyl-Δ<sup>2</sup>-butene are also formed. Similar changes occur when thorium oxide at 350° is used as catalyst.

The value found for the molecular refraction of methyltetramethylene confirms the value 0.46 for the increment for a four-membered ring. In the case of ethyltetramethylene the increment is 0.09 (cf. Eisenlohr, "Spectrochemie organischer Verbindungen"; Zelinski, A., 1908, i, 15). By investigation of the azine of cyclobutaldehyde (this aldehyde being an intermediate compound in the preparation of methyltetramethylene), the refractive coefficient of the azine group is found to be 6.25; the mean of this and of the values obtained by the author for two other azines is 6.28.  
T. H. PORE.

**spirocycloDecane and its catalytic isomerisation.** N. D. ZELINSKI and N. I. SCHUIKIN (J. Russ. Phys. Chem. Soc., 1929, 61, 2245—2252).—See A., 1929, 1287.

**Catalytic hydrogenation of unsaturated compounds.** V. Hydrogenation of cyclic ethylenic derivatives and of their mixtures. S. V. LEBEDEV and M. S. PLATONOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2151—2174, and J.C.S., 1930, 321—336).—Study of the hydrogenation curves of a number of ethylenic derivatives, mainly those with a double linking in a cyclohexane ring, and of about 40 mixtures of such compounds with one another and with open-chain ethylenic derivatives gives results which conform to the general rules followed by the hydrogenation of open-chain ethylenic compounds alone. Cyclo disubstituted ethylenic derivatives are hydrogenated more readily than trisubstituted ones and these more readily than tetrasubstituted ones. Mixtures of cyclic ethylenic derivatives of similar degrees of substitution are hydrogenated at a common rate, the hydrogenation curves being continuous. The components of mixtures of cyclic ethylenic derivatives of different degrees of substitution are hydrogenated successively in the order stated above. The curves for such mixtures always have a break, which corresponds closely with the end of the hydrogenation of the first component and often coincides with a minimum velocity of reaction. Moreover, the different parts of the curve do not differ essentially from the individual curves for

the separate components, but the actual velocity of hydrogenation of any component may be greatly changed in a mixture.

The hydrogenation of mixtures of cyclic with open-chain ethylenic derivatives of the same degree of substitution proceeds as follows. In mixtures of cyclic with open-chain (*s*- or *as*-) disubstituted compounds, the components are hydrogenated simultaneously, the curves being continuous. In mixtures of cyclic with open-chain trisubstituted compounds, the latter are hydrogenated first owing to their more ready absorption by platinum-black; hence the curves show pronounced breaks. In a mixture of a cyclic with an open-chain tetrasubstituted compound, the latter is hydrogenated far more rapidly than the former.

Consecutive hydrogenation occurs also with a mixture of a cyclic with an open-chain ethylene derivative having a different degree of substitution, the component with the lower degree being hydrogenated first. The curves for mixtures of disubstituted cyclic or open-chain (*s*- or *as*-) compounds with cyclic tri- or tetra-substituted compounds show much sharper breaks than those for mixtures of the disubstituted compounds with open-chain tri- or tetra-substituted compounds. In mixtures containing one component with a conjugated system of double linkings, divergences from the above regularities occur. Anhydrides of maleic and citraconic acids, unlike the acids themselves, are toxic to platinum-black.

Examination of the hydrogenation curves of ethylenic derivatives and of mixtures of these with ethylenic derivatives of known structure may give indications concerning the individuality and structure (degree of substitution at the double linking) of the former. To determine the structure of cyclic ethylenic derivatives by the method of hydrogenation, this must be carried out on mixtures of the compounds with known cyclic compounds. T. H. POPE.

**Absorption of ozone by benzenoid and acetylenic systems.** G. BRUS and G. PEYRESBLANQUES (Compt. rend., 1930, 190, 685—686; cf. this vol., 449).—Even when in large excess benzene and its homologues do not absorb ozone completely. Substances of the type of styrene and phenylcyclohexene add ozone first at the ethylenic double linking, and only when this addition is complete is the nucleus attacked. Acetylenic compounds are intermediate between ethylenic and benzenoid compounds in their behaviour towards ozone, and ozonisation curves may be used to distinguish sharply between these three classes of compounds. These conclusions are contrasted with those of Molinari (cf. A., 1907, i, 1039; Harries, A., 1908, i, 75). H. A. PIGGOTT.

***p*-Divinylbenzene and *p*-diacetylenylbenzene.** LESPIEAU and DELUCHAT (Compt. rend., 1930, 190, 683—684).—*p*-Divinylbenzene, obtained by distilling *p*-di- $\alpha$ -bromoethylbenzene with quinoline (Ingle, A., 1894, i, 589), has been obtained crystalline, m. p. 31°, b. p. 52°/4 mm.,  $d_4^{20}$  0.913,  $n_D^{20}$  1.5820. It rapidly polymerises to an amorphous powder insoluble in the usual solvents, which becomes yellow and decomposes when heated. The tetrabromo-derivative (Ingle, loc. cit.) yields with alcoholic potassium hydroxide *p*-diacetylenylbenzene, m. p. 95°, stable in the dark but turning

violet in light. Ammoniacal cuprous chloride and ammoniacal or alcoholic silver nitrate yield yellow precipitates, the silver salt exploding at 280°.

H. A. PIGGOTT.

**Preparation and application of higher esters of *p*-toluenesulphonic acid.** R. K. SLOTTA and W. FRANKE (Ber., 1930, 63, [B], 678—691).—Technical *p*-toluenesulphonyl chloride is freed from *p*-toluenesulphonic acid and hydrogen chloride by agitation with water at 100°. It is converted by boiling hydrochloric acid into *p*-toluenesulphonic acid, m. p. (monohydrate) 106°, m. p. (anhydrous) 38°; the formation of a tetrahydrate is not observed. *n*-Propyl *p*-toluenesulphonate, b. p. 182°/18 mm., 178°/13 mm., is obtained in 74% yield by gradually heating a mixture of 1 mol. of chloride and 1.2 mols. of the alcohol to a temperature not exceeding 125°; the hydrogen chloride liberated during the change is removed continuously in a current of air. The crude material contains 4—8% of di-*n*-propyl ether; it is better used as such, since slight decomposition during distillation involves the presence of 2—5% of *p*-toluenesulphonic acid in the distillate. *n*-Butyl *p*-toluenesulphonate, b. p. 146°/1 mm., is prepared similarly, but with addition of anhydrous sodium carbonate; the crude product contains di-*n*-butyl ether and 95% of ester.

Phenol in presence of aqueous sodium hydroxide is etherified by the *n*-propyl ester to the extent of 30%, whilst in presence of acetone and potassium carbonate phenol and  $\beta$ -naphthol afford 70% of ether. Otherwise it is necessary to operate in alcoholic solution on the water-bath in presence of potassium hydroxide. The following data are recorded: phenyl *n*-propyl ether, b. p. 106°/60 mm., 189°/760 mm., *n*-butyl ether, b. p. 92—94°/17 mm., 206°/760 mm.; *o*-tolyl *n*-propyl ether, b. p. 92°/18 mm., 201°/750 mm.;  $\alpha$ -naphthyl *n*-propyl ether, b. p. 166—167°/18 mm., 285°/760 mm., *n*-butyl ether, b. p. 174°/20 mm., 310°/760 mm.;  $\beta$ -naphthyl *n*-propyl ether, b. p. 167°/17 mm., m. p. 40°, *n*-butyl ether, b. p. 162°/9 mm., m. p. 35°. Pyrocatechol when treated with a molecular quantity of alkyl *p*-toluenesulphonate and 0.95 mol. of potassium hydroxide rapidly gives a 50% yield of the mono-ether, which passes slowly into the dialkyl compound; the di-*n*-propyl, b. p. 117—120°/12 mm., 234—237°/760 mm., *n*-propyl, b. p. 110°/15 mm., 219—222°/741 mm., di-*n*-butyl, b. p. 135—138°/12 mm., 241—243°/765 mm., and *n*-butyl, b. p. 127°/17 mm., 239°/760 mm., ethers are described. Alkylation at the sulphur atom is effected by heating with the calculated amounts of ester and alkali hydroxide, frequently without solvent, in about 80% yield. *p*-Tolyl *n*-propyl sulphide, b. p. 128—133°/20 mm., 242°/743 mm., *p*-tolyl *n*-butyl sulphide, b. p. 142—145°/18 mm., and di-*p*-tolyl disulphide, m. p. 47—48°, are described.

Primary aromatic amines give dialkylamines in yield up to 80% from 1 mol. of base, 2 mols. of ester, and 2 mols. of potassium hydroxide, and monoalkylamines from 2 mols. of base and 1 mol. of ester, whereby the *p*-toluenesulphonate of the base is also produced. The propyl- and butyl-anilines are described.  $\beta$ -Naphthylamine gives *n*-propyl- $\beta$ -naphthylamine, b. p. 198—200°/20 mm., di-*n*-propyl- $\beta$ -naphthylamine, b. p.



205—210°/17 mm., 330°/743 mm. (*picrate*, m. p. 165°), *n*-butyl- $\beta$ -naphthylamine, b. p. 195—196°/12 mm. (*hydrochloride*, m. p. 192° after softening at 186°), and *di*-*n*-butyl- $\beta$ -naphthylamine, b. p. 198—202°/12 mm., 354°/759 mm. (*picrate*, m. p. 151°);  $\beta$ -naphthylamine *p*-toluenesulphonate, m. p. 218°, is incidentally described. 2-Aminopyridine, in presence of ether and sodamide, is readily propylated, but di-butylated only to a small extent. 2-*Di*-*n*-propylaminopyridine, b. p. 130—131°/17 mm. (*picrate*, m. p. 138·5°), 2-propylaminopyridine, b. p. 145—160°/21 mm. (*picrate*, m. p. 163°), 2-butylaminopyridine, b. p. 124—126°/16 mm., m. p. 45° (*picrate*, m. p. 138°), and 2-*di*-*n*-butylaminopyridine, b. p. 163°/20 mm. (*picrate*, m. p. 136—137°), are described.

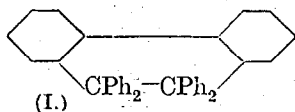
The applicability of the propyl ester to *C*-alkylation is shown in the instance of ethyl malonate.

H. WREN.

Separation of xylenes. III. Isolation of *o*-xylene from its isomerides. A. NAKATSUCHI (J. Soc. Chem. Ind. Japan, 1930, 33, 65—66B).—The solubilities at 25° of calcium and sodium *m*-, *o*-, and *p*-xylenesulphonates are 32·67, 21·91, 11·81, 64·73, 26·68, and 20·02 g. per 100 g. of water, respectively. The solubilities of calcium and sodium *p*-xylene-sulphonates in saturated aqueous solutions of calcium and of sodium *o*-xylenesulphonates have also been measured at 25°. Pure *o*-xylene was obtained from solvent naphtha by fractional distillation, selective hydrolysis of xylenesulphonic acids, and fractional crystallisation of the xylenesulphonates. Sodium *o*-xylenesulphonate is decomposed by sulphuric acid at 160°.

A. I. VOGEL.

Polyphenyl substituted derivatives of *oo'*-ditolyl. II. P. G. SERGEEV (J. Russ. Phys. Chem. Soc., 1929, 61, 1421—1449; cf. A., 1926, 610).—A detailed account of the attempts to synthesise the hydrocarbon (I), which, however, could not be obtained. The hydrocarbon [ $\text{C}_6\text{H}_4\cdot\text{CHPh}_2$ ]<sub>2</sub>, m. p. 236—237°, on bromination in sun-



light, yielded a dark brownish-red *dibromide*, [ $\text{C}_6\text{H}_4\cdot\text{CPh}_2\text{Br}$ ]<sub>2</sub>, m. p. 192—194°, which was hydrolysed in aqueous alcohol to the carbinol

$\text{C}_6\text{H}_4\cdot\text{CPh}_2\text{OH}$ . This carbinol can also be obtained by Grignard's method from magnesium phenyl bromide and methyl 9:9'-diphenylfluorene-carboxylate or benzoyldiphenylfluorene,

$\text{C}_6\text{H}_4\cdot\text{CPh}_2\text{Bz}$  [which is formed (*loc. cit.*) from the keto-carbinol  $\text{C}_6\text{H}_4\text{Bz}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$  or

$\text{C}_6\text{H}_4\cdot\text{CPh}_2\text{OH}$  by the action of acid reagents].

The dibromide was very unstable, and could not be hydrolysed to give either the glycol or the corresponding oxide. Another method of obtaining the hydrocarbon started with the carbinol,  $\text{CHPh}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$ , or its *bromide*. The carbinol was synthesised by Grignard's method from the lactone of *o*-benzhydryl-diphenyl-*o'*-carboxylic acid, m. p. 178—179°. The acid itself was obtained by Grignard's method from diphenic anhydride and magnesium phenyl bromide,

when *o*-diphenylmethylol-*o'*-carboxylic acid, m. p. 220—221°, giving a lactone, m. p. 189—190°, on dehydration, was obtained as an intermediate product, and could be reduced by halogen acids to yield a 9:9'-diphenylfluorene-5-carboxylic acid, m. p. 256—257°, which could be made to lose carbon dioxide and yield 9:9'-diphenylfluorene. The formation and behaviour of this acid indicated that a similar reaction might take place by reduction of the glycol, [ $\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{OH}$ ]<sub>2</sub>, and that instead of the hydrocarbon, [ $\text{C}_6\text{H}_4\cdot\text{CHPh}_2$ ]<sub>2</sub>, m. p. 236—237°, a mixture of hydrocarbons of the structure  $\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_3\cdot\text{CHPh}_2$  is formed.

By boiling the carbinol with hydriodic acid, the above hydrocarbon (5-benzhydryl-9:9'-diphenylfluorene, m. p. 219—220°), was obtained, identical with the reduction product of the fluorene-carbinol, m. p. 252—253°,  $\text{C}_6\text{H}_4\cdot\text{CPh}_2\cdot\text{C}_6\text{H}_3\cdot\text{CPh}_2\cdot\text{OH}$ , prepared by Grignard's method from the ester of 9:9'-diphenylfluorene-5-carboxylic acid. All other attempts to synthesise the hydrocarbon yielded only benzhydryl-diphenylfluorene.

M. ZVEGINTZOV.

New method of preparing free radicals of the triarylmethyl series. A. E. ARBUSOV and B. A. ARBUSOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1923—1931; cf. A., 1929, 1053).—The action of triaryl bromides on sodium diethyl phosphite in ether was investigated. Triphenylmethyl bromide and sodium diethyl phosphite gave instead of the expected ester of the substituted phosphinic acid, an orange solution of free triphenylmethyl, which deposited the peroxide, m. p. 186°. If diphenyl- $\alpha$ -naphthylmethyl bromide or didiphenylphenylmethyl bromide were used instead of triphenylmethyl bromide, the corresponding diphenyl- $\alpha$ -naphthylmethyl and didiphenylphenylmethyl were obtained. Distillation of the mother-liquor yielded a liquid, b. p. 146—149°, of a sky-blue colour, becoming yellow on keeping, which, it is suggested, is the free radical diethylphosphone,  $\text{PO}(\text{OEt})_2$ .

M. ZVEGINTZOV.

Reduction of triphenylhalogenomethanes. J. C. THOMAS, S. T. BOWDEN, and W. J. JONES (J.C.S., 1930, 473—478).—Cadmium, thallium, lead, tin, arsenic, antimony, bismuth, selenium, tellurium, and iron react with triphenyl-chloro- and -bromo-methanes in benzene, toluene, and ether. The rate of reaction varies considerably, iron being most and lead least reactive. Triphenylchloromethane is not attacked by cobalt or nickel, and only slightly attacked by manganese and chromium in benzene, toluene, bromobenzene, hexane, or ether; in *n*-hexane reduction is effected by few metals only, and even with mercury or silver is much slower than in benzene. It is suggested that the influence of the solvent is due to either one or both of two factors, viz., dissolution or disintegration of the metallic halide, and the effect of the solvent on the molecular state of the halide in solution and on the metal-solution interfacial phenomena.

Triphenylbromomethane is rapidly reduced by zinc and tin, the metallic bromide produced forming with unchanged initial material highly coloured additive compounds. Finely-divided iron with triphenyl-

chloromethane in benzene solution produces a greenish-yellow solution which does not contain free triphenylmethyl; possibly it is present as a ferrous chloride complex. Aluminium, when pure, seems to be without action on triphenylchloromethane in benzene, although the technical metal reacts to form an aluminium chloride double compound. Cobalt, manganese, and chromium reduce triphenylchloromethane in acetone solution completely to triphenylmethyl, although in the other solvents no action occurs. Calcium is quite non-reactive in all solvents with the possible exception of acetone; magnesium reacts well only in ethereal solution, and then forms magnesium triphenylmethyl chloride.

Triphenylbromomethane reacts slowly with acetone in the cold, triphenylcarbinol being isolated in small yield. It also forms additive products with aluminium bromide,  $\text{CPh}_3\text{Br}\cdot\text{AlBr}_3$ , m. p. 120—123°, zinc bromide,  $\text{CPh}_3\text{Br}\cdot\text{ZnBr}_2$ , a dark red oil, and stannic bromide,  $\text{CPh}_3\text{Br}\cdot\text{SnBr}_4$ , m. p. 171°. H. A. PIGGOTT.

**Organo-alkali compounds.** IV. Electrolytic character of organo-alkali compounds. K. ZIEGLER and H. WOLLSCHITT. V. Synthesis of simple lithium alkyls. K. ZIEGLER and H. COLONIUS. VI. Mode of reaction of solid alkali metals. K. ZIEGLER and O. SCHÄFER (Annalen, 1930, 479, 123—134, 135—149, 150—179).—IV. The conductivity of solutions of sodium triphenylmethyl in ether approaches with dilution a minimum value of about  $0.5 \times 10^{-2}$  at 0° (cf. Schlenk and Marcus, A., 1914, i, 823). The conductivity is much greater in pyridine solution, and also increases with dilution. The conductivity-volume curves for sodium and potassium triphenylmethyl (from triphenylmethane and potassium phenylisopropyl) and sodium *pp'*-trinitrotriphenylmethyl are very similar. These sodium derivatives behave as heteropolar, strongly dissociated salts. The use of pyridine as a solvent is, however, limited, since an unexplained reaction occurs with many alkali compounds. Treatment of an ethereal solution of sodium triphenylmethyl with a small amount of pyridine gives a sparingly soluble, red, pyridine additive compound. The remainder of the paper is a criticism of Schlenk and Bergmann's explanation (A., 1928, 1035) of the addition of sodium and lithium to stilbene and isostilbene.

V. Lithium *n*-butyl reacts with *n*-butyl halides much more readily in ether than in benzene; reaction is fastest with the iodide and slowest with the chloride. Little reaction occurs with halogenobenzenes in either solvent. When an ethereal solution of *n*-butyl chloride or bromide (not iodide) is treated with lithium, lithium *n*-butyl is obtained in 50—60% and 15% yield, respectively. The yield is improved considerably when benzene is used as the solvent. Lithium and bromobenzene in benzene afford 75% of lithium phenyl. When lithium *n*-butyl in cyclohexane solution is shaken with mercury, mercury dibutyl is formed. The reaction between mercury dibutyl and lithium is reversible (cf. Schlenk and Holtz, A., 1917, i, 255). A similar decomposition does not occur with 40% sodium amalgam. Lithium alkyls could not be prepared by Spencer and Price's method (J.C.S., 1910, 97, 385).

VI. When *as*-diphenylethylene is treated with sodium in presence of ether and 2 mols. of indene two reactions occur: (a) the formation of  $\alpha\alpha\delta$ -tetraphenylbutane and sodium indene, (b) the production of *as*-diphenylethane and sodium indene. Reaction a occurs only to the extent of 20%. Two atoms of sodium are used and reaction b does not proceed by the reduction of the ethylene with hydrogen liberated from sodium and indene (under the experimental conditions used these substances undergo practically no reaction). These results support the previously proposed mechanism (A., 1929, 1092) of the addition of sodium to *as*-diphenylethylene. *as*-Diphenylethane and potassium phenylisopropyl react, yielding potassium  $\alpha\alpha$ -diphenylethyl, decomposed by carbon dioxide to  $\alpha\alpha$ -diphenylpropionic acid. Treatment of benzylidenedianiline with sodium in presence of indene furnishes benzylaniline, m. p. 36° (lit. 32°), and sodium indene; some 1- $\alpha$ -anilinobenzylindene, m. p. 248°, is formed as a by-product.  $\alpha\gamma\gamma$ -Triphenyl- $\Delta^{\alpha}$ -butenoic acid is obtained by decomposition of the reaction product from  $\alpha\gamma$ - or  $\alpha\gamma\gamma$ -triphenyl- $\Delta^{\alpha}$ -propylene and potassium phenylisopropyl.

The following is included in a reply to Schlenk and Bergmann's criticism (see below) of Ziegler's view of the addition of sodium to *as*-diphenylethylene. When disodiotriphenylethane is treated with liquid ammonia and then with methyl iodide,  $\alpha\beta$ -triphenylpropane is produced. This proves the intermediate formation of the compound  $\text{CNaPh}_2\cdot\text{CH}_2\text{Ph}$ . Decomposition of the product formed from sodium  $\alpha\alpha$ -diphenylethyl (prepared from the corresponding methyl ether) and  $\alpha\alpha$ -diphenyl- $\Delta^{\alpha}$ -propylene with carbon dioxide gives  $\alpha\alpha$ -diphenylpropionic and  $\gamma\gamma$ -diphenyl- $\Delta^{\beta}$ -butenoic acids. The last-named acid results from the change  $\text{CNaMePh}_2 + \text{CPh}_2\cdot\text{CHMe} \rightarrow \text{CHMePh}_2 + \text{CPh}_2\cdot\text{CH}\cdot\text{CH}_2\text{Na}$ .

A solution of lithium benzyl (prepared from mercury dibenzyl and lithium butyl) in ether does not alter until after one week. H. BURTON.

**Production of styrene and homologues thereof.** NAUGATUCK CHEM. CO.—See B., 1930, 276.

**Mechanism of the addition of sodium to double linkings.** W. SCHLENK and E. BERGMANN (Annalen, 1930, 479, 58—77).—Ziegler's conception (A., 1929, 1092) of the mode of addition of sodium to *as*-diphenylethylene is criticised, and held to be mainly untenable in view of the work now described. Disodiotriphenylethane and benzylidenefluorene do not undergo an additive reaction; an equilibrium mixture of the reactants, triphenylethylene, and  $\alpha\delta$ -disodio- $\beta\gamma$ -diphenyl- $\alpha\delta$ -di(diphenylene)butane is produced. A similar reaction is also observed with disodiotriphenylethane and *as*-diphenylethylene. The reaction product from lithium and  $\alpha\alpha$ -diphenyl- $\beta\beta$ -dimethylethylene (A., 1928, 1032) gives with benzyl chloride a mixture of the corresponding ethane and a hydrocarbon,  $\text{C}_{23}\text{H}_{22}$ , m. p. 85—86°, saturated towards bromine and cold chromic acid. This hydrocarbon is not  $\alpha\alpha\delta$ -triphenyl- $\beta$ -methyl- $\Delta^{\alpha}$ -butene. It is suggested that ring closure has occurred with the formation of either 1-phenyl-3-benzyl-2-methyl- or 1-phenyl-2- $\beta$ -phenylethyl-hydrindene. *as*-Diphenyldimethylethane, b. p. 158—159°/19 mm., is conveniently prepared in quantitative

yield by the successive action of sodium and isopropyl chloride on diphenylmethyl methyl ether.  $\alpha\beta$ -Triphenyl- $\gamma$ -methylbutane, b. p. 225—227°/20 mm., m. p. 80°, is prepared similarly from diphenylbenzylmethyl methyl ether. Magnesium methyl iodide and  $\beta$ -phenylpropaldehyde furnish  $\beta$ -phenylethylmethylcarbinol, b. p. 129—130°/15 mm.; the corresponding chloride decomposes on distillation in a vacuum. Successive treatment of diphenylmethyl methyl ether with sodium and benzylacetone gives diphenylmethane and  $\alpha\alpha$ -triphenyl- $\beta$ -methylbutan- $\beta$ -ol, m. p. 67°, reduced by a mixture of red phosphorus, hydriodic and acetic acids to  $\alpha\alpha$ -triphenyl- $\beta$ -methylbutane, m. p. 69°.

$\alpha\alpha$ -Diphenyl- $\beta\beta$ -dimethylethylene is considered to be capable of reacting in the tautomeric form  $\text{CPh}_2\cdot\text{CMe}\cdot\text{CH}_2$ . A similar change is suggested for dimethylfulvene (1-isopropylidenecyclopentadiene), since treatment of this with sodium triphenylmethyl in ether yields triphenylmethane; the original fulvene is isolated by decomposition of the reaction product with water. Similar results are found with 1-isopropylideneindene and 9-isopropylidene fluorene. Further evidence for such tautomerism is also furnished by the observation that  $\alpha\alpha$ -diphenyl- $\beta$ -benzylethylene is converted by treatment with sulphuric acid into 1:3-diphenylhydrindene.

Addition of a solution of benzylidene fluorene in toluene to a solution of sodium in liquid ammonia and subsequent treatment of the mixture with benzyl chloride gives 9:9-dibenzylfluorene and a small amount of  $\alpha\gamma\delta\epsilon$ -tetraphenyl- $\beta\epsilon$ -di(diphenylene)- $n$ -hexane, m. p. 304—306°. The dibenzylfluorene is formed

thus:  $\text{CR}_2\cdot\text{CHPh} \longrightarrow \text{CNaR}_2\cdot\text{CHPh} \xrightarrow{\text{NaNH}_2} \text{CNaR}_2\cdot\text{CH}_2\text{Ph} + \text{NaNH}_2$  ( $\text{R}=\text{C}_6\text{H}_4$ ). The authors consider their previously proposed mechanism for alkali metal addition (*loc. cit.*) to be satisfactory.

H. BURTON.

"Disproportionate alkali metal addition" and the mechanism of the reaction. W. SCHLENK and E. BERGMANN [with O. BLUM-BERGMANN] (Annalen, 1930, 479, 78—89).—Treatment of the reaction product (A) from  $\alpha\alpha$ -diphenyl- $\beta$ -benzylethylene and lithium (A., 1928, 1032) with benzyl chloride affords a mixture of  $\alpha\beta\delta$ -tetraphenylbutane, m. p. 172°, and  $\alpha\gamma\delta$ -tetraphenyl- $\Delta^a$ -butene, m. p. 63°. The former of these is synthesised from sodium diphenylbenzylmethyl (prepared from the corresponding methyl ether) and  $\beta$ -phenylethyl chloride or from sodium diphenyl- $\beta$ -phenylethylmethyl ( $\alpha\alpha\gamma$ -triphenylpropyl) and benzyl chloride.  $\alpha\alpha\gamma$ -Triphenylpropyl methyl and ethyl ethers have m. p. 110° and 86°, respectively. When either  $\gamma$ -methoxy- $\alpha\alpha\gamma$ - or  $\alpha\gamma\gamma$ -triphenyl- $\Delta^a$ -propene is treated first with sodium and then with benzyl chloride the same  $\alpha\gamma\delta$ -tetraphenyl- $\Delta^a$ -butene is obtained. This is reduced catalytically to  $\alpha\gamma\delta$ -tetraphenylbutane, b. p. 270—273°/21 mm. Decomposition of A with carbon dioxide gives  $\alpha\gamma\gamma$ -triphenyl- $\Delta^b$ -butenoic acid (I), m. p. 166—167°, and  $\alpha\alpha\gamma$ -triphenylbutyric acid (II), m. p. 182° after sintering at 178°. The last-named acid (with m. p. 183.5—184°) is synthesised by the successive action of sodium and carbon dioxide on  $\alpha\alpha\gamma$ -triphenylpropyl methyl ether, whilst the former is obtained similarly from either of the above methoxypropenes.  $\alpha\gamma\gamma$ -Triphenylbutyric

acid has m. p. 111—113°. When A is decomposed with phenylthiocarbimide the thioanilides of I and II, m. p. 122—124.5° and 124—126°, respectively, are obtained. These are synthesised from phenylthiocarbimide and the requisite sodium compound. Decomposition of A with diphenylmethyl bromide gives tetraphenylethane and 1:3-diphenylhydrindene. The mechanism of the initial reaction is considered to

be:  $2\text{CPh}_2\cdot\text{CH}\cdot\text{CH}_2\text{Ph} + 2\text{Li} \longrightarrow 2\text{CPh}_2\cdot\text{Li}\cdot\text{CH}\cdot\text{CH}_2\text{Ph} \longrightarrow \text{CPh}_2\cdot\text{Li}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph} + \text{CPh}_2\cdot\text{Li}\cdot\text{CH}\cdot\text{CHPh}$ . The compound  $\text{CPh}_2\cdot\text{CMe}\cdot\text{CH}_2\text{K}$  described by Ziegler (A., 1929, 1092) is considered to be  $\text{CKPh}_2\cdot\text{CMe}\cdot\text{CH}_2$ .

H. BURTON.

Relationship between the degree of saturation of the ethylenic linking and its capacity for alkali metal addition. W. SCHLENK and E. BERGMANN (Annalen, 1930, 479, 42—57).—Sodium does not combine with  $\alpha\alpha$ -di- $p$ -tolyl- $\beta\beta$ -dimethyl-,  $\alpha\alpha$ -diphenyl- $\beta$ -ethyl-, - $\beta$ - $n$ -propyl-, or - $\beta$ - $n$ -butyl-ethylenes (cf. the case of  $\alpha\alpha$ -diphenyl- $\beta$ -methylethylene; A., 1928, 1032). Consideration of the addition of sodium to aryl-ethylenes, fulvenes, styrene, and naphthalene (*loc. cit.*) leads to the conclusion that the more partial valency there exists on an ethylenic carbon atom, the smaller is its capacity for the addition of an alkali metal. Conversely, addition is facile when the amount of residual affinity is small (e.g., as in tetraphenylethylene).

[With S. FUJISE].—Magnesium  $p$ -tolyl bromide and ethyl isobutyrate afford di- $p$ -tolylisopropylcarbinol, m. p. 99°, converted by way of its chloride into  $\alpha\alpha$ -di- $p$ -tolyl- $\beta\beta$ -dimethylethylene, m. p. 55°.  $\alpha\alpha$ -Diphenyl- $\beta$ -ethyl-, b. p. 157—158°/14 mm., - $\beta$ - $n$ -propyl-, b. p. 174—175°/14 mm., and - $\beta$ - $n$ -butyl-ethylenes, b. p. 184°/15 mm., are prepared similarly. Diphenyl- $n$ -amylcarbinol has b. p. 199—200°/13 mm., m. p. 47°.  $\alpha$ -Methylstilbene and sodium react rapidly in ether. Decomposition of the additive compound with alcohol gives  $\alpha\beta$ -diphenylpropane, b. p. 155—157°/22 mm. Similar decomposition of the product from sodium and anisylidene fluorene affords  $\alpha\beta$ -dianisyl- $\alpha\beta$ -difluorenyl-ethane, m. p. above 300° (cf. *loc. cit.*).  $\alpha$ -Naphthaldehyde, obtained in 90% yield by acid hydrolysis of the acetal from magnesium  $\alpha$ -naphthyl bromide and ethyl orthoformate, condenses with fluorene in presence of alcoholic sodium ethoxide forming  $\alpha$ -naphthylidene fluorene, m. p. 149—150°, and some  $\alpha$ -naphthyl- $\delta$ -diphenylene- $\Delta^a\gamma$ -butadiene, m. p. 174—175°. The production of the last-named compound is probably due to the intermediate formation of acetaldehyde. Sodium and naphthylidene fluorene react slowly in ether, yielding an indigo-blue additive compound, decomposed by alcohol to 9- $\alpha$ -naphthylmethylfluorene, m. p. 135°. This is also obtained by catalytic reduction of  $\alpha$ -naphthylidene fluorene. 2:7-Dibromo- $\alpha$ -naphthylidene fluorene has m. p. 190—191°.

When phenylbenzylmethylcarbinyl chloride is heated with pyridine,  $\alpha$ -methylstilbene, m. p. 83°, and an isomeride, b. p. 167°/24 mm., are obtained. Treatment of the former hydrocarbon with bromine in carbon disulphide gives the dibromide, m. p. 132° (decomp.; lit. 127—135°), and a compound,  $\text{C}_{15}\text{H}_{13}\text{Br}_3$  (?), m. p. 85°.

Oxidation of  $\alpha\beta$ -triphenyl- $\Delta^a$ -propene by Lévy's

method (A., 1921, i, 233, 861) furnishes benzophenone, acetophenone, a compound,  $C_{26}H_{20}O$ , m. p. 175—176°, and triphenylmethyl methyl ketone, m. p. 143—144° (cf. Wieland and others, A., 1927, 237). The last-named ketone is formed from the intermediate  $\alpha\beta$ -triphenylpropane- $\alpha\beta$ -diol by a pinacol-pinacolin change; it is obtained directly from magnesium methyl iodide and benzoyldiphenylcarbinol. H. BURTON.

**Action of aromatic sulphonyl chlorides on the sodium derivatives of acetylenic hydrocarbons.** M. BOURGUEL and R. TRUCHET (Compt. rend., 1930, 190, 753—755).—Treatment of the sodium derivative of phenylacetylene with benzene- or *p*-toluene-sulphonyl chloride in presence of ether affords  $\alpha$ -chloro- $\beta$ -phenylacetylene, b. p. 71.5—72°/15 mm.,  $d_{15}^{25}$  1.126,  $n_D^{25}$  1.576, and sodium benzene- or *p*-toluene-sulphinate.  $\alpha$ -Chloro- $\Delta^a$ -heptinene, b. p. 141—142°/760 mm.,  $d_{15}^{25}$  0.918,  $n_D^{25}$  1.441, is prepared similarly from the sodium derivative of  $\Delta^a$ -heptinene. The sodium atom in sodium benzenesulphinate is considered to be attached directly to the sulphur atom. H. BURTON.

**Highly polymerised compounds. XXXV. Poly- $\alpha$ -phenylbutadiene.** H. STAUDINGER and A. A. ASHDOWN (Ber., 1930, 63, [B], 717—721; cf. this vol., 333).— $\alpha$ -Phenylbutadiene is converted by treatment with stannic chloride in cold carbon tetrachloride into a colourless, amorphous polymeride ( $C_{10}H_{10}$ )<sub>12</sub>, m. p. 140° after softening at 130°. Determination of mol. wt. in freezing benzene of the material after 4, 9, and 19 precipitations from ether by alcohol give consistent values and the product is therefore regarded as a polymeric homologous material. Like other hemicolloids it can be separated into more and less freely soluble portions. With  $\alpha$ -phenylbutadiene, polymerisation is complicated by the production of cyclic compounds and the material contains less than one double linking per unit molecule. When heated above 200° it gives liquid products of lower mol. wt. in which the presence of the monomeride cannot be established. Phenylsuccinic acid is not formed by its oxidation or ozonisation.

H. WREN.

**Substitution processes in doubly-unsaturated hydrocarbons. II.** P. W. NEBER, F. FÖHR, and P. BAUER (Annalen, 1930, 478, 197—218).—A previous investigation (A., 1926, 1119) has been extended to include the effect of substitution in the benzene ring on the position occupied by the remaining nitro-group when  $\alpha$ -cyano- $\alpha\delta$ -diphenyl- $\Delta^a$ -butadiene is treated with nitrogen peroxide and one of the two entering nitro-groups is removed by treatment with alcohol. The  $\alpha$ -*p*-nitro-, and *m*- and *p*-bromo-derivatives yield the  $\gamma$ -nitro-compounds in the same way as the unsubstituted compound. When the  $\alpha$ -cyano-group is replaced by the carbomethoxy- or nitro-group, the nitro-group is left in the  $\delta$ -position.

$\gamma$ -Nitro- $\alpha$ -cyano- $\delta$ -phenyl- $\alpha$ -*p*-nitrophenyl- $\Delta^a$ -butadiene, prepared by keeping the dinitro-compound in alcoholic solution, yields with methyl-alcoholic potassium methoxide the potassium salt of the aci-form of  $\gamma$ -nitro- $\alpha$ -cyano- $\delta$ -methoxy- $\delta$ -phenyl- $\alpha$ -*p*-nitrophenyl- $\Delta^a$ -butene, m. p. 165°, which yields with sodium hypobromite  $\gamma$ -bromo- $\gamma$ -nitro- $\alpha$ -cyano- $\delta$ -methoxy- $\delta$ -phenyl- $\alpha$ -*p*-nitrophenyl- $\Delta^a$ -butene, m. p. 129°. Decomposition

of the potassium salt by methyl-alcoholic sulphuric acid yields benzaldehyde, methyl alcohol, and  $\gamma$ -nitro- $\alpha$ -*p*-nitrophenylcrotonamide (not isolated), and the last-named yields  $\beta$ -carboxy-*p*-nitrocinnamylhydroxamic anhydride, m. p. 203° (sinters at 190°). The presence of the *p*-nitro-group apparently prevents decomposition of this by alkali to *p*-nitrophenylmaleic anhydride.  $\gamma$ -Nitro- $\alpha$ -cyano- $\delta$ -phenyl- $\alpha$ -*p*-bromo-phenyl- $\Delta^a$ -butadiene yields analogously the unstable  $\gamma$ -nitro- $\alpha$ -*p*-bromophenylcrotonamide, m. p. 200° (decomp., darkens at 170°),  $\beta$ -carboxy-*p*-bromocinnamylhydroxamic anhydride, m. p. 162° (sinters at 155°), and *p*-bromophenylmaleic anhydride, m. p. 156°.  $\gamma$ -Nitro- $\alpha$ -*m*-bromophenylcrotonamide, sinters 145°, decomp. 180°, and  $\beta$ -carboxy-*m*-bromocinnamylhydroxamic anhydride, m. p. 167—168° (sinters 158°), but not the corresponding maleic anhydride, are obtained analogously from the *m*-bromo-compound.

Phenylcinnamenylacrylonitrile is converted by bromine in chloroform into  $\gamma\delta$ (?)-dibromo- $\alpha$ -cyano- $\alpha\delta$ -diphenyl- $\Delta^a$ -butene, m. p. 118°, which yields with methyl-alcoholic potassium hydroxide  $\gamma$ (?)-bromo- $\alpha$ -cyano- $\alpha\delta$ -diphenyl- $\Delta^a$ -butadiene, m. p. 92°.

Methyl phenylcinnamenylacrylate is converted by nitrogen peroxide in ethereal solution into the dinitro-compound (not isolated), which yields with alcoholic ammonia methyl  $\delta$ -nitro- $\alpha\delta$ -diphenyl- $\Delta^a$ -pentadienoate, m. p. 154°. A small amount of an isomeride, m. p. 116°, is formed if the dinitro-compound is decomposed with alcohol. The  $\delta$ -nitro-compound is converted by potassium methoxide and sodium hypobromite successively into methyl  $\delta$ -bromo- $\delta$ -nitro- $\gamma$ -methoxy- $\alpha\delta$ -diphenyl- $\Delta^a$ -pentenoate, m. p. 111°, which is reconverted by potassium methoxide into the intermediately formed potassium salt. If, however, the  $\delta$ -nitro-compound is treated with hot alcoholic potassium methoxide or with concentrated potassium methoxide solution, it yields an unstable dipotassium salt,  $CPh(CO_2K):CH:CO:CPh:NO_2K$  or  $CPh(CO_2K):CH:CH(OH):CPh:NO_2K$ , which is decomposed by dilute sulphuric acid to give phenylmaleic anhydride and phenylnitromethane, characterised by conversion into 7-nitrostilbene.

$\alpha$ -Nitro- $\alpha\delta$ -diphenyl- $\Delta^a$ -butadiene is converted by treatment with nitrogen peroxide in ether and subsequent decomposition with ammonia solution into  $\alpha\delta$ -dinitro- $\alpha\delta$ -diphenyl- $\Delta^a$ -butadiene, m. p. 225° (decomp., sinters at 215°) (cf. Wieland and Stenzl, A., 1908, i, 517), accompanied by a small quantity of an isomeride, m. p. 154° (decomp.). Treatment of the  $\alpha\delta$ -dinitro-compound with potassium methoxide and sulphuric acid successively yields  $\alpha\delta$ -dinitro- $\gamma$ -methoxy- $\alpha\delta$ -diphenyl- $\Delta^a$ -butene, m. p. 142°. Oxidation by permanganate in acetone, or ozonolysis, yields benzaldehyde and benzoic acid, and the other usual methods of determining the constitution also fail. However, hydrogenation in acetic acid in presence of platinum with increasing quantities of hydrogen led to the successive isolation of  $\alpha$ -oximino- $\alpha\delta$ -diphenyl- $\Delta^a$ -butene, m. p. 108—110°, a mixture of two isomeric  $\delta$ -nitro- $\alpha$ -oximino- $\alpha\delta$ -diphenyl- $\Delta^a$ -butenes, m. p. 107° and m. p. 128°, and ultimately  $\delta$ -amino- $\alpha$ -oximino- $\alpha\delta$ -diphenyl- $\Delta^a$ -butenyl acetate, m. p. 146—147° (decomp.), accompanied by a third isomeric  $\delta$ -nitro- $\alpha$ -oximino- $\alpha\delta$ -diphenyl- $\Delta^a$ -butene, m. p. 130°. The  $\delta$ -amino-compound, m. p. 95°

(*acetyl* derivative, m. p. 203°), yields the known 2:5-diphenylpyrrole when boiled for 48 hrs. with dilute sulphuric acid. R. K. CALLOW.

**1-Methylnaphthalene.** I. R. E. STEIGER (Helv. Chim. Acta, 1930, 13, 173—186).—Treatment of 1-methylnaphthalene with chlorosulphonic acid in presence of carbon tetrachloride at 0° (cf. Veselý and others; A., 1929, 1288) affords 73% of 1-methylnaphthalene-4-sulphonic acid (*potassium* salt), some *di-α-4-methyl-naphthyl sulphone*, m. p. 255—256° (all m. p. are corr.), and an isomeric sulphonic acid. Fusion of the crude potassium salts with potassium hydroxide gives 4-methyl- $\alpha$ -naphthol and a small amount of a *dihydroxydimethyldinaphthyl*, m. p. about 220° (*diacetate*, m. p. 236.5—237°). Nitration of 1-methylnaphthalene-4-sulphonyl chloride, m. p. 80.8—81° [corresponding amide, m. p. 177° (lit. 174°)], with nitric acid (*d* 1.475) at -5° to 0° furnishes a mixture of the 5- and 8-nitro-derivatives (cf. *loc. cit.*). The former is hydrolysed by *N*-sodium hydroxide to the sodium salt (+2.5H<sub>2</sub>O) of 5-nitro-1-methylnaphthalene-4-sulphonic acid, which is reduced by iron and water containing a trace of acetic acid to 5-amino-1-methylnaphthalene-4-sulphonic acid (sodium salt +0.5H<sub>2</sub>O). Diazotisation of this amino-acid gives 5-hydroxy-1-methylnaphthalene-4-sulphonolactone, m. p. 161—161.5°. 8-Nitro-1-methylnaphthalene-4-sulphonyl chloride, -4-sulphonodithylamide, m. p. 130—131°, -4-sulphonanilide, m. p. 131—132°, and 5-nitro-1-methylnaphthalene-4-sulphonanilide (?), m. p. 257.5° (from the chloride and aniline), are all light-sensitive.

H. BURTON.

**Bromo- and dinitro-derivatives of 1-methylnaphthalene.** V. VESELÝ, F. ŠTURSA, H. OLEJNÍČEK, and E. REIN (Coll. Czech. Chem. Comm., 1930, 2, 145—157).—By the action of sulphuric acid-nitric acid (*d* 1.52) mixtures on 4- or 5-nitro-1-methylnaphthalene in acetic acid solution or of nitric acid (*d* 1.52) on 1-methylnaphthalene in the same solvent 4:5-dinitro-1-methylnaphthalene, m. p. 142—143°, was obtained. Reduction with alcoholic ammonium sulphide of the material left after removal of the 4:5-dinitro-compound from the product of nitration led to 2-nitro-4-amino-1-methylnaphthalene, m. p. 131—132° (*acetyl* derivative, m. p. 230—231°), which, by diazotisation and treatment with sodium nitrite and copper-bronze, gave 2:4-dinitro-1-methylnaphthalene, m. p. 160—161°. This compound was reduced in acetic acid solution (saturated with hydrogen chloride) by stannous chloride, 2-nitro-4-amino-1-methylnaphthalene, m. p. 132—133°, and 4-nitro-2-amino-1-methylnaphthalene, m. p. 126—128° (*acetyl* derivative, m. p. 203—204°), being formed.

The following substances were prepared by standard methods: 4-bromo-2-amino-1-methylnaphthalene, m. p. 78° (*acetyl* derivative, m. p. 223—224°); 4-bromo-1-methyl- $\beta$ -naphthol, m. p. 108—109°; 2:4-dibromo-1-methylnaphthalene, m. p. 58—59°; 2-bromo-4-nitro-1-methylnaphthalene, m. p. 138—139°; 2-bromo-4-amino-1-methylnaphthalene, m. p. 118—119° (*acetyl* derivative, m. p. 206—207°); 2-bromo-1-methylnaphthalene, m. p. 35—36° (*picrate*, m. p. 105—106°); 3-bromo-4-methyl- $\alpha$ -naphthol, m. p. 128—129°; 3-bromo-1-methylnaphthalene, m. p. 46—57° (*picrate*,

m. p. 83—84°); 5-bromo-1-methylnaphthalene, m. p. 63—64° (*picrate*, m. p. 110—111°); and 8-bromo-1-methylnaphthalene, m. p. 80° (*picrate*, m. p. 152—153°).

By the nitration of 8-nitro-1-methylnaphthalene with sulphuric-nitric acid mixture in acetic acid solution 4:8-dinitro-1-methylnaphthalene (?), m. p. 120—121°, was obtained. R. J. W. LE FÈVRE.

**Synthesis of alkyl-naphthalenes.** I. 1-Methyl-5-, -6-, and -7-ethylnaphthalenes. J. HARVEY, I. M. HEILBRON, and D. G. WILKINSON (J.C.S., 1930, 423—431).—*o*-Tolualdehyde and ethyl  $\alpha$ -bromobutyrate were condensed in the presence of zinc to form ethyl  $\beta$ -hydroxy- $\beta$ -*o*-tolyl- $\alpha$ -ethylpropionate, b. p. 164—166°/12 mm., converted by successive treatment with phosphorus tribromide and diethylaniline into ethyl *o*-methyl- $\alpha$ -ethylcinnamate, b. p. 144°/15 mm. This when reduced with sodium in absolute alcohol yielded  $\gamma$ -*o*-tolyl- $\beta$ -ethylpropyl alcohol, b. p. 145°/15 mm., and  $\beta$ -*o*-tolyl- $\alpha$ -ethylpropionic acid, b. p. 173—175°/12 mm., m. p. 53—54°: the latter on esterification and reduction by the same method gave a further quantity of the *o*-tolylethylpropyl alcohol. This alcohol was converted into  $\gamma$ -*o*-tolyl- $\beta$ -ethylpropyl bromide, b. p. 136—138°/12 mm., and thence through the nitrile into  $\gamma$ -*o*-tolyl- $\beta$ -ethylbutyric acid, b. p. 186°/13 mm. The acid chloride, b. p. 149—150°/12 mm., under the influence of aluminium chloride condensed to 5-keto-1-methyl-7-ethyl-5:6:7:8-tetrahydronaphthalene, b. p. 165°/12 mm., m. p. 38°, reduced by Clemmensen's method to 1-methyl-7-ethyl-5:6:7:8-tetrahydronaphthalene, b. p. 129—131°/14 mm., which, when dehydrogenated with selenium, yielded 1-methyl-7-ethylnaphthalene, b. p. 133°/12 mm.,  $n_D^{20}$  1.5970 (*picrate*, m. p. 97°).

5-Keto-1-methyl-5:6:7:8-tetrahydronaphthalene, m. p. 50—51°, was prepared in a similar manner to its lower homologue starting from ethyl *o*-methylcinnamate, b. p. 157°/25 mm. (Young, A., 1892, 1221), by means of the intermediates:  $\gamma$ -*o*-tolylpropyl alcohol, b. p. 136°/15 mm. (*urethane*, m. p. 58°),  $\beta$ -*o*-tolylpropionic acid, m. p. 105° (ethyl ester, b. p. 141°/22 mm.; cf. Young, *loc. cit.*);  $\gamma$ -*o*-tolylpropyl bromide, b. p. 124°/17 mm.;  $\gamma$ -*o*-tolylbutyric acid, m. p. 60° (chloride, b. p. 143°/17 mm.). It yielded with magnesium ethyl iodide a carbinol, dehydrated by acetic anhydride to 1-methyl-5-ethyl-7:8-dihydronaphthalene, b. p. 130—131°/12 mm., which when heated with selenium gave 1-methyl-5-ethylnaphthalene, m. p. 40°,  $n_D^{20}$  1.600 (*picrate*, m. p. 97°).

2-Methylstyryl ethyl ketone, b. p. 150—153°/14 mm., (phototropic semicarbazone, m. p. 176—178°), obtained by condensing *o*-tolualdehyde with methyl ethyl ketone in presence of sodium hydroxide, was reduced by hydrogen and palladium to  $\beta$ -*o*-tolyl-diethyl ketone, b. p. 140—143°/16 mm. (*semicarbazone*, m. p. 160°). Further reduction with sodium and alcohol gave  $\gamma$ -*o*-tolyl- $\alpha$ -ethylpropyl alcohol, b. p. 145—146°/14 mm. This was subjected to parallel processes to those used for 1-methyl-7-ethylnaphthalene, the following products being isolated in the synthesis of 1-methyl-6-ethylnaphthalene, b. p. 140°/12 mm.,  $n_D^{20}$  1.598 (*picrate*, m. p. 82°);  $\gamma$ -*o*-tolyl- $\alpha$ -ethylpropyl bromide, b. p. 149—151°/18 mm.;  $\gamma$ -*o*-tolyl- $\alpha$ -ethylbutyric acid, b. p. 195—

196°/18 mm. (chloride, b. p. 158—160°/18 mm.); 5-keto-1-methyl-6-ethyl-5:6:7:8-tetrahydronaphthalene, b. p. 172°/19 mm. H. A. PIGGOTT.

**New class of coloured hydrocarbons.** M. MAXIM (Bul. Soc. Chim. România, 1930, 11, 109—122).—See this vol., 334.

**Rubrene. XIII. Preparation of rubrene.** C. MOUREU, C. DUFRAISSE, and P. LOTTE (Bull. Soc. chim., 1930, [iv], 47, 216—221).—The conversion of diphenylphenylacetylenylmethyl chloride (A., 1923, i, 921) into rubrene is a strongly exothermic reaction which takes place at the ordinary temperature and through at least one intermediate stage (cf. A., 1929, 922). It is not pyrogenic and can give high yields of rubrene. The strongly exothermic character sometimes causes the reaction to become violent and excessive rise of temperature favours the formation of resinous substances and of "satellites" of rubrene, up to twelve in number. Dilution favours side-reactions and acid catalysts the formation of  $\psi$ -rubrene (cf. A., 1929, 549). The yields are improved in presence of tertiary bases, and with 2% of quinoline up to 78% of rubrene may be obtained, the formation of resinous substances being diminished, and the white fluorescent substance (A., 1926, 945) is not formed. Purification by dissolution in naphthalene is then unnecessary, the product being extracted with acetone and dissolved in cold benzene, giving about 45% of purified product. The m. p. affords little criterion of purity and if the fluorescent substance is absent, microscopic examination of the crystals deposited by evaporation from carbon disulphide and light petroleum gives the best indication of purity. R. BRIGHTMAN.

**Rubrene. XIV. Yellow and brown satellite hydrocarbons of rubrene.** C. MOUREU, C. DUFRAISSE, and P. LOTTE (Bull. Soc. chim., 1930, [iv], 47, 221—225).—Yellow and brown crystalline hydrocarbons,  $C_{42}H_{28}$ , (?)  $C_{42}H_{30}$  ( $+x C_6H_6$ ), m. p. 249°, "satellites" of rubrene, are obtained from the acetone extract (cf. preceding abstract). The amount of "solvent of crystallisation" (benzene) varies considerably without affecting the m. p. Cryoscopic determinations in benzene indicate a mol. wt. of about 610. R. BRIGHTMAN.

**Quaternary iodides from phenylglycine, and the corresponding betaines.** L. PIAUX (Compt. rend., 1930, 190, 645—647).—Quaternary iodides of the type  $(NPhRR' \cdot CH_2 \cdot CO_2Et)I$  are obtained by addition in the cold of (a) R'I to disubstituted glycine esters,  $NPhR \cdot CH_2 \cdot CO_2Et$ , (b) ethyl iodoacetate to disubstituted anilines  $NPhRR'$ . Phenyltrimethylcarbethoxymethylammonium iodide, m. p. 129° (decomp.; M.b.; cf. lit.), and phenylcarbethoxymethyl-diethylammonium iodide, m. p. 127.5° (decomp.; M.b.), are resolved into their components, ethyl iodoacetate and dimethyl- or diethyl-aniline, above their m. p. Ethyl iodide and phenylmethylglycine ester do not interact, but phenylmethylcarbethoxymethylammonium iodide, obtained by process (b), dissociates in the cold, and is stable only in the presence of an excess of one of its components. By treatment with silver oxide and water, the above iodides are quantitatively converted into the corresponding betaines: phenyltrimethylbetaine, m. p. 124° (M.b.;

cf. Willstätter, A., 1904, i, 235); phenyl-diethylbetaine, m. p. 207° (decomp.; M.b.); phenyl-ethylmethylbetaine, a syrup; phenyl methylcarbethoxymethyl-ethylammonium iodide, m. p. 165° (decomp.). The following are also described: phenyl-trimethylammonium iodide, m. p. 224° (M.b.); phenyl-dimethyl-ethylammonium iodide, m. p. 134° (decomp.; M.b.); (M.b.=Maquenne block).

C. W. SHOPPEE.

**Mechanism of the action of the Grignard reagent on N-disubstituted crotonamides.** N. MAXIM (Bul. Soc. Chim. România, 1929, 11, 123—129).—In contradistinction to magnesium ethyl and phenyl bromides, which react with disubstituted crotonamides to form compounds of the type  $CHMe(Et \text{ or } Ph) \cdot CH_2 \cdot CO \cdot NR_2$  (Maxim, A., 1929, 431), magnesium methyl iodide with croton-diphenylamide yields only a small amount of isovaler-diphenylamide, m. p. 93.5° (identified by comparison with the product synthesised by the action of isovaleryl chloride on diphenylamine), and as principal product a substance,  $C_{33}H_{34}O_2N_2$ , m. p. 135°, to which the structure  $NPh_2 \cdot CHMe \cdot CH(CO \cdot NPh_2) \cdot CO \cdot CH_2 \cdot CHMe_2$  is assigned. A mechanism for the formation of this compound is suggested. Alcoholic potassium hydroxide hydrolyses it to the corresponding acid, m. p. 158°, whilst 40% hydrobromic acid yields an isomeric acid of m. p. 133°; the existence of these two acids is ascribed to the presence of two asymmetric carbon atoms. Bromine is absorbed in the cold to form a nonabromo-compound,  $C_{33}H_{25}O_2N_2Br_9$ , m. p. 185°.

H. A. PIGGOTT.

**Nature of the alternating effect in carbon chains. XXXII. Directive influence of  $\psi$ -basic systems in aromatic substitution.** Nitration of benzylidene-*m*-nitroaniline. J. W. BAKER and C. K. INGOLD (J.C.S., 1930, 431—440; cf. Baker, A., 1929, 1447).—The claim of Flürscheim and Holmes (A., 1928, 1126) that benzylidene-*m*-nitroaniline nitrates as such and not as the salt in fuming sulphuric acid (5% free  $SO_3$ ) to form a higher proportion of *m*-derivative than is given by benzaldehyde is contrary to all theories of aromatic substitution based on the electronic theory of valency. It is shown by partition experiments of the base between 5% oleum and light petroleum (b. p. 110—120°) or carbon tetrachloride, that the free base is absent from the oleum solution, since none is removed by the organic solvent. Further, by cooling a warm, saturated solution of the base in 5% oleum or by dilution with ether, the hydrogen sulphate, m. p. 225° (decomp. with previous darkening), of the base is isolated. That the pseudo-base is nitrated as its sulphate  $\{CHPh \cdot NH \cdot C_6H_4 \cdot NO_2\}^+ X^-$  is proved by the fact that, contrary to Flürscheim and Holmes (*loc. cit.*), the amount of *m*-substitution produced in 5% oleum ( $89.1 \pm 0.3\%$ ) suffers a larger repression (to  $83.7 \pm 0.2\%$ ) in the presence of added ammonium sulphate than does the true base diethylbenzylamine under the same conditions ( $61.0 \pm 1.3$  and  $61.9 \pm 0.3\%$  *m*, respectively), since in the case of the Schiff's base the change ion  $\rightarrow$  salt is followed by a further *m*-repressing change salt  $\rightarrow \psi$ -salt, that is, pole  $\rightarrow$  dipole  $\rightarrow$  neutral form. Nitration of benzaldehyde with absolute nitric acid (*d* 1.53) and acetic anhydride



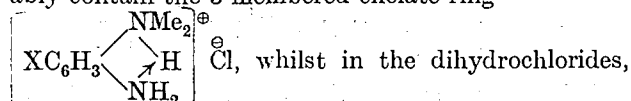
at 35° gives 37.4% of the *m*-nitro-derivative, but since *p*-nitrobenzylidene diacetate can be isolated from the product it follows that addition of the reagent to benzaldehyde occurs. Similarly, when a solution of *m*-nitrobenzylidene-*m*-nitroaniline in a mixture of nitric acid and acetic anhydride is evaporated to constant weight in a vacuum at the ordinary temperature a gain in weight (42.4%) corresponding with the addition of 1 mol. of acetyl nitrate (38.8%) occurs. Moreover, if the solution is cooled to -30° colourless crystals of an additive compound, m. p. 50–55° (decomp.; in a sealed tube), may be isolated with suitable precautions. This compound readily decomposes, giving nitrous gases and a red gum. Hence, as in the case of benzaldehyde, the proportion of *m*-isomeride (40.7%) formed when benzylidene-*m*-nitroaniline is nitrated with nitric acid and acetic anhydride at 35° does not correspond with the nitration of the free base, but of an additive compound.

J. W. BAKER.

**3-Halogeno-6-nitro- and -6-amino-dimethylanilines.** H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 497–501).—Dimethylamine in boiling alcohol, in the absence of any catalyst, readily replaces the 2-halogeno-substituent in 2:4-dihalogenonitrobenzenes and thus are obtained: 3-*chloro*-, m. p. 49° (*picrate*, m. p. 70°), 3-*bromo*-, m. p. 58.5° (*picrate*, m. p. 85°), and 3-*iodo*-, m. p. 52° (*picrate*, m. p. 104°), -6-nitrodimethylaniline. The low m. p. of the 2-nitrodialkylanilines in contrast to the high m. p. of the 4-nitro-derivatives is probably due to co-ordin-

ation  $\begin{array}{c} \text{NO}_2\text{O} \\ | \\ \text{N}=\text{R}_2 \end{array}$  (cf. Bennett and Willis, A., 1929, 436),

the general effect of a halogen substituent, which is discussed, being to raise the m. p. of these substituted dialkylanilines. The low m. p. of the picrates suggests chelation,  $o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2 \rightarrow \text{HO}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$ , the m. p. rising (I > Br > Cl) with increase in salt-like character. Reduction of the above halogenonitrodialkylanilines with iron powder and 50% acetic acid gives: 3-*chloro*- (*hydrochloride*; *dihydrochloride*; *picrate*, m. p. 151°), 3-*bromo*- (*hydrochloride*; *dihydrochloride*; *picrate*, m. p. 137°), and 3-*iodo*- (*hydrochloride*; *dihydrochloride*; *picrate*, m. p. 167°) -6-aminodimethylaniline. The monohydrochlorides probably contain the 5-membered chelate ring



the stability of which diminishes in the order Cl > Br > I, the general (inductive) effect of the halogen atom weakens the union of the chelating electrons on the *p*-amino-nitrogen so that the hydrogen is completely captured by the dimethylamino-group, leaving the amino-group free for further salt formation. *o*-Nitrodialkylaniline (*picrate*, m. p. 103°) is reduced to *o*-aminodimethylaniline, b. p. 212° (*monohydrochloride*; *picrate*, m. p. 136°).

J. W. BAKER.

**Catalytic preparation of primary and secondary amines.** A. GUYOT and M. FOURNIER (Bull. Soc. chim., 1930, [iv], 47, 203–210).—A more de-

tailed account of work already published (this vol., 203).

**Monoacyl derivatives of benzidine.** I. V. HOPPER and J. R. ALEXANDER (J. Roy. Tech. Coll. Glasgow, 1930, 2, 200–202).—Repetition of the preparation of the monoacetyl and monobenzenesulphonyl derivatives of benzidine by the methods of Schmidt and Schultz (A., 1881, 909) and Hinsberg (A., 1893, i, 168), respectively, gave meagre yields of the monoacyl derivatives, although the diacyl compounds were always obtained in abundant yield, even in presence of a large excess of benzidine. Modified methods were tried without better results; similar yields were obtained with acetic anhydride or benzenesulphonyl chloride in dilute acetic acid, and preparations in which benzidine sulphate were used yielded only the diacyl derivatives.

R. K. CALLOW.

**Parachor of azo-compounds.** H. LINDEMANN and R. GROGER (Ber., 1930, 63, [B], 715–717).—The doubts cast by Sidgwick (A., 1929, 805) on the validity of the use of the parachor in elucidating the constitution of the azides (Lindemann and Thiele, A., 1928, 937) are considered unjustified, since the results obtained with a series of azides all point in the same direction. The suggestion of Mumford and Phillips (A., 1929, 1219) that the double linking between two nitrogen atoms has a lower parachor value than the corresponding carbon-carbon linking is negated by observations on azo-compounds for which the following data are cited: azobenzene,  $d_4^{25}$  1.035,  $\gamma$  35.5; *o*-methylazobenzene,  $d_4^{25}$  1.067,  $\gamma$  40.5; *m*-methylazobenzene,  $d_4^{25}$  1.061,  $\gamma$  40.7; *oo*-dimethylazobenzene,  $d_4^{25}$  1.021,  $\gamma$  35.2; *mm'*-dimethylazobenzene,  $d_4^{25}$  1.014,  $\gamma$  35.2; ethyl benzene-azoformate,  $d_4^{25}$  1.106,  $\gamma$  38.9; diethyl azoformate,  $d_4^{25}$  1.110,  $\gamma$  33.4.

H. WREN.

**Azomethine azo-dyes.** R. N. SEN and A. K. SEN (J. Indian Chem. Soc., 1930, 7, 11–17).—Sodium 4:4'-dialdehydoazobenzene-3:3'-disulphonate (Green and Crosland, J.C.S., 1906, 89, 1613) (*barium salt*; *disemicarbazone*) condenses with aniline and  $\alpha$ - and  $\beta$ -naphthylamine to give, respectively, the compounds  $\text{C}_{26}\text{H}_{18}\text{O}_6\text{N}_4\text{S}_2\text{Na}_2$ ,  $\text{C}_{34}\text{H}_{24}\text{O}_6\text{N}_4\text{S}_2$ , and  $\text{C}_{34}\text{H}_{22}\text{O}_6\text{N}_4\text{S}_2\text{Na}_2$ . With diamines the very insoluble condensation products contain no free aldehyde or amino-groups and are therefore assumed to be polymembered ring structures of the type  $\text{R} \left\langle \begin{array}{c} \text{N}:\text{CHR}' \\ \text{N}:\text{CHR}' \end{array} \right\rangle \text{N}_2$  ( $\text{R}' = \text{C}_6\text{H}_3\cdot\text{SO}_3\text{H}$ ), and thus with hydrazine, *o*-phenylenediamine, benzidine, rosaniline, and safranine the compounds  $\text{C}_{14}\text{H}_8\text{O}_6\text{N}_4\text{S}_2\text{Na}_2$ ,  $\text{C}_{20}\text{H}_{14}\text{O}_6\text{N}_4\text{S}_2$  (*disodium salt*),  $\text{C}_{26}\text{H}_{18}\text{O}_6\text{N}_4\text{S}_2$ ,  $\text{C}_{33}\text{H}_{22}\text{O}_6\text{N}_4\text{S}_2$ , and  $\text{C}_{34}\text{H}_{26}\text{O}_7\text{N}_6\text{S}_2$ , respectively, are obtained. Two mols. of the aldehyde condense with 3 mols. of chrysoidine to give the compound

$\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_3[\text{N}:\text{CHR}'\cdot\text{N}_2\cdot\text{R}'\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3(\text{NH}_2)\cdot\text{N}:\text{NPh}]_2$

4-Hydroxy-4'-aldehydoazobenzene-3-carboxylic-3'-sulphonic acid was prepared by permanganate oxidation of Hessian-yellow and was condensed with aniline, benzidine, chrysoidine, rosaniline, and safranine to yield the compounds  $\text{C}_{20}\text{H}_{15}\text{O}_6\text{N}_3\text{S}$ ,  $\text{C}_{40}\text{H}_{28}\text{O}_{12}\text{N}_6\text{S}_2$ ,  $\text{C}_{49}\text{H}_{20}\text{O}_{12}\text{N}_8\text{S}_2$ ,  $\text{C}_{47}\text{H}_{33}\text{O}_{12}\text{N}_7\text{S}_2$ , and

$C_{48}H_{36}O_{13}N_8S_8$ , respectively. The dyeing properties of these azomethine azo-dyes are described and it is concluded that introduction of an azomethine group in the *p*-position to the azo-group lightens the colour unless it forms part of an aldazine group  $\cdot CH:N:N:CH \cdot$ , in which case it deepens the colour. The presence of the auxochromic hydroxyl group in the *p*-position to the azo-group has no effect. J. W. BAKER.

**Sodation of the cyclanols.** S. SABETAY and J. BLÉGER (Bull. Soc. chim., 1930, [iv], 47, 214—216).—Sodium derivatives of the cyclanol series are readily obtained by adding the cyclanol to a solution of an alkoxide in excess of the alcohol and distilling. Thus, when 1:2-cyclohexanediol is added to a solution of the sodium derivative of diethylcarbinol, and the diethylcarbinol removed by distillation at  $210^\circ/3-5$  mm., the disodio-derivative of the diol is obtained. With methyl iodide at  $130^\circ$  this yields more than 60% of 1:2-cyclohexanediol dimethyl ether. Quinitol behaves similarly. R. BRIGHTMAN.

**Stereoisomeric cyclohexane derivatives.** K. VON AUWERS and F. DERSCH (J. pr. Chem., 1930, [ii], 124, 209—239).—An investigation of *cis*- and *trans*-2-methylcyclohexanols has been made in which the results of Gough, Hunter, and Kenyon (A., 1926, 1032) are generally confirmed and attention is given particularly to the question of inversion. Preparation of the *p*-nitrobenzoate and hydrogen phthalate in pyridine, of the acetate by means of acetyl chloride alone, and of the phenylcarbamate of *trans*-2-methylcyclohexanol, or the hydrolysis of these esters does not affect the configuration, for the carbinol recovered from any of these esters yielded the pure *p*-nitrobenzoate, m. p.  $65^\circ$ . Anomalous results were, however, obtained with a specimen of *cis*-2-methylcyclohexanol prepared by Skita's method (A., 1923, i, 460); the viscosity of the product indicated a high proportion of the *cis*-isomeride, but it yielded esters of the *trans*-isomeride, from the mother-liquors of which no compounds of sharp m. p. could be isolated. It is probable that inversion of the *cis*-isomeride occurs very readily, and it is suggested that inversion is accelerated in presence of the *trans*-isomeride. The pure *cis*-isomeride, prepared from the *p*-toluenesulphonate of the *trans*-isomeride, yielded a *p*-nitrobenzoate, m. p.  $52^\circ$ , and a phenylcarbamate, m. p.  $88^\circ$  (m. p. of both depressed by the *trans*-compounds), but it is uncertain whether these compounds or those of lower m. p. described by Gough, Hunter, and Kenyon are actually pure *cis*-compounds.

The increased likelihood of inversion in reactions in which the hydroxyl group is replaced is illustrated by the results of Gutt (A., 1907, i, 508) and Zelinski (A., 1908, i, 864), who respectively obtained *trans*- and *cis*-2-methylcyclohexanecarboxylic acids from *trans*-2-methylcyclohexanol by way of the chloride. When their work was repeated it was found only possible to obtain the chloride of lower specific gravity described by Zelinski, either from the *cis*- or *trans*-carbinols. The *cis*- and *trans*-acids were isolated from different preparations, but it appeared to be entirely a matter of chance which acid was obtained as the ultimate product. Again, the *cis*-acid was obtained from the *trans*-carbinol by way of the iodide,

whether the last-named compound was prepared from the carbinol by boiling with hydriodic acid or by heating at  $100^\circ$  as described by Skita (the reaction was incomplete at the ordinary temperature).

Values of *b*, *p*, *d*, *n* for different wave-lengths, molecular refractivity, and dispersivity for different temperatures, exaltation of molecular refraction, and viscosities of *cis*- and *trans*-2-methylcyclohexanols, their acetates, chlorides, and iodides, and of *cis*- and *trans*-2-methylcyclohexanecarboxylic acids and their chlorides and ethyl esters are tabulated, and it is concluded that physical constants give no clue to configuration, except in the case of the viscosities of the 2-methylcyclohexanols, but the authors do not agree with Gough, Hunter, and Kenyon that the composition of mixtures of the carbinols can be determined from the viscosity.

The question of the determination of the configuration of trisubstituted cyclohexane derivatives is discussed, and the work of Skita (A., 1924, i, 25) is criticised.

The isomeric cyclohexane-1:2-diols have been examined. They are best prepared by the method of Derx (A., 1922, i, 651). The acetone compound of the *cis*-diol has  $d^{20}_D$  0.980,  $n^{20}_D$  1.4479. The acetates, prepared by the action of acetyl chloride, yield the unchanged diols when hydrolysed; there is no evidence of inversion. The *cis*-diacetate has *b*. p.  $120^\circ/15$  mm.,  $d^{20}_D$  1.090,  $n^{20}_D$  1.4500, and the *trans*-diacetate, *b*. p.  $123^\circ/14$  mm.,  $d^{20}_D$  1.077,  $n^{20}_D$  1.4464. In both the diols and the diacetates the exaltation of molecular refractivity is lower for the *cis*- than for the *trans*-isomeride. R. K. CALLOW.

**Methylcycloheptanols.** M. GODCHOT and (MLLE.) G. CAUQUIL (Compt. rend., 1930, 190, 642—643).—Reduction with sodium and alcohol of 2:2-dimethylcycloheptanone (A., 1929, 560) furnishes 2:2-dimethylcycloheptanol, *b*. p.  $196-197^\circ/760$  mm.,  $d^{12}_D$  0.9008,  $n^{20}_D$  1.4699 (hydrogen phthalate, m. p.  $148^\circ$ ; phenylurethane, m. p.  $97^\circ$ ). Similar treatment of 2-methylcycloheptanone yields almost exclusively *trans*-2-methylcycloheptanol, *b*. p.  $194^\circ/768$  mm.,  $d^{15}_D$  0.9422,  $n^{15}_D$  1.4740,  $\eta^{15}$  0.5083 (hydrogen phthalate, m. p.  $98^\circ$ ; phenylurethane, m. p.  $59-60^\circ$ ), whilst catalytic reduction with platinum in glacial acetic acid affords *cis*-2-methylcycloheptanol, *b*. p.  $191^\circ/753$  mm.,  $d^{15}_D$  0.9492,  $n^{15}_D$  1.4762,  $\eta^{15}$  0.4519 (hydrogen phthalate, m. p.  $86^\circ$ ; phenylurethane, m. p.  $40-41^\circ$ ). The isomerides are purified through the hydrogen phthalates.

C. W. SHOPPEE.

**Colour and constitution from the viewpoint of recent electronic theory.** II. H. H. HODGSON (J. Soc. Dyers and Col., 1930, 46, 39—44; cf. A., 1929, 1298).—The formation of 3:4:6-tribromophenol by dibromination of *m*-bromophenol is shown to be in accordance with electronic theory. An electronic interpretation of the Reimer-Tiemann reaction as applied to phenol, *o*- and *m*-cresol, *o*- and *m*-chlorophenol, *o*- and *m*-fluorophenol, and salicylic acid in conjunction with chloroform and bromoform is given. The theory is used to explain the properties of abnormal benzene derivatives in which co-ordination effects have to be taken into account. It is used to account for the volatility and non-volatility

in steam of a number of substituted benzaldehydes. The hypsochromic effect of the *o*-methylthiol group in azo-compounds, compared with the methoxy-group, is attributed to co-ordination between the methylthiol and azo-groups. In the *para*-position to the azo-group, the methylthiol group is more bathochromic than the methoxyl group. N. CHAPPELL.

#### New compounds of nickel with nitrophenols.

II. A. BERNARDI (Gazzetta, 1930, 60, 166—168).—Nickel hydroxide combines with *o*-nitrophenol in boiling alcoholic solution to give the garnet-red compound,  $[\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{O}]_2\text{Ni}$ . With 2:4-dinitrophenol under the same conditions the yellow complex,  $\text{Ni}[\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}]_2\cdot\text{Ni}(\text{OH})\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot 0.2\text{EtOH}$ , is obtained, which by desiccation loses alcohol to give the compound  $\text{Ni}[\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}]_2\cdot\text{Ni}(\text{OH})\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2\text{O}$ . Picric acid furnishes the yellow compound  $[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\text{Ni}\cdot 1.5\text{EtOH}$ . C. W. SHOPPEE.

#### Compounds of manganese with nitrophenols.

III. A. BERNARDI (Gazzetta, 1930, 60, 169—171).—Manganese hydroxide combines with *o*-nitrophenol to yield the compound  $[\text{C}_6\text{H}_4(\text{NO}_2)\cdot\text{O}]_2\text{Mn}$ ; 2:4-dinitrophenol and picric acid similarly afford the compounds (I) and (II), rose and brownish-yellow, respectively.  $\{(\text{EtOH})_3\text{Mn}_2\text{OH}[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]\}$  (II)  $\{\text{Mn}_2\text{OH}[\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}]_2[\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}]\}$  (I)

C. W. SHOPPEE.

Relation between constitution and sharp taste of acylamides. T. SZÉKI (Arch. Pharm., 1930, 268, 151—157).—The acylamides are obtained from the amine and acid chloride in benzene at the ordinary temperature, or at the b. p., in presence of anhydrous sodium carbonate. The position of each compound in an ascending scale of pungency is given by the figure in parentheses. The marked pungency of guaiacylamine derivatives disproves the statement of Ott and Zimmermann (A., 1922, i, 137; cf. Nelson, A., 1920, i, 154, 380) that this property is absent in derivatives of aromatic amines. The following are described: *acyl-4-hydroxy-3-methoxyanilides*: isobutyryl- (1), m. p. 142°; *n-heptoyl-* (3), m. p. 108—112°;  $\Delta^a$ -*nonenoyl-* (3), m. p. 93°; *decoyl-* (3), m. p. 100°, and  $\Delta^a$ -*undecenoyl-* (3), m. p. 89°; and *acyl-p-hydroxyanilides*:  $\Delta^a$ -*nonenoyl-* (2), m. p. 108—110° [ $\Delta^a$ -*nonenoate* (1), m. p. 84°]; *decoyl-* (2), m. p. 125.5°, and *oleyl-* (1), m. p. 93—95°; also *p-heptoylamidophenyl heptate* (1), m. p. 119°;  $\Delta^a$ -*undecenoylamidophenyl undecenoate* (2), m. p. 111°; *p-nonoylamidophenyl nonoate* (1), m. p. 121°, and *4-hydroxy-2:3-dimethoxydecoylanilide*, m. p. 119°, which has no pungent taste. H. E. F. NOTTON.

Formation of 2:4-dinitro- $\alpha$ -naphthol by nitration of naphthalene in absence or presence of mercury. W. ENZ and F. PFISTER (Helv. Chim. Acta, 1930, 13, 194—196).—Technical  $\alpha$ -nitronaphthalene contains a small amount of 2:4-dinitro- $\alpha$ -naphthol, m. p. 137.5° (corr.). Nitration of naphthalene with nitric acid (*d* 1.33) at the ordinary temperature in absence and presence of mercury gives an increased amount of the naphthol with rise in the quantity of mercury used. H. BURTON.

Catalytic reactions in organic chemistry. II. *cyclohexylethanol* and its transformations. Linalool and its transformation under the influence of alumina. N. A. ROZANOV, TJASCHELOV, and NIKIFOROV (J. Russ. Phys. Chem. Soc., 1929, 61, 2309—2312).—When heated with anhydrous oxalic acid, *cyclohexylethanol* undergoes normal dehydration, giving *cyclohexylethylene*. In presence of thoria, however, the product of this reaction is dicyclooctane,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2$ , either the dehydration being abnormal or the normal dehydration product undergoing subsequent polymerisation. The dehydration of linalool under the influence of alumina leads to ring closure, with formation of dipentene by way of camphene as an intermediate product. T. H. POPE.

"Oxidising" action of alkalis. III. *Aromatic alcohols*. G. LOCK (Ber., 1930, 63, [B], 551—559; cf. A., 1929, 67, 814).—Benzyl alcohol is converted by potassium hydroxide at about 240° into potassium benzoate, toluene, and hydrogen. The same products are obtained from benzaldehyde and potassium hydroxide, the change being preceded by the Cannizzaro reaction. Nef's observation that hydrogen is evolved in small amount when benzaldehyde is dropped on to potassium hydroxide at 180° is confirmed, but the action is due to local superheating caused by the preliminary disproportionation. Reaction between *o*- or *p*-hydroxybenzyl alcohol and potassium hydroxide commences at about 165—170°, whereas with the *meta*-derivative its incidence is observed at about 190°; in every case the products are hydrogen and the corresponding acid in yield of about 90%. Sodium hydroxide resembles potassium hydroxide in its action towards *o*-hydroxybenzyl alcohol, but the change does not occur below 190°; with lithium hydroxide, evolution of hydrogen is not observed below 260°. Barium hydroxide has no appreciable effect below 200° and salicylic acid is produced only in traces at 225—245°.

Hydrogen and the corresponding hydroxy-acid are obtained in good yield by the action of potassium hydroxide on the following: 3-aldehydo-5-hydroxymethyl-*p*-cresol, 5-hydroxymethylsalicylaldehyde, 3-aldehydo-*p*-cresol, 5-aldehydo-*o*-cresol, and 3-aldehydo-*o*-cresol. 3-Aldehydo-*p*-cresol is transformed by formaldehyde and hydrochloric acid into 3-aldehydo-5-chloromethyl-*p*-cresol, m. p. 96° (corr.), readily hydrolysed to 3-aldehydo-5-hydroxymethyl-*p*-cresol, m. p. 77.5° (corr.). H. WREN.

Colour reaction of Japanese acid clay towards leucomalachite-green hydrochloride. N. KAMEYAMA and S. OKA.—See this vol., 538.

Colour reactions and absorption spectra of sterols in relation to structure. I. M. HEILBRON and F. S. SPRING (Biochem. J., 1930, 24, 133—135).—Selective absorption of sterols is conditioned by the presence of two ethylenic linkings in the molecule, one of which must apparently be in the  $\Delta^{1:3}$ - (or  $\Delta^{1:2}$ )-position. The Tortelli-Jaffé reagent appears to be specific for sterol derivatives containing a linking inert to hydrogenation, possibly in position  $\Delta^{10:19}$ . This reaction has been modified and made more sensitive. S. S. ZILVA.

**New cases of stereoisomerism in the cholesterol group.** S. MINOVICI and M. VANGHELOVICI (Bul. Soc. Chim. România, 1929, 11, 69—80).—A continuation of the work of Windaus and Stein (A., 1904, i, 1010) and the present authors on the production of stereoisomerides in the cholesterol group due to the different planes of the adjacent *cyclopentene* and *cyclohexane* rings in Wieland's formula. An analogous series of operations to that described by Windaus in the case of  $\beta$ -chlorocholestanone, m. p. 180°, has been carried out with the  $\alpha$ -chlorocholestanone of Mauthner and Suida and yields isomeric products up to the final stage (A., 1904, i, 49), m. p. 129°. With fuming nitric acid in acetic acid solution,  $\alpha$ -chlorocholestanone gives a dibasic acid,

$\text{CO}_2\text{H}\cdot\text{C}_{22}\text{H}_{39}\left\langle\begin{array}{c}\text{CH}(\text{CO}_2\text{H}) \\ \text{CH}_2\end{array}\right\rangle\text{CHCl}$ , m. p. 263—264°, the

*cyclopentene* ring being ruptured. A more soluble substance, of m. p. about 100° and of unknown constitution, is also produced. Potassium hydroxide converts this chloro-acid into the *hydroxy-acid*, m. p. 221°, and this with chromium trioxide in acetic acid yields the *keto-acid*, m. p. 213°, more prolonged action of the oxidising agent yielding a tribasic acid,  $(\text{CO}_2\text{H})_2\text{C}_{22}\text{H}_{39}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 190°, by rupture of the *cyclohexanone* ring in the keto-acid and loss of carbon dioxide. On the theory put forward in this and earlier papers as to the structure of  $\alpha$ -chlorocholestanone, the final product should have been the tetracarboxylic acid of Windaus (*loc. cit.*). The reason for this discrepancy has not yet been satisfactorily explained.

H. A. PIGGOTT.

**Action of benzamide on semicarbazide hydrochloride.** I. K. MACUREVITCH (J. Russ. Phys. Chem. Soc., 1929, 61, 1591—1594).—On heating benzamide with semicarbazide hydrochloride to 190—200°, *s*-dibenzoylhydrazine, m. p. 234—235° (decomp.), is obtained, together with ammonia and ammonium chloride, instead of the expected dibenzoylcarbamide.

M. ZVEGINZOV.

**Condensation products of benzhydroxymethylamide.** L. MONTI (Gazzetta, 1930, 60, 39—42).—In presence of concentrated sulphuric acid, *N*-hydroxymethylbenzamide (cf. Einhorn, A., 1905, i, 344) readily condenses with  $\beta$ -diketones forming compounds to which, owing to the reactivity usually exhibited by a methylene group between two carbonyl groups, the general formula  $\text{COPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{R})_2$  is attributed.  $\alpha$ -Benzamido- $\beta$ -benzoyl- $\beta$ -acetyl-ethane,  $\text{CHBzAc}\cdot\text{CH}_2\cdot\text{NHBz}$ , m. p. 108—109°, is thus obtained from benzoylacetone, and  $\alpha$ -benzamido- $\beta$ - $\beta$ -dibenzoyl-ethane, m. p. 158—160°, from dibenzoylacetophenone. Similar condensation of antipyrine with benzhydroxymethylamide gives a compound, m. p. 128—130° (+ $\text{H}_2\text{O}$ ) or 140° (anhydrous), which is probably 4-benzamidomethyl-1-phenyl-2:3-dimethylpyrazolone,  $\begin{array}{c}\text{NMe}\cdot\text{CMe} \\ \text{NPh}\cdot\text{CO}\end{array}\text{C}\cdot\text{CH}_2\cdot\text{NHBz}$ , and is

analogous to the compound obtained by Einhorn and Mauermayer from methylolchloroacetamide and 1-phenyl-3-methylpyrazolone (A., 1906, i, 252). Benzhydroxymethylamide reacts with acetylacetone to give a semi-solid product not yet purified, but does not react with camphor and coumarin. T. H. POPE.

**Interaction of ethyl *l*-mandelate and thionyl chloride in the presence of pyridine. Mechanism of the replacement of hydroxyl by chlorine by means of thionyl chloride.** J. KENYON, A. G. LIPSCOMB, and H. PHILLIPS (J.C.S., 1930, 415—423).—Ethyl *l*-mandelate is converted by the action of thionyl chloride in the presence of potassium carbonate into ethyl *l*-phenylchloroacetate (McKenzie and Barrow, *ibid.*, 1911, 99, 1910), but in the presence of 1—2 mols. of a tertiary base in dry ether at 0° the *d*-ester is formed, although *l*- $\beta$ -octanol is similarly converted both in the absence (Levene and Mikeska, J. Biol. Chem., 1924, 59, 45) and in the presence (McKenzie and Tudhope, A., 1925, i, 226) of pyridine into *d*- $\beta$ -chloro-octane. In both cases it is suggested that unstable intermediates of the same type,

$\text{CHMe}(\text{C}_6\text{H}_{13})\cdot\text{O}\cdot\overset{+}{\text{S}}\text{O}\cdot\overset{+}{\text{NC}}_5\text{H}_5\cdot\text{Cl}$  (I) and

$\text{CHPh}(\text{CO}_2\text{Et})\cdot\text{O}\cdot\overset{+}{\text{S}}\text{O}\cdot\overset{+}{\text{NC}}_5\text{H}_5\cdot\text{Cl}$  (II), are formed, and since Houssa, Kenyon, and Phillips (A., 1929, 1164) have shown that conversion of *l*- $\beta$ -octanol into *d*- $\beta$ -chloro-octane involves inversion, it is probable that similar inversion is involved in the conversion of ethyl *l*-mandelate into ethyl *d*-phenylchloroacetate. These conversions, and others mentioned in the last paper cited, all involve the formation of an intermediate complex of the type postulated above, and it is assumed that these decompose leaving the asymmetric carbon atom positively charged and that this unites with the negative chloride ion making inversion possible. Thus the decomposition of *l*-octyl chlorosulphonate is represented:  $\text{l-CHMe}\cdot\text{C}_6\text{H}_{13}\cdot\text{O}\cdot\overset{+}{\text{S}}\text{O}\cdot\text{Cl} \rightarrow (\text{d or l?}) \text{CHMe}\cdot\text{C}_6\text{H}_{13} + \text{SO}_2 + \text{Cl}$ . Although there is no experimental proof that the formation of a carbonium cation is attended by a Walden inversion, or whether such a cation is capable even of momentary existence in an optically active state, the semipinacolic deamination of *l*- $\beta$ -amino- $\alpha$ -diphenyl-*n*-propyl alcohol to a *d*-ketone (McKenzie and others, A., 1926, 610) may be represented:

$\text{CPh}_2(\text{OH})\cdot\text{CHMe}\cdot\text{NH}_2 \rightarrow \text{CPh}_2(\text{OH})\cdot\text{CHMe}\cdot\text{N}^+\cdot\text{N}\cdot\text{OH} \rightarrow \text{CPh}_2(\text{O})\cdot\text{CHMe}\cdot\text{N}^+\cdot\text{N} \rightarrow \text{PhCO}\cdot\text{CHMe}\cdot\text{N}^+\cdot\text{N}\cdot\text{Ph} \rightarrow \text{PhCO}\cdot\text{CHMePh}$ . In the action of thionyl chloride on ethyl *l*-mandelate there are two possible mechanisms:  $\text{CPh}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{O}\cdot\overset{+}{\text{S}}\text{O}\cdot\text{Cl} \xrightarrow{\text{A}} \text{CHPh}\cdot\text{CO}_2\text{Et} + \text{SO}_2 + \text{Cl}$  or  $\xrightarrow{\text{B}} \text{CHPh}\cdot\text{CO}_2\text{Et} + \text{SO}_2 + \text{Cl}$ , of which only B differentiates the decomposition from that of *l*- $\beta$ -octyl chlorosulphonate, the phenyl group conferring on the asymmetric carbon atom the power to retain its electrons during the decomposition. The action of pyridine to form the complex II (above) increases the positive character and hence the electron-retaining power of the chlorosulphoxy-group; which is then able to overcome the electron-retaining power of the asymmetric carbon attached to the phenyl group, and a Walden inversion occurs.

J. W. BAKER.

**Thiochaulmoogra compounds. Thiochaulmoogramide, anilide, and toluidides.** I. DE SANTOS and A. P. WEST (Philippine J. Sci., 1930, 41, 373—379).—By heating the amide, anilide, *o*-, *m*-, and *p*-toluidides [best prepared by Goldberg's method

(A., 1906, i, 426), by the action of the amide on the appropriate bromohydrocarbon in the presence of copper powder] of chaulmoogric acid with powdered phosphorus pentasulphide in boiling benzene are obtained *thiochaulmoogramide*, m. p. 75—76°; *anilide*, m. p. 55—57°; *o*-, m. p. 98—100°; *m*-, m. p. 78—79°; and *p*-, m. p. 80°, *toluidides*. J. W. BAKER.

**Derivatives of 6-amino-3-hydroxybenzoic acid.**  
**II.** E. PUXEDDU and G. SANNA (Gazzetta, 1930, 60, 126—133; cf. A., 1929, 1295).—Methyl 6-chloroacetamido-3-hydroxybenzoate reacts with diethylamine to give *methyl 6-diethylaminoacetamido-3-hydroxybenzoate*, m. p. 87—88° [hydrochloride, m. p. 180—181° (decomp.)]; *ethyl 6-chloroacetamido-3-hydroxybenzoate*, m. p. 177—178°, obtained by treatment of ethyl 6-amino-3-hydroxybenzoate with chloroacetyl chloride in benzene, similarly affords *ethyl 6-diethylaminoacetamido-3-hydroxybenzoate*, m. p. 93° (hydrochloride, m. p. 154°). The last-named ester and its methyl analogue may possess pharmacological applications.

6-Amino-3-hydroxybenzoic acid condenses with boiling ethyl acetoacetate (cf. Niementowski, A., 1907, i, 1081) to yield 40% of an acidic compound,  $C_{22}H_{16}O_7N_2$ , m. p. 256° (decomp.) (cf. Froelicher and Cohen, J.C.S., 1921, 119, 1425); the acid reacts with ethyl chloroformate in 10% aqueous potassium carbonate solution to furnish 6-carbethoxycarbonyl-3-hydroxybenzoic acid, m. p. 163—165°, and with oxalyl chloride in benzene to afford 4 : 4'-dihydroxyoxanilide-2 : 2'-dicarboxylic acid, m. p. 220—221°. Attempts to obtain condensation products from methyl 6-amino-3-hydroxybenzoate with antipyrine, pyrazolone, and salipyrin were unsuccessful.

C. W. SHOPPEE.

**Stereochemistry of some alicyclic ring-systems.** M. QUDRAT-I-KHODA (J. Indian Chem. Soc., 1930, 7, 79—81).—Experimental work on the stability of some cyclohexanespirocyclopropane derivatives is foreshadowed.

J. W. BAKER.

**$\gamma$ -Resorcylic acid [2 : 6-dihydroxybenzoic acid].**  
**II.** F. MAUTHNER (J. pr. Chem., 1920, [ii], 124, 319—322).—2 : 6-Dimethoxybenzoic acid, prepared by the method previously described (A., 1929, 697) and now slightly improved, yields 2 : 6-dihydroxybenzoic acid ( $\gamma$ -resorcylic acid), m. p. 148—172° (decomp., according to rate of heating), when heated with aluminium chloride in benzene solution. The preparation and separation of  $\beta$ - and  $\gamma$ -resorcylic acids by Brunner's method is also described. *Methyl 2 : 6-dihydroxybenzoate*, m. p. 67—68°, is obtained from the acid in 33% yield, contrary to Victor Meyer's rule, with methyl-alcoholic hydrogen chloride. *Methyl 2 : 6-dimethoxybenzoate* could not be induced to condense with ethyl acetate and sodium, nor could the desired keto-acid be obtained by treating the nitrile with magnesium methyl iodide.

R. K. CALLOW.

**Synthesis of capsaicin.** E. SPÄTH and S. F. DARLING (Ber., 1930, 63, [B], 737—743; cf. Nelson and Dawson, A., 1923, i, 1108; Felmayer, Diss., Wien, 1923).—The action of zinc isobutyl iodide on ethadipyl chloride yields *ethyl  $\epsilon$ -keto- $\eta$ -methylnonoate*, hydrolysed to  *$\epsilon$ -keto- $\eta$ -methylnonoic acid*, m. p. 39—40° (*semicarbazone*, m. p. 139—140°). The acid is

reduced by hydrogen in presence of palladised charcoal or, preferably, by sodium and alcohol to  *$\epsilon$ -hydroxy- $\eta$ -methylnonoic acid*, b. p. 135—140°/0.01 mm. (bath temperature), converted by successive treatment with fuming hydrobromic acid at 100—105° and diazomethane into *methyl  $\epsilon$ -bromo- $\eta$ -methylnonoate*, b. p. 105—112°/0.4 mm. (bath temperature). Successive treatment of the ester with quinoline at 210—240° and sodium hydroxide affords a mixture of decenoic acids, transformed by purified thionyl chloride at the laboratory temperature into the chlorides, from which, after reaction with veratrylamine in ether, *capsaicin methyl ether*, m. p. 75—76°, is obtained, identical with the product prepared from diazomethane and natural capsaicin. Hydrolysis of the amide with aqueous methyl-alcoholic hydrochloric acid followed by treatment of the product with potassium hydroxide leads to the homogeneous  *$\eta$ -methyl- $\Delta^6$ -nonenoic acid*, which is converted into the corresponding chloride and then allowed to react with vanillylamine in nitrobenzene, thereby giving a product, m. p. 64—65°, identical with natural capsaicin.

H. WREN.

**Transformation of ethyl oxindonecarboxylate into a naphthalenecarboxylic ester.** A. HANTZSCH and E. CZAPP (Ber., 1930, 63, [B], 566—567).—Ethyl oxindonecarboxylate is converted by an excess of diazomethane in methyl alcohol through the unstable *O*-methyl ether into *ethyl 4-methoxy- $\alpha$ -naphthol-2-carboxylate*, m. p. 87—88°, hydrolysed to the corresponding acid, m. p. 180° (decomp.), which passes by loss of carbon dioxide into 4-methoxy- $\alpha$ -naphthol, m. p. 130°.

H. WREN.

**Configuration of polymethylenedicarboxylic acids.** IV. Ring-strain and dissociation constants of *trans*-polymethylenedicarboxylic acids. V. Dissociation constants of *cis*-polymethylenedicarboxylic acids. A. WASSERMANN (Helv. Chim. Acta, 1930, 13, 207—222, 223—236; cf. A., 1928, 239, 240).—In Bjerrum's equation (A., 1923, i, 1059) as modified by Ebert (A., 1925, i, 230):  $\log K_1 - \log K_2 - 0.60 = n + x$ ,  $K_1$  and  $K_2$  are the first and second dissociation constants of a dicarboxylic acid,  $n$ , for a given solvent, depends only on the distance apart of the carboxyl groups, whilst  $x$  is a measure of the capacity for polarisation of the carbon atoms to which the carboxyl groups are attached and should be affected by the condition of the linkings joining them. In the *trans*-polymethylene-1 : 2-dicarboxylic acids for which  $n$  is constant, the values of  $n + x$  increase from fumaric acid to cyclopentane-1 : 2-dicarboxylic acid, whilst  $K_1$  and  $K_2$  decrease. Thus, increasing ring-tension is accompanied by increasing capacity for polarisation of the ring carbon atoms. The same effect is observed in *trans*-cyclobutane- and -cyclopentane-1 : 3-dicarboxylic acids. The acids with larger rings are not available for comparison, owing to their non-planar configurations. *trans*-Oxidomethylenedicarboxylic acid has a greater ring-strain than cyclopropane-1 : 2-dicarboxylic acid.

Unlike the *trans*-derivatives, the *cis*-polymethylene-1 : 2-dicarboxylic acids show a decrease in  $n + x$  from maleic acid to a minimum at cyclobutane-1 : 2-dicarboxylic acid.  $K_1$  shows a steady increase from the 2-ring to the 5-ring, but  $K_2$  is again abnormal. Similar

results are obtained with *cis*-cyclobutane- and -cyclopentane-1:3-dicarboxylic acids. Values calculated from Bjerrum's equation are tabulated for the ratio of the distances apart of the two ionising groups in each pair of *cis*- and *trans*-acids. These are also anomalous except in the case of those acids the *cis*-forms of which do not readily yield anhydrides. The effects of lactone formation and of solvent action on the results are discussed. Values of  $K_1$  and  $K_2$  have been determined for the *cis*- and *trans*-forms of cyclopropane- and cyclopentane-1:2-dicarboxylic acids, cyclobutane- and cyclopentane-1:3-dicarboxylic acids, and oxidoethyl-endicarboxylic acid. H. E. F. NOTTON.

#### 4-Bromophthalic anhydride and derivatives.

I and II. H. WALDMANN [with H. MATHIOWETZ] (J. pr. Chem., 1930, [ii], 126, 65—68, 69—75).—I. 4-Bromophthalic acid may be prepared by bromination of phthalic acid in alkaline solution at 60°. An excess of bromine over the amount necessary to react completely with the free alkali is used. The acid was characterised by the following derivatives: anhydride, b. p. 305—309°, m. p. 107° (cf. Stephens, A., 1922, i, 141); methyl ester, b. p. 303—306°, m. p. 40°; chloride, b. p. 293—298°; imide, m. p. 229.5°, and 4-bromo-anthranilic acid (by the Hofmann reaction), m. p. 224°.

II. 4-Bromophthalic anhydride is condensed with benzene, bromo- and chloro-benzene in presence of aluminium chloride, the orientation of the *o*-benzoylbenzoic acids produced being determined, when unknown, by further condensation to the corresponding halogenated anthraquinones. The preparation of some  $\psi$ -chlorides and  $\psi$ -esters is described. 4-Bromo-2-benzoylbenzoic acid, m. p. 191° (cf. Stephens, A., 1922, i, 141) ( $\psi$ -chloride, m. p. 189—191°;  $\psi$ -methyl ester, m. p. 183°, readily isomerises by heating with methyl alcohol and a drop of sulphuric acid to the normal methyl ester, m. p. 129°); 4-bromo-2-p-bromobenzoylbenzoic acid, m. p. 207.5—208.5° ( $\psi$ -chloride, m. p. 135—139°;  $\psi$ -methyl ester, m. p. 132°; methyl ester, m. p. 122.5°); 4-bromo-2-p-chlorobenzoylbenzoic acid, m. p. 203.5°; 4-chloro-2-p-bromobenzoylbenzoic acid, m. p. 201°, from 4-chlorophthalic anhydride and bromobenzene: the last two acids both give 2-chloro-6-bromoanthraquinone, m. p. 285° (identified by conversion into the known 2:6-diaminoanthraquinone), on ring-closure. H. A. PIGGOTT.

Halogenated derivatives of terephthalic acid. I. G. FARBININD. A.-G.—See B., 1930, 275.

Derivatives of 3-bromoacenaphthene. K. DZIEWOŃSKI, (MLLE.) J. SCHOENÓVNA, and (MLLE.) A. GLAZNERÓVNA (Bull. Acad. Polonaise, 1929, A, 636—649).—Oxidation of 3-bromoacenaphthene by means of sodium dichromate in acetic acid solution at 30° yields, besides 4-bromonaphthalic acid, 3-bromoacenaphthenequinone, m. p. 235—236° (Graebe, A., 1903, i, 408, gives m. p. 194°) [monophenylhydrazone, m. p. 179—180°; diphenylhydrazone, m. p. 225—226° (lit. 153° and 134°, respectively); dioxime, m. p. 230—231° (decomp.); 3-bromoacenaphthaphenazine, from the foregoing quinone and *o*-phenylenediamine, m. p. 261—263°, and 3:3'-dibromodiacenedione, ( $C_{10}H_8Br_2 \cdot \overset{O}{\underset{CO}{\parallel}} \cdot \overset{O}{\underset{CO}{\parallel}}$ ), m. p. 320—321° (for nomenclature, cf. A., 1926, 160).

Nitration of 3-bromoacenaphthene in acetic acid solution gives mainly 3-bromo-4-nitroacenaphthene, m. p. 159—161°, converted by sodium hyposulphite into 3-bromo-4-aminoacenaphthene, m. p. 133°. The orientation of these derivatives is established by the further reduction of the latter, by means of sodium amalgam and alcohol, to the known 3-aminoacenaphthene. 3-Bromo-4-nitroacenaphthene is oxidised by sodium dichromate to 4-bromo-5-nitronaphthalic acid, m. p. 295° (anhydride, m. p. 312°; methyl ester, m. p. 162°).

Two isomeric sulphonic acids, termed " $\alpha$ " and " $\beta$ ", respectively, are obtained by the interaction of chlorosulphonic acid and 3-bromoacenaphthene at the ordinary temperature, and are separated by means of their sodium salts. 3-Bromoacenaphthene- $\alpha$ -sulphonic acid forms the more sparingly soluble sodium salt (aniline salt, m. p. 260—261°;  $\beta$ -naphthylamine salt, m. p. 265—266°; chloride, m. p. 134—135°; amide, m. p. 137—138°); oxidation affords 3-bromo- $\alpha$ -sulphonaphthalic anhydride, isolated as its sodium salt.

3-Bromoacenaphthene- $\beta$ -sulphonic acid (aniline salt, m. p. 256—257°; chloride, m. p. 192—193°; amide, m. p. 233—234°; ethyl ester, m. p. 140—141°) yields a similar naphthalic acid on oxidation. Sulphonation with sulphuric acid (*d* 1.84) at 80—90° converts 3-bromoacenaphthene into a disulphonic acid, isolated as the barium salt; the disodium salt (+3H<sub>2</sub>O) is readily soluble in water [dichloride, m. p. 181—182°; diamide, m. p. 289° (decomp.); ethyl ester, m. p. 164°]. R. CHILD.

Action of acids on  $\beta\gamma$ -oxido-*n*-propylphthalimide. M. WEIZMANN and S. MALKOWA (Compt. rend., 1930, 190, 495—496).—Glycerol epibromohydrin condenses with potassium phthalimide to yield  $\beta\gamma$ -oxido-*n*-propylphthalimide, m. p. 93—94°, which is converted by hydrochloric, hydrobromic, and hydriodic acids into  $\gamma$ -chloro- (I), m. p. 96—97°,  $\gamma$ -bromo- (II), m. p. 112°, and  $\gamma$ -iodo- $\beta$ -hydroxy-*n*-propylphthalimide, m. p. 124° (cf. Gabriel and Ohle, A., 1917, i, 565), respectively. Further treatment of I and II with hydrochloric or hydrobromic acid affords  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-propylamine hydrochloride, m. p. 101—102°, and  $\gamma$ -bromo- $\beta$ -hydroxy-*n*-propylamine hydrobromide, m. p. 113—113.5°, converted by benzaldehyde in the presence of sodium carbonate into the 2-phenyl-5-chloromethyl- and 2-phenyl-5-bromo-methyl-oxazolidines described by Bergmann, Radt, and Brandt (A., 1921, i, 688); further treatment of the iodo-compound leads to decomposition with liberation of iodine. C. W. SHOPPEE.

Quinovic acid. II. H. WIELAND and T. HOSHINO (Annalen, 1930, 479, 179—210).—The compound  $C_{30}H_{40}O_6$  (now termed *novicquinone*), previously obtained by oxidising novic acid with chromic acid (A., 1927, 562), is an *o*-quinone, since, on treatment with methyl-alcoholic potassium hydroxide, it undergoes a benzilic acid rearrangement forming a *hydroxy-acid*,  $C_{30}H_{42}O_7(+Et_2O)$ , m. p. (ether-free) 183—185°. Oxidation of this with chromic oxide in acetic acid solution gives a *ketodilactone*,  $C_{29}H_{40}O_5$ , m. p. 198—199° (titrates with hot alcoholic potassium hydroxide as a monobasic acid), which on reduction with sodium and alcohol furnishes a mixture of a *monocarboxylic*



acid,  $C_{28}H_{44}O_3$ , m. p. 244—245° after sintering at 239°, and a *dicarboxylic acid*,  $C_{29}H_{44}O_5$ , decomp. 330°. Catalytic reduction (Adams) of novicquinone in acetic acid solution yields the corresponding *quinol*,  $C_{30}H_{42}O_6$ , m. p. 267—268°, an alkaline solution of which undergoes atmospheric oxidation, and subsequent rearrangement into the above hydroxy-acid. When novicquinone is exposed to light a colourless modification is obtained. The quinone is probably a dilactone formed from novic acid by oxidation of a tertiary carbon atom and subsequent elimination of water (lactonisation). Novic acid is unaffected by treatment with amalgamated zinc and hydrochloric acid, sodium and alcohol, or hydriodic acid at 180°.

Oxidation of the unsaturated anhydroquinovic acid,  $C_{30}H_{44}O_4$ , m. p. 235° (cf. *loc. cit.*), with dilute alkaline potassium permanganate gives two isomeric monobasic (lactonic) acids,  $C_{30}H_{44}O_5$ , m. p. 241—242° and 285—286°, formed by elimination of 1 mol. of water from the intermediate dihydroxydicarboxylic acid. The former of these is converted into a *substance*, m. p. 211°, by boiling with 25% methyl-alcoholic potassium hydroxide solution, and subsequent acidification of the deep orange-yellow, fluorescent, alkaline solution. Both acids are oxidised by chromic oxide in acetic acid solution to novicquinone, further lactonisation occurring during the oxidation.

Oxidation of tribenzoylquinovic acid with chromic and acetic acids affords a *compound*,  $C_{37}H_{46}O_6$ , m. p. 189—190°, and a *benzoylquinone*,  $C_{37}H_{44}O_8$ , m. p. 285—286° (decomp.). The last-named substance, on treatment with 10% methyl-alcoholic potassium hydroxide, is hydrolysed and then rearranged into a *hydroxy-acid*,  $C_{30}H_{42}O_8 + H_2O$ , m. p. 220—221° (decomp.), oxidised further to a mixture of a dibasic acid,  $C_{29}H_{38}O_9$ , m. p. 286—287° (decomp.) after previous sintering (*methyl ester*, m. p. 231—232°), and a neutral *compound*,  $C_{29}H_{36}O_8$ , m. p. 316° (decomp.). The compound  $C_{37}H_{46}O_6$  is hydrolysed by 10% methyl-alcoholic potassium hydroxide to a *hydroxydilactone*,  $C_{33}H_{42}O_5$ , m. p. 258—259° (decomp.), re-benzoylated in pyridine to the original substance, and oxidised further to an acid,  $C_{30}H_{40}O_8$ , m. p. 352° (decomp.) after darkening at 330°. *Dimethyl benzoylquinovate*, m. p. 235—236°, is oxidised by chromic and acetic acids to two isomeric *substances*,  $C_{39}H_{52}O_7$ , m. p. 242—243° and 298—299°, respectively, whilst *dimethyl acetylquinovate*, m. p. 208—209°, furnishes similarly a *compound*,  $C_{34}H_{50}O_7$ , m. p. 239—240°.

Oxidation of pyroquinovic acid (*loc. cit.*) with dilute potassium permanganate at 0° gives a mixture of a *dihydroxylactone*,  $C_{29}H_{44}O_5$ , m. p. 314° (decomp.) [*diacetyl derivative*, m. p. 303° (decomp.)], and an acid,  $C_{29}H_{44}O_4$ , m. p. 310° (decomp.), whilst chromic acid oxidation affords a neutral *compound*,  $C_{27}H_{40}O_4$ , m. p. 238—239°, and a *keto-acid* (I),  $C_{24}H_{34}O_4$ , m. p. 295° (decomp.; *methyl ester*, m. p. 215—216°); I is also formed by oxidation of pyroquinovic acid with potassium permanganate in acetic acid solution. Pyroquinovic acid contains one double linking and a secondary hydroxyl group; it is presumed that during the oxidation with aqueous permanganate, glycol formation, oxidation of the secondary alcoholic grouping and a tertiary carbon atom, and subsequent elimination of water between the carboxyl and one

of the three hydroxyl groups occur, thus giving the above dihydroxylactone. Acetylpyroquinovic acid (*loc. cit.*) is oxidised by chromic acid to a mixture of two neutral *substances*,  $C_{25}H_{34}O_4$  and  $C_{29}H_{44}O_5$ , m. p. 292—293° (decomp.) and 290—291°, respectively, and the *acetyl derivative*, m. p. 292—293°, of a *hydroxy-acid*,  $C_{24}H_{36}O_4$ , m. p. 298°. This acid contains a secondary alcoholic grouping; on further oxidation it yields I. Treatment of pyroquinovic acid with bromine in ethereal solution furnishes a *bromolactone* (II),  $C_{29}H_{45}O_3Br$ , m. p. 192° (decomp.), presumably

formed thus:  $CBr \cdot CBr \dots CO_2H \longrightarrow \cdot CBr \cdot \overset{\overset{O}{\parallel}}{C} \dots CO$ . Mono- and di-acetylpyroquinovic acids furnish similarly the same acetylated *bromolactone* (III),  $C_{31}H_{47}O_4Br$ , m. p. 195° (decomp.). When II is heated with pyridine, hydrogen bromide is evolved and a *hydroxy-acid*,  $C_{29}H_{44}O_3$ , m. p. 245—246°, results. The *acetyl derivative*, m. p. about 265° (decomp.), of this is also formed from III by treatment with pyridine. Oxidation of the hydroxy-acid with dilute potassium permanganate gives the two compounds obtained similarly from pyroquinovic acid, whilst chromic acid oxidation affords I. When pyroquinovic acid is treated with slightly alkaline sodium hypobromite a *bromolactone*,  $C_{29}H_{43}O_3Br$ , m. p. 190° after darkening at 160°, is obtained. This is probably derived from II by oxidation of a secondary alcoholic grouping. The formation of pyroquinovic acid from quinovic acid (*loc. cit.*) probably involves the opening of a ring.

H. BURTON.

Degradation of humic acids to *benzenecarboxylic acids* and *nitrophenols*. W. FUCHS and W. STENGEL (Annalen, 1930, 478, 267—283).—"Nitrohumic acid," which is considered to be a nitroso-derivative of a hydroxyketocarboxylic acid, has been further oxidised and the products have been examined. Comparative experiments showed that a maximum yield (50%) of ether-soluble material in the product is obtained when nitrohumic acid is treated for 45 min. with six parts of dilute nitric acid (1 : 1) at 90°, and the treatment then repeated. Attempts to fractionate the ethereal extract were unsuccessful, and a method is described in which the aqueous extract (71%) is precipitated successively with milk of lime and silver nitrate, and the calcium and silver salts obtained are then refractionated. The calcium salts consist largely of oxalate. The silver salts are converted into methyl esters by successive treatment with methyl alcohol and hydrogen chloride and with diazomethane. These methyl esters are partly soluble in ether, and the soluble fraction can be fractionally distilled at 60—190°/0.0001 mm. to give limpid and then viscous oils, and from the latter crystals separate on cooling. In the crystalline material the methyl esters of mellitic, benzenepentacarboxylic, pyromellitic, mellophanic, and trimelic acids have been identified. The yellow filtrate from the silver salts contains nitrophenols. When silver has been removed, extraction with ether and extraction of the ether with benzene yields a solution which affords the picrate with naphthalene. In one case a *compound*, m. p. 174—183°, was isolated from the ethereal solution. Preferably, however, the aqueous solution is treated with acridine hydrochloride, when acridine picrate is obtained in a yield

corresponding with 40 g. of picric acid from 900 g. of nitrohumic acid, and an acridine compound, m. p. 169°, may also be isolated. R. K. CALLOW.

**Reduction of *m*-nitrobenzaldehyde and its derivatives in neutral solution.** W. M. CUMMING and J. C. EATON (J. Roy. Tech. Coll. Glasgow, 1930, 2, 191—195).—In confirmation of the view that an organo-zinc compound is an intermediate stage in such reactions (Cumming and Howie, A., 1929, 693), it is found that reduction of *m*-nitrobenzaldehyde with zinc and ammonium chloride in aqueous alcohol at 70° yields a solution which deposits the compound  $9\text{Zn}(\text{OH})_2 \cdot \text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl} \cdot 2\text{C}_{14}\text{H}_{10}\text{O}_3\text{N}_2$  as an insoluble, amorphous, yellow powder. *m*-Azoxybenzaldehyde is obtained from the filtrate in small quantity, and from the organo-zinc compound by crystallisation from formic acid, or by treatment with acids or alkalis, ammonia, ammonium or zinc chloride, or hot potassium hydrogen sulphite solutions. When the compound of *m*-nitrobenzaldehyde with potassium hydrogen sulphite is reduced, the compound  $\text{NH}_4\text{Cl} \cdot \text{ZnCl}_2 \cdot 5\text{Zn}(\text{OH})_2$  is obtained, but no reduction product can be isolated. Steam-distillation of the organo-zinc compound with ferric chloride solution yields *m*-nitrosobenzaldehyde. Reduction of *m*-nitrobenzaldehyde to the hydrazo-compound does not take place with zinc and ammonium chloride.

*m*-Nitrobenzoic acid and *m*-nitrobenzyl alcohol are reduced by the same method to the azoxy-compounds. Efflorescent double basic zinc salts are formed to which formulæ cannot be assigned.

R. K. CALLOW.

**Constitution of cryptal.** A. R. PENFOLD and J. L. SIMONSEN (J.C.S., 1930, 403—406).—*l*-Cryptal (oily phenylhydrazone; *p*-nitrophenylhydrazone, m. p. 167°), which is mixed with cuminaldehyde and phellendral in "aromadendral" (Penfold, J.C.S., 1922, 121, 266), is converted quantitatively by oxidation with potassium permanganate at 0° into *d*- $\alpha$ -isopropylglutaric acid, and is therefore 4-isopropyl- $\Delta^2$ -cyclohexenaldehyde, oxidation probably proceeding through the glycol and the enol form of the corresponding cyclohexadione. Attempts to oxidise cryptal to the corresponding cyclohexenecarboxylic acid were unsuccessful, oxidation with silver oxide proceeding smoothly but giving a non-crystalline product, probably a mixture of  $\alpha\beta$ - and  $\beta\gamma$ -isomerides. The oxime, b. p. 150°/17 mm.,  $n_D^{20}$  1.5139, of cryptal is converted by heating with acetic anhydride and sodium acetate into an optically inactive substance,  $\text{C}_{22}\text{H}_{30}\text{O}_5$ , b. p. 200—210°/23 mm., m. p. 102—103°, only a trace of the impure nitrile being obtained. The biogenetic relation of cuminaldehyde, phellendral, and cryptal to  $\alpha$ -phellandrene is discussed.

J. W. BAKER.

**Oxidation of cyclopolymethylene ketones with hydrogen peroxide and ozone.** M. STOLL and W. SCHERRER (Helv. Chim. Acta, 1930, 13, 142—153).—Dissolution of cyclohexanone in 30% hydrogen peroxide and subsequent dilution with water affords 1-hydroxy-1-cyclohexyl peroxide (+0.5H<sub>2</sub>O) (I), m. p. 62—63°, which cannot be freed from water of crystallisation owing to its ready decomposition. When distilled with benzene it regenerates the original

reagents, and on hydrolysis with *N*-sodium hydroxide solution gives mainly cyclohexanone together with small amounts of adipic and  $\epsilon$ -hydroxyhexoic acids. Treatment of cyclohexanone with 55% hydrogen peroxide at 35° and subsequent addition of 10% hydrochloric acid gives 1-hydroxy-1-cyclohexyl hydrogen peroxide, decomp. 50°/22 mm. Treatment of an ethereal solution of I with cold 90% sulphuric acid furnishes

the peroxide,  $\text{C}_6\text{H}_{10}\text{O}_3$ , m. p. 131—133°, which when heated at 80°/vac. passes into a sodium hydroxide-soluble resinous product; the residue from this preparation is converted by alcoholic sulphuric acid into neutral products (impure ethyl  $\epsilon$ -hydroxyhexoate), probably formed by way of 1-hydroxy- $\Delta^1$ -cyclohexene oxide and  $\epsilon$ -hydroxyhexoic acid lactone. Exaltone (cyclopentadecanone) reacts with hydrogen peroxide only in presence of sulphuric acid, yielding a non-homogeneous peroxide derivative, m. p. 96—118°, decomp. 125°, hydrolysed by potassium hydroxide solution to exaltone and a small amount of  $\xi$ -hydroxypentadecic acid. When a mixture of exaltone and 55% hydrogen peroxide is treated with an excess of sulphuric acid, peroxide, tridecane- $\alpha\gamma$ -dicarboxylic acid, a neutral product, m. p. 150—158° (reduced by zinc dust and acetic acid to exaltone; cf. Ruzicka and Stoll, A., 1929, 68), a ketone (semicarbazone, m. p. 40—60°), and other neutral products are produced. Exaltolide (*loc. cit.*) is converted by alcoholic sulphuric acid into ethyl  $\xi$ -hydroxypentadecate, b. p. 151—155°/0.12 mm.

Treatment of cyclohexanone and exaltone with ozone in carbon tetrachloride solution furnishes adipic and tridecane- $\alpha\gamma$ -dicarboxylic acids, respectively. Ozonisation of exaltone in acetic acid solution affords some tridecane- $\alpha\gamma$ -dicarboxylic acid; dilution of the acetic acid solution and subsequent extraction with light petroleum affords an acid,  $\text{C}_{15}\text{H}_{30}\text{O}_5$ , m. p. 85—87°, and a neutral peroxidic product,  $\text{C}_{15}\text{H}_{28}\text{O}_4$ . The ozone molecule appears to add to the keto-group (or to the enol form) with subsequent change of the enol ozonide to a peroxidic acid and thence to the dicarboxylic acid. The action of Caro's acid on the ketones (*loc. cit.*) is considered to involve addition to the carbonyl group with subsequent formation of peroxide and hydroxycyclene oxide. H. BURTON.

**Properties of the carbonyl group.** R. CORNUBERT and R. HUMEAU (Compt. rend., 1930, 190, 643—645; cf. Bull. Soc. chim., 1928, [iv], 43, 807).—3-Methyl-2:2:6:6-tetra-*n*-propylcyclohexanone is inactive toward magnesium methyl iodide, semicarbazide, and hydroxylamine under various conditions, although traces of nitrogenous material were found in the last case. On the contrary, the ketone is reduced with great ease by sodium and alcohol to 3-methyl-2:2:6:6-tetra-*n*-propylcyclohexanol (acetyl derivative, b. p. 182—184°/23 mm.). C. W. SHOPPEE.

**Catalytic reactions in organic chemistry. III. Isomeric transformations of a seven-membered ring.** N. A. ROZANOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2313—2318).—When heated with anhydrous oxalic acid, cycloheptanone undergoes normal dehydration to cycloheptene, but in presence of thoria partial isomerisation of the seven- to a six-membered ring

occurs, methylenecyclohexane being formed. When catalytically reduced under the influence of finely-divided nickel, cycloheptene also undergoes isomerisation, methylcyclohexane being obtained. cyclo-Heptylcarbinol, obtained by treating the magnesium compound of iodocycloheptane with trioxymethylene, has b. p. 204—206°/49 mm.,  $d_4^{20}$  0.9315,  $n_D^{20}$  1.4685, molecular refraction increment -0.14; when dehydrated by heating with oxalic acid, it gives methylenecycloheptane,  $C_8H_{14}$ , b. p. 139—143°/749 mm.,  $d_4^{20}$  0.8185,  $n_D^{20}$  1.4599, molecular refraction increment 0.36, but dehydration under the influence of thoria yields cyclooctene, b. p. 145—146°,  $d_4^{20}$  0.8415,  $n_D^{20}$  1.4678, molecular refraction increment -0.12. T. H. POPE.

**Catalytic reactions in organic chemistry.**  
**I. Preparation of cycloheptanone and cyclooctanone.** N. A. ROZANOV and BELIKOV (J. Russ. Phys. Chem. Soc., 1929, 61, 2303—2308).—Suberic acid, prepared by Markownikoff's method (A., 1894, i, 172), may be separated from the accompanying azelaic acid by esterification, followed by fractional distillation of the methyl esters in a vacuum. The catalytic preparation of the corresponding cyclic ketones from these acids is best carried out at 300—350° in presence of thoria, cycloheptanone (suberone) and cyclooctanone (azelaone) being thus obtained. Dry distillation of sebatic acid with thoria at 300—350° yields no cyclic ketone. T. H. POPE.

**Isomerism of oximes.** M. BUSCH and R. KÄMMERER (Ber., 1930, 63, [B], 649—658; cf. Busch and others, A., 1925, i, 40; Raikowa, *ibid.*, 1929, 911, 1276).—Phenacyl-*p*-toluidine is converted by hydroxylamine hydrochloride and sodium acetate in aqueous alcohol into a mixture of the corresponding *n*-oxime, m. p. 92°, and *h*-oxime, m. p. 97°, which is separated into its components by taking advantage of their differing rates of crystallisation from alcohol. Both forms are stable in boiling alcohol. When kept molten for half an hour the *n*-oxime yields the other variety only in traces, whereas the reverse change occurs to 60% extent. Both varieties dissolve immediately in aqueous-alcoholic potassium hydroxide and separate unchanged when the solutions are acidified with acetic acid. Since the *h*-oxime is transformed by phosphorus pentachloride in presence of ether into *p*-toluidinoacetanilide, m. p. 99° (lit. m. p. 82—83°; hydrochloride, m. p. 216°), it receives the configuration  $\text{Ph}\cdot\text{C}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_7$ . With the

*n*-oxime the action follows a more complex course, giving mainly the *h*-oxime and thence *p*-toluidinoacetanilide with smaller amounts of a base,  $\text{C}_{15}\text{H}_{14}\text{ON}_2$ , m. p. 222° after softening at 210°, from which benzoic acid cannot be obtained. With concentrated alcoholic hydrogen chloride this base affords a dihydrochloride which becomes converted when warmed into phenacyl-*p*-toluidine hydrochloride. With reserve, the formation of the base is formulated,  $\text{Ph}\cdot\text{C}\cdot\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_7$ ,  $\text{OH}\cdot\text{NH}$

$\xrightarrow{-\text{H}_2}$   $\text{CPh}\cdot\text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_7$ . The base yields a nitrosoamine and is converted by alcoholic potassium hydroxide into a compound (?)  $\text{CPh}\cdot\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_7$ ,

m. p. 133° (hydrochloride; sulphate, m. p. 200°). The inability of the *n*-oxime to undergo the Beckmann rearrangement finds its most plausible explanation in the hydroxyamino-formulation, and this view is strengthened by the behaviour of the isomerides towards benzaldehyde. The *h*-compound affords diphenyl-*p*-tolylloxidiazine,  $\text{N}\langle\text{CPh}\cdot\text{CH}_2\rangle\text{N}\cdot\text{C}_6\text{H}_7$ , m. p. 141°, converted by alcoholic potassium hydroxide into ammonia, benzaldehyde, benzoic acid, and *p*-toluidine. The *n*-oxime affords a mixture of diphenyl-*p*-tolylloxidiazine and 2:4-diphenyl-1-*p*-tolyl-oximinazole, m. p. 206°. The last-named compound yields benzaldehyde when boiled with dilute sulphuric acid; it is transformed by alcoholic potassium hydroxide into diphenyl-*p*-tolyliminazole, m. p. 148° (hydrochloride, m. p. 91°). The simultaneous formation of oxidiazine and oximinazole is possible only on the assumption of the  $\psi$ -oxime structure. In alcoholic solution the *h*-oxime affords a yellow, the *n*-oxime a dark red coloration.

Contrary to Raikowa, the proximity of methyl or methylene to the oxime group does not necessitate the absence of isomerism, and, if only one oxime exists, it is not necessarily the  $\psi$ -form. Thus phenacylaniline affords a single oxime,  $\text{C}_{14}\text{H}_{14}\text{ON}_2$ , m. p. 105—106°, which does not exhibit the ferric chloride reaction. Since it gives anilinoacetanilide, m. p. 112°, when treated with phosphorus pentachloride in ether it appears to have the *syn*-methyl configuration. With benzaldehyde it affords triphenyloxidiazine, m. p. 125°. H. WREN.

**Nitration of 4-methoxy- and 4-ethoxy-benzophenone.** J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 383—395).—4-Methoxybenzophenone is nitrated by acetic anhydride and absolute nitric acid at 0° to 3-nitro-4-methoxybenzophenone, converted by boiling aqueous-alcoholic methylamine solution into 3-nitro-4-methylaminobenzophenone, m. p. 200°. When absolute nitric acid was used at -15°, 3:3':5-trinitro-4-methoxybenzophenone, m. p. 184°, 2':3:5-trinitro-4-methoxybenzophenone, m. p. 138° (lit. 142°), and 2:4-dinitroanisole, accompanied by mixed nitrobenzoic acids, were isolated.

By the interaction of nitric acid at -15° with 4-ethoxybenzophenone there are obtained a mixture of nitrobenzoic acids, 2:2-dinitrophenetole, m. p. 86°, 3:3':5-trinitro-4-ethoxybenzophenone, m. p. 134°, and 2':3:5-trinitro-4-ethoxybenzophenone, m. p. 102°. It is considered that a side reaction accompanies the main nitration:  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{COPh} + \text{NO}_2\cdot\text{OH} \rightarrow \text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 + \text{Ph}\cdot\text{CO}_2\text{H}$ , the products so formed being then nitrated further.

Nitration of 3:3'-dinitro-4-methoxybenzophenone with absolute nitric acid at -15° gives 3:3':5-trinitro-4-methoxybenzophenone, m. p. 183°, which on boiling with absolute nitric acid and concentrated sulphuric acid gives 2:4:6-trinitroanisole contaminated with higher-melting products. Absolute nitric acid and 2':3-dinitro-4-methoxybenzophenone, m. p. 131°, at -15° yield 2':3:5-trinitro-4-methoxybenzophenone, m. p. 142°. 3:3'-Dinitro-4-ethoxybenzophenone, m. p. 115°, gives under the same conditions 3:3':5-trinitro-4-ethoxybenzophenone accompanied

by a little *m*-nitrobenzoic acid. 2':3-Dinitro-4-ethoxybenzophenone, m. p. 151°, with absolute nitric acid gives 2':3:5-trinitro-4-ethoxybenzophenone. 3:3':5- and 2':3:5-Trinitro-4-methylaminobenzophenones, m. p. 157—158° and 191°, respectively, are also described.

R. J. W. LE FÈVRE.

**$\alpha$ -Trisubstituted aryl ketones.** (MME.) BRUZAU (Compt. rend., 1930, 190, 496—499).—Phenyldimethylacetoneitrile and magnesium phenyl bromide react in toluene or xylene to give *phenyl  $\alpha$ -phenylisopropyl ketimine hydrobromide* (I), m. p. 240—241°, which by hydrolysis furnishes *phenyl  $\alpha$ -phenylisopropyl ketone*, m. p. 46—47° (oxime, m. p. 192—193°; *semicarbazone*, m. p. 177—178°, both readily obtained directly from I), also prepared from methyldeoxybenzoin by methylation with sodamide and methyl iodide. With magnesium *p*-tolyl bromide is obtained *p*-tolyl  $\alpha$ -phenylisopropyl ketimine hydrobromide (II), m. p. 246—247°, hydrolysed to *p*-tolyl  $\alpha$ -phenylisopropyl ketone, m. p. 60—61° (oxime, m. p. 205—206°; *semicarbazone*, m. p. 223—224°, both also obtained directly from II). Magnesium *p*-anisyl bromide affords *p*-anisyl  $\alpha$ -phenylisopropyl ketimine hydrobromide (III), m. p. 205—206°, hydrolysed to *p*-anisyl  $\alpha$ -phenylisopropyl ketone, m. p. 100—101°, the oxime, m. p. 193—194°, and *semicarbazone*, m. p. 210—211°, of which were prepared from III, but not from the ketone. Using toluene as medium, the yields of the three ketones are 27, 50, and 57%, whilst with xylene all three yields range from 60 to 70%. Diphenylethylacetoneitrile and magnesium benzyl chloride do not give a ketone, but afford dibenzyl, a hydrocarbon derived from the nitrile, and magnesium cyanide (cf. A., 1928, 522).

C. W. SHOPPEE.

**Reaction of aldehydes.** IV. R. DE FAZI and F. MONFORTE (Atti R. Accad. Lincei, 1929, [vi], 10, 653—655).—The reaction of acenaphthenone with cyclic aldehydes to give compounds yielding a violet-red coloration with concentrated sulphuric acid (A., 1924, i, 1319) is shown by phenylacetaldehyde, resorcyaldehyde, *o*- and *p*-nitrobenzaldehydes, and salicylaldehyde, the compounds formed being phenylethylideneacenaphthenone, 2:4-dihydroxybenzylideneacenaphthenone, 2- and 4-nitrobenzylideneacenaphthenones, and 2-hydroxybenzylideneacenaphthenone, respectively. Either alone or in alcoholic solution, these products give the characteristic violet-red colour with sulphuric acid. Gugliemelli and Delmon's view that the coloration is due to condensation products of fluorene (A., 1918, i, 161) is untenable.

T. H. POPE.

**Desylanilides.** I. V. HOPPER and J. R. ALEXANDER (J. Roy. Tech. Coll. Glasgow, 1930, 2, 196—200).—*Desyl-p*-acetamidoanilide, m. p. 230—240° [*di*-hydrochloride, m. p. 187.5° (decomp. from 165°); *sulphate*, m. p. 175—178°; *N*-nitroso-derivative, m. p. 180° (decomp.); *N*-acetyl derivative, m. p. 217°], is obtained by heating benzoin with *p*-aminoacetanilide at 135—145°. It is only slightly hydrolysed by acids. When heated with excess of aniline it yields desylanilide. Solutions of desyl-*p*-acetamidoanilide, particularly alcoholic solutions containing a trace of alkali, are readily oxidised in air to *benzil-p*-acetamidoanil, m. p. 190° (also prepared by heating benzil with

*p*-aminoacetanilide), which is readily hydrolysed to benzil and *p*-aminoacetanilide. *Desyl-p*-toluidide, m. p. 144°, and desylanilide are similarly oxidised to *benzil-p*-toluidide and anilide, respectively.

R. K. CALLOW.

**Condensation of methyl isobutyl ketone with anisaldehyde.** II. Phototropy of semicarbazones of ethylenic ketones. C. V. GHEORGHIU and B. ARVENTIEV (Bull. Soc. chim., 1930, [iv], 47, 195—203).— $\alpha$ -Ethylenic ketones,  $\text{CHPh}:\text{CH}\cdot\text{COR}$ , yield semicarbazones which become coloured on exposure to light, the semicarbazones of  $\gamma$ -ethylenic ketones,  $\text{CHPh}:\text{CR}'\cdot\text{COR}$ , remaining colourless. Thus in presence of 10% sodium hydroxide anisaldehyde and methyl isobutyl ketone yield *p*-methoxystyryl isobutyl ketone, m. p. 46°, b. p. 190—191°/12 mm. [*dibromide*, m. p. 115° (decomp.)], giving a colourless  $\gamma$ -semicarbazone, m. p. 155—158°, which turns intense yellow in diffused light and is not decolorised by sunlight (cf. A., 1928, 522), but yields the colourless form on recrystallisation. Condensation in presence of hydrogen chloride probably yields a little of the  $\gamma$ -ketone, since the mother-liquors from the semicarbazone yield a colourless substance, m. p. 186—188°, unchanged by light. Similarly, *p*-methoxystyryl ethyl ketone, b. p. 182—185°/10 mm., m. p. 59° (some *dimeride*, m. p. 194°, is formed when the condensation is effected in alcohol), yields a colourless  $\gamma$ -semicarbazone, m. p. 172°, which turns yellow immediately in light and is decolorised when heated to its m. p., whilst  $\alpha$ -methyl-*p*-methoxybenzylidene-methyl methyl ketone, m. p. 28°, b. p. 168—170°/10 mm., yields a colourless *semicarbazone*, m. p. 201° (decomp.), unchanged by light. *Styryl ethyl ketone* yields a colourless *semicarbazone*, m. p. 173°, yellow on exposure to light, which is not decolorised on insolation, whilst the *semicarbazone*, m. p. 204°, of methylstyryl methyl ketone is unchanged by light. Similarly, the semicarbazones of the  $\alpha$ -ethylenic ketones turn yellow in presence of sodium methoxide, and are decolorised again by addition of acetic and hydrochloric acids. With ferric chloride the two kinds of ketone show similar differences (cf. Stobbe and Bremer, A., 1929, 1301).

R. BRIGHTMAN.

**Heteropolar compounds of carbon.** XI. Influence of substituents on halochromism in chalkone and triphenylmethane derivatives. W. DILTHEY, L. NEUHAUS, E. REIS, and W. SCHOMMER (J. pr. Chem., 1930, [ii], 124, 81—126).—The influence of various substituents, especially the nitro-group and the halogens, on the halochromism of chalkone and certain triphenylmethane derivatives and the effect of interchange of oxygen, sulphur, and selenium in triarylmethane and diphenyl derivatives have been investigated (cf. A., 1929, 1301). The standard of comparison in chalkones was the initial colour produced on dissolution in concentrated sulphuric acid (Pfeiffer, "Organische Molekülverbindungen," 2nd Ed., p. 68). The amino- and the dimethylamino-groups in the 4'-position have little effect in the benzaldehyde series, but have a slight bathochromic influence in the anisaldehyde series. The nitro-group has a bathochromic effect only when present in the phenyl adjacent to the carbonyl group, otherwise it

exerts a hypsochromic action. Thus with 3'-nitro-chalkone a bathochromic influence is present, but with the introduction of further nitro-groups in the 2- and 3-positions a hypsochromic effect is observed. The nitro-group in the 4-position exerts an anomalous bathochromic influence. Halogens in the 4-position usually have a hypsochromic effect, but the effect is very much smaller than that of the nitro-group. An interpretation of these results is given which is based on the effect of the introduction of positive and negative auxochromic groups in either of the two phenyl nuclei in the intramolecular dipole

$\text{R}\ddot{\text{C}}\text{H}\cdot\ddot{\text{C}}\text{H}\cdot\ddot{\text{C}}\text{R}'\cdot\ddot{\text{O}}$  or  $\text{R}\ddot{\text{C}}\text{H}\cdot\text{CH}:\ddot{\text{C}}\text{R}'\cdot\ddot{\text{O}}$ . The phenylthiol group in the 4-position exerts a powerful bathochromic influence. Substitution of sulphur for oxygen in diphenyl oxide derivatives results in an appreciable bathochromic effect, which is further slightly increased by selenium; this effect is also apparent in the dichalkones and in triarylmethane derivatives with oxygen, sulphur, and selenium bridges.

The following compounds were prepared: 4'-amino-chalkone, m. p. 108°, from *p*-aminoacetophenone and benzaldehyde in the presence of alcohol and hydrochloric acid at 0° [hydrochloride; perchlorate, m. p. 196° (decomp.); acetate, m. p. 161°]; 4'-amino-4-methoxychalkone, m. p. 198° (hydrochloride); 4'-dimethylamino-4-methoxychalkone, m. p. 132°, from anisaldehyde, *p*-dimethylaminoacetophenone, and sodium methoxide; diphenyl sulphide (I), b. p. 157–158°/16 mm., best prepared from benzene, sulphur, and aluminium chloride; 4-acetyldiphenyl sulphide (II), m. p. 65°, from I and acetyl chloride in the presence of aluminium chloride and carbon disulphide; 4-benzylidenecetyldiphenyl sulphide, m. p. 95°, from II, benzaldehyde, and excess of methyl-alcoholic sodium methoxide (dibromide, m. p. 146–147°); 4-anisylidenecetyldiphenyl sulphide, m. p. 110°; 4-piperonylidenecetyldiphenyl sulphide, m. p. 94–95°; 4:4'-di-benzylidenediacetyldiphenyl sulphide, m. p. 150–151° [tetrabromide, m. p. 220° (decomp.)]; 4:4'-di-*p*-anisylidenediacetyldiphenyl sulphide, m. p. 178–179°; 4:4'-dipiperonylidenediacetyldiphenyl sulphide, m. p. 150°; 4:4'-dicinnamylidenediacetyldiphenyl sulphide, m. p. 176°; 4-benzoyldiphenyl sulphide, m. p. 71–72°, from diphenyl sulphide and benzoyl chloride in the presence of carbon disulphide and aluminium chloride [oxime, m. p. 150° (slow decomp.)]; 4:4'-dibenzoyldiphenyl sulphide, m. p. 169° [dioxime, m. p. 203° (decomp.)]; 4:4'-di(chlorodiphenylmethyl)diphenyl sulphide (III), m. p. 162–163°, from magnesium phenyl bromide and dibenzoyldiphenyl sulphide in benzene solution; 4:4'-dibenzoyldiphenyl selenide (IV), m. p. 159–160°, from diphenyl selenide, benzoyl chloride, and excess of aluminium chloride; 4:4'-dibenzhydryl selenide, m. p. 113–114°, prepared in 75% yield by reduction of IV with zinc dust in alkaline solution; 4:4'-di(chlorodiphenylmethyl)diphenyl selenide, m. p. 152° (decomp.), from magnesium phenyl bromide and dibenzoyldiphenyl selenide in toluene solution; 4:4'-diacetyldiphenyl selenide (V), m. p. 91–92°, from diphenyl selenide, acetyl chloride, and aluminium chloride in carbon disulphide solution (70% yield); diphenylselenone-4:4'-dicarboxylic acid (VI), m. p. above 350°, by oxidation of V with potassium permanganate; diphenyl selenide-4:4'-di-

carboxylic acid, m. p. 321–323°, by reduction of VI with zinc dust in acetic acid solution; 4:4'-dibenzylidenediacetyldiphenyl selenide, m. p. 155–156°, from diacetyldiphenyl selenide, benzaldehyde, and methyl-alcoholic sodium methoxide at the ordinary temperature; 4:4'-di-*p*-anisylidenediacetyldiphenyl selenide, m. p. 157–158°; 4:4'-dipiperonylidenediacetyldiphenyl selenide, m. p. 195–196°; 4:4'-dicinnamylidenediacetyldiphenyl selenide, m. p. 166° (decomp.), from diacetyldiphenyl selenide, cinnamaldehyde, and methyl-alcoholic sodium hydroxide in 60% yield; 4:4'-dicinnamylidenediacetyldiphenyl ether, m. p. 178–179°; 4:4'-dipiperonylidenediacetyldiphenyl ether, m. p. 175–176°; *pp'*-di-4-benzoylphenoxydiphenyl ether, m. p. 205–206°, from *pp'*-diphenoxydiphenyl ether, benzoyl chloride, and aluminium chloride in carbon disulphide solution [dioxime, m. p. 196–197° (decomp.)]; 4-nitro-4'-acetyldiphenyl, m. p. 152–153°, from nitrodiphenyl and acetyl chloride by the Friedel-Crafts reaction; 4-nitro-4'-benzylidenecetyldiphenyl, m. p. 165–166°; 4-nitro-4'-*p*-anisylidenecetyldiphenyl, m. p. 198–199°; 3:2'-dinitrochalkone, m. p. 195–196° (decomp.), from *m*-nitrobenzaldehyde, *o*-nitroacetophenone, and methyl-alcoholic sodium hydroxide; 2:3'-dinitrochalkone, m. p. 160–161°; 4:3'-dinitrochalkone, m. p. 223–224° (sinters at 200°); 4-chlorochalkone, m. p. 103–104° and 115–116°, from *p*-chlorobenzaldehyde and acetophenone.

A. I. VOGEL.

**Preparation of chalkones.** L. MONTI (Gazzetta, 1930, 60, 43–49).—Simonis and Lear's method of preparing chalkones (A., 1927, 154) was not new, having been first used by Stockhausen and Gattermann (A., 1893, i, 163). Attempts now described to obtain additive compounds of ethers of polyhydric phenols and chalkones, similar to the compound  $\text{C}_{27}\text{H}_{30}\text{O}_7$ , obtained by Bargellini and Finkelstein (A., 1913, i, 59), have proved unsuccessful. Thus, the interaction of veratrole and phenyl styryl ketone (chalkone) or of 2'-hydroxy-3':4'-dimethoxychalkone and the trimethyl ether of pyrogallol, in presence of aluminium chloride and in carbon disulphide solution, yielded only the unchanged chalkone. In the action of cinnamoyl chloride on various phenolic ethers under similar conditions, the chalkones formed were accompanied by small proportions of other substances of which only the m. p. could be determined.

Veratrole and cinnamoyl chloride give 3':4'-dimethoxychalkone and a compound, m. p. 122°, which is probably the same chalkone with one of the methoxyl groups hydrolysed. *p*-Chloroanisole and cinnamoyl chloride give, not 5'-chloro-2'-methoxychalkone, but 5'-chloro-2'-hydroxychalkone,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CO}\cdot\text{CH}:\text{CHPh}$ , m. p. 109–110°. Pyrogallol trimethyl ether and cinnamoyl chloride give 2'-hydroxy-3':4'-dimethoxychalkone and a small amount of a compound, m. p. 152–153°. 3-Methoxy-2-naphthyl styryl ketone, m. p. 138–140°, is obtained from  $\beta$ -naphthyl methyl ether and cinnamoyl chloride.

T. H. POPE.

**Sulphur-containing dyes. I. Derivatives of alkyl- and aryl-thioldiphenylmethane.** M. V. BETRABET and G. C. CHAKRAVARTI (J. Indian Chem. Soc., 1930, 7, 21–30).—Condensation of benzhydrol (or substituted benzhydrols) with various aliphatic and aromatic mercaptans in the presence of concen-

trated sulphuric acid at the ordinary temperature yields methanesulphonic acid derivatives:

$$\text{CHAr}_2\cdot\text{OH} + \text{R}\cdot\text{SH} \longrightarrow \text{CHAr}_2\cdot\text{SR} \xrightarrow{\text{H}_2\text{SO}_4} \text{CAr}_2(\text{SO}_3\text{H})\cdot\text{SR}$$

which react further with the same or a different mercaptan and sulphuric acid:  $\text{R}'\cdot\text{SH} + \text{H}_2\text{SO}_4 \longrightarrow \text{R}'\cdot\text{S}\cdot\text{OH} + \text{SO}_2 + \text{H}_2\text{O}$ ;  $\text{CAr}_2(\text{SO}_3\text{H})\cdot\text{SR} + \text{R}'\cdot\text{S}\cdot\text{OH} \rightleftharpoons \text{CAr}_2(\text{SR})\cdot\text{SR}' + \text{H}_2\text{SO}_4$ , the disulphides so formed being secondary products of the condensation. The reversible nature of the last reaction is confirmed by the conversion of the disulphides into the original sulphonie acids by the action of concentrated sulphuric acid. Thus from the appropriate diphenylcarbinol (or the intermediate sulphonie acid) and mercaptan are obtained:  $\alpha$ -p-tolylthiol-, m. p. 158—159° (potassium salt),  $\alpha$ -phenylthiol-, m. p. 191—195° (potassium salt),  $\alpha$ -n-butylthiol-, m. p. 146—147° (potassium salt), and  $\alpha$ -benzylthiol-, m. p. 223—225° (potassium salt), -2:4-dihydroxydiphenylmethanesulphonic acid, together with  $\alpha$ -di-p-tolylthiol-, not melting at 300° (potassium and silver salts),  $\alpha$ -di-n-butylthiol-, m. p. 250° (decomp.) (potassium salt),  $\alpha$ -phenylthiol- $\alpha$ -n-butylthiol-, decomp. above 250°, and  $\alpha$ -phenylthiol- $\alpha$ -p-tolylthiol-, decomp. at high temperature, -2:4-dihydroxydiphenylmethane;  $\alpha$ -p-tolylthiol-, m. p. 160—161° (potassium salt), and  $\alpha$ -n-butylthiol-, decomp. 265° (potassium salt), -2:4-dihydroxy-4'-methoxydiphenylmethanesulphonic acid:  $\alpha$ -p-tolylthiol-diphenylmethanesulphonic acid, m. p. 163—164°,  $\alpha$ -diphenylthiol-, m. p. 221—223°, and  $\alpha$ -di-p-tolylthiol-, m. p. 251—252°, -diphenylmethane.

These sulphonie acids dye wool in fawn to buff shades; they do not dye cotton. J. W. BAKER.

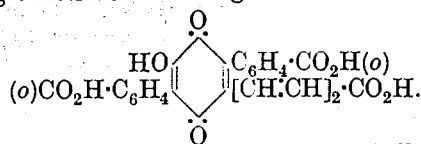
**peri-Benzoyl and -benzyl derivatives of naphthalene.** K. DZIEWOŃSKI, J. AUERBACH, and J. MOSZEW (Bull. Acad. Polonaise, 1929, A, 658—663). —1-Benzoyl-8-benzyl-naphthalene, m. p. 142° (oxime, m. p. 220—222°), is prepared by the action of benzyl chloride on 1-benzoylnaphthalene in the presence of aluminium chloride at 160—170°. Oxidation of this with nitric acid yields 1:8-dibenzoylnaphthalene (bisphenylhydrazone, m. p. 270—271°; *dioxime*, m. p. 270°) (cf. A., 1929, 56, 1054). R. CHILD.

**New reaction for aryl aldehydes.** M. V. IONESCU (Bull. Soc. chim., 1930, [iv], 47, 210—214; cf. A., 1928, 422).—The formation of arylidene-indandiones by condensation with indandione in presence of piperidine in alcoholic solution is proposed as a test for aryl aldehydes. The following indandiones, most of which appear to be new, are described: o-toluylidene-, m. p. 150—152°; m-toluylidene-, m. p. 157°; p-toluylidene-, m. p. 133—135°; (cf. *loc. cit.*); o-chlorobenzylidene-, m. p. 130—132°; m-chlorobenzylidene-, m. p. 178—179°; p-chlorobenzylidene-, m. p. 177—178°; o-nitrobenzylidene-, m. p. 183°; m-nitrobenzylidene-, m. p. 246—247°; p-nitrobenzylidene-, m. p. 228—230°; furfurylidene-, m. p. 199—201°; o-methoxybenzylidene-, m. p. 162—163°; anisylidene-, m. p. 155—157°; salicylidene-, m. p. 195°; m-hydroxybenzylidene-, m. p. 222°; p-hydroxybenzylidene-, m. p. 240°; resorcyldene-, m. p. 205—207°; vanillylidene-, m. p. 210—212°; piperonylidene-, m. p. 205—206°; protocatchuylidene-, m. p. 255—256°; 2:3-dimethoxysalicylidene-, m. p. 222—225°; 2:4-methoxysalicylidene-, m. p. 211—217°; 5-nitrosali-

cyldene-, m. p. 260—265°; 4-bromosalicyldene-, m. p. 229—230°; homosalicyldene-, m. p. 193—196°; cinnamylidene-, m. p. 150—151°;  $\alpha$ -methylcinnamylidene-, m. p. 162—164°;  $\alpha$ -chlorocinnamylidene-, m. p. 189—191°; o-nitrocinnamylidene-, m. p. 218—220°; m-nitrocinnamylidene-, m. p. 255—256°; piperonylacrylidene-, m. p. 224—226°; asarylidene-, m. p. 206°; p-methoxynaphthalidene-, m. p. 210—212°;  $\alpha$ -hydroxynaphthalidene-, m. p. 247°;  $\beta$ -hydroxynaphthalidene-, m. p. 221°; p-dimethylaminobenzylidene-, m. p. 198—200°; o-phthalylidene-, m. p. 170°; isophthalylidene-, m. p. 274°; terephthalylidene-, m. p. 320°; and 1-naphthalidene-, m. p. 172°. R. BRIGHTMAN.

**Dioximes.** LXII. G. PONZIO and G. CARTA-SATTA.—See this vol., 621.

**Colouring matters of fungi.** VIII. Red colouring matter of fly fungus [*Amanita muscaria*, L.]. F. KÖGL and H. ERXLEBEN (Annalen, 1930, 479, 11—26).—The skins from 500 kg. of the fungus are extracted with alcohol at 0° in the absence of light, and the colouring matter (to which the name muscarufin is assigned) is precipitated as the crude silver salt. This is decomposed with methyl-alcoholic hydrogen chloride, and the resulting acid product freed from accompanying substances by extraction with ether and chloroform. Further purification is effected by precipitating the crude muscarufin from its aqueous solution with acetone and finally crystallising from 80% alcohol. Muscarufin,  $\text{C}_{25}\text{H}_{16}\text{O}_9$ , m. p. 275.5° (red sodium salt), is thus obtained as orange-red needles (rhombs from water; crystallographic data by STEINMETZ) in a yield of 850 mg. Electrometric titration indicates that it is a tribasic acid. Muscarufin contains one hydroxyl group, since it furnishes a *monoacetyl* derivative, m. p. 197°. Methylation with diazomethane affords an impure *tetra-methyl* derivative, m. p. 203°, and treatment with zinc dust and acetic anhydride in presence of a small amount of sodium acetate gives the *triacetyl* derivative, m. p. 184°, of *leucomuscarufin*, m. p. 192°, thus indicating that muscarufin is a quinone. Catalytic reduction (Adams) of muscarufin in 96% alcohol furnishes *hexahydromuscarufin*, m. p. 200° (*triacetyl* derivative, m. p. 192°), thus showing the presence of two double linkings. Distillation with zinc dust affords p-diphenylbenzene, thus showing a relationship between muscarufin, polyporic acid (A., 1926, 407), and atromentin (A., 1928, 1250). Oxidation of an alkaline solution of muscarufin (1 mol.) with hydrogen peroxide gives phthalic acid (1.39 mol.); a mixture of phthalic and adipic acids is obtained by similar oxidation of the hexahydro-derivative. The presence of the  $\text{C}[\text{CH}:\text{CH}]_2\cdot\text{CO}_2\text{H}$  grouping is indicated, and confirmed by the condensation of triacetyl-leucomuscarufin with maleic anhydride in benzene to the compound,  $\text{C}_{35}\text{H}_{26}\text{O}_{15}$ , m. p. 286°. Muscarufin is optically inactive. The following constitution is assigned to muscarufin:

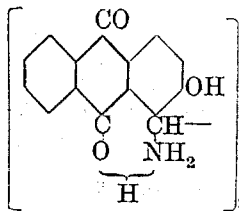


H. BURTON.



**Derivatives of hydroxyaminomethylanthraquinones and dihydroxydianthraquinonylethylenes.** II. H. DE DIESBACH, P. GÜBSE, and H. LEMPEN (Helv. Chim. Acta, 1930, 13, 120—137; cf. A., 1929, 70).—Treatment of *s*-di-( $\alpha$ -2-hydroxyanthraquinonyl)ethylene (*loc. cit.*) in aqueous suspension with chlorine and bromine gives the *dichloride* and *dibromide*, respectively. Whereas the original ethylenic compound dissolves in alkali hydroxide to a blue solution, the colour being ascribed to radical formation (cf. Scholl, A., 1927, 675), the dihalides afford brown solutions which possess only slight tinctorial properties (no radical formation). Treatment of the dibromide with boiling 10% alkali hydroxide solution in a current of oxygen affords some 3-bromo-2-hydroxyanthraquinone-1-carboxylic acid, m. p. 248°. The ethylene derivative is converted by treatment with chlorine in cold sulphuric acid or in trichlorobenzene at 130—140°, and by sulphuryl chloride in trichlorobenzene at 100°, into the *dichloride* of *s*-di-( $\alpha$ -3-chloro-2-hydroxyanthraquinonyl)ethylene (I). The last-named compound is produced from the ethylene derivative and sulphuryl chloride in nitrobenzene. 3-Chloro-2-hydroxyanthraquinone reacts with *N*-methyloltrichloroacetamide in cold sulphuric acid, forming 3-chloro-2-hydroxy-1-trichloroacetamidomethylanthraquinone, m. p. 246°. This is hydrolysed by boiling 10% sodium hydroxide solution in an atmosphere of hydrogen to 3-chloro-2-hydroxy-1:9(N)-isopyrroleanthrone (cf. *loc. cit.*), whilst hydrolysis in presence of oxygen gives *s*-di-( $\alpha$ -3-chloro-2-hydroxyanthraquinonyl)ethylene, not melted at 360°, identical with I. This is nitrated and oxidised by treatment with nitric and sulphuric acids to a 3-chloro-(?)-nitro-2-hydroxyanthraquinone-1-carboxylic acid, m. p. 124°. The introduction of the chlorine atoms in the 3:3'-positions depresses the reactivity of the double linking, and addition of chlorine is possible only with sulphuryl chloride in trichlorobenzene. *s*-Di-( $\alpha$ -2-hydroxy-3-carboxyanthraquinonyl)ethylene (*loc. cit.*) and bromine in aqueous suspension furnish a *dibromide*, oxidised by gaseous oxygen in presence of alkali to 2-hydroxyanthraquinone-1:3-dicarboxylic acid.

Treatment of *s*-di-( $\alpha$ -2-hydroxyanthraquinonyl)ethylene or its dihalides with alcoholic ammonia at 120°, gives *s*-di-( $\alpha$ -2-hydroxyanthraquinonyl)ethylenediamine (*loc. cit.*), which dissolves in sulphuric acid to a blue solution and in alkali hydroxide to a brown solution. Reaction is presumed to occur through an intermediate (radical) with the annexed constitution; this reduced form gives a green coloration with sulphuric acid and a blue coloration with alkali hydroxide. The ethylene and aniline at 180° yield the reduced form of



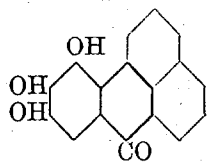
*s*-NN-diphenyldi-( $\alpha$ -2-hydroxyanthraquinonyl)ethylenediamine, which on keeping for some days passes into the normal form; when the reaction is carried out at 100° the normal form is produced, although the presence of the reduced phase can be shown after reaction has proceeded for a short time. Similarly, *s*-di-( $\alpha$ -3-chloro-2-hydroxyanthraquinonyl)ethylene and am-

monia yield *s*-di-( $\alpha$ -3-chloro-2-hydroxyanthraquinonyl)ethylenediamine, but with aniline the reduced form of *s*-NN-diphenyldi-( $\alpha$ -3-anilino-2-hydroxyanthraquinonyl)ethylenediamine results. 3-Chloro-2-hydroxyanthraquinone and *N*-methylolphthalimide react in cold sulphuric acid forming 3-chloro-2-hydroxy-1-anthraquinonylmethylphthalamic acid, m. p. 222°, which on hydrolysis with 10% sodium hydroxide solution and subsequent acidification gives the *phthalate* of 3-chloro-2-hydroxy-1-aminomethylanthraquinone. When this salt is heated with acetic acid at 170° in absence of air the reduced form of *s*-di-( $\alpha$ -3-chloro-2-hydroxyanthraquinonyl)ethylenediamine is obtained. This is readily oxidised to the above normal form.

Treatment of *s*-di-( $\alpha$ -2-hydroxyanthraquinonyl)ethylene with potassium nitrate in presence of a large excess of cold sulphuric acid gives 50% of *s*-dinitrodi-( $\alpha$ -3-nitro-2-hydroxyanthraquinonyl)ethane, oxidised slowly by gaseous oxygen in presence of boiling alkali to 3-nitro-2-hydroxyanthraquinone-1-carboxylic acid, m. p. 220°. When the nitration is carried out at 60—70° with an excess of potassium nitrate a *hexanitro*-derivative and a *dinitro*-2-hydroxyanthraquinone-1-carboxylic acid, m. p. 223°, are obtained. Treatment of the above tetranitro-derivative with sodium sulphide in slightly alkaline solution, and subsequent boiling with sodium chloride solution and dilute hydrochloric acid, gives the reduced (radical) form of *s*-di-( $\alpha$ -2:3-dihydroxyanthraquinonyl)ethylenediamine, which on keeping passes into the normal form. H. BURTON.

**Reduction products of the hydroxyanthraquinones.** XI. E. J. CROSS and A. G. PERKIN (J.C.S., 1930, 292—308).—In the reduction of hydroxyanthraquinones containing an  $\alpha$ -hydroxyl group the carbonyl group further from this hydroxyl group is preferably reduced yielding a 1-hydroxy-9-anthranol (or anthrone—in cases where both terms may apply anthranol is used in this abstract); if, however, this hydroxyl group is acetylated, then the adjacent carbonyl group is reduced producing a 4-acetoxyanthranol. It is inferred that the chelate linking between the  $\alpha$ -hydroxyl and carbonyl groups is responsible for the protection of the latter during reduction. The structure of the hydroxyanthranols is determined by conversion into hydroxybenzanthrones, which are tested for the presence or absence of an  $\alpha$ -hydroxyl group by methyl iodide and alkali (J.C.S., 1922, 121, 474). The  $\alpha$ -hydroxyl group of the hydroxybenzanthrones is also very resistant to alkylation. The method of reduction is to add stannous chloride in hydrochloric acid to an acetic acid solution of the acyl compound. The results indicate that generally reduction occurs before hydrolysis. Triacetylanthragallol thus treated gives a small amount of 1:2:3-trihydroxy-9-anthranol, and as main product 2:3:4-trihydroxy-9-anthranol, m. p. above 300° (2:3:4-triacetoxy-9-anthranol acetate, m. p. 199—201°). The anthranol is best purified by hydrolysis of the acetyl compound in presence of stannous chloride. It does not react with benzoquinone. The acetyl compound, oxidised with chromic acid in acetic acid, yields an orange substance, m. p. 218—220°, probably 2:3-diacetyl-

anthragallol, as it gives triacetylanthragallol on acetylation. With glycerol and sulphuric acid the anthranol yields, in small amount, *benzanthragallol*, m. p. above 290° (*triacetyl* compound, m. p. 221—223°). Unlike *isobenzanthragallol*, similarly formed from 1:2:3-trihydroxy-9-anthranol, this yields a



*trimethyl ether*, m. p. 143—144°, with methyl iodide or methyl sulphate and alkali and is therefore 8:9:10-trihydroxybenzanthrone (annexed formula). This is regarded as affording conclusive proof of the orientation of these compounds, and the conclusion of Green (A., 1927, 1079), based on the action of thionyl chloride, that 1:2:3-trihydroxy-9-anthranol, also produced by reduction of anthragallol, is really the 2:3:4-compound is disproved.

2:3-Diacetylanthragallol on reduction gives 1:2:3-trihydroxy-9-anthranol only, thus behaving like anthragallol. *Tribenzoylanthragallol*, m. p. 213—215°, gives *dibenzoyl-2:3:4-trihydroxy-9-anthranol*, m. p. 212—214°, identified by conversion into 2:3:4-triacetoxy-9-anthranol acetate. *Dibenzoylanthragallol*, on the other hand, gives *dibenzoyl-1:2:3-trihydroxyanthranol*, m. p. 188—190° (identified by conversion into monoacetyl-1:2:3-trihydroxyanthranol, m. p. 239—240°), and *monobenzoyl-1:2:3-trihydroxy-9-anthranol*, m. p. 213—216°. *Triethylcarbonatoanthragallol*, m. p. 103—105°, kept over-night as a suspension in pyridine, or in solution in acetic acid containing stannous chloride and hydrochloric acid, is converted into the diethylcarbonato-compound. Consequently it gives on reduction 1-hydroxy-2:3-diethylcarbonato-9-anthranol, m. p. 131—132°, and *dicarbethoxy-2:3:4-trihydroxy-9-anthranol*, m. p. 156—158°, the configuration of these products being confirmed by hydrolysis followed by acetylation. Diethylcarbonatoanthragallol gives the former, m. p. 131—132°, and *monoethylcarbonato-1:2:3-trihydroxy-9-anthranol*, m. p. 218—219°.

2-Acetylalizarin on reduction gives 1:2-dihydroxy-9-anthranol, which on acetylation gives 1:2-diacetoxy-9-anthranol acetate, m. p. 185—187°, whereas diacetylalizarin gives mainly the 3:4-compound (deoxyalizarin) with only a trace of the 1:2-compound. Acetylalizarin 2-methyl ether gives 4-hydroxy-3-methoxy-9-anthranol, and alizarin gives a mixture of 1:2- and 3:4-dihydroxy-9-anthranols. 1-Acetoxyanthraquinone yields 4-hydroxy-9-anthranol, m. p. 240—242° (*acetyl-4-hydroxy-9-anthranol*, m. p. 173—175°). Diacetylchrysazine yields 4:5-dihydroxy-9-anthranol, m. p. about 293—295° (*monoacetyl* compound, m. p. 220—222°). 2-Acetoxyanthraquinone gives 3-hydroxy-9-anthranol.

Alizarin, heated with sulphuric acid, glycerol, and aniline sulphate, yields a small quantity of *isobenzalizarin*, isolated as monoacetyl compound, m. p. 243—245°. 1:2:3-Trihydroxy-9-anthranol with boroacetic anhydride in acetic anhydride containing a little pyridine gives 2-acetylanthragallol *boroacetate*, a dull orange crystalline substance, decomposed slowly by cold and rapidly by hot water to 2-acetylanthragallolanthranol. This derivative affords further confirmation of the orientation

assigned to the anthranol by Cross and Perkin (A., 1927, 771).

H. A. PIGGOTT.

**Perylene and its derivatives. XXVIII.** A. ZINKE and R. WENGER (Monatsh., 1930, 55, 52—57).—When perylene in sulphuric acid solution is treated with manganese dioxide anthraquinol-1:5-dicarboxydilactone (I) is formed, which with concentrated nitric acid and glacial acetic acid yields anthraquinone-1:5-dicarboxylic acid (II) (also produced by oxidation of perylene with chromic acid or of perylene-3:9-quinone with manganese dioxide or with chromic acid). Distillation of I or II with zinc dust yielded anthracene.

A. I. VOGEL.

**Linear pentacene series. XVIII.** Two isomeric dibromo-derivatives of linear pentacene-5:7:12:14-diquinone. G. MACHEK (Monatsh., 1930, 55, 47—51).—Treatment of diaminopentacenediquinone, decomp. above 450° (cf. A., 1929, 1453), in glacial acetic acid-acetic anhydride suspension with hydrobromic acid, followed by diazotisation with amyl nitrite and subsequent heating of the resultant *perbromide*, yields 1:8-dibromopentacene-5:7:12:14-diquinone, m. p. 453—455°. 1:11-Dibromopentacene-5:7:12:14-diquinone, m. p. 314—316°, is similarly prepared from the diaminopentacenediquinone, decomp. 389—390° (*loc. cit.*).

A. I. VOGEL.

**Constitution of Chinese tannin.** O. T. SCHMIDT (Annalen, 1930, 479, 1—10).—Hydrolysis of Chinese tannin by Feist and Haun's method (A., 1914, i, 195) gives little or no dextrose; the method is unsuitable. Hydrolysis of the tannin used by Mitchell (A., 1923, ii, 188) and Nierenstein (cf. A., 1925, i, 951) by Fischer and Freudenberg's method (A., 1912, i, 471), and determination of the sugar formed by three different methods, gives a dextrose value of 7—8%.

The action of brewer's bottom yeast on a 5% tannin solution has been investigated. Fermentation does not occur and there is only a slight change in the optical activity of the solution. The yeast also loses its power to ferment dextrose after having been in contact with the tannin solution. These results are in agreement with those of van Tieghem (Ann. Sci. nat. Botanique, 1867, [v], 8, 210). Chinese tannin is not a glucoside; the constitution assigned to it by Fischer (*loc. cit.*; A., 1919, i, 278) is correct.

H. BURTON.

**Syntheses of d-glucoacetosyringone and d-glucosyringaldehyde.** F. MAUTHNER (J. pr. Chem., 1930, [ii], 124, 313—318).—By condensing 4-hydroxy-3:5-dimethoxyacetophenone (A., 1929, 701) with acetobromoglucose in aqueous acetone solution there is obtained *tetra-acetylglucoacetosyringone*, m. p. 119—120°. This is converted by prolonged treatment with cold 6% barium hydroxide solution into *d-glucoacetosyringone*, m. p. 208—209°, which is not known to occur naturally. In a similar way 4-hydroxy-3:5-dimethoxybenzaldehyde is converted into *tetra-acetylglucosyringaldehyde*, m. p. 158—159°. The glucoside is decomposed by barium hydroxide, but the acetyl derivative is hydrolysed by 2.5% ammonia solution to give *d-glucosyringaldehyde*, m. p. 210—211°, [ $\alpha$ ]<sub>D</sub> -12.83°, which is probably, in spite of the higher m. p., identical with

the product obtained from syringin by Körner (A., 1889, 159). R. K. CALLOW.

**Constitution of aloins. II.** C. S. GIBSON and J. L. SIMONSEN (J.C.S., 1930, 553—561).—Bromination of barbaloin with bromine in hydrobromic acid (*d* 1.5) at 0° gives *tribromobarbaloin*,  $C_{20}H_{15}O_9Br_3$ , decomp. 291° (darkens at 284°), which is not hydrolysed by hot 50% sulphuric acid or by 3% methylalcoholic hydrogen bromide in a sealed tube at 110°, and is converted by boiling acetic anhydride containing two drops of sulphuric acid into an amorphous *hexa-acetyl* derivative, m. p. 185—187° (softens at 173°). Barbaloin therefore contains six hydroxyl groups and not five as postulated by Léger (A., 1917, i, 276, for references). Moreover methylation of *tribromobarbaloin* with methyl sulphate yields a pentamethyl ether,  $C_{20}H_{18}O_9Br_3Me(OH)(OMe)_5$ , m. p. 128—130° (one methyl group having been introduced into the nucleus), which yields an *acetyl* derivative, m. p. 102—105° (softens at 90°). These substances are regarded as true derivatives of barbaloin. The compound obtained by the action of bromine water on barbaloin is considered, contrary to Léger's view, to be an oxidation product, *tribromonorbarbaloin*, m. p. 193—194° (softens 188°; decomp. 223°), which, contrary to Léger's suggestion (*loc. cit.*), has the composition  $C_{16}H_{10}O_2Br_3(OH)_5$ , since with acetic anhydride it yields a *penta-acetyl* derivative, m. p. 139—140° (softens 128°), and forms a *pentamethyl ether*, m. p. 115—116° (softens 101°). Acetylation with acetyl chloride gives a different *acetyl* derivative,  $C_{16}H_{11}O_3Br_3(OAc)_4$ , m. p. 137—138°. On the basis of these results and of mol. wt. determinations (Sugden), the authors, whilst confirming Léger's experimental results and accepting his composition  $C_{20}H_{18}O_9$  for barbaloin, cannot accept the suggestion that this substance is a simple arabinoside. Attempts to reduce barbaloin gave unsatisfactory results. It is not reduced by hydrogen and a platinum oxide catalyst (King), whilst sodium and alcohol or hydriodic acid and phosphorus give bright red products resembling phlobaphens. Acetylation-reduction gives only a colourless gum which could not be purified.

J. W. BAKER.

**Constituents of *Arctium Lappa*. II.** J. SHINODA (J. Pharm. Soc. Japan., 1929, 49, 183—184).—Arctigenin (A., 1929, 1347) gives with diazoethane a syrupy *ethyl ether*, which is oxidised by permanganate in alkaline solution to veratric acid, a substance, m. p. 90—95°, and an acid, m. p. 192° (anilide, m. p. 209°), apparently identical with vanillic acid *ethyl ether*. Methylarctigenin is hydrolysed by alkali to *methylarctigenic acid*, from which it is re-formed by heating, or by treatment with diazomethane. It is concluded that arctigenin contains a 3:4-dimethoxyphenyl and a 4-hydroxy-3-methoxyphenyl nucleus united by a straight hydrocarbon chain,  $C_6H_{10}$ , to which is attached the lactone grouping. H. E. F. NORTON.

**Plant colouring matters. XIX. Zeaxanthin and xanthophyll.** P. KARRER, H. WEHRLI, and A. HELFENSTEIN (Helv. Chim. Acta, 1930, 13, 268—273).—Zeaxanthin (A., 1929, 1077) absorbs 36.65% of its weight of oxygen when exposed to the atmo-

sphere for 110 days. An alcoholic solution shows two absorption bands with maxima at 451 and 486  $\mu$ . Oxidation of both zeaxanthin and xanthophyll with potassium permanganate furnishes some *as*-dimethylsuccinic acid. Application of the Zerevitinov method to various carotenoids shows that zeaxanthin, xanthophyll, and lutein contain two, and fucoxanthin contains six hydroxyl groups. Xanthophyll is probably a dihydroxycarotene. H. BURTON.

**Rotenone, the active constituent of *Derris* root. IV. Isomeric relationships between rotenone and isorotenone.** S. TAKEI, M. KOIDE, and S. MIYAJIMA (Ber., 1930, 63, [B], 508—511; cf. this vol., 216).—Rotenone is isomerised simply and in good yield to isorotenone, m. p. 178°, by treatment with a boiling mixture of glacial acetic and sulphuric acids. Whereas rotenone is converted by alcoholic potassium hydroxide into tubaic acid, isorotenone affords the isomeric rotenic acid, m. p. 182°. Hydrogenation of rotenone in presence of acetic acid and palladised barium sulphate yields hydrototenone,  $C_{23}H_{24}O_6$ , m. p. 215° (*oxime*, m. p. 255°), hydrolysed to hydro-tubaic acid, m. p. 166°. It does not become isomerised when treated with acetic and sulphuric acids. Rotenone and hydrototenone are strongly optically active, whereas isorotenone is only feebly active. The reducible double linking present in rotenone is absent from isorotenone. Tubaic acid is converted by acetic and sulphuric acids into rotenic acid. The relationship of rotenone to isorotenone depends therefore on the isomerisation of the tubaic acid residue in rotenone to the rotenic acid residue in isorotenone; the reducible double linking and an asymmetric carbon atom in rotenone belong to the tubaic acid residue. The last-named group therefore plays a highly important part in rotenone, since isorotenone, in which it appears to be transformed into the rotenic acid residue, is not toxic to animals.

The physiological action of aqueous solutions of sodium tubaate, hydrotubaate, and rotenate and of rotenone, hydrototenone, and isorotenone emulsified in olive oil and soap has been investigated towards *Cobitis fossilis*. Rotenic is ten times as poisonous as tubaic acid. Rotenone is ten times as toxic as potassium cyanide, whereas isorotenone is inactive.

H. WREN.

**Compounds of *k*-strophanthidin. I.** G. FARBENIND.—See B., 1930, 394.

**Isoprene and caoutchouc. XVII. Fractionation of balata.** H. STAUDINGER and H. F. BONDY. XVIII. Determinations of viscosity of balata. H. STAUDINGER and E. O. LEUPOLD. XIX. Molecular size of caoutchouc and balata. H. STAUDINGER and H. F. BONDY (Ber., 1930, 63, [B], 724—730; 730—733; 734—736; cf. A., 1929, 1307).—XVII. Balata latex is diluted with water until an approximately 4% solution is obtained, which is poured into methyl alcohol. The precipitated balata is dissolved in carbon tetrachloride, from which it is obtained by use of methyl alcohol. The product is divided into fractions by crystallisation from toluene or xylene. The most sparingly soluble fractions give solutions with the highest viscosity and with increase in solubility the viscosity of the solution

diminishes. It therefore appears that balata is a mixture of polymer-homologues differentiated by the length of the molecules. The possibility that balata contains cyclic products to a greater or smaller degree is negated by the observation that one double linking is present in the unit molecule of the original balata, the first and last fractions as shown by the behaviour towards iodine chloride. The possibility of a degradation of balata by oxygen is excluded by working in an atmosphere of carbon dioxide. The deviations from the Hagen-Poiseuille law are most marked with the most highly viscous solutions containing the largest molecules.

XVIII. Balata solutions contain macromolecules, since the specific viscosity of a 0.025*M*-solution in tetrahydronaphthalene in an atmosphere of nitrogen is unchanged by rise in temperature from 20° to 60° and only alters slightly with 0.05- and 0.1*M*-solutions. Dissolved balata is degraded with extraordinary ease by minute amounts of oxygen.

XIX. The mol. wt. of caoutchouc and balata can be determined by measurement of the viscosity in accordance with the expression  $M = \eta_{sp}/cK_m$ .  $K_m$  is evaluated by observations with solutions of gutta-percha and caoutchouc degraded in tetrahydronaphthalene or xylene to products of which the mol. wt. is determined in benzene. The constant has the same value for either hydrocarbon. The viscosity of caoutchouc and balata is determined at such concentration that solutions of the eucolloids and hemicolloids are approximately equally viscous. From the results so obtained the specific viscosity of a unit molar solution is calculated on the assumption that it increases proportionately with the concentration. For an unfractionated balata the mol. wt. 51,000 is deduced, whereas for caoutchoucs of greater and smaller solubilities in ether the values 52,000 and 73,000 are found.

H. WREN.

**Dihydroperillamine and its reaction with nitrous acid.** W. W. WILLIAMS (J. Russ. Phys. Chem. Soc., 1929, 64, 1573—1590).—The preparation and properties of dihydroperillamine,  $C_9H_{15} \cdot CH_2 \cdot NH_2$ , and its reaction with nitrous acid were investigated.

Perillaldehyde, b. p. 108.5—109°/12 mm.,  $d_{20}^{20}$  0.9626,  $n_D^{20}$  1.5064 (semicarbazone, m. p. 197°), was obtained from the essential oil of *Siler trilobum*, Scop., and the oxime, m. p. 100—101°, transformed into the nitrile of perillal acid, b. p. 116—117°/11 mm.,  $d_{20}^{20}$  0.9487,  $n_D^{20}$  1.4982, by heating with acetic anhydride and fused sodium acetate. The nitrile was reduced by sodium ethoxide, when dihydroperillamine (I), b. p. 99—101°/12 mm.,  $n_D^{20}$  1.4871, was obtained. As by-products, a compound,  $C_{10}H_{21}ON$ , m. p. 115—116.5°, was obtained, probably the amine oxide (hydrochloride, m. p. 127.5—128°). Small quantities of two further compounds which could not be identified were isolated.

Treatment of dihydroperillamine with nitrous acid gave a mixture of alcohols and a hydrocarbon,  $C_{10}H_{18}$ , b. p. 72—75°/18 mm.,  $d_{20}^{20}$  0.8594,  $n_D^{20}$  1.4769 (nitroschloride, m. p. 68.5°), possessing two double linkings and similar to  $\beta$ -phellandrene. The mixture of alcohols was fractionated, and was found

to contain: (a) a tertiary alcohol, which could not be isolated, since on distillation it lost water to give the hydrocarbon  $C_{10}H_{16}$ , (b) a primary alcohol,  $C_{10}H_{17} \cdot OH$ , b. p. 109—113°/13 mm.,  $d_{20}^{20}$  0.9401,  $n_D^{20}$  1.4878, possessing one double linking, which on oxidation yielded an aldehyde, b. p. 93—96°/12 mm.,  $d_{20}^{20}$  0.9375,  $n_D^{20}$  1.4817 (semicarbazone, m. p. 123—124°), and (1) a secondary alcohol, b. p. 104—108°/13 mm.,  $d_{20}^{20}$  0.9350,  $n_D^{20}$  1.4849, which could be oxidised to a ketone, b. p. 92—97°/12 mm.,  $d_{20}^{20}$  0.9319,  $n_D^{20}$  1.4789. A mechanism for the formation of the above series of products is suggested.

M. ZVEGINTZOV.

**Condensation of pulegone with aldehydes.** H. THOMS and K. SOLTNER (Arch. Pharm., 1930, 268, 157—166).—Attempts to condense pulegone with acetaldehyde, isobutaldehyde, heptaldehyde, citronellal, citral,  $\alpha$ -diphenylbutaldol, and tetrahydrocinnamaldehyde were unsuccessful. Anisaldehyde and pulegone in aqueous alcohol in presence of sodium hydroxide (cf. Rupe and Schäfer, A., 1928, 645) give  $\alpha$ -anisylidenepulegone, b. p. 230—232°/12 mm., which is hydrogenated in presence of palladised charcoal to p-methoxybenzylmenthone, b. p. 161—163°/0.7 mm.,  $d_{16}^{16}$  1.023,  $n_D^{16}$  1.5188. Piperonylidenepulegone, b. p. 218—220°/0.25 mm., reduced similarly to 3:4-methylenedioxybenzylmenthone, b. p. 202—204°/0.25 mm.,  $d_{16}^{16}$  1.1027,  $n_D^{16}$  1.5300; furfurylidenepulegone, b. p. 168—170°/0.25 mm., reduced to tetrahydro- $\alpha$ -furfurylmenthone, b. p. 160—162°/0.3 mm.,  $d_{16}^{16}$  1.0105,  $n_D^{16}$  1.4960; and cinnamylidenepulegone, b. p. 168—203°/2.3 mm., are prepared similarly. The last-named was hydrogenated on one occasion to  $\gamma$ -phenylpropylmenthone, b. p. 160—165°/2 mm.,  $d_{17}^{17}$  1.0154,  $n_D^{17}$  1.5398, but subsequent preparations appeared to contain a dihydrocinnamylidenementhone. Some derivatives of pulegonylacetic acid (amide, m. p. 134—135°) will be described in full later.

H. E. F. NOTTON.

**Pinane; determination of nopinene.** P. LIPP [with H. WITGERT] (Ber., 1930, 63, [B], 411—416).—Catalytic hydrogenation of  $\beta$ -pinene at the atmospheric temperature without solvent in the presence of platinum according to Fokin and Willstätter proceeds normally, yielding pinane identical with that derived from  $\alpha$ -pinene. There is no reason to assume that a change in the carbon skeleton of pinene occurs during hydrogenation or to doubt the homogeneity of nopinene. Repetition of the work of Zelinski and Levina (A., 1929, 450) shows that the hydrogenation of nopinene in an atmosphere of hydrogen is accompanied by the isomerisation of  $\beta$ - to  $\alpha$ -pinene and the production of *p*-cymene. In a current of hydrogen reaction proceeds further, giving a hydrocarbon  $C_{10}H_{20}$ , b. p. 166—167° (corr.),  $d_{15}^{15}$  0.8286,  $n_D^{15}$  1.4476, which is not regarded as *p*-menthane.

Ozonisation of camphene or nopinene with the 9% gas in aqueous suspension at 0° or in the absence of solvent (cf. Escourrou, A., 1928, 1357) is accompanied by slight formation of carbon dioxide as well as ozonide production and fission, so that the method is quantitatively invalid. Observation of the index of refraction is the most convenient criterion of homogeneity of nopinene preparation.

H. WREN.

**Certain transformations of bornyl chloride.** I. I. VANIN and A. A. TSCHERNOJAROV (J. Russ. Phys.

Chem. Soc., 1929, **61**, 2279—2290).—When heated with nickel carbonate at 125—135°, bornyl chloride yields camphene, m. p. 50°, whilst at 165—175° the reaction gives a series of liquid hydrocarbons,  $C_{10}H_{16}$ , of various b. p. Three of these, forming the bulk of the product, yield esters of isoborneol when heated with acetic and sulphuric acids and are hence "liquid camphenes." They are being investigated further.

T. H. POPE.

**Camphor acetal.** A. E. ARBUSOV (J. Russ. Phys. Chem. Soc., 1929, **61**, 1595—1597; cf. A., 1908, i, 555).—Earlier experiments on the preparation of camphor acetal by the action of ethyl orthoformate on camphor in alcoholic solution have been repeated in greater detail. The acetal is colourless and has b. p. 106°/11.5 mm.,  $d_4^{20}$  0.9633,  $[\alpha]_D^{20}$  +21.31°. Careful fractionation gives rise to a certain quantity of acetal having a yellow colour and a characteristic odour which, however, disappears on keeping. M. ZVEGINTZOV.

**$\alpha$ -Furylacetic [furan-2-acetic] acid and an interesting isomerisation in the furan series.** T. REICHSTEIN (Ber., 1930, **63**, [B], 749—754).—2-Chloromethylfuran, b. p. 37°/15 mm., is readily obtained by addition of a mixture of furfuryl alcohol, pyridine, and anhydrous ether to well-cooled thionyl chloride somewhat diluted with pentane. It is converted by aqueous potassium cyanide into a mixture of (mainly) 5-methylfuran-2-nitrile and 2-furfurylacetonitrile, which on hydrolysis yields 5-methylfuran-2-carboxylic acid, m. p. 109—110° (corr.) [described by Kirner and Richter (A., 1929, 1458) as furan-2-acetic acid], and the true furan-2-acetic acid, m. p. 67—68.5° (corr.) [corresponding chloride, b. p. about 65°/1 mm.; anilide, m. p. 84—85° (corr.)]. The structure of the last-named acid follows from its formation by treatment of 2-furoylformic acid, b. p. 105°/1 mm., m. p. 97—98.5° (corr.) [cf. Fischer and Brauns, A., 1913, i, 501], with hydrazine hydrate and sodium ethoxide.

[By M. KERSCHBAUM.]—Sodium 2-furylglycidate is converted by hydroxylamine hydrochloride into 2-furylacetaldoxime, b. p. 75—77°/2 mm., m. p. 63°, transformed by boiling acetic anhydride into 2-furylacetonitrile, b. p. 69—73°/10 mm., which passes without isomerisation when treated with ethyl-alcoholic hydrogen chloride or potassium hydroxide into furan-2-acetic acid, m. p. 67—68°. The acid is also obtained by the action of silver oxide on 2-furylacetaldehyde, b. p. about 58°/10 mm. [semicarbazone, m. p. 131—132° (corr.)], obtained from sodium 2-furylglycidate and aqueous oxalic acid. Methyl 2-furylglycidate, b. p. about 95°/2 mm., and ethyl 2-furylglycidate, b. p. about 105°/2 mm., are incidentally described.

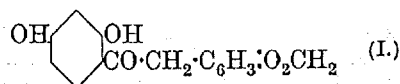
$\gamma$ -Methyl- $\Delta^8$ -butenyl bromide, b. p. 59—60°/60 mm., is converted through the cyanide into homogeneous  $\gamma$ -methyl- $\Delta^8$ -pentoic acid, b. p. 83—85°/3 mm., 106—107°/14 mm. [chloride, b. p. about 55°/12 mm.; anilide, m. p. 105.5—106.5° (corr.); dibromide, m. p. 102—103.5° (corr.)], hydrogenated to  $\gamma$ -methylvaleric acid [anilide, m. p. 121.5—113.5° (corr.)].  $\Delta^8$ -Butenyl bromide, analogously but in poorer yield, affords  $\Delta^8$ -pentoic acid, wandering of the double linking taking place probably during the protracted

alkaline hydrolysis. In both cases therefore the main change is normal.

H. WREN.

**Syntheses of the isoflavone,  $\psi$ -baptigenin.** E. SPÄTH and E. LEDERER (Ber., 1930, **63**, [B], 743—748; cf. Späth and Schmidt, A., 1929, 1458).—3:4-Methylenedioxyphenylmethylcarbinol is oxidised by potassium dichromate and sulphuric acid to acetopiperone, m. p. 81°, which is transformed by bromine in glacial acetic acid under the influence of the light from a quartz lamp into  $\omega$ -bromoacetopiperone, m. p. 86—87°, oxidised to piperonylic acid. With resorcinol and sodium hydroxide in aqueous acetone the bromo-compound affords  $\omega$ -m-hydroxyphenylacetopiperone, m. p. 140—141°. Transformation of the ketone into the corresponding cyanohydrin does not proceed smoothly, but the crude product, after treatment according to Hoesch, gives unchanged ketone and  $\psi$ -baptigenin, m. p. 296—298°, when sublimed in a high vacuum. The methyl ether, m. p. 179—180°, from the synthetic product is identical with that of the natural substance; it is also derived from  $\omega$ -m-methoxyphenylacetopiperone, m. p. 106—107°.

$\psi$ -Baptigenetin is condensed with ethyl formate and sodium followed by treatment of the product with alcohol and fuming hydrochloric acid and sublimation in a high vacuum into  $\psi$ -baptigenin mixed with unchanged ketone. The constitution I is confirmed



for  $\psi$ -baptigenetin by removal of the methylenedioxy-group from its dimethyl ether by phloroglucinol and sulphuric acid followed by oxidation of the resulting material to 2:4-dimethoxybenzoic acid.

H. WREN.

**Synthesis of methysticin.** W. LAMPE and Z. SANDROWSKI (Rocz. Chem., 1930, **10**, 199—210).—Ethyl  $\gamma$ -cinnamoyl- $\gamma$ -carbethoxyacetoacetate, m. p. 45—47° (copper salt, m. p. 135—137°), is prepared by condensing cinnamoyl chloride with ethyl sodioacetonedicarboxylate; the corresponding free acid, m. p. 88—90°, is converted by sulphuric acid into 6-styryl-5-carbethoxypyronone, m. p. 158—160° (acetyl derivative, m. p. 124—126°); this, on hydrolysis, gives 6-styryl-5-carboxypyronone, m. p. 203° (decomp.). All attempts to eliminate the carboxyl group, with the object of synthesising methysticin from 6-styrylpyronone, proved unsuccessful. An attempted synthesis of 6-(3':4'-methylenedioxy-styryl)pyronone was for the same reason unsuccessful. Ethyl  $\gamma$ -piperonylacryloyl- $\gamma$ -carbethoxyacetoacetate, m. p. 100—102° (prepared by condensing piperonylacryloyl chloride with ethyl sodioacetonedicarboxylate), and acetic anhydride give 6-(3:4-methylenedioxy-styryl)-5-carbethoxy-4-acetylpyronone, m. p. 197—199°, which affords on alkaline hydrolysis 6-(3:4-methylenedioxy-styryl)-5-carbethoxypyronone, m. p. 165—168°, together with the corresponding 5-carboxy-derivative, m. p. 225° (decomp.). The carbethoxy-derivative is hydrogenated in presence of palladium to 6-(3:4-methylenedioxyphenylethyl)-5-carbethoxypyronone, m. p. 106—108°, whilst, under similar conditions, the free acid gives the corresponding carboxy-derivative, m. p. 195°.

R. TRUSZKOWSKI.

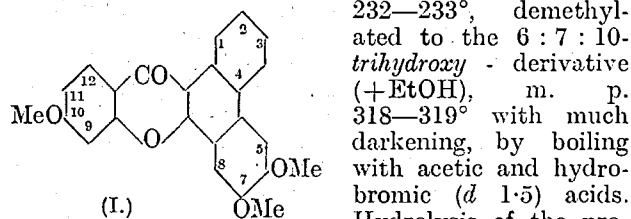
**Substituted diaryl ethers. III. New synthesis of substituted xanthhydrols.** J. REILLY and P. J. DRUMM (J.C.S., 1930, 455—458).—The product obtained by the condensation of di-*p*-tolyl ether with benzoyl chloride in the presence of aluminium chloride is not a ketone as previously described (A., 1928, 63), but the isomeric 9-phenyl-2:7-dimethyl-xanthhydrol, identical with a specimen obtained by the action of magnesium phenyl bromide on 2:7-dimethylxanthone. The xanthhydrol is converted by the action of diethylaniline in boiling acetic acid into 4'-diethylamino-9:9-diphenyl-2:7-dimethylxanthen, m. p. 183—184°, by the action of dry hydrogen chloride in ether (containing a few drops of acetyl chloride) into the *chloride hydrochloride*, m. p. 147—149°, which loses 1 mol. of hydrogen chloride at 130°, giving an unstable *chloride* (*ferrichloride*, m. p. 181°), and by bromine in acetic acid on its solution in acetic acid saturated with hydrogen bromide, into a *tribromide*, m. p. 145—146° (decomp.). Reduction of 9-phenyl-2:7-dimethylxanthhydrol with zinc dust and 80% acetic acid (or by formic acid or acetic acid alone, unless absolutely pure) gives 9-phenyl-2:7-dimethylxanthen, identical with a specimen obtained by Feuerstein and Lipp (A., 1902, i, 768), which is re-oxidised to the xanthhydrol with lead peroxide in hot 80% acetic acid. J. W. BAKER.

**Bivalency of carbon. III. Experiments on xanthhydrol, dixanthhydrol ether, and xanthhydrol chloride.** F. G. KNY-JONES and A. M. WARD (J.C.S., 1930, 535—542).—Xanthhydrol chloride [best prepared by the action of thionyl chloride on xanthhydrol or its ether in boiling light petroleum (b. p. 40—60°)] is instantly decomposed at the ordinary temperature by anhydrous alcohol into xanthen (main product) and xanthone, and by trituration with water for 0.5 hr. into the same products, together with some xanthhydrol. Xanthhydrol, which is stable to boiling 0.1*N*-sodium hydroxide, is readily decomposed (5 min.) by boiling 0.1*N*-aqueous hydrochloric acid (and with increasing hydrochloric acid concentration up to 5*N*), and more slowly (1 hr.) by boiling 0.05*N*-alcoholic hydrogen chloride, into xanthen and xanthone. Xanthhydrol ether (best prepared by heating moist xanthhydrol at 150—155° and finally at 175°, extraction of the product with spirit, and crystallisation from xylene), m. p. 219° (Meyer and Saul, A., 1893, i, 471, whose method of preparation gives incomplete conversion, give m. p. 206°), is similarly decomposed by short boiling (0.5 hr.) with 0.1*N*-aqueous hydrochloric acid, and dissolves readily in 0.05*N*-alcoholic hydrogen chloride with conversion into xanthhydrol. Xanthhydrol, its chloride and ether, are therefore far more reactive than benzhydrol, dibenzhydrol ether, and diphenylchloromethane, and a general comparison of these reactions with those of the systems  $\text{CHR}'\text{R}''\text{Cl}$  and  $\text{CR}'\text{R}''\text{R}'''\text{Cl}$  suggests that the decompositions

involve an ionisation mechanism,  $\text{CHR}-\text{O}-\overset{\text{H}}{\underset{|}{\text{C}}}-\text{CR} \rightarrow \text{CH}_2\text{R} + \text{RC}:\text{O} \left( \text{R} = \text{O} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \right)$ , rather than one involving bivalent carbon, since xanthhydrol deriv-

atives exhibit certain reactions which in the triphenylmethane series have been regarded as evidence of the formation of ions. Thus dixanthhydrol ether in chloroform solution gives a precipitate of Prussian-blue when shaken with an aqueous solution of potassium ferricyanide and ferrous chloride (cf. Conant and Evans, A., 1929, 934; Conant and Sloan, A., 1924, i, 304), whilst in all the above experiments with hydrochloric acid a yellowish-green colour is first developed and subsequently disappears (cf. Boyd and Hardy, A., 1928, 516). J. W. BAKER.

**Colloidal phenoxides. II. Phenanthraxanthones.** W. BAKER (J.C.S., 1930, 261—268).—A continuation of the attempts to prepare a  $\gamma$ -pyrone which will give a fluorescent gel when dissolved in alkali hydroxide (cf. this vol., 217). Nitration of 7-methoxy-3-phenyl-2-(3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone with nitric and acetic acids affords 7-methoxy-3-phenyl-2-(6-nitro-3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone, m. p. 222°, reduced by tin and alcoholic hydrochloric acid to the corresponding amino-compound, m. p. 208° [*chlorostannate*, m. p. 240° (decomp.) after darkening at 200°; *hydrochloride*, loses hydrogen chloride at 100°]. Dissolution of this base in methyl-alcoholic sulphuric acid, diazotisation, and subsequent boiling gives 6:7:10-trimethoxyphenanthraxanthone (I), m. p.



232—233°, demethylated to the 6:7:10-trihydroxy-derivative (+EtOH), m. p. 318—319° with much darkening, by boiling with acetic and hydrobromic (*d* 1.5) acids. Hydrolysis of the product formed from 2:4-dihydroxyphenyl benzyl ketone, *o*-nitrobenzoic anhydride (modified method of preparation given), and sodium *o*-nitrobenzoate at 153° with alcoholic potassium hydroxide furnishes 7-hydroxy-3-phenyl-2-*o*-nitrophenylbenzo- $\gamma$ -pyrone, m. p. 268°. The methyl ether, m. p. 183°, of this is reduced to 7-methoxy-3-phenyl-2-*o*-aminophenylbenzo- $\gamma$ -pyrone, m. p. 213°, converted as above into 10-methoxyphenanthraxanthone, m. p. 248—249°. Demethylation of this yields 10-hydroxyphenanthraxanthone, m. p. 325—326° with slight darkening (*acetyl* derivative, m. p. 234—235°), which on dissolution in sodium hydroxide gives an unstable gel possessing no marked fluorescence.

The Hoesch condensation of resorcinol and *o*-nitrophenylacetonitrile gives 2:4-dihydroxyphenyl *o*-nitrobenzyl ketone, m. p. 159—161°, converted by treatment with benzoic anhydride and sodium benzoate at 180—190° and subsequent hydrolysis into 7-hydroxy-2-phenyl-3-*o*-nitrophenylbenzo- $\gamma$ -pyrone, m. p. 267°. Reduction of the methyl ether, m. p. 178°, of this pyrone furnishes an amorphous product showing some of the properties of a secondary amine.

H. BURTON.

**Determination of the configuration of 2:6-diphenylpenthian-4-one.** F. ARNDT and E. SCHAUDER (Ber., 1930, 63, [B], 313—316).—The *A* form of 2:6-diphenylpenthian-4-one, m. p. 113—114° (Arndt, Nachtwey, and Pusch, A., 1925, i, 1307; for nomen-



clature see Bennett and Scoria, A., 1927, 228), is converted by magnesium methyl bromide into a mixture of the two varieties of 2 : 6-diphenyl-4-methylpenthi-4-ol, m. p. 90—91°, and 173°, respectively, transformed by phosphoric oxide in presence of boiling light petroleum into (?) 2 : 6-diphenyl-4-methyl- $\Delta^3$ -penthiene, m. p. 83—84°. 2 : 6-Diphenylpenthi-4-one B, m. p. 87—88°, is transformed by magnesium methyl bromide into a non-crystalline material, converted by phosphoric oxide into an isomeric diphenylmethylpenthiene, m. p. 74—75°. The *cis*- and *trans*-configurations are therefore assigned respectively to the ketones, m. p. 113—114° and 87—88°. Reduction of the compound of m. p. 113—114° with amalgamated zinc and concentrated hydrochloric acid affords *cis*-2 : 6-diphenylpenthi-4-ol, m. p. 98°; *trans*-2 : 6-diphenylpenthi-4-ol, m. p. 142°, is obtained similarly from the ketone of m. p. 87—88°. H. WREN.

**Derivatives of 2-keto-1 : 2-dihydrothionaphthen SS-dioxide.** A. COHEN and S. SMILES (J.C.S., 1930, 406—414).—A satisfactory synthesis of these derivatives,  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} CHR$  (I), consists in the action of alcoholic sodium ethoxide on sulphone esters  $CH_2R \cdot CO_2 \cdot C_6H_4 \cdot SO_2 \cdot CH_2R$  (II) (prepared by the action of an alkali *o*-carboxybenzenesulphinate on the appropriate halogeno-derivative) or by direct action of sodium ethoxide on the ethyl ester of the sulphone acid  $C_6H_4(SO_2 \cdot CH_2R) \cdot CO_2H$  (III), in which case admixture of the product with the ether

$C_6H_4 \begin{smallmatrix} \text{C(OR)} \\ \text{SO}_2 \end{smallmatrix} CR$  is avoided. Thus are obtained : phenacyl-*o*-carbophenacylphenylsulphone (II,  $R=Bz$ ), m. p. 164°; *o*-carboxyphenylbenzylsulphone (III,  $R=Ph$ ), m. p. 126—128° (potassium salt); *o*-nitrobenzyl ester, m. p. 156° (II,  $R=O \cdot NO_2 \cdot C_6H_4$ ), of *o*-carboxyphenyl-*o*-nitrobenzylsulphone; ethylenedio-carboxyphenylsulphone (III,  $R=CH_2$ ), m. p. 250° (ethyl ester, m. p. 150°); 2-keto-1-benzoyl- (I,  $R=Bz$ ), m. p. 188° [also by oxidation of the corresponding 1 : 2-dihydrothionaphthen with 30% hydrogen peroxide; 1-bromo-derivative, m. p. 168°; diphenylhydrazone, m. p. 243°; converted by 1 mol. of alcoholic phenylhydrazine into 1 : 3-diphenylthionaphthapyrazole 5 : 5-dioxide,  $C_6H_4 \cdot C \cdot NPh \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} C \cdot CPh \gg N$ , m. p. 225°, and by boiling acetic anhydride and borodiacetic anhydride into the borodiacetate,  $C_6H_4 \cdot COB(OAc)_2 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} C \cdot CPh : O$ , m. p. 220° (decomp.), readily decomposed by cold water], 2-keto-1-phenyl- (I,  $R=Ph$ ), m. p. 174° (1-bromo-derivative, m. p. 170°; also obtained, together with the benzyl ether, m. p. 146°, of 2-hydroxy-1-phenylthionaphthen SS-dioxide by the action of sodium ethoxide on the product of the interaction of potassium *o*-carboxybenzenesulphinate and benzyl chloride); 2-keto-1-acetyl- (I,  $R=Ac$ ), m. p. 164° (monophenylhydrazone, m. p. 210°, dehydrated by acetic acid containing a few drops of sulphuric acid at 90° to 1-phenyl-3-methylthionaphthapyrazole 5 : 5-dioxide, m. p. 180°); 2-keto-1-*o*-nitrophenyl- (I,  $R=O \cdot NO_2 \cdot C_6H_4$ ), m. p. 187° (reduced by zinc dust and acetic acid to

thionaphthindole dioxide,  $C_6H_4 \cdot C \cdot NH \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} C \cdot C_6H_4$ , m. p. 220°),

1 : 2-dihydrothionaphthen SS-dioxide. Reduction of the corresponding 1-*p*-nitrophenyl derivative (A., 1929, 62; 1-bromo-derivative, m. p. 155°) with alkaline sodium hyposulphite yields the unstable 2-keto-1-*p*-aminophenyl-1 : 2-dihydrothionaphthen SS-dioxide, m. p. about 180° (acetyl derivative, m. p. 226°). The presence of a substituent in the 1-position greatly increases the stability of the thionaphthen dioxide ring and most of the above derivatives are stable to hot aqueous sodium hydroxide. The bromo-derivatives described above are obtained by direct bromination in acetic acid, with the exception of the parent 2-keto-1 : 2-dihydrothionaphthen SS-dioxide which yields the 1 : 1-dibromo-derivative, m. p. 148°. The 1-bromo-derivative, m. p. 149—150°, is obtained by bromination of the corresponding 1-carboxy-derivative (Feist, A., 1926, 74) and elimination of carbon dioxide. The bromine in all these derivatives is readily removed as hypobromite by the action of alkali hydroxides. 2-Keto-1-phenyl-1 : 2-dihydrothionaphthen SS-dioxide is converted by the action of either concentrated hydrochloric acid and ethyl nitrite at 90°, or of a mixture of chromic and acetic acids, into the 1-oxide,  $[C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} CPh]_2 O$ , m. p. 220°, but an excess of nitrous acid converts 2-keto-1 : 2-dihydrothionaphthen SS-dioxide into the nitroso-oximino-derivative, m. p. 173°, formed by complete replacement of the 1-hydrogen atoms, and containing the group  $>C(NO) \cdot N(OH) \cdot C(NO) <$ . The 1-benzoyl compound is not attacked by nitrous acid, but the 1-*p*-aminophenyl derivative is converted into a substance to which the constitution 2-keto-1-*p*-quino-1 : 2-dihydrothionaphthen SS-dioxide hydroxide,  $[C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{SO}_2 \end{smallmatrix} C : C_6H_4 : O \rightarrow H] OH$ , decomp. 123° (chloroplatinate; ferrichloride), is assigned. The borodiacetate of 2-keto-1-phenyl-1 : 2-dihydrothionaphthen is only slowly decomposed by boiling water. J. W. BAKER.

**5-Halogeno-3-methylhydroxythionaphthens [6-halogeno-4-methylthioindoxyls].** I. G. FAR-BENIND.—See B., 1930, 362.

**Imide and amide chlorides of non-aromatic acids.** V. J. VON BRAUN and A. HEYMONS (Ber., 1930, 63, [B], 502—507; cf. this vol., 466).—The conversion of acid amides  $CH_2R \cdot CO \cdot NHR'$  and  $CHR_2 \cdot CO \cdot NHR'$  (in which *R* and *R'* are aliphatic or aromatic residues) by an excess of phosphorus pentachloride into stable imide chlorides hydrolysable to chlorinated acids (cf. A., 1927, 547) can also be effected when *R* and *R'* are united to form a ring. Piperidone is converted by 3 mols. of phosphorus pentachloride in xylene at a final temperature of 140° into the imide chloride,  $[CH_2]_3 \begin{smallmatrix} \text{CCl}_2 \\ \text{N} \end{smallmatrix} > C \cdot Cl$ , m. p. 27°, very readily transformed by water into 3 : 3-dichloropiperidone, m. p. 166°. The last-named compound is converted by evaporation with concentrated hydrochloric acid into  $\alpha$ -dichloro- $\delta$ -aminovaleric acid hydrochloride, m. p. 183° ( $\alpha$ -dichloro- $\delta$ -benzamidovaleric acid, m. p. 152°), converted by boiling alcohol into a compound,  $C_5H_9O_2NCl_2$ , m. p. 200°.  $\epsilon$ -Leucinelactam is converted by phosphorus pentachloride and treatment of the product with water into 3 : 3-dichloroleucine-

lactam, m. p. 125° (yield 30—40%), converted by hydrochloric acid into  $\alpha$ -dichloro- $\varepsilon$ -aminohexanoic acid hydrochloride, m. p. 191°. Much less favourable results are obtained with pyrrolidone, which, after treatment as outlined above, gives 3:3-dichloro-pyrrolidone, m. p. 132°, in very small yield.

The product obtained by the action of concentrated sulphuric acid on *o*-methylcyclohexanoneoxime (Wallach, A., 1906, i, 514) is identified as the lactam,  $[\text{CH}_2]_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CHMe} \end{smallmatrix} \text{NH}$ , since it is converted by successive treatment with phosphorus pentachloride and water into the dichloro-derivative,  $\text{C}_7\text{H}_{11}\text{ONCl}_2$ , m. p. 133—135°, and thence into the hydrochloride of the chlorinated amino-acid,  $\text{C}_7\text{H}_{14}\text{O}_2\text{NCl}_3$ , m. p. 151° after softening at 148°. The lactam is also produced from *o*-methylcyclohexanone and azoimide together with the tetrazole derivative,  $\text{C}_7\text{H}_{12}\text{N}_4$ , b. p. about 185°/15 mm., m. p. 32°.

H. WREN.

**Modification of Gattermann's method for the preparation of phenol- and pyrrole-aldehydes.** C. D. NENITZESCU and D. ISACESCU (Bul. Soc. Chim. România, 1929, 11, 135—139).—The phenol or pyrrole, and an excess of formamide or formanilide, is treated in absolute ether with phosphorus oxychloride. With formamide the aldimine hydrochloride is precipitated, and with formanilide that of the aldehyde anil. These are hydrolysed to the aldehyde. In some cases the hydrochlorides are converted into free base before hydrolysis. The formamide method with resorcinol and the formanilide method with 2:4-dimethylpyrrole yield resorcyraldehyde, m. p. 134—135°, and 3:5-dimethylpyrrole-2-aldehyde, m. p. 90°, respectively. Ethyl 2:5-dimethylpyrrole-3-carboxylate (formanilide) gives 3-carbethoxy-2:5-dimethylpyrrole-4-aldehyde anil hydrochloride, m. p. 221°. The base with boiling water gives the aldehyde, m. p. 151°. Similarly, from ethyl 3:5-dimethylpyrrole-4-carboxylate [?] the 2-aldehyde, m. p. 145°, is formed in good yield. 3:5-Dimethylpyrrole, its 2-carbethoxy-derivative (but see above), and 2-methylindole give only complex insoluble substances.

H. A. PIGGOTT.

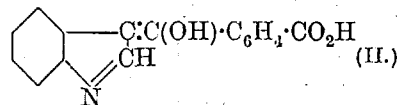
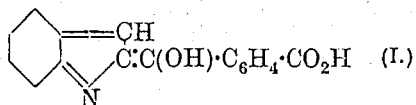
**Syntheses by means of magnesylpyrroles.** Series II. XIII. Reactions with phthalyl chloride and with phthalic anhydride. B. ODDO and C. TOFFOLI (Gazzetta, 1930, 60, 3—13).—Unlike other magnesylindoles, magnesyl-3-methylindoles give mainly *N*-substituted derivatives when they react with phthalyl chloride or phthalic anhydride. 3-Methylindole-1-phthaloin lactoid,

$\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{N} \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CMe} \end{smallmatrix}$ , m. p. 216°, formed in almost theoretical yield when phthalyl chloride and magnesylskatole interact, is accompanied by a small proportion of 3-methylindole-2-phthaloin,

$\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \begin{smallmatrix} \text{CMe} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p. 185—190°.

The interaction of magnesylskatole and phthalic anhydride gives *N*-(3-methylindolyl)hydroxyhydrophthalide,  $\text{CO} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C}(\text{OH}) \cdot \text{N} \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CMe}$ , m. p. 211°, whilst that of magnesylindole and phthalic anhydride yields 2-indolidenphenylcarbinol-*o*-carboxylic acid (I), m. p.

155.5°, and 3-indolidenphenylcarbinol-*o*-carboxylic acid (II), m. p. 179.5°, which are the products of hydrolysis of the corresponding phthalides.



T. H. POPE.

**Syntheses by means of magnesylpyrroles.** Series II. XIV. Reactions between magnesylpyrroles and ketones. B. ODDO and L. PEROTTI (Gazzetta, 1930, 60, 13—21).—The interaction of acetone and magnesylpyrrole gives principally di-

pyrrylphenylmethylmethane,  $\begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CMePh} \end{smallmatrix}$ , m. p.

232°, together with pyrrylphenylmethylcarbinol,

$\begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CMePh} \cdot \text{OH} \end{smallmatrix}$ , m. p. 264—265°, which gives

pyrrolenophenylmethylmethane,  $\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{CPhMe} \end{smallmatrix}$ , as

hydrochloride when dry hydrogen chloride is passed through its ethereal solution. Condensation of acetophenone with magnesyl-2-methylindole gives only di-2-methylindylphenylmethylmethane,

$\begin{smallmatrix} \text{C} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \begin{smallmatrix} \text{C} \\ \diagup \quad \diagdown \\ \text{CMe} \end{smallmatrix} \text{CPhMe}$ , m. p. 130—132°. Mag-

nesylindole and acetone give di-3-indolyl dimethylmethane (cf. Scholtz, A., 1913, i, 520; Majima and Kotake, A., 1923, i, 150); magnesyl-2-methylindole and acetone, di-2-methylindyl dimethylmethane, m. p. 197° (cf. Scholtz, loc. cit.); magnesyl-2-methylindole and dipropyl ketone, di-2-methylindyl dipropylmethane,  $\text{CPr}_2 \cdot (\text{C}_6\text{H}_7\text{NH})_2$ , m. p. 222°; and magnesyl-2-methylindole and methyl *p*-tolyl ketone, di-2-methylindyl-*p*-tolylmethylmethane,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{CMe} \cdot (\text{C}_6\text{H}_7\text{NH})_2$ , m. p. 187°.

T. H. POPE.

**Reactions of magnesium pyrryl and indolyl compounds.** C. D. NENITZESCU (Bul. Soc. Chim. România, 1929, 11, 130—134).—Magnesium pyrryl compounds and Michler's ketone give violet-red dyes not isolated on account of their high solubility. They are turned yellow by alkalis, but regain their colour on treatment with acids. The corresponding indolyl compounds give no trace of colour. *N*-Formylpiperidine and magnesium 2:4-dimethylpyrryl bromide do not give the expected aldehyde, but *N*-(di-2:4-dimethylpyrryl-5-methyl)piperidine, m. p. 133°. This when heated alone or with acids gives piperidine and the orange-yellow dye, bis-(2:4-dimethylpyrryl)-methane, m. p. 117° (cf. A., 1915, i, 309) [hydrochloride, dark orange, m. p. 227° (blackens 208°)]. With formyl derivatives of less basic amines the dye is obtained direct, but not in a pure state. A slight reaction only is observed with the magnesium com-

pounds of indole and 2-methylindole. From a consideration of these and previously known reactions in this series, particularly the reaction with Michler's ketone (cf. Gilman and Schulze, A., 1925, ii, 1011; 1928, 160; Gilman and Heck, A., 1929, 303), it might be assumed that in the pyrrole series the magnesium is attached to carbon and in the indole series to nitrogen. The author, however, considers that they are *N*-derivatives in every case, the difference being one of reactivity. The reaction with Michler's ketone then loses its value as a reagent for *C*-magnesium compounds. H. A. PIGGOTT.

**Preparation of 3:5-dimethylpyridine and 2:3:5-trimethylpyridine.** (MLLE.) M. P. OPARINA (J. Russ. Phys. Chem. Soc., 1929, 61, 2001—2010).—Condensation of propaldehyde with ammonia in presence of alumina yields, as secondary product, a small proportion of 3:5-dimethylpyridine (cf. Tschitschibabin and Oparina, A., 1923, i, 1123), which may result from the condensation with ammonia of propaldehyde (2 mols.) and formaldehyde (1 mol.), the latter being formed from the propaldehyde at the high temperature of the reaction. Actually condensation of propaldehyde (2 mols.) with diethylformal (1 mol.) gives 3:5-dimethylpyridine as principal product, together with 3:5-lutidine, pyridine,  $\beta$ -picoline, 3:4-dimethylpyridine, and a base giving a picrate, m. p. 183°. The formation of pyridine and  $\beta$ -picoline in this reaction is explained by the presence of admixed acetaldehyde in the propaldehyde. The picrate, m. p. 183°, proves to be that of 2:3:5-trimethylpyridine, b. p. 182—183.3° (uncorr.), obtainable from low-temperature tar and (1) by the condensation of propaldehyde (2 mols.) and acetaldehyde (1 mol.) with ammonia in presence of alumina, or (2) by the action of methyl iodide on 3:5-dimethylpyridine, no 3:4:5-trimethylpyridine being formed in either case. On oxidation with dilute permanganate solution, this base gives pyridine-2:3:5-tricarboxylic acid as final product, but if insufficient permanganate is used, a mixture of 2:5-dimethylpyridine-3-carboxylic acid, m. p. 185—186°, and 2:3-dimethylpyridine-5-carboxylic acid, m. p. 195—197°, is obtained. T. H. POPE.

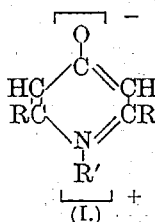
**2-Methyl-5-isopropylpyridine.** (MLLE.) M. P. OPARINA (J. Russ. Phys. Chem. Soc., 1929, 61, 2011—2015).—Treatment of 5-acetyl-2-methylpyridine (cf. Benary and Psille, A., 1924, i, 872) or ethyl 2-methylpyridine-5-carboxylate with magnesium methyl iodide yields 2-methylpyridine-5-dimethylcarbinol,  $C_9H_{13}NMe_2 \cdot CMe_2 \cdot OH$ , m. p. 57—58°, b. p. 138—140°/15 mm., which, on reduction with hydriodic acid and red phosphorus, gives 2-methyl-5-isopropylpyridine, b. p. 190—191°,  $d_4^{20}$  0.9237,  $d_4^{25}$  0.9114; the picrate of this base has m. p. 167.5° (cf. Curtius and Bertho, A., 1926, 509) and the chloroplatinate, m. p. 137—138° or 93—94° (+H<sub>2</sub>O), has the normal composition,  $(C_9H_{14}NCl)_2PtCl_6$ . T. H. POPE.

**Reactivity of halogen atoms in compounds of the pyridine series. I. Halides of 2-stilbazole.** J. W. BLOOD and B. D. SHAW (J.C.S., 1930, 504—507).—Treatment of 2-stilbazole (2-styrylpyridine) dibromide, m. p. 172° (lit. 166—167°), with pyridine,

alcoholic potassium iodide, hydriodic acid, or phenol affords 2-stilbazole [*hydrobromide* + H<sub>2</sub>O, m. p. (anhydrous) 188—189°; *hydriodide* + 2H<sub>2</sub>O, m. p. (anhydrous) 182—184°]. 2-Stilbazole is also formed when the quantity of reagent is equivalent to one bromine atom, indicating that replacement of one bromine atom with hydrogen and subsequent loss of hydrogen bromide occur. With piperidine or alcoholic sodium ethoxide, *bromostilbazole*, m. p. 74—75°, is obtained. Alcoholic potassium hydroxide solution at the ordinary temperature produces 9% of stilbazole and 50% of bromostilbazole. Small amounts of oily products, which solidify on keeping, are also formed. Similar results are found using *stilbazole dichloride*, m. p. 153—154°, obtained together with the *tetrachloride*, m. p. 180—181°, from equimolecular amounts of 2-stilbazole and chlorine in carbon tetrachloride. *Chlorostilbazole* has m. p. 63°. H. BURTON.

**Constitution of so-called "4-pyridones."** F. ARNDT and A. KALISCHEK (Ber., 1930, 63, [B], 587—596).—The possibility of assigning the betaine structure I to 4-pyridones has been examined (cf. Arndt and others, A., 1925, i, 57). Contrary to Smirnov, 1-*p*-tolyl-4-keto-1:4-dihydropyridine-2:6-dicarboxylic acid, m. p. 192° (decomp.), is colourless and his phenylhydrazone is the phenylhydrazine salt of the acid. 1-Phenylchilidamic acid is converted by ethyl alcohol and hydrogen chloride into the monohydrated ethyl ester, m. p. 65—66°, giving, with phosphorus pentasulphide in boiling benzene, *ethyl 4-thio-1-phenylchilidamate*, m. p. 130°, which is devoid of ketonic properties. Attempts to prepare 1-acyl-4-pyridones were fruitless. 4-Hydroxypyridine is transformed by cold acetic anhydride into 4-acetoxypyridine, m. p. (indef.) 140—150°, which is immediately hydrolysed by water. When heated alone or with acetic anhydride it passes into *di-4-pyridyl ether*, m. p. 177—178° (*picrate*, m. p. 198° after softening; 4-hydroxypyridine *picrate* has m. p. 238°). In presence of pyridine, 4-hydroxypyridine is converted by the requisite acid chloride into the corresponding *o*-benzoyl derivative, m. p. 81°, and *o*-*p*-toluenesulphonyl compound, m. p. about 105° in a preheated bath (*perchlorate*, m. p. 162°; *picrate*, m. p. 128° after softening). The last-named substance passes when warmed in presence of water vapour into *di-4-pyridyl ether p-toluenesulphonate*, m. p. 224° (decomp.). The ether is also produced during the distillation of chilidamic acid and is separated from 4-hydroxypyridine by extraction with dry benzene. The experiments afford no support to the pyridone formula, but the great volatility of the acetoxy-derivative in comparison with that of the parent compound is explicable by a betaine structure of the latter.

4-Hydroxypiperidine hydrochloride, obtained by reduction of 4-hydroxypyridine, is converted by *p*-toluenesulphonyl chloride and sodium hydroxide into 1-*p*-toluenesulphonyl-4-hydroxypiperidine, m. p. 131—132° (1-*p*-toluenesulphonylpiperidine has m. p. 95—96°). It is oxidised by chromium trioxide in



glacial acetic acid to 1-*p*-toluenesulphonyl-4-ketopiperidine, m. p. 128° [semicarbazone, m. p. 220° (decomp.)], which is brominated to 3:5-dibromo-1-*p*-toluenesulphonyl-4-ketopiperidine, m. p. 191°. The last-named compound appears to lose the toluenesulphonyl group or to suffer fission of the ring when warmed with pyridine.

H. WREN.

**Preparation of quinoline by Skraup's reaction.** G. DARZENS, R. DELABY, and (Mlle.) J. HIRON (Bull. Soc. chim., 1930, [iv], 47, 227—232).—Consistent and higher yields of quinoline are obtained by adding the sulphuric acid gradually, decreasing the proportion of glycerol from 3.0 to 1.7 mols. per mol. of aniline, and effecting the condensation in presence of a dehydrating or an oxidation catalyst. Thus, by heating a mixture of aniline (1 mol.), glycerol (1.73 mols.), nitrobenzene (0.55 mol.), 0.5 g. of vanadic acid, 2.5 g. of thoria and sulphuric acid *d* 1.84 (1.25 mol.) for 10 hrs. at 150°, and, after cooling, adding successively a further 0.5, 0.5, and 0.25 mol. of sulphuric acid, heating for 10 hrs., 3 hrs., and 3 hrs. after the respective additions, yields of quinoline amounting to 72% on the aniline or 42% on the glycerol are uniformly obtained. The excess of aniline may be removed by diazotisation in sulphuric acid or the quinoline may be precipitated as chlorozincate (Wyler, A., 1927, 365); the latter process gives a purer product. With mechanical agitation and continuous addition of sulphuric acid *d* 1.84 (105 c.c.) to a mixture of glycerol (150 g.), aniline (70 g.), and nitrobenzene (45 g.) in presence of 0.5 g. of vanadic acid yields of 82% on the aniline and 48% on the glycerol used are obtained.

R. BRIGHTMAN.

**Complex compounds of benzylquinoline chloride or bromide with metallic salts.** J. MICHAILENKO (J. Russ. Phys. Chem. Soc., 1929, 61, 2253—2267).—Benzylquinoline chloride and bromide readily form complex compounds of the types  $(C_9H_7N \cdot CH_2PhX)_2RX_2$  and  $C_9H_7N \cdot CH_2PhX \cdot RX_3$ , where X is chlorine or bromine and R is copper, cobalt, zinc, cadmium, manganese, iron, or aluminium. Compounds of the former type are analogous, in mode of formation, form, and chemical relationships, to the simplest compounds of the type  $2RX \cdot R'X_2$ , where R is hydrogen or a univalent metal and X is a halogen. The cation  $[C_9H_7N \cdot CH_2Ph]^+$  is a complex cation of the ammonium type, being a tetrasubstituted ammonium in which three hydrogen atoms are replaced by the tervalent group  $C_9H_7$ , and the fourth hydrogen by the benzyl radical. These complex compounds are prepared by mixing benzylquinoline chloride or bromide with the heavy metal salt in aqueous or alcoholic solution. In aqueous solution they behave like mixtures of the component salts, all four chlorine atoms being precipitated by silver nitrate and the heavy metal by hydrogen sulphide or alkali carbonate or hydroxide. Compounds of the second of the two types are regarded as salts formed by the cation  $[C_9H_7N \cdot CH_2Ph]^+$  and the complex anion  $[R'''X_4]^-$ .

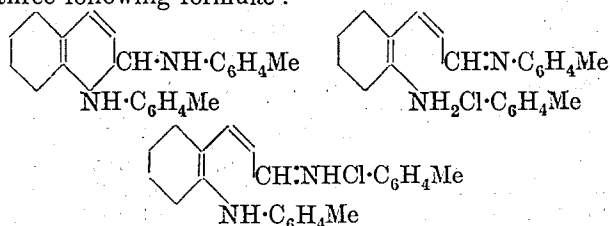
The compounds prepared are: [With I. MOLODYX.— $(C_9H_7N \cdot CH_2PhCl)_2CuCl_2$ , m. p. 150° (decomp.);  $C_9H_7N \cdot CH_2PhBr$ , m. p. 182°, 120° (+2H<sub>2</sub>O), 139° (+H<sub>2</sub>O);  $(C_9H_7N \cdot CH_2PhCl)_2CuBr_2$  or

$(C_9H_7N \cdot CH_2PhBr)_2CuCl_2$ , cinnamon-black crystals; an isomeric dark red crystalline compound, m. p. 167° (decomp.);  $(C_9H_7N \cdot CH_2PhBr)_2CuBr_2$ , m. p. about 154° (decomp.). [With A. KRYLEVSKA.]— $(C_9H_7N \cdot CH_2PhCl)_2CoCl_2$ , m. p. 210°;  $(C_9H_7N \cdot CH_2PhBr)_2CoBr_2$ , m. p. 164°. [With N. ZVORYKINA.]— $(C_9H_7N \cdot CH_2PhBr)_2ZnBr_2 \cdot 2H_2O$ , m. p. 173°;  $[(C_9H_7N \cdot CH_2Ph)_2][ZnCl_2Br_2]$  (?), m. p. 195°;  $(C_9H_7N \cdot CH_2Ph)_2CdBr_2$ , m. p. 158°;  $(C_9H_7N \cdot CH_2PhBr)_2MnBr_2$  (?), m. p. 165°. [With N. KUDRJASHEVA.]— $C_9H_7N \cdot CH_2PhCl \cdot FeCl_3 \cdot H_2O$ , m. p. 95°;  $C_9H_7N \cdot CH_2PhBr \cdot FeBr_3$  (?), m. p. 130° (? + H<sub>2</sub>O);  $C_9H_7N \cdot CH_2Ph \cdot ONO_2$ , m. p. 121—122°.

T. H. POPE.

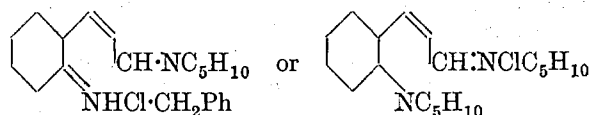
**Action of amines on benzylquinoline chloride.** J. MICHAILENKO and B. MINOFIEV (J. Russ. Phys. Chem. Soc., 1929, 61, 2269—2277).—Benzylquinoline chloride reacts with aniline,  $\alpha$ - and  $\beta$ -naphthylamines, sulphanilic acid, pyrrole, *m*-nitroaniline, *p*-toluidine, diphenylamine, and piperidine, giving deep red or yellow compounds, but only with the four last bases have the resulting products been separated.

*p*-Toluidine and benzylquinoline chloride give a ruby-red compound, m. p. 148°, having one of the three following formulæ:



Similarly, diphenylamine gives a red compound,  $C_6H_5 \cdot \text{quinoline} \cdot CH \cdot CH \cdot C_6H_5 \cdot NPh_2 + EtOH$ , m. p. 148°.

Piperidine yields a deep red compound, m. p. 84°, which has the properties of a basic dye and the structure



*m*-Nitroaniline gives a yellow compound, m. p. 84° (? 184°).

T. H. POPE.

**Synthesis of quinoline derivatives.** K. MURAKAMI (Sci. Rep. Tôhoku, 1929, 18, 643—649).—Condensation of zingerone with paraldehyde, propaldehyde, and *n*-butaldehyde in presence of alcoholic hydrochloric acid, and subsequent treatment of the reaction mixture with aniline, affords, instead of the expected quinoline derivative (cf. John and others, A., 1925, i, 1451), 2-methyl-, 3-methyl-2-ethyl-, m. p. 57—57.5° [picrate, m. p. 190—192° (decomp.)], and 3-ethyl-2-*n*-propyl-quinoline (picrate, m. p. 164—166°; hydrochloride, m. p. 169.5—170°; mercurichloride, m. p. 126°; dichromate), respectively. These quinoline derivatives result from 2 mols. of the aldehyde and 1 mol. of aniline. 4-Hydroxy-3-methoxystyryl methyl, heptynyl, and octenyl ketones, and 3:4-dimethoxystyryl methyl ketone furnish traces of quinoline derivatives when condensed with aniline under various conditions.

H. BURTON.

Quinoline compounds containing an aliphatic amino-substituted side-chain. I. G. FARBENIND.—See B., 1930, 349.

Phenylcarboxylic acid compounds [carboxy-anilinoquinolines]. I. G. FARBENIND.—See B., 1930, 302.

Pyrazolines derived from 4-hydroxy-3-methoxystyryl alkyl and phenyl ketones and  $\beta$ -4-hydroxy-3-methoxyphenylethyl  $n$ - $\Delta^8$ -octenyl ketone. K. MURAKAMI (Sci. Rep. Tôhoku, 1929, 18, 651—660).—Treatment of an alcoholic solution of a 4-hydroxy-3-methoxystyryl alkyl ketone with phenylhydrazine and acetic acid (cf. von Auwers, A., 1909, i, 59; 1910, i, 70) affords 1-phenyl-5-(4'-hydroxy-3'-methoxyphenyl)-3-alkylpyrazolines, of which the following are described: 3-methyl, m. p. 136—136.5°; 3-ethyl, m. p. 100—101°; 3-n-propyl, m. p. 94.5—95°; 3-n-butyl, m. p. 105.5°; 3-n-amyl, m. p. 81.5°; 3-n-hexyl, m. p. 68°; 3-n-octyl, m. p. 75.5—76°; 3-n-heptadecyl, m. p. 82.5—83.5°; 3-isobutyl, m. p. 132.5—133°, and 3-tert.-butyl, m. p. 101°. 1:3-Diphenyl-5-(4'-hydroxy-3'-methoxyphenyl)pyrazoline, m. p. 160—161°, is obtained similarly from phenyl 4-hydroxy-3-methoxystyryl ketone.  $\beta$ -4-Hydroxy-3-methoxyphenylethyl  $n$ - $\Delta^8$ -octenyl ketone furnishes an oily pyrazoline derivative.

H. BURTON.

Pungent principles of ginger. VI. Colour reaction of shogaol and methylgingerol. H. NOMURA, K. IWAMOTO, and K. MURAKAMI (Sci. Rep. Tôhoku, 1929, 18, 661—664).—4-Hydroxy-3-methoxystyryl  $n$ -heptyl ketone, phenylhydrazine, and acetic acid react in methyl-alcoholic solution forming 1-phenyl-5-(4'-hydroxy-3'-methoxyphenyl)-3-n-heptylpyrazoline, m. p. 78—79°. Similar treatment of  $\beta$ -4-hydroxy-3-methoxyphenylethyl  $n$ - $\Delta^8$ -heptenyl ketone affords an oily pyrazoline derivative. Since shogaol also furnishes an oily pyrazoline, the presence of an  $\alpha\beta$ -unsaturated linking is confirmed (cf. A., 1927, 770). Methylgingerol (A., 1928, 1375) affords an oily pyrazoline, thus indicating that it has the constitution  $C_6H_3(OMe)_2[CH_2]_2COCH_2CH(OH)[CH_2]_4Me$ . The oily products are identified as pyrazolines by the Knorr colour reaction (A., 1893, i, 229).

H. BURTON.

Reactions of antipyrine. L. EKKERT (Pharm. Zentr., 1930, 71, 180).—Some colour reactions with  $p$ -dimethylamidobenzaldehyde in sulphuric acid are described. The reaction product gives a red dye on treatment with perchloric acid; the colour is discharged on addition of ammonia. S. I. LEVY.

$N$ -Acylpyrazolones as acylating agents. J. S. AGGARWAL and J. N. RAY (J.C.S., 1930, 492—493).—Ethyl acetoacetate condenses with phenylacetylhydrazine in presence of small amounts of alcohol and piperidine at 100°, forming 3-methyl-5-pyrazolone (I) and  $s$ -di(phenylacetyl)hydrazine. When the condensation is carried out at the ordinary temperature, 1-phenylacetyl-3-methyl-5-pyrazolone, m. p. 134—136°, results. This and aniline at 130—140° give phenylacetanilide and I; phenylacetylhydrazine and aniline, under the same conditions, do not afford the anilide. Similarly, ethyl acetoacetate and benzoylhydrazine

afford either 1-benzoyl-3-methyl-5-pyrazolone or  $s$ -di-benzoylhydrazine and I. H. BURTON.

New methods of forming 2:5-dimethylpiperazine. M. GODCHOT and M. MOUSSERON (Compt. rend., 1930, 190, 798—800).—When 2:5-dimethylpyrazine is passed with a current of hydrogen over reduced nickel at 150—160°, *trans*-2:5-dimethylpiperazine, m. p. 118° (Kipping and Pope, A., 1926, 739), is formed exclusively. When the reduction is effected with hydrogen and platinum-black in acetic acid the product is mainly the *trans*-isomeride, but a trace of the *cis*-compound can be separated by Stoehr's method (A., 1893, i, 486). Similar reduction of *iso*-nitrosoacetone converts it directly into *trans*-2:5-dimethylpiperazine in good yield. J. W. BAKER.

cycloDipeptides of asparagine. C. RAVENNA and R. NUCCORINI (Gazzetta, 1930, 60, 140—143).—Self-condensation of asparagine in glycerol at 160—170° (cf. Shibata, A., 1927, 891) affords a viscous syrup, which by treatment with 0.33*N*-barium hydroxide is converted into the  $\beta$ -dipeptide of aspartic acid (A., 1920, i, 150, 151, 600; cf. A., 1922, i, 180). The production of the  $\beta$ -dipeptide is held to indicate the pre-existence in the condensation product of the corresponding cyclo-dipeptide

$CO_2H \cdot CH < \begin{smallmatrix} NH \cdot CO \cdot CH_2 \\ CH_2 \cdot CO \cdot NH \end{smallmatrix} > CH \cdot CO_2H$ , which arises by elimination of ammonia from the amino- and carboxyl-amido-group of 2 mols. of asparagine.

C. W. SHOPPEE.

Constitution of anserine. II. W. KEIL (Z. physiol. Chem., 1930, 187, 1—6; cf. A., 1929, 944).—Anserine reacts with  $\gamma$ -trinitrotoluene to give *dinitrotolylanserine*, which on hydrolysis with 30% sulphuric acid yields  $\beta$ -dinitrotolylalanine, showing the presence of a  $\beta$ -alanine side-chain. Distillation of anserine with soda-lime yields 1:5-dimethylglyoxaline. Anserine is thus ( $\beta$ -alanyl)amino- $\beta$ -( $N$ -methyl-5-iminazolyl)propionic acid. J. H. BIRKINSHAW.

Formation of 4(5)-aminoglyoxalines. I. I. E. BALABAN (J.C.S., 1930, 268—273).—Ethyl glyoxaline-4(5)-carboxylate and hydrazine hydrate at 100° give *glyoxaline-4(5)-carboxyhydrazide* (+H<sub>2</sub>O), m. p. 213° [*picrate*, m. p. 223° (decomp.)], converted by nitrous acid into *glyoxaline-4(5)-carboxyazide*, decomp. 137°. With boiling methyl and ethyl alcohols this furnishes 4(5)-*carbomethoxyaminoglyoxaline*, m. p. 175° [*picrate*, decomp. 243° after blackening at about 240°], and 4(5)-*carbethoxyaminoglyoxaline*, m. p. 180° [*picrate*, decomp. 210°], respectively. The *nitrate*, decomp. 143°, of the last-named substance on treatment with sulphuric acid affords 5(4)-*nitro-4(5)-carbethoxyaminoglyoxaline*, m. p. 234° (decomp.). Attempts to obtain the amino-derivatives from these carbamates were unsuccessful. The above azide is decomposed by boiling water, yielding a green solution from which a *picrate*,  $C_7H_8ON_6 \cdot 2C_6H_5O_7N_3$ , chars at 230° after previous darkening, can be obtained.

5-Chloro-4-nitro-1-methylglyoxaline and 3.5% alcoholic ammonia at 140° give 4-nitro-5-amino-1-methylglyoxaline, m. p. 303° (decomp.), which is decomposed by 16% hydrochloric acid at the ordinary temperature to nitrous acid and  $\alpha$ -methylamino- $\alpha$ -hydroxyacetamide, m. p. 140°. Fission of the gly-

oxaline molecule occurs between the 1:2- and 2:3-positions; formic acid is eliminated and the intermediate  $\alpha$ -amino- $\alpha$ -methylaminoacetamide reacts with the nitrous acid.

4(5)-Nitro- and 4(5)-nitro-2-methyl-glyoxalines could not be reduced to the corresponding amines by various standard methods. H. BURTON.

**Nitration of phenyl substituents of heterocyclic nuclei.** R. FORSYTH and F. L. PYMAN (J.C.S., 1930, 397—403).—Nitration of 2-phenyl-1-methylglyoxaline [nitrate, m. p. 126—127° (all m. p. are corr.)] by the method previously described (A., 1925, i, 157) gives 39% of the *p*-nitrophenyl derivative; crude *p*-nitrobenzoic acid (4.4% yield) is also isolated by permanganate oxidation of the by-products. Similarly, 1-phenylglyoxaline (dinitrate, m. p. 82—86°) furnishes 58% of 1-*p*-nitrophenylglyoxaline, m. p. 204—205° [hydrochloride, m. p. 293—294° (decomp.)]; 4-phenylpiperidine (nitrate, m. p. 139°) affords 8, 3, and 52.5% of the *o*- [hydriodide + H<sub>2</sub>O, m. p. (anhydrous) 160—161°; nitrate, m. p. 131—132°], *m*- (hydriodide, m. p. 236°; nitrate, m. p. 205—206°), and *p*-nitro-derivatives (hydriodide, m. p. 189—190°; nitrate, m. p. 162—163°), respectively; 4-hydroxy-2-phenyl-6-methylpyrimidine yields 50% of the *m*-nitrophenyl derivative, m. p. 257° (lit. 254°), and phenylacetamide (nitrate, m. p. 168—169°) gives 75% of *p*-nitrophenylacetamide [nitrate + 0.5H<sub>2</sub>O, m. p. (anhydrous) 157°; picrate, m. p. 210°]. Addition of 2-phenylglyoxaline nitrate to sulphuric acid and keeping the mixture at the ordinary temperature for 60 hrs. results in the formation of 57% of the *p*-nitro-derivative (cf. *loc. cit.*).

Hydrogen chloride converts an ethereal-alcoholic suspension of *p*-nitrophenylacetoneitrile into *p*-nitrophenylacetiminoethyl ether hydrochloride, m. p. 191—192° (decomp.) after softening at about 188° when heated slowly from the ordinary temperature, decomposes when placed in a bath at 150°. Prolonged treatment of this with alcoholic ammonia at 30°, acidification of the alcohol-free solution with hydrochloric acid, subsequent treatment with silver nitrate, and evaporation of the residual aqueous solution affords *p*-nitrophenylacetamide nitrate. H. BURTON.

**Mixed acid anhydrides.** K. VON AUWERS and E. WOLTER (Ber., 1930, 63, [B], 479—482; cf. A., 1929, 75).—Hydroindazolecarboxylic acid is converted by boiling acetyl chloride into a mixture of acetic 1-acetyl-tetrahydroindazole-3-carboxylic anhydride,

$\text{AcN} \langle \text{C}_6\text{H}_5 \rangle \text{N} \rangle \text{C} \cdot \text{CO} \cdot \text{OAc}$ , m. p. 76.5—77.5°, and 1-acetyltetrahydroindazole-3-carboxylic acid, m. p. 187.5—188.5°, the relative proportion of the mixed anhydride increasing with the duration of heating. Similarly, hydroindazolecarboxylic acid is transformed by prolonged ebullition with methyl chloroformate into the mixed ester,  $\text{CO}_2\text{Me} \cdot \text{N} \langle \text{C}_6\text{H}_5 \rangle \text{N} \rangle \text{C} \cdot \text{CO} \cdot \text{O} \cdot \text{CO}_2\text{Me}$ , m. p. 86—87°. The corresponding ethyl ester, which could not be caused to solidify, loses carbon dioxide when heated in a vacuum and passes into ethyl tetrahydroindazole-1:3-dicarboxylate with a small proportion of diketopiperazine derivative. The production of mixed anhydride appears to depend on the acid

chloride used, since boiling propionyl chloride affords 1-propionyltetrahydroindazole-3-carboxylic acid, m. p. 157—158° after softening, and boiling isovaleryl chloride yields exclusively diketopiperazine, m. p. 298° (decomp.). Unexpectedly, the last-named substance is exclusively formed by the action of methyl chloroformate on the acid in the presence of pyridine whereas it is not formed in traces in the absence of the base. Diketopiperazine is produced by the action of a large excess of boiling thionyl chloride on hydroindazolecarboxylic acid. H. WREN.

**Polymerisation of indole. I. Preparation of di-indole.** O. SCHMITZ-DUMONT and B. NICOLAJANNIS (Ber., 1930, 63, [B], 323—328).—The action of hydrogen chloride on a solution of indole in benzene leads to the separation of di-indole hydrochloride,  $(\text{C}_8\text{H}_7\text{N})_2\text{HCl}$ , converted by warm aqueous ammonia into di-indole, m. p. 108°. The picrate, indef. m. p., from which di-indole is regenerated by ammonia, and the additive compound with trinitrobenzene are described. Depolymerisation of di-indole to indole occurs when it is heated at 200—220°/2 mm. With tin tetrabromide in benzene, the compound  $\text{SnBr}_4 \cdot 2(\text{C}_8\text{H}_7\text{N})_2$ , m. p. 114° (decomp.) after darkening at about 100°, is obtained, converted by ammonia or sodium hydroxide into di-indole. Treatment of di-indole with benzoyl chloride and anhydrous sodium carbonate in benzene gives a product,  $\text{C}_{23}\text{H}_{18}\text{ON}_2$ , m. p. (indef.) 152° after softening at 139°. H. WREN.

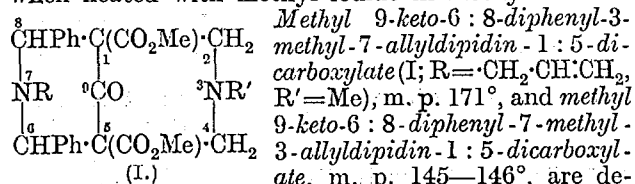
**Hydrogenation of octahydrophenazine.** M. GODCHOT and M. MOUSSERON (Compt. rend., 1930, 190, 442—443).—1:2:3:4:6:7:8:9-Octahydrophenazine (A., 1925, i, 436) is reduced by sodium and alcohol to tetradecahydrophenazine (+EtOH), m. p. 133—134° (dinitroso-compound, m. p. 161—162°), which forms an acid urate soluble in water, and gives phenazine when distilled with zinc dust. The same compound is formed when octahydrophenazine and hydrogen are passed over nickel at 170°, but the catalyst soon loses its activity. Hydrogenation in acetic acid in presence of platinum-black yields an isomeric tetradecahydrophenazine, m. p. 107°, b. p. 170°/15 mm. (dinitroso-compound, m. p. 182°).

R. K. CALLOW.

**Derivatives of a condensed dicyclic system formed from two piperidine rings.** C. MANNICH and P. MOHS (Ber., 1930, 63, [B], 608—612).—Methyl 4-keto-2:6-diphenyl-1-methylpiperidine-3:5-dicarboxylate, m. p. 137—138° (hydrochloride, decomp. 195°), is prepared in about 65% yield by the action of methylamine on benzaldehyde and ethyl acetonedicarboxylate. Methyl 4-keto-2:6-diphenyl-1-allylpiperidine-3:5-dicarboxylate, m. p. 159—160°, methyl 4-keto-2:6-di-*p*-anisyl-1-allylpiperidine-3:5-dicarboxylate, m. p. 158°, and methyl 4-keto-2:6-diphenyl-1- $\beta$ -hydroxyethylpiperidine-3:5-dicarboxylate, m. p. 123—124° (hydrochloride, m. p. 153—154°), are analogously prepared. Addition of a second piperidine ring to methyl 4-keto-2:6-diphenyl-1-methylpiperidine-3:5-dicarboxylate by the action of formaldehyde and methylamine affords methyl 9-keto-6:8-diphenyl-3:7-dimethyldipidine-1:5-dicarboxylate (I; R=R'=Me), m. p. 184—185° [unstable dihydrochloride; monohydrochloride, m. p. 191—192° (de-



comp.], which undergoes extensive decomposition when heated with methyl iodide in methyl alcohol.



**Product of the action of propionic anhydride on 2-methylpyridine.** A. E. TSCHITSCHIBABIN and F. N. STEPANOV (Ber., 1930, 63, [B], 470-472; cf. A., 1929, 704).—The view that the compound obtained by Scholtz from 2-methylpyridine and propionic anhydride is 3-propionyl-1-methylindolizine (*loc. cit.*) is confirmed by the conversion of the substance by hydrochloric acid into propionic acid and 1-methylindolizine, b. p. 230°. The position of the methyl group in the indolizine nucleus follows from the mode of formation of the compound and its non-identity with the known 2-methylindolizine. H. WREN.

**Dyes of the phenonaphthazine series from 3-arylamino-1 : 8-naphthasultam compounds.** W. NEELMEIER and others.—See B., 1930, 411.

**Acid dyes of the phenonaphthasafraanine series.** J. R. GEIGY A.-G.—See B., 1930, 364.

**Vat dyes of the anthraquinone series.** I. G. FARBENIND.—See B., 1930, 365.

**Methylketoylacetic [3-acetyl-2-methylindole- $\omega$ -carboxylic] acid and some of its derivatives.** A. ALBANESE (Gazzetta, 1930, 60, 21-26; cf. Oddo and Albanese, A., 1928, 185).—Ethyl 3-acetyl-2-methylindole- $\omega$ -carboxylate, m. p. 95°, obtained by the interaction of ethylmalonyl chloride and magnesylmethylketole, yields no silver derivative by replacement of the iminic hydrogen, shows feebly basic properties, dissolves slowly in concentrated hydrochloric acid, and gives crystalline precipitates with auric and platonic chlorides; it may, therefore, be capable of assuming a pseudo-enolic or quaternary basic form. The free acid has been described by Mingoia (A., 1929, 579). The action of dilute alkali on the ester gives 3-acetyl-2-methylindole, obtained also by careful heating of the acid. Treatment of the ester with phenylhydrazine gives the phenylhydrazone, which then loses a molecule of alcohol to form 2-methylindolylphenylpyrazolone,  $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{C} \langle \text{CH}_2 \cdot \text{CO} \rangle \text{N} \cdot \text{NMe}$ ,

m. p. 258°, which gives the characteristic reactions of the pyrazolones and various colorations with concentrated acids. With semicarbazide the ester reacts with difficulty, giving the semicarbazone, m. p. 199°, which does not yield the corresponding pyrazolone derivative, but with nitrous acid gives a compound, m. p. 233°, not analysed. By ammonia and absolute alcohol in a sealed tube, ethyl 3-acetyl-2-methylindole- $\omega$ -carboxylate is converted into 2-methylketoyl-3-acetamide,  $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 197°.

T. H. POPE.

**Formation of heterocyclic compounds from ethyl carbethoxythiocarbamate.** P. C. GUHA and S. R. A. SALETORÉ (J. Indian Inst. Sci., 1930, 13A, 11-20).—See A., 1929, 1317.

**Tetrazole derivatives.** R. STOLLÉ and F. HENKE-STARK (J. pr. Chem., 1930, [ii], 124, 261-300).—The decomposition of phenylthiocarbamyl azide by alkalis to give 1-phenyl-5-thioitetrazole (cf. Freund and Hempel, A., 1895, i, 193; Oliveri-Mandalà, A., 1914, i, 1144) is accompanied by a secondary decomposition into phenylthiocarbimide and sodium azide, and also, when alcoholic sodium ethoxide is employed, phenylthiocarbamate and small amounts of phenylcyanamide. The addition of sodium azide depresses the formation of phenylthiocarbimide, and this reversal of the reaction can be applied to give a convenient method of preparation of phenylthiocarbamyl azide by treating phenylthiocarbimide in alcoholic solution with excess of sodium azide in a current of carbon dioxide. The action of excess of sodium azide on phenylthiocarbimide in alcoholic solution at low temperature yields phenylcyanamide.

1-Phenyl-5-methylthioitetrazole (Freund and Hempel, *loc. cit.*) is obtained by the action of diazomethane on 1-phenyl-5-thioitetrazole (I). It is oxidised by acid permanganate to 5-(1-phenyltetrazolyl)methylsulphone, m. p. 84°, which is converted by prolonged heating with 10% sodium hydroxide into 1-phenyl-5-hydroxytetrazole. 1-Phenyl-5-benzylthioitetrazole, m. p. 71°, is obtained from benzyl chloride and the sodium salt of I.

1-Methyl-5-thioitetrazole (II), m. p. 126°, is prepared by the interaction of sodium azide and methylthiocarbimide in a stream of carbon dioxide. It is oxidised by dilute nitric acid to 1-methyltetrazole (additive compound with silver nitrate, decomp. 107°), thus resembling 5-thioitetrazole and differing from I, which yields the disulphide. 1-Methyltetrazole is formed by the action of diazomethane on tetrazole. Oxidation of II by boiling with aqueous ferric chloride gives a small yield of 5 : 5'-di-(1-methyltetrazolyl)sulphide, m. p. 184° (decomp. on further heating). Oxidation of II with dilute hydrogen peroxide yields 5 : 5'-di-(1-methyltetrazolyl) disulphide, m. p. 113° (decomp. 170-230°), which is decomposed by dilute sodium hydroxide solution in the cold to give II and the 5-sulphinic acid, which is decomposed by acids. Oxidation of II by concentrated hydrogen peroxide yields 1-methyltetrazole. In these two reactions the methyl resembles the phenyl derivative. Decomposition of 5 : 5'-di-(1-phenyltetrazolyl) disulphide by aqueous alkali yields analogously I, a little 1-phenyltetrazole, and a compound, m. p. 134°, whilst boiling with sodium methoxide solution yields the thiol and the additive compound of triphenylmelamine and phenylcyanamide. Oxidation of II by permanganate yields, analogously to the phenyl derivative, 1-methyltetrazole-5-sulphonic acid, decomp. with darkening at 321° (silver salt), which is decomposed by warm potassium hydroxide solution to give 5-hydroxy-1-methyltetrazole, m. p. 122°, which is neutralised by alkali as a monobasic acid and yields a monosilver salt. 1-Phenyltetrazole-5-sulphonic acid, which is also obtained by oxidation of the 5 : 5'-disulphide by

permanganate, and is conveniently prepared directly from the 5-thiol by oxidation with permanganate, is analogously decomposed by alkali to give 5-hydroxy-1-phenyltetrazole (*acetyl* derivative, m. p. 103°), which yields with bromine in aqueous hydrobromic acid 5-hydroxy-1-*p*-bromophenyltetrazole, m. p. 216° (decomp.).

1-Phenyltetrazole (Freund and Paradies, A., 1901, i, 770) is conveniently prepared by treating 1-phenyl-5-thioltetrazole in solution in dilute ammonia with concentrated hydrogen peroxide. It yields additive compounds with silver nitrate, decomp. 126°, and with mercuric chloride, m. p. 147°. It yields with acetic anhydride *N*-acetyl-*N'*-phenylcarbamide, by way of phenylcyanamide, which also yields the same product. It gives a compound with magnesium methyl iodide. It reacts with mercuric acetate to give 5-acetatomercuri-1-phenyltetrazole, decomp. 140°, which is converted by hot concentrated sulphuric acid into 1-phenyltetrazole, and by chlorine or bromine into the 5-chloro- or 5-bromo-derivative; 5-iodo-1-phenyltetrazole, decomp. with darkening at 140°, is obtained by the action of iodine in potassium iodide solution. The action of benzoyl chloride in benzene on the acetatomercuri-compound yields *N*-benzoyl-*N'*-phenylcarbamide, derived from benzoylphenylcarbodi-imide by the action of water; in a carefully dried solution the product is benzanilide. 1-Phenyltetrazole is decomposed by boiling with 10% sodium hydroxide solution to give phenylcyanamide, and 1-*p*-nitrophenyltetrazole similarly yields *p*-nitrophenylcyanamide.

The interaction of sodium azide and phenylthiocarbimide in a current of carbon dioxide yields no 5-thiol-1-benzoyltetrazole, but only benzoylcyanamide. Azoimide and phenylthiocarbimide explode when warmed in benzene solution. Benzoylcyanamide does not react with sodium azide and carbon dioxide, but it reacts when heated under pressure with azoimide in benzene solution to give 5-benzamidotetrazole. Similarly phenylmethylcyanamide yields 5-(phenylmethylamino)tetrazole, m. p. 139°, phenylethylcyanamide yields 5-(phenylethylamino)tetrazole, m. p. 170°, and phenylbenzylcyanamide yields 5-(phenylbenzylamino)tetrazole, m. p. 144°. Under the same conditions, however, phenylcyanamide and benzoylphenylcyanamide both yield 5-amino-1-phenyltetrazole. In the latter case the benzoyl group appears to be removed before condensation takes place; phenylcarbimide and phenylcarbamiyl azide are obtained as by-products. Phenylcarbamiyl azide is obtained when benzazide is heated with azoimide in benzene. *N*-Benzoyl-*N'*-phenylthiocarbimide in alcoholic solution reacts with sodium azide and lead dioxide in a current of carbon dioxide to give 5-anilinetetrazole, m. p. 206° (decomp.), and 5-benzamido-1-phenyltetrazole, m. p. 157° (after sintering), identical with the product of benzoylation of 5-amino-1-phenyltetrazole in pyridine. 5-Benzamido-2-phenyltetrazole, m. p. 164°, is prepared from the corresponding amine. The reaction of *N*-benzoyl-*N'*-phenylthiocarbimide appears to take place with the intermediate formation of benzoylphenylcarbodi-imide, which then adds on azoimide in two ways. 5-Benzamido-1-phenyltetrazole may be titrated with alkali hydroxide, evidently forming a compound with the metal attached to the 4-position.

The 2-phenyl-compound is soluble in excess of alkali. The reactions with silver nitrate and mercuric chloride solutions of most of the compounds prepared are described.

R. K. CALLOW.

**Action of diazo-compounds on tetrazolyl disulphides.** R. STOLLÉ and H. PERREY (Ber., 1930, 63, [B], 670—677).—Methylenedi-1-phenyl-4 : 5-dihydro-5-tetrazolyl disulphide (Stollé and others, A., 1929, 828) in acetic acid is reduced by zinc dust and hydrochloric acid to a mixture of 5-thiol-1-phenyltetrazole, m. p. 151°, and 4-thio-1-phenyl-4-methyl-4 : 5-dihydro-5-tetrazole, m. p. 49° (additive compound, C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>S<sub>2</sub>HgCl<sub>2</sub>, m. p. 145°, decomp. about 220°). The methylene compound is converted by boiling methanol into polythioformaldehyde, 1-phenyl-5-tetrazolyl methyl sulphide, m. p. 84°, 5-hydroxy-1-phenyltetrazole, m. p. 186°, and 5-thiol-1-phenyltetrazole, m. p. 151°. Bromine water appears to transform methylenedi-1-phenyl-4 : 5-dihydro-5-tetrazolyl disulphide into the compound I (R=Ph), m. p. 134°. Methylenedi-1-*p*-tolyl-4 : 5-dihydro-5-tetrazolyl disulphide (*loc. cit.*) is reduced to 5-thiol-1-*p*-tolyltetrazole, m. p. 156°, and 5-thio-1-*p*-tolyl-4-methyl-4 : 5-dihydro-5-tetrazole, m. p. 111°, converted by bromine water into 5-keto-1-*p*-tolyl-4-methyl-4 : 5-dihydro-5-tetrazole, m. p. 70°; 5-thiol-1-*p*-tolyltetrazole is conveniently prepared from sodium azide and *p*-tolylthiocarbimide. Compounds, m. p. 125° and 172°, respectively, constituted according to I (R=*o*- or *p*-MeC<sub>6</sub>H<sub>4</sub>), are obtained by the action of bromine water on methylenedi-1-(*o*- or *p*-)tolyl-4 : 5-dihydro-5-tetrazolyl disulphides.

The action of iodine on the silver salt of 5-thiol-1-*o*-tolyltetrazole leads to the formation of di-1-*o*-tolyl-5-tetrazolyl disulphide, m. p. 102°. Di-1-*m*-xylyl-5-tetrazolyl disulphide, from 5-thiol-1-*m*-xylyltetrazole and dilute nitric acid, has m. p. 114°. The action of 40% formaldehyde on 5-thiol-1-phenyltetrazole leads to the formation of 1-phenyl-5-tetrazolyl hydroxymethyl sulphide, m. p. 99°, which with hydrogen chloride in chloroform gives the non-crystalline chloromethyl compound, transformed by ethyl alcohol into 1-phenyl-5-tetrazolyl ethoxymethyl sulphide, m. p. 56°.

H. WREN.

**Chlorophylls. X. Behaviour of chlorophyll derivatives with hydrogen iodide and acetic acid and with sulphuric acid.** H. FISCHER, A. MERKA, and E. PLÖTZ (Annalen, 1930, 478, 283—302).—A systematic investigation has been made of the action of hydrogen iodide and acetic acid on certain hæmin and chlorophyll derivatives, and a micro-method of separating the products from 0.5 g. of starting material has been applied. The reaction is carried out at 100°, or at 130° in certain cases. It is found that cryptopyrrole is hydrogenated at 200°, cryptopyrrolecarboxylic acid is destroyed at 160°, but largely unchanged at 130°, whilst opsopyrrolecarboxylic acid is largely destroyed at 130°. The degradation products identified include opsopyrrole (a), hæmopyrrole (b), cryptopyrrole (c), and the derived carboxylic acids, (d), (e), and (f), respectively. At 100° hæmin yields (a), (b), (c), (d), and (e); meso-

hæmin ester yields (a), (b), (c), (d), (e), and (f); phylloporphyrin yields (b), (c), (d), and (e); phæophorbide *a* yields (a), (b), (d), (e), phyllopyrrole (?), and a compound (? *bis*trimethylpyrrole) isolated as the *picrate*, m. p. 149°; chlorin *e* yields (b), (c), (d), and (e); methylchlorophyllide yields (b), (c), and (e); mesorhodin yields (b) and (e). At 130° rhodoporphyrin yields (b), (c), (d), and (e); phæophorbide *b* yields (b) and (e); rhodin *g* yields (b) and (c); allomerised phæophorbide *a* yields (a), (b), (d), and (e); allomerised methylchlorophyllide yields (a), (b), and (e); bilirubin yields (c) and (f); pyroporphyrin yields (b), (d), and (e). In the comparison and discussion of results the chief points of interest are the following. Low yields are obtained with chlorophyll derivatives, and much tar is formed. Incomplete reduction does not account for this, for the yields are not increased at 130°. The presence of, or the possibility of the formation of, free methine groups appears to have no effect on the course of the reaction. Comparison of chlorophyll *a* and *b* is afforded by the cases of phæophorbide *b* and rhodin *g* and of phæophorbide *a* and chlorin *e*. The yield of hæmopyrrole and hæmopyrrolecarboxylic acid is much reduced in the first two cases, and much tar is formed. The gases evolved have been examined. No hydrocarbons can be detected. It appears from these results and results with simpler pyrrole derivatives that nuclear carboxyl or carbethoxyl groups are lost with the evolution of carbon dioxide, but glyoxylic acid groups are unaffected. Phylloerythrin gives no carbon dioxide, in harmony with the assumption of the presence of a pyridone ring.

Decomposition by heating with 85% sulphuric acid has been applied to a number of compounds. In this case carbon dioxide and carbon monoxide are evolved from derivatives of chlorophyll in which the presence of a glyoxylic acid residue may be assumed, but hæmin, mesohæmin, and bilirubin also behave in the same way. That a methene bridge can give rise to carbon dioxide and monoxide is demonstrated by the decomposition of the methene from cryptopyrrolealdehyde and cryptopyrrolecarboxylic acid. Treatment of hæmin with 85% sulphuric acid yields a compound,  $C_{34}H_{36}O_{10}N_4S$ . R. K. CALLOW.

**Porphyrin syntheses. XXVII. Synthesis of a porphintripropionic acid, its chlorin and rhodin; coprorhodin and ætiochlorin.** H. FISCHER, K. PLATZ, H. HELBERGER, and H. NIEMER (Annalen, 1930, 479, 26–42).—The methene from cryptopyrrolealdehyde and cryptopyrrolecarboxylic acid is brominated in acetic acid solution to (3-methyl-5-bromo-methyl-4-β-carboxyethylpyrrol)-(3-methyl-4-ethyl-5-bromomethylpyrrolenyl)methene hydrobromide, darkens at 180°, not melted at 275°. This is condensed with bis-(5-bromo-4-methyl-3-β-carboxyethylpyrrol)methene hydrobromide in presence of hydrobromic and acetic acids, or by the usual fusion method, forming “porphintripropionic acid” (1:4:6:7-tetramethyl-8-ethylporphin-2:3:5-tripropionic acid) {dihydrochloride; copper salt; ethyl ester, m. p. 167°; methyl ester, m. p. 175° [(corr.); iron salt (hæmin),  $C_{38}H_{42}O_8N_4ClFe$ , m. p. 233° (corr.); copper salt, m. p. 214° (corr.)}. This acid is stable towards alkoxide, but treatment with fuming sulphuric acid gives

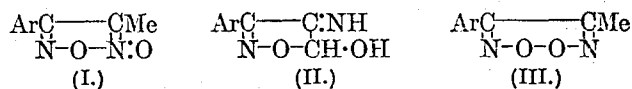
rhodindicarboxylic acid,  $C_{35}H_{36}O_8N_4$  (methyl ester, m. p. 222°; acetyl derivative, not melted at 280°). Treatment of the complex iron salt of the above tri-carboxylic acid with sodium and amyl alcohol, subsequent removal of iron, and oxidation (atmospheric) of the intermediate perhydro-derivative gives chlorin-tricarboxylic acid,  $C_{35}H_{40}O_8N_4$ , not melted at 285° [methyl ester, m. p. 166° (corr.) (copper salt)]. Treatment of this acid with concentrated methyl-alcoholic potassium hydroxide in presence of a stream of air furnishes the above porphintripropionic acid.

When coproporphyrin I methyl ester is treated with fuming sulphuric acid at 40° for a short time, coprorhodin I,  $C_{36}H_{36}O_7N_4$  (trimethyl ester, m. p. 227°), is obtained; when heated at 60–70° for some time, the rhodin decomposes.

Treatment of ætiohæmin with sodium and methyl alcohol yields methoxyætiohæmin,  $C_{33}H_{39}ON_4Fe$ ; with sodium and alcohol at 165°, ethoxyætiohæmin is produced. Removal of iron from the last-named compound by treatment with 18% hydrochloric acid furnishes a small amount of ætiochlorin,  $C_{32}H_{40}N_4$  (copper salt), which contains no active hydrogen (Zerevitinov). Similar treatment of the former hæmin regenerates ætiohæmin.

Spectrochemical data for most of the compounds are recorded. H. BURTON.

**Dioximes. LXII.** G. PONZIO and G. CARTA-SATTA (Gazzetta, 1930, 60, 150–158).—The present work together with previous papers (A., 1928, 888; 1929, 334, 1072; this vol., 226) enables the following generalisations to be made: (a) the β-forms of aryl-methylglyoximes,  $ArC:(N\cdot OH)\cdot CMe\cdot N\cdot OH$ , furnish two isomeric dioxime peroxides by dehydrogenation, whilst the α-forms yield only a single dioxime peroxide; (b) the isomeric peroxides come into equilibrium when heated; (c) of the two glyoxime peroxides, that considered to be an oxadiazole *N*-oxide (I) has the higher m. p., and is reduced by phosphorus pentachloride to the corresponding arylmethylfurazan, and isomerised by alcoholic sodium ethoxide to the γ-aryl-β-imino-α-hydroxyisooxazoline (II); (d) the peroxide considered to be a dioxdiazine (III) has the lower m. p., and is stable to phosphorus pentachloride and to alcoholic sodium ethoxide.



3:4-Methylenedioxyphenylmethyloxadiazole *N*-oxide, m. p. 124.5° (cf. Angeli, A., 1893, i, 196, 261), when dissolved in boiling acetic anhydride, propionic anhydride, aniline, or chloroacetic acid is converted (35%) into 4-(3':4'-methylenedioxyphenyl)-5-methyl-1:2:3:6-dioxdiazine (IV), m. p. 116°, which is reconverted (60%) into the oxadiazole-*N*-oxide under the same conditions; the reaction velocity increases with rising b. p. of the solvent. The oxadiazole *N*-oxide, m. p. 124.5°, reacts with phosphorus pentachloride at 125°, undergoing reduction to 3:4-methylenedioxyphenylmethylyfurazan, m. p. 84° (cf. *loc. cit.*), and with bromine in glacial acetic acid at 100°, giving 3:4-methylenedioxy-2(?)-bromophenylmethyloxadiazole *N*-oxide, (V), m. p. 112° (cf. *loc. cit.*), isomerised

incompletely at 140–150° to 4-(3': 4'-methylenedioxy-2'(?)-bromophenyl)-5-methyl-1:2:3:6-dioxdiazine, m. p. 112°, also obtained from (IV) by bromination in glacial acetic acid. Brief treatment with alcoholic sodium ethoxide converts the oxadiazole *N*-oxide into the isomeric 4-imino-5-hydroxy-3-(3': 4'-methylenedioxyphenyl)isooxazoline (VI), m. p. 185° (decomp.) (cf. *loc. cit.*); similar treatment of (V) affords 4-imino-5-hydroxy-3-(3': 4'-methylenedioxy-2'(?)-bromophenyl)isooxazoline. By reduction with zinc and acetic acid, the oxadiazole *N*-oxide yields the  $\alpha$ -form of 3:4-methylenedioxyphenylmethylglyoxime, m. p. 163° (cf. *loc. cit.*), oxidised by 10% sodium hypochlorite in 10% sodium hydroxide to the same oxadiazole *N*-oxide exclusively, and affording in aqueous-alcoholic solution at 100° with nickel acetate and acetic acid a red nickel complex decomposed by hydrochloric acid in the presence of ether to give the  $\beta$ -form of 3:4-methylenedioxyphenylmethylglyoxime, m. p. 207–209° (decomp.) (cf. *loc. cit.*), which is oxidised by 10% sodium hypochlorite in 10% sodium hydroxide to furnish, in quantitative yield, a mixture of the oxadiazole *N*-oxide, m. p. 124.5°, and its isomeric dioxdiazine (IV).

The isooxazoline (VI) by treatment with ethereal hydrochloric acid at 0° gives 5-chloro-4-amino-3-(3': 4'-methylenedioxyphenyl)isooxazole, m. p. 105–106° (acetyl derivative, m. p. 181°; benzoyl derivative, m. p. 167), converted by hydrazine hydrate at 100° into 4-amino-5-hydroxy-3-(3': 4'-methylenedioxyphenyl)isooxazole, m. p. 146° (decomp.), which is slowly isomerised to its precursor (VI) in 10% sodium hydroxide, and is readily transformed by hydrochloric acid into the above chloroisooxazole.

3:4-Dimethoxyallylbenzene, b. p. 245–249°, obtained by methylating eugenol with methyl sulphate and 10% sodium hydroxide, is converted by boiling alcoholic potassium hydroxide into 3:4-dimethoxypropenylbenzene, which by treatment with sodium nitrite and glacial acetic acid yields 3:4-dimethoxyphenylmethyloxadiazole *N*-oxide, m. p. 118° after purification with stannous chloride and hydrochloric acid (cf. Malagnini, A., 1895, i, 35). The last-named compound is reduced by phosphorus pentachloride at 120° to 3:4-dimethoxyphenylmethylfuran, m. p. 74° (cf. *loc. cit.*), and is isomerised in boiling propionic acid to 4-(3': 4'-dimethoxyphenyl)-5-methyl-1:2:3:6-dioxdiazine, m. p. 95°, which is unaffected by phosphorus pentachloride or boiling alcoholic sodium ethoxide and reacts with bromine in glacial acetic acid to give 4-(3': 4'-dimethoxy-2'(?)-bromophenyl)-5-methyl-1:2:3:6-dioxdiazine, m. p. 109°, also unaffected by hot alcoholic sodium ethoxide. The isomeric 3:4-dimethoxy-2'(?)-bromophenylmethyl-oxadiazole *N*-oxide, m. p. 135° (cf. *loc. cit.*), is converted by sodium ethoxide into 2-imino-1-hydroxy-3-(3': 4'-dimethoxy-2'(?)-bromophenyl)isooxazoline. The dimethoxyoxadiazole *N*-oxide, m. p. 118°, by the action of sodium ethoxide affords 4-imino-5-hydroxy-3-(3': 4'-dimethoxyphenyl)isooxazoline (VII), m. p. 171° (decomp.), converted by ethereal hydrochloric acid into 5-chloro-4-amino-3-(3': 4'-dimethoxyphenyl)isooxazole, m. p. 130° (decomp.) [acetyl derivative, m. p. 160° (decomp.); benzoyl derivative, m. p. 163°], which by treatment with hydrazine hydrate yields

4-amino-5-hydroxy-3-(3': 4'-dimethoxyphenyl)isooxazole, m. p. 107° (decomp.), slowly reconverted by 10% sodium hydroxide into its precursor (VII) and giving the above chloroisooxazole with ethereal hydrochloric acid.

C. W. SHOPPEE.

**Action of nitric acid on acetylene. II.** A. QUILICO and M. FRERI (Gazzetta, 1930, 60, 172–184; cf. this vol., 449).—Slow passage of acetylene containing acetone vapour through nitric acid (*d* 1.52) for 3–4 days gives, in addition to compounds previously described, 4:5'-diisooxazolyl ketone,  $\text{CH}\cdot\text{CH} \begin{array}{c} \diagup \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{CH} \cdot \text{O} \\ \diagdown \text{N} \rightarrow \text{O} \quad \diagup \text{CH} \cdot \text{N} \end{array}$  (I), m. p. 76°, b. p. 150°/15–20 mm. (phenylhydrazone, m. p. 72°; *p*-nitrophenylhydrazone, m. p. 215°; *p*-bromophenylhydrazone, m. p. 160°; dioxime, m. p. 111°). By oxidation with powdered potassium permanganate at 0° in either acid or alkaline suspension, the ketone (I) yields carbon dioxide, hydrocyanic acid, and isooxazole-5-carboxylic acid, m. p. 149° (silver salt; amide, m. p. 145–146°). The ketone (I) is stable to strong mineral acids, but undergoes fission in the presence of 10% aqueous or 15% methyl-alcoholic potassium hydroxide to give isooxazole-5-carboxylic acid in almost theoretical yield, and cyanoacetaldehyde, isolated and identified as benzeneazocycanoacetaldehyde, m. p. 168° (cf. lit.), and as the *p*-nitrophenylhydrazone, m. p. 153–154°. The mode of formation of the ketone and the mechanism of the production of above degradation compounds are discussed.

C. W. SHOPPEE.

**Derivative of a condensed, dicyclic system from a pyran and piperidine ring.** C. MANNICH and M. W. MÜCK (Ber., 1930, 63, [B], 604–608).—Ethyl 2:6-dimethyltetrahydro-4-pyrone-3:5-dicarboxylate is converted by formaldehyde and methylamine into a compound I (*R*=Me) which, by reason of the presence of a pyran and piperidine ring, is designated ethyl 9-keto-3:6:8-trimethylpydin-1:5-dicarboxylate, m. p. 86° (monohydrated hydrochloride, m. p. 155–156°; methiodide, m. p. 175–176°). The presence of the ketonic group cannot be detected by the customary reagents and a reduction to the corresponding alcohol has not been effected. The base is remarkably stable towards acids, but decomposed in a complicated manner by alkali hydroxide, giving acetone and  $\alpha$ -methylaminomethylcrotonic acid [hydrobromide, m. p. 212–213° (decomp.); benzoyl derivative, m. p. 148–149°].

In individual experiments, ethyl 2:6-diphenyltetrahydro-4-pyrone-3:5-dicarboxylate, formaldehyde, and methylamine give ethyl 9-keto-6:8-diphenyl-3-methylpydin-1:5-dicarboxylate as the  $\alpha$ -form, m. p. 193° (hydrochloride, m. p. 216° when rapidly heated), or the  $\beta$ -variety, m. p. 133–134° [hydrochloride, m. p. 196° (decomp.)]. The stereoisomeride of high m. p. can be transformed into that of low m. p. through the hydrochloride, but the reverse conversion cannot be effected. The bases are decomposed by warm water at different rates with production of benzaldehyde.

Ethyl 2:6-dimethyltetrahydro-4-pyrone-3:5-di-

carboxylate, piperidine, and formaldehyde yield the unstable base  $\text{CHMe} \cdot \text{O} \cdot \text{CHMe} \cdot \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{NC}_5\text{H}_{11} \\ \text{CH}(\text{CO}_2\text{Et}) - \text{CO} \end{smallmatrix}$ , isolated as the sodium salt of the enolic form, m. p. 212–213° (decomp.) [corresponding *picrate*, m. p. 133°, and *chloroplatinate*, decomp. 161–162°]. The sodium salt of the enolic form of ethyl 4-keto-2:6-dimethyl-3-diethylaminomethylpyran-3:5-dicarboxylate is analogously obtained. H. WREN.

**Condensation of aldehydes and ketones with thiosemicarbazides.** M. BUSCH [with E. WAGNER and W. RENNER] (J. pr. Chem., 1930, [ii], 124, 301–312).—The interaction of  $\alpha\delta$ -diphenylthiosemicarbazide and benzaldehyde in alcoholic hydrochloric acid (Busch and Ridder, A., 1897, i, 381) is now differently interpreted. Instead of the ultimate formation of a thiodiazoloneanil, the reaction is considered to consist in the condensation of the aldehyde with the enolic form of the semicarbazide to give a thiazdimethylene derivative,  $\text{NPh} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{NPh} \\ \text{S} \end{smallmatrix} \text{CPh}$  (I), which then by isomerisation and elimination of hydrogen yields 2-benzeneazo-3:4-diphenylthiazmethine,

$\text{NPh} \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{NPh} \\ \text{S} \end{smallmatrix} \text{CPh}$  (II). The hydrochloride of I is

precipitated as a colourless oil by the addition of ether in the first phase of the reaction, and the salt of the base yields benzaldehyde when warmed with dilute sulphuric acid. If the reaction mixture is kept, oxidation takes place to the yellow hydrochloride of II, which is decomposable only by 40% sulphuric acid, or hydrochloric acid at 130°. The compounds from *m*-nitrobenzaldehyde and cinnamaldehyde previously described are also now formulated as thiazdimethine derivatives, but the colourless product from acetaldehyde and  $\alpha\delta$ -diphenylsemicarbazide appears to be 2-keto-3-phenyl-4-methylthiazdimethylenephénylhydrazone, curiously stable to oxidation. II is transformed slowly into triphenylendothiotriazole (Busch, Kamphausen, and Schneider, A., 1903, i, 530; Busch and Holzmann, A., 1901, i, 234).

The formation of stable colourless products from alkyl thiosemicarbazides and aldehydes or ketones can take place either, as from  $\alpha\delta$ -trialkylthiosemicarbazides, with the formation of a thiodiazole, or of thiazdimethylene derivatives in which isomerisation and oxidation to a thiazmethine is prevented by the replacement of one of the mobile hydrogen atoms. Thus  $\alpha\delta$ -diphenyl- $\delta$ -methylthiosemicarbazide and benzaldehyde yield 2-phenylmethylamino-4:5-diphenyl-4:5-dihydrothiodiazole, m. p. 123°;  $\alpha\delta$ -diphenylthiosemicarbazide and acetone yield 2-keto-3-phenyl-4:4-dimethylthiazdimethylenephénylhydrazone hydrochloride, m. p. 155°;  $\alpha\delta$ -diphenyl- $\alpha$ -methylthiosemicarbazide and benzaldehyde yield 2-keto-3:4-diphenylthiazdimethylenephénylmethylhydrazone hydrochloride, m. p. 185–186°, yellow (also obtainable from benzylidenethiosemicarbazide), which yields with ammonia a colourless desmotropic form of the base, m. p. about 90°.  $\delta$ -Phenylthiosemicarbazide and benzaldehyde (2 mols.) yield 2-keto-3:4-diphenylthiazdimethylenephénylhydrazone hydrochloride, m. p. 145–150° (base, yellow). R. K. CALLOW.

**Synthesis of pilopinic acid and structure of pilocarpine.** A. E. TSCHITSCHIBABIN and N. A. PREOBRASHENSKI.—See this vol., 452.

**Microchemical reactions for pilocarpine.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 285–287).—A résumé of the literature is given. The most sensitive reaction, that with gold chloride, will indicate 1 mg. at a dilution of 1:2000. S. I. LEVY.

**Nature of the reaction of eserine [physostigmine] obtained with an acetic acid solution of benzidine and hydrogen peroxide and its application to the colorimetric determination of eserine.** M. MOKRAGNATZ (Bull. Soc. Chim. biol., 1930, 12, 34–43).—By replacing acetic acid with acetic anhydride in the author's test for eserine an almost colourless reagent is obtained giving the same violet colour, which may then be used for the colorimetric determination of eserine (cf. A., 1928, 1264).

P. W. CLUTTERBUCK.

**Reactions of atropine and some related compounds.** L. EKKERT (Pharm. Zentr., 1930, 71, 180–181).—Colour reactions on warming with sulphuric acid and *p*-dimethylaminobenzaldehyde, cooling, and diluting are described. S. I. LEVY.

**Alkaloid amine oxides and their transformations.** M. POLONOVSKI (Bull. Soc. chim. Belg., 1930, 39, 1–39).—A lecture in which the methods of formation, properties, and molecular transformations of amine oxides ("genalkaloids") are dealt with on the basis of the author's theory of structure with special reference to the stereochemical relationships of scopalamine and scopinium derivatives to  $\psi$ -scopine derivatives. J. W. BAKER.

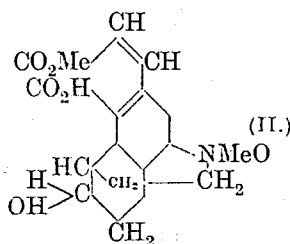
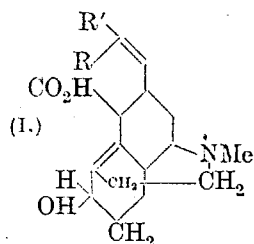
**Microchemical reactions of cocaine.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 229–232).—A résumé of the tests given in the literature. The most sensitive reagents are gold and platinum chlorides, each of which will detect 2 mg. at a dilution of 1:1000. S. I. LEVY.

**Harmine.** H. KREITMAIR (Mercks Jahresber., 1929, 42, 5–19; Chem. Zentr., 1929, ii, 2465).—The identity of banisterine and harmine is shown by pharmacological tests. The pharmacological properties of harmaline are recorded. A. A. ELDRIDGE.

**Harmine.** O. WOLFES and O. IVERS (Mercks Jahresber., 1929, 42, 5–19; Chem. Zentr., 1929, ii, 2465).—*N*-Benzyltetrahydroharmine,  $\text{C}_{20}\text{H}_{22}\text{O}_2\text{N}$ , from tetrahydroharmine and benzyl chloride in boiling methyl alcohol, has m. p. 109–110° (hydrochloride, m. p. 236°). A. A. ELDRIDGE.

**Action of ozone on hydrogenated and non-hydrogenated bases of the morphine group.** E. SPEYER and L. F. ROELL (Ber., 1930, 63, [B], 539–551).—Treatment of  $\alpha$ -ozodihydrocodeine hydrochloride with methyl-alcoholic sodium methoxide at 5° followed by hydrogen chloride affords the non-crystalline  $\beta$ -ozodihydrocodeine (hydriodide, decomp. 220°,  $[\alpha]_D^{20} +52.5$  in water); if reaction is effected at 50°, non-crystalline  $\gamma$ -ozodihydrocodeine [hydriodide, m. p. 219–220° (decomp.) after softening at 215°,  $[\alpha]_D^{20} +17.6$  in water] results. During the reaction, the carbomethoxy-group of  $\alpha$ -ozodihydrocodeine becomes hydrolysed and the carboxyl group is

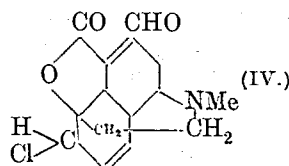
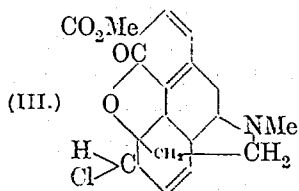
subsequently esterified. The compounds described previously (A., 1929, 336) as  $\beta$ - and  $\gamma$ -ozodihydrocodeine are therefore  $\beta$ - and  $\gamma$ -*ozoethylidihydromorphine* I ( $R' = CO_2Et$  or  $H$ ,  $R = H$  or  $CO_2Et$ ). Ozonisation of  $\beta$ -*ozoethylidihydromorphine* in dilute acetic acid and addition of phenylhydrazine to the resulting mixture yields ethyl glyoxylate phenylhydrazone, m. p.  $130^\circ$ , and  $\beta$ -*dihydrocodinalphenylhydrazone* (monohydrated acetate, m. p.  $205$ – $206^\circ$ );  $\beta$ -*dihydrocodinaloxime dihydrate*, decomp.  $267$ – $287^\circ$ , according to the rate of heating (*hydrochloride*, decomp.  $266^\circ$ ), and the corresponding *semicarbazone*, decomp.  $247^\circ$ , are described. Since identical products are derived from  $\gamma$ -ozodihydromorphine, the  $\beta$ - and  $\gamma$ -compounds are regarded as *cis-trans*-isomerides.



Methyl 5-deoxydihydromorphinate is transformed by ozone in presence of dilute acetic acid into the corresponding *N-oxide*, decomp.  $183^\circ$ ,  $[\alpha]_D^{25} +19.7^\circ$  in water (*hydrochloride*, decomp.  $195$ – $199^\circ$ ; *picrate*, decomp.  $196^\circ$ ), also prepared by the action of hydrogen peroxide on the ester, into which it is readily re-converted by catalytic hydrogenation or by sulphurous acid.

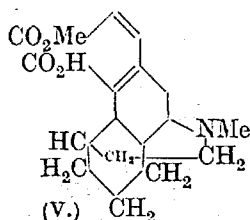
Dihydrocodeinone is transformed by ozone into 6-ketodihydrocodinol, isolated as the *disemicarbazone*,  $C_{17}H_{23}O_4N_7$ , decomp.  $280^\circ$ .

In agreement with Wieland and Small (A., 1929, 81), ozonisation of  $\alpha$ -chlorocodide yields a compound,  $C_{18}H_{23}O_4NCl$  (Wieland's chlorocodizone), which is devoid of aldehyde properties. On the assumption that ozonolysis follows a normal course the compound is re-named *ozo- $\alpha$ -chlorocodide* (m. p.  $104$ – $105^\circ$ ,  $[\alpha]_D^{25} -231^\circ$  in alcohol), and to it the structure III is



assigned; the hydrochloride, decomp.  $213^\circ$ , *hydrobromide*, decomp.  $201^\circ$ , *hydriodide*, decomp.  $174^\circ$  after softening at  $160^\circ$ , and *picrate*, m. p.  $171^\circ$ , are described.

Ozonisation of *ozo- $\alpha$ -chlorocodide* affords  $\alpha$ -*chlorocodinal* (IV) isolated as the amorphous *phenylhydrazone*,  $C_{21}H_{22}O_2N_3Cl$ . *Ozo- $\alpha$ -chlorocodide* is readily hydrolysed by 15% sulphuric acid to  $\alpha$ -*chloromorphinic acid*,  $C_{17}H_{20}O_5NCl \cdot H_2O$ , decomp.  $192^\circ$ , and is converted by hydrogen in presence of palladised charcoal into *methyl 6-deoxydihydromorphinate*



(V), isolated as the *picrate*, m. p. about  $200$ – $205^\circ$  after softening at  $170^\circ$ , decomp.  $221^\circ$ . Similarly,  $\beta$ -*chlorocodide* is ozonised to *ozo- $\beta$ -chlorocodide*, isolated as the *picrate*,  $C_{18}H_{20}O_4NCl \cdot C_6H_2(NO_2)_3 \cdot OH$ , decomp.  $217^\circ$ .

Codeine and morphine in presence of 30% formic acid are readily ozonised to codinal, isolated as the *phenylhydrazone*,  $C_{21}H_{23}O_3N_3 \cdot 1.5H_2O$ , decomp.  $215^\circ$ . Ozonolysis appears to follow the course taken in the production of *ozo- $\alpha$ -* and *- $\beta$ -chlorocodide*.

H. WREN.

#### *Strychnos* alkaloids. LIV. Relationship of the three $C_{17}$ series of the degradation of brucine.

H. LEUCHS and A. HOFFMANN (Ber., 1930, 63, [B], 439–448; cf. A., 1929, 1470).—Hydrolysis of the alkaloid,  $C_{17}H_{20}O_3N_2Br_2$ , obtained by oxidation of cactochelin with bromine, yields the substance,  $C_{17}H_{22}O_5N_2$ , oxidised by chromic acid to the acid,  $C_{17}H_{26}O_6N_2$ , identical with the compound obtained directly from brucine by Wieland and Münster (A., 1929, 707), with whose formulation the authors now concur (cf. *ibid.*, 1320). According to its mode of origin, Wieland's acid must contain the reactive C:C linking, two carboxyls, a ketonic group, and an oxygen atom possibly in ethereal union. It is oxidised by bromine to the salt,  $C_{17}H_{20}O_8N_2 \cdot HBr$ , darkening and softening at  $280$ – $310^\circ$  (*disemicarbazone*,  $C_{19}H_{26}O_8N_3 \cdot HBr$ , darkening at  $280^\circ$ , but not molten below  $305^\circ$ ), which is oxidised by mercuric oxide to the acid,  $C_{17}H_{20}O_8N_2$ , identical with the compound derived from Hanssen's acid (A., 1929, 944) to which the formula  $C_{17}H_{18}O_8N_2$  was ascribed; the corresponding dianhydride, (now)  $C_{17}H_{16}O_6N_2$ , darkening above  $240^\circ$ , after softening, *diamide*,  $C_{17}H_{22}O_6N_4$ , darkening at  $255^\circ$  after softening at  $240^\circ$ , and *monoamide hydrochloride*,  $C_{17}H_{21}O_7N_3 \cdot HCl$ , are described.

During the attack of chromic acid on Hanssen's  $C_{19}$  acid and brucine an amido-group is hydrolysed and one of the two C:C linkings is oxidised in such a manner that oxalic acid (transitorily) and a ketone are formed. The other C:C group remains intact and the successive action of bromine and mercuric oxide yields the ketonic acid,  $C_{17}H_{20}O_8N_2$ . In the reduced Hanssen acid, the group C:C is not present and the substance is not attacked by chromic acid. The  $C_{17}$  alkaloid series is genetically related to the Wieland acid, which can arise only by the production of two new carboxyl groups.

The reactive C:C linking is also present in the  $C_{16}$  Hanssen acid which does not contain the ketonic group. The acid  $C_{16}H_{20}O_4N_2$  (cf. Wieland and Münster, *loc. cit.*) is oxidised by bromine in hydrobromic acid to the salt  $C_{16}H_{20}O_6N_2 \cdot 2HBr$ , m. p.  $290$ – $295^\circ$  (decomp.) after darkening at  $230^\circ$ , which affords a *semicarbazone*,  $C_{17}H_{23}O_6N_5 \cdot HBr$ , decomp.  $240^\circ$  after becoming yellow at  $230^\circ$ , and is oxidised by mercuric oxide to the substance  $C_{16}H_{20}O_7N_2$ , isolated as the *hydrobromide*. Similarly, the amino-acid,  $C_{17}H_{22}O_4N_2$ , yields a compound,  $C_{17}H_{22}O_6N_2 \cdot HBr$ , darkening at  $260^\circ$ , but not molten below  $310^\circ$  [*semicarbazone*, m. p.  $260^\circ$  (decomp.) after softening and darkening at  $240^\circ$ ], oxidised by mercuric oxide to the substance,  $C_{17}H_{22}O_7N_2 \cdot HBr$ , decomp. about  $255^\circ$  after softening at  $235^\circ$ .



Although absorption of bromine occurs, similar products could not be isolated from the base  $C_{17}H_{22}O_3N_2$  and from a new alkaloid,  $C_{17}H_{22}O_3N_2$ , m. p. 130°, and 160—165° after partial re-solidification, derived from the alkaloid,  $C_{17}H_{20}O_3N_2Br_2$ , by Clemmensen's method. Unsuccessful attempts to oxidise the last-named compound with chromic acid are described.

H. WREN.

**Strychnine and brucine. IX. Preparation of some isomerides of di- and tri-nitrostrychols.** J. N. ASHLEY, (the late) W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1930, 382—395).—Dinitrostrychol-carboxylic acid is obtained by a modification of the method described by Tafel (A., 1898, i, 706). Dinitrostrychol, m. p. 282° (lit. 284°), is readily converted by warm nitric acid (*d* 1.5) into trinitrostrychol (Tafel, *loc. cit.*). Dinitrostrychol monomethyl ether is hydrolysed by 1% sodium hydroxide solution at 40°; with cold 8% sodium hydroxide solution the ether gives a deep red sodium salt. The disodium salt of dinitrostrychol and alcoholic ethylene dibromide afford a small amount of (probably) the monoethyl ether, m. p. 186—187°, whilst the dipotassium salt and oxalyl chloride in toluene furnish a poor yield of a substance, m. p. 161°, oxidised by boiling nitric acid (*d* 1.42) to a compound, m. p. 278—279° (decomp.). Syntheses of 6:8-dinitro-2:4-, -2:5-, and -2:7-dihydroxyquinolines are described; none of these is identical with dinitrostrychol.

2:4-Dihydroxyquinoline [2(or 4)-*acetyl* derivative, m. p. 214—215°; 2(or 4)-*p-nitrobenzoyl* derivative, m. p. 247° (decomp.)], prepared by a slight modification of Camps' method (A., 1900, i, 310), is converted by Gabriel's method (A., 1919, i, 38) into 3-nitro-2:4-dihydroxyquinoline [*monoacetyl* derivative, m. p. 194° (decomp.)], which on distillation with soda-lime gives a small amount of aniline. Treatment of 2:4-dihydroxyquinoline with potassium nitrate and sulphuric acid below 5°, with subsequent addition of nitric acid to the mixture, gives 3:6-dinitro-2:4-dihydroxyquinoline, m. p. 200° (decomp.) [*sodium salt*], which is stable to 10% sodium hydroxide solution at 145°. The *acetate*, m. p. 190° (decomp.), of this is converted by potassium nitrate and 10% oleum at 85—95° into 3:6:8-trinitro-2:4-dihydroxyquinoline, m. p. 192—193° (decomp.) [*acetyl* derivative, m. p. 158° (decomp.)], which is not identical with trinitrostrychol. This trinitro-derivative is degraded by nitric (*d* 1.5) and acetic acids to picric acid, whilst trinitrostrychol is not. 6:8-Dinitro-2:4-dihydroxyquinoline could not be obtained (attempted ring closure) from *methyl* and *ethyl* 3:5-dinitro-2-acetamidobenzoates, m. p. 172—173° and 174°, respectively. 3:5-Dinitro-2-methoxy- and 2-chloro-3:5-dinitro-benzoyl chlorides, m. p. 37—38° and 62°, respectively, do not condense with ethyl sodioacetoacetate.

6:8-Dinitro-2:5-, m. p. 261° (decomp.) (*acetyl* derivative, m. p. 178°), and 6:8-dinitro-2:7-dihydroxyquinolines, not melted at 310°, are obtained from 5- and 7-aminocarbostyrils, respectively, by diazotisation, decomposition of the diazo-solutions, and subsequent nitration; the intermediate compounds were not isolated. Both dinitro-derivatives are degraded by nitric acid to styphnic acid; the 2:5-

derivative is the more stable. An improved preparation of 7-nitrocarbostyryl from 7-nitroquinoline is given.

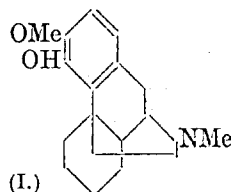
Oxidation of 2-nitro-*p*-tolyl methyl ether with potassium permanganate solution affords 35% of 3-nitroanisic acid, m. p. 195—196° (*ethyl ester*, m. p. 71—72°; acid *chloride*, m. p. 56°). 2-Nitroanisoyl chloride and ethyl sodioacetoacetate in ether yield the corresponding acetoacetate (*potassium salt*), hydrolysed by dilute sulphuric acid to 2-nitro-4-methoxyacetophenone. Condensation of this ketone with ethyl oxalate in presence of sodium ethoxide solution, subsequent dilution with water, and acidification with hydrochloric acid furnishes 2-nitro-4-methoxybenzoylpyruvic acid, m. p. 161°, reduced by ferrous hydroxide to 4-hydroxy-7-methoxyquinoline-2-carboxylic acid (7-methoxykynurenic acid), m. p. 278° (decomp.). This is nitrated by nitric acid (*d* 1.5) at 30° to the 3(or 8)-nitro-derivative, m. p. 250° (decomp.), and further to the 3:6:8-trinitro-derivative, not melted at 310°. Exhaustive nitration of decarboxylated 7-methoxykynurenic acid affords specimens of 3:6:8-trinitro-derivatives differing from trinitrostrychol in their behaviour towards hot aqueous sodium hydroxide; the pale yellow solution of trinitrostrychol in dilute sodium hydroxide solution becomes deep brown when heated. It is considered that strychnine is not 4:7-dihydroxyquinoline.

The Reimer-Tiemann reaction with *m*-nitrophenol gives 3% of 6-nitrosalicylaldehyde, m. p. 54—55°; the *methyl ether*, m. p. 111°, when treated with aqueous sodium hydroxide in acetone solution affords dimethoxyindigotin.

H. BURTON.

**Constitution of dihydrothebaine, dehydroxytetrahydrocodeine, and  $\beta$ -tetrahydrodeoxycodine.** H. KONDO and E. OCHIAI (Ber., 1930, 63, [B], 646—649).—Methylsinomenine is catalytically reduced in presence of palladised charcoal to dihydro-methylsinomenine [*semicarbazone*, m. p. 220° (decomp.); *dihydrated hydrochloride*, m. p. 150° (decomp.)], [ $\alpha$ ]<sub>D</sub><sup>20</sup> +35.05° in water, converted by amalgamated zinc and concentrated hydrochloric acid into deoxytetrahydrosinomenine methyl ether (*hydriodide* and its *monohydrate*, m. p. 104—106°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +20.53° in water; *methiodide*, m. p. 257—258°). The same methyl ether methiodide is obtained by the successive action of methyl sulphate and sodium hydroxide and potassium iodide on deoxytetrahydrosinomenine (cf. A., 1929, 1088). In the last-named compound the hydroxyl group must be attached to the C-4 atom. Since deoxytetrahydrosinomenine is the optical

antipode of dihydrothebaine (Speyer and Siebert, A., 1921, i, 685) it must have the same constitution I, and since dehydroxytetrahydrocodeine (Mannich and Löwenheim, A., 1921, i, 124) and  $\beta$ -tetrahydrodeoxycodine (Freund, A., 1920, i, 757) are identical therewith it is proposed to designate them "dihydrothebaine." H. WREN.



(I.)

**Microchemical reactions of apomorphine.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 321—322).—Suitable reactions for microscopic tests are described.

By addition of one drop of concentrated chloral hydrate solution and a drop of gold chloride solution to the solution of the hydrochloride, a fine reddish-brown precipitate of needle crystals is obtained. The test will detect 1 mg. at a dilution of 1 : 1000.

S. I. LEVY.

**Ultra-violet absorption spectrum of chelidonine.** V. BRUSTIER (Compt. rend., 1930, 190, 499—501).—The ultra-violet absorption spectrum of chelidonine (maximum at  $\lambda$  2280.9) although larger and approximately ten times as intense, is closely similar to that of morphine and diionine; chelidonine is therefore considered to be derived from phenanthrene and not from isoquinoline (cf. A., 1924, i, 1227).

C. W. SHOPPEE.

**Sinomenine and disinomenine. XIV. Bromosinomeninone.** K. GOTO and T. NAMBO (Bull. Chem. Soc. Japan, 1930, 5, 73—77).—When bromosinomenine (Goto and Nakamura, A., 1929, 1469) or its hydrobromide is heated with 2*N*-hydrochloric acid, it is converted into bromosinomeninone, m. p. 227° (decomp.),  $[\alpha]_D^{25} +54.5^\circ$  (in alcohol) (semicarbazone, decomp. 118°; methiodide, m. p. 244—246°), the dioxime, m. p. 189° (decomp.), of which is also obtained by the action of bromine in acetic acid on sinomenine hydrate dioxime. A solution of bromosinomeninone in 1% hydrochloric acid is converted by addition of 7*N*-ammonia solution into bromosinomeninonimine, sinters 233°, not melting at 300°,  $[\alpha]_D^{25} +110.9^\circ$  (in chloroform), which is hydrolysed by warm 10% sodium hydroxide to bromosinomeninone, and gives an oxime, sinters 208°, decomp. 300°, converted by 2*N*-sodium carbonate into the mono- or di-oxime of bromosinomeninone according to the conditions.

J. W. BAKER.

**$\gamma$ -Phenyl- $\alpha$ -methylpropyldimethylarsine,  $\beta$ -benzylbutyldimethylarsine, and some related compounds.** A. BREWIN and E. E. TURNER (J.C.S., 1930, 502—504).—Reduction of ethyl  $\alpha$ -benzylbutyrate (prepared by way of benzylidenemalononic acid, benzylmalonic acid, its ethyl ester, ethyl benzylethylmalonate, and  $\alpha$ -benzylbutyric acid) with sodium and alcohol affords a 73% yield of  $\beta$ -benzylbutyl alcohol (corresponding bromide, b. p. 135°/20 mm.). Magnesium  $\beta$ -benzylbutyl bromide and iododimethylarsine in ether-benzene solution furnish  $\beta$ -benzylbutyldimethylarsine, b. p. 150°/20 mm. Magnesium  $\beta$ -phenylethyl bromide reacts with benzaldehyde and *m*-chlorobenzaldehyde forming  $\alpha\gamma$ -diphenylpropyl alcohol (corresponding bromide, b. p. 185—190°/30 mm.) and  $\gamma$ -phenyl- $\alpha$ -*m*-chlorophenylpropyl alcohol, b. p. 210—215°/25 mm. (corresponding bromide, b. p. 200—205°/30 mm.), respectively. Neither of these bromides reacts with magnesium. The Grignard reagent from  $\gamma$ -bromobutylbenzene, b. p. 118—119°/14 mm. (the corresponding alcohol is prepared from magnesium  $\beta$ -phenylethyl bromide and acetaldehyde), and iododimethylarsine afford 56% of  $\gamma$ -phenyl- $\alpha$ -methylpropyldimethylarsine, b. p. 143—145°/20 mm. (methiodide, m. p. 156° after softening at 153°). The dichloride of this undergoes thermal decomposition mainly to  $\gamma$ -chlorobutylbenzene and chlorodimethylarsine. The arsines described could not be converted into cyclic arsines.

H. BURTON.

**Synthesis of  $\alpha$ -chlorostyryldichloroarsine.** V. IPATIEV, G. RAZUBAIEV, and A. SIZOV (J. Russ. Phys. Chem. Soc., 1928, 61, 1869—1874; cf. Turner, J.C.S., 1925, 127, 996).—The preparation and properties of  $\alpha$ -chlorostyryldichloroarsine are described. Phenylacetylene and arsenic trichloride when heated for 30 hrs. under reflux gave a mixture of the arsine and the initial materials which could not be separated by distillation, but by freezing yielded the pure arsine, m. p. 40.6—41.2°, which decomposed when heated above 110°. On heating it with dilute sodium hydroxide to 110—120°,  $\alpha$ -chlorostyrylarsine oxide, m. p. 115—117°, was obtained, whilst oxidation with hydrogen peroxide yielded  $\alpha$ -chlorostyrylarsinic acid, m. p. 179—180°.

M. ZVEGINZOV.

**Arsenic derivatives of 2-methylthiophen. IV.** C. FINZI (Gazzetta, 1930, 60, 159—165; cf. A., 1926, 186).—2-Methylthiophen-5-mercuric chloride, m. p. 204°, obtained in almost theoretical yield from 2-methylthiophen by treatment with aqueous mercuric chloride in the presence of sodium acetate, condenses with arsenious chloride in benzene to give 2-methylthiophen-5-arsenious chloride, oxidised by alkaline hydrogen peroxide to 2-methylthiophen-5-arsinic acid, m. p. 132°, which loses 1 mol. of water by drying to give 2-methylthiophen-5-arsenic oxide. Nitration of 2-methylthiophen-5-arsinic acid in the presence of concentrated sulphuric acid yields 3-nitro-2-methylthiophen-5-arsinic acid, m. p. above 270° (decomp.), reduced in alcoholic solution by 4% sodium amalgam to 3-amino-2-methylthiophen-5-arsinic acid, decomp. about 270° without melting (hydrochloride; acetyl derivative, m. p. above 260°). Reduction (50% hypophosphorous acid at 60—70°) of 2-methylthiophen-5-arsinic acid gives 2 : 2'-dimethyl-5 : 5'-arsenothiophen, m. p. 62—130°. 3-Nitro-2-methylthiophen-5-arsinic acid is similarly reduced at 80—85° to 3 : 3'-dinitro-2 : 2'-dimethyl-5 : 5'-arsenothiophen, decomp. 185—225°; the arsenothiophens are reconverted into the corresponding arsinic acid by oxidation with iodine or hydrogen peroxide. C. W. SHOPPEE.

**Arsenic compounds of pyrrole and indoles. Q.** MINGOIA (Gazzetta, 1930, 60, 134—140).—Diazotised *p*-aminophenylarsinic acid couples with pyrrole, indole, 2-methylindole, and 3-methylindole in cold alkaline aqueous-alcoholic solution to give, respectively : 2-benzeneazopyrrole-4'-arsinic acid (ammonium, lead, barium, silver, copper, iron, zinc, tin, and manganese salts); 3-benzeneazoindole-4'-arsinic acid (ammonium and lead salts); 3-benzeneazo-2-methylindole-4'-arsinic acid (ammonium, lead, and mercuric salts); 2-benzeneazo-3-methylindole-4'-arsinic acid (ammonium and mercuric salts). The foregoing substances are intensely coloured (reddish-brown) and without m. p.; they are readily soluble in alkali hydroxides or carbonates.

C. W. SHOPPEE.

**Preparation and properties of derivatives of phenarsazine.** O. A. ZEIDE and I. M. GORSKI (J. Russ. Phys. Chem. Soc., 1929, 61, 1563—1571).—The action of Grignard reagents on 10-chloro-5 : 10-dihydrophenarsazine was investigated. The methyl (m. p. 107—108°), ethyl (m. p. 71—72°), phenyl (m. p. 148—149°), and  $\alpha$ -naphthyl (m. p. 154—155°) derivatives are prepared by the above method. The action of

chlorine on these compounds gave perchlorides, whilst gaseous hydrogen chloride decomposed them, giving the corresponding substituted dichloroarsine and diphenylamine hydrochloride. M. ZVEGINTZOV.

**Reduction of derivatives of dihydrophenarsazine.** G. RAZUBAIEV and A. BENEDIKTOV (Ber., 1930, 63, [B], 343—346; cf. Wieland and Rheinheimer, A., 1921, i, 371; Razubaiev, A., 1929, 585, 834).—Direct determination of the hydrogen absorbed during the reduction of 10-chloro-5:10-dihydrophenarsazine is impossible, since the compound is not affected by magnesium or sodium amalgam in acetic acid or alcoholic hydrogen chloride. It is therefore treated with zinc dust and acetic acid and, by measurement of the oxygen absorbed in re-oxidation of the reduced product, it is shown that approximately 2 atoms of hydrogen are required for the reduction. The compound produced cannot be isolated from the solution, which, on addition of water, appears to deposit the oxide,  $C_{24}H_{22}ON_2As_2$ . The last-named compound is very unstable and is slowly oxidised by air to 5:10-dihydrophenarsazine. It dissolves readily in a solution of iodine in acetone or alcohol, evolving hydrogen iodide and producing 10-iodo-9:10-dihydrophenarsazine; in presence of water, further oxidation to phenarsazinic acid occurs. With concentrated sulphuric acid the oxide evolves sulphur dioxide and gives the intensely red solution characteristic of dihydrophenarsazine derivatives.

Phenarsazinic acid, 10:10-dimethyl- and 10-methyl-10-ethyl-5:10-dihydrophenarsazine, and the iodides, perchloride, and perbromide of 10-methyl-5:10-dihydrophenarsazine which contain quinquevalent arsenic give pale greenish-yellow solutions in concentrated sulphuric acid and no coloration when warmed with formic acid. Compounds containing tervalent arsenic in which halogen, oxygen, methoxy-, ethoxy-, acetoxy-, formoxy-, or similar group is attached to arsenic yield intensely red solutions in sulphuric acid and, with few exceptions, are reduced by formic acid with production of a cherry-red colour sensitive to atmospheric oxygen. If an alkyl or aryl group is united to the arsenic atom, the sulphuric acid solutions are much less intensely coloured and marked colorations are not produced by formic acid.

H. WREN.

**Uranium salts.** S. WEIL and S. ROSENBLUMÓWNA (Bull. Trav. Inst. pharm. État, Warsaw, 1928, 10 pp.; Chem. Zentr., 1929, ii, 2222).—The following salts are described: uranium  $\alpha$ -phenyl-,  $UO(C_6H_5N.C_6H_5.CO_2)_2.3H_2O$ , and  $\alpha$ -salicyl-cinchoninate,  $UOC_6H_4O_5N.H_2O$ ; uranyl  $\alpha$ -salicylcinchoninate,  $UO_2C_6H_4O_5N.4H_2O$ ; uranium sulphosalicylate,  $C_{14}H_8O_{12}S_2U$ , and salicylate,  $C_{14}H_8O_6U.4H_2O$ ; uranyl salicylate,  $C_{14}H_{10}O_6UO_2.5H_2O$ ; uranium naphthalene-2-sulphonate,  $UO(C_{10}H_7SO_3)_2$ ; uranyl *p*-aminophenylarsinate,  $C_{12}H_{14}O_6N_2As_2UO_2.H_2O$ , methylarsinate,  $CH_3AsO_3UO_2.1.5H_2O$ , *m*-nitro-*p*-hydroxyphenylarsinate,  $C_{12}H_{10}O_{12}N_2As_2UO_2.2H_2O$ , and *m*-nitroarsanilate,  $(+2H_2O)$ ; and uranyl compounds of guaiacol,  $C_{14}H_8O_6U.4H_2O$ , and salvarsan,  $(C_{12}H_{10}O_2N_2As_2UO_2OH)_2.5H_2O$ . A. A. ELDRIDGE.

**Phosphonocarboxylic acids containing an asymmetrical phosphorus atom.** A. E. ARBUSOV

and B. A. ARBUSOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1599—1607).—Earlier attempts to prepare optically active isomerides of phosphinic acid derivatives are briefly summarised, and the preparation of *phenylphosphoneacetic acid*,  $OH.PPhO.CH_2.CO_2H$ , and *phenyl- $\alpha$ -phosphonepropionic acids*,  $OH.PPhO.CHMe.CO_2H$ , is described. Phenylphosphoneacetic acid, m. p. 121.5—122.5°, was obtained as the *ethyl ester*, b. p. 195—198°/7 mm.,  $d_4^{20}$  1.1223, by the action of diisobutyl phenylphosphite,  $PPh(OC_4H_9)_2$ , b. p. 134.5°/7 mm. (from phosphenyl chloride and sodium isobutoxide), on ethyl bromoacetate. The alkaloid salts of the acid could not be resolved into optically active components. *Phenyl- $\alpha$ -phosphonepropionic acid*, m. p. 168—169°, was prepared by the same method as the ethyl ester, b. p. 191—193°/7 mm.,  $d_4^{20}$  1.10535, from diisobutyl phenylphosphite and ethyl  $\alpha$ -bromopropionate.

M. ZVEGINTZOV.

**Phosphinic acids containing an asymmetrical phosphorus atom.** A. E. ARBUSOV and I. ARBUSOV (J. Russ. Phys. Chem. Soc., 1929, 61, 1905—1908).—Phenylisobutylphosphinic acid and phenyltriphenylmethylphosphinic acid were synthesised, and unsuccessful attempts made to resolve them into optical isomerides by salt formation with alkaloids.

*Phenylisobutylphosphinic acid*, m. p. 64—65°, was obtained by the action of isobutyl iodide on the ester,  $PPh(OC_4H_9)_2$ , at 160° in a sealed tube. It did not give crystallisable salts with alkalis or alkaloids.

The ester  $PPh(OC_4H_9)_2$  and triphenylmethyl bromide under similar conditions yielded *phenyltriphenylmethylphosphinic acid*, m. p. 287—288°, which gave crystalline salts with the alkali metals but not with alkaloids.

M. ZVEGINTZOV.

**Preparation of thiophosphinic acids containing asymmetric phosphorus.** A. E. ARBUSOV and G. X. KAMAT (J. Russ. Phys. Chem. Soc., 1929, 61, 2037—2042).—Various acids of the types  $PRR'S.OH$  and  $PRR'S.SH$  have been prepared with the object of obtaining them in optically active forms. The only one to be obtained crystalline is phenylbenzylmonothiophosphinic acid, which is being investigated further. The compound  $PPh(SET)_2$ , b. p. 143—144°/3.5 mm.,  $d_4^{20}$  1.1417, prepared by treating mercaptan (1 mol.) in ethereal solution with sodium and phosphenyl chloride (0.5 mol.) forms a crystalline compound with cuprous bromide. At 150° it combines with sulphur giving rise to the compound  $C_{10}H_{15}S_3P$ , b. p. 191—192°/3.5 mm.,  $d_4^{20}$  1.2201, which is hydrolysed by sodium ethoxide to the crystalline salt,  $PPhS(SET).ONa$ , but the corresponding acid could not be obtained crystalline. When heated with ethyl iodide in a sealed tube at 130°, the thio-ether  $PPh(SET)_2$  undergoes isomerisation to the compound,  $PPhEt(SET).S$ , b. p. 169—170°/3.5 mm.,  $d_4^{20}$  1.1693, which, with sodium ethoxide, gives the crystalline sodium salt of phenylethylmonothiophosphinic acid,  $PPhEt(ONa).S$ , but the corresponding acid was obtained only as a syrup. The isobutyl ether,  $PPh(SC_4H_9)_2$ , b. p. 191—192°/12.5 mm.,  $d_4^{20}$  1.0637, forms the compound  $S.PPh(SC_4H_9)_2$ , with flowers of sulphur, and, when treated with bromoacetic acid, yields a product giving the crystalline sodium salt,

$\text{S:PPh(ONa)·CH}_2\text{·CO}_2\text{Na}$ ; the corresponding acid and its cinchonine and brucine salts did not crystallise.

The action of ethyl  $\beta$ -iodopropionate on the thio-ether  $\text{PPh(SC}_4\text{H}_9)_2$  gives the compound  $\text{C}_{13}\text{H}_{19}\text{O}_2\text{S}_2\text{P}$ , b. p.  $200\text{--}206^\circ/4.5\text{ mm.}$ , but hydrolysis of this failed to give a crystalline acid. Treatment of the thio-ether,  $\text{PPh(SEt)}_2$  with benzyl chloride at  $200^\circ$  gave the compound  $[\text{S:PPh(CH}_2\text{Ph)·S}]_2(?)$ , m. p.  $145\text{--}146^\circ$ , and the oily compound  $\text{S:PPh(CH}_2\text{Ph)·SEt}$ , b. p.  $210\text{--}218^\circ/3\text{ mm.}$ ,  $d_4^{20} 1.826$ . The action of benzyl chloride on the ether  $\text{PPh(SC}_4\text{H}_9)_2$  at  $210^\circ$  gave the compound, m. p.  $145\text{--}146^\circ$ , similarly obtained from the ether,  $\text{PPh(SEt)}_2$ , but vacuum distillation of the residue led to rapid decomposition, so that this residue was hydrolysed directly, with formation of *phenylbenzylmonothio-phosphinic acid*,  $\text{S:PPh(CH}_2\text{Ph)·OH}$ , m. p.  $173\text{--}174^\circ$ .

T. H. POPE.

**Indolylphosphines.** Q. MINGOIA (Gazzetta, 1930, 60, 144—149).—Magnesiumindole (prepared from indole, magnesium, and ethyl bromide) reacts with phosphorus trichloride in ether to give *tri-3-indolylphosphine*, m. p.  $195\text{--}196^\circ$ , together with a small quantity of *tri-1-indolylphosphine*, m. p.  $223\text{--}225^\circ$ , from which the former is separated by treatment with acetone. Magnesium-2-methylindole and phosphorus trichloride similarly furnish only *tri-2-methyl-1-indolylphosphine*, m. p.  $180^\circ$ , and magnesium-3-methylindole affords *tri-3-methyl-2-indolylphosphine*, m. p.  $156\text{--}158^\circ$  (*methiodide*, m. p.  $171^\circ$ ). These phosphines are colourless and odourless; the 2- and 3-indolyl compounds give *N*-silver derivatives soluble in ammonia and are unaffected by boiling concentrated alkali hydroxide. The 1-indolyl derivatives, on the other hand, form no silver compounds and give phosphine with boiling water or moist solvents.

C. W. SHOPPEE.

**Action of selenoxanthhydrol on carbamides and carbamic esters.** F. FRANÇOIS (Compt. rend., 1930, 190, 800—802).—Selenoxanthhydrol reacts, in alcoholic acetic acid, with carbamide and thiocarbamide, monosubstituted carbamides and urethanes to give derivatives of the type  $\text{CO(NHX)}_2$ ,

$\text{NHR·CO·NHX}$ , and  $\text{NHX·CO}_2\text{R}$  ( $\text{X}=\text{CH}<\text{C}_6\text{H}_4>\text{Se}$ )

respectively, and thus are prepared: *di(selenoxanthyl)-carbamide*, m. p. about  $300^\circ$  (decomp.) (quantitative precipitation), and *-thiocarbamide*, m. p.  $190\text{--}230^\circ$  (decomp., according to conditions of heating); *selenoxanthylphenyl-carbamide*, m. p.  $234^\circ$  (decomp.), and *-thiocarbamide*, m. p.  $145^\circ$ ; and *selenoxanthylurethane*, m. p.  $179.5\text{--}181^\circ$ .

J. W. BAKER.

**Peptone.** VI. A. BERNARDI and (MISS) M. A. SCHWARZ (Annali Chim. Appl., 1930, 20, 49—56).—When formed in the solution, cupric hydroxide decomposes Witte's peptone into simpler substances by a gradual demolition of the protein molecule, the products obtained showing different colour reactions (A., 1927, 582). Hydrolysis by means of dilute hydrochloric acid of the compound  $\text{C}_{51}\text{H}_{44}\text{O}_{24}\text{N}_{14}\text{S}$  obtained, with others, in this way, leads to further degradation of the protein molecule with gradual loss of the characteristic chromogenic groups, the final products being apparently diketopiperazine compounds or hydroxyamino-acids.

T. H. POPE.

**Oxygen residue of proteins.** Z. STARY (Z. physiol. Chem., 1930, 186, 137—140).—A dried gelatin hydrolysate on elementary analysis gave figures agreeing closely with the figures for the amino-acids contained therein, taking into account the yields. The unhydrolysed gelatin, on the other hand, gave a much higher sulphur and oxygen content. This indicates the presence of groups containing oxygen (and hydrogen) which on acid hydrolysis serve for fission of the  $\text{·CO·NH·}$  linkings.

J. H. BIRKINSHAW.

**Denaturation of proteins.** VI. Titration of the basic and acidic groups in egg-albumin. N. BOOTH (Biochem. J., 1930, 24, 158—168).—By using Harris' method of titration with acid (J.C.S., 1923, 123, 3294) and Kerridge's glass electrode with alkali it was found that in neither case did heat-denaturation affect the number of titratable groups. The change of one titratable group, if such occurs, is beyond the limits of experimental error. The number of free amino-groups (27) found by analysis agrees with the acid titration values. No "zwitterion" formation accompanying denaturation is to be detected in titratability of the protein. Haemoglobin undergoes denaturation during the titration for all  $p_{\text{H}}$  values less than 4 and greater than 10 (cf. Lewis, A., 1927, 270). Egg-albumin can be titrated in the undenaturated state owing to the relative slowness of denaturation even at  $p_{\text{H}}$  1 and  $25^\circ$ . S. S. ZILVA.

**Application of azeotropy to qualitative organic analysis.** M. LECAT (Z. physikal. Chem., 1930, 146, 232—244).—A method is outlined whereby the character of an unknown substance can be ascertained from an experimental determination of the azeotropic deviation of a binary system consisting of it and a suitable comparison substance. The substance under investigation should vaporise without decomposition and both it and the standard substance should be as pure as possible.

F. L. USHER.

**Sulphoiodic oxidation of organic substances.** **Xanthyl derivatives.** L. CUNY and J. ROBERT (J. Pharm. Chim., 1930, [viii], 11, 241—258).—The micro-determination of dixanthylcarbamide and related xanthyl derivatives by complete oxidation with sulphuric and iodic acids has been worked out and the effect of varying conditions studied. Oxidation of dixanthylcarbamide,  $5\text{C}_{27}\text{H}_{20}\text{O}_3\text{N}_2 + 116\text{HIO}_3 + 5\text{H}_2\text{SO}_4 + 5\text{H}_2\text{O} = 135\text{CO}_2 + 58\text{I}_2 + 5(\text{NH}_4)_2\text{SO}_4 + 98\text{H}_2\text{O}$ , is incomplete at  $100^\circ$  and even at  $150\text{--}160^\circ$ , but at  $260^\circ$  (phosphoric acid bath) it is almost quantitative and is complete in 5 min. Dixanthylcarbamide (about 60 mg.) is heated at this temperature with 10 c.c. of 2*N*-iodic acid and 50 c.c. of sulphuric acid ( $d$  1.838) until iodine ceases to be evolved, 300—400 c.c. of water are added, and boiling is continued until all traces of iodine are expelled. After cooling, 200 c.c. of water, 160 c.c. of sodium carbonate solution, and 25 c.c. of 20% potassium iodide solution are added and the excess of iodic acid is determined by titration of the liberated iodine with 0.2*N*-sodium thiosulphate solution. After allowing for the corresponding volume of thiosulphate solution required in a blank experiment, 1 c.c. of *N*-sodium thiosulphate corresponds with 3.017 mg.

of dixanthylcarbamide. The error is  $-0.1$  to  $-0.8\%$ . Dilution of the sulphuric acid to lower the b. p. and hence the temperature of oxidation cannot be carried beyond  $75\%$  acid, otherwise an insoluble substance, oxidised only with extreme difficulty, is formed and the results are low. Alternatively, determination of the weight of carbon dioxide produced may be used and the detailed technique of this method is given. The results so obtained are rather lower (error,  $-0.7$  to  $-2.7\%$ ) than those obtained by titration of the excess of iodic acid, but this is shown not to be due to the formation of carbon monoxide, but probably results from the sudden and rapid evolution of carbon dioxide, traces of which escape absorption. The method is successfully applied to the determination of xanthhydrol, xanthone, xanthene, dixanthylsuccinamide, xanthylphenylacetamide, xanthylphenylthiocarbamide, xanthylantipyrine, and dixanthylveronal, 1 c.c. of *N*-sodium thiosulphate solution corresponding with 2.8448, 2.916, 2.527, 3.0512, 2.7925, 2.9432, 2.7380, and 3.0909 mg. of these substances, respectively. The uses of iodic acid as an oxidising agent are summarised.

J. W. BAKER.

**Determination of nitrogen in organic compounds by hydrogenation.** H. TER MEULEN (Rec. trav. chim., 1930, 49, 396—400).—The author describes improvements and modifications of the method (cf. A., 1925, ii, 66). R. J. W. LE FÈVRE.

**Micro-determination of mercury in organic compounds.** J. J. RUTGERS (Compt. rend., 1930, 190, 746—748).—The substance (about 5 mg.) is ignited in a current of oxygen saturated with the vapours of aqua regia, and the mercuric chloride formed decomposed electrolytically in aqueous solution using a slight modification of the method described by Verdino (A., 1928, 386). The method is rapid and gives accurate results.

H. BURTON.

**Microchemistry of cytisine.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 205—207).—A biblio-

graphy of the literature is given. The most sensitive reagents are gold and platinum chlorides and potassium mercuric iodide, each of which will detect 2 mg. at a dilution of 1:1000. S. I. LEVY.

**Microchemical contributions.** C. VAN ZIJP (Pharm. Weekblad, 1930, 67, 189—198).—Acetylsalicylic acid may readily be recognised under the microscope from the optical properties of the crystals and the characteristic formation and appearance of the copper and silver salts. Salicylic acid in solution or moistened gives needle crystal growth with solid lead acetate or carbonate; sodium uranate, bromine, and manganese sulphate in presence of ammonia also give excellent crystals. The most suitable reactions for atophan (phenyleinchroninic acid) are with concentrated hydriodic acid, iodine in potassium iodide solution, and concentrated nitric acid; for benzoic acid, the copper salt formed by adding a crystal to copper acetate solution; for cinnamic acid, with cadmium acetate and with barium hydroxide; for anisic acid, with silver acetate and with barium and strontium hydroxides; for fumaric acid, with barium acetate or carbonate, and lead and copper acetates; for saccharin, excellent results are obtained with mercuric chloride and cadmium acetate and with iodine. Sublimed cantharidin gives good crystal formation on treatment with lime-water or strontium hydroxide; guanine responds to the same treatment, and gives good crystals with picric and iodic acids. Boric acid gives a good test with berberine. The employment of iodic acid for the microchemical detection of alkaline-earth salts is discussed. Methods of manipulation are described in each case.

S. I. LEVY.

**Reactions of antifebrin and phenacetin.** L. EKKERT (Pharm. Zentr., 1930, 71, 179).—Some colour reactions with sulphuric acid, alone and with subsequent addition of alkalis, are described.

S. I. LEVY.

## Biochemistry.

**Blood of tropical inhabitants.** PARJONO, W. RADSMAN, and M. JOENES (Arch. Néerland. Physiol., 1930, 15, 73—96).—The respective values for oxygen absorption capacity, iron content, and haemoglobin content of Europeans were 21.4 vol.%, 5.63 mg. per 10 c.c., 94.6; for prosperous natives 21.6 vol.%, 5.75 mg. per 10 c.c., 92; for the poor working classes 19.6 vol.%, 5.11 mg. per 10 c.c., 85.4. The deficiency in the case of the poor is correlated with the frequent occurrence of intestinal worms. T. R. SESHADRI.

**Composition of normal rat blood.** A. K. ANDERSON, H. E. HONEYWELL, A. C. SANTY, and S. PEDERSEN (J. Biol. Chem., 1930, 86, 157—160).—Figures are given for the non-protein constituents of the blood of normal rats at various ages.

C. R. HARRINGTON.

**Permeability [of blood-corpuscles to water].** W. SPRANGER (Biochem. Z., 1930, 218, 341—354; cf. A., 1929, 845).—The resistance of red blood-

corpuscles from the sheep to permeation by water is lowered by treatment with albumin, lecithin, or sodium oleate and raised by treatment with cholesterol, cholesteryl ester, or triolein. When substances of the one type are combined with those of the other so as to reproduce the conditions in blood-serum, the permeability is normal. The bearing of these and other results on the applications of the author's theories to the behaviour of living protoplasm is considered. W. MCCARTNEY.

**Enzymes of leucocytes. IV. Peptidases of blood-serum.** W. GRASSMANN and W. HEYDE (Z. physiol. Chem., 1930, 188, 69—80; cf. this vol., 234).—The normal sera of the pig, sheep, rabbit, calf, ox, horse, and man contain peptidases. The dipeptidase action (leucylglycine) is small and disappears on keeping; the tripeptidase action (leucylglycylglycine) is much stronger and stable. The optimum  $p_H$  is 7.4—7.5. The polypeptidase content of serum is

characteristic for each animal species. The activity of ox-serum is 2—3 times, of rabbit- and sheep-serum 5 times, and of pig-serum 10 times that of human serum. The method of obtaining the serum has no effect on the enzyme content. In pathological conditions the peptidase content may vary greatly from the normal. J. H. BIRKINSHAW.

**Electrical conductivity of leucocytes.** G. ENDRES (Z. Biol., 1930, 90, 63—69).—The addition of 0.2% of saponin to a suspension of red blood-corpuscles in plasma produces hæmolysis as evidenced by the increase in electrical conductivity. When the red cells are replaced by leucocytes or platelets, there is no change in conductivity on addition of saponin. Cooling the cell suspensions to  $-8^{\circ}$  to  $-12^{\circ}$  does not affect the conductivity. In all cases the resistance-capacity is measured by comparison with 0.1*M*-potassium chloride. The physico-chemical properties of the leucocytes are distinct from those of the erythrocytes under these conditions.

P. G. MARSHALL.

**Viscosimetric studies of the coagulation of hæmoglobin.** S. L. PURKO (J. Russ. Phys. Chem. Soc., 1929, 61, 2043—2048).—See A., 1929, 1382.

**Protein coagulation and its reversal. Preparation of insoluble globin, soluble globin, and hæm.** M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1930, 13, 469—476; cf. this vol., 102).—By the use of acid acetone hæmoglobin may be rapidly separated into a precipitate of denatured globin and an acetone solution of hæm. By gradual neutralisation the denatured globin may be largely converted into a soluble, apparently native form which can combine with hæm to form hæmoglobin. The hæm is obtained in acetone-free slightly alkaline solution avoiding the modifying effect of strong alkali.

T. R. SESHADRI.

**Protein coagulation and its reversal. Reversal of coagulation of hæmoglobin.** A. E. MIRSKY and M. L. ANSON (J. Gen. Physiol., 1930, 13, 477—481).—The technique for the reversal of coagulation of hæmoglobin is improved. Several methods for preparing soluble crystalline hæmoglobin from that denatured by hydrochloric or trichloroacetic acid are described, the maximum yield being about 75%.

T. R. SESHADRI.

**Preparation and coupling of globin.** A. HAMSIK (Z. physiol. Chem., 1930, 187, 229—237).—A method for the preparation of globin and hæmatin from ox-blood is described. The globin retained its power of uniting with hæmatin to form synthetic methæmoglobin from which hæmoglobin, oxy- and carboxy-hæmoglobin were obtained. Both globin and hæmatin solutions on keeping lose their power of combination.

J. H. BIRKINSHAW.

**Determination of the proteins of blood-serum by alcoholic precipitation.** A. GRIGAUT, A. BOUTROUX, and A. CODOUNIS (Bull. Soc. Chim. biol., 1930, 12, 20—24).—Refractometric methods for determination of serum-proteins always give high results. A method is described in which the protein is precipitated with alcohol, the precipitate extracted continuously with boiling alcohol, and the residual protein determined either gravimetrically or by the

nitrometric method. The treatment with alcohol removes salts and lipins and the two methods then give comparative results. P. W. CLUTTERBUCK.

**Iodometric micro-determination of blood-urea. I. Sulpho-iodic oxidation.** L. CUNY and J. ROBERT (Bull. Soc. Chim. biol., 1930, 12, 171—195).—The urea in 0.5 c.c. of blood is determined by precipitating it with xanthhydrol and oxidising the dixanthylcarbamide with a mixture of sulphuric acid and potassium iodate. The potassium iodate remaining is determined by titration of iodine liberated after the addition of potassium iodide.

W. O. KERMACK.

**Comparative determination of urea in urine and in blood by the hypobromite and urease methods.** L. AMBARD and F. SCHMID (Bull. Soc. Chim. biol., 1930, 12, 231—240).—Determinations of urea in blood and urine by the hypobromite and urease methods give results in fairly close agreement, those by the former method tending to be slightly higher than those by the latter. W. O. KERMACK.

**Determination of uric acid in blood.** O. FOLIN [with A. SVEDBERG and K. JONES] (J. Biol. Chem., 1930, 86, 179—187).—The method for the determination of uric acid in blood (A., 1924, ii, 634) is improved by employing protein-free extracts of unlaked blood prepared as described by the author (cf. below). Addition of carbamide to the sodium cyanide solution inhibits the decomposition of the latter and the formation of turbidities during the determination; further improvement is effected by the removal of carbonate from the cyanide by treatment with calcium oxide.

C. R. HARINGTON.

**Determination of uric acid in blood.** R. A. TRELLES and R. FERRAMOLA (Semana Méd., 1929, 36, 1711—1712).—For whole blood Benedict's method, and for plasma or serum Flotow's method, is preferred. Normal serum or plasma contains 40—50 mg. of uric acid per litre; for whole blood the values are usually 5—10% higher. CHEMICAL ABSTRACTS.

**Regulation of blood-cholesterol and the lungs.** M. BUGNARD (Bull. Soc. Chim. biol., 1930, 12, 97—104).—The distribution of cholesterol between plasma and corpuscles is determined by the reaction of the medium. In the lungs, cholesterol passes from plasma to corpuscles and the reverse occurs in the tissues, thus explaining the difference in cholesterol content of the serum of venous and arterial blood.

P. W. CLUTTERBUCK.

**Lipæmia. I. Determination of lipins in blood or plasma.** R. B. ESQUIVEL and G. M. GRAMAJO (Semana Méd., 1929, 36, 1507—1514).—Bang's method is inexact; Bloor's method was used for total lipins and cholesterol, and Whitehorn's method for lecithin. CHEMICAL ABSTRACTS.

**Analysis of unlaked blood.** O. FOLIN (J. Biol. Chem., 1930, 86, 173—178).—In order to eliminate the disturbing effects of products of disintegration of the red blood-corpuscles, a modification of the original method of Folin and Wu for the preparation of blood for analysis is proposed. Whole blood is added to a mixture of sodium tungstate solution and sulphuric acid rendered hypertonic by the addition



of sodium sulphate; the mixture of cells and precipitated plasma-proteins is separated rapidly on the centrifuge, yielding a solution suitable for analysis.

C. R. HARINGTON.

**Blood samples for determination of alcohol content.** E. M. P. WIDMARK (Biochem. Z., 1930, 218, 465—467).—A method (cf. A., 1922, ii, 789) of taking and preserving blood samples with which three micro-analyses can be made is described. The alcohol content of the samples remains unchanged for at least 4 days.

W. MCCARTNEY.

**Apparatus for micro-determination of blood-sugar.** H. J. FUCHS (Biochem. Z., 1930, 218, 487—490).—An improved micro-pipette and micro-burette are described.

W. MCCARTNEY.

**Validity of blood-sugar values from immediate reduction.** V. Justification for the determination of blood-sugar in the plasma. G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1930, 12, 196—212).—Considerations are advanced in favour of the determination of the plasma-sugar rather than of the whole blood-sugar. The imperfect permeability of the blood-corpuscles to dextrose may result in a difference in the concentrations of dextrose in the red blood-corpuscles and in the plasma, and the plasma-sugar is considered to be more immediately available for the tissues. If sodium fluoride (0.2%) is added to prevent clotting, the plasma-sugar remains constant for periods up to 1 hr.

W. O. KERMACK.

**Does cabbage fed to rabbits increase the calcium of the blood-serum?** K. CULHANE (J. Biol. Chem., 1930, 86, 113—116).—A reply to Kapsinow and Underhill (A., 1929, 843); the author's original conclusions (A., 1927, 904) are maintained.

C. R. HARINGTON.

**Determination of phosphorus in blood.** A. IONESCU-MATIU and (ILLE.) M. VITNER (Bul. Soc. Chim. România, 1929, 11, 103—108).—An application of the method of Bell and Doisy (A., 1920, ii, 769) as modified by Bordeianu (B., 1927, 422). One c.c. of the blood is diluted to 4 c.c. with water and 1 c.c. of trichloroacetic acid added gradually; after keeping it is further diluted to 10 c.c. and filtered. To 5 c.c. of the filtrate are added 1 c.c. of a solution of potassium dihydrogen phosphate containing 0.25 g.  $P_2O_5$  in 100 c.c., 2 c.c. of a freshly-prepared 10% solution of *p*-hydroxyphenylglycine, and 5 c.c. of a solution of 150 g. ammonium molybdate in 1000 c.c. water and 1000 c.c. nitric acid of  $d_{1.20}$ . This solution is compared in a colorimeter with 5 c.c. of water similarly treated, the difference in concentrations multiplied by two giving the weight in g. of saline phosphorus per 1000 c.c. of blood. For the determination of total phosphorus 1 c.c. of blood is heated with 3 c.c. of concentrated nitric acid, 0.2 g. of potassium permanganate added, and, when the reaction has subsided, again heated gently. If the solution is still brown after a few minutes, the permanganate treatment is repeated. Any excess of permanganate is destroyed with ammonium oxalate, 10 c.c. of water are added, and the liquid is evaporated to dryness. The residue is redissolved in water and diluted to 10 c.c. The colorimetric determination is then

carried out as before with 5 c.c. of this liquid, no additional standard phosphate being added, however; hence the blank is made up from 4 c.c. of water. The method can be employed in presence of dextrose, glycerophosphates, and the hexosephosphates.

H. A. PIGGOTT.

**Blood coagulation. Affinity of hæmolytic systems for the complement in circulating blood.** M. VON FALKENHAUSEN (Biochem. Z., 1930, 218, 453—458).—Observations of the times required for the coagulation of blood from guinea-pigs which had received intrajugular injections of erythrocytes from wethers show that, in circulating blood, a temporary inhibitory effect on the power to coagulate occurs only when the erythrocytes have been highly sensitised, since only then has prothrombin a greater affinity for the erythrocytes than for antiprothrombin. Weakly sensitised erythrocytes have no effect on the time of coagulation or on the titre of the complement, and the obscure results obtained with moderately sensitised erythrocytes are to be explained by the suppression of the affinity of prothrombin for antiprothrombin, thrombokinase, and sensitised erythrocytes. These results support the view that there is no free complement in circulating blood.

W. MCCARTNEY.

**Human isohæmolysin.** S. HIGUCHI (Deut. Z. ges. gerichtl. Med., 1929, 13, 428—440; Chem. Zentr., 1929, ii, 2472).—The isohæmolysin is present in the globulin, but not in the euglobulin or albumin fraction of the serum; it is decomposed in 20 min. at 63°.

A. A. ELDRIDGE.

**Immunological specificity of chemically altered proteins. Halogenated and nitrated proteins.** A. WORMALL (J. Exp. Med., 1930, 51, 295—317).—Iodinated and brominated serum-proteins have lost their original species specificity, but have a new specificity due to halogenation. As the halogenated proteins do not give Millon's reaction it is probable that 3:5-dihalogenated tyrosine derivatives are formed, and it is this grouping which gives the protein its specificity. Diazotised and nitrated proteins react with any nitroprotein antiserum; it is suggested that both these types of compounds possess a quinonoid structure.

E. BOYLAND.

**Preparation of cerebroside.** I. H. PAGE (Biochem. Z., 1930, 219, 161—164).—If in Rosenheim's method for the separation of cerebroside pyridine is replaced by tetralin, the yield is improved by 30—40%.

P. W. CLUTTERBUCK.

**Egg-lecithin.** T. HATAKEYAMA (Z. physiol. Chem., 1930, 187, 120—126).—In order to obtain a quantitative separation of the fatty acids of lecithin, crystalline lecithin-cadmium chloride was hydrolysed with alcoholic potassium hydroxide in presence of deoxycholic acid. The mixture of choleic acids, m. p. 184—185°, was heated with xylene to form xylene-choleic acid and free fatty acids, which were then fractionated from acetone solution or by making use of the differing solubilities of the barium salts. Stearic, palmitic, oleic, and arachidonic acids were obtained, the last-named in high yield, indicating that at least one egg-lecithin contains only arachidonic acid. *Arachidoncholeic acid*,  $SC_{24}H_{40}O_4, C_{20}H_{32}O_2$ ,

m. p. 183°, was prepared and, by hydrogenation, *arachincholeic acid*,  $\text{SC}_{24}\text{H}_{40}\text{O}_4$ ,  $\text{C}_{20}\text{H}_{40}\text{O}_2$ , m. p. 189°.

J. H. BIRKINSHAW.

**Preformation of oxysterol in animal organs and tissues.** I. LIFSCHÜTZ (Arch. Pharm., 1930, 268, 166—170).—The following experiments show that the oxysterol previously detected in animal fats is not formed by atmospheric oxidation of cholesterol during the process of extraction (cf. A., 1913, ii, 350). The fat extracted from ox-blood which has been evaporated to dryness in a vacuum at the lowest possible temperature contains considerable amounts of oxysterol. Dog's liver, freed from blood and dried in air by gentle heating, contains cholesterol, but no oxysterol. Dried lipin-free human blood oxidises cholesterol in acetic acid in presence of air at 60—65° to oxysterol, although neither the blood nor the cholesterol alone gives oxysterol under these conditions. The nature and applicability of the acetic-sulphuric acid reaction for oxysterol is discussed. H. E. F. NOTTON.

**Production of large quantities of the cholesterol-free portions of the unsaponifiable fraction of liver.** S. J. THANNHAUSER and F. FROMM (Z. physiol. Chem., 1930, 187, 173—182).—The unsaponifiable matter of liver can be extracted with methylene chloride, trichloroethylene, or ethylene chloride in addition to ether. The extraction on a large scale is described. The unsaponifiable matter of ox and dog bile does not contain the unsaturated hydrocarbon of m. p. 128—129° isolated from liver by Channon and Marrian (A., 1926, 638). In some of the liver extractions a crystalline oxidation product, m. p. 220°, was obtained. J. H. BIRKINSHAW.

**Distribution of cholesterol and its esters in the suprarenal capsules.** A. LEULIER and L. REVOL (Compt. rend., 1930, 190, 657—659).—Determination of the total cholesterol and of cholesterol esters in the suprarenal cortex and medulla (sheep and ox) shows that the latter contains a greater proportion of the total cholesterol, and that this is very largely composed of free cholesterol. On the contrary, the cortex of the horse is much richer in total cholesterol than the medulla; the content of free cholesterol is, however, the same in both capsules as in the sheep and the ox, the difference being due to the presence of a large quantity of cholesterol esters.

C. W. SHOPPEE.

**Colour reactions for thymonucleic acid and its determination in animal organs.** Z. DISCHE (Mikrochem., 1930, 8, 4—32).—The characteristic blue colour given by a solution of diphenylamine in acetic acid containing an optimum concentration of sulphuric acid with a solution of thymonucleic acid has been utilised for the micro-determination of the latter in 1—2 g. of animal organs. Carbohydrates and other interfering substances are without influence except in much larger concentrations than they are usually found in animal tissues; of greater influence are salts of weak acids and protein decomposition products. The material is first digested with 1% pepsin in 0.1N-hydrochloric acid at 40° and the residue is extracted with N-sodium hydroxide for 2 hrs. at 100°. The liquid is then cooled, acetic acid is added, and to

the filtrate alcohol is added to precipitate the thymonucleic acid. It is concluded that the sugar attached to the purine bases is different from that of the pyrimidine bases. The analytical results obtained in the case of thymus agree with previous determination by other methods, whereas for liver and spleen they are widely different.

T. R. SESHADRI.

**Basic amino-acids of wool.** H. B. VICKERY and R. J. BLOCK (J. Biol. Chem., 1930, 86, 107—111).—Sheep wool contains histidine 0.66, arginine 7.8, and lysine 2.3%.

C. R. HARRINGTON.

**Occurrence of metallic elements in biological material.** W. B. S. BISHOP (J. Cancer Res. Comm. Sydney, 1930, 1, 242—253).—The elements of groups I and II in the periodic table are widely distributed. Group III is the poorest as regards biological occurrence, the presence of aluminium in animal tissues being much in dispute. Lead (group IV) is the first toxic element occurring in tissues. Arsenic and vanadium are biologically the most interesting members of group V, the latter being but slowly eliminated after injection. The carcinogenic action of tar does not depend on its arsenic content. Manganese is found in small amount in animal tissues, but is not related to sarcomata or carcinomata. Copper is connected with haemoglobin formation, whilst zinc may play some part in reproduction.

P. G. MARSHALL.

**The iodine problem.** E. GLIMM (Biochem. Z., 1930, 219, 148—154).—The iodine contents of a number of food materials obtained in the Danzig area are found to be much greater than those recorded by Fellenberg for similar Swiss foodstuffs. The outer layers of the cereal grains are richer in iodine than the inner and the meal is therefore poorer than the bran. The iodine contents of 58 thyroid glands of Danzig people were determined. The iodine content of stillborn child's gland is extremely low and the mean content of 48 glands of adults is 10.4 mg.

P. W. CLUTTERBUCK.

**Amylase of ox and horse saliva.** T. CHRZASZCZ and Z. SCHECHTLOWNA (Biochem. Z., 1930, 219, 30—50).—The amount of saliva secreted is least during rest (especially at night) and most during feeding, a greater quantity being obtained with dry fodder. A cow of average size secretes 28 litres per day, but individual differences are large. The  $p_H$  of ox saliva is 8.55—8.90 except during rumination, when it falls to 8.00. The  $p_H$  of horse saliva is 8.5—8.6. Ox and horse saliva contains amylase which may be separated by the alcohol and adsorption methods. The optimal  $p_H$  for ox saliva amylase in phosphate buffer at the optimal temperature (45° for ox, 50° for horse) is 6.5—6.6 and for horse saliva, 6.2. The diastatic power of horse saliva is 2—4 times that of ox. The saliva contains least amylase during rest and in the morning and most after feeding. The kind of fodder, the age, sex, and minor ailments of the animal have no influence on the amount of amylase. Yeast complement, blood-serum, and sodium chloride (optimal 1.5%) influence favourably the action of the amylase. The diastatic power of saliva increases on keeping at 20—25°, due to the

development of bacteria and not to the conversion of a proenzymic form of amylase.

P. W. CLUTTERBUCK.

**Inhibition of enzyme action. Influence of organic fatty acids on the hydrolysis of starch by human saliva.** V. BORISSOVSKI and N. VEDENSKI (Biochem. Z., 1930, 219, 72—78).—Surface-active fatty acids (butyric, valeric, and heptic acids) are absorbed by starch grains and form thereon a uni-molecular surface layer which inhibits the action of ptyalin.

P. W. CLUTTERBUCK.

**Surface activity of human saliva.** V. BORISSOVSKI and N. VEDENSKI (Biochem. Z., 1930, 219, 79—86).—Tables show the surface activity (ergs/cm.<sup>2</sup>) of samples of human saliva over a range of temperature from 0° to 80° using both dry food material and 0.1% hydrochloric acid to stimulate secretion. The surface tension varies considerably in different individuals and the surface energy-temperature curves are very different according to the method of secretion, acid secretion yielding a saliva poor, and food secretion a saliva rich in surface-active material.

P. W. CLUTTERBUCK.

**Basal secretion of the stomach. III. Influence of feeding bone and other hard objects.** R. K. S. LIM, H. C. HOU, H. C. CHANG, and T. P. FENG (Chinese J. Physiol., 1930, 4, 1—20).—The gastric secretion in dogs with Pavlov and other pouches is investigated. Feeding of pieces of bone gives rise to a much higher elevation of the basal secretion than the response to a meat meal. The ingestion of pieces of hard material such as brass tubing has a stimulating effect similar to that of bone. The mechanism of the pyloric hormone is apparently connected with mechanical stimulation.

F. O. HOWITT.

**Bile acids of rabbit-bile.** S. OKAMURA and T. OKAMURA (Z. physiol. Chem., 1930, 188, 11—16).—From the bile of rabbits collected in winter deoxycholic acid was isolated as the principal bile acid. From fistula-bile deoxycholic acid could not be isolated, but a small amount of a crystalline cholic acid, m. p. 196—197°, was obtained.

J. H. BIRKINSHAW.

**Urinary bile pigment.** J. DECADE (Bull. Soc. Chim. biol., 1930, 12, 130—131).—Urine (10 c.c.) is first titrated to phenolphthalein with 0.1N-sodium hydroxide (=x c.c.). For the test, to 10 c.c. of filtered urine are added 4 drops of alcoholic phenolphthalein and then 3x c.c. of 0.1N-sodium hydroxide. A coral-red colour is obtained in presence of bile pigment.

P. W. CLUTTERBUCK.

**Reduction of mercury salts by normal urine.** H. PÉNAU and G. TANRET (Bull. Soc. Chim. biol., 1930, 12, 67—87).—A more detailed account of work already abstracted (A., 1929, 1480).

**Detection of sugar in urine with o-nitrophenyl-propionic acid.** H. SZANCER (Pharm. Zentr., 1930, 71, 225—227).—Unlike Nylander's and Haine's reagents, o-nitrophenylpropionic acid is reduced by hydrogen sulphide, and urine containing this product must first be treated with lead acetate before testing for sugar.

P. G. MARSHALL.

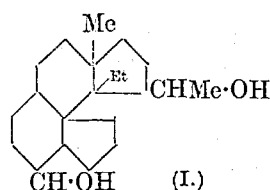
**Passage of alcohol into the urine by diffusion.** E. M. P. WIDMARK (Biochem. Z., 1930, 218, 445—452).—In the determination, by the dichromate method, of the alcohol content of urine this must be made alkaline, since otherwise incorrect results due to the action of reducing substances are obtained. When alkaline urine is used alcohol contents of the same order as those of normal blood are found. Criticisms of the view that alcohol passes into the urine by diffusion only depend on determinations which were inaccurate for the reason given and the view has been confirmed.

W. MCCARTNEY.

**Adenosine from human urine.** H. O. CALVERY (J. Biol. Chem., 1930, 86, 263—266).—Urine was freed from phosphate by shaking with calcium oxide, and the filtrate was treated with copper sulphate; the precipitate was decomposed, and the precipitation and decomposition were repeated. The solution was cleared by treatment with lead acetate and acetic acid, and the filtrate made alkaline with ammonia. The resulting lead precipitate was decomposed and the precipitation and decomposition were repeated; treatment of the concentrated solution with picric acid yielded adenosine picrate amounting to about 300 mg. from 80 litres of urine.

C. R. HARRINGTON.

**Pregnandiol, a sterol derivative from the urine of pregnancy.** A. BUTENANDT (Ber., 1930, 63, [B], 659—663; cf. this vol., 118).—Pregnandiol, m. p. 234—235°, isolated from the urine of pregnant women (cf. Marrian, A., 1929, 1495), in all probability has the composition C<sub>21</sub>H<sub>36</sub>O<sub>2</sub>. The formation of a diacetate, m. p. 180° (the existence of a second variety, m. p. 166°, is indicated), establishes the presence of two hydroxyl groups. The alcohol is saturated and does not react with bromine and the acetate is not affected by catalytic hydrogenation. Cautious treatment of pregnandiol with chromic acid in acetic acid yields *pregnandione*, C<sub>21</sub>H<sub>32</sub>O<sub>2</sub>, m. p. 123° (dioxime, decomp. above 250°), whereas more drastic treatment leads to a ketodicarboxylic acid, C<sub>21</sub>H<sub>32</sub>O<sub>5</sub>, m. p. 270° (decomp.) (*methylester*, m. p. 113°). One ketonic group of pregnandione is therefore present in a hydrogenated ring and the presence of an aromatic nucleus is excluded. Pregnandiol contains, therefore, four hydrogenated rings



in the molecule and appears to be closely related chemically to the sterols and bile acids. Since the diketone gives a positive iodoform reaction with alkaline iodine solution it must contain the  $\cdot\text{CO}\cdot\text{CH}_3$  group. The structure I is suggested for pregnandiol.

H. WREN.

**Decolorisation of urine.** C. OTTO (Pharm. Ztg., 1930, 75, 319—320).—The effect of various decolorising agents in the quantitative analysis of urine, especially the polarimetric determination of dextrose, is discussed.

W. O. KERMACK.

**Sulphate content of amyloid organs.** H. HEINLEIN (Arch. exp. Path. Pharm., 1930, 149, 119—128).—Various human organs which had undergone amyloid changes showed no significant increase

in total sulphur, but had an abnormally high sulphate-sulphur content. Diseased organs which had not undergone amyloid changes occasionally showed high sulphate-sulphur. W. O. KERMAK.

**Serum-iron in experimental anaemia.** H. H. RIECKER and M. E. WINTERS (Amer. J. Physiol., 1930, 92, 196—204).—Experimental anaemia following haemorrhage reduces the serum-iron of dogs, but this rises again on feeding with iron in the food or as ferric citrate. The serum-iron and haemoglobin of the blood are not directly related. E. BOYLAND.

**Endogenous uric acid and haematopoiesis. II. Haemolysis by phenylhydrazine hydrochloride.** J. KRAFKA, jun. (J. Biol. Chem., 1930, 86, 223—230).—Anaemia induced by administration of phenylhydrazine hydrochloride to a Dalmatian hound was accompanied by marked increase in the excretion of uric acid and in the number of reticulocytes. The peak of the reticulocyte count occurred 3—4 days later than that of the uric acid excretion. The previous suggestion (A., 1929, 1195) as to the origin of the uric acid from the nuclei of the erythroblasts is confirmed. C. R. HARRINGTON.

**Compounds from the urine of persons suffering from Amentia and Dementia praecox.** S. GULLOTTA (Biochem. Z., 1930, 218, 472—480).—The urine of persons suffering from *Amentia* and incipient *Dementia praecox* contains substances with the properties of phenol or indole compounds. From such urine by mild acid hydrolysis and subsequent treatment with dichlorobenzenediazonium chloride a red azo-dye, m. p. 68°, can be isolated, and from the hydrolysed urine of *Amentia* patients, by extraction with ether, *p*-hydroxyphenylacrylic acid can be obtained. The dye is identical with that obtained by Hermanns (A., 1922, i, 1091) from the urine of tuberculous persons. W. MCCARTNEY.

**Water content of heart muscle in beri-beri columbarum.** C. NEWCOMB (Indian J. Med. Res., 1930, 17, 1—14).—Beri-beri diet in pigeons produces in the majority of cases a diminution in the size of heart and an increase in the water content of the heart-muscle (polyneuritis *columbarum* and starvation), and in the minority of cases an increase in the size of the heart and some increase in the water content of the muscle (beri-beri *columbarum*). The large heart of beri-beri *columbarum* is not to be explained by water retention. T. R. SESHADRI.

**Analysis of small urinary calculi.** C. NEWCOMB (Indian J. Med. Res., 1930, 17, 1—13).—Micro-methods for the determination of phosphate, total nitrogen, calcium, magnesium, oxalate, and carbonate and qualitative tests for uric acid, cysteine, creatinine, and cholesterol are described. T. R. SESHADRI.

**Phylloerythrin in gall-stones of cattle.** H. FISCHER and R. HESS (Z. physiol. Chem., 1930, 187, 133—136).—Phylloerythrin was isolated from the ethereal extract of ox gall-stones after treatment with hydrochloric acid. J. H. BIRKINSHAW.

**Zinc and cancer.** A. ZLATAROV (Bull. Soc. Chim. biol., 1930, 12, 44).—It is suggested that accumulation of zinc is one defence of the organism against the

abnormal metabolism of the cancer cell, the zinc tending to inhibit the enhanced activity of proteolytic enzymes and catalase, to stimulate the decreased activity of peroxidase, and to oppose the increased colloidal activity of the cancer cell, thus tending to re-establish normal cellular respiration.

P. W. CLUTTERBUCK.

**Biological chemistry of zinc.** M. ANDRETT-CHEWA (Bull. Soc. Chim. biol., 1930, 12, 45—57).—The zinc ion when present above a minimal concentration readily coagulates boiled and unboiled milk and accelerates the clotting of milk by rennin. Zinc inhibits the action of proteolytic enzymes, trypsin being more sensitive to it than pepsin; the effect is modified by the anion in the case of pepsin, but not of trypsin. 0.001*M*-Solutions of zinc salts retard spontaneous oxidation of quinol and pyrogallol and accelerate the action of peroxidase. True oxidase and catalase reactions are inhibited by zinc salts.

P. W. CLUTTERBUCK.

**Activation of proteolysis in malignant tumours.** E. WALDSCHMIDT-LEITZ and A. SCHÄFFNER (Naturwiss., 1930, 18, 280—281).—As previously shown (A., 1929, 344), proteolysis by catheptic enzymes in animal organs and tissues is activated by hydrocyanic acid and hydrogen sulphide, which also check cell respiration. In the cell itself, however, there is a natural activator, zookinase, which increases in quantity by autolysis of the tissues and may be separated by extraction with aqueous alcohol. These observations suggest that there is a connexion between arrest of cell respiration and increased proteolytic activity in malignant tumours, and that the same substance is responsible for both phenomena. This view is supported by the fact that cysteine and glutathione activate cathepsin similarly to hydrogen sulphide, because these thiol compounds can also check cell respiration. Zookinase is probably, therefore, a compound of similar constitution. The proteolytic activator in malignant tumours possesses properties similar to those of the activator formed by autolysis in normal organs, and its quantity increases with the ripening of the tumour. The degree of activation of the cathepsin of rat sarcoma 14 days old was found to be 28%, but after a further 29 days it had practically doubled. At the same time there was a marked increase in the amount of amino-polypeptidase and dipeptidase. The increased proteolysis is probably the result and not the cause of arrested cell respiration. M. S. BURR.

**Relation of vitamin-B to tumour growth.** W. NAKAHARA (J. Cancer Res., 1929, 13, 363—366).—Rous chicken sarcoma is devoid of vitamin-B, but small quantities are present in rat sarcoma and carcinoma. Vitamin-B is not essential for the growth of transplanted tumours in rats and fowls.

CHEMICAL ABSTRACTS.

**X- and  $\gamma$ -Radiation measurement and the new international *r* unit.** J. G. STEPHENS (J. Cancer Res. Comm. Sydney, 1930, 1, 222—231).—Radiation is specified clinically by determining (a) the wavelength, (b) the amount of energy in the radiation, and (c) the degree of polarisation. The *r* unit, which measures the total ionic charge under certain con-

ditions, is used to express energy in the radiation in terms of the ionisation in air. It is suggested that the ionisation in liquids such as hexane or light petroleum would be of advantage by reducing the size of apparatus and giving larger ionisation currents.

P. G. MARSHALL.

**Variations of plasma-cholesterol in hog cholera.** R. E. SHORE (J. Exp. Med., 1930, 51, 179—187).—Swine infected with hog cholera have alternating periods of hypocholesterolaemia and hypercholesterolaemia.

E. BOYLAND.

**Calcium metabolism in chorea.** E. C. WARNER (Lancet, 1930, i, 339—342).—Chorea is accompanied by a low serum-calcium which causes increased nervous excitability. On recovery the serum-calcium content rises.

E. BOYLAND.

**Cystinuria. Excretion of a complex which decomposes in the urine with liberation of cystine.** E. BRAND, M. M. HARRIS, and S. BILOON (J. Biol. Chem., 1930, 86, 315—331).—The apparent cystine content of the urine of cystinuric patients, as determined by the method of Sullivan (A., 1926, 1266), increases markedly if the urine is kept for 24 hrs. This fact, together with the increase in the apparent cystine content which occurs when the urine is hydrolysed by acid, and the slowness with which cystine separates from urine, are taken to indicate the excretion by the cystinuric of a cystine complex, possibly a peptide, from which cystine is slowly liberated. Cystinuria may be detected by the magenta colour given by the urine with sodium nitroprusside 5—10 min. after treatment with sodium cyanide. Cystinuria may be accompanied by a variability in the excretion of creatinine.

C. R. HARRINGTON.

**Hydrogen-ion concentration of official test-water used in dermatology. II. Buffer capacity.** A. PERÜTZ and B. LUSTIG (Arch. exp. Path. Pharm., 1930, 149, 321—325).—The buffering capacity of acetic acid-alumina solution (approx. 0.05*N*-basic aluminium acetate), aqua Goulardi (1:10), boric acid (1.5%), and resorcinol solutions (1%) decreases in the above order.

W. O. KERMACK.

**Range of effective iodine dosage in exophthalmic goitre. II, III. Effect on basal metabolism of daily administration of iodine.** II. W. O. THOMPSON, E. G. THORP, P. K. THOMPSON, and A. C. COHEN. III. W. O. THOMPSON, A. C. COHEN, P. K. THOMPSON, E. G. THORP, and A. G. BRAILEY (Arch. Int. Med., 1930, 45, 420—429, 430—455).—II. In 20 cases of exophthalmic goitre the administration of iodine solution (approx. 3 mg. of iodine) caused a significant reduction (i.e., greater than 10 points) of the basal metabolism in 13 subjects, 5 showed no change, and 2 an increase, whilst 7 showed a lower metabolism on the subsequent administration of 60 times the amount daily.

III. In 14 cases of exophthalmic goitre on administration of iodine solution (approx. 1.5 mg. of iodine) 7 showed a significant reduction of basal metabolism, 6 no change, and 1 an increase. The average reduction of the basal metabolism was 9 points. The minimum dose to produce a maximum reduction in basal

metabolism is about 6 mg. of iodine per day. In approximately 50% of the cases the smallest dose that will produce any effect is greater than 1.5 mg. per day; administration of a smaller amount may interfere with the effect of larger doses given immediately afterwards.

C. C. N. VASS.

**Metabolism of under-nourished children. VIII. Effect of high- and low-protein diets on the excretion of creatine, creatinine, and ammonia.** C. C. WANG and M. KAUCHER. IX. Basal metabolism, caloric balance, and protein metabolism during a period of gain in weight. C. C. WANG, R. KERN, and M. KAUCHER (Amer. J. Dis. Children, 1929, 38, 468—475, 476—480).—In under-nourished children the retention of nitrogen is greater than normally; the excretion of creatine, creatinine, and ammonia and the basal metabolism are unaffected.

CHEMICAL ABSTRACTS.

**Artificial alteration of the reaction of waters in the campaign against *Anopheles* larvæ and on the absorbing power of peat.** A. N. ADOVA and I. A. SMORODINCEV (Bull. Soc. Chim. biol., 1930, 12, 213—230).—The effect of Sphagnum peat and Carex peat on the reaction of solutions of various acids, sodium hydroxide, and certain salts has been investigated. The Sphagnum peat is the more acid, and more effectively reduces the  $p_H$  of the alkaline solutions in which it is immersed, whereas the Carex peat has the greater influence in increasing the  $p_H$  of the more strongly acid solutions. These results bear on the method proposed for the destruction of *Anopheles* larvæ by acidification of the water in which they breed.

W. O. KERMACK.

**Metabolism of women during the reproductive cycle. I. Calcium and phosphorus utilisation in pregnancy.** I. G. MACY, H. A. HUNSCHER, B. NIMS, and S. S. MCCOSH. II. Calcium and phosphorus utilisation in lactation. H. A. HUNSCHER. III. Calcium, phosphorus, and nitrogen utilisation in lactation with and without supplementation of the diet with cod-liver oil and yeast. I. G. MACY, H. A. HUNSCHER, S. S. MCCOSH, and B. NIMS (J. Biol. Chem., 1930, 86, 17—35, 37—57, 59—74).—I. Periods of negative calcium balance were observed during the pregnancy of each of three normal women; considerable quantities of phosphorus were retained by all the women during pregnancy, a negative phosphorus balance being observed on two occasions only.

II. In normal women the calcium and phosphorus balances are negative early in the lactation period; the loss of calcium increases until the sixth month of lactation and then diminishes, until, at the end of the period, the calcium balance is positive. The heavy loss of calcium occurs mainly through the faeces.

III. Supplementation of the diet of lactating women with cod-liver oil and yeast diminished the above-mentioned faecal excretion of calcium and led to general improvement in the assimilation of both calcium and phosphorus. Nitrogenous metabolism was not affected by the dietary supplements.

C. R. HARRINGTON.

**Retention of nitrogen, calcium, phosphorus, and magnesium by pregnant women.** C. M.

COONS and K. BLUNT (J. Biol. Chem., 1930, 86, 1—16).—Although considerable individual variations were observed, there was a general tendency for the retention of calcium and phosphorus by pregnant women to increase in the middle and later stages of pregnancy. The retention of calcium was not affected by variation in the intake of magnesium. Nitrogen retention varied with the intake of protein, but was usually highest in the middle period of pregnancy, whilst the increase in calcium retention was most marked towards the end.

C. R. HARINGTON.

**Diet and calcium assimilation. XIII. Influence of irradiated yeast on the calcium and phosphorus metabolism of milking cows.** E. B. HART, H. STEENBOCK, O. L. KLINE, and G. C. HUMPHREY (J. Biol. Chem., 1930, 86, 145—155).—Addition of irradiated yeast to the diet of milking cows produced no change in the assimilation of calcium and phosphorus or in the quality or quantity of the milk.

C. R. HARINGTON.

**Physiological effect of rations restricted principally or solely to lucerne. I. Calcium, phosphorus, and nitrogen metabolism of dairy cattle.** J. R. HAAG, J. S. JONES, I. R. JONES, and P. M. BRANDT (J. Dairy Sci., 1929, 12, 445—455).—Cows in early lactation were always in negative phosphorus balance, were usually in positive calcium balance, and were in negative nitrogen balance when the hay contained less than 2% N on feeding lucerne hay alone. Addition of disodium hydrogen phosphate caused a slight positive phosphorus balance.

CHEMICAL ABSTRACTS.

**Iodine metabolism.** C. NEWCOMB and G. SANKARAN (Trans. F. E. A. T. M. Congr., 1927, 329—334).—Iodine excretion per litre of urine under normal conditions is constant. Daily total excretion is chiefly dependent on the amount of urine excreted. It can be raised by increasing the amount of urine, but it is not reduced much below the normal on days of starvation when the iodine content of urine becomes higher.

T. R. SESHADRI.

**Salt licks.** C. NEWCOMB (Trans. F. E. A. T. M. Congr., 1927, 450—452).—From analysis of samples of salt licks from different parts of South India it is shown that the essential constituent is neither sodium nor iodine.

T. R. SESHADRI.

**Influence of a low-fat diet on fat metabolism during lactation.** L. A. MAYNARD and C. M. MCKAY (J. Nutrition, 1929, 2, 67—81).—A ration low in fat content diminished the volume of milk secreted by cows and goats without significantly altering its fat content, and diminished the blood-lipins. The fat had a lower iodine value than normally.

CHEMICAL ABSTRACTS.

**Relation of lipins to physiological activity. I. Changes in the lipin content of the corpus luteum of the sow.** W. R. BLOOR, R. OKEY, and G. W. CORNER (J. Biol. Chem., 1930, 86, 291—306).—The lipins of the corpus luteum of the sow have been studied during the cycle of changes of the tissue. The phospholipin content increases with the growth of the tissue to the period of maximum activity; if

pregnancy ensues, the high level of phospholipin is maintained; otherwise it falls off with the degeneration of the corpus luteum. The free cholesterol content increases slightly during the development of the corpus luteum, and remains constant while the latter is active. The cholesteryl ester content remains constant during development of the corpus luteum and increases during degeneration; in pregnancy it falls to a low level.

C. R. HARINGTON.

**Variations in lipins of uterine mucosa of the pig.** R. OKEY, W. R. BLOOR, and G. W. CORNER (J. Biol. Chem., 1930, 86, 307—314).—The total lipin content of the pig's uterine mucosa in the resting condition is (calculated on the dry weight) about the same as that of ox lung, kidney, and pancreas. Proliferation of the tissue is accompanied by increase in the percentages of lecithin and of free cholesterol, whilst the small amount of cholesteryl esters shows no change.

C. R. HARINGTON.

**Nature of the liver-fat and subcutaneous fat produced in animals kept in low-pressure atmospheres.** G. MONASTERIO (Biochem. Z., 1930, 218, 331—340).—Guinea-pigs fed on hay and carrots were kept for 3 days in air at pressures of 330—300 mm. and then their liver-fat and subcutaneous fat were extracted successively with acetone, ether, and alcohol. The phosphorus, nitrogen, and (where possible) cholesterol contents of the extracts were determined, as were also their iodine, saponification, and acid values. Compared with the fats of normal animals those of the experimental animals showed no qualitative differences, but the liver-fats of the experimental animals contained increased amounts of neutral fat (soluble in acetone), of phosphatide, and (probably) of cholesterol.

W. MCCARTNEY.

**Effect of ingestion of sodium tartrate by normal and pathological animals.** E. AUBEL and P. MAURIAC (Bull. Soc. Chim. biol., 1930, 12, 112—127).—Ingestion of tartrate is followed by excretion of carbonates, due probably to the combustion of pyruvic acid arising from tartaric acid under the action of intestinal bacteria. Tartrate did not appear to be toxic even to the dog, which was more sensitive than either man or rabbit, no albuminuria or change of urinary volume being detected.

P. W. CLUTTERBUCK.

**Perfusion of sugar through the tortoise.** F. LIEBEN and G. EHRLICH (Biochem. Z., 1930, 219, 145—147).—When dextrose and laevulose each in 0.25% solution are simultaneously perfused, both sugars are utilised, a greater amount of laevulose than of dextrose disappearing. Since, however, laevulose may be partly converted into dextrose and the latter may be liberated from the liver as a result of stimulation during the experiment, a strict comparison of the rate of utilisation of the two sugars is not possible (cf. A., 1928, 1276).

P. W. CLUTTERBUCK.

**Relationship between lactic acid and carbohydrate in isolated liver tissue.** A. CARRUTHERS (Chinese J. Physiol., 1930, 4, 65—71).—Sections of liver tissue (of rat) respiring in an atmosphere of oxygen and placed in buffered Ringer solution do not bring about a synthesis of carbohydrate from added



lactic acid. The results are not in accord with those of Takane (A., 1926, 754) on isolated liver-tissue and of Cori and Cori (A., 1929, 467) on the intact animal. The carbohydrate systems of muscle and liver are compared. F. O. HOWITT.

**Oxidative breakdown of carbohydrates in mammalian muscle, and especially the formation of succinic from pyruvic acid.** E. TOENNIESSEN and E. BRINKMANN (Z. physiol. Chem., 1930, 187, 137—159).—The muscular system of the rabbit was perfused with a solution of pyruvic acid. With free access of oxygen 75% of the pyruvic acid disappeared in 1 hr. Acetic and succinic acids were detected neither in the muscle nor in the perfusion liquid. Formic acid was the only decomposition product observed. Similar results were obtained with restricted oxygen supply as regards the liquid, but succinic acid was now present in the muscle and larger amounts of formic acid, but no acetic, fumaric, or malic acid. When Ringer solution alone was employed, only small amounts of formic acid were detected in the perfusion fluid. Perfusion with acetic acid does not yield succinic acid; the formation of the latter cannot therefore take place by way of acetic acid. A primary oxidation and condensation of 2 mols. of pyruvic acid giving a diketoadipic acid is suggested. J. H. BIRKINSHAW.

**Hexosediphosphate in muscle activity.** N. E. FREEMAN (Amer. J. Physiol., 1930, 92, 107—116).—The presence of sodium hexosediphosphate in the Ringer solution perfusing a frog's heart increases the muscular efficiency, but this is probably due only to the increased buffering action of the ester.

E. BOYLAND.

**Behaviour of pyrophosphoric acid and of lactacidogen in muscular work.** G. EMBDEN, J. HEFTER, and M. LEHNARTZ (Z. physiol. Chem., 1930, 187, 53—83).—Changes in the phosphoric acid content of the frog's gastrocnemius after electrical stimulation were followed. After stimulation until no further contraction occurred, resting in oxygen produced an increase in pyrophosphoric acid, but no increase in lactacidogen as compared with the fatigued muscle. The increase in pyrophosphoric acid was often far greater than corresponded with the amount of orthophosphoric acid disappearing. With stronger stimulation there was no increase in pyrophosphoric acid after resting. Of loaded and unloaded muscles undergoing contraction by immersion in liquid air, the hydrolysed extract from the loaded muscle contains more orthophosphoric acid. There is evidence for a fission of adenylic or inosic acid at the moment of contraction and probably also a corresponding increase of pyrophosphoric acid (or the adenylic acid complex). J. H. BIRKINSHAW.

**Utilisation of the energy of oxidation of alcohol in muscular work.** W. FLEISCHMANN (Biochem. Z., 1930, 219, 7—29).—The respiratory quotient of isolated frog's muscle was, in the normal condition 1.06, and in presence of alcohol 0.87. Skeletal, heart, and smooth muscle pulps (of guinea-pig, dog, etc.) are able, in presence of a fixing agent, to oxidise alcohol to acetaldehyde, the reaction being completely inhibited by 0.002*N*-hydrogen cyanide. In

the absence of a fixing agent, the aldehyde is further oxidised. The oxidation energy of these reactions is utilised in the aerobic phase of the contraction process, the muscle thus being able to use directly a substance other than carbohydrate.

P. W. CLUTTERBUCK.

**X-Ray diagram of muscle contraction.** G. BOEHM and K. F. SCHOTZKY (Naturwiss., 1930, 18, 282).—By an improved method of X-ray photography by which photographs may be obtained with very brief exposures (Siemann and Schotzky, this vol., 138, 299), X-ray diagrams of living muscle in a state of rest and of excitation, as well as diagrams of dried muscle, have been obtained and compared.

M. S. BURR.

**Glycogen and carbohydrate reserves of the fasting animal.** H. BIERRY (Compt. rend., 1930, 190, 649—651).—Experiments with dogs kept on water only show that in general after 28 days, glycogen is present in the liver (1.48%) and in the muscles (0.15%). In two cases only, in which the percentage of free sugar in the blood was very low and that of protein-sugar very high, glycogen had almost disappeared from the liver and muscle. Similar experiments with frogs after 2½ months' fast indicate that the liver contains 2% and muscle 0.30% of glycogen; if the fast was prolonged to the extreme limit the figures became 0.30% and 0.10% of glycogen, respectively. C. W. SHOPPEE.

**Effect of deprivation or absorption of water on metabolism in starvation.** V. AXENOV (Z. Biol., 1930, 90, 50—56).—The body-weight rises slightly on the intake of water during starvation owing to retention by the tissues. The urine-nitrogen rises (both in deprivation and absorption of water) from less than 1% to 2.25%, but the total volume secreted in 24 hrs. increases only slightly after drinking 1—2 litres of water. Uric acid excretion is slightly greater during the periods of water absorption, whilst sodium chloride excretion is but little affected. Acetone excretion is somewhat variable. P. G. MARSHALL.

**Electrolyte content and chemical composition of frog nerve and the changes produced by stimulation.** F. ROEDER (Biochem. Z., 1930, 218, 404—411).—Nerves from the frog were electrically stimulated for 4—8 hrs. and the potassium, calcium, nitrogen, and phosphorus contents of the various portions of the nerves were then determined. In the portions nearest to the place of stimulation the amounts of potassium and calcium had decreased after stimulation, whilst in the portions nearer to the muscles the amounts of these elements had increased. In both stimulated and unstimulated nerves there was more phosphorus and more nitrogen in the distal than in the proximal portions. The nitrogen content of the nerves did not change as a result of stimulation, but this caused an increase in the phosphorus content of their middle portions. In different batches of nerves considerable differences, both in the total content of electrolytes and in the way in which they were distributed in the fibres, were found.

W. MCCARTNEY.

**Metabolism of sulphur. XVII. Rate of oxidation of cystine in the rabbit.** G. STEARNS and

H. B. LEWIS (J. Biol. Chem., 1930, 86, 93—105).—After oral administration of cystine to rabbits 60—80% of the sulphur is excreted as inorganic sulphate within 24 hrs. After subcutaneous injection of cystine a similar result is observed if absorption be slow; if absorption be rapid a large part of the cystine is excreted in the urine unchanged, sometimes with accompanying pathological changes in the kidney.

C. R. HARRINGTON.

**Copper salts in nutrition.** J. M. EVVARD, V. E. NELSON, and W. E. SEWELL (Proc. Iowa Acad. Sci., 1928, 35, 211—215).—Copper fed to rats and pigs as sulphate plays an important part in promoting growth. Storage of copper is chiefly confined to the liver.

CHEMICAL ABSTRACTS.

**Quantitative relations of the dry matter of the food consumed, the heat produced, the gaseous outgo, and the insensible loss in body-weight of cattle.** M. KRISS (J. Agric. Res., 1930, 40, 283—295).—A mathematical analysis of the results of biometrical studies leads to the conclusion that for practical purposes the dry matter of the feed of steers and cows is a better basis for predicting the heat production of the cattle than would be the insensible loss in body-weight.

E. HOLMES.

**Dietary properties of the flat bean (*Dolichos lablab*, L.).** T. T. CHEN (Chinese J. Physiol., 1930, 4, 73—77).—Feeding experiments with rats show that when fed at a level of 55—60%, the bean does not promote normal growth. Deficiencies in protein quality, mineral salts, and vitamins A and B are shown by control experiments.

F. O. HOWITT.

**Nutritive value of milk.** III. Supplementary value of various constituents of synthetic basal rations. W. E. KRAUSS (J. Dairy Sci., 1929, 12, 438—444).—An exclusive milk diet fed to rats is deficient in copper and iron; prevention of nutritional anaemia by supplementary foods was in general parallel to the copper and iron content. Cod-liver oil, gelatin, rice polishings, wheat germ oil, and irradiated milk were ineffective.

CHEMICAL ABSTRACTS.

**Deaminocaseinogen.** II. H. STEUDEL (Z. physiol. Chem., 1930, 187, 203—206; cf. A., 1929, 1188).—Rats fed on a complete diet in which deaminocaseinogen replaces caseinogen showed a decline in weight. Growth was not improved by addition of lysine to the ration, which was refused by dogs after the first day.

J. H. BIRKINSHAW.

**Biological value of the proteins of barley, rice, kaoliang, and millet.** T. W. LI (Chinese J. Physiol., 1930, 4, 49—58).—The biological values (100 × nitrogen retained/nitrogen absorbed) of cereal proteins common in North China were determined by the method of Mitchell (A., 1924, i, 453). For rice, barley, millet, and kaoliang at a level of 10% intake, the values are 77, 64, 57, and 56, respectively (cf. 52 for white flour; Mitchell and Carman, A., 1926, 754).

F. O. HOWITT.

**Nutritive value for rats of a pure flesh diet, prepared from raw, cooked, and autoclaved muscle.** A. SCHEUNERT and H. BISCHOFF (Biochem. Z., 1930, 219, 186—197).—Feeding experiments lasting more than 200 days were carried out using young

white rats and a diet consisting of salts, vitamins, and flesh both raw, cooked for 1.5 hrs., and autoclaved for 1 hr. at 1 and 4 atm. with and without addition of caseinogen. No decisive differences were obtained between raw and cooked flesh, and addition of caseinogen had but slight effect. Addition of salts and vitamins does not make flesh a complete diet, but the normal method of cooking does not decrease the food value of the flesh.

P. W. CLUTTERBUCK.

**Action of sodium chloride on nitrogen metabolism.** E. F. TERROINE and T. REICHELT (Compt. rend., 1930, 190, 768—770).—Administration of sodium chloride (0.1 g. of sodium per kg. body-weight per day) to the rabbit, sheep, and pig generally causes an increase in the nitrogen retention and, hence, growth of the animal. The ratio K:Na in the food-stuff should not exceed 3.

H. BURTON.

**Growth of infants from the point of view of physical measurements and of nitrogen metabolism.** II. Creatine. III. Uric acid. A. L. DANIELS and L. M. HEJINIAN (Amer. J. Dis. Children, 1929, 38, 499—506, 507—512).—Increase in creatine excretion is associated with increase in the amount of protein ingested and with increase of urinary nitrogen, but not with age, muscle development, or volume of urine. Excretion of uric acid increases with height and age, but is apparently not related to the amount of protein ingested or to the urinary creatinine.

CHEMICAL ABSTRACTS.

**Embryochemical investigations with the injection method.** II. Carbamide formation in the hen's embryo. J. KAIEDA. III. Behaviour of cholesterol in the incubated hen's egg after adrenaline and ephedrine injections. K. KUSUI (Z. physiol. Chem., 1930, 187, 207—209, 210—213; cf. A., 1929, 1334).—II. Hens' eggs were injected with amino-acids and incubated for 16 days. In all cases except with cysteine and serine injections there was an increase of carbamide. Ammonium carbamate produced an increase but the carbonate gave none.

III. Hens' eggs fresh and at varying periods of incubation were injected with 0.1 c.c. of 0.1% adrenaline or of 4% ephedrine solution and the free cholesterol and cholesteryl ester were determined after further incubation. Both adrenaline and ephedrine considerably increased the free cholesterol partly at the expense of the ester, the total cholesterol showing a slight increase over the controls.

J. H. BIRKINSHAW.

**Comparative influence of sunlight, iron preparations, and vitamins in the maintenance of health.** C. C. PALIT, R. K. KAUL, and N. R. DHAR (J. Physical Chem., 1930, 34, 737—742).—Pigeons and rats receiving sunlight but no vitamin-A, -B, or -C and fed on polished rice maintained good health for three weeks. Without sunlight stomacheic and eye troubles developed as well as polyneuritis and paralysis. Leafy vegetables and tomatoes are less effective than sunlight in preventing these diseases but colloidal ferric hydroxide and ferric chloride are as effective as the vegetables.

L. S. THEOBALD.

**Origin of light erythema.** F. ELLINGER (Arch. exp. Path. Pharm., 1930, 149, 343—347).—Extracts prepared from pig skin in the normal condition and

after ultra-violet irradiation, when tested as to their effect on the blood-pressure of the cat and on the surviving guinea-pig intestine, showed no significant difference. The experiments fail to support, but do not disprove, the view that a histamine-like substance is responsible for the erythema following irradiation.

W. O. KERMACK.

**Permeability of surface of marine animals.** A. BETHE (J. Gen. Physiol., 1930, 13, 437—444).—Observations on changes of body-volume and chlorine content of blood with the common crab and sea-slug in sea-water diluted with distilled water or with a solution of non-electrolyte isotonic with sea-water show that their surfaces are permeable not only to water but also to both salts and their ions. It is concluded that their skins serve only as a protecting barrier preventing loss of body-colloids.

T. R. SESHADRI.

**Isoelectric point and diffusion potential of ions in a living body.** T. SHITO (Hokkaido J. Med., 1929, 7, 297—304).—The isoelectric point of cow's bladder is  $p_{H}$  5.58—5.81. CHEMICAL ABSTRACTS.

**Penetration of methylene-blue into living cells.** M. M. BROOKS (Nature, 1930, 125, 599).—A reply to Irwin (A., 1928, 793). It is maintained that under carefully controlled conditions methylene-blue as such penetrates normal living cells. L. S. THEOBALD.

**Catalytic effect of dyes on oxygen consumption of living cells.** E. S. G. BARRON and Z. A. HOFFMAN (J. Gen. Physiol., 1930, 13, 483—494).—Dyes which can be reversibly oxidised and reduced act as catalysts for some oxidative processes taking place in the living cells, as is manifested by an increase in their oxygen consumption. The catalytic power is conditioned by the reduction potential of the dye and the permeability of the cell surface. When the reduction potential of the dye is towards the positive side of the aerobic reduction potential of the cell the catalytic power is maximum and when towards the negative side the catalytic power decreases and disappears. When a dye cannot penetrate into the cell, its effect is greatly diminished as in this case only those processes taking place at the outer surface can be activated.

T. R. SESHADRI.

**Distribution of bromine in the organism.** M. A. B. TOXOPÉUS (Arch. exp. Path. Pharm., 1930, 149, 263—273).—Sodium bromide administered by mouth to dogs is accumulated chiefly in the muscle (37%), skin (16%), and blood (9%). The ratio of bromide to chloride is highest in the muscles. A method for the determination of bromine and chlorine in animal organs is described. W. O. KERMACK.

**Distribution of thorium in the animal organism.** G. VON HEVESY and O. H. WAGNER (Arch. exp. Path. Pharm., 1930, 149, 336—342).—After subcutaneous administration of thorium nitrate to mice about 99% of the thorium is excreted in 9 days, of which 36% is in the faeces and 64% in the urine. Bismuth is taken up selectively by malignant tumours, but not thorium or lead.

W. O. KERMACK.

**Action and excretion of nitrates.** N. M. KEITH, M. WHELAN, and E. G. BANNICK (Proc. Staff Mayo

Clinic, 1929, 4, 362).—Ingestion of sodium or ammonium nitrate (10 g. daily for 4—5 days) is followed by immediate urinary excretion of 75% of the nitrate, the total eventual excretion being 90%; blood-nitrate varies from a trace to 2—3 mg. per 100 c.c. Diuresis causes an increased excretion of chlorine, ammonia, and total fixed base. Excretion of urea is increased.

CHEMICAL ABSTRACTS.

**Iodinated proteins.** J. SCHWAIBOLD (Biochem. Z., 1930, 218, 355—360).—Products formed from iodinated protein material by the successive action of pepsin and trypsin act on tadpoles in the same way as do active thyroid preparations or large doses of 3:5-di-iodotyrosine. The iodine in the products is mainly organic and does not behave towards nitrous acid or hydrogen peroxide as does the iodine in the original material.

W. MCCARTNEY.

**Action of purine bases on the pupil.** J. ETTINGER (Russ. J. Physiol., 1929, 12, 631—641).—Preparations containing caffeine, theobromine, theophylline, and uric acid have a dilating action on the isolated frog's eye, which in the case of caffeine is proportional to the concentration of the compound. The method for determining the concentration of adrenaline in blood by means of its action on the isolated frog's eye may therefore be vitiated by the presence of purine bases in the blood.

W. O. KERMACK.

**Toxicity of vapours of cyclopentane and its homologues.** N. V. LAZAREV and S. N. KREMEVA (Arch. exp. Path. Pharm., 1930, 149, 116—118).—The toxicities of cyclopentane and of its methyl, ethyl, and propyl derivatives on white mice are comparable to those of the open-chain hydrocarbons containing a similar number of carbon atoms.

W. O. KERMACK.

**Detoxication of chloroform.** H. FÜHNER (Deut. med. Woch., 1929, 55, 1331—1332; Chem. Zentr., 1929, ii, 2476).—The toxic after-effect of chloroform, which is attributed to an oxidation product formed by the organism, is diminished by using chloroform containing 10% of alcohol, and by previous oral administration of alcohol, whereby the stability of the chloroform is increased. Possibly anti-catalysts, such as cysteine, insulin, sugar, etc., arrest the oxidation.

A. A. ELDRIDGE.

**Effect of ethyl alcohol on the growth of chicks.** W. E. ELHARDT (Amer. J. Physiol., 1930, 92, 450—452).—Chicks receiving 15% of alcohol in their diet grew faster than controls.

E. BOYLAND.

**Work of the heart in absence of oxygen.** V. Inhibition of the action of hydrocyanic acid by dihydroxyacetone and glyceraldehyde. H. CASER (Arch. exp. Path. Pharm., 1930, 149, 240—246).—The poisoning effect of hydrocyanic acid on the heart, as well as the stopping of the respiration of bird erythrocytes, is removed by dihydroxyacetone and glyceraldehyde. They do not act in absence of oxygen. These substances act by removing hydrocyanic acid through cyanohydrin formation.

T. R. SESHADRI.

**Is the inhibition of caffeine action on muscle by sodium salicylate and novocaine hydrochloride due to complex formation?** K. ZIPF (Z. physiol.

Chem., 1930, 187, 214—228).—The increase in solubility of caffeine produced by certain salts runs parallel with the change in the partition coefficient chloroform/water, but not with the f. p. changes. The specific conductivity of the salts is only slightly lowered by caffeine. These facts indicate that complex formation does not occur. The decrease in f.-p. depression of a sodium salicylate solution is accounted for largely by polymerisation of the caffeine molecules and to a smaller degree by the formation of slightly dissociated caffeine salicylate as evidenced by the slight decrease in electrical conductivity. Caffeine behaves similarly in novocaine hydrochloride. The novocaine base probably polymerises also in novocaine hydrochloride, thus increasing its solubility. J. H. BIRKINSHAW.

**Effect of some tetanic poisons on sugar and lactic acid content of blood.** M. BÖMER (Arch. exp. Path. Pharm., 1930, 149, 247—256).—As had been observed with picrotoxin and santonin, simultaneous increase of sugar and lactic acid in blood was established in the case of "cardiazol" and in some experiments with cocaine. With cocaine a regular influence could not be detected. "Hexetone," strychnine, and caffeine partially lower the blood-lactic acid; the blood-sugar curve is not affected.

T. R. SESHADRI.

**Pharmacology of xysmalobinum.** J. M. WATT (J. Pharm. Exp. Ther., 1930, 38, 261—270).—Xysmalobinum, a glucoside from the root of *Xysmalobinum undulatum*, has a digitalis-like action on the heart, contracts smooth muscle, stimulates the secretion of saliva, and produces a marked diuresis in the rabbit.

W. O. KERMACK.

**Blood composition of animals under pathological conditions. II. Experiments with lupins.** A. A. HORVATH (J. Pharm. Exp. Ther., 1930, 38, 303—311).—Sheep to which 20 g. of lupin flour were administered per day for 2 months showed no toxic symptoms, but had a blood-sugar value below normal. Similar effects on the blood-sugar were observed in the case of hens, and in these cases the blood-uric acid was generally raised. In rabbits, administration of sparteine sulphate decreases the blood-sugar and increases the blood-creatinine.

W. O. KERMACK.

**Inactivation of catalase. II. Inactivation by ultra-violet irradiation at varying  $p_H$ .** S. MORGULIS [with L. SHUMAKER] (J. Biol. Chem., 1930, 86, 75—85).—At  $p_H$  6—8 the inactivation of catalase by ultra-violet irradiation proceeds at a uniform rate; at more acid or alkaline reactions the initial rate of inactivation diminishes considerably with lapse of time; in fact, at  $p_H$  11.0 this effect is so pronounced that the enzyme is actually stabilised against the inactivating action of the irradiation. The conclusions of Pincussen (A., 1926, 432) are criticised.

C. R. HARRINGTON.

**Effect of  $p_H$  value on the inactivation temperature of fruit oxidase.** W. Y. FONG and W. V. CRUESS (Plant Physiol., 1929, 4, 537—541).—Resistance to heat was greatest at  $p_H$  5—7; at  $p_H$  2—2.2 or 12 the peroxidase was inactivated at the ordinary temperature in 12 hrs. or less.

CHEMICAL ABSTRACTS.

**Insoluble tyrosinase of the velvet-bean seed coat.** E. R. MILLER (Plant Physiol., 1929, 4, 507—517).—The enzyme may be a peroxide.

CHEMICAL ABSTRACTS.

**Dextrins. I. Action of amylase from cholam (*Sorghum vulgare*) on potato starch.** V. N. PATWARDHAN (J. Indian Inst. Sci., 1930, 13A, 31—37).—Four different dextrins have been isolated from the products of the action of the amylase of cholam on potato starch. Dextrin I, isolated from the reaction mixture when it just failed to give a purple colour with iodine, has  $[\alpha] +174.0^\circ$ . Dextrin II, obtained after about 80% of starch had been converted into maltose and equilibrium established, has  $[\alpha] +155.9^\circ$ . Dextrins III and IV were isolated by acting on starch for 16 hrs. with alcohol-dried amylase from ungerminated cholam, when 66% of non-saccharine solids were obtained and separated into two fractions, of which one, dextrin III,  $[\alpha] +170.6^\circ$ , was non-reducing and the other, dextrin IV,  $[\alpha] +184.2^\circ$ , was feebly reducing. Dextrins I and II dissolved in cold, but dextrins III and IV only in boiling water. The dextrins were hydrolysed by the enzymes from malted and ungerminated cholam, the latter attacking them more readily. W. O. KERMACK.

**Dextrins. II. Amylase from Ragi (*Eleusine Coracana*).** V. N. PATWARDHAN and N. NARAYANA (J. Indian Inst. Sci., 1930, 13A, 38—41).—The amylase of Ragi malt which is more active than that from cholam malt or maize malt, but less than that from malted barley, has optimum activity at 55—60°, but does not lose its activity very rapidly at higher temperatures. The optimum reaction is at  $p_H$  4.86—5.07. The enzyme loses its activity when dialysed at 0—3° in presence of toluene, and it is not reactivated by the addition of salt, buffer solutions of known  $p_H$ , or asparagine, nor by the addition of boiled undialysed enzyme. W. O. KERMACK.

**Influence of aliphatic amines and their hydrochlorides on the amylolytic activity of saliva and pancreatin.** F. CAUJOLLE and J. MOLINIER (Compt. rend., 1930, 190, 695—696).—A continuation of the work of Desgrez and Moog (A., 1921, i. 282). The action of methyl-, ethyl-, *n*-propyl-, isobutyl-, isoamyl-, allyl-, dimethyl-, diethyl-, trimethyl-, and triethyl-amines on the amylolytic activity (1% starch solution) of human saliva and glycerinated pancreatin is one of inhibition, and decreases with increase of mol. wt. of the amine. Ethylamine, however, is exceptional, being much more powerful than methylamine. The amine hydrochlorides, on the contrary, increase the hydrolytic action, the effect again diminishing with increase of mol. wt. These amines do not destroy the amylases, for if they are converted in the reaction medium into their hydrochlorides, the enzyme assumes the enhanced activity due to the latter. H. A. PIGGOTT.

**Influence of ultra-violet light on invertase. I. Ultra-violet spectra of invertase of varying degree of purity.** G. GORBACH and K. LERCH (Biochem. Z., 1930, 219, 122—135).—The ultra-violet spectra of various invertase preparations show an absorption band at 270  $\mu\mu$ , the sharpness of which is greatest in autolysates and decreases with decrease of purity.

Irradiation sufficient to inactivate the preparations does not appreciably change the absorption. Pure tryptophan shows a similar absorption at 270  $\mu$  and the absorption of the enzyme preparations must be ascribed to their tryptophan content. Tryptophan carries the enzymically active group and to some extent protects it from the action of ultra-violet light.

P. W. CLUTTERBUCK.

**Enzymic breakdown of carbohydrate.** R. NILSSON (Arkiv Kemi, Min., Geol., 1930, 10, A, No. 7, 135 pp.).—In the case of yeast and of muscle, the effect of sodium fluoride is to cause reactions to proceed as in the absence of co-zymase. In the presence of sodium fluoride esterification of dextrose to hexosephosphate is not brought about by dried yeast, but both in yeast and in muscle the preformed glycogen is esterified to yield hexosephosphates. In the case of yeast the inorganic phosphate which disappears is quantitatively accounted for as crude hexosemonophosphate, essentially identical with Robison's ester. This esterification is approximately proportional to the extent of autofermentation of the yeast when zymase is present and practically zero in zymase-free preparations. In presence of sucrose and sodium fluoride an increased production of hexosemonophosphate occurred. No evidence could be obtained of the participation of Robison's ester in the synthesis of liver-glycogen. Galactose was esterified by a dried yeast suitable for fermenting that sugar, the products being a hexosediphosphate identical with Harden's ester and a new *hexosemonophosphate* (barium salt,  $[\alpha]_D^{20} + 48.3^\circ$ ; *strychnine* salt,  $[\alpha]_D^{20} - 26^\circ$ ). Esterification of dextrose unaccompanied by production of carbon dioxide occurs in the presence of sodium fluoride, provided hexosediphosphate is added, the degree of esterification being approximately proportional to the quantity of hexosediphosphate present, provided the concentration of the latter is small. The ester formed was levorotatory. Certain yeasts ferment dextrose readily but do not attack acetaldehyde. The property of attacking acetaldehyde also appears to be related to that of autofermentation, and in the case of a yeast which does not undergo autofermentation and so does not attack acetaldehyde, the addition of hexosediphosphate with dextrose brings about rapid utilisation of acetaldehyde at first. If sodium fluoride is also added so as to depress fermentation, utilisation of acetaldehyde continues for a longer time. In this way fermentation mixtures were obtained in which the rate of utilisation of acetaldehyde was comparable with the rate of fermentation. Of the acetaldehyde which disappears more than 90% is found as alcohol, acetic acid not being detected. Accompanying the disappearance of acetaldehyde was a considerable esterification of phosphate with the formation of a compound having the composition of a *monophosphoglyceric acid*,  $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OPO}_3\text{H}_2)\cdot\text{CO}_2\text{H}$  (?) (barium salt,  $[\alpha]_D^{20} - 11.1^\circ$ ; *strychnine* salt,  $[\alpha]_D^{20} - 21.6^\circ$ ). Similar relations hold for the transformation of acetaldehyde by dry muscle. Acetaldehyde is not attacked by dry yeast in the absence of phosphate, even although dextrose and hexosediphosphoric acid are also present; arsenate can take the place of phosphate. Whilst, however, the phosphate disappears in the course of the

utilisation of the acetaldehyde, no decrease in the quantity of arsenate present could be observed. Fluorides and oxalates exert no influence on pyruvic acid fermentation.

W. O. KERMACK.

**Mechanism of changes in phosphorus compounds in muscle autolysis.** D. FERDMANN (Z. physiol. Chem., 1930, 187, 160—170).—In autolysis of pigeon's breast-muscle ground up with quartz sand ortho- and pyro-phosphoric acid disappear, giving rise to hexosemonophosphoric acid. In autolysis of minced muscle of rabbits and pigeons in presence of lactate ions, inorganic phosphoric acids disappear and the reducing power of the precipitate of phosphorus compounds is lowered. In autolysis in presence of fluoride or of starch, the inorganic phosphoric acids disappear, but the precipitate of phosphorus compounds, which is non-reducing in the case of fluoride, has increased reducing power in the case of starch. The possibility of the formation of a new series of phosphorus compounds is indicated.

J. H. BIRKINSHAW.

**Effect of various substances of the quinine group on the enzymic functions of the organism.**  
**XIII. Peptic digestion of muscle-protein in presence of quinine.** J. A. SMORODINCEV and E. A. SVESCHNIKOVA (Biochem. Z., 1930, 218, 269—282; A., 1929, 848).—The peptic digestion of muscle-protein (ox) is inhibited by the chlorides of sodium and potassium and by quinine hydrochloride in 0.025*M*-concentration, the effect of quinine hydrochloride being more powerful than that of the other chlorides. Neither quinine hydrochloride (0.1—0.001%) nor sodium or potassium chloride (0.015—0.019% or 0.00015—0.00019%) influences the peptic digestion of myosin, but more concentrated solutions of quinine hydrochloride (0.6—1.0%) have an inhibiting effect, since they shift the reaction of the medium from the optimum for the action of pepsin. At 38° muscle-protein is digested by pepsin three times as fast as egg-albumin.

W. MCCARTNEY.

**Specificity of animal proteases.** **XVIII. Proteolytic system in animal organs.** E. WALDSCHMIDT-LEITZ, A. SCHÄFFNER, J. J. BEK, and E. BLUM (Z. physiol. Chem., 1930, 188, 17—47; cf. A., 1929, 1338).—Enzyme solutions from fresh animal organs were prepared and the activities determined. Cathepsin from spleen or liver activated by hydrogen sulphide (which gives the maximum activity) had a  $p_H$  optimum of 4 on gelatin. Catheptic polypeptidase on benzoylglucylglycine had a  $p_H$  optimum of 4.2. The reaction was linear. Aminopolypeptidase on *dl*-leucylglucylglycine had an optimum  $p_H$  of 8.0 and linear reaction. The natural activator of cathepsin (zookinase) was most easily separated by making use of its solubility in 70% aqueous alcohol or acetone. The zookinase content of organs increases on autolysis. Cathepsin is completely activated by hydrogen cyanide or hydrogen sulphide. Since it is difficult to obtain the catheptic free from the ereptic enzymes, it is preferable to inhibit the latter by mercuric chloride, hydrogen sulphide, or hydrogen cyanide. Cathepsin may be freed from catheptic polypeptidase by making use of the greater stability of the former at  $p_H$  3.5 or by selective adsorption of the latter with

ferric hydroxide at  $p_{\text{H}}$  3.8. The ereptic enzymes are prepared by adsorption on aluminium hydroxide; elution gives aminopolypeptidase and dipeptidase free from catheptic action. The dipeptidase is more readily adsorbed by ferric hydroxide; separation of the two enzymes is thus effected. The activity and specificity of similar enzymes of animals and plants are compared. J. H. BIRKINSHAW.

**Homogeneity of intestinal dipeptidase.** K. LINDERSTRÖM-LANG (Z. physiol. Chem., 1930, 188, 48—68).—By means of affinity measurements it is shown in the hydrolysis of alanyl- and leucyl-glycine that the relative enzyme concentration can be determined with some degree of exactitude. The action of inhibitors can probably be neglected. The previous conception of the presence of two distinct enzymes in intestinal erepsin is substantiated. Peptidase II is probably to be regarded as a "leucyl-peptidase" which hydrolyses any leucylpeptide. A method for the determination of the relative affinity of an enzyme towards two substrates depends on a comparison of the hydrolysis of each substrate separately, and of the mixture. The affinity of peptidase I for leucylglycine is probably 16 times that for alanyl-glycine. As a measure of fission titration of the amino-groups with hydrochloric acid in acetone to naphthyl-red was employed. J. H. BIRKINSHAW.

**Purification of urease by crystallisation and the elementary composition of the crystals.** J. B. SUMNER (Ber., 1930, 63, [B], 582—586; cf. A., 1928, 329, 1401).—Extraction of jack-bean meal from specially selected stock by the process described previously (A., 1926, 1061) permits the isolation of crystals of very high urease activity which increases somewhat after one, two, or three re-dissolutions, whereas a decrease in activity would be expected if the activity were caused by accompanying or adsorbed urease. Two such highly active specimens, re-dissolved once and twice respectively, proved to be proteins on the basis of elementary analysis. H. WREN.

**Mechanism of urease activation.** H. MÜNCH (Z. physiol. Chem., 1930, 187, 241—251).—The dissociation constant of the urease-substrate complex was 0.007—0.009. The value was unchanged on addition of hydrocyanic acid or glycine, although the reaction velocity was more than doubled. This indicates that no enzyme-activator complex is formed which exhibits a higher affinity for carbamide than the unactivated enzyme, but does not preclude the removal of an inhibitor by the activator.

J. H. BIRKINSHAW.

**Mechanism of urease action.** O. AMBROS and H. MÜNCH (Z. physiol. Chem., 1930, 187, 252—263).—The following substances, each containing a group similar in structure to some part of the carbamide molecule in its various possible forms, were found to have no effect on the dissociation constant of the urease-carbamide complex: thiocarbamide, methyl-carbamide, *s*- and *as*-dimethylcarbamide, guanidine carbonate, succinimide, acetophenone, acetamide, glycerol, mannitol, ethylene glycol, betaine hydrochloride. J. H. BIRKINSHAW.

**Fermentation in maceration juice.** S. KOSTYTSCHEV (Biochem. Z., 1930, 218, 402—403).—A reply

to Lebedev (this vol., 113) and a criticism of his procedure. W. MCCARTNEY.

**Survival of dried yeast.** N. A. KRASSILNIKOV (Z. physiol. Chem., 1930, 187, 277—280).—Zymin preparations produced by prolonged treatment of yeast with water-free acetone or alcohol and ether show a considerable number of cells capable of growth as evidenced by colony formation on beer-wort gelatin. Treatment with aqueous organic solvents causes death of all cells. J. H. BIRKINSHAW.

**Phosphatide content of yeast.** B. REWALD (Biochem. Z., 1930, 218, 481—484).—Fairly pure phosphatide was obtained from two kinds of fresh moist yeast by extraction with alcohol, dissolution of the extract in ether or chloroform, and precipitation by acetone. The yeasts contained 1.25 and 1.37% of phosphatide. W. MCCARTNEY.

**Determination of purine bases in yeast nucleic acid.** D. ASSENHAJN (Acta Biol. Exp., Warsaw, 1929, 4, 167—174).—The values found for the total purine content of hydrolysed yeast nucleic acid are 6.6% lower than theoretical using the method of double precipitation as copper salts, and 17% lower using Steudel's method, in which purine bases are precipitated once as copper and once as silver salts. Where the individual purines are isolated from the precipitate, however, the values obtained for the above two methods are, respectively, 11.6 and 2.8% lower than theoretical, so that the total yield of isolated purines is from 81 to 83% of that present in nucleic acid, irrespective of the method used.

R. TRUSZKOWSKI.

**Nitrates as a source of nitrogen for the growth of yeast.** K. PIRSCHLE (Biochem. Z., 1930, 218, 412—444).—Ammonium salts are much more favourable as sources of nitrogen to the growth of yeast than are nitrates because these are reduced to nitrites which act as poisons. If the accumulation of nitrites is prevented by aëration or addition of hydrogen peroxide, then nitrates act as satisfactorily as do ammonium salts. The reaction of the source of nitrogen, the concentration of the alcohol formed, the concentration of sugar in the nutrient medium, and the nature of the gases in presence of which the growth of the yeast takes place also influence that growth, but to a smaller extent. When nitrates are used as a source of nitrogen the normally rapidly occurring decolorisation of methylene-blue does not take place or does so very slowly.

W. MCCARTNEY.

**Nitrogen distribution in the yeast proteins produced from ammonium sulphate as sole source of nitrogen.** Y. TOMODA and M. WADANO (J. Soc. Chem. Ind. Japan, 1930, 33, 27—28B).—*Saccharomyces Saké*, grown on a medium containing ammonium sulphate as the sole source of nitrogen, contained 46.7% of crude protein, the amino-acid composition of which resembles that of the protein of beer yeast. K. V. THIMANN.

**Behaviour of benzoylmethylcarbinol with fermenting yeast.** F. VON FALKENHAUSEN (Biochem. Z., 1930, 219, 241—247).—When 70 g. of benzoylmethylcarbinol (*semicarbazone*, m. p. 194°;



thiosemicarbazone, m.p. 205–206°) were slowly dropped into a vigorously fermenting sugar solution over a period of 2 days, the yeast centrifuged off, and the liquid extracted with ether, a product was obtained which on fractionation gave 39 g. of unchanged carbinol and 11.2 g. of phenylmethyl ethylene glycol,  $\alpha_D -16.8^\circ$ , which on oxidation with nitric acid gave the ketol,  $\alpha_D -65.1^\circ$  (*p*-nitrophenylosazone, m.p. 265°).  
P. W. CLUTTERBUCK.

**Desmolytic system of *Torula colliculosa*. I.** Glycolase and production of methylglyoxal. I. YAMASAKI (Biochem. Z., 1930, 218, 468–471).—From magnesium hexosediphosphate by the action of *T. colliculosa* methylglyoxal was obtained in a yield of 77% of the possible amount. W. MCCARTNEY.

**Desmolytic system of *Torula colliculosa*. II.** Carboxylase. I. YAMASAKI (Biochem. Z., 1930, 219, 252–254).—When an acetate-buffered solution of sulphite-pyruvic acid is treated with a dry preparation of *T. colliculosa*, the amount of carbon dioxide obtained is 86.4% and of acetaldehyde is 87.7% of the theoretical. P. W. CLUTTERBUCK.

**Proportion of acetic, succinic, fumaric, and oxalic acids in cultures of *Mucor stolonifer* and some other moulds.** W. S. BUTKEWITSCH and M. W. FEDEROV (Biochem. Z., 1930, 219, 87–102).—Repetition of the author's experiments (A., 1929, 724) confirms the result that, in sugar cultures of *M. stolonifer*, fumaric acid predominates, succinic acid forming only 10–13% of the total acids. When the mould is grown on acetic acid, succinic acid forms 80% and fumaric acid 20% of the ether-soluble acids. On sugar-acetic acid mixtures, fumaric forms 74% and succinic 26% of the total acids. Comparative experiments on the action of the mould on succinic acid and sugar together and separately show a greater production of fumaric acid in the former case, indicating that the conversion of succinic into fumaric acid is assisted by the presence of sugar. Prolonged action of the mould on acetic acid leads to the production of oxalic acid. The amount of oxalic acid obtained was considerable only on succinic acid, was much less in presence simultaneously of sugar, and amounts only to a trace on sugar alone. By the action of *M. mucedo* on calcium acetate considerable amounts of succinic and oxalic acids were formed. The above and similar results with *Aspergillus niger* and *A. oryzae* suggest that succinic acid is an intermediate product in the conversion of acetic into oxalic acid.

P. W. CLUTTERBUCK.

**Transformation of ethyl alcohol in cultures of *Mucor stolonifer*.** W. S. BUTKEWITSCH and M. W. FEDEROV (Biochem. Z., 1930, 219, 103–121).—*M. stolonifer* is able to form succinic and fumaric acids from sugar, acetic acid, or ethyl alcohol, fumaric acid predominating from sugar and alcohol, whereas succinic acid predominates from acetic acid. In aerobic sugar cultures, ethyl alcohol initially accumulates to form about 2% of the medium and then gradually disappears, the amount of succinic and fumaric acids then increasing even after all the sugar has been utilised. If, however, the culture is rendered anaerobic while sugar still remains, the amount of

alcohol may increase to 3.5%. In aerobic cultures, the production of carbon dioxide shows two maxima, the first depending on the fermentation of sugar and the second on the utilisation of acids formed in the culture. It is suggested that in the conversion of sugar into succinic and fumaric acids, the formation of alcohol (possibly from aldehyde) and its oxidation to acetic acid are intermediate stages in the reaction.

P. W. CLUTTERBUCK.

**Energy of growth. XIII. Energy yield in the development of *Aspergillus niger* on various ternary substances.** E. F. TERROINE and R. BONNET (Bull. Soc. Chim. biol., 1930, 12, 10–19).—In the development of *A. niger* a greater energy yield was obtained on polyalcohols and sugars containing a ketonic group than on the corresponding hydroxylic and aldehydic substances, whilst on lactic acid a loss of 12 g.-cal. per mol. was obtained, a value considerably below that of Meyerhof and Aubel for animals. Arabinose, xylose, erythritol, and glycerol give energy yields identical with that of dextrose.

P. W. CLUTTERBUCK.

**Acid formation from raffinose by *Aspergillus niger*.** H. AMELUNG (Z. physiol. Chem., 1930, 187, 171–172).—*A. niger japonicus* produces citric acid from raffinose. Only the laevulose portion of the molecule is attacked; the melibiose is unchanged.

J. H. BIRKINSHAW.

**Localisation of oxidising enzymes in the cell of fungi.** J. NARUTOWICZ (Bull. Soc. Amis sci. Poznan, 1928, 2, 68–69).—The appearance of phenolases (oxidases and peroxidases) in the inner, protoplasmic part only of the cell or the hyphae shortly after treatment with a solution of benzidine in acetone and hydrogen peroxide shows that oxidising centres do not pre-exist in the cells of *Rhizopus nigricans*, *Botrytis cinerea*, and *Saccharomyces*.

CHEMICAL ABSTRACTS.

**Reducing sugar formed from starch and cellulose by bacterial action.** W. H. PETERSON, S. W. SCOTT, and W. S. THOMPSON (Biochem. Z., 1930, 219, 1–6).—The reducing sugar obtained as an end-product of bacterial fermentation of starch and cellulose was dextrose. Intermediate formation of maltose and cellobiose respectively was not, but in the cellulose fermentation the presence of a soluble polysaccharide was, detected.

P. W. CLUTTERBUCK.

**Determination of reducing sugar in bacteriological media.** M. C. MAGEE and H. G. SMITH (J. Bact., 1930, 19, 125–132).—The method of Stiles, Petersen, and Fred (*ibid.*, 1926, 12, 427) is unsatisfactory whether basic lead acetate or any other protein precipitant is used. Benedict's method gives inconsistent results. Schaffer and Hartmann's process (B., 1921, 361A) used without preliminary clarification of the liquid, proved the least unsatisfactory of the methods examined.

A. G. POLLARD.

***Bacillus thermofibrincolus* n. sp. I.** A. ITANO and S. ARAKAWA (Ber. Ohara inst. landw. Forsch., 1929, 4, 265–271).—A new species of organism, for which the above name is proposed, has been isolated. It decomposes cellulose vigorously at 65°.

O. J. WALKER.

**Fermentation of dihydroxyacetone.** A. I. VIRTANEN, H. KARSTRÖM, and O. TURPEINEN (Z. physiol. Chem., 1930, **187**, 7—44; see this vol., 114).—*B. coli* acclimatised to dihydroxyacetone by cultivation in a nutrient medium containing 0.22% of this substance, fermented it more rapidly than dextrose. The rate of fermentation of dextrose was unaffected by the composition of the nutrient solution. The optimum phosphate concentration is 0.5—1.0%  $P_2O_5$ .

J. H. BIRKINSHAW.

**Fermentation of glyceric acid.** A. I. VIRTANEN and E. PELTOLA (Z. physiol. Chem., 1930, **187**, 45—52).—*dl*-Glyceric acid is fermented by *B. coli* to acetic and formic acids, and the latter yields hydrogen and carbon dioxide. The fermentation usually ceases when the *l*-acid has disappeared, but in one case the *d*-acid was also fermented. The rate of fermentation is less than for dihydroxyacetone.

Both glycerol and glyceric acid yield some aldehyde in the Fürth-Charnass method for the determination of lactic acid.

J. H. BIRKINSHAW.

**Formation of melanin by bacteria.** (MISS) B. LLOYD and A. JOHNSTON (J. Roy. Tech. Coll. Glasgow, 1930, **2**, 346—353).—Examination of an agar-blackening organism from sea-water has shown that pigment production increases with rise of temperature and with vigour of the culture. It occurs only in presence of atmospheric oxygen and when tyrosine is a constituent of the medium. The optimum  $p_H$  is 7.8. Tyrosinase has been shown to be present. A substance with the properties of melanin can be isolated by cultivation in a salt solution containing tyrosine. The organism grows equally well on media which are free from tyrosine, and the formation of melanin is not an essential phase in its metabolism.

R. K. CALLOW.

**Degradation of caseinogen by lactic acid bacteria.** A. I. VIRTANEN and E. LUNDMARK (Suomen Kem., 1929, **2**, 86—91).—The degradation of caseinogen by lactic acid bacteria is an enzyme reaction independent of the vitality of the cells, since cells killed with toluene produce degradation with the same velocity as living cells. It is still not known whether there are several proteolytic enzymes in *B. casei*  $\alpha$  which, acting successively, bring about the degradation of caseinogen, or whether this degradation is produced by a single trypsin-like enzyme. Gelatin is broken down by *B. casei*  $\alpha$  with practically the same velocity as caseinogen. Amino-acids are more rapidly split off from caseinogen degraded by pepsin than from unchanged caseinogen.

S. K. TWEEDY.

**Effect of autolysis in sterile tissues on subsequent bacterial decomposition.** N. E. GIBBONS and G. B. REED (J. Bact., 1930, **19**, 73—88).—Protein decomposition in fish muscle and guinea-pig kidney by autolysis and by bacterial action is examined. Infection of autolysed tissue with *Prot. vulgaris* results in utilisation of the products of autolysis by the organism followed by accelerated protein decomposition with a rapid increase in the non-protein- and ammoniacal nitrogen. The period of autolysis before infection does not affect the growth rate of the organism, but markedly influences the course of nitrogen transformation.

A. G. POLLARD.

**Bacterial denitrification.** J. A. CRANSTON and (MISS) B. LLOYD (J. Roy. Tech. Coll. Glasgow, 1930, **2**, 301—315).—The general mechanism of denitrification is closely connected with respiration. Denitrification occurs only when the supply of atmospheric oxygen is less than the demand. Denitrification by a marine bacillus ("organism XIV") grown in a broth containing nitrite has been studied. Pure nitrogen is evolved. Measurements have been made of the rate of evolution of gas from the beginning of regular growth to the death of the organism, and it is found that when the food supply is short the rate of decrease in the number of bacilli is then logarithmic. The changes in the  $p_H$  of the medium during growth are determined by the formation of carbon dioxide from free oxygen and of carbonate from alkali nitrite. The effect of rise in temperature is to stimulate attainment of maximum development. Some experiments are described in which methylene-blue and indigo are reduced by the organism.

R. K. CALLOW.

**Detection of ammonia production by bacteria in agar slants.** P. A. HANSEN (J. Bact., 1930, **19**, 223—229).—The culture is treated with 1 c.c. of a 2% solution of thymol in sodium hydroxide followed by 1 c.c. of a 0.2*N*-solution of hypobromite. The formation of a blue colour after 20 min. indicates the presence of ammonia. Ether extracts the colour with the formation of a deep reddish-violet solution.

A. G. POLLARD.

**Formation of enzymes in bacteria.** H. KARSTRÖM (Suomen Kem., 1929, **2**, 63—72).—The effect of bacteria, capable of degrading sugars, on six carbohydrates, after cultivation in buffered and other media was investigated. The nature of the cultivating solution is a decisive factor in the formation of enzymes. Only dextrose and sucrose are always fermented independently of previous treatment, except that sucrose is not affected by bacteria cultivated in a medium containing dextrose. These facts are utilised for classifying the specific enzymes formed by a given species of bacterium.

S. K. TWEEDY.

**Diagnosis of the tubercle bacillus.** A. Z. ABUSHADY (J. Egyptian Med. Assoc., 1930, **13**, 40—43).—The use of fat-staining dyes, particularly Nile-blue sulphate, is recommended for staining tubercle bacilli. In sputum no organisms, cocci, or bacilli other than tubercle give a positive reaction.

F. O. HOWITT.

**Non-logarithmic order of death of some bacteria.** O. RAHN (J. Gen. Physiol., 1930, **13**, 395—407; cf. this vol., 116).—The apparent exceptions to logarithmic order of death are explained. The commonly occurring decreasing death rate is accounted for by the assumption of variation in resistance of the cells under test. The few cases of increasing death rates like *Staphylococci* are due to their marked tendency for clustering and to errors of counting living bacteria by the plating method where a cluster of several cells can be counted only as one cell.

T. R. SESHADRI.

**Filtration of bacteriophage.** N. W. LARKUM and M. F. SEMMES (J. Bact., 1930, **19**, 213—222).—Bacteriophage is removed from suspensions by Mandler

and Seitz filters at  $p_H$  4.5–5.0 and  $p_H$  9.0–10.0. Within these  $p_H$  ranges the bacteriophage passes plaster of Paris filters, but is retained by them at  $p_H$  7.0. The bacteriophage is adsorbed by protein in these suspensions. A. G. POLLARD.

**Oligodynamic effect of metallic salt solutions.** S. HOCs (Helv. Chim. Acta, 1930, 13, 153–172).—The bactericidal action of solutions of the following metallic salts has been investigated: cobalt chloride, nitrate, and sulphate, manganous chloride and sulphate, chrome alum, nickel, cadmium, aluminium, and zinc sulphates, ferric, stannous, and strontium chlorides, potassium antimonyl tartrate, lead and bismuth nitrates, and potassium arsenite. These are all inactive towards *Bacillus coli*, or toxic only in relatively concentrated solutions (cf. Egg and Jung, A., 1929, 1494). The oligodynamic action of most of these salts on *Spirogyra* has also been investigated. Solutions of silver nitrate, copper sulphate, and mercuric chloride, of metallic concentrations 1, 63, and 20  $\gamma$  per litre, respectively, are capable of bringing about shrinkage of the chlorophyll bands without plasmolysis. The following salts, however, are either unable to cause oligodynamic injury or can produce it in relatively strong concentrations only: cobalt, strontium, stannous, cadmium, manganous, and ferric chlorides, chrome alum, nickel, zinc, and aluminium sulphates, lead nitrate, potassium arsenite, and potassium antimonyl tartrate. The oligodynamic action of the silver ion is so characteristic that it may be used for the determination of silver in solutions of concentrations 1–100  $\gamma$  per litre. M. S. BURR.

**Influence of certain inorganic salts on the germicidal activity of hydrogen peroxide.** H. R. DITTMAR, I. L. BALDWIN, and S. B. MILLER (J. Bact., 1930, 19, 203–211).—Ferric and copper sulphates increased the germicidal action of hydrogen peroxide toward *Es. coli* and *Staphylococcus aureus*, the optimum concentration being 0.1 millimol. per 120 c.c. of solution. Potassium dichromate activated by cobalt or manganous sulphate had a similar effect. The toxicity of hydrogen peroxide in these experiments is ascribed directly to its oxidising action. A. G. POLLARD.

**Germicidal efficiency of "electrolytic chlorine" and formalin on bacterial spores.** C. S. R. AYYAR (Agric. J. India, 1930, 25, 53–57).—A commercial disinfectant obtained by electrolysis of rock salt and stabilising with lime, containing approximately 2% of available chlorine, was more effective against *B. mycoides* than was formalin at much greater concentration, but was ineffective against *B. subtilis* even after 30 min. contact. E. HOLMES.

**Chemotherapeutic equilibria.** A. E. STEARN and E. W. STEARN (J. Exp. Med., 1930, 51, 341–356).—The bacteriostatic action of dyes, which appear to combine with protein in the blood, is very rapid. The disappearance of the colour of a dye such as gentian-violet need not be accompanied by disappearance of therapeutic effect. E. BOYLAND.

**Compound formation of crystal-violet with nucleic acid and gelatin and its significance in dye bacteriostasis.** A. E. STEARN (J. Bact., 1930,

19, 133–143).—Conductivity measurements indicate the formation of non-ionised compounds of crystal-violet with gelatin and with nucleic acid. The inhibition of the normal functioning of these typical cell constituents due to combination with the dye explains the bacteriostatic effect of the latter.

A. G. POLLARD.  
**Growth of anaerobes in crystal-violet bile media.** C. F. POE (J. Bact., 1930, 19, 117–124).—Addition of crystal-violet (1 in 75,000) to lactose broth inhibits the development of most anaerobes. This effect is nullified by additions of bile to the media. *B. welchii* withstands a dye concentration of 1:20,000. A. G. POLLARD.

**Mechanism of adrenaline action. V. Changes in liver-glycogen and blood-lactic acid after injection of adrenaline and insulin.** G. T. CORI, C. F. CORI, and K. W. BUCHWALD (J. Biol. Chem., 1930, 86, 375–388).—Injection of adrenaline was followed, in normal rats, by preliminary decrease and later rise in the liver-glycogen; the lactic acid of the blood at first increased and returned to normal in 3 hrs. at which time the blood-sugar was still high. Since the total sugar mobilised from the liver during 1 hr. after injection of adrenaline was only one fourth of the amount which could be utilised in this time, the previous suggestion (this vol., 116) that adrenaline hyperglycaemia is associated with decreased utilisation of sugar is confirmed. Injection of insulin alone produced no immediate change in the liver-glycogen or blood-sugar, but both were reduced after 1 hr.; insulin administered simultaneously with adrenaline inhibited the mobilisation of sugar from the liver, but did not prevent the increase in the lactic acid of the blood. C. R. HARRINGTON.

**Apparent rôle of the thymus in calcium metabolism.** L. J. HARRIS (Nature, 1930, 125, 346).—The hypothesis that the thymus is concerned in promoting calcification explains many observations hitherto overlooked or forgotten.

L. S. THEOBALD.  
**Blood-phosphorus and serum-calcium in parathyroid deficiency. Effect of the parathyroid hormone.** J. N. ESAU and O. O. STOLAND (Amer. J. Physiol., 1930, 92, 1–24, 25–34).—The symptoms of parathyroid deficiency are accompanied by increase of the ratios of inorganic and total phosphorus to calcium. This may be due to disturbance of the phosphocreatine metabolism. Treatment with "parathormone" reduces the blood-phosphorus.

E. BOYLAND.  
**Influence of the intersecretory glands on the carbohydrate metabolism of animals which hibernate.** S. MIYAMURA (Folia endocrinol. Japon., 1928, 4, 51–52).—The effect of removal of the thyroid, suprarenals, and sex glands from toads is described. CHEMICAL ABSTRACTS.

**Internal secretion and blood-calcium.** S. NISHIMURA (Folia endocrinol. Japon., 1928, 4, 73–74).—Administration of thyroid substance increases the blood-calcium in man or animals, whilst thyroidectomy decreases it. It is increased by splenectomy but unchanged or slightly increased by the double operation, and diminished by thymectomy alone or

with thyroidectomy. It is also increased in diabetes mellitus and dystrophia adiposogenitalis; sex-gland substance lowers the blood-calcium, whilst castration, ovariectomy, or ligation of the vas deferens increases it.

#### CHEMICAL ABSTRACTS.

**Relation of carbohydrate metabolism to out-side temperature, thyroid gland, and insulin.** S. MIYAMURA (Japan. J. Int. Secret., 1929, 4, 2103—2129).—Exposure of rats to low temperatures ( $5-10^{\circ}$ ) decreased the liver- and muscle-glycogen; the rate of decrease was augmented by feeding thyroid gland, whilst the decrease was inhibited by removal of the gland or by injection of insulin. Poisoning by insulin was more frequent with rats kept at  $5-10^{\circ}$  or  $30-35^{\circ}$  than at normal temperatures.

#### CHEMICAL ABSTRACTS.

**Metabolism of cold-blooded animals. IV. Effect of oxygen and insulin on the gaseous exchange of the heart.** G. EISMAYER and H. QUINCKE (Z. Biol., 1930, 90, 57—62).—Small doses of insulin have little effect on the oxygen consumption, whilst larger doses produce a rise in the respiratory quotient with an attendant lowering of the ability to perform work. With a lowering of the oxygen content of the perfusion fluid below 8 vol.-% the oxygen consumption gradually falls, although it is unaffected when the oxygen content is 7.8 to 14.3 vol.-%.

P. G. MARSHALL.

**Non-identity of insulinoid of yeast and insulin.** M. A. BORVIN (Bull. Soc. Chim. biol., 1930, 12, 244—252).—No insulin could be separated by isoelectric precipitation from alcoholic extracts of yeast exhibiting hypoglycaemic activity. By identical methods about 50% of insulin added to yeast was recovered. The insulin-like substance present in certain yeasts is not identical with insulin.

W. O. KERMAK.

**Insulin-like properties of "uvursin," "oxycatalyst," and *Solanum sanitwongsei* berries.** M. L. LONG and F. BISCHOFF (J. Pharm. Exp. Ther., 1930, 38, 313—325).—"Uvursin," "oxycatalyst," and *Solanum sanitwongsei* berries, the first two of which are commercial anti-diabetic preparations, have no hypoglycaemic activity when administered to rabbits.

W. O. KERMAK.

**Effect of insulin on avitaminosis-B.** S. OMURA (Japan. J. Int. Secret., 1929, 4, 2163—2179).—Injection of insulin, especially together with dextrose, into rats with avitaminosis-B reduces the amount of fat in various organs.

#### CHEMICAL ABSTRACTS.

**Chemistry of insulin. V.** K. FREUDENBERG, W. DIRSCHERL, and H. EYER (Z. physiol. Chem., 1930, 187, 89—119; cf. A., 1929, 357).—Highly active insulin coagulates in hot dilute hydrochloric acid giving an active product (about 20 units per mg.). This form and the crystalline variety contain no removable methyl groups. Insulin inactivated by formaldehyde is partly regenerated by very dilute hydrochloric acid. The combination of insulin with formaldehyde and with the acetyl group suggests the presence of an imino-group. The rate of removal of ammonia (or primary amine) by dilute alkali hydroxide runs parallel with the disappearance of physiological activity. There is a corresponding change in optical

activity. Reduction produces similar changes. The mol. wt. estimated from the ammonia removed is about 8000. The prosthetic group must have high optical activity. The ultra-violet absorption of insulin is accounted for by the tyrosine and cystine content. Crystalline insulin shows no X-ray interference.

J. H. BIRKINSHAW.

**Plant secretin in Japanese vegetables.** O. OKANO (Folia endocrinol. Japon., 1928, 4, 57—58).—In addition to the plant secretin described by Bickel and having an irritant action on the isolated rabbit intestine, a substance having an inhibiting action thereon and having an effect like that of adrenaline on the blood-pressure and respiration of the rabbit and on the isolated heart and peripheral blood-vessels of the frog has been extracted.

#### CHEMICAL ABSTRACTS.

**Sexual hormone (feminin).** E. GLIMM and F. WADEHN (Biochem. Z., 1930, 219, 155—160).—The feminin (oestrus-producing substances) content of children's urine is about 100—200 mouse units per litre and increases to 500 units at puberty. About 1000 units are excreted daily by man, whilst urine during labour contains up to 150,000 units. Feminin arises only in part from food. A fraction is always present in urine in the ether-insoluble form (*V*-feminin), but this is not identical with the ether-insoluble substance obtained by heating alkaline feminin solutions (see A., 1929, 725).

P. W. CLUTTERBUCK.

**Female sexual hormone. III. Physiological activity of crystalline female sexual hormone in the Allen-Doisy test.** A. BÜTENANDT and E. VON ZIEGNER (Z. physiol. Chem., 1930, 188, 1—10; cf. this vol., 118).—Tests of the activity of various samples of crystalline "progynon" according to different methods gave results concordant in themselves but differing according to the technique adopted. The single injection method gave the value 8—9 million mouse units per g., for 2—3 injections in 12—14 hrs. the value was 15 million, 4—6 injections in 36—40 hrs. gave 30 million, in 48 hrs. 40 million.

J. H. BIRKINSHAW.

**Ovary-stimulating hormone of the placenta.** J. B. COLLIP (Nature, 1930, 125, 444).—Human or ox placenta contains an ovary-stimulating hormone which when injected into rats and mice causes prematurity. The active principle is micro-crystalline and 0.0015 g. represents one rat unit, and active extracts freed from protein, lipin, or oestrin have been standardised in terms of rat units. They withstand digestion with pepsin and trypsin without appreciable loss of physiological activity. Oral administration is almost as effective as subcutaneous. This hormone is considered to be not identical with the anterior pituitary ovary principle, "*Rho* 1," of Weisner (Edinburgh Med. J., 1930, 73).

L. S. THEOBALD.

**Presence of a hyogenic substance in the mouse placenta.** L. MIRSKAIA (Proc. Roy. Soc. Edin., 1929, 50, 104—112).—Immature female mice into which were implanted mouse placental tissue developed changes characteristic of pseudo-pregnancy but no such changes took place in ovariectomised animals. It is concluded that mouse placenta contains a factor

possibly identical with the *Rho* 2 factor of the anterior pituitary lobe, capable of stimulating the formation of *beta* factor by the ovary. W. O. KERMACK.

**Vitamins and foodstuffs.** E. C. VAN LEERSUM (Chem. Weekblad, 1930, 27, 122—129).—A general account of the occurrence, properties, and methods of assay of vitamins. S. I. LEVY.

**Inheritance of vitamin-A in maize.** II. Vitamin-A in hybrid red maize. S. M. HAUGE. III. Vitamin-A content in relation to yellow endosperm. S. M. HAUGE and J. F. TROST (J. Biol. Chem., 1930, 86, 161—165, 167—172).—II. In hybrid red maize producing a mixture of grains with red and colourless pericarp and yellow and white endosperm, the vitamin-A is confined to the grains with yellow endosperm and bears no relation to the colour of the pericarp.

III. Comparison of pure yellow maize with crossed yellow-white varieties shows that the vitamin-A content bears a quantitative genetic relationship to the content of yellow pigment. C. R. HARRINGTON.

**Colorimetric determination of vitamin-A.** T. MOORE (Lancet, 1929, ii, 219—220).—The trustworthiness of the antimony chloride reaction for vitamin-A is discussed and it is emphasised that before a general conclusion as to validity can be reached further tests should be performed on substances other than cod-liver oil. Absence of a blue coloration with antimony chloride appears to be a sound indication of the absence of vitamin-A.

L. S. THEOBALD.

**Vitamin activity of carotene.** M. JAVILLIER and (MLLE.) L. ÉMERIQUE (Compt. rend., 1930, 190, 655—657).—A preparation of carotene from spinach, which had been preserved in an atmosphere of hydrogen and exposed to feeble diffused light for 40 years, exhibited the physiological properties of vitamin-A. Its activity was about 100,000 units per g., and it was capable of curing avitaminosis-A in young rats when administered in doses of 0.007—0.2 mg. per day per 100 g. of rat; it also possessed preventive properties. C. W. SHOPPEE.

**Influence of hydrogen-ion concentration on the fractionation of the water-soluble vitamins.** M. J. OTERO (Semana méd., 1929, 36, 1712—1714).—The filtered acetic acid (0.01%) extract of yeast is evaporated at 100° (1 c.c.=2 g. of yeast); addition of alcohol to 52% at  $p_H$  4.5 leaves most of the vitamin in solution. Precipitation at 79% alcohol is optimal at  $p_H$  5.5. CHEMICAL ABSTRACTS.

**Change of fat content of blood of animals fed with vitamin-poor food.** T. FUKUDA (Med. News, Japan, 1929, No. 1243, 20—35).—In birds with avitaminosis-B or -C chiefly the blood-fat soluble in alcohol is increased, that soluble in light petroleum being unchanged; in avitaminosis-A the reverse holds. In general, avitaminosis is accompanied by derangement of fat metabolism. CHEMICAL ABSTRACTS.

**Rickets in chickens.** IV. Effect of heat and exposure to air on the stability of vitamin-D. G. F. HEUSER and L. C. NORRIS (Amer. J. Dis. Children, 1929, 38, 481—489).—The vitamin-D of cod-liver oil is partly destroyed by exposure at 100°

for 12 hrs. to air free from moisture and carbon dioxide, and completely destroyed in 48 hrs.

CHEMICAL ABSTRACTS.

**Mode of action of irradiated ergosterol.** W. BAUER and A. MARBLE (New England J. Med., 1929, 201, 809—811).—The hypercalcaemia and increased bone-calcification produced appear to be due to increased absorption of calcium from the gastrointestinal tract. CHEMICAL ABSTRACTS.

**Effects and secondary effects of irradiated ergosterol.** H. SEEL (Münch. med. Woch., 1929, 76, 1413—1417; Chem. Zentr., 1929, ii, 2473).—The antirachitic effect is demonstrable with doses of 0.1—0.0001 mg. The effect of irradiated ergosterol on metabolism is not considered to be specific.

A. A. ELDRIDGE.

**Toxic effects of irradiated ergosterol.** J. C. HOYLE (J. Pharm. Exp. Ther., 1930, 38, 271—289).—On a synthetic diet, but not on a diet of bread and milk, rats exhibit toxic symptoms when given excessive quantities of ergosterol irradiated in alcohol, whether or not air is admitted during evaporation of the solvent. Prolonged administration of irradiated ergosterol to rats on a bread and milk diet, however, produces urinary calculi and the animals fail to gain weight at the normal rate. W. O. KERMACK.

**Prolonged feeding experiments with activated ergosterol.** I. C. E. BILLS and A. M. WIRICK (J. Biol. Chem., 1930, 86, 117—128).—Growing rats have been kept for extended periods on an adequate diet to which were added varying amounts of irradiated ergosterol. The latter produced no definite injury until 4000 times the minimum antirachitic dose was given; 40,000 times the minimum dose was strongly toxic. The toxicity was increased by simultaneous administration of calcium carbonate and possibly slightly lessened by sodium phosphate.

C. R. HARRINGTON.

**Effect of irradiated ergosterol on thyreoparathyroidectomised dogs.** J. H. JONES, M. RAPAPORT, and H. L. HODES (J. Biol. Chem., 1930, 86, 267—283).—Hypercalcaemia accompanied by loss of appetite, but not by increased blood concentration or viscosity, could be produced in normal dogs by administration of 10 mg. of irradiated ergosterol *per diem*. Pre-operative treatment with irradiated ergosterol prevented the development of tetany in thyreoparathyroidectomised dogs, whilst post-operative treatment caused hypercalcaemia with relief of toxic symptoms. It must therefore be concluded that the irradiated ergosterol does not act through stimulation of the parathyroid glands (cf. Demole and Christ, this vol., 242). C. R. HARRINGTON.

**Rickets in rats.** XI. Alteration of calcium and phosphorus metabolism of normal and rachitic rats produced by irradiated ergosterol. H. B. BROWN and A. T. SHOHL (J. Biol. Chem., 1930, 86, 245—262).—Beneficial effects were observed as the result of administration of doses of irradiated ergosterol up to 0.1 mg. *per diem* to normal rats, the retention of calcium and calcification of the bones being improved; doses of 0.5—2.0 mg. *per diem* were toxic, causing increased urinary excretion of calcium, decalcification of the bones, and pathological calcific-

ation of other tissues. Rachitic rats were more resistant to the toxic effects of irradiated ergosterol than normal animals; the rickets could be cured without great improvement in the general condition of the animals, and without change in the ratio of calcium and phosphorus retained, the latter being determined by the mineral composition of the diet.

C. R. HARRINGTON.

**Variations of carbon dioxide in the neighbourhood of vegetation in the open air and in a closed space.** P. JACCARD (Bull. Soc. Chim. biol., 1930, 12, 156—170).—Observations are recorded on the concentration of carbon dioxide in the atmosphere in the neighbourhood of vegetation which show the presence of diurnal and seasonal variation. Experiments have also been carried out on the diffusion of carbon dioxide and on the uptake of carbon dioxide in closed spaces.

W. O. KERMACK.

**Physiological action of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays of radium on the dynamics of carbon dioxide assimilation.** J. STOKLASA, J. HOUBAN, and J. PĚNKAVA (Biochem. Z., 1930, 218, 361—396).—The effects of the rays on the growth and metabolism of plants and in particular on their respiratory processes have been studied.  $\alpha$ -Rays increase the consumption of oxygen and depress the process of assimilation, hence inhibiting photosynthesis. Combined  $\beta$ - and  $\gamma$ -rays stimulate the activity of cells containing chlorophyll, promote photosynthesis, and raise the respiratory coefficient.  $\gamma$ -Rays stimulate the assimilation of carbon dioxide and depress the respiratory processes. Although the effect of the  $\beta$ -rays alone cannot be directly determined it can be deduced that they first depress and then stimulate the assimilation of carbon dioxide.

W. MCCARTNEY.

**Use of dyes for the localisation of transpiration over the leaf surface.** R. B. HARVEY (Ecology, 1930, 11, 233—235).—Changes in the rate of transpiration over leaf surfaces due to differences in illumination, air movement, or injury may be followed by the local accumulation of dye in the leaf following immersion of the petiole in a 0.1% solution of light-green S.F.

A. G. POLLARD.

**Composition and growth initiation of dormant Bartlett pear shoots as influenced by temperature.** F. E. GARDNER (Plant Physiol., 1929, 4, 405—434).—Trees kept in a warm greenhouse remained dormant and there was little change in the composition of the shoots; trees kept at 20° or exposed to low outdoor temperatures broke their rest period and the shoots showed an increase in hexoses, sucrose, and organic acids and a decrease in starch. Various other constituents were unaffected. Although growth did not take place in the absence of the changes, it has not been established that they are necessary for the initiation of growth.

CHEMICAL ABSTRACTS.

**Rice starch. I. Chemical changes of starch during germination of rice in the dark. II. Effect of temperature on germination of rice in the dark.** W. S. TAO (Bull. Chem. Soc. Japan, 1930, 5, 64—69, 69—73).—I. The average moisture, ash, total nitrogen, fat, protein, reducing sugar, soluble polysaccharide, starch, cellulose, and pentosan

contents of rice seeds (Asahi) both before and after germination in the dark (the seeds being steeped, previously to germination, in distilled water until they had absorbed 50% of their weight) have been determined. In agreement with previous investigations it is found that loss in weight occurs during germination, the chief decrease occurring in the starch content, whilst the amount of reducing sugars and soluble polysaccharides increases (but not in an amount equivalent to the starch destroyed). The total fat content remains almost unchanged. On the basis of these results it is suggested that the starch is transformed by hydrolysis into polysaccharides and simple sugars, and a portion of the latter is oxidised to carbon dioxide and water, the energy thus liberated being utilised for the germination of the seeds, and thus it is calculated that the energy required for the germination of one rice grain is about 3000 g.-cal.

II. The effect of temperature on the composition of the germinated seeds has been studied at 20°, 35°, and 40°. The greatest total loss in weight (30%) and the greatest percentage loss of starch occurs at 35° (optimum germination temperature). In all cases the content of reducing sugars and soluble polysaccharides in the seedlings increases inversely to the decrease in the starch content, the formation of the former products being favoured at 20°, whilst conversion of polysaccharides into simple reducing sugars is comparatively great at 40°.

J. W. BAKER.

**Rust diseases of cereals. II. Adsorption of copper by rust spores (*Tilletia tritici*, Bjerk., Winter) of wheat.** J. BODNÁR and A. TERÉNYI (Z. physiol. Chem., 1930, 186, 157—182; cf. A., 1927, 600).—Of the copper adsorbed by wheat rust spores from copper sulphate solution, 55% replaces hydrogen ions and 45% metallic ions. More copper is adsorbed from copper acetate and copper ammonium sulphate solutions than from sulphate solutions. The absolute and relative absorption values (representing copper sulphate as 1) are 2 and 3, respectively. The spores are not killed by treatment with copper solution, since after treatment with acid they germinate on calcium nitrate solution or in moist ground. Copper present as the complex cuprammonium ion penetrates to the interior and kills the spores. The critical concentration of copper in the spores for germination is 0.5%; above this value the spores will not germinate; if the copper content is lowered by acid treatment below this critical level, germination ensues. Germination in dilute copper salt solution is preceded by adsorption; copper being thus removed from solution the spores can germinate provided the critical value in the spores is not exceeded.

J. H. BIRKINSHAW.

**Specific colour reaction for histamine.** W. ZIMMERMANN (Z. physiol. Chem., 1930, 186, 260—262).—Dilute solutions of histamine salts with small amounts of cobalt nitrate, on addition of alkali give a violet precipitate or coloration. The mixture is decolorised by oxidation (e.g., atmospheric oxygen) or reduction. The reaction is specific for histamine and may be used to follow the putrefactive decomposition of a histidine solution.

J. H. BIRKINSHAW.



# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JUNE, 1930.

### General, Physical, and Inorganic Chemistry.

**Intensity of multiple lines in the Balmer series.** J. BLATON (*Z. Physik*, 1930, **61**, 263—273).—Mathematical. Certain multiple lines due to a single-electron atomic system are excluded on first approximation calculations, but a closer investigation of the appropriate vector potential gives finite values for their intensities. The results are applied to the Balmer series. A. B. D. CASSIE.

**Hydrogen and helium lines as standards of wave-length.** W. G. PENNEY (*Phil. Mag.*, 1930, [vii], **9**, 661—664).—Calculations have been made of the wave-numbers of the centres of gravity of the components of the first three lines in the Lyman series for hydrogen and helium, and also of the first six lines in the Balmer series of hydrogen, as well as those of the corresponding lines in the spectrum of  $\text{He}^+$ , with the view of employing them as standards of wave-length, especially in the far ultra-violet.

M. S. BURR.  
**New bands in the molecular spectrum of hydrogen.** D. S. JOG (*Nature*, 1930, **125**, 709).—A number of bands due to forbidden transitions has been identified. L. S. THEOBALD.

**Near infra-red spectrum of helium and mercury.** II. T. TAKAMINE and T. SUGA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **13**, 1—6; cf. A., 1929, 1116).—The apparatus previously employed has been modified so as to obtain larger dispersion. With helium, although an improved spectrogram has been obtained, the dispersion is still insufficient to allow accurate measurement of wave-length for analysis in the near infra-red as the intensity falls rapidly near the region  $\lambda$  9200 Å., where new bands would be expected. In the mercury arc spectrum ( $\text{Hg I}$ ), besides the lines assigned by McLennan and others to  $3^3P_1 - m^3D_2$ , there appear to be two other sets forming series of the type  $\nu = x - m^3S$  and  $\nu = x - m^3D$ . The final term  $x$  is an unknown energy level with the value  $15299 \text{ cm}^{-1}$ , probably of the nature of a  $P$  term, common to both series. A. J. MEE.

**Spectrophotometric study of the absorption of helium in the bright and dark sunspots.** N. PERRAKIS (*J. Phys. Radium*, 1930, [vii], **1**, 126—131; cf. A., 1929, 223).—Values for the wave-length, intensity, and excitation potential of a number of helium lines as observed in the chromosphere and in the laboratory are compared and tabulated. The strongest are the triplet lines  $D_3$  ( $\lambda$  5875.62) and  $\lambda$  4477.451. Visual and spectrophotometric observations were made over a period of 6 months, and

photomicrographs are given showing the line and its absorption in the neighbourhood of a sunspot and in the interval separating members of a group. Absorption was relatively strong in the bright patches remote from the dark spots, the line, however, appearing stronger in the spots. N. M. BRIGHT.

**Electronic fine structure in helium bands.** S. IMANISHI (*Nature*, 1930, **125**, 529).—Measurements of the doublet separations of the band 6400 Å. of helium are recorded. L. S. THEOBALD.

**Alternating intensities and isotope effect in the blue-green absorption bands of  $\text{Li}_2$ .** A. HARVEY and F. A. JENKINS (*Physical Rev.*, 1930, [ii], **35**, 789—801).—Spectrograms taken with low or high dispersion allow a quantum analysis of the vibrational and rotational structures of the blue-green lithium bands; these show close analogy with the corresponding sodium system (cf. Loomis, A., 1928, 1068). The analysis given by Wurm (cf. this vol., **1**, 123) is extended, and redetermined molecular constants are given which are in close agreement with his values. An expression is found for the band heads. Wave-numbers of the rotational structure lines of the (0,1) band are tabulated, and the assignment of this system to the electronic transition  $^1\Pi \leftarrow ^1\Sigma$  is confirmed. An accurate representation of the wave-numbers of the lines of the (0,0) band is deduced; the origin of this band is  $20,395.96 \text{ cm}^{-1}$ . The vibrational isotope effect is established by the identification of three band heads (1,0), (2,0), and (3,0), due to  $\text{Li}^6\text{Li}^7$ , found in their calculated positions. The rotational isotope effect is shown by two faint series agreeing with theoretical equations for the  $Q$  and  $P$  branches due to  $\text{Li}^6\text{Li}^7$ . The alternation ratio of the intensities of successive lines in the  $\text{Li}_2^7$  bands is determined by a new method depending partly on the theory of intensity distribution in this type of bands (cf. Mulliken, A., 1927, 394). The best value is found from the  $Q$  branches of the (0,0) and (1,0) band as  $1.78 \pm 0.2$ ; evidence indicates a true value of 1.67 corresponding with a nuclear spin of the lithium atom of  $3/2(\hbar/2\pi)$ , which disagrees with the value found by Schüller and Brück from hyperfine structure (cf. this vol., 124). In agreement with theory, the isotope lines due to the unsymmetrical molecule  $\text{Li}^6\text{Li}^7$  show no alteration.

N. M. BRIGHT.  
**Simple "eigenfunction" for the ground state of lithium-like atomic systems.** V. GUILLEMIN, jun., and C. ZENER (*Z. Physik*, 1930, **61**, 199—205).—Mathematical. A simple eigenfunction for lithium-

like atomic systems is deduced from a function asymptotically accurate with increasing distance from the nucleus. Values of parameters in this function are deduced by the variation method. The function is then used to calculate ionisation potentials for the sequence Li to  $C^{++}$ ; the results agree with experiment.

A. B. D. CASSIE.

**Reversal in the spectra of beryllium.** H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1930, 6, 12—14).—Grating photographs and photometric curves were obtained of the spectra of beryllium excited by a condenser and by a transformer discharge. Self-reversal was observed for the strong lines 3322 ( $2^3P_{0,1,2}-2^3S_1$ ) and 2495 ( $2^3P_{0,1,2}-3^3D$ ) in Be I, and the doublet 3132 ( $1^2S_{1/2}-2P_{3/2,1/2}$ ) in Be II, obtained by the disruptive discharge. No reversal was observed with the ordinary discharge, but the lines are associated with ghosts. The reversals resemble those for thallium (cf. A., 1927, 706).

N. M. BLIGH.

**Intensities in the atmospheric oxygen (intercombination) bands.** W. H. J. CHILDS and R. MECKE (Nature, 1930, 125, 599—600).—Exact intensity measurements of the *A* group of the absorption bands of oxygen at 7600 Å. have been made; the law  $J=J_0e^{-kx}$  holds for these lines, and for the strongest an absorption  $(J_0-J)/J_0$  of 27% is found. The summation rule  $P_2(j)+P_3(j)+R_2(j)+R_1(j)=2j+1$  holds only for higher values of *j*.

L. S. THEOBALD.

**Stark effect in oxygen.** M. KIUTI, K. OCHIAI, and Y. NISHIMURA (Japan. J. Phys., 1929, 5, 139—144; cf. A., 1929, 1349).—The Stark effect in oxygen was photographed for electric field intensities up to 180,000 volts/cm. For comparison, over each of the Lo Surdo spectra the neon and helium lines were photographed. The lines of the diffuse series  $2p - nd$  were accompanied by new lines interpreted as combination lines  $2p-5d$ ,  $-5f$ ,  $-5g$ ,  $-5s$ , and  $-5p$  forming the group  $2p-5q$ . The observed and calculated  $5q$  terms are tabulated. The electric shifts were measured at their maximum separations and the field intensity was calculated. The components of  $2p-5s$ ,  $-5d$ , and  $-5f$  were displaced to the red, and of  $2p-5g$  and  $-5p$  to the violet. The separations in wave-numbers are given graphically.

N. M. BLIGH.

**Interaction of Stark effect and electron spin in alkali atoms.** V. ROJANSKY (Physical Rev., 1930, [ii], 35, 782—788; cf. Ladenburg, A., 1929, 972).—Theoretical. It is shown by quantum mechanics that when the Stark effect in alkali metal atoms is in weak fields, it is a second order effect. When it is large enough to be comparable with the multiplet structure, there appears, due to the interaction of the Stark effect and spin, an effect analogous to the Paschen-Back effect in its influence on the multiplet structure, causing a distortion of the multiplet structure and a redistribution of the intensities of the spectral lines.

N. M. BLIGH.

**Band systems of alkali vapours.** W. WEIZEL and M. KULP (Ann. Physik, 1930, [v], 4, 971—984).—The band systems for the molecules  $Na_2$ ,  $K_2$ , NaK, NaCs, LiK, LiRb, LiCs, and NaRb have been arranged

in term schemes. The lines used were those found by Walter and Barratt (A., 1928, 812, 1307). The oscillation quanta of the fundamental terms and higher terms can be determined approximately, and these are compared for the different molecules considered.

A. J. MEE.

**Ultra-violet band spectrum of sodium-potassium molecule.** Y. UCHIDA (Japan. J. Phys., 1929, 5, 145—152).—Theoretical. The band heads due to sodium-potassium vapour in the ultra-violet found by Walter and Barratt (cf. A., 1928, 812) are subjected to vibrational quantum number analysis; the frequencies of the bands are arranged in an  $n'' - n'$  diagram, with the intensities and frequencies of the heads. The intensity distribution among the heads is compared with the corresponding Condon parabolas constructed from the potential energy functions for the two electronic states. The yellow-green and ultra-violet bands of NaK are assumed to correspond respectively with the green and 330  $\mu$  bands of  $Na_2$ ; the constants of the NaK molecule are intermediate between those of  $Na_2$  and  $K_2$  and the oscillation frequency is found to be inversely proportional to the atomic number. The NaK molecule dissociates by the absorption of ultra-violet light into a normal sodium and an excited potassium atom.

N. M. BLIGH.

**Ultra-violet reflecting power of aluminium and several other metals.** W. W. COBLENTZ and R. STAIR (Bur. Stand. J. Res., 1930, 4, 189—193).—The ultra-violet reflecting powers of aluminium, duralumin, tin, and rhodium have been determined. Aluminium is comparable with chromium, the reflecting power increasing from 50% at 300  $\mu$  to 75% at 550  $\mu$ . The reflectivity is higher than that of chromium in the visible spectrum. Duralumin is similar to aluminium, whilst tin has a lower reflecting power which diminishes rapidly with tarnishing. The reflectivity of rhodium increases from 30% at 260  $\mu$  to 45% at 365  $\mu$ .

C. J. SMITHELLS.

**Variation of relative intensities of components of rotation doublets in the resonance spectrum of sulphur.** P. SWINGS (Compt. rend., 1930, 190, 965—967; cf. this vol., 124).—The intensities of the components  $C_1$ ,  $C_2$  ( $\lambda_1 > \lambda_2$ ) of the doublets 4546—4543 (series *A*) and 4531—4528 (series *B*), excited, respectively, by the mercury lines 3132 and 3126 Å., have been determined under pressures of 1—10 mm. In both cases the intensities of the  $C_1$  components increase with pressure relatively to those of the  $C_2$  components. In series *A* the intensities of  $C_1$  are equal to those of  $C_2$  for pressures not greater than 0.4 mm., in *B* they are definitely less at low pressures. It is shown that this variation is not due to reabsorption by sulphur vapour. Raising the temperature (e.g., from 400° to 580°), density remaining constant, has a similar but much smaller effect.

C. A. SILBERRAD.

**Structure of the spectrum of ionised argon (A II).** T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 198—212).—In continuation of previous work (A., 1928, 1293; 1929, 3, 111) the analysis of the A II spectrum has been extended. A large number of new levels has been detected. These

belong to three term systems corresponding with the ground levels  $^3P$ ,  $^1D$ , and  $^1S$  of the ion  $A^{++}$ . The interpretation of lines in the extreme ultra-violet given by Compton and co-workers (A., 1929, 1206) is extended and corrected. Data for 360 new lines are given. M. S. BURR.

**Spark spectrum of argon. III.** T. L. DE BRUIN (Z. Physik, 1930, 61, 307—320).—See preceding abstract.

**Blue absorption band spectrum of potassium.** H. YAMAMOTO (Japan. J. Phys., 1929, 5, 153—156; cf. Walter and Barratt, A., 1928, 812).—The potassium absorption band system corresponding with the  $330\mu$  system of sodium was photographed and analysed by the assignment of vibrational quantum numbers to the band heads. Wave-lengths and intensities are tabulated and the series of band heads are arranged in an  $n'' - n'$  diagram. An expression is given for the frequencies of the heads, which, on comparison with that found by Frederickson and Watson (cf. A., 1927, 1122) for the near red system, shows that both systems have the same initial absorption levels. N. M. BLIGH.

**Pressure effects in the band spectrum of calcium hydride.** B. GRUNDSTRÖM and E. HULTHÉN (Nature, 1930, 125, 634—635).—The entire spectrum of calcium hydride is increased with an increase in pressure of hydrogen from 10 mm. to 7 atm. In the  $C$ -band at  $\lambda$  3533 the  $P$ - and  $R$ -branches are strongly developed to about  $J = 40$  at high pressures and in addition new bands appear; the vibrational quantum numbers of these are recorded, and the results are discussed. L. S. THEOBALD.

**Dissociation energy of  $Zn_2$  molecules.** S. MROZOWSKI (Nature, 1930, 125, 528—529).—The energy of evaporation of  $Zn_2$  molecules calculated from optical data is  $32 \pm 3$  kg.-cal./mol.

L. S. THEOBALD.

**Spark spectra of selenium and tellurium.** L. BLOCH and E. BLOCH (Ann. Physique, 1930, [x], 13, 233—262; cf. A., 1927, 1117).—Using the oscillating electrodeless discharge, the spark spectra of selenium and tellurium were investigated for the ranges 6783—2196 and 7246—2207 Å., respectively. The spectra of Se II, Se III, Se IV, Te II, Te III, and Te IV were separated, a large number of new lines was detected, and wave-lengths, intensities, and orders of more than 1200 lines for each element are tabulated.

N. M. BLIGH.

**Spectrum of bromine in different stages of ionisation.** S. C. DEB (Proc. Roy. Soc., 1930, A, 127, 197—217).—The spectrum of bromine in its different stages of ionisation (from  $Br^+$  to  $Br^{++++}$ ) has been classified, using Bloch's data (A., 1927, 802) and those given in Kayser's "Handbuch der Spectroscopie." Additional data have been obtained in the region 4000—7500 Å. and assigned to  $Br^{++}$ . The spectrum was obtained by passing a condensed discharge through a spectrum tube of special design, similar to that described by Majumdar (A., 1929, 1117), with nickel electrodes. About 230 lines, of which 60 were new, were measured. Approximate values of 19.1 and 25.9 volts are found for the ionis-

ation potentials of  $Br^+$  and  $Br^{++}$ . The classification illustrates the use of the extension of the irregular doublet law and the horizontal comparison method of Saha and Majumdar.

L. L. BIRCUMSHAW.

**New band group in the ultra-violet absorption spectrum of selenium vapour.** (MLLE.) M. MORACZEWSKA (Bull. Acad. Polonaise, 1930, A, 17—19).—A new band group has been observed in the absorption spectrum of selenium vapour in the spectral region 2100—2300 Å. Like other selenium bands they are degraded towards the red, but unlike the visible band series no rotational fine structure could be detected with the dispersion employed. The frequencies of 12 band heads have been measured and are expressed by the formula  $\nu = 43,210 + 368n - 0.2n^2$ . Since the bands appear in the saturated selenium vapour at relatively low temperature,  $200^\circ$  ( $p = 0.001$  mm.) to  $400^\circ$  ( $p = 4$  mm.), and since the mean frequency difference is  $363\text{ cm.}^{-1}$  as against  $200\text{—}250\text{ cm.}^{-1}$  for the bands in the visible region, it is suggested either that the carrier of this spectrum is not  $Se_2$  but a polyatomic selenium molecule, or, more probably, that this spectrum corresponds with a different electron jump from that corresponding with the bands previously observed.

J. W. SMITH.

**Band spectra of cadmium and bismuth.** S. BARRATT and A. R. BONAR (Phil. Mag., 1930, [vii], 9, 519—524).—The band system 2856—2644 Å., previously attributed to cadmium suboxide by Barratt and Walter (A., 1929, 237), has been definitely identified with the spectrum of bismuth vapour. It is attributed to the molecular spectrum, the molecule being  $Bi_2$ . Nineteen wave-lengths have been identified with those previously attributed to cadmium molecules. On the assumption that on dissociation of the molecule there results one normal atom and one excited atom associated with the wave-length 3067 Å. the heat of formation of the molecule is calculated as 18.5 kg.-cal. per mol.

A. E. MITCHELL.

**Second spark spectrum of antimony and a note on the first spark spectrum of tin.** R. J. LANG (Physical Rev., 1930, [ii], 35, 445—451).—The vacuum spark spectrum of antimony was measured over the range 6600—600 Å., and the Paschen hollow-cathode spectrum over the range 5200—1950 Å.; about 60 lines of the former spectrum are classified as transitions between terms of Sb III. Corresponding with the deepest term value an ionisation potential of approximately 24.7 volts is calculated. The hollow cathode spectrum of tin was photographed between 6000 and 2000 Å. (cf. Green and Loring, A., 1927, 912) and new term values for Sn II are tabulated.

N. M. BLIGH.

**Analysis of the spectrum of Hg II.** W. M. HICKS (Phil. Mag., 1930, [vii], 9, 673—740; cf. Paschen, A., 1929, 365).—Results of a detailed analysis of the Hg II spectrum are tabulated, discussed, and compared with those of Paschen. The line  $n = 35,104$  is taken as  $S_{2,2}$  in each case, but different values are given for the  $p_{1,2}$  term, and this discrepancy is discussed. The lowest  $p_2$  level is shown to be multiple, producing a number of different doublet separations. If the various  $p_2$  were equally

normal there should be a corresponding number of independent  $D$  series; evidence for their existence was found and is given for one, with corresponding  $F'$  and  $G$  series. Evidence of the satelloidal effect was found. Instances of the re-emission by the nucleus of radiation of frequency  $E = nh\nu$ , where  $n$  is not restricted to unity (cf. A., 1929, 1354), and their relation to the non-appearance of certain lines are given and discussed. N. M. BLIGH.

**Band spectra of mercury, cadmium, and zinc halides.** K. WIELAND (Helv. phys. Acta, 1929, 2, 46—94; Chem. Zentr., 1929, ii, 3106).—The spectra of mercury, cadmium, and zinc chlorides, bromides, and iodides, excited at a high temperature, were photographed between 7000 and 2200 Å. The band systems were grouped in three classes according to their regularities. A. A. ELDRIDGE.

**Band spectrum of ionised mercury hydride.** T. HORI (Z. Physik, 1930, 61, 481—489).—An arc discharge between mercury and tungsten electrodes in an atmosphere of hydrogen at 2 mm. pressure was used as a source of ionised mercury hydride and the spectrum investigated between 2200 and 2550 Å. Band edges are located at 2264, 2287, 2367, 2388, 2413, 2475, and 2493 Å. and correspond with  $^1\Sigma \rightarrow ^1\Sigma$  transitions. Molecular constants for the initial and final states are calculated and tabulated. By means of a cyclic process and an equation connecting the ionisation potentials and dissociation energies of neutral and ionised mercury hydride the value 9.26 volts is deduced for the ionisation potential of mercury hydride. This value is in good agreement with the value for gold (9.2 volts) and the values of the ionisation potentials of neighbouring elements in the periodic system are discussed. Further, it is shown that the excited  $^1\Sigma$  state results from dissociation in the  $2D^{1/2}_{5/2}$  term. W. R. ANGUS.

**Intensity measurements in the arc spectrum of thallium.** O. U. VONWILLER (Physical Rev., 1930, [ii], 35, 802—808).—Measurements of the ratio of the intensities of the lines  $2p_2 - 2s$ ,  $2p_1 - 2s$  in the arc spectrum with a current of 1.6 amp. were made by the photographic method, using alloys of chemically pure lead and thallium in varying proportions. The ratio increased with decreasing concentration of thallium to a limit at about 0.01%. The limiting value for  $\bar{a}_2/\bar{a}_1$  is 0.388, where  $I = a^2\nu^4$ . Measurements of the intensity ratios of doublets in the principal series  $2s - mp_1$ ,  $2s - mp_2$  were made for  $m = 4, 5, 6$ , and 7, the values obtained for  $\bar{a}_1/\bar{a}_2$  being 4.5, 5.7, 6.4, and 7, which were independent of the concentration of thallium and of the current over a limited range. The variation with wave-length of the fraction of light transmitted through the antimony film reducer was measured. The diffraction effects found by Shenstone (cf. A., 1929, 1208) were observed, and photometer diagrams are given. N. M. BLIGH.

**Zeeman effect and hyperfine structure.** F. STARK (Physikal. Z., 1930, 31, 375).—Mathematical. The work of Schüler and Brück on the hyperfine structure of a series of elements has been carried out for a strong magnetic field. The case of a magnetic field weak in comparison with the nuclear impulse

moment and the coupling is now treated. A numerical example on the separation of the cadmium lines is given. A. J. MEE.

**Nuclear spin and hyperfine structure.** H. E. WHITE (Physical Rev., 1930, [ii], 35, 441—444; cf. this vol., 265).—Theoretical. Assuming that hyperfine structure in spectral lines originates in the coupling of a nuclear spin with electron resultant  $J$ , gross structure and hyperfine structure are compared from Jackson's relation (cf. A., 1929, 1),  $\Delta\nu_g/\Delta\nu_f = m_e/4im_n$ , where  $\Delta\nu_g$  is a gross or multiplet and  $\Delta\nu_f$  the corresponding hyperfine structure separation,  $m_e$  the mass of an electron, and  $m_n$  the mass of the nucleus. Satisfactory agreement with experiment is found for atomic systems with electron configurations showing  $LS$  or  $jj$  coupling. The case of other electronic configurations is considered. N. M. BLIGH.

**Effect of hyperfine structure due to nuclear spin on polarisation of resonance radiation.** A. ELLET (Physical Rev., 1930, [ii], 35, 588—594).—The effect of hyperfine structure when due to a nuclear moment, on the polarisation of resonance radiation may be calculated from Heisenberg's extension of the principle of spectroscopic stability. On Schüler and Brück's assumption (cf. A., 1929, 967) that the nuclear moment of the thallium atom is  $\frac{1}{2}$ , the  $\lambda\lambda$  3776 and 5350 lines should show no polarisation,  $\lambda$  2768 should show 33.3—35.1% parallel, and  $\lambda$  3530 41.8—48.8% perpendicular to the electric vector of a plane-polarised exciting beam. These values are compared with the observed values of Gülke (cf. this vol., 16). Sodium resonance radiation excited by plane-polarised  $D_1$  and  $D_2$  lines should show 33.3 and 16.6% polarisation for nuclear moment of  $\frac{1}{2}$  and 1, respectively. The observed value is 16.3%, but band spectra observations indicate a higher nuclear moment. N. M. BLIGH.

**Effect of a nucleus spin on the optical spectra.** II. J. HARGREAVES (Proc. Roy. Soc., 1930, A, 127, 141—154).—The method previously applied to the investigation of the effect of a nuclear spin of half a quantum on the optical spectra of an atom with a central field (A., 1929, 972) is extended to the case of an atom with a nuclear spin of  $i_n$  quanta (where  $2i_n$  is an integer). A general solution is given of the cases where  $i_n = 1, 3/2$ , and  $9/2$ , the last case being of special interest, since it has been found by Back and Goudsmidt (A., 1928, 340) that the hyperfine structure of bismuth is due to a spin of  $9/2$  quanta. The calculated intensities of the components of the lines  $p_{3/2} \rightarrow s_{1/2}$  and  $p_{1/2} \rightarrow s_{1/2}$  are in fair agreement with Back and Goudsmidt's values. The  $P \rightarrow S$  transitions for  $i_n = 1$  and  $i_n = 3/2$  are also calculated. L. L. BIRCUMSHAW.

**Intensity anomaly of Stark-effect lines in very strong fields.** C. LANZOS (Naturwiss., 1930, 18, 329—330).—Theoretical. The physical interpretation of the effect of an electric field on the characteristic function is given. A. J. MEE.

**Application of electron scattering to the problem of free rotation.** R. WIERL (Physikal. Z., 1930, 31, 366—367; cf. this vol., 390).—By applying Debye's method to the photographs obtained in the

method previously used to show inner molecular interference through the scattering of rapid electrons, the distance apart of the scattering atoms in the molecule can be found. In the case of carbon tetrachloride the four chlorine atoms are at equal distances from each other. The scattering power is for the central carbon atom only one eighth of that for the chlorine atoms, and can be neglected. The accuracy of this is proved by the photograph in which the ratio of the sines of half the angles of scattering for the first maxima was 5 : 9 : 13. This agrees with the simple sine function,  $\sin x/x$ . The same ratio for the ring diameter is found for dichloroethylene. For  $\alpha\beta$ -dichloroethane and oxalyl chloride the ratio is 5 : 7.8. This indicates the existence of more than one effective molecular distance in the substance under consideration. In  $\alpha\beta$ -dichloroethane it would appear that there are two kinds of molecules present in approximately the same amounts, one corresponding with the *cis*-, the other with the *trans*-form. The two Cl-Cl distances are  $4.4 \pm 0.1$  and  $3.2 \pm 0.1$  Å. Free rotation is restricted. The results of a calculation for the case of free rotation are not in agreement with experiment.

A. J. MEE.

**Plasmoidal high-frequency oscillatory discharges in "non-conducting" vacua.** R. W. WOOD (Physical Rev., 1930, [ii], 35, 673—693; cf. A., 1929, 1350).—A new type of vacuum tube discharge is described; it is excited, using external electrodes, by comparatively low-voltage high-frequency oscillations, in which luminous masses of various shapes are observed. They are formed of singly-ionised oxygen or carbon monoxide molecules, and by analogy with Langmuir's observations (cf. A., 1928, 1168) are termed "plasmoids." The behaviour in magnetic fields of a red phosphorescence of the glass wall when the tube contains oxygen at low pressure was studied; it appears when a plasmoid is deflected against the wall by a magnet. A green phosphorescence is caused by the impact of high-velocity electrons from the inner glass surface when the external cathode is excited by higher voltages. Clean-up effects are described, a sealed-off tube showing either the atomic hydrogen spectrum or the green discharge of molecular oxygen. Changes of pressure as the spectrum alters were investigated by a vibrating quartz fibre manometer. The spectra of the plasmoids, their dark sheaths, and the less luminous surrounding gas were investigated by projecting their images on the slit of a spectroscope. The band spectrum of oxygen is seen in the whole tube, but is concentrated in the plasmoids and diluted in their dark sheaths; atomic lines also appear, the local concentration being different for singly- and doubly-ionised oxygen. There are two types of discharge, one at very low potentials and a more brilliant one appearing as the potential is raised. Plasmoids appear to form with both types, their shape and distribution in the tube changing on passing from one type to the other.

N. M. BLIGH.

**Cause of the change in intensity of the lines and bands in atomic and molecular spectra.** H. DESLANDRES (Compt. rend., 1930, 190, 836—840).—The author's law (A., 1920, ii, 69; 1929, 223) that the

frequency of the brightest portions of certain line and band spectra is an approximate multiple of the infra-red frequency 1062.5 ( $d_1$ ) is extended to certain lines of the Balmer and Paschen series of hydrogen and to the ultimate, and in some cases the penultimate, lines of the nitrogen spectrum of the terrestrial aurora borealis and of the  $\text{CO}^+$  spectra of the tails of comets. Examples are cited of the reinforcement in intensity of such lines compared with other lines of the same element and of the same multiplet, the ratio of the intensities being higher than that obtained in the laboratory. The fact that this variation is more marked for the eclipse of 1905 than for that of 1926 (1905 being a year of maximum sunspot activity when helium should be more abundant in the solar atmosphere) supports the author's theory (A., 1924, ii, 577) of a connexion between  $d_1$  and the internal vibrations of the  $\alpha$ -particle.

J. GRANT.

**Zeeman effect of quadrupole lines.** A. RUBINOWICZ (Z. Physik, 1930, 61, 338—348).—Mathematical. The intensity and polarisation ratios for the split components are investigated. It is shown that for the longitudinal Zeeman effect the position of the quadrupole lines and polarisation of the split components are the same as for dipole lines. For the transverse effect, however, the components corresponding with  $\Delta m = \pm 1$  appear as  $\pi$ - and those corresponding with  $\Delta m = \pm 0$  as  $\sigma$ -components. The components corresponding with  $\Delta m = 0$  are lacking in both cases. The intensities of the single components are given, and it is shown that there are summation laws similar to those for dipole lines.

A. J. MEE.

**Cathode dark space in the Geissler discharge.** E. C. CHILDS (Phil. Mag., 1930, [vii], 9, 529—546).—An apparatus has been devised for the determination of the relative merits of Aston's law with reference to the cathode dark space in a Geissler tube, and Langmuir's space-charge law. The balance of evidence from the experiments appears to be in favour of the former.

M. S. BURR.

**Identification of Al III and of Al II in stellar spectra.** O. STRUVE (Astrophys. J., 1930, 71, 67—69).—Five lines, previously unidentified, in the star 88  $\gamma$  Pegasi of spectral type B2 are due to Al III. These new lines have been observed in many stars and appear to reach maximum intensity in the spectral types B1 to B2. Lines previously measured by Baxandall in  $\alpha$  Cygni are attributed to Al II.

L. S. THEOBALD.

**Distinction between scattering and absorption.** J. Q. STEWART and S. A. KORFF (Astrophys. J., 1930, 71, 62—66).—A method capable of distinguishing between scattering and absorption in the formation of dark lines when light is transmitted through a vapour is described and discussed. With sodium vapour scattering predominates at the edges but absorption occurs in the cores.

L. S. THEOBALD.

**Spectrum of the chromosphere.** S. A. MITCHELL (Astrophys. J., 1930, 71, 1—61).—The spectrum of the chromosphere is revised, utilising the spectra of the eclipses of 1905 and 1925. It is concluded that the Fraunhofer spectrum is essentially an arc spectrum, that of the chromosphere more closely resembles the

spark spectrum, whilst the flash spectrum is a reversal of the Fraunhofer spectrum. The spectrum of the chromosphere differs greatly from the ordinary solar spectrum in the intensities of the lines; enhanced lines are specially prominent in the former. For each element in a given state of ionisation there is a close connexion between intensity and height. The greatest heights in the chromosphere are reached by  $\text{Ca}^+$  at 14,000 km. and by  $\text{H}_\alpha$  of hydrogen at 12,000 km.

L. S. THEOBALD.

#### Axiality of light emission and atomic structure.

VI. Consequences of the elementary phenomena of light emission. VII. Physical criticism of a Sommerfeld theorem. J. STARK (Ann. Physik, 1930, [v], 4, 685—709, 710—724).—VI. The theory is based on the Bohr energy condition, the correspondence principle, the conception of the light quantum, and the energy relations holding in the process of emission of a quantum. A transition in which an electron changes its position into the direction of an electric field will yield a line of which the frequency will be decreased by the presence of the field; if the change is to a more transverse position the frequency will be increased. Thus in the linear Stark effect the sign of the frequency change of a line is proportional to the strength of the field applied and to the change of its projection in the direction of the field during the transition. The effect observed with hydrogen lines must mean that the excited hydrogen atom can set in two opposite directions in the field. When the electron at the end of the oscillation takes up a certain direction in the lower level, the excess of energy is sent out of the electromagnetic field between the electron and its ion in nearly the opposite direction as a light quantum. The addition of an external field will thus influence the relative intensities of lines in a given direction. In the case of canal rays there is an asymmetry of emission conditioned by the arrangement and motion of emitters with respect to the axis. This asymmetry follows, as far as is known, the same law as the asymmetry caused by application of an external electric field. It is possible to superpose the longitudinal and transverse effects due to the electric field upon the longitudinal effect in the canal rays, and a table of experimental results of relative intensities in these cases is given for the hydrogen atom. These figures indicate that the angle between the axis and the equilibrium position of a hydrogen electron in the field due to its ion is greater for  $d^3$  than for  $p^2$  series, and greater for  $p^3$  than for  $s$ .

VII. The theorem concerned states that the structures of atoms of certain elements are not axial but spherically symmetrical. Sommerfeld is thus giving a physical significance to the  $\psi$ -function. The question of whether the electric and magnetic fields are metaphysical and fundamentally unobservable is discussed. If this is so a physical interpretation of the  $\psi$ -function is untenable. The behaviour of an electron in a stationary state and in a transition between stationary states is considered on the basis of Sommerfeld's  $\psi$ -interpretation. The experiment of Fraser (cf. A., 1927, 399) on canal rays is criticised; it provides no evidence for the conclusion that the hydrogen atom in its state of lowest energy is spherically symmetrical.

A. J. MEE.

Production of diffraction gratings by the photography of interference fringes. G. SIMON (Ann. Physique, 1930, [x], 13, 131—231).—The problem of obtaining single order diffraction gratings on a transparent support for the study of the infra-red was investigated theoretically and practically. Daguerreotype plates were found to give reflexion gratings, and also transmission gratings capable of reproduction. To obtain gratings of larger extent it was found possible to juxtapose on the same plate two photographic reproductions, interferometry methods being used to ensure a correct junction. Gratings of 15—20 cm. surface were obtained by the juxtaposition of a number of grating elements obtained by photographing equidistant fringes given by the interference of parallel beams.

N. M. BLIGH.

Separation of angles in the two-electron problem. G. BREIT (Physical Rev., 1930, [ii], 35, 569—578).—Mathematical.

N. M. BLIGH.

Singular behaviour of striæ in the positive column of an electrical discharge through hydrogen. J. ZELENY (Nature, 1930, 125, 562—563).—Descriptive.

L. S. THEOBALD.

Afterglow in air. J. KAPLAN (Physical Rev., 1930, [ii], 35, 600—604; cf. A., 1928, 604; Herzberg, *ibid.*, 457).—The active material in the air afterglow produced by an uncondensed discharge through various mixtures of oxygen and nitrogen at 0.5 mm. pressure was passed into another discharge tube having internal electrodes, and through which a feeble current from a small spark coil was passed. The resulting spectrum was photographed and the  $\beta$  bands of nitric oxide were found to be very strongly excited. They correspond with transitions from the  $B_0$  to the various  $X$  vibrational levels, whereas in the afterglow of active nitrogen they correspond with transitions from several  $B$  levels to the various  $X$  levels, the difference indicating two possible methods, excitation by recombination and by collisions of the second kind, for exciting these unusual bands.

N. M. BLIGH.

Dependence of line absorption on brightness in the arc light. C. WEISS (Ann. Physik, 1930, [v], 4, 923—942).—Experiments for determining the line absorption as a function of the brightness, using a carbon arc for a source, are described. The function calculated is, for fairly small and large brightnesses, the same for line absorption as for an undistorted dispersion distribution. For small and medium brightnesses no deviations from this are to be expected. The function agrees with that of Ladenburg and Reiche.

A. J. MEE.

Can light nuclei exist in different quantum states? W. HEITLER (Naturwiss., 1930, 18, 332).—From the size of intensity changes in the band spectra of molecules with two equal nuclei, the amount of nuclear spin can be calculated. In some cases (*e.g.*, lithium and sodium) the intensity ratio is so small that the nuclear spin would have to be very large. The results can, however, be explained on the assumption that the nucleus can exist in different quantum states of which the life period is very large. Two nuclei in different states are, in the quantum mechanics



sense, unequal particles. This would lead to the required result regarding intensities in band spectra.

A. J. MEE.

**Proof of the existence of a  $K_2$  molecule bound by polarisation forces.** H. KUHN (Naturwiss., 1930, 18, 332—333).—The absorption spectrum of potassium vapour at relatively high pressures has been investigated. On the short-wave side there is a small band, the distance between the lines of the series being about 2.7 Å. The origin of these lines must be some potassium combination, from their position in the spectrum. They must also be due to some outer loosely-bound molecule. It is concluded that the molecule in question is the  $K_2$  molecule. There are theoretical grounds for anticipating the existence of such a molecule.

A. J. MEE.

**Temperature determination of the electric arc from the band spectrum.** L. S. ORNSTEIN and W. R. VAN WIJK (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 44—46).—Calculations have been made of the temperature of the inner and outer zones of an aluminium-carbon arc from measurements of the line intensities of the cyanogen and aluminium band spectra, on the assumption that a distribution of the rotation states occurs in the arc corresponding with the actual temperature of the gases. Values of 5000° and 2800° Abs. are suggested for the maximum temperatures of the two zones in an arc of length about 1.5 cm. (9 amp., 220 volts.).

F. G. TRYHORN.

**Polarisation, light scattering, photo-effect, and Compton effect on the tubes of force theory of light quanta.** W. ANDERSON (Z. Physik, 1930, 61, 566—575).—Electron waves are associated with the classical electro-magnetic tubes that tend towards the equatorial plane as the velocity of the electron approaches that of light (cf. this vol., 25). They are non-polarisable, as experiment shows. The photon is conceived as an electric doublet the axis of which lies in the plane perpendicular to its velocity. These models predict that radiant energy of long wave-length (wireless waves) should experience only small deflexions on encounter with a free electron, energy of medium wave-length, large deflexions, and energy of very short wave-length, small deflexions. If the photon is to lose its energy to an atomic system, its wave-length must not be too small. This minimum wave-length capable of photo-emission is 0.47 Å. for the hydrogen atom. Wave-lengths less than 0.47 Å. may collide with, and displace, a bound electron, but the photon is not absorbed as in the photo-electric effect. This is, in fact, the Compton effect.

A. B. D. CASSIE.

**Angular intensity distribution of continuous X-ray spectrum.** II. Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 23—47; cf. this vol., 4).—Mathematical. The earlier work assumed that emission of radiation is measured by the retarded co-ordinate matrix. This is incorrect, the emission being measured rather by the retarded current matrix. The previous work is corrected, and angular intensity distribution curves of the continuous X-rays emitted from a very thin aluminium target are given for various applied voltages and compared

with the experimental curves. The observed curves are generally flatter than those calculated, although the difference is not so great with the corrected theory.

A. J. MEE.

**X-Ray scattering powers of nickel and oxygen in nickel oxide.** R. W. G. WYCKOFF (Physical Rev., 1930, [ii], 35, 583—587; cf. Z. Krist., 1929, 72, 319).—Atomic scattering factor curves for the nickel and oxygen atoms in nickel monoxide were obtained from measurements of the intensities of the principal powder reflexions of molybdenum, copper, and nickel  $K\alpha$  radiations. The scattering power of oxygen with respect to sodium chloride remains nearly constant, but that of nickel shows relatively large differences.

N. M. BLYTH.

**Soft X-rays of manganese.** F. C. CHALKLIN (Phil. Mag., 1930, [vii], 9, 847—857; cf. A., 1929, 692).—The validity in the soft X-ray region of the theory of critical potentials of iron, cobalt, nickel, and copper, when applied to manganese, was investigated by determining the critical potentials of manganese by two variations of the photo-electric method. Two critical potential series were obtained; the scheme does not account for discontinuities found above 280 volts.

N. M. BLYTH.

**L Series spectra of the elements from calcium to zinc.** C. E. HOWE (Physical Rev., 1930, [ii], 35, 717—725; cf. Thoræus, A., 1926, 329).—Using the first inside order of a plane grating,  $L$  lines of the elements zinc, copper, nickel, cobalt, iron, manganese, chromium, vanadium, titanium, and calcium were measured and tabulated, and a Moseley diagram of the results is given. Separation of the  $L\alpha$  and  $L\beta$  and of the  $Ll$  and  $L\eta$  lines was obtained. The results are somewhat higher than those obtained by crystal measurements, but are in agreement with the work of other investigators. The failure of the  $L\alpha$  and  $L\beta$  calcium lines to appear is in accord with Foote's extension of Stoner's arrangement of the electrons.

N. M. BLYTH.

**L Series of element 91—protoactinium.** H. BRUTHE and A. VON GROSSE (Z. Physik, 1930, 61, 170—173).—Using a Bragg X-ray spectrograph, the  $L$  series of protoactinium has been exhaustively examined and evaluated. The  $K$  lines of silver, molybdenum, strontium, and bromine (which appear in the  $L$  region of protoactinium) were used as reference lines in assigning values to the twenty-one lines recorded. The purity of the pentoxide is discussed. A table gives the symbols for the lines, the mean distance from the reference line, dispersion, and wave-lengths of the protoactinium lines. The position of the lines is discussed in relation to lines of other elements.

W. R. ANGUS.

**Scattering and diffraction of cathode rays.** P. WHITE (Phil. Mag., 1930, [vii], 9, 641—661).—The angular distribution of electrons of above 30 kilovolts, after scattering by sputtered films of gold of about 200 Å. in thickness, has been found by measuring with a photometer, ring photographs of the type obtained by Thomson and Reid with microcrystalline films (A., 1927, 605; 1928, 3, 938). A method for calculating, from the photographic densities, the number of electrons falling on unit area is described.

The relative intensities of the profile of the rings, central spot, and general background have been measured.  
M. S. BURR.

**Measurement of absorbing power of materials by the stationary wave method.** A. H. DAVIS and E. J. EVANS (Proc. Roy. Soc., 1930, A, 127, 89—110).—The theory and application of the stationary wave method for determining the absorption coefficient of a material are discussed, and an apparatus by means of which the absorbing powers of a large number of materials have been measured is described. Experiments were also carried out to determine the influence on the absorption coefficient of the thickness of the specimen, its distance from the backing-plate, the presence of perforations in the specimen, and of membranes fastened to the surface. A comparison of the values obtained by the stationary wave and the reverberation methods indicates that the former are generally lower than the latter.

L. L. BIRCUMSHAW.

**Increase of photo-electric effect of potassium by means of hydrogen.** R. FLEISCHER and H. TEICHMANN (Z. Physik, 1930, 61, 227—233).—Gas-free potassium is vaporised on to gas-free platinum foil and the wave-length-photo-electric sensitivity curve determined, a maximum being found at 334 m $\mu$ . Then pure hydrogen at 15 mm. pressure is admitted for 15 min.; after evacuation a large decrease in the sensitivity is observed, and only a small increase occurs on keeping in a high vacuum for 24 hrs. A further layer of potassium is then vaporised on to the potassium film previously saturated with hydrogen, and a large increase in the sensitivity is observed with a maximum at 436 m $\mu$  characteristic of the influence of hydrogen. On another platinum foil potassium was vaporised first in high vacuum, when a maximum occurred at 365 m $\mu$ , then in an atmosphere of hydrogen at  $10^{-2}$  mm., when the characteristic maximum at 436 m $\mu$  was observed. It is therefore deduced that the selective sensitivity at 436 m $\mu$  is due to the influence of potassium vapour on molecular hydrogen. Further experiments in which a potassium layer is bombarded with H<sup>+</sup> ions under 300 volts and of current strength  $3.2 \times 10^{-8}$  amp. without developing selective sensitivity show that Suhrmann (A., 1929, 229) must have used larger currents and that therefore his theory that hydrogen ions are the origin of the effect is incorrect, as with larger currents potassium will be vaporised.

H. A. JAIN.

**Ionisation potential of a two-electron atomic system.** B. N. FINKELSTEIN (Z. Physik, 1930, 61, 234—235).—Hylleraas' formula (cf. this vol., 267) gives an electron affinity of 15.6 kg.-cal. per mol. for the hydrogen atom. Possible relations for the electron affinities of heavier atoms are discussed.

A. B. D. CASSIE.

**Characteristic energy losses of electrons scattered from incandescent solids.** E. RUDBERG (Proc. Roy. Soc., 1930, A, 127, 111—140).—In continuation of previous work (this vol., 526) a study has been made of the velocity distribution of an initially homogeneous beam of electrons after scattering from the surface of targets of the following

substances kept at incandescence: copper, silver, gold, platinum, and the oxides of magnesium, calcium, strontium, and barium, the oxides being deposited on a roughened platinum surface. An improved form of the apparatus is described, and two methods are used to obtain the velocity distribution, either the magnetic field or the potential of the entire system being varied by small steps. The investigation is confined to scattered electrons for which the energy lost in the collision does not exceed 50 volts. The distribution with respect to energy among the scattered electrons has a sharp peak, corresponding with truly reflected electrons, and several smaller maxima for slightly lower values of the energy, the position of which with respect to the reflected peak remains constant over the wide range of bombarding voltages used. These are regarded as characteristic of the substance composing the target. Measurements made with an apparatus in which the electron gun and target could be rotated show that the shape of the distribution curve is almost the same for all angles of scattering, over a range of about 70°. Tables are given showing the positions of the maxima for the different targets. The smallest values recorded are those for the first maxima in the cases of copper and silver; for all the metals tested a prominent maximum follows in the neighbourhood of 7 volts, then a broader maximum near 25 or 26 volts, and a fainter indication of a similar feature near 35 volts. No noticeable regularities are observed among the values recorded for the oxides. In an attempt to interpret the results it is suggested that the characteristics shown by the maxima indicate that they are due to inelastic collisions with the target atoms involving definite energy changes, such as excitation and ionisation. L. L. BIRCUMSHAW.

**Potential relations in the striated positive column of electrical discharges through hydrogen.** J. ZELENY (Physical Rev., 1930, [ii], 35, 699—704; cf. Thomson, A., 1929, 1356).—Theoretical. To explain the many-lined visible spectrum from the striæ in the positive column of a discharge through hydrogen it is necessary to produce excited states at least 3 volts above the lowest excited level of 11.5 volts, and an energy not far below the ionisation potential of 16.1 volts is required. A process by which excitation of molecules to the required levels and ionisation might occur at equal intervals throughout the positive column is described. In certain cases when the voltage drop between striæ is several volts below the ionisation potential it is assumed that the electrons acquire energy for ionisation from collisions of the second kind with molecules of impurities coming from the walls of the tube, the influence of which is discussed. N. M. BLIGH.

**Ionisation of helium by potassium positive ions.** R. M. SUTTON and J. C. MOUTON (Physical Rev., 1930, [ii], 35, 694—698).—The apparatus previously employed for argon and neon was modified (cf. A., 1929, 483), and the ionisation of carefully purified helium was investigated, using potassium positive ions up to 750 volts accelerating potential. The ionisation properties of the gas were particularly sensitive to impurities. At pressures between 0.01

and 0.1 mm. and above 150 or 200 volts accelerating potential there was definite evidence of ionisation, the effect being much smaller than for argon and neon.

N. M. BLIGH.

**Properties of ionised gases in high-frequency electromagnetic fields.** C. GUTTON (Compt. rend., 1930, 190, 844—847).—The results obtained by H. Gutton (A., 1927, 294) are independent of the dimensions of the apparatus used and indicate that the ionisation of a gas corresponding with resonance (when the frequencies of the field and electronic oscillations coincide) is due to the existence of an oscillation period of the electrons of the gas. A valve oscillator was used to demonstrate that the amplitude of the electronic oscillations increases when the ionisation increases and their period approaches that of resonance. There is a consequent further increase in ionisation, and stability is attained when a state corresponding with that of resonance is reached.

J. GRANT.

**Thermionic emission and electrical conductivity of oxide cathodes.** A. L. REIMANN and R. MURGOCI (Phil. Mag., 1930, [vii], 9, 440—464).—The results of Horton (*ibid.*, 1906, 11, 505) and Spanner (Ann. Physik, 1924, 75, 609) that the electrical conductivity  $C$  of an activated alkaline-earth oxide varies with the temperature  $T$  according to a law  $C = \alpha e^{-\beta/T}$ , where  $\alpha$  and  $\beta$  are constants, has been confirmed. During the activation both the thermionic emission and the conductivity increase similarly, whilst both are similarly destroyed by exposure of the oxide to oxygen, a discharge in carbon monoxide, or a discharge in hydrogen. Cathode recovery is possible only a few times after treatment with oxygen or carbon monoxide, but it may be reactivated as desired after destruction by hydrogen. These results in conjunction with those of other observers lead to the conclusion that the oxide coating conducts the space current electrolytically, practically only the metallic ions being mobile whilst the oxygen ions play scarcely any part in the electrolysis. It also follows that the whole surface of each crystal of oxide in an activated cathode is covered by a mobile monatomic layer of alkaline-earth metal, the passage of space current being accompanied by a continual circulation of this metal. It is estimated that at the usual operating temperatures of such cathodes the average life of alkaline-earth metal particles is of the order of  $10^{-3}$  sec. The coating is considered to be in imperfect contact with the metallic core space current passing from the core to the oxide mainly in the form of thermionically emitted electrons, and it is suggested that a sufficiently copious supply of these would be made possible by the contamination of the core surface by adsorbed barium or barium and oxygen.

A. E. MITCHELL.

**The hydrogen molecule ion.** E. TELLER (Z. Physik, 1930, 61, 458—480).—The excited states of the hydrogen molecule ion, which on separation of the nuclei gives a proton and a neutral or excited hydrogen atom, are determined. Only the  $3d\sigma$  state is stable. Its energy of dissociation is 1.35 volts. The hydrogen molecule ion should have no band spectrum in the ultra-violet.

A. B. D. CASSIE.

**Anode rays of sodium, potassium, calcium, and barium.** A. POIROT (Compt. rend., 1930, 190, 735—736; cf. A., 1929, 970).—By the method previously described, using a current of about 0.5 milliamp. the nitrates give stable and long-continued emission of anode rays of sodium, potassium, calcium, and barium. Addition of any other salt is disadvantageous. The voltage in the tube varied from a few hundredths of a volt for sodium to several thousands for barium; the duration of emission depends on the metal and varied from 3 to 10 hrs. The colour of the discharge indicates that the atoms carry only a single charge. Apart from the metal under examination the spectrograms show faintly only hydrogen rays and a band spectrum due to the lubricants.

C. A. SILBERRAD.

**Behaviour of electrons in magnetic fields.** V. A. BAILEY (Phil. Mag., 1930, [vii], 9, 560—567, 625—628).—A new method for measuring the drift velocity of electrons in gases in uniform electric fields has been devised; it can be employed even in the presence of negative ions. Use is made of the reduction of the divergence of an electronic stream, which occurs when a uniform magnetic field is applied in the same direction as the electric field. The method has been tested by means of hydrogen and is found to be satisfactory.

Four additional variations of the method of applying the experimental results are described. M. S. BURR.

**Dissociation of the atoms of metals into ions and electrons, and the osmotic theory of the origin of the electric current.** L. PISARSHEVSKI (J. Chim. phys., 1930, 27, 98—117).—Theoretical. The author considers that in solid metals there is an equilibrium between atoms, ions, and electrons, analogous to the electrolytic dissociation of salts, and in the light of this theory discusses the mechanism of galvanic action.

C. W. GIBBY.

**Absorption coefficient for slow electrons in cadmium and zinc vapours.** R. B. BRODE (Physical Rev., 1930, [ii], 35, 504—508).—Using the apparatus previously described for mercury (cf. A., 1929, 1123) the variation with the electron velocity of the absorption coefficient  $\alpha$  or the effective collision cross-section was measured in the vapours of cadmium and zinc. The curves found were similar to those for mercury. The magnitudes of the maxima for  $\alpha$  are of the order: cadmium 130, zinc 75, mercury 60.

N. M. BLIGH.

**Energy exchange within molecules and between molecules by collision.** O. K. RICE (Z. physikal. Chem., 1930, B, 7, 226—233).—Theoretical. It has been observed that the reaction velocities of decomposition of several ethers and of propaldehyde, which decompose unimolecularly in the gaseous state, decrease at higher pressures to a greater extent than is to be expected theoretically. The velocity of activation by shock is, therefore, not so great as might be supposed for such complicated molecules. Two explanations are suggested. Either the energy exchange within the molecule is limited to a small portion, so that it behaves as a smaller molecule, or the energy exchange between molecules due to shock is relatively small. The fact that hydrogen has

approximately the same activation efficiency as organic molecules seems to support the former view. Various theoretical considerations in relation to energy exchange are discussed and it is shown that, if the first suggestion is correct, the specific reaction velocity at high pressures should be independent of pressure, should decrease at somewhat lower pressures, and, at still lower pressures, should again attain a constant but smaller value. M. S. BURR.

**Effect of water vapour on diffusion coefficients and mobilities of ions in air.** J. J. NOLAN and T. E. NEVIN (Proc. Roy. Soc., 1930, A, 127, 155—174).—The variation of the diffusion coefficient of ions in air with the water-vapour content has been studied by Townsend's method, and found to be of a totally different character from what might have been expected from Tyndall and Grindley's mobility observations (cf. A., 1926, 219), the values for ions of both signs exhibiting a periodic variation with the vapour pressure. This result is verified by determinations of the variation of the sum of the mobilities of positive and negative ions, derived from conductivity observations in weak fields. The Rutherford-Child surface ionisation method of measuring the positive and negative mobilities separately in fields of different strengths provides further confirmation. An increase in the field strength from 1 to 1.4 volts per cm. causes the periodic variation to disappear, and in higher fields the mobility varies in the manner observed by Tyndall and Grindley (*loc. cit.*). Using the Rutherford-Franck alternating-field method, with an apparatus of the type described by Nolan (A., 1924, ii, 661), results are obtained which confirm the observations of previous investigators for both positive and negative ions. Over a wide range of humidity, water vapour has no effect on the positive mobility, but below a vapour pressure of 0.8 mm. the value rises rapidly, reaching 1.65 cm./sec. per volt/cm. in dry air. The ionic recombination coefficient is shown to vary considerably with the humidity and has a maximum value, about four times that in dry air, at a vapour pressure of 4 mm.

L. L. BIRCUMSHAW.

**Ions produced by discharges at liquid surfaces.** J. ZELENY (Nature, 1930, 125, 706).—Electric transfer is effected by liquid droplets only in certain cases (cf. Nolan and O'Keeffe, this vol., 269).

L. S. THEOBALD.

**Effect of end losses on the characteristics of filaments of tungsten and other materials.** I. LANGMUIR, S. MACLANE, and (Miss) K. B. BLODGETT (Physical Rev., 1930, [ii], 35, 478—503).—Tables and formulae are deduced for the calculation of the effect of the leads on the properties of any long tungsten filament for which the current and diameter are known. The theory is extended to the cases of filaments in gases, filaments of other materials, and short filaments to which the first results do not apply.

N. M. BLIGH.

**Recombinations of electrons and positive ions in the upper atmosphere.** T. L. ECKERSLEY (Nature, 1930, 125, 669—670).—The value of the recombination coefficient of electrons and ions is approximately  $8.75 \times 10^{-11}$  cm.<sup>2</sup>/sec. and the distance

to which the electron must approach a positive ion in order to be captured is of the magnitude  $1.4 \times 10^{-9}$  cm. The mean free life of an electron between ionisation and recombination is about 5 hrs.

L. S. THEOBALD.

**Relativistic electron.** R. ZAYCOFF (Z. Physik, 1930, 61, 395—410).—Mathematical. A theory for the explanation of the equilibrium of the electron is proposed.

A. J. MEE.

**Direct evidence for the formation of ions by an ion stream.** H. KALLMANN and B. ROSEN (Naturwiss., 1930, 18, 355).—A stream of ions was passed between the poles of an analysing magnet and then near to a wire electrode. This electrode can collect only slowly moving ions, *i.e.*, ions not in the original stream. Ions were collected on the electrode when ionised nitrogen molecules traversed nitrogen molecules, and when ionised argon atoms traversed argon atoms, but not when ionised nitrogen atoms traversed nitrogen molecules. This agrees with deductions from experiments on the selective absorption of streaming ions (this vol., 16).

A. B. D. CASSIE.

**Sorption and chemical reactions in atomic rays.** M. LANCUCKI (Bull. Acad. Polonaise, 1930, A, 20—29).—A study has been made of the close relationship which exists between the absorption of nitrogen in an electrical discharge tube, using iron or aluminium electrodes, and the disintegration of these metals. The amounts of nitrogen absorbed and of iron disintegrated are equiatomic and depend on the gas pressure, the cathode fall, the current density, and the temperature of the cathode. If the cathode be constructed of iron nitride, the latter is disintegrated without absorption of nitrogen. The iron nitride formed by this process is not ferro-magnetic.

J. W. SMITH.

**Masses of the proton and electron.** H. T. FLINT (Proc. Physical Soc., 1930, 42, 239—244).—A principle of minimum proper time has been proposed, which states that in association with the electron and proton no proper time less than  $h/m_0c^2$  and  $h/M_0c^2$ , respectively, will be observed. It has also been deduced by Fürth (cf. A., 1929, 1123) with the help of Heisenberg's uncertainty principle, and is here applied to the deduction of an equation for the ratio of the masses of the proton and electron. The result is in agreement with the experimental value. The possibility of explaining the asymmetry with regard to mass of the proton and electron by a difference in the metric of space in the two cases is discussed.

N. M. BLIGH.

**Frequency of occurrence of the disintegrative synthesis of oxygen 17 from nitrogen 14 and helium.** W. D. HARKINS and A. E. SCHUB (Physical Rev., 1930, [ii], 35, 809—813; cf. A., 1927, 183).—Using a modified Wilson-Shimizu apparatus 39,000 photographs were taken of the tracks in nitrogen of  $\alpha$ -rays from thorium-C and -C'. Two disintegrative syntheses were obtained of oxygen of mass 17 and isotopic number 1 by the attachment of the  $\alpha$ -particle in each case to the nucleus of a nitrogen atom, in general one of mass 14 and isotopic number 0. The number of disintegrative syntheses per million  $\alpha$ -tracks is 8. The abundance of the different

atomic species of oxygen and nitrogen in the earth's crust is tabulated, and the mechanism of their formation is discussed. Isotope 17 is less abundant and less stable than isotope 18. N. M. BLOCH.

**Supposed transmutation of lead effected by sunlight.** N. V. KARPEN (Bull. Acad. Sci. Roumaine, 1929, 12, [7—10], 60).—The previous statement of Maracineanu (cf. this vol., 270) as to the transmutation of lead into gold, mercury, and helium under the influence of solar rays is refuted. H. F. HARWOOD.

**Ranges of  $\alpha$ -particles.** G. I. HARPER and E. SALAMAN (Proc. Roy. Soc., 1930, A, 127, 175—185).—The extrapolated ranges have been measured for  $\alpha$ -particles from radium- $C'$ , thorium- $C$  and - $C'$ , and polonium in air, oxygen, nitrogen, argon, and hydrogen, only the portion of the Bragg curve from the maximum to the end of the range being experimentally determined. To obtain this portion of the Bragg curve the distance of the source from the ionisation chamber was varied, the pressure being kept constant during one set of observations. Whilst the results for polonium agree well with those of Curie (A., 1925, ii, 834), Joliot and Onoda (A., 1928, 1069), and Onoda (A., 1928, 1169), the ranges in air found for thorium- $C'$ , radium- $C'$ , and thorium- $C$  are all smaller than those previously obtained. The deviation is greatest for the particles from thorium- $C$ , and appears to be definitely outside the range of experimental error. In the case of argon and hydrogen the ranges agree with those calculated from the stopping powers obtained by Gurney (A., 1925, ii, 256). The values for the ranges, calculated from the initial velocities of the  $\alpha$ -particles measured by Briggs (A., 1927, 393) and Lawrence (A., 1929, 370), are not in agreement with the observed values. It is shown that the theory of Gaunt of the stopping power of the hydrogen atom (A., 1927, 606) can be extended to the case of molecular hydrogen if a new value of the ratio of  $j'$  to  $w'$ ,  $(1.20 \pm 0.02) \times 10^{-16}$ , is used.

L. L. BIRCUMSHAW.

**Range of the  $\alpha$ -particle of thorium.** J. L. NICKERSON (Trans. Nova Scotian Inst. Sci., 1930, 17, 172—174).—Using Wilson's chamber method a value of 2.75  $\pm$  0.1 cm. has been obtained for the range of the  $\alpha$ -particle from thorium. J. W. SMITH.

**Distribution in time of the scintillations produced by the  $\alpha$ -particles from a weak source.** N. FEATHER (Physical Rev., 1930, [ii], 35, 705—716).—Evidence has been found that at high concentrations (cf. Kutzner, A., 1927, 1003) and at very low temperatures (cf. Pokrowski, this vol., 9) radioactive disintegration may depart slightly from a perfectly time-random process. Using gold leaf which had been exposed to radon as a weak source of polonium the record of more than 10,000 scintillations produced by  $\alpha$ -particles was obtained and analysed. There was no evidence against the validity of the Marsden-Barratt distribution formula under these conditions. The effect of intense  $\gamma$ -radiation on the rate of disintegration in a weak source was investigated, with negative results (cf. Pokrowski, this vol., 393).

N. M. BLOCH.

**Indeterminacy of the energy of primary  $\beta$ -particles and induced  $H$ -particles.** E. GUTH

and T. SEXL (Naturwiss., 1930, 18, 183—184).—A theoretical discussion of the energy of primary  $\beta$ -particles and induced  $H$ -particles. R. W. LUNT.

**Absorption of  $\beta$ -rays.** J. A. CHALMERS (Proc. Camb. Phil. Soc., 1930, 26, 252—257).—The absorption curve for  $\beta$ -rays is calculated on the assumption that absorption by a larger thickness of matter is the sum of the absorptions by a series of thinner sheets (each of thickness 0.0001 g./cm.<sup>2</sup>). The conditions assumed are those in Schonland's experiments (Proc. Roy. Soc., 1925, A, 108, 187), where  $\beta$ -rays of velocity 0.52 of that of light were incident normally on aluminium. Scattering is deemed to occur at the centre of each sheet, and the beam unabsorbed after passing through a sheet is grouped into "direction-groups," rays travelling at inclinations of 0—30°, 30—60°, etc. to the original direction being treated as travelling at inclinations of 15°, 45°, etc. thereto. The rays in each such group are grouped into "velocity-groups" of  $\beta = 0.52$ —0.51, 0.51—0.50, etc. The results are in substantial agreement with experiment (cf. Schonland, *loc. cit.*; Eddy, A., 1929, 234), and imply that loss of velocity and scattering are sufficient to explain the phenomena of absorption. C. A. SILBERRAD.

**Complexity of nitrogen.** A. SMITS and J. DE GRUYTER (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 86—95, and Physikal. Z., 1930, 31, 435—440).—A confirmation of the prediction on the ground of quantum mechanics that nitrogen should exhibit molecular complexity has been obtained from a study of the vapour pressure of nitrogen at its b. p. It was found that a rapidly boiled-off portion of the nitrogen had a vapour pressure 0.1 mm. higher than the bulk of the liquid, and that this elevated pressure fell in the course of a few minutes to the normal value. This difference in vapour pressure would correspond with a difference in b. p. of about 0.025°, which is a value greater than can be attributed to experimental error. Three possible types of ( $T$ ,  $X$ ) diagrams for nitrogen are discussed. F. G. TRYBORN.

**Exit gas from an ammonia discharge tube.** G. I. LAVIN and J. R. BATES (Nature, 1930, 125, 709).—After passage through a discharge tube, ammonia contains a gas which reduces cupric oxide and a zinc oxide-chromium oxide catalyst. Small solid particles become incandescent. Solid ammonia condensed in liquid air at 1.5 m. from the discharge tube gives an intense bluish-green glow when the active gas is passed over it. The glow is not affected by the introduction of zinc catalyst in the gas stream nor is it produced by the passage of active nitrogen over solid ammonia. The presence of atomic hydrogen together with a compound of hydrogen and nitrogen, possibly  $NH$  or  $NH_2$ , in the exit gas from an ammonia discharge tube appears likely. L. S. THEOBALD.

**Charging of small suspended particles in the corona discharge.** W. DEUTSCH (Ann. Physik, 1930, [v], 4, 823—828; cf. Schweitzer, this vol., 271).—Reference is made to theories and experiments published before those of Schweitzer, with special mention of gas purification. A. J. MEE.

**Origin of the chemical elements.** S. B. STONE (J. Physical Chem., 1930, 34, 821—841).—Theoretical. The assumption that the formation of atoms results from a union of hydrogen and helium nuclei indicates (i) an upper limit of 340 for atomic weights, (ii) the concentration of matter into the lighter elements and into the  $4K$  type of atom, (iii) the possibility of slight variations in any one given type of atom, suggesting the existence of a fine structure in mass spectrum lines, and explains (iv) the evolution of the radioactive elements on thermodynamic lines. An explanation of cosmic rays in terms of a kinetic hypothesis is developed and differs from that of Millikan and Cameron in requiring the presence of a large quantity of soft radiation in the helium band and the absence of an iron band. A satisfactory ionisation-depth curve has been constructed. A magnetic hypothesis of the mechanism of atomic formation is suggested.

L. S. THEOBALD.

**Theory of the interaction of field and matter.** J. R. OPPENHEIMER (Physical Rev., 1930, [ii], 35, 461—477).—Mathematical. A method is developed for the systematic integration of the relativistic wave equations for the coupling of electrons and protons with each other and with the electromagnetic field. Since the present theory does not allow the elimination of the interaction of a charge with its own field the correct values for the energy levels and the frequency of the absorption and emission lines of an atom cannot be predicted. N. M. BLIGH.

**Possible influence of the mosaic structure of crystals on the determination of Avogadro's number.** F. ZWICKY (Proc. Nat. Acad. Sci., 1930, 16, 211—215).—The values for the charge of the electron as found by Millikan's oil drop method and Avogadro's number deduced therefrom are lower by 0.4—0.7% than those derived from absolute determinations of the wave-lengths of X-rays. This discrepancy is attributed to the treatment of the crystal lattice as a uniform instead of a mosaic structure (cf. this vol., 139). The calculated correction for rock salt is of the order found experimentally. A difference should be found in the wave-lengths of X-rays measured by two different crystals. The existence of surface cracks (cf. A., 1929, 630) should have no effect. N. M. BLIGH.

**Equilibrium between matter and radiation.** L. S. KASSEL (Physical Rev., 1930, [ii], 35, 778—781; cf. Zwicky, A., 1928, 1096).—Theoretical. The equilibrium concentration of electrons and protons, the ratio of the energy in the form of matter to that in the form of radiation, is calculated on the basis of Dirac's theory of the proton (cf. this vol., 271) and is found to be of the order of magnitude found in previous calculations. N. M. BLIGH.

**Wave mechanics and homo- and hetero-polar compounds.** A. T. WILLIAMS (Physikal. Z., 1930, 31, 367—368).—Theoretical. Polar compounds are explained on the basis of wave mechanics, especially from Kossel's point of view. A. J. MEE.

**Nuclear size and radiation properties of non-metallic bodies.** F. SKAUPY and G. LIEBMAN (Physikal. Z., 1930, 31, 373—374).—The effect of

nuclear size on reflexion and absorption and emission of radiation was determined. A curve is drawn showing the dependence of absorption for a given wave-length on nuclear size. The curve reaches a maximum and then decreases with decreasing nuclear size. The colour of powdered crystals depends not only on the absorption index, but also on the nuclear size of the powder. It is usually brighter for a powder than for a compact mineral. A. J. MEE.

**Effect of hydrogen and water on radiation from cyanogen-oxygen flame.** K. TAWADA (Nature, 1930, 125, 705—706).—Previous results are quoted (Garner and Tawada, this vol., 263).

L. S. THEOBALD.

**Emission spectrum of benzene in the region 2500—3000 Å.** J. B. AUSTIN and I. A. BLACK (Physical Rev., 1930, [ii], 35, 452—460; cf. McVicker and others, J.C.S., 1923, 123, 642).—The ultra-violet emission band spectrum of benzene vapour, excited by a Tesla discharge, was photographed and the wave-lengths of more than 100 bands between 2400 and 3000 Å. were measured. Equations are given to represent all the main bands. Evidence is presented that the bands are due to benzene and not to decomposition products, and the applicability of the data to spectroscopic analysis is discussed. N. M. BLIGH.

**Absorption spectrum of chlorine monoxide.** C. F. GOODEVE and J. I. WALLACE (Trans. Faraday Soc., 1930, 26, 254—260).—The extinction coefficient-frequency curve (2284—6200 Å.) of chlorine monoxide prepared by passing chlorine and air through a reaction vessel containing equal weights of mercuric oxide and sand at 9° shows three regions, viz., a rapid rise in absorption from 16,000 to a constant value at about 20,000  $\text{cm}^{-1}$ ; a further rise to a maximum at 23,600  $\text{cm}^{-1}$  with a slight irregularity at 21,000  $\text{cm}^{-1}$ ; and a high double maximum at 35,000 and 39,000  $\text{cm}^{-1}$ . Thermochemical evidence supports the interpretation of these regions as due to dissociation into (1)  $\text{Cl}_2 + \text{O}$ , (2)  $\text{ClO} + \text{Cl}$ , and (3)  $\text{Cl} + \text{Cl} + \text{O}$ , respectively. Photochemical evidence supports the formation of "chloric oxide" ( $\text{ClO}$ ) as an appreciably stable compound, and in this connexion the predissociation absorption and series convergence limit of chlorine dioxide are also discussed.

J. GRANT.

**Absorption spectrum of selenium dioxide.** S. F. EVANS (Nature, 1930, 125, 528).—A banded structure for selenium dioxide extending over the range 3840—5740 Å. has been observed between 250° and 400°.

L. S. THEOBALD.

**Absorption spectra of salt solutions. II. Absorption spectra due to oxyacidic anions. III. Absorption spectra due to cations.** S. KATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 7—21, 49—58; cf. this vol., 519).—II. The oxyacidic anions are classified into two groups according to differences in the absorption spectra which are due to changes in valency. The first group contains those anions which give a general absorption edge on the comparatively more refrangible side. If these are reduced to their oxyacids containing the same elements but with lower valency, no selective absorption occurs in the visible and infra-red regions, and the



edge of the general absorption is displaced towards the longer wave-lengths. The elements combined with oxygen in these oxyacidic anions occur in the sub-groups in the periodic system and change their valency by two units on reduction. The following conclusions have been reached after a study of the absorption spectra. The degree of stability of the oxyacidic anions containing the elements at their maximum valency as well as that of the reduced oxyacidic anions decreases with the increasing atomic number of the element. The anions containing the elements at their maximum valency are more stable in solution than the reduced ions. Throughout, the absorption due to the anions depends on the valency of the elements combined with oxygen in them. In the second group are placed those oxyacidic anions which give the general absorption edge on the relatively less refrangible side. When these are reduced there appear selective absorption spectra in the visible and infra-red regions, and the general absorption edge is displaced towards the shorter wave-lengths. In these cases the elements combined with oxygen in the anions on reduction change their valencies only by one unit. These anions are less stable in solution than those in the first class. Compounds containing an element of higher valency are more difficult to convert into those containing the same element at a lower valency and in these compounds the wave-length of the absorption edge shifts to the shorter-wave side.

III. Cations which give selective absorption spectra in the visible and infra-red regions are discussed. In the majority of cases the absorption due to cations is due to the change of electron spins in the outside incomplete *d*-shell, the transition taking place between the normal state and the next higher energy levels of atom-ions. The effect of surrounding atoms and molecules on the selective absorption is discussed. The smaller are the selective absorption frequencies the more stable are the ions. A. J. MEE.

Ultra-violet absorption of inorganic salt solutions. II. Absorption of alkaline-earth halides. J. VON KOCZKÁS (Z. Physik, 1930, 61, 545—547).—Aqueous solutions of the chlorides of calcium, strontium, and barium exhibit a selective absorption band in the middle ultra-violet region with the centres of each band at approximately the same place (this vol., 132). An examination of aqueous solutions of bromides and iodides of these metals revealed no absorption maximum corresponding with that obtained with the chlorides, but the absorption curves indicate the existence of an absorption maximum outside the measurable spectral range. The amount of the ultra-violet absorption increases with increasing at. wt.—Ba>Sr>Ca and I>Br>Cl—in agreement with Müller's results for aqueous solutions of alkali halides (A., 1927, 185). W. R. ANGUS.

Light absorption and constitution of complex salts. II. Aliphatic amino-acids and inner complex salts of copper. H. LEY and F. VAN-HEIDEN (Z. anorg. Chem., 1930, 188, 240—258; cf. A., 1927, 1009).—A continuation of previous work. The molar extinctions of the copper salts of amino-acetic,  $\alpha$ -aminopropionic, piperidinoacetic, picolinic,

and  $\alpha\beta$ -diaminopropionic acids have been determined. When concentrated ammonia solution is present there is evidence, especially in the case of piperidinoacetic acid, that the anion of the complex salt is eliminated with formation of the tetramminecopper cation. The extent to which a similar action occurs in the other compounds studied has been investigated by measuring their electrical conductivity in the presence of varying concentrations of ammonia.  $\alpha\beta$ -Diaminopropionic acid has been separately studied, and its acid and first and second basic ionisation constants have been determined to be  $3.4 \times 10^{-8}$  and  $1.9 \times 10^{-13}$ , respectively. F. L. USHER.

Absorption spectra in the vapour state of methyl halides and other methyl compounds in the ultra-violet and Schumann region. G. HERZBERG and G. SCHEIBE (Z. physikal. Chem., 1930, B, 7, 390—406).—The interpretation of the observations previously recorded (this vol., 10) is discussed. The continuous absorption bands are attributed to dissociation of the molecule into the methyl group and either a halogen, hydroxyl, or cyanide group, one product of dissociation being excited, whereas the discontinuous bands are considered to indicate transition into several excited electronic states, 1090 and 1080  $\text{cm}^{-1}$  being principal vibration frequencies in the first and second states, respectively, of methyl iodide. R. CUTHILL.

Absorption of agar-agar and *Conophallus Konjak* in the ultra-violet region. S. DOTE and T. SHIDEI (Japan. J. Phys., 1929, 5, 157—160).—With the view of providing a film for photographic plates more transparent than gelatin to short wave-length ultra-violet rays, the absorption of films and solutions of agar-agar and *Conophallus Konjak*, and of commercial viscose film was photographed, and absorption curves were constructed. The films were more transparent than the corresponding solutions, which were themselves more transparent than gelatin, especially in the extreme ultra-violet.

N. M. BRIGHT.

The asymmetrical rotator and its infra-red spectrum. C. R. BAILEY, A. B. D. CASSIE, and W. R. ANGUS (Trans. Faraday Soc., 1930, 26, 197—202).—Lütgemeier's expressions (A., 1926, 991) for the energy of an asymmetrical rotator when spinning (i) about its axis of least inertia, and (ii) about its axis of greatest inertia are used to predict line separations in the vibrational-rotational spectra of asymmetrical molecules. There are two distinct sets of line separations, depending on the distribution of the total angular momentum between the spin and precessional momenta. A. B. D. CASSIE.

Infra-red spectrum of water vapour. C. R. BAILEY (Trans. Faraday Soc., 1930, 26, 203—211).—Present data on the infra-red spectrum of water vapour are resolved as far as possible, and the appropriate line separations are determined. Approximate values for the moments of inertia of the water molecule are used to calculate second order parameters in the formulæ (cf. preceding abstract) for rotational line separations. The observed values of the separations, when inserted in these formulæ, then give corrected values for the moments of inertia, viz., 2.91, 1.91 and

$0.97 \times 10^{-40}$  g.-cm.<sup>2</sup> Two fundamental frequencies, 1607 cm.<sup>-1</sup> and 3864 cm.<sup>-1</sup>, appear sufficient to account for the vibrational-rotational bands. Molecular models for water are discussed; the isosceles triangle of side  $1.07 \times 10^{-8}$  cm. and of angle 64° is favoured.

A. B. D. CASSIE.

**Spectroscopic evidence of two types of ammonia molecule.** J. W. ELLIS (Physical Rev., 1930, [ii], 35, 595—599).—The equation for the anharmonic frequencies arising from vibratory energy changes in ammonia molecules in solution (cf. Badger and Meeke, A., 1929, 1363) differs from that for the gas (this vol., 521) by the presence of a constant term and a larger coefficient for the  $n^2$  term. The wavelength 2.916  $\mu$  for the ammonia solution band was confirmed by observations on a solution in carbon tetrachloride. The constant term is interpreted as measuring the energy required to change the molecule from an  $\alpha$ - to a  $\beta$ -form of greater potential energy, and the greater coefficient, indicating a more rapid approach of the energy terms towards confluence, is assumed to arise from the proximity of the molecules of the solvent. The existence of a constant in the infra-red formula assists the interpretation of the Raman spectrum of ammonia, liquid and in solution.

N. M. BLIGH.

**Near infra-red absorption spectrum of calcite.** J. W. ELLIS (Proc. Nat. Acad. Sci., 1930, 16, 315—320).—Sections of crystals, thicker than those used by previous investigators, have been examined with a registering spectrograph and three new bands have been found at 1.65, 1.56, and 1.47  $\mu$ . These bands have a doublet structure. The doublet structure of a number of bands previously reported has been definitely established. The influence of plane-polarised light on the bands is discussed; it was found that all the bands disappear almost entirely when the light is nearly completely plane-polarised at right angles to the optic axis. The bands observed by infra-red and Raman methods are tabulated and arranged as combinations of three fundamental frequencies. (Cf. Schaefer and others, A., 1927, 5.)

W. R. ANGUS.

**Infra-red absorption of some organic liquids.** E. K. PLYLER and T. BURDINE (Physical Rev., 1930, [ii], 35, 605—612).—With the object of tracing similarities in the near infra-red absorption bands of organic liquids of different types, investigations of bands in the region 1—8  $\mu$  were made on methyl, ethyl, propyl, butyl, isopropyl, isoamyl, and isobutyl alcohols (cf. Sappenfield, A., 1929, 236), *o*- and *m*-nitrotoluene, methyl and ethyl sulphate, nitromethane, nitrobenzene, and ethyl acetoacetate, using the method previously described (cf. A., 1929, 1215). Percentage transmission-wave-length curves for each substance are given. The bands in the region 1—3  $\mu$  are classified as overtones or combination bands of the assumed fundamental bands for the alcohols at about 3, 3.4, 6.8, and 9.8  $\mu$ . Intensity relations are discussed, and shown to be in general agreement with combinations attributed to the different bands. Combinations of the fundamentals at 3.4 and 6.8  $\mu$  are given for *m*-nitrotoluene, methyl sulphate, and nitromethane. It is suggested that the similarity in the spectra of different organic

compounds in the region 1—3  $\mu$  is due to the combinations of bands having fundamentals at 3.3 and 6.8  $\mu$  common to these compounds. N. M. BLIGH.

**Infra-red spectrum of diamond by infra-red spectrometer and Raman methods.** R. ROBERTSON and J. J. FOX (Nature, 1930, 125, 704).—The spectra of seven diamonds obtained by the infra-red spectrometer show apparently three fundamental frequencies and one combination band; the wave numbers have the approximate values  $\nu_1=1246$ ,  $\nu_2=2086$ ,  $\nu_3=2438$ , and  $\nu_2+\nu_1=3353$  cm.<sup>-1</sup> The spectrum obtained by the Raman method using the line  $\lambda$  4358 shows a sharp line at approximately  $\lambda$  4629.

L. S. THEOBALD.

**Raman effect in diamond.** C. RAMASWAMY (Nature, 1930, 125, 704).—The mercury lines 4046.6 and 4358.3 Å. each excite a single, sharp, and intense Raman line in the diamond, the wave-number shifts being 1331 cm.<sup>-1</sup> and 1333 cm.<sup>-1</sup>, respectively. A diffuse band at 4155 Å. is also shown.

L. S. THEOBALD.

**Raman effect in water.** I. R. RAO (Nature, 1930, 125, 600).—Pure water gives diffuse bands corresponding with the wave-lengths 3.12, 2.93, and 2.79  $\mu$ . In solutions of electrolytes these bands become sharper with increase in concentration. The 3.12  $\mu$  band gradually diminishes to zero intensity; the 2.79  $\mu$  band, which is weakest in pure water, increases in intensity with concentration until it reaches that of the central band, which is the strongest band in pure water. A similar behaviour accompanies a rise in temperature. With ice, the band 3.12  $\mu$  is stronger in intensity than in pure water, whilst the 2.79  $\mu$  band is weaker still.

L. S. THEOBALD.

**Raman spectra of some compounds containing the  $S_mO_n$  or  $RO_4$  group.** H. NISÉ (Japan. J. Phys., 1929, 5, 119—137).—With the object of comparing with the known infra-red absorption spectra, of investigating the influence of the R atom in the  $RO_4$  group on the wave-number shift, and of studying in various concentrations sulphuric acid and its derivatives, the Raman spectra of a number of compounds were photographed, using Wood's arrangement for liquids (cf. A., 1928, 1306), and a method previously described for crystals (cf. A., 1929, 742). For aqueous solutions of lithium, sodium, potassium, ammonium, magnesium, zinc, and cadmium sulphates, three diffuse lines and an intense line due to the  $SO_4$  group, corresponding with a wave-number shift of about 980 cm.<sup>-1</sup>, were found. Gypsum and barytes gave spectra approximately similar to those of the sulphate solutions. The  $NH_4$  group gave a characteristic band. The spectrum of potassium hydrogen sulphate solution indicated ions in successive stages of dissociation; the wave-number shifts of the corresponding lines due to  $SO_3$ ,  $SO_4$ , and  $HSO_4$  groups are not equal. Solutions of compounds containing the  $RO_4$  group were investigated, where R=Se, Te, Cr, Mo, W, P, As, V, I, and Cl, and showed an intense line and decreasing shift with increase in the atomic number of R, but an increasing shift in the chromium group. The Raman spectrum of sulphuric acid solution showed lines due to  $HSO_4$  and  $SO_4$  groups.

and was greatly influenced by concentration; results for the line due to the  $\text{SO}_4$  group were inconsistent with those from infra-red investigations. The spectrum of chlorosulphonic acid resembles that of sulphuric acid, and in both were found lines corresponding with the principal infra-red absorption maxima for gaseous sulphur dioxide; a preliminary study on the polarisation of these lines is given. Similarity exists between the Raman spectra of sodium metabisulphite and dithionate (cf. Pringsheim and Yost, A., 1929, 1362), and of sodium thiosulphate and sulphate solutions, the thiosulphate being regarded as sulphate in which one atom of sulphur replaces an oxygen atom, and of potassium pyrosulphate and potassium hydrogen sulphate. N. M. BLIGH.

**Raman spectrum of crystalline and dissolved nitrates.** W. GERLACH (Naturwiss., 1930, 18, 182).—In lithium, sodium, and potassium nitrate solutions the separation of the water doublet at 4655 Å. increases approximately linearly with the concentration, whilst in the solutions of the corresponding chlorides the doublet disappears with increasing concentration. The same doublet appears in the spectrum of suspensions of the finely-divided salts. New lines are reported corresponding with  $\Delta\nu=720\text{ cm}^{-1}$ ,  $\lambda=13.9\text{ }\mu$ , which, it is thought, may be identified with the nitric acid frequency difference  $\Delta\nu=697$  reported by Carrelli, Pringsheim, and Rosen (cf. A., 1929, 120). R. W. LUNT.

**Raman spectra of nitric acid and aqueous solutions of certain nitrates.** I. KISHI (Mem. Coll. Sci. Kyoto, 1930, 13, 163–167).—New Raman lines were found at 4259 Å. with nitric acid, 4496 and 4166 Å. with sodium nitrate, and 4566, 4495, 4259, 4225, and 4165 Å. with ammonium nitrate. Raman lines having a difference of  $1042\text{ cm}^{-1}$  in the wave-number were found for all nitrates examined, and other lines having a difference of  $700\text{ cm}^{-1}$  in the case of nitric acid, sodium, potassium, ammonium, cadmium, and lead nitrates. C. J. SMITHELLS.

**Raman effect and chemistry.** A. DADIEU and K. W. F. KOHLRAUSCH (Ber., 1930, 63, [B], 251–282; cf. A., 1929, 866, 977; Raman and Krishnan, A., 1928, 1075; Landsberg and Mandelstam, *ibid.*, 936, 1306).—The incidence of the effect is not restricted to liquids, since solids and gases also give displaced lines. The number and position of the Raman lines are, within the limits of accuracy of measurement, independent of the state of aggregation and, in solution, of the nature of the solvent. Changes of temperature influence the intensity relationships, but not the position of the lines provided that alteration of molecular structure is not induced. In the few cases examined, the lines of the same spectrum frequently exhibit different states of polarisation.

A modified type of apparatus is described and the Raman spectra of about 70 compounds (mainly organic) have been determined. Lines occur in the region above  $\nu'=2800\text{ cm}^{-1}$  only when hydrogen atoms are present in the molecule and in the interval, 600–2800  $\text{cm}^{-1}$  only when the molecule contains double, triple, or particularly stable linkings. In general, the frequency increases with increasing firmness of union and decreasing mass of the vibrating

portions. Lines characterised by great permanence are observed to occur in almost the same positions in spite of variations in the molecule as a whole provided that it contains a definite linking, for example, C:O or C:C. These vibrations which are only secondarily influenced by the structure of the molecule are termed "internal vibrations" and their permanence allows them to be recognised readily and assigned to definite groups in the molecule. The following are described in detail. All compounds containing the aliphatic C-H linking exhibit a Raman frequency at about  $\nu'=2930\text{ cm}^{-1}$ ; the line is often diffuse, varies appreciably in position, and frequently becomes divided into two or more lines but it is not shown by compounds from which this group is absent. All aromatic hydrocarbons and their derivatives exhibit a well-defined line at  $\nu'=3050\text{ cm}^{-1}$  which is generally remarkably sharp and only little influenced in its position by neighbouring substituents. If the substituent contains the aliphatic C-H linking (toluene, xylene) the line 2930 also appears; unexpectedly, this is also the case with benzene. The ethylenic linking causes the appearance of a line about  $\nu'=1600\text{ cm}^{-1}$  which varies very little in position, whereas for the acetylenic linking the line at about  $\nu'=1960\text{ cm}^{-1}$  is characteristic. For the C:O linking the position of the line lies between 1640 and 1730, but is very constant for analogously constituted compounds. The influence of substituents is particularly marked (see later). The C:N and  $\text{NO}_2$  groups cause lines at about  $\nu'=2200$  and  $1400\text{ cm}^{-1}$ , respectively. Almost without exception, compounds in which at least two hydrogen atoms are attached to the same carbon atom exhibit a line of very constant frequency at 1440. The benzene nucleus is characterised by a series of very persistent frequencies at 604, 997, 1176, 1368 (?), a double line at 1590, and the aromatic C-H line at 3050. Simple substitution has little influence on the position of the lines, whereas double substitution causes fission and displacement of the lower frequencies without greatly affecting the higher frequencies. It does not appear possible at present to assign a definite internal vibration to the C-halogen linking.

Since in a given class of compound, the position of the lines varies relatively slightly with the different members, it follows that the effect is due to vibrations of the same masses and that the shift of the lines from compound to compound is due to slight change in the firmness of union. This constitutive influence is considered in detail with respect to the C-H and C-O linking. In the case of compounds containing the acetyl group, the second substituent has a loosening effect in the sequence  $\text{OAlk} < \text{H} < \text{Alk} < \text{Ar} < \text{OH}$ , whereas with the constant grouping  $\text{H}\cdot\text{CO}-$  the sequence is  $\text{Alk} < \text{OAlk} < \text{Ar} < \text{NH} < \text{OH}$ . With respect to individual compounds, the line at  $1310\text{ cm}^{-1}$  observed with nitric acid (about 60%) and sodium nitrite but not with nitrates (cf. Carrelli, Pringsheim, and Rosen, A., 1929, 120) is found in organic nitro-compounds and therefore the presence of the undissociated molecule  $\text{HO}\cdot\text{NO}_2$  in nitric acid is regarded as established. The frequency at  $2155\text{ cm}^{-1}$  observed for carbon monoxide by Rasetti (A., 1929, 241) is closely allied to that observed for the N:N and C:C

linkings, whereas the frequencies of the double linking lie between 1500 and 1700  $\text{cm}^{-1}$ ; the structure  $\text{C}:\text{O}$  appears therefore to be established. For benzene, the Raman spectra support the Kekulé constitution (cf. A., 1929, 976). For allylthiocarbimide the constitution  $\text{CH}_2:\text{CH}:\text{CH}_2\cdot\text{N} \leq \text{C} \begin{smallmatrix} \diagup \\ \text{S} \end{smallmatrix}$  is suggested.

Attempts are made, with the aid of definite assumptions concerning the oscillation process, to reduce the observations to a quantitative basis. The connexion between the Raman frequencies and infra-red absorption spectra and energy of disruption is considered.

H. WREN.

**Raman effect. VI. Raman spectra of organic substances.** A. DADIEU and K. W. F. KOHLRAUSCH (Monatsh., 1930, 55, 201—224).—The Raman spectrum of acetone has been repeated (cf. A., 1929, 866; this vol., 14) and is found to be similar to that obtained by Dickinson and Dillon (A., 1929, 741). The other substances investigated are zinc acetate, acetonitrile, *n*-butyl bromide, allyl alcohol, *m*-dichlorobenzene, diphenyl, benzoic acid, methyl and ethyl benzoate, ethyl succinate, malonate, and oxalate. Tables of Raman frequencies and relative intensities of the lines are given for each substance. The frequency  $\nu=1440 \text{ cm}^{-1}$  is assigned to the C-H linking, and  $2246 \text{ cm}^{-1}$  to the C-N linking; the C-C linking is characterised by a line at  $1645 \text{ cm}^{-1}$ , whilst all the esters give lines corresponding with the characteristic frequencies of the C-O linking. The similarity in the spectra of derivatives of the same substance is discussed and illustrated by the derivatives of acetic acid (esters and inorganic salts) and by benzene and its substitution products. The relation between chemical binding and Raman frequency is discussed. To each chemical binding is assigned a definite frequency, and also a definite value of a constant,  $k$ , which is given by  $\nu=k\sqrt{A/u}$ , where  $\nu$  is the Raman frequency characteristic of the linking,  $A$  the value for the thermochemical dissociation of the linking expressed in kg.-cal./mol., and  $u=m_1m_2/(m_1+m_2)$  is the reduced mass. Results obtained from sixteen linkings are collected in a table. The value of  $k$  depends on the type of the linking, thus H-H=293; C-H=292; H-Cl=294; O-H=300; N-H=329; C-O=326; C'O=325; C'O=352.

W. R. ANGUS.

**Theory of polarisation of scattering in crystals.** M. LEONTOVITSCH (Z. Physik, 1930, 61, 548—556).—The possible theoretical significance of the results of Cabannes (A., 1929, 378, 627) and Menzies (*ibid.*, 1361) on the polarisation of the scattered radiation in quartz and calcite is discussed. The classical tensor method is used.

A. B. D. CASSIR.

**Combination scattering in absorption and Fraunhofer lines.** F. BORYSCHANSKAJA and G. LANDSBERG (Naturwiss., 1930, 18, 183).—Combination scattering has hitherto been found in emission spectra only. If the exciting radiation is a continuous source with sharp absorption lines, the scattered light should show, not only absorption lines of unmodified frequency  $\nu$ , but also lines of frequency  $\nu-\nu'$ , where  $\nu'$  is the natural frequency of the scattering medium. Such "false" absorption (combination)

lines corresponding with  $\lambda=21.5 \mu$  have been found in quartz, when a continuous source filtered through a neodymium-praseodymium solution so as to produce a band is passed into a clear quartz crystal. A similar explanation is put forward for the weakest Fraunhofer lines. It is also suggested that atmospheric scattering should result in very faint Fraunhofer lines close to the true lines, but these have not yet been observed.

J. J. FOX.

**Volume light effect (longitudinal scattering) for light rays passing through different media.** J. PLOTNIKOV and L. ŠPLAIT (Physikal. Z., 1930, 31, 369—372).—The expected existence of a longitudinal scattering of light rays on passing through different media is proved experimentally for long and short waves. There is a complicated relationship between the wave-length and the molecular size of the medium. The higher is the mol. wt. of the medium the longer is the wave-length for which the effect can be observed. Three spectral ranges were used which were obtained by the use of glass filters placed in front of a carbon arc. The following media were used: resin (artificial and natural), gelatin, collodion, paraffin, paraffin oil, light petroleum, machine oil, glycerol, ethylene glycol, ethyl alcohol, methyl alcohol, water, solutions of alcohol in water. An unusual occurrence was noted with ethyl alcohol; it not only gave a strong scattering effect in the infra-red, but the addition of one drop of alcohol to water was sufficient to produce this effect. Many substances gave dark rings of different widths and intensities. The scattering effect caused no polarisation of the scattered light.

A. J. MEE.

**Water as an activator of luminescence.** J. EWLES (Nature, 1930, 125, 706—707).—Many white substances such as salts or silica, when wet, show a bright blue luminescence when irradiated by a mercury-vapour lamp through a screen excluding the visible region. In most cases, also, there is a transient phosphorescence. The intensity of the luminescence varies with the amount of water present. In the case of lithium fluoride, two optima, corresponding with the existence of  $\text{LiF}\cdot\text{H}_2\text{O}$  and  $\text{LiF}\cdot 2\text{H}_2\text{O}$ , are shown.

L. S. THEOBALD.

**Luminescence from solidified gases at the temperature of liquid helium.** L. VEGARD and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 10—16).—Spectrographic investigations have been made of the luminescence of solid nitrogen and nitrogen-neon mixtures produced by bombardment with cathode rays of high velocity at the temperature of liquid helium. The nitrogen luminescence is not polarised to any noticeable degree, and all four of the bands at 5577.2, 5205, 6325, and 5947 Å. appear in the afterglow. Previous results regarding the motion and contraction of the band at 5577.2 Å. have been confirmed, and this figure represents the limit obtained as the nitrogen concentration approaches zero. In addition to these four bands the spectra contain lines belonging to the series  $C$ ,  $\eta$ ,  $\epsilon$ ,  $\alpha$ ,  $\zeta$ ,  $b'$ , and perhaps  $\gamma$ . The  $\text{N}_2$  band (5205 Å.) consists of two parts, one a diffuse band with two maxima (5209, 5202) stretching across the spectrum, and the other of a short band restricted to the middle part of the spectrum, and consisting of

four maxima, 5243, 5236, 5229, 5221 Å. The four doublets 3163.6 3149.6, 3104.5 3090.5, 2906.9 2895.2, and 2841.6 2830.2 Å. have been observed in the direct light from pure neon. These give a frequency difference between the components which is constant within the limit of error. These doublets are possibly due to vibrations of molecules. F. G. TRYHORN.

**Fluorescence of praseodymium and neodymium glasses.** P. PRINGSHEIM and S. SCHLITZ (Z. Physik, 1930, 61, 297—306).—The discontinuity in the fluorescence spectra of praseodymium, neodymium, and didymium glasses is not only due to the superposition of a discontinuous absorption spectrum, but is primarily due to an emission process. The praseodymium glass shows more independent groups of fluorescence bands with unequal distribution of excitation, and quite different relative intensities for different samples of glass. The fluorescence of neodymium glasses is much weaker, but many didymium glasses, on the contrary, show very strong fluorescence, the spectrum agreeing fairly closely with that for neodymium glass. The intensities of the fluorescence of praseodymium and neodymium glasses depend a good deal on the accurate preparation of the glass. A. J. MEE.

**Structure and power of light emission of solid carbon monoxide.** L. VEGARD (Z. Physik, 1930, 61, 185—190).—In order to elucidate difficult points in the behaviour of solid  $\alpha$ -nitrogen, solid carbon monoxide has been examined at liquid hydrogen temperatures. The number of outer electrons is the same in each case and the spatial distribution, lattice dimensions, and atomic separations have been found to be approximately the same. The great similarity is illustrated by the reproduction of X-ray (powder) diagrams of the two substances. Values of the parameters, relative intensities, atomic separation, and density are calculated. An extraordinary difference exists between the two substances in their power of emitting light. Solid carbon monoxide is excited by very weak light and does not exhibit phosphorescence. W. R. ANGUS.

**Fluorescent and phosphorescent substances.** J. R. PARTINGTON (Nature, 1930, 125, 636).—Cadmium tungstate and barium and magnesium platinocyanides, which fluoresce strongly under the influence of X-rays, have, according to Werner's formulation, an atom of high stopping power with four light atoms or radicals arranged about it, whilst a bivalent positive ion is present in each case. L. S. THEOBALD.

**Composition of calcium-strontium-samarium sulphide mixed phosphors.** E. RUMPF and M. TRAVNIČEK (Ann. Physik, 1930, [v], 4, 725—732).—It has been shown that there is proportionality between lattice constant and the positions of the phosphorescence bands, but for this the mean lattice constant was used, and not the principal one. The amount of deviation due to this is shown. During the preparation of the sulphide phosphors mixed crystals of the calcium-strontium-fluorine series with high strontium content were formed. The fluorine was combined chiefly with strontium, but the presence of this series must make a difference in the atomic concentrations

used in obtaining previous results. Assuming that all the fluorine was combined with strontium, a correction can be made which will give the true atomic concentrations of the sulphides. Pure calcium-strontium sulphide mixed crystals appear to obey Vegard's additive law. If the assumption is made that the displacement of the sharp principal red line of the calcium-strontium-samarium sulphide mixed phosphors is proportional to the change of the lattice constant of the calcium-strontium sulphide mixed crystal system, results are obtained which cannot be confirmed by experiment. The formula  $\nu = 158 \times 10^3 + 1795\alpha$  where  $\alpha$  is the principal lattice constant expresses the facts more closely. There is thus a linear relationship between the wave numbers of the phosphorescence bands and the principal lattice constant. Experiments on the ageing of these phosphors were carried out, but led to no results. A. J. MEE.

**Light emission of some alkali halide phosphors containing thallium.** W. VON MEYEREN (Z. Physik, 1930, 61, 321—331).—The distribution of the light emitted by a number of alkali halide phosphors containing thallium was determined by a photographic-photometric method. Monochromatic light was used for the excitation, and only emission bands were investigated, the maximum wave-length being 430 m $\mu$ . The emission is identical for fluorescence and phosphorescence, and is independent of the wave-length of the exciting light. The simplest distribution is given by the chloride phosphors of sodium and potassium. They show only one uniform emission band throughout the whole temperature range of  $-183^\circ$  to  $150^\circ$ . Experiments were also made using cathode rays for the excitation of thallium phosphors, as it was possible that there were further emission bands when the excitation was in the Schumann ultra-violet range, but these led to no definite results. A. J. MEE.

**Ionisation potential of CN and C<sub>2</sub> molecules.** H. KALLMANN and B. ROSEN (Z. Physik, 1930, 61, 332—337; cf. this vol., 398).—Another method is used for the determination of the ionisation potentials of the cyanogen and carbon (C<sub>2</sub>) molecules, the ionisation chamber containing also a gas of known ionisation potential (in this case argon). The selective ionic absorption was then determined. The results show that the values previously arrived at of 14 volts for the ionisation potential of the CN molecule and 12 volts for the C<sub>2</sub> molecule are correct. The formation of C<sub>2</sub> from dicyanogen is correctly represented by the equation  $(CN)_2 \longrightarrow C_2^+ + N_2$ . Incidentally it is also shown that the ionisation work of oxygen, O<sub>2</sub>, is less than 13.5 volts. A. J. MEE.

**Dielectric behaviour of hydrated oxides.** L. HAVESTADT and R. FRICKE (Z. anorg. Chem., 1930, 188, 357—395).—The dielectric constants of hydrated oxides of beryllium, aluminium, gallium, silicon, tin, thorium, and chromium have been measured, and parallel observations have been made on their X-ray interference patterns, ultra-microscopic appearance, cataphoresis, and fluxional birefringence, with the object of securing information regarding their chemical character under conditions

least likely to change it. The dielectric constants were usually higher than that of water, the highest value observed being 112 in the case of thorium hydroxide. The "ageing" of the oxides was shown by characteristic changes in the dielectric constants, increase of the latter corresponding with the growth of crystal structure indicated by X-ray analysis. The dielectric constants of non-crystalline oxides always decreased with time. The magnitude of the electric charge of the particles deduced from measurements of cataphoretic velocity was reflected in the dielectric constant, which increased with the former in consequence of the enhanced polarity. Amorphous aluminium hydroxide precipitated from cold acid solution changes under water to böhmite and finally to bayerite. Amorphous beryllium hydroxide similarly becomes crystalline. A crystalline hydroxide of gallium having the composition  $\text{Ga}_2\text{O}_3 \cdot 1.66\text{H}_2\text{O}$  was prepared, which gave an X-ray diagram different from that of gallium oxide prepared by heating the hydroxide. F. L. USHER.

**Properties of the chlorides of sulphur. III. Dielectric constants.** T. M. LOWRY and G. JESSOP (J.S.C., 1930, 782—792; cf. A., 1927, 505; 1929, 978).—The dielectric constants of mixtures of sulphur chloride and chlorine have been measured over the range of composition from monochloride to chlorine, from the ordinary temperature down to the f. p. The results confirm the dissociation of dichloride into monochloride and chlorine, but give no indication of the formation of the tetrachloride. The dielectric constant of solid chlorine is almost identical with that of the liquid; those of mixtures increase on solidification, passing through a maximum near the composition of the tetrachloride. Sulphur tetrachloride dissolved in chlorine and in liquid hydrogen chloride has no electrical conductivity. C. W. GIBBY.

**Measurement of the dielectric constant and index of refraction of water and aqueous solutions of potassium chloride at high frequencies.** F. H. DRAKE, G. W. PIERCE, and M. T. DOW (Physical Rev., 1930, [ii], 35, 613—622).—The method employed depends on the measurement of standing electric waves between a pipe and a concentric wire, the liquid being the dielectric between the two; frequencies were measured by a piezo-crystal and zero beat method, half wave-lengths within the dielectric being obtained by moving a piston in the liquid and observing reactions on the source. The dielectric constant of distilled water measured with a vacuum tube source of voltage was 78.57 at 25°, independent of the period within the range  $(1.31-8.49) \times 10^{-8}$  sec., corresponding with vacuum wave-lengths of 3.918—25.47 metres. An empirical equation is found for the temperature coefficient between 10° and 60°. With distilled water, tap water, and aqueous potassium chloride solutions of conductivity range 0.97— $178 \times 10^7$  e.s.u., the dielectric constant was only slightly dependent on the ionic concentration and nearly the same as for pure water. N. M. BLIGH.

**Measurements of the dielectric constants of conducting media.** J. WYMAN, jun. (Physical Rev., 1930, [ii], 35, 623—634).—A method of measuring the dielectric constant of small amounts of dilute

solutions, suitable for biological substances, is described. Small rigid resonators were made, having natural periods determined by the medium in which they are immersed, and in contrast to the usual procedure, the frequency of the oscillator is tuned to the resonator, first in air, then in the liquid. Values for the dielectric constant of water for the frequency range  $1.4-8.1 \times 10^{-8}$  were in good agreement with those by a different method (cf. preceding abstract). The difficulties of salt solutions are discussed and it is shown that the method can be adapted to liquids having conductivities up to 100 times that of water. N. M. BLIGH.

**Dielectric constants of liquids. II. Temperature coefficient of the dielectric constant of water.** G. DEVOTO (Gazzetta, 1930, 60, 208—212).—Measurements have been made for water at temperatures between 3.8° and 39.2° for a wave-length of about 90 cm. These values are in excellent agreement with those found by Koekel using a much higher wave-length. At 25° the coefficient is  $-0.392$ . The use is discussed of the temperature coefficient in the evaluation of the integral heat of dilution of a solution by the Debye-Hückel equation. F. G. TRYHORN.

**Dielectric constant and molecular structure of carbon disulphide.** C. T. ZAHN (Physical Rev., 1930, [ii], 35, 848—854; cf. A., 1928, 1172; Ghosh and others, A., 1929, 1365).—Using the radio frequency heterodyne method, the dielectric constant of carbon disulphide vapour was measured at various temperatures and pressures. The value 22.36 is obtained for the molecular polarisation, which is independent of the temperature, the electric moment being zero. The structure of the molecule is concluded to be rectilinear and symmetrical. N. M. BLIGH.

**Variation of dielectric constant with temperature. I. Electric moments of the carbon disulphide and nitrous oxide molecules.** C. H. SCHWINGEL and J. W. WILLIAMS (Physical Rev., 1930, [ii], 35, 855—862; cf. preceding abstract).—An apparatus for the determination of dielectric constants of gases and vapours and their dependence on temperature over a range of several hundred degrees is described. The electric moments of gaseous carbon disulphide and nitrous oxide were found to be zero, indicating a linear arrangement of the three atoms in each molecule. N. M. BLIGH.

**Determination of electric moments of molecules from the temperature variation of the dielectric constant.** R. SÄNGER (Physikal. Z., 1930, 31, 306—315).—It is emphasised that measurements of the temperature variation of the dielectric constant of gases and vapours can be used for an accurate determination of their electric moment only when the equation of state of the gases is known with a corresponding accuracy. Correction is made to the values obtained by Säger and Steiger (this vol., 275) for the electric moments of water and ethyl ether. Using the Beattie-Keyes equation of state for ether, the corrected value for the moment is shown to be  $1.146 \pm 0.012 \times 10^{-18}$  e.s.u. A small correction is made to the previous value for the moment of water,



which was obtained by use of a simplified equation for the molecular polarisation; the exact equation gives the value  $1.842 \pm 0.008 \times 10^{-18}$  if the result at the lowest temperature is rejected owing to the association of the water. Using these accurate values and the available data for the dispersion, the infra-red term of the static molecular polarisation  $A$ , is calculated for water to be  $0.08 \pm 0.06$  and for ether  $4.47 \pm 1.00$ . The low value for water is shown to agree with the intensity of the infra-red absorption bands of water vapour. Using the results of lines for the infra-red absorption spectra, the value of  $A$ , for hydrogen chloride and bromide is calculated to be 0.41 and 0.50, respectively, in disagreement with the values 1.34 and 0.22 which are calculated from the dielectric measurements of Zahn. This is explained by the inaccurate values for the density used by Zahn. Conflicting theories of the molecular structure of the ethers are discussed and further progress with vapours is shown to be expected by the method of Raman and Krishnan through accurate measurement of the Kerr effect.

H. A. JAHN.

**Dielectric constants of binary mixtures. IX. Electric moments of substituted phenols and their relation to the stereochemistry of the oxygen atom.** J. W. WILLIAMS and J. M. FOGELBERG (J. Amer. Chem. Soc., 1930, 52, 1356—1363; cf. A., 1927, 819).—The following electric moments are recorded: *o*-, *m*-, and *p*-chlorophenol, 1.43, 2.17, and  $2.68 \times 10^{-18}$  e.s.u., respectively; *o*-, *m*-, and *p*-nitrophenol, 3.10, 3.90, and 5.05; *o*- and *p*-bromophenol, 1.36, and 2.86; *o*- and *p*-anisidine, 1.50, and 1.80; *m*-aminophenol, 1.83. The compounds are regarded as derivatives of oxygen in which the valency linkings subtend an angle of less than  $180^\circ$ . Dipole moments can be calculated only if the stereochemistry and mutual electrical interactions of the substituent groups are known.

J. G. A. GRIFFITHS.

**Electric moments of aromatic diamines.** J. W. WILLIAMS and J. M. FOGELBERG (Physikal. Z., 1930, 31, 363—365).—From the theories accepted at present, and from the knowledge of the structure of the ammonia molecule it would be expected that *p*-phenylenediamine would be polar and possess a finite electric moment. The value of this electric moment for the compound has therefore been redetermined. As the solubility of *p*-phenylenediamine in the non-polar substance benzene is small, it is difficult to obtain accurate results. In order to confirm them the dipole moments of *o*- and *m*-phenylenediamine were also found. As a rule, for benzene substitution products the *ortho*-compound has the largest, and the *para*-compound the smallest moment, whilst that of the *meta*-compound lies between the two. In the case of the phenylenediamines, however, the *meta*-compound has a considerably larger moment than either of the other two, a fact which has not yet been explained. Hence, little light is thrown by this expected confirmatory method on the value of the moment of the *para*-compound. This uncertainty also calls in question the structure of the benzidine molecule.

A. J. MEE.

**Dipole moment of some organic halides.** D. N. S. GUPTA (Nature, 1930, 125, 600).—The

dipole moments of propyl chloride, allyl chloride, and propyl bromide, determined by a heterodyne method, are 2.07, 1.99, and  $1.78 \times 10^{-18}$  e.s.u., respectively.

L. S. THEOBALD.

**Dipole moments of butyl halides.** A. PARTS (Z. physikal. Chem., 1930, B, 7, 327—338).—The dielectric constants of all the butyl chlorides, bromides, and iodides have been measured at  $20^\circ$ , and in some cases also at  $10^\circ$ ,  $30^\circ$ , and  $50^\circ$ , the dipole moments being calculated from the results. The dipole moments of the chlorides are the same as those of the corresponding bromides, and a similar relationship exists between the normal compounds and the corresponding isocompounds. The tertiary halides always have the greatest dipole moment and the normal compounds the least.

R. CUTHILL.

**Dipoles in relation to the anomalous properties of dielectrics.** S. WHITEHEAD (Phil. Mag., 1930, [vii], 9, 865—880).—Mathematical. The anomalous decrease, in the neighbourhood of 1000 cycles, of the power factor expressing the losses at low stresses is investigated by the application of Debye's dipole theory.

N. M. BLIGH.

**Refraction of electric waves ( $\lambda = 12$  cm.) in some electrolytes.** K. ZAKRZEWSKI and T. NAYDER (Bull. Acad. Polonaise, 1930, A, 30—41).—Measurements have been made of the refractive index of water and of aqueous solutions for damped electrical waves of wave-length 12 cm. The method employed consists in measuring the deviation produced in a narrow pencil of waves by a hollow glass prism filled with the liquid. The angle of the prism used was very small ( $3^\circ 56'$ ), but large enough to eliminate inaccuracy due to reflexions on the interior of the prism. The oscillator and detector were of the types described by Zakrzewski (A., 1928, 347). Within experimental error the refractive index of water for this wave-length is the same as that for very long waves. The refractive indices of copper sulphate of up to 3% concentration and of sodium chloride solutions of up to 1% show no perceptible difference from those of pure water.

J. W. SMITH.

**Molecular volume of hydrocarbons and other compounds at low temperature.** W. HEUSE (Z. physikal. Chem., 1930, 147, 266—274).—Measurements have been made at  $20^\circ$  Abs. (in a few cases at  $80^\circ$  Abs.) of the molecular volumes of methane and homologues, benzene and homologues, ethylene, ammonia, carbon dioxide, acetone, bromine, chlorine, nitric oxide, nitrous oxide, and ice. In the case of ethylene and of the aromatic hydrocarbons the agreement between the experimental values and those calculated from the volumes of the constituents is good, but in the methane series the deviations are considerable, and the molecular volume does not increase regularly with the number of carbon atoms (see this vol., 677).

O. J. WALKER.

**Racemic isohydrobenzoin and its decomposition into optical antipodes by spontaneous crystallisation.** E. OTT (Z. anorg. Chem., 1930, 188, 47—51; cf. Read and Steele, A., 1927, 557).—Contrary to the conclusions of Read and Steele, racemic isohydrobenzoin can give definite enantiomorphic crystals of the optically active constituents

by a single crystallisation from ether. A curve is given showing the specific rotation of the *l*-form for different wave-lengths. F. L. USHER.

**Ellipsoidal polarimetry in the study of circular dichroism.** G. BRUNAT (Bull. Soc. chim., 1930, [iv], 47, 251—261).—The change in sign of rotatory dispersion on passing through an absorption band, observed by Cotton (Ann. Chim. Phys., 1896, 8, 347), is associated with circular dichroism. The Cotton effect should not be shown by a mixture of a transparent active substance and a coloured inactive one, as the absorbing electrons belong to a symmetrical molecule. The detection of the Cotton effect by measurements of rotation involves the whole of the rotatory dispersion curve, maxima and changes of sign alone not being characteristic, but the detection of circular dichroism proves the existence of the effect. Apparatus for use in this connexion is described. C. W. GIBBY.

**Photochemical production of optically active substances.** W. KUHN and E. KNOPF (Naturwiss., 1930, 18, 183).—In agreement with theory, it has been found that the difference between the absorption coefficients of  $\alpha$ -azidopropiondimethylamide for right and left circularly polarised light of  $\lambda$  2900 Å. is about 2—3%. The optically active amide is decomposed in this region with a quantum efficiency of unity with the evolution of nitrogen. The hexane solution of the racemic amide when decomposed to the extent of 40% by irradiation with circularly polarised light of  $\lambda$  = 2900 exhibits a rotation of +0.78° and -1.04° corresponding with right and left polarisation, respectively. R. W. LUNT.

**Magnetic birefringence of organic substances in the fused condition.** C. SALCEANU (Compt. rend., 1930, 190, 737—739).—Using the method of Cotton and Dupouy (*ibid.*, 602) and a special arrangement for heating, the magnetic double refraction of 2-methylnaphthalene (m. p. 32.5°) has been determined for  $\lambda$  = 578 m $\mu$  at eight temperatures from 36.5° (4.75°) to 89° (3.84°), that of nitrobenzene measured similarly at 20° being 4.74°. At 62° the values for  $\lambda$  = 578, 546, and 436 m $\mu$  are respectively 4.27°, 4.37°, and 6.15°; *C* at 36.5° is  $2.465 \times 10^{-12}$ . C. A. SILBERRAD.

**Magnetic birefringence of ethyl alcohol, water, and of aqueous solutions of nitrates.** M. A. HAQUE (Compt. rend., 1930, 190, 789—790).—The method of Cotton and Dupouy (*ibid.*, 602) gave the values of  $C_m \times 10^{14}$ /mass of active substance per 100 c.c. for ethyl alcohol (15°) -1.27, distilled water (16.6°) -0.39, sodium and ammonium nitrates (17.1°, corrected for the birefringence of the water) +3.1 and +2.8, respectively. These are in close agreement with the observed and calculated results of Ramanadham (A., 1929, 1128, 1223), except for water, where the value is lower. J. GRANT.

**Paramagnetic rotary dispersion of aqueous solutions of cobalt sulphate in the visible and ultra-violet regions of the spectrum.** R. W. ROBERTS (Phil. Mag., 1930, [vii], 9, 361—390).—The magnetic rotations of several solutions of cobalt sulphate in water have been examined at the ordinary

temperature in the visible and ultra-violet spectral regions. The rotation of the solutions was found to be negative in the red and ultra-violet regions, becoming positive in the neighbourhood of the 5100 Å. band. The refractive indices of the solutions at different wave-lengths have been measured and used to calculate the corresponding molecular refractivities. From these the characteristic frequencies of the electrons responsible for the refraction have been calculated by Heydweiller's modification (Physikal. Z., 1925, 26, 526) of Drude's dispersion theory. The value of  $SO_4^{--}$  in cobalt sulphate then agrees with Heydweiller's value for  $SO_4^{--}$  in lithium sulphate, whilst that for  $Co^{++}$  is greater than the corresponding value for  $Li^{++}$ . The magnetic measurements have been used with Ladenburg's dispersion formula to calculate the frequency of the ultra-violet paramagnetic band and its moment. A. E. MITCHELL.

**Stereochemical researches: principle of privileged structure.** J. TIMMERMANS (J. Chim. phys., 1930, 27, 64—74).—Free rotation about a single linking as postulated by van't Hoff is not in accordance with experimental facts. Certain of the possible positions must be privileged, particularly in the crystalline state. C. W. GIBBY.

**Subsidiary valency and crystal structure.** E. HERTEL (Z. physikal. Chem., 1930, B, 7, 188—209).—The crystal structure of the following nitro-compounds has been investigated by means of the Weissenberg and Böhm X-ray goniometer: 4:6-dinitro-*m*-xylene, *o*-, *m*-, and *p*-dinitrobenzene, and 2:6-dinitrophenol. The dimensions obtained for *o*-dinitrobenzene are practically identical with those given by Bragg (J.C.S., 1922, 121, 2772), but the dimensions obtained for the other two dinitrobenzenes are quite different from Bragg's values. The structures of dinitroxylenes and *m*- and *p*-dinitrobenzene are discussed with the aid of diagrams of models. The characteristic symmetry of the molecules of dinitroxylenes, the dinitrobenzenes, *s*-trinitrobenzene, and di- and tri-nitrophenol is compared. It has been shown that the subsidiary valencies which are responsible for the formation of the molecular compounds typical of the polynitro-compounds are also influential in the building up of the crystal structure of the nitro-compounds by bringing about the formation of chains, networks, and lattices. M. S. BURR.

**Interpretation of simple chemical reactions.** R. MECKE (Z. physikal. Chem., 1930, B, 7, 108—129).—A general account of the results of recent spectroscopic investigations and their bearing on the mechanism of decomposition of simple molecules such as those of water, carbon dioxide, methane, formaldehyde, nitrous oxide, and nitrogen peroxide. F. L. USHER.

**Cybotactic (molecular group) condition in liquids; nature of the association of octyl alcohol molecules.** G. W. STEWART (Physical Rev., 1930, [ii], 35, 726—732; cf. A., 1928, 224).—Experimental evidence for the molecular group theory of the nature of liquids is summarised. X-Ray diffraction measurements were made for 22 octyl alcohols, and relative ionisation current-diffraction angle curves are given. The value of the effective diameter

of the primary normal alcohols is approximately 4.5 Å. The increase for OH and Me in a branch is approximately 0.0 and 0.24 to 0.75 Å., respectively. Two types of association were found: (1) an attachment of the OH group at the end or next to the end of a molecule, when two molecules associate end to end in one line, and (2) the OH group is attached to any other carbon atom when the molecules are arranged side by side.

N. M. BLIGH.

**Parachor and molecular volume.** A. FERGUSON (*Nature*, 1930, 125, 597—598).—It is maintained that the parachor is not a molecular volume and it should be treated strictly as an individual concept.

L. S. THEOBALD.

**Surface energy of solids. I. Surface energy of barium sulphate.** B. BRUZS (*J. Physical Chem.*, 1930, 34, 621—626).—The surface energy of barium sulphate has been determined by an application of the calorimetric method to the system barium chloride-manganous sulphate-water and the theoretical value of 310 ergs/cm.<sup>2</sup> given by the lattice theory is supported. The surface energy of barium sulphate increases by 2200 g.-cal./g.-mol. with an increase in concentration of the manganous sulphate solution from *M* to 3*M*. The existence of a region of maximum grain size for certain concentrations has been established.

L. S. THEOBALD.

**Structure of the capillary layer in dipole liquids.** H. F. HERTLEIN (*Ann. Physik*, 1930, [v], 1, 898—922).—Theoretical. The forces between dipole molecules are considered, and can be made up of two parts, cohesion forces and expansion forces. The former are electrostatic and can be calculated. The general method of calculating the density changes in the capillary layer, assuming that the molecules are rigid spheres, is given. The potential energy and law of force are then calculated for a dipole liquid, and it is shown that for the assumptions given there can be no equilibrium in the capillary layer. It is impossible for a surface layer to be formed if the molecules in it are arranged in the disorderly way in which they exist in the body of the liquid; it is necessary to assume that in the surface layer they are arranged more or less parallel, and that therefore the negative potential energy of a single molecule is much greater than that calculated for particles which are completely disordered. The amount of this increase in the potential energy can be calculated and the maximum is in the neighbourhood of 0.5*V*<sub>0</sub>, where *V*<sub>0</sub> is the potential energy of a molecule in the homogeneous liquid. It has been assumed that the density of the capillary layer forms a transition between the densities of the liquid and the saturated vapour, and that the change is linear; this is impossible. There must be a very rapid fall in the density on the liquid side of the layer and a very gradual one on the vapour side.

A. J. MEE.

**Recrystallisation of metals and dynamic aggregation in glass.** E. BERGER (*Naturwiss.*, 1930, 18, 333—334).—The physical properties of glass, e.g., refraction, are dependent on the heat treatment the glass has received, all the equilibrium values of the property concerned lying on two curves, the intersection of which gives the transition temperature

between the brittle and viscous states of glass. There must be for glass a progressive dynamic aggregation (polymerisation, association, etc.) as the temperature falls. The velocity with which these equilibrium states are attained is given by the equation  $dn/dz = C/z$ , where *n* is the refractive index, or other property, *z* the time at the temperature *T*, and *C* a term depending on the original and final value of the property and on the temperature. A similar formula holds for the recrystallisation of metals isothermally. The change of the nuclear distance *a* is given by the equation  $da/dz = C/z$ . There is a similarity between the growth of the particles in glass and the growth of crystal nuclei in metals.

A. J. MEE.

**Correction factors in the photographic measurement of X-ray intensities in crystal analysis.** E. G. COX and W. F. B. SHAW (*Proc. Roy. Soc.*, 1930, A, 127, 71—88).—Possible sources of error in the measurement of the integrated intensities of X-ray reflexions by crystals from photographic records are discussed. These are of two kinds: (1) a geometrical factor, dependent only on the angle of reflexion and the orientation of the reflecting plane with respect to the axis of rotation. It is shown that to every point on a photograph there corresponds a correction factor by which the measured intensity must be multiplied in order to eliminate this effect; (2) an error due to obliquity of incidence of the reflected X-rays on the photographic film. In this case the magnitude of the correction factor depends on the angle of incidence, the type of film or plate employed, and the wavelength of the monochromatic X-ray beam used. The validity of the ordinary polarisation factor is discussed. Evidence is adduced to show that characteristic X-ray beams contain not more than 1% of plane-polarised radiation, and that the maximum error involved in assuming the polarisation factor to have the value  $0.5(1 + \cos^2 2\theta)$  is 0.5%. Some experimental figures are quoted to show that the correction factors give reasonably concordant results when applied to actual measurements on X-ray photographs.

L. L. BIRCUMSHAW.

**New X-ray spectrograph with absolute zero determination without a divided circle, and the zero method of Cornu.** H. SEEMANN (*Z. Physik*, 1930, 61, 416—434).—A new X-ray spectrograph is described. The method at present almost universally used for the determination of the zero point with the Bragg spectrograph is that due to Cornu (1880). An arrangement is shown for the determination of the zero point by this method, using a pin-hole camera, and the new spectrograph employs a pin-hole camera, but has a new method for determining the zero point. The crystal is mounted on a table on a rod which can rotate through 180° about a vertical axis with accuracy, obviating the use of a divided circle. The rotation can take place in either direction, and the table is accurately fixed in position by contact screws. The principle of the method and the sources of error are discussed.

A. J. MEE.

**Variation of the rotating crystal method suitable for investigations of crystal structure by X-rays.** W. LINNIK (*Z. Physik*, 1930, 61, 220—226).—The crystal and photographic plate are at rest

relative to one another, whilst the incident beam moves about a line joining the centre of the crystal and the centre of the photographic plate. Reflexion occurs when the incident beam is appropriately oriented with respect to the reflecting planes. The paths traced on the photographic plate by reflected radiation give the inclination of the axis of the reflecting planes to the line joining the centres of the crystal and plate, the order of the crystal symmetry, and the grating constant. The apparatus used is described in detail, and photographs for rock-salt and quartz crystals are reproduced.

A. B. D. CASSIE.

**X-Ray intensity measurements with deformed crystals.** J. HENGSTENBERG and H. MARK (Z. Physik, 1930, 61, 435—453).—The application of X-ray intensity measurements to the study of small changes in structure due to mechanical, chemical, heat, and electrical influences is discussed. Reflexions from the cubic faces of sylvine during distortion were obtained with an ionisation spectrometer. The increase in (200) and (400) reflexions with distortion is due to an increase in mosaic-like structure, whilst diminution in (600), (800), and (1000) reflexions is due to deformation of the grating elements. Measurements of line width show disturbances at the slip planes to be local; a 3.8% compression disturbs 2.25% of the atoms with a maximum amplitude one eighth of the atomic spacing. A. B. D. CASSIE.

**Intensity measurements of diffuse X-rays reflected from distorted sylvine.** R. BRILL (Z. Physik, 1930, 61, 454—457).—An apparatus for X-ray measurements, using the Geiger counter method, is described. Measurements show an increase in intensity of diffuse radiation with deformation of the crystal. A. B. D. CASSIE.

**Precision measurements of X-ray reflexions from crystal powders.** J. BRENTANO (Phil. Mag., 1930, [vii], 9, 525—528).—The agreement between the results of Fuller (A., 1929, 1367) and of Brentano and Adamson (*ibid.*, 493) for the space lattice of cadmium oxide is discussed. The relative advantages of the powder-rod method and the focussing method used by Brentano and Adamson are outlined. The merits of cadmium oxide as a standard of reference in X-ray precision measurements are discussed.

A. E. MITCHELL.

**Lloyd's single mirror fringes with X-rays.** W. LINNIK (Naturwiss., 1930, 18, 354).—Interference fringes were obtained with X-rays, using a glass plate of area  $10 \times 4$  cm. as a mirror. Conditions necessary for the production of successful fringes are given.

A. B. D. CASSIE.

**Testing of monocrystalline wires.** W. J. DE HAAS and P. M. VAN ALPHEN (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 128—129).—A rapid method is described for testing monocrystalline thin wires by taking a series of Laue photographs along the whole length of the wire. If the wire is monocrystalline the Laue spots will lie on straight lines parallel to the direction of displacement. Twisting of the wire can be detected by this method, and also the effects of mechanical disturbances which cannot be observed visually.

M. S. BURR.

**Experimental evidence of the mosaic structure of bismuth single crystals.** A. GOETZ (Proc. Nat. Acad. Sci., 1930, 16, 99—105).—Microscopical examination has been made of crystal faces after cleavage of single bismuth crystals grown to a size of 200—300 mm. by 2—7 mm. in any desired orientation. Faint lines were detectable under high magnification on fresh unetched (111) planes which intersected one another at  $60^\circ$  and formed a regular triangular pattern. The basal side of the smallest triangle in such a pattern was determined as  $1.4 \times 10^{-3} \pm 0.2 \mu$ . Confirmatory evidence of the individual qualities of these triangular units was obtained from an examination of etched surfaces. It is concluded that the bismuth crystal consists of blocks of a definite size which is independent of the perfection of the crystal so long as it is not plastically deformed. When deformation causes twinning, the thickness of the smallest twin lamella is approximately twice the size of one block. The observations follow qualitatively the predictions of the theory of Zwicky, and the fact that the parameter of the blocks is 40% too high for agreement with the theory is attributed to lack of knowledge of the Poisson number for bismuth crystals.

Reasons are given supporting the suggestion that the blocks described may be the smallest units in the crystal above the lattice unit. The chemical behaviour of the surfaces leads to the concept of the blocks as ideal crystals surrounded by a very thin shell of higher density.

F. G. TRYHORN.

**Structure of thin layers of metals.** Z. DEBINSKA (Spraw. Prace Polsk. Towarz. Fizycz., 1929, 4, 59—68; Chem. Zentr., 1929, ii, 2974).—Thin metallic films, especially when obtained by vacuum distillation, exhibit orientation of the microcrystals, the degree of orientation depending on the nature of the carrier.

A. A. ELDRIDGE.

**Stability of metallic crystal lattices.** R. H. CANFIELD (Physical Rev., 1930, [ii], 35, 530—542).—Theoretical. Born's theory of homopolar crystal lattices is applied to cases in which the lattice is in equilibrium as regards displacement of one atom, unidirectional extension, and simple shear. It is shown that each postulate leads to a restrictive condition on the symmetry and pattern of the possible lattices, in agreement with the high symmetry observed. If these equilibria are stable the lattice is shown to be in equilibrium against relative motion of portions; hence "mosaic" crystals cannot be configurations of minimum potential energy.

N. M. BLIGH.

**The crystal of tungsten obtained by deposition.** T. FUJIWARA (Mem. Coll. Sci. Kyōtō, 1930, 13, 149—161).—Crystals of tungsten deposited by the action of water vapour on polycrystalline and single-crystal tungsten rods heated in wet hydrogen were examined. In the first case the crystals were rhombic dodecahedra with (110) crystal faces, sometimes appearing as hexagonal prisms. Some of the crystals were laminated. Similar crystals deposited on the etched surface of single-crystal rods had the same orientation as the parent crystal, to which they were united by a (110) plane.

C. J. SMITHELLS.

**Recrystallisation of aluminium.** I. K. TANAKA (Mem. Coll. Sci. Kyōtō, 1930, 13, 117—125).—Crystals produced by recrystallisation in slightly deformed single crystals of aluminium tend to have a definite orientation with reference to that of the mother crystal. The orientation is little affected by the direction of the stress applied before annealing, or the type of deformation produced by the stress.

C. J. SMITHELLS.

**Arrangement of microcrystals in bent wires of tungsten and molybdenum.** T. FUJIWARA (Mem. Coll. Sci. Kyōtō, 1930, 13, 109—115).—The crystal fragments resulting from bending a single-crystal tungsten wire are so oriented that they retain closely the same position as the original crystal with respect to the wire axis. The arrangement of the fibrous structure of a hard-drawn molybdenum wire with respect to the axis of the wire is retained after bending.

C. J. SMITHELLS.

**Arrangement of microcrystals in a fractured single-crystal aluminium wire.** K. FUJII (Mem. Coll. Sci. Kyōtō, 1930, 13, 101—108).—The arrangement of the microcrystals formed when a single-crystal aluminium wire is broken in tension was determined by means of X-rays. The crystal fragments form an imperfect fibre structure on that plane perpendicular to the (221) planes which makes the smallest angle with the wire cross-section. Near the point of fracture the wire extends 120—130% and the crystal fragments on either side have suffered rotation of about 95° at this point.

C. J. SMITHELLS.

**Preparation of single crystals of bismuth.** L. SCHUBNIKOV (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 327—331).—A method is described whereby single bismuth crystals may be prepared of any predetermined geometric form and with the axis oriented in any required direction. The molten metal is pressed into a mould of the desired dimensions constructed of quartz plates coated with a little paraffin wax and containing a small crystal of the metal, oriented in the required direction, which serves to seed the melt. It is relatively easy to prepare crystals in this manner with the major axis at right angles to the length of the specimen, but more difficulty is experienced when the major axis is required to be parallel with the length, as in this case twinning frequently occurs.

J. W. SMITH.

**Crystal structure of neon.** J. DE SMEDT, W. H. KEESOM, and H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 255—257).—Using a form of the apparatus previously described (A., 1925, ii, 484), adapted so that the solidified neon could be cooled to liquid helium temperatures, Debye-Scherrer diagrams of solid neon have been obtained. Only four sharp and intense lines originating from neon could be observed, the spacings corresponding with a face-centred cubic lattice, the lattice constant being 4.52 Å. The density is 1.44<sub>3</sub> at a temperature slightly above the b. p. of helium. The ratio of the distance between the centres of the nearest neighbouring neon atoms (3.20 Å.) to the diameter of the neon atom calculated from viscosity data (2.36 Å.) is 1.35, as against 1.29 for argon.

J. W. SMITH.

**Crystal structure of white phosphorus.** G. NATTA and L. PASSERINI (Nature, 1930, 125, 707—708).—Contrary to Young (Centr. Min., 1926, 107), no appreciable transformation of white into red phosphorus occurs under the influence of X-rays of long wave-length. The 22 lines obtained with the K radiations of an iron anticathode indicate a lattice constant (cubic system) of 7.17 Å. for the elementary cell.

L. S. THEOBALD.

**Space-group of alkali sulphates.** A. OGG (Phil. Mag., 1930, [vii], 9, 665—667).—The author's conclusion (A., 1928, 223) that the space-group of the alkali sulphates is  $P_2^1$  has been confirmed by the experimental work of Taylor and Boyer (A., 1929, 243). Further, the shortest distance between the atomic centres of the metals and oxygen, in the structure given by the author, is in agreement with the sum of the atomic radii calculated by Pauling on the basis of wave mechanics.

M. S. BURR.

**Structure of sulphides and sulpho-salts.** J. W. GRUNER (Amer. Min., 1929, 14, 470—481).—Sulpho-salts differ from sulphides in that the metals occupy at least two structurally non-equivalent positions. Structural radicals are not distinguishable except in the pyrite group, pentlandite, and sylvanite. The commonest arrangements of the sulphur atoms involve close packing of cubic face-centred and hexagonal types. Except for the larger lattices of the molybdenite group, most sulphides and sulpho-salts have the sulphur atoms arranged at the corners of regular or slightly distorted tetrahedra.

CHEMICAL ABSTRACTS.

**X-Ray spectroscopic investigations of some solid chloro-salts.** I. O. STELLING and F. OLSSON (Z. physikal. Chem., 1930, B, 7, 210—225).—X-Ray K absorption spectra are recorded for 25 solid double salts of chlorides of the alkali metals and ammonium with chlorides of the heavy metals manganese, iron, cobalt, nickel, copper, zinc, cadmium, tin, antimony, and platinum, including also the compound of tetraethylammonium chloride with manganic chloride,  $(Et_4N)_2MnCl_5$ . All give two well-marked absorption bands of similar type, except the zinc salts, which give one band. These bands appear to be characteristic of non-ionic chlorine (A., 1927, 391). The wave-lengths are in good agreement with those of the simple heavy metals in the salts. The conception of a complex ion  $(MCl_x)$  with non-polar linking seems to be supported by the results.

M. S. BURR.

**Crystal structure of potassium chlorate.** W. H. ZACHARIASEN (Z. Krist., 1929, 71, 501—516; Chem. Zentr., 1929, ii, 3103).—Potassium chlorate, monoclinic, holohedral, has  $a$  4.647,  $b$  5.585,  $c$  7.085 Å.,  $\beta$  109° 38'; the unit cell contains 2 mols. The space-group is  $C_{2h}^2$ , and  $d_{calc}$  2.28.

A. A. ELDRIDGE.

**Crystal structure of sodium chlorate.** W. H. ZACHARIASEN (K. Krist., 1929, 71, 517—529; Chem. Zentr., 1929, ii, 3103).—Sodium chlorate, cubic tetartohedral, has  $a$  6.570 Å.; the unit cell contains 4 mols., and the space-group is  $T$ .

A. A. ELDRIDGE.

**X-Ray investigation of nitrides of molybdenum and tungsten.** G. HÄGG (Z. physikal. Chem., 1930,

B, 7, 339—362).—By heating molybdenum in ammonia, products containing up to 48 at.-% of nitrogen have been obtained, and by X-ray examination the presence of three intermediate nitride phases has been demonstrated. The  $\gamma$  phase consists of metal atoms arranged in a face-centred cubic lattice, the nitrogen atoms apparently being contained in the larger interstices of the lattice, and below about 700° is homogeneous only if the nitrogen content lies within narrow limits about 33 at.-%. In the  $\delta$  phase, which would probably be homogeneous for about 50 at.-% N, the metal atoms form a simple hexagonal lattice, and the structure is similar to that of tungsten carbide (Westgren and Phragmén, A., 1926, 1084). The  $\beta$  phase, which is homogeneous for about 28 at.-% N, has its metal atoms in a face-centred tetragonal lattice, and is stable only above about 600°. In the system tungsten–nitrogen the  $\beta$  phase, which has the lowest nitrogen content, is similar in structure to the  $\gamma$  phase in the previous system. There is no evidence that nitrogen dissolves in either metal.

R. CUTHILL.

**Crystal structure of calcium carbide.** M. VON STACKELBERG (Naturwiss., 1930, 18, 305—306).—Accurate X-ray investigation by the Weissenberg–Böhm method have shown that calcium carbide crystals are tetragonal. The rectangular pieces split from the carbide give a wrong form of X-ray diagram. There is a coalescence of three faces the  $c$  axes of which lie at right angles to each other in three-directional space. Each rotation diagram therefore gives the superposition of three rotation diagrams (of which two are identical) of the tetragonal crystal in three directions mutually perpendicular. This coalescence, detectable by the polarisation microscope, is possible because of the slight difference between  $c$  and  $a$ :  $a=5.48$ ,  $c=6.37$  Å.,  $c/a=1.16$ . There are at least four molecules in the crystal and the calculated density is 2.21, in good agreement with the experimental value of 2.1. The calcium atoms are disposed in a face-centred lattice and the carbon atoms form two face-centred lattices. The relationship to the crystal structure of the carbides of barium, cerium, and strontium is considered.

W. R. ANGUS.

**K-X-Ray absorption spectra of chlorine in stereoisomeric organic compounds.** O. STELLING (Z. physikal. Chem., 1930, B, 7, 325—326).—As in the case of complex inorganic chlorine compounds (cf. A., 1927, 391), organic *cis*- and *trans*-chloro-compounds show different  $K$  absorption spectra due to the chlorine, but unlike the former compounds it is the shorter wave-length edge which is the more strongly influenced by the spatial configuration of the molecule. Both the active forms and the racemic form of dichlorosuccinic acid give almost identical results, but the *meso*-form shows a lower value for the shorter wave-length edge. Similarly, monochlorofumaric acid shows a lower wave-length of this edge than monochloromaleic acid, and the value for the former compound is almost identical with that of *meso*-dichlorosuccinic acid.

J. W. SMITH.

**Internal and surface structure of long-chain organic liquids.** J. J. TRILLAT (Compt. rend., 1930, 190, 858—860).—If errors due to diffraction of

the continuous background (this vol., 19) are eliminated, then the molecular spacings of long-chain organic compounds determined from X-ray diagrams by Bragg's formula are in agreement with those obtained by other methods. In addition, evidence is obtained of the formation of chains of molecules. The author's tangential drop method (A., 1929, 630) shows that the surface structures of such fluids differ from their internal structures by reason of the discontinuity of the magnetic field in the former case.

J. GRANT.

**Crystal structure of picric acid.** M. A. BREDIG and H. MÖLLER (Z. Krist., 1929, 71, 331—342; Chem. Zentr., 1929, ii, 3103).—The space-group is  $C_{2h}^2$ ; the translation lattice is the simple rhombic lattice. The unit cell contains 8 mols.

A. A. ELDRIDGE.

**X-Ray diffraction in liquids. II. Benzene, cyclohexane, and their homologues.** S. TANAKA and A. TSUJI (Mem. Coll. Sci. Kyōtō, 1930, 13, 169—173; cf. this vol., 527).—X-Ray diffraction patterns of 14 hydrocarbons were obtained. The diffraction band of benzene shows two maxima, and assuming the benzene molecule to have a flat disc form this gives 4.76 and 3.12 Å. for its diameter and thickness. *cyclo*Hexane and its homologues give single sharp maxima, indicating a spherical molecule. The substitution of a methyl group produces uniform increase in diameter.

C. J. SMITHELLS.

**Determination of purity of liquid isomerides by X-ray diffraction.** G. W. STEWART (Proc. Iowa Acad. Sci., 1928, 35, 251).—The presence of isomerides, e.g., of aliphatic hydrocarbons, is detected by displacement of the diffraction peaks.

CHEMICAL ABSTRACTS.

**Cellulose space lattice.** O. L. SPONSLER (Nature, 1930, 125, 633—634).—New data showing the relationship between planes parallel to the long axis have been obtained from diffraction patterns of *Valonia ventricosa*. The diffraction maxima agree with an elementary cell in which the planes (010) are parallel to the surface of the cell-wall and are represented by planes spaced 6.10 Å.; the planes (100) are perpendicular to the surface and are represented by 5.33 Å. spacings, whilst the diagonals (110) are spaced 3.93 Å. The axial dimensions for cellulose are  $a$  10.7,  $b$  12.2,  $c$  10.3 Å.; the angles between them are nearly right angles.

L. S. THEOBALD.

**Cellulose space lattice.** W. H. BRAGG (Nature, 1930, 125, 634).—The results of Mark and co-workers are practically equivalent to those of Sponser (see preceding abstract).

L. S. THEOBALD.

**Structure of andalusite,  $Al_2SiO_5$ .** W. H. TAYLOR (Z. Krist., 1929, 71, 205—218; Chem. Zentr., 1929, ii, 2990).—The unit cell has  $a$  7.76,  $b$  7.90,  $c$  5.56 Å.; space-group  $V_2^2$ .

A. A. ELDRIDGE.

**Fine structure of gypsum.** E. ONORATO (Z. Krist., 1929, 71, 277—325; Chem. Zentr., 1929, ii, 3102—3103).—The lattice constants of gypsum are:  $a_0$  10.47,  $b_0$  15.15,  $c_0$  6.28 Å. ( $a:b:c=0.6895:1:0.4132$ ; crystallographically  $a:b:c=0.6910:1:0.4145$ ); the unit cell contains 8 mols. The space-group is  $C_{2h}^2$ .

A. A. ELDRIDGE.



**Diamagnetic simple salt of nickel.** D. M. BOSE (Nature, 1930, 125, 708).—Dutt has shown that the compound  $\text{Ni}(\text{CN})_2 \cdot 7\text{H}_2\text{O}$  is paramagnetic, but becomes progressively less paramagnetic on dehydration and on complete dehydration would probably become diamagnetic. L. S. THEOBALD.

**Influence of chemical colloidisation on the anomalous diamagnetism of bismuth and antimony.** V. I. VAIDYANATHAN (Nature, 1930, 125, 672).—The specific diamagnetic susceptibility of colloidal antimony with a particle size of  $100 \mu\mu$  and prepared by reducing potassium antimonate by means of sodium hydrosulphide is reduced to a value of  $0.31 \times 10^{-6}$ . Colloidal bismuth, prepared by reducing bismuth tartrate with stannous chloride in alkaline solution, gave a value of  $0.25 \times 10^{-6}$  unit.

L. S. THEOBALD.

**Magnetisation curve of single iron crystals.** D. FOSTER and R. M. BOZORTH (Nature, 1930, 125, 525).—The abrupt changes in slope of this curve observed by previous investigators are due to incorrect measurements of field intensities; when actual magnetising fields are measured directly no breaks occur.

L. S. THEOBALD.

**Diamagnetism of electrons in metals.** F. BITTER (Proc. Nat. Acad. Sci., 1930, 16, 95—98).—On the basis of the wave structure of the electron a formula for the diamagnetic susceptibility of free electrons is obtained having the same form as the classical formula with the substitution for  $\lambda$ , the mean free path, of the term  $\alpha/4$ , where  $\alpha$  is the grating constant of the cubic lattice under consideration. Whereas the values given by the classical formula were much too large, those given by the new formula in cases where it may properly be applied are lower than the paramagnetism of the free electrons. A quantitative check with experiment cannot be undertaken in the case of the heavy elements potassium, rubidium, caesium, copper, silver, and gold, because  $K_p$  and  $K_d$  are both small compared with the diamagnetism of the atoms of the lattice.

F. G. TRYHORN.

**Diamagnetism of ferromagnetic substances.** R. GANS (Naturwiss., 1930, 18, 184—185).—Weber's theory of magnetism is interpreted in the light of present knowledge. Weber's and Ampère's molecular circuits are identified with the magnetic moment of the rotating electrons of para- and ferro-magnetics, and the induction effect with the Larmor precession of diamagnetics. Weber was unable to show a diamagnetic effect in ferromagnetic substances. In a saturated ferromagnetic substance, where the molecular circuits are oriented to a maximum, then, with increasing external field, a diamagnetic effect should manifest itself. With external fields of about 500 gauss it is shown that permalloy and mu-metal can be diamagnetic, although both are strong ferromagnetic substances.

J. FARQUHARSON.

**Theory of ferromagnetism.** F. BLOCH (Z. Physik, 1930, 61, 206—219).—Theoretical. By an application of wave mechanics to the exchange of electrons in a crystal a theory of higher multiplets is derived (cf. Slater, this vol., 126; Bloch, A., 1929, 1360). Various types of space-lattice are considered,

and, at the low temperatures at which ferromagnetism can occur, magnetic saturation is described by an equation of the form  $M(T) = M(0)[1 - (T/0)^{3/2}]$ .

J. FARQUHARSON.

**Magnetic characteristics of nickel.** F. TYLER (Phil. Mag., 1930, [vii], 9, 1026—1038).—Quantum and classical theory curves for the variation of the spontaneous magnetisation with temperature below the Curie point are obtained and compared with experimental results; curves corresponding with large external fields are also considered. Results indicate that the carriers have a moment of one Bohr magneton. There is evidence of anomalies in the variation in magnetisation close to the Curie point (cf. Forrer, A., 1929, 752, 1224). Magnetic data above the Curie point are discussed. Most of the characteristics can be explained by assuming that the carriers are free electrons the numbers of which may vary (cf. Dorfman, *ibid.*, 751).

N. M. BLIGH.

**Barkhausen effect. II. Determination of the average size of the discontinuities in magnetisation.** R. M. BOZORTH and (MISS) J. F. DILLINGER (Physical Rev., 1930, [ii], 35, 733—752; cf. A., 1929, 1224).—The discontinuities in magnetisation, when a continuously varying magnetic field is applied to a ferromagnetic substance, have been examined in wires of iron, nickel, and iron-nickel alloys. An expression is derived and experimental methods are described for determining their average size for a given material in a given state of magnetisation.

N. M. BLIGH.

**Chemical and magnetic study of the complex derivatives of the triazine nucleus.** P. PASCAL and R. LECUIR (Compt. rend., 1930, 190, 784—786).—The complexities of a number of the triazinetricarboxylates of the metals of the iron group (A., 1929, 1083) have been determined from the difference between the observed magnetic susceptibilities and those calculated by Wiedemann's method. The red salt,  $\text{Co}''_3(\text{CO}_2\text{CN})_6 \cdot 9\text{H}_2\text{O}$ , and the white salt,  $\text{Ni}_3(\text{CO}_2\text{CN})_6 \cdot 4\text{H}_2\text{O}$ , behave as the mixtures  $[\text{Co}''_3(\text{CO}_2\text{CN})_6 + 9\text{Co}''(\text{NH}_4)_2(\text{C}_2\text{O}_4)_2]$  and  $[2\text{Ni}_3(\text{CO}_2\text{CN})_6 + 3\text{Ni}(\text{NH}_4)_2(\text{C}_2\text{O}_4)_2]$ , respectively. The complex compounds,  $\text{Co}''_2[\text{Co}(\text{C}_3\text{N}_3\text{O}_3)_2]$  (bluish-green),  $\text{Co}''_2\text{H}_2(\text{C}_3\text{N}_3\text{O}_3)_2 \cdot 6\text{H}_2\text{O}$  (mauve needles, and  $\text{Co}''_2\text{H}_4(\text{C}_3\text{N}_3\text{O}_3)_2 \cdot 3\text{H}_2\text{O}$  (red needles) were prepared by the hydrolysis of sodium cyanurate in the presence of decreasing amounts of cobaltous sulphate and their formulæ established.

J. GRANT.

**Magnetostriction constant for alternating magnetic fields.** F. D. SMITH (Proc. Physical Soc., 1930, 42, 181—191).—The magnetostriction constant for the Joule effect is the same as the constant in the relation between the alternating intensity of magnetisation produced by an alternating strain, and was measured for various values of the magnetic field with a ring of the alloy Fe 60, Ni 40%. It is shown that the magnetostriction effect for steady magnetising fields can be inferred from measurements with alternating magnetic fields if the reversible and differential permeability of the alloy are known.

N. M. BLIGH.

**Magnetic properties of rocks.** G. GRENET (Ann. Physique, 1930, [x], 13, 263—348).—A brief historical

and critical survey of the subject is given. Using a modified Curie-Cheneveau magnetic balance, and a Hughes induction balance adapted for rapidly measuring magnetisation coefficients, the relation between the susceptibilities and compositions of rocks was investigated. Magnetisation coefficients and susceptibilities are tabulated for about 140 minerals and 280 samples of rock. For the rocks, values are also given of the percentage of magnetite present. Magnetic properties were most marked in rocks rich in ferromagnetic elements. The increase in susceptibility of certain rocks after heating is discussed.

N. M. BLIGH.

**Mechanism of ionic conduction in solid compounds [of the class of] "good conductors."** W. JOST (Z. physikal. Chem., 1930, B, 7, 234—242).—Polemical against Smekal (this vol., 140).

M. S. BURR.

**Anomalous after-effect of dielectrics for their apparent resistivity.** H. SAEGUSA and S. SHIMIZU (Phil. Mag., 1930, [vii], 9, 474—488).—Resistivity measurements have been made on a quartz plate cut normal to the optic axis. It is found that following the application of any potential the resistivity returns to a normal figure only after considerable time, the duration depending on the magnitude of the initial applied potential. This after-effect appears at the limit potential and is of the same magnitude whether the initial applied potential is negative or positive. The after-effect increases rapidly with the time of application of the initial potential and finally tends to a constant value. If the initial potential is less than that applied in determining the resistivity the after-effect is comparatively small.

A. E. MITCHELL.

**Application of the Kerr effect for the investigation of the distribution of the electric field in dielectrics and the determination of some Kerr constants.** G. J. DILLON (Z. Physik, 1930, 61, 386—394).—A method, using the Kerr effect, is given for the investigation of the distribution of the electric field in transparent dielectrics, and is applied to nitrobenzene. The field changes considerably for constant current, and round the cathode is about twice as strong as round the anode. For a changing current the field in the neighbourhood of the electrodes is stronger than that in the middle. The accuracy of the method is considerable, and it has the advantage that the whole field is investigated simultaneously, so that it is possible to determine not only the distribution of the field, but also its variation, if any, in the course of time. Some Kerr constants were determined by the method of compensation. Solutions of substances existing in the liquid crystalline state were used. Benzene itself and benzene solutions of two cholesteryl esters and of ethyl azoxybenzoate were investigated. The results show that the Kerr constants of the solutions and of the solvent differ little from one another.

A. J. MEE.

**Crystal detectors.** J. VREDE (Physikal. Z., 1930, 31, 323—332).—A continuation of the work of Trey (A., 1926, 115) and of Lüke (A., 1927, 402). Chemically-prepared lead sulphide which was made a good detector by gently heating is shown to have

less detecting power after subliming in a vacuum, when it gives off large volumes of gas, and on resubliming is shown to have completely lost its action. The crystal did not regain its power of detecting on treatment with water, sulphur, lead sulphate, or hydrogen sulphide. Pure tellurium is not a detector. Cuprous iodide, prepared in a vacuum, but containing excess of iodine, has good detecting power. A large series of pure oxides, nitrides, and carbides was investigated and shown to be without detecting power. Various theories of the detecting action of crystals are discussed. The action is shown to be related to the Peltier effect and it is pointed out that galena has a high place in the thermo-electric series.

H. A. JAHN.

**Colour of alloys.** M. KURODA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 12, 308—320).—An apparatus was devised by which the residual light, after multiple reflexions from a metal surface, of a divided beam of light could be compared with the original beam after dispersion in a spectroscope. The spectra obtained were compared visually, and the intensity of the comparison spectra was altered by a neutral calibrated wedge. Preliminary experiments indicated that four successive reflexions were sufficient to define the spectral characteristics of the reflected light, and also if inequalities of the surface due to the mechanical processes of preparation were placed parallel to the incident beam of light no serious errors were made. Four types of binary alloys were examined: copper-bismuth, copper-silver, copper-nickel, and copper-zinc. The results showed that eutectic alloys and alloys of agglomerate structure have the reflexion characteristics indicated by composition. Solid solutions are more complicated. The dilution ratio expected by comparison with liquid solutions did not apply to the reflexion characteristics obtained.

J. O. CUTTER.

**Dynamic method for the determination of the dependence on temperature of the elastic constants of specimens in the form of rods at low temperatures.** E. GOENS (Ann. Physik, 1930, [v], 4, 733—777).—A method for the simultaneous determination of the temperature coefficients of the moduli of torsion and elasticity of specimens in the form of rods over a low temperature range is described. The method is intended to be of special use in determining the temperature coefficients of the elastic constants of single metallic crystals, although here it is applied to aluminium and iron in the polycrystalline form. The absolute values of the constants cannot be generally found by this method, but the torsional modulus can be determined with accuracy. The method depends on the measurement of torsional and transversal oscillations of the test piece, which is symmetrically loaded at its ends. The frequency of the oscillations is determined electrically, as they are made audible by an electrodynamic method. The theory of the method is given, and it is tested on specimens of aluminium and iron. Certain corrections have to be made to get accurate results. The temperature coefficients of the two moduli were determined for the metals over the range  $-195^{\circ}$  to  $18^{\circ}$ . When compared with other earlier results, it is found that they deviate considerably from those of

Schaefer (Ann. Physik, 1901, 5, 220) for aluminium, but that the value for the temperature coefficient of the torsional modulus is in satisfactory agreement with that obtained by Guye and Fréedericksz (Compt. rend., 1909, 149, 1066). For iron the deviations are smaller.

A. J. MEE.

**Hardness and pressure of flow of metals at different temperatures.** V. SCHISCHOKIN (Z. anorg. Chem., 1930, 189, 263—282).—The Brinell hardness and pressure of flow of the following easily fusible metals have been investigated: bismuth, thallium, tin, lead, cadmium, and zinc. With rising temperature the hardness of bismuth, lead, and zinc decreases along a uniform curve. The curve for thallium has a break between 215° and 231°, for cadmium at about 100°, and for tin a slight one at 155—165°. The break in the thallium curve corresponds with the transition point, but the transition point for cadmium is 65°. By plotting the logarithm of the hardness against temperature a break is also obtained for zinc at 175—185°. The transition temperature of zinc is 170°. The pressure of flow also falls with rising temperature and is represented by a smooth curve for tin, lead, cadmium, and bismuth. Thallium has a sharp break corresponding with the transition point. The dependence of the Brinell hardness  $H$  on the temperature  $t$  is given by an exponential function of the form  $H = \kappa e^{-at}$ , and similarly for the flow pressure  $F$ . The temperature coefficients of  $F$  and  $H$  are similar and are lowest for the pure metals, admixture with another metal causing an increase in the temperature coefficients.

M. S. BURR.

**Cohesion in univalent metals.** J. C. SLATER (Physical Rev., 1930, [ii], 35, 509—529).—Theoretical. The Sommerfeld-Heisenberg-Bloch theory of metallic structure is extended to explain cohesive forces; calculations for atoms with one valency electron are in qualitative agreement with experiment. Conductivity and ferromagnetism are considered; it is shown that metals of the alkali type cannot be ferromagnetic, a property which appears to require a group of electrons responsible for cohesion, and a group of smaller orbit, producing the magnetism, as shown by the iron and similar groups.

N. M. BLIGH.

**Influence of very slight impurities on the cohesion limits of rock-salt crystals.** F. BLANK and A. SMEKAL (Naturwiss., 1930, 18, 306—307).—The cohesion limits are increased by the addition of slight impurities. When  $10^{-5}$  mol. of lead chloride is added to a fused crystal of the purest synthetic rock-salt the increase is three-fold. Theories of the influence of impurities on lattice structure are discussed.

W. R. ANGUS.

**Lattice energies and compressibilities of alkali hydrides.** J. KASARNOVSKI (Z. Physik, 1930, 61, 236—238).—Bethe's value (this vol., 132) for the electron-affinity of hydrogen is used as a basis for calculating the lattice energies of the alkali and alkaline-earth hydrides. The repulsion exponents and compressibilities of the alkali hydrides have also been calculated.

W. R. ANGUS.

**Behaviour of single crystals in brittle regions of  $\alpha$ -iron and  $\alpha$ -brass.** F. SAUERWALD, B.

SCHMIDT, and H. DIENENTHAL (Z. Physik, 1930, 61, 153—157).—The cleavage of single iron crystals at low temperatures is shown by X-ray examination to take place along the cubic planes of the crystal. Single crystals of pure brass were fractured at 616° and 715° and shown to be readily plastic, the slipping taking place along an octahedral plane of the crystal. Test pieces containing various numbers of single crystals were examined and the plasticity of the single crystals was shown to be much influenced by increase in the number of crystals present in unit volume.

H. A. JAHN.

**Calculation of mol. wts. of liquids from pressure coefficients.** R. O. HERZOG (Z. physikal. Chem., 1930, 147, 118—124).—The utility as a means of calculating the mol. wt.  $M$  of a non-associated liquid of the equations  $s = a/(M/d)^2 T$  and  $s = R/(M/d - b)$ , where  $d$  is the density,  $T$  the temperature (Abs.),  $a$  and  $b$  are the van der Waals constants, and  $R$  has the value 3.04 litre-atm., is demonstrated by means of existing data for the pressure coefficient,  $s$ , i.e., the quotient of the coefficient of expansion by the compressibility coefficient, the values of  $a$  and  $b$  being calculated by the additive principle (cf. van Laar, "Die Zustandsgleichung von Gasen und Flüssigkeiten," Leipzig, 1924, p. 111). The second equation can also be used for calculating the degree of association of associated liquids.

R. CUTHILL.

**Relation between mol. wt. and m. p. of organic compounds.** J. B. AUSTIN (J. Amer. Chem. Soc., 1930, 52, 1049—1053).—Starting with Lindemann's formula for the characteristic vibrations of the atoms in a monatomic solid and introducing a number of simplifying assumptions, the relation  $\log M = A + BT$  [where  $M$  = mol. wt.,  $T$  = m. p. (Abs.),  $A$  and  $B$  are constants] is derived for members of homologous series.

R. K. CALLOW.

**Application of dialysis coefficient in the determination of mol. wt.** H. BRINTZINGER (Naturwiss., 1930, 18, 354—355; cf. A., 1929, 1003).—Using light permeable membranes of cellophane dialysis coefficients are measured and from them mol. wts. are calculated according to the equation  $\lambda_1 \sqrt{M_1} = \lambda_2 \sqrt{M_2}$ .

W. R. ANGUS.

**Measurements with liquid helium. VII. Curves of transition to superconductivity for tantalum and thorium.** W. MEISSNER (Z. Physik, 1930, 61, 191—198).—Four specimens of tantalum, one of which was relatively pure, were investigated. The pure metal transforms into the superconductive state in a smaller temperature interval than the others. The middle of the transition curves occurs at approximately 4.36° Abs. for all four specimens. Thorium transforms in a comparatively large temperature interval. This may be due to the use of an imperfect crystal.

A. B. D. CASSIE.

**Increase in resistance produced magnetically in monocrystals of bismuth at low temperatures.** L. SCHUBNIKOW and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 130—133).—The resistance of two monocrystalline bismuth wires, with the chief axis parallel to the length of the wire, has been determined for different positions of the wire in

magnetic fields of varying strength and at temperatures in the neighbourhood of 14–20° Abs. The ratio  $R_H/R_0$  has been plotted against the field strength  $H$ ,  $R_H$  being the resistance in the field  $H$  at the temperature of the experiment and  $R_0$  the resistance at the temperature of melting ice without field.

M. S. BURR.

**Superconductivity of alloys.** W. J. DE HAAS, E. VAN AUBEL, and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 258–261; cf. A., 1929, 496, 652, 1135).—Like the compounds  $\text{Cu}_3\text{Sn}$  and  $\text{Cu}_4\text{Sn}$ ,  $\text{AuSn}$  does not become superconducting down to 1.43° Abs. The transition point of  $\text{Hg}_5\text{Ti}_2$  (3.82° Abs.) lies a little below that of mercury and considerably above that of pure thallium, whilst that of  $\text{PbTi}_2$  (4.05° Abs.) also lies between the transition points of lead and of thallium. Thallium containing 3% of silver, which must be composed of thallium, silver, and a solid solution of thallium in silver, becomes superconducting at 2.67° Abs., or 0.3° higher than pure thallium.

J. W. SMITH.

**Influence of magnetic fields on superconductors.** W. J. DE HAAS and J. VOOGD (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 262–272).—Like the alloys previously investigated (cf. A., 1929, 496), the magnetic threshold values of  $\text{PbTi}_2$  and  $\text{Sb}_3\text{Sn}_3$  rise more rapidly with lowering of temperature than do those of the pure metals. Lead-bismuth alloys require very high magnetic fields to disturb the superconductivity, the magnetic fields required being the higher the greater is the bismuth content. A solenoid made of a saturated solution of bismuth in lead should be able to generate magnetic fields of 14,000 gauss at the b. p. of helium without development of heat, and at 2° Abs. even fields of 19,000 gauss. Lead-tin-bismuth and lead-tin-bismuth-cadmium alloys show magnetic disturbance at about the same field strength as the lead-bismuth eutectic mixture. These, as well as the lead-bismuth alloys, give indications of a small hysteresis in the magnetic transition figure.

J. W. SMITH.

**Apparent deviation from Ohm's law for metals at high current densities.** H. M. BARLOW (Phil. Mag., 1930, [vii], **9**, 1041–1055; cf. Bridgman, Proc. Amer. Acad. Arts Sci., 1922, **57**, 131; Compton, A., 1926, 1086).—Bridgman found a variation in the resistance of conducting films at high current densities and with the alternating current frequency when a large direct current and a small alternating current were passed through the film at the same time. An investigation was made, using an improved form of Bridgman's apparatus, and curves are given of the variation differences between alternating and direct current resistances with the alternating current, the direct current density, and frequency of the alternating current. Ohm's law was found to be rigidly true for a gold conductor carrying a current density of  $2 \times 10^6$  amp./cm.<sup>2</sup>, and for a platinum conductor at  $1.3 \times 10^5$  amp./cm.<sup>2</sup> Bridgman's assumption of a sinusoidal variation of resistance with the alternating current is not supported.

N. M. BLIGH.

**Electrical conductivity of fused silica.** H. J. SEEMANN (Z. Physik, 1930, **61**, 576–577).—Polemical, against Lauster (cf. this vol., 142).

A. B. D. CASSIE.

**Electrical conductivity of fused silica.** F. LAUSTER (Z. Physik, 1930, **61**, 578–580).—A reply to Seemann (preceding abstract). Photomicrographs of specimens of fused silica are reproduced.

A. B. D. CASSIE.

**Magnetic susceptibility of manganocyanide ion.** S. FREED and C. KASPER (J. Amer. Chem. Soc., 1930, **52**, 1012–1013).—The magnetic susceptibility of the manganocyanide ion is found to be  $1650 \times 10^{-6} \pm 5\%$  by the Gouy method.

J. G. A. GRIFFITHS.

**Magnetic moment of the atomic nucleus.** J. DORFMAN (Compt. rend., 1930, **190**, 924–925).—Calculating  $\chi_c$  for lithium (6) by a method analogous to that of Cabrera (A., 1925, ii, 1107) as  $-24.1 \times 10^{-6}$ , and  $\chi_i$  on the assumption that the magnetic moment of the nucleus is one Bohr magneton, the value obtained for the susceptibility is  $\chi (= \chi_c + \chi_i) = +43.72 \times 10^{-6}$ , which disagrees with Pascal's experimental value,  $-24.3 \times 10^{-6}$ . It is inferred that if the nucleus of Li(6) possesses any magnetic moment at all it does not exceed  $M_B/10$ . Similar calculations lead to similar conclusions regarding atoms containing 2, 3, 4, 5, 6, and 7 electrons. This implies that the moment of the pivoting electron is without effect in the nucleus, a conclusion in agreement with spectroscopic data. Various explanations are suggested, the one preferred being that the moment of the pivoting electron is compensated in some way in the nucleus.

C. A. SILBERRAD.

**Measurements of sound-velocities in air, oxygen, and carbon dioxide at temperatures from 900° to 1200°, with special reference to the temperature coefficients of molecular heats.** F. E. KING and J. R. PARTINGTON (Phil. Mag., 1930, [vii], **9**, 1020–1026).—With the apparatus and method previously described (cf. A., 1929, 128) measurements were extended to higher temperatures. Sound velocities, molecular heats, and their ratios are tabulated.

N. M. BLIGH.

**Specific heats of metals and alloys at low temperatures.** A. EUCKEN and H. WERTH (Z. anorg. Chem., 1930, **188**, 152–172).—The variation with temperature of the specific heats of copper, nickel,  $\alpha$ -iron, constantan, and three alloys of iron and manganese has been determined down to 15° Abs. Below 20° Abs. none of the substances obeys the Debye equation ( $C_v = \alpha T^3$ ); electrolytic iron, however, does so between 26° and 40° Abs. The specific heats of constantan are given satisfactorily from those of the components by the Kopp-Neumann additive rule, and the latter has been used to calculate the specific heat of  $\gamma$ -iron from the observed values for the iron-manganese alloys examined. With the data for the at. heats of  $\alpha$ - and  $\gamma$ -iron the values of the entropy integrals in the Nernst heat theorem have been calculated, and these point to a finite entropy difference at 0° Abs., which, however, is of the same order as the experimental error. At liquid air temperature there is, with nickel or copper, no marked difference between the specific heats of recrystallised and stamped metals, but at the temperature of liquid hydrogen that of stamped nickel is about 3% lower than that of the recrystallised metal.

F. L. USHER.

**Heats of association of acetic and heptonic acids in the vapour state.** (Miss) T. M. FENTON and W. E. GARNER (J.C.S., 1930, 694—700).—The vapour densities of acetic and heptonic acids have been measured over the ranges 110—184° and 185—230°, respectively. The heat of association of acetic acid is calculated to be 13,790 g.-cal. per mol.; that of heptonic acid varies with the temperature and has an average value of 7050 g.-cal. per mol. over the range studied.

C. W. GIBBY.

**Simple equation for the Joule-Thomson effect in real gases.** J. A. BEATTIE (Physical Rev., 1930, [ii], 35, 643—648).—Mainly mathematical. From the Beattie-Bridgeman equation of state simple approximate relations are derived for  $\mu C_p$  and the pressure variation of  $C_p$  expressed as functions of  $p$  and  $T$  (cf. Bridgeman, A., 1929, 1136). The resulting values for the Joule-Thomson coefficient  $\mu$  agree well with the observed values in the case of air, and fairly well for ammonia. The approximate equation for  $\mu C_p$  gives values for the inversion temperatures of the Joule-Thomson effect for air in good agreement with experiment. N. M. BLIGH.

**Thermal data on organic compounds. VI. Heat capacities, entropies, and free energies of some saturated, non-benzenoid hydrocarbons.** G. S. PARKS, H. M. HUFFMAN, and S. B. THOMAS (J. Amer. Chem. Soc., 1930, 52, 1032—1041).—The following heats of fusion are recorded (g.-cal. per g. at the m. p.):  $\beta$ -methylbutane, 16.94;  $n$ -hexane, 34.89;  $n$ -heptane, 33.78;  $\beta$ -methylhexane, 21.16;  $n$ -octane, 42.04;  $\beta\beta\beta$ -trimethylpentane, 18.92; eicosane, 52.0; cyclohexane, 7.41. Solid transitions are exhibited by hexamethylethane at 148.1° Abs. and by cyclohexane at 185.9° Abs., the respective heats of transition being 4.20 and 19.07 g.-cal./g. The molar entropy at 25° of liquid aliphatic hydrocarbons having a straight chain of  $n$  carbon atoms and  $r$  methyl branches is  $25.0 + 7.7n - 4.5r$  (g.-cal./1°),  $r$  being zero for normal hydrocarbons. The entropy of cyclohexane is much smaller than that of  $n$ -hexane, whereas the free energy is much larger. A free energy increase of 600 g.-cal./mol. occurs between successive members of an ascending homologous series of normal hydrocarbons; the free energy of a branched hydrocarbon is higher than that of the corresponding normal compound, and is greater the more extensive is the branching (cf. A., 1929, 990).

S. K. TWEEDY.

**Thermal data on organic compounds. VII. Heat capacities, entropies, and free energies of twelve aromatic hydrocarbons.** H. M. HUFFMAN, G. S. PARKS, and A. C. DANIELS (J. Amer. Chem. Soc., 1930, 52, 1547—1558).—The specific heats of benzene, ethylbenzene, *tert.*-butylbenzene, *o*-, *m*-, and *p*-xylenes, diphenylmethane, hexamethylbenzene, diphenyl, triphenylmethane, dibenzyl, and naphthalene have been measured over a wide range of temperature by the method previously described (A., 1925, ii, 491). The heats of fusion of the first seven of the hydrocarbon have also been determined. The entropies of the hydrocarbons, calculated from the heat capacity data, agree fairly well with those obtained from the empirical equation  $S_{298} = 25.0 + 7.7n - 4.5r +$

$19.5p$  (cf. preceding abstract), where  $n$ =total number of carbon atoms outside the benzene ring,  $p$ =number of phenyl groups in the molecule, and  $r$ =number of hydrocarbon groups in excess of 2 attached to any carbon atom in the aliphatic chain. The free energies have also been calculated. The introduction of a phenyl group into a saturated aliphatic hydrocarbon raises the free energy level by about 35,000 g.-cal., and the simple alkylbenzenes have approximately the same free energies, slightly lower than the value for benzene. The free energy change for the hydrogenation of benzene to cyclohexane is calculated by two different methods to be about -23,000 g.-cal.

H. BURTON.

**Entropy of solids at very low temperatures.** H. LUDLOFF (Naturwiss., 1930, 18, 182).—The entropy of solids at temperatures in the neighbourhood of 0° Abs. is discussed in the light of the new statistics with particular reference to the vapour-pressure constant.

R. W. LUNT.

**Specific heat of chlorine.** J. R. PARTINGTON (Z. physikal. Chem., 1930, B, 7, 319—323).—The criticism by Eucken and Hoffmann (A., 1929, 1372) of the use of the Berthelot equation of state for the calculation of the specific heat of chlorine (cf. A., 1914, ii, 529) is held to be unjustified, since this equation gives good agreement with the experimental measurements of the density of chlorine at various temperatures. Other data, not quoted by Eucken and Hoffmann, agree better with the low values obtained by the author.

J. W. SMITH.

**Specific heat of chlorine.** A. EUCKEN (Z. physikal. Chem., 1930, B, 7, 324).—Polemical against Partington (cf. preceding abstract). The Callendar equation of state is held to be preferable to that of Berthelot for use in these calculations.

J. W. SMITH.

**Isotherms of carbon dioxide between 0° and 100°.** G. P. NIJHOFF, A. J. J. GERVEN, and A. MICHELS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 72—73; cf. A., 1929, 128).—Preliminary data of isotherms measured up to 2000 atm. pressure are given.

F. G. TRYHORN.

**Dilatometric observation of the transition point of methane.** W. HEUSE (Z. physikal. Chem., 1930, 147, 282—287).—The transition point of methane at 20.4° Abs. found by Clusius (A., 1929, 635) is not sharp. The change in volume takes place between 20.15° and 20.45° Abs. and is probably due to a change within the molecule and not to a lattice change.

O. J. WALKER.

**Preparation and characteristic data of [hydrocarbons].** W. FISCHER and W. KLEMM (Z. physikal. Chem., 1930, 147, 275—281).—The methods of preparation of the hydrocarbons used by Heuse (see this vol., 667) for molecular volume measurements are described and their experimentally determined vapour pressures and densities tabulated.

O. J. WALKER.

**Specific heat of solid substances at the temperatures obtainable with the aid of liquid helium. II. Measurements of the at. heats of lead and of bismuth.** W. H. KEESOM and J. N.

VAN DEN ENDE (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 243—254).—The experiments of Keesom and Andrews (A., 1927, 1131) on the at. heat of lead have been repeated over the temperature range 2—17° Abs. Improvement in the heat insulation of the calorimeter and in the arrangements for temperature measurement have enabled more regular results to be obtained. Similar measurements have also been made with bismuth, and the at. heats of these metals at temperatures between 3° and 20° Abs. are given in tabular form. J. W. SMITH.

**Effect of a permanent electrical dipole on the internal latent heat of vaporisation of a liquid.** A. R. MARTIN (Phil. Mag., 1930, [vii], **9**, 422—425).—The work of vaporising a single molecule is regarded as the change in the energy in the medium resulting from the transfer of the molecule to a vacuum from a medium of dielectric constant equal to that of the liquid. Then if the molecule be regarded entirely as a permanent electrical dipole the energy change is given by the expression  $\mu^2(1-1/D)/3a^3$  previously described (A., 1929, 143), where  $\mu$ =moment of the dipole,  $a$ =radius of the molecule, and  $D$ =dielectric constant of the liquid. Values of  $a$  have been calculated for a number of compounds, mainly organic, in which allowance has been made for that part of the latent heat not due to the dipole by subtracting from the total latent heats values for the alkyl and phenyl groups based on the latent heats of the parent hydrocarbons. The molecular radii so calculated are of the correct order of magnitude, although smaller than those indicated by gaseous viscosities.

A. E. MITCHELL.

**Physical chemistry of sulphur trioxide.** R. GRAU and W. A. ROTH (Z. anorg. Chem., 1930, **188**, 173—185).—The vapour pressures of sulphur trioxide have been determined by a static method between 15° and 45°. Above 25° the results are in agreement with those of previous workers. Heats of dissolution of both the liquid and solid modifications have been measured. The variability of the values obtained with the solid trioxide indicates that it consists of more than one substance. For the heat of dissolution of the liquid in 5000 mols. of water the value  $41.18 \pm 0.02$  kg.-cal. per mol. is obtained. The heat of vaporisation of liquid sulphur trioxide has been directly determined. The value obtained,  $-10.0$  kg.-cal. per mol., is regarded as approximate, but is in agreement with the value ( $-10.16$  to  $-10.3$ ) deduced from the vapour pressures by means of the Clausius-Clapeyron equation. F. L. USHER.

**Vapour pressure of solid nitrous oxide.** H. K. BLACK, G. VAN PRAAGH, and B. TOPLEY (Trans. Faraday Soc., 1930, **26**, 196—197).—The vapour pressure of solid nitrous oxide was measured with a McLeod gauge, the following corrected values\* being obtained: at  $-150.0^\circ$   $0.306$  mm., at  $-160.0^\circ$   $0.030$  mm., and at  $-170.0^\circ$   $0.0013$  mm.

C. J. SMITHELLS.

**New vapour-pressure measurements of sodium and determination of its chemical constant.** R. LADENBURG and E. THIELE (Z. physikal. Chem., 1930, **B**, **7**, 161—187).—Vapour-pressure measurements of sodium between  $614^\circ$  and  $771^\circ$  Abs. have

been made by an improved method of flow with an accuracy of 1—2%. Argon was used as the inert gas. The results are best represented by the equation  $\log(pT^{1.52}) = -26400/4.573T + 12.439$ , determined by a graphical method, or by  $\log(pT^{1.78}) = -26167/4.573T + 11.396$ , calculated by the method of least squares. Partial pressures of atomic and molecular sodium have been calculated on the basis of a heat of dissociation of the sodium molecule of 18,000 g.-cal./g.-mol. Between  $496^\circ$  and  $771^\circ$  Abs.  $\log p_{Na} = -26077/4.573T - 1.178 \log T + 11.329$ . At the b. p.,  $1156^\circ$  Abs., and  $759$  mm.,  $p_{Na}$  is  $614$  mm. and  $p_{Na_2}$  is  $1.45$  mm. Taking into consideration the optical data of Ladenburg, Minkowski, and others on magnetorotation in the  $D$  lines, the chemical constant of sodium is  $0.78 \pm 0.10$ . The classical value is  $-1.588 + 1.5 \log M = 0.455$  and the difference is therefore  $0.32 \pm 0.10$ . This is in agreement with Schottky's theory, according to which the difference is  $\log g$ , where  $g$  is the quantum weight of the sodium atom in the normal state and equals 2. M. S. BURR.

**Vapour pressure of some stannanes.** R. H. BULLARD and A. C. HAUSSMANN (J. Physical Chem., 1930, **34**, 743—747).—The vapour pressures of tetramethyl-, trimethylethyl-, and trimethyl- $n$ -propyl-stannane have been determined between  $0^\circ$  and  $80^\circ$ ,  $0^\circ$  and  $111^\circ$ , and  $13^\circ$  and  $132^\circ$ , respectively. The corresponding b. p. are  $78.0^\circ$ ,  $108.2^\circ$ , and  $130.8^\circ$ , respectively, whilst the calculated molal heats of vaporisation at the b. p. are  $7406$ ,  $8338$ , and  $8913$ , respectively. The molal entropies indicate that these liquids are normal or non-polar. L. S. THEOBALD.

**Vapour-pressure curves and the calculation of van der Waals'  $a$  constants for metals and salts.** J. A. M. VAN LIEMPT (Z. anorg. Chem., 1930, **189**, 287—288).—A criticism of a publication by Lorenz and Herz (this vol., 403). M. S. BURR.

**Method of calculating the numerical equation of state for helium below  $6^\circ$  Abs., and of determining the relative importance of gas degeneracy and inter-atomic forces.** M. C. JOHNSON (Proc. Physical Soc., 1930, **42**, 170—180).—It is shown that theories of gas degeneracy, or the effect of non-Maxwellian distribution of molecular velocities, cannot be verified by specific heat measurements unless account is taken of the rapid increase at the lowest temperatures and highest pressures of gas imperfection, or the effect of intermolecular forces. From a thermodynamic calculation of the sum of degeneracy and imperfection at  $4^\circ$  and  $5^\circ$  Abs. for helium an approximate test of theories of degeneracy can be made. The method is applied to Berthelot's equation of state and to Fermi's expressions for strong and weak degeneracy (cf. A., 1926, 657); the latter, giving the better agreement with available data, indicates that degeneracy comprises 15% of the total departure of helium from the ideal gas laws at  $4^\circ$  and  $5^\circ$  Abs., the remainder being due to true imperfection or intermolecular forces. N. M. BLIGH.

**Compressibility isotherms of hydrogen, nitrogen, and a 3 : 1 mixture of these gases at  $-70^\circ$ ,  $-50^\circ$ ,  $-25^\circ$ , and  $20^\circ$ , and at pressures to 1000 atm.** E. P. BARTLETT, H. C. HETHERINGTON, H. M.



KVALNES, and T. H. TREMBARNE (J. Amer. Chem. Soc., 1930, 52, 1363—1373).—An extension of previous work (A., 1928, 698) on the above gases. Compressibility data are recorded. At about 380 atm., nitrogen exhibits a constant deviation from the ideal gas law for the range  $-70^{\circ}$  to  $100^{\circ}$ .

J. G. A. GRIFFITHS.

Compressibility isotherms of carbon monoxide at temperatures from  $-70^{\circ}$  to  $200^{\circ}$  and at pressures to 1000 atm. E. P. BARTLETT, H. C. HETHERINGTON, H. M. KVALNES, and T. H. TREMBARNE (J. Amer. Chem. Soc., 1930, 52, 1374—1382).—The formation of carbon dioxide and iron carbonyl in steel cylinders of carbon monoxide under high pressure has been examined. The data recorded show that carbon monoxide and nitrogen exhibit similar compressibility phenomena. Carbon monoxide is slightly more compressible in the low pressure range, and slightly less compressible in the high pressure range. At 375 atm., the volume is a linear function of the absolute temperature for the range  $-70^{\circ}$  to  $200^{\circ}$  (cf. nitrogen, preceding abstract).

J. G. A. GRIFFITHS.

Constants of the Beattie-Bridgeman equation of state with Bartlett's  $P$ - $V$ - $T$  data on nitrogen. W. E. DEMING and L. E. SHUPE (J. Amer. Chem. Soc., 1930, 52, 1382—1389).—Bartlett's compressibility data (A., 1928, 698) for nitrogen in the range  $-70^{\circ}$  to  $400^{\circ}$  are reproduced with a root mean square deviation of 0.50% at 4 c.c./g. and 0.78% at 3 c.c./g., by inserting the values  $r=2.92861$ ,  $A_0=1528.5$ ,  $a=0.2748$ ,  $a'=0.9084$ ,  $B_0=1.643$ ,  $b=-0.9235$ ,  $c=2.2 \times 10^6$  (units: atm., c.c./g.) in the Beattie-Bridgeman equation of state (A., 1927, 819),  $a'$  being the additional constant in the relation  $A=A_0(1-a/v-a'/v^2)$ . The discrepancy between observed and calculated pressures becomes very large at low temperatures and low volumes.

J. G. A. GRIFFITHS.

Limiting value for the expansion and elastic coefficients of gases. II. Neon. W. HEUSE and J. OTTO (Ann. Physik, 1930, [v], 4, 778—780).—Earlier work (A., 1926, 786) has given a relatively small value for the limiting value compared with that for helium and other gases recently determined (A., 1929, 1226). A redetermination is made, using the same method as was employed for helium, with a better result.

A. J. MEE.

Relation of fluidity of liquids to temperature. S. E. SHEPPARD (Nature, 1930, 125, 709).—Concerning priority.

L. S. THEOBALD.

Viscosity of vapours of organic compounds. II. T. TITANI (Bull. Chem. Soc. Japan, 1930, 5, 98—108; cf. A., 1929, 993).—The viscosities of ethane, propane, isobutane, *n*-butane, ethylene, propylene,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -butylene, isopropylethylene, acetylene, allylene, trimethylene, methyl ether, methyl chloride, methyl bromide, and sulphur dioxide have been measured at temperatures between  $20^{\circ}$  and  $120^{\circ}$ . In every case Sutherland's formula applies satisfactorily. Tabulated values are given for Sutherland's constant, mean free path, and molecular diameters. In general, good agreement obtains between values of the molecular diameters computed

from the viscosity data and from critical data, respectively. The molecular volumes at the b. p. are found to be approximately three times as large as the actual volume of the molecules.

F. G. TRYHORN.

Hydrodynamics of systems of variable viscosity. III. M. REINER (Kolloid-Z., 1930, 50, 199—207; cf. A., 1927, 1138; 1928, 235).—Equations applicable to viscosity measurements with the capillary and the rotating viscosimeters are tested by reference to experimental results recorded in the literature.

E. S. HEDGES.

Coefficient of diffusion of water vapour. W. E. SUMMERHAYS (Proc. Physical Soc., 1930, 42, 218—225).—A method is described by which water vapour was allowed to diffuse down a vertical tube about 2 in. in diameter, a steady concentration gradient being maintained from approximate saturation to dryness at the top and bottom, respectively. The gradient was measured by two catharometers at known distances apart, and the mass of vapour passing in an observed time was weighed. The value obtained was 0.282 cm.<sup>2</sup>/sec. at mean temperature  $16.1^{\circ}$ . An indirect method based on the analogy between thermal conductivity and diffusion was unsatisfactory.

N. M. BLYCH.

Mixtures of vapours of iodine and various solvents. M. CHATELET (Compt. rend., 1930, 190, 927—929).—When a solution of iodine in benzene is vaporised the spectrum shows a band which cannot be attributed to either of the constituents. To verify the assumption that this is due to molecular combination, the specific volume at  $100^{\circ}$  of the mixed vapour from solutions of iodine in a series of solvents has been determined, and found to be always less than that of the pure solvent. The number of molecules of the following solvents associated with one of iodine is calculated to be: benzene 10, methyl alcohol 14.9, ethyl alcohol 13, propyl alcohol 11.2, acetone 12, ethyl acetate 9. It is further shown that the number of associated molecules of solvent is approximately inversely proportional to the mean free path of the iodine molecule.

C. A. SILBERRAD.

Comparison of analyses by specific gravity and refraction. I. Solutions of phenol in water. N. SCHOORL (Pharm. Weekblad, 1930, 67, 302—306).—Comparison of published results shows that the change in refractive index for a given change in concentration is much greater than the corresponding change in specific gravity, whilst the temperature coefficient is much lower for refractive indices.

S. I. LEVY.

Viscosity and diffusion in glycerol-water mixtures. II. Z. V. VOLKOVA (Z. physikal. Chem., 1930, 147, 206—214; cf. this vol., 146).—In continuation of previous work, the diffusion coefficients of potassium iodide, sodium, potassium, and barium chlorides, and sucrose in different glycerol-water mixtures have been measured. For all mixtures of specific volume between 0.7988 and 0.8700 the same equation represents the relation between specific volume and fluidity and between specific volume and diffusion. For the specific volume interval 0.8700—1.00117 the diffusion curve deviates from the fluidity

curve, due to a marked increase in the quotient of fluidity by diffusion, which is a constant characteristic of the salt at the lower specific volumes. The heats of dilution of glycerol-water mixtures, determined by Fricke (A., 1928, 134), also follow the fluidity-volume curve between the specific volumes 0.7966 and 0.8300. M. S. BURR.

**Viscosity formula for binary mixtures, having regard to the degrees of association of the constituents.** V. T. ISHIKAWA (Bull. Chem. Soc. Japan., 1930, 5, 47—54).—The formula previously derived (A., 1929, 387) has been adapted for the case of a solid dissolved in an inert liquid, and in its modified form is shown to be valid for a number of solutions. H. F. GILLBE.

**Vapour pressures of solutions and the Ramsay-Young rule. Application to the complete system water-ammonia.** F. C. KRACEK (J. Physical Chem., 1930, 34, 499—521).—A systematic method for the treatment of vapour-pressure data for solutions based on the Ramsay-Young rule that the ratio of the absolute b. p. of two substances at various vapour pressures varies linearly with temperature has been developed and applied to the system water-ammonia for vapour pressures up to  $10^4$  mm. The vapour-pressure curve for saturated solutions of ammonia in water has been calculated. Thermodynamic relations connecting heat of vaporisation with the Ramsay-Young rule have been derived and in the case of the system ammonia-water these yield calculated values for  $25^\circ$  in good agreement with those obtained by experiment. The method gives no information concerning the formation of compounds between the components of the system. L. S. THEOBALD.

**Binary systems for which the b. p. curves are practically straight lines.** M. LECAT (Ann. Soc. Sci. Bruxelles, 1930, 50, 13—17).—Examples of systems in which the b. p. is practically a straight line function of the composition are shown in tabular form. In many such systems thermal effects are shown when the components are mixed. J. O. CUTTER.

**New azeotropic binary systems.** M. LECAT (Ann. Soc. Sci. Bruxelles, 1930, 50, 21—33).—A further list (No. 15) of 270 normal azeotropic mixtures, showing the characteristic data relating to composition and temperature. J. O. CUTTER.

**Physical methods of separating constant-boiling mixtures.** A. A. SUNIER and C. ROSENBLUM (Ind. Eng. Chem. [Anal.], 1930, 2, 109—113).—A review of the physical methods of separation of the components of constant-boiling mixtures. The methods fall into two classes, dependent on the utilisation of differences in the mass or in the vapour pressure of the components. To the first class belong atmolysis, non-equilibrium evaporation, thermal diffusion, and centrifuging, whilst the second class includes methods based on reduction of pressure, formation of three-component systems by the addition of a liquid or solid, and the production of solid phases. The method of separation by selective adsorption of one component by a silica gel does not come under either of the above headings, and appears to be promising. H. F. HARWOOD.

**Effect of temperature on the molecular surface energy of binary mixtures. II. Water and nicotine.** W. F. SEYER and A. F. GALLAUGHER (J. Amer. Chem. Soc., 1930, 52, 1448—1456).—The densities and surface tensions of nicotine between  $-50^\circ$  and  $94^\circ$  and of its aqueous solutions between  $0^\circ$  and  $95^\circ$  have been determined. Molecular surface energies and Eötvös constants,  $K_e$ , are recorded. The presence of nicotine hydrates is inferred from the existence of maxima in the concentration-surface tension curves at 36% and 72% of nicotine. The maxima disappear above  $40^\circ$ . Nicotine is not associated, and  $K_e$  is between 2.4 and 2.8. J. G. A. GRIFFITHS.

**Form of the property curves in binary systems in the formation of an undissociated compound, in which the given property is expressed in an ideal system by a straight line.** V. Y. ANOSOV (Bull. inst. rech. biol. univ. Perm, 1929, 6, 486—487).—Mathematical. When concentrations are expressed in mol. fractions it is impossible to find a property which is additive in an ideal system as well as in a system with a non-dissociating compound. CHEMICAL ABSTRACTS.

**Relation between the molar and weight concentration curves for the same property of a binary system.** V. Y. ANOSOV (Bull. inst. rech. biol. univ. Perm, 1929, 6, 501—502).—In non-ideal systems the property curves expressed in terms of weight and molar concentration are similar. CHEMICAL ABSTRACTS.

**Relation between temperature coefficients of reciprocal properties.** V. Y. ANOSOV (Bull. inst. rech. biol. univ. Perm, 1929, 6, 515).—Theoretical. The true temperature coefficient of a given property is equal to that of the reciprocal property with the opposite sign; equations for the calculation of the average temperature coefficient of the reciprocal property are given. CHEMICAL ABSTRACTS.

**Relation between the curves for reciprocal properties of binary systems.** V. Y. ANOSOV (Bull. inst. rech. biol. univ. Perm, 1929, 6, 511—512).—In non-ideal systems either of two reciprocal properties may be used in determining the equilibrium; in systems approaching ideal an additive property should be selected. CHEMICAL ABSTRACTS.

**Lead-magnesium alloys.** C. L. ACKERMANN (Metall.-Wirt., 1929, 8, 701—702; Chem. Zentr., 1930, i, 124—125).—A study of physical properties. A. A. ELDRIDGE.

**System copper-zinc.** C. H. JOHANNSON (Z. anorg. Chem., 1930, 187, 334—336).—A criticism of the conclusion of Ruer and Kremers (this vol., 161) that the transformation of  $\beta$ -brass cannot take place in a homogeneous phase. The anomalous specific heat at constant pressure is attributed to the rotational energy of the zinc atom in the lattice structure. M. S. BURR.

**Nickel-chromium system.** Y. MATSUNAGA (J. Study Met., Japan, 1929, 6, 207—215).—The components are miscible in all proportions in the liquid phase; in the solid phase the eutectic, m. p.  $1346^\circ$ , contains 49% Ni. The solid solubility of the  $\alpha$ -phase corresponds with 47 and 44% Cr and that of the

$\beta$ -phase with 37 and 7% Ni at the eutectic and ordinary temperatures, respectively. The best workable acid-resisting alloy contains 15–35% Cr.

#### CHEMICAL ABSTRACTS.

**X-Ray investigation of the nickel-cobalt and iron-cobalt systems.** A. ÔSAWA (Sci. Rep. Tôhoku, 1930, 19, 109–121).—In nickel-cobalt alloys, the lattice constant and concentration are linearly related to each other, i.e., Vegard's law holds. The lattice constant  $a$  of face-centred cubic cobalt at the ordinary temperature is 3.525 Å. In the case of the  $\alpha$ -solid solution in the iron-cobalt system, Vegard's law does not hold. The lattice constant-concentration curve can be represented by an equation of the second order. The axial ratio of hexagonal cobalt is considerably decreased by the addition of nickel, but is increased by the addition of iron.

W. E. DOWNEY.

**System chromium-carbon.** A. WESTGREN and G. PIIRAGMÉN (Z. anorg. Chem., 1930, 187, 401–403).—The results of Kraiczek and Sauerwald (this vol., 147) contradict in certain important respects those previously obtained by the authors (B., 1928, 408). The chromium-chromium carbide eutectic is, according to the latter, at 3.4% carbon and not 4.5%. A cubic carbide of the formula  $\text{Cr}_7\text{C}_3$  is indicated both by X-ray and micrographic observations in addition to the carbides  $\text{Cr}_4\text{C}$  and  $\text{Cr}_3\text{C}_2$ . There is no series of mixed crystals in the concentration interval round 9% carbon. These discrepancies are attributed to an error on the part of Kraiczek and Sauerwald in the preparation of sections for examination.

M. S. BURR.

**Vanadium-carbon system.** A. ÔSAWA and M. ÔYA (Sci. Rep. Tôhoku, 1930, 19, 95–108).—Microscopic and X-ray observations show that three solid phases occur in this system,  $\alpha$ ,  $\beta$ , and  $\epsilon$ , the two latter corresponding with the compounds  $\text{V}_5\text{C}$  and  $\text{V}_4\text{C}_3$ . The crystal form of  $\text{V}_5\text{C}$  is hexagonal, having an axial ratio of 1.59, and the atomic distribution is hexagonal close-packed. The crystal form of  $\text{V}_4\text{C}_3$  is cubic, having a face-centred distribution of vanadium atoms. Eutectic mixtures are formed by the  $\alpha$ -phase (a vanadium solid solution) and the  $\beta$ -phase, and also by the  $\beta$ - and  $\epsilon$ -phases.

W. E. DOWNEY.

**Quantitative X-ray analysis of iron and of iron-manganese alloys.** S. SHIMURA and K. WADA (J. Iron Steel Inst. Japan, 1929, 15, 393–402).—The manganese (6–7%) could be determined with a maximum error of 0.2%.

#### CHEMICAL ABSTRACTS.

**Barium-tin alloys.** K. W. RAY and R. G. THOMPSON (Metals and Alloys, 1930, 1, 314–316).—The alloys were prepared by electrolysis of a eutectic mixture of potassium and barium chlorides over a molten tin cathode in a chromium-plated iron crucible, a carbon rod being used as anode. The compounds  $\text{BaSn}_3$  and  $\text{BaSn}_5$  are present in alloys containing up to 28% Ba.  $\text{BaSn}_3$  is stable, and  $\text{BaSn}_5$  unstable, above 422°. In alloys containing less than 18.79% Ba,  $\text{BaSn}_5$  is the only solid phase stable between the m. p. of tin and 422°. The alloys corrode rapidly in air to form a film of oxide and carbonate, and then corrosion proceeds slowly;

with water, hydrogen is evolved. Addition of barium increases the hardness, brittleness, and rate of corrosion, whilst the density is decreased.

#### CHEMICAL ABSTRACTS.

**Hall effect, electrical conductivity, and thermo-electric power of the lead-antimony series of alloys.** E. STEPHENS (Phil. Mag., 1930, [vii], 9, 547–560; cf. A., 1929, 384, 1224).—Successive determinations of the electrical resistance of the alloys at 0° were made until annealing produced no further variation. The temperature coefficients of resistance, thermo-electric power, and Hall effect were then determined for the alloys in this final state. The curves relating these constants to the concentration of one metal are continuous and without irregularities; but there is no indication of any close connexion between the different phenomena. Annealing reduces the resistance of all the alloys.

M. S. BURR.

**Transitions in the solid state of silver-cadmium alloys.** W. FRAENKEL and A. WOLF (Z. anorg. Chem., 1930, 189, 145–167).—Silver-cadmium alloys, containing 40–60 at.-% of silver, have been investigated by thermal, electric, volumetric, and micrographic methods. The cooling curves for alloys containing 43–57% Ag indicate the existence of transition points, the maximum halts being obtained with approximately 50% alloys. For alloys with more than 50% Ag the upper and lower transition points are at 430° and 211°, respectively. With decreasing silver content the upper is replaced by one at 450° and the transition is delayed at the lower temperature. At the transition points volume expansion takes place on heating. There is an abrupt increase of the electrical resistance at 211° and the temperature coefficient of resistance increases suddenly at 430°. Micrographic investigation supports these conclusions. The results have been represented diagrammatically and the different alloys compared as regards colour and hardness. The modifications stable at higher temperatures cannot be supercooled, but at about 150° the lower transition can be followed kinetically by the dilatometer.

M. S. BURR.

**Relation between the colours and the microstructures of some binary and ternary silver alloys, with visible rays.** S. UENO (Mem. Coll. Sci. Kyôtô, 1930, 13, 141–147).—The intensity of reflexion for the  $c$  line in the hydrogen spectrum was determined for three series of silver alloys. In the silver-aluminium system there is a maximum at  $\text{AlAg}_3$ , a break at  $\text{AlAg}_2$ , and a minimum at the eutectic. In the silver-aluminium-10% zinc system there is a minimum at 30% Al, and breaks at 5% and 10% Al. In the silver-copper-30% zinc system there is a minimum at 20% Ag and a maximum at 50% Ag.

C. J. SMITHELLS.

**Binary system bismuth-tellurium.** F. KÖRBER and U. HASCHIMOTO (Z. anorg. Chem., 1930, 188, 114–126).—Thermal analysis of the above system, whilst establishing the existence of mixed crystals of bismuth and bismuth telluride,  $\text{Bi}_2\text{Te}_3$ , gives no trustworthy indication of the solubility of tellurium in the compound. The variations of electrical con-

ductivity, of thermo-electric power, and of magnetic susceptibility with composition indicate mutual solubility of tellurium and bismuth telluride or, alternatively, the existence of a second compound such as  $\text{BiTe}_2$ . X-Ray analysis shows conclusively that no compound other than  $\text{Bi}_2\text{Te}_3$  is formed. The conclusion reached is that the electrical and magnetic properties of the system must be ascribed to solubility of tellurium in the telluride despite the absence of confirmation by thermal analysis.

F. L. USHER.

**Inactivation of the surface of metals by diffusion. IV. Diffusion of molybdenum and iron in the solid state.** G. GRUBE and F. LIEBERWIRTH (*Z. anorg. Chem.*, 1930, **188**, 274—289; cf. A., 1928, 138).—The diffusion of molybdenum into iron has been studied by heating cylindrical rods of very pure iron embedded in powdered molybdenum in a stream of hydrogen at temperatures from 1000° to 1300°. At the latter temperature the molybdenum after 24 hrs. was present to the extent of 0.25% at a depth of 1.5 mm. The coefficient of diffusion increases with the distance from the surface, and attains an approximately constant value in the innermost layers examined. Homogeneous alloys have been prepared by heating compressed mixtures of powdered molybdenum and iron for 72 hrs. at 1250°, and a micrographic examination of the resulting specimens supports the observations of Sykes made by the usual method. Experiments in which rods of alloy of varying composition were subjected to the action of 0.1*N*-hydrochloric or sulphuric acid show that the presence of molybdenum in the mixed crystals exercises a powerful protective action, which is greatest at about 5% Mo. In alloys with higher molybdenum content, in which micrographic examination reveals a heterogeneous structure, the protective action is less marked.

F. L. USHER.

**Ternary system aluminium-magnesium-zinc.**

I. S. NISHIHARA (*Suiyokaishi*, 1929, **5**, 783—790).—Alloys containing less than 20%  $\text{MgZn}_2$  show a eutectic line at 469°; the maximum and minimum solubilities of the compound  $\text{MgZn}_2$  on the aluminium side are 19.5 and 3%, respectively. The ageing of the alloys was studied.

CHEMICAL ABSTRACTS.

**Thermo-electric force coefficient of some pure metals and alloys down to the temperature of liquid hydrogen and calculation of the Thomson effect.** G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON, and J. O. LINDE (*Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 17—31, 32—43; cf. A., 1929, 385).—I. The thermo-electric force, and its temperature coefficient, have been determined over the range 20° to -256° for copper, silver, gold, iron, palladium, platinum, and lead. The measurements were made against a standard silver-gold alloy, and from the results the temperature function of the Thomson effect has been computed. The form of this function is very similar for the metals copper, silver, and gold, a marked minimum occurring at 88°, 75°, and 76°, respectively. At a very low temperature a maximum occurs in the curve for copper. The curves for palladium and platinum are similar to that for iron; at high temperatures negative values

approximately proportional to the absolute temperature are found, whilst at lower temperatures slight maxima are obtained on the positive side at 37° Abs. for palladium and 34° Abs. for platinum. The Thomson effect for lead is small and its values are a little uncertain.

II. Similar measurements have been made for alloys of copper with small amounts of iron, cobalt, nickel, palladium, arsenic, and gold, for alloys of platinum containing 1.9—17.4% Rh, and for a ternary alloy of platinum, palladium, and gold. Like most dilute alloys, all the copper alloys are thermo-electrically negative against the pure metal, whilst the platinum-rhodium alloys are positive against the pure metals. The thermo-electric coefficients of copper alloys with small amounts of iron against pure copper rise with decreasing temperature. The results both for pure metals and for alloys tend to verify the generalisation that the Thomson effect and the thermo-electric coefficient approach zero value as the temperature approaches 0° Abs.

F. G. TRYHORN.

**Artificially coloured crystals as examples of the so-called anomalous mixed crystals.** K. SPANGENBERG and A. NEUHAUS (*Chem. Erde*, 1930, **5**, 437—528).—A detailed review is given of artificially coloured mixed crystals (*e.g.*, ferric chloride in ammonium chloride, methylene-blue in lead nitrate, etc.) and of the influence of such substances in solution on the habit of the crystals. It is considered that these are not true mixed crystals, but represent an inclusion of foreign material adapted to the structure of the host. In this connexion the composite crystals formed by the regular intergrowths of various minerals and salts are considered in detail from a structural point of view.

L. J. SPENCER.

**Anomalous crystallised mixed systems with organic components or of an organic component in an inorganic host.** A. NEUHAUS (*Chem. Erde*, 1930, **5**, 529—553).—Various inorganic salts when crystallised from solution may take up organic colouring matters; *e.g.*, barium, lead, and strontium nitrates readily take up methylene-blue, sodium and potassium chlorides take up murexide, and potassium sulphate takes up ponceau-red and Bismarck-brown. Similar anomalous crystals are also formed by certain pairs of organic compounds, *e.g.* naphthalene and dihydronaphthalene. Crystals of this kind are considered in detail especially from a structural point of view.

L. J. SPENCER.

**Anomalous crystallised mixed systems of the type iron ammonium chloride.** A. NEUHAUS (*Chem. Erde*, 1930, **5**, 554—624).—Ammonium chloride may take up varying amounts of  $\text{FeCl}_3 \cdot \text{H}_2\text{O}$  (up to 7.5%), giving distorted cubic crystals showing optical anomalies. Crystals of a similar nature are formed with  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  (up to 19%) and  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$  (up to 14%). It is concluded that these are not double salts nor true mixed crystals, but rather represent the inclusion of foreign matter along certain faces in the ammonium chloride crystals. The systems  $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ , and  $\text{NiCl}_2 \cdot \text{H}_2\text{O}$  were also studied in this connexion and data are given for some new crystalline hydrates.

L. J. SPENCER.

**Volume change during formation of binary compounds.** C. DEL FRESNO (Z. Elektrochem., 1930, 36, 163—165).—The changes of volume which accompany the formation of the alkali and alkaline-earth hydrides, halides, oxides, and sulphides follow a course parallel with that of the heats of formation.

H. F. GILLBE.

**Solubility of inert gases in water.** S. VALENTINER (Z. Physik, 1930, 64, 563—565; cf. A., 1927, 508).—The solubilities of helium in water at different temperatures (cf. A., 1922, ii, 642) taken as Ostwald solubilities were, in fact, Bunsen solubilities. This changes the coefficients in the solubility formula.

A. B. D. CASSIE.

**Solubility of ferrous sulphate.** F. K. CAMERON (J. Physical Chem., 1930, 34, 692—710).—The solubility of ferrous sulphate in aqueous solutions of sulphuric acid at 0°, 25°, 55°, 65°, and 75° has been determined together with the composition of the solid phases in contact with the solutions. The stable solid phase in contact with solution at 75° is the dihydrate, the solubility at this temperature being 31.04 g. of ferrous sulphate per 100 g. of solution. The general properties of aqueous solutions of ferrous sulphate are discussed.

L. S. THEOBALD.

**Tricalcium phosphate and water.** H. DANNEEL and K. W. FRÖHLICH (Z. anorg. Chem., 1930, 188, 14—31).—The wide variation of the figures given in the literature for the solubility of tricalcium phosphate in water is largely due to the fact that a substance having the composition  $\text{Ca}_3\text{P}_2\text{O}_8$  has hitherto seldom been obtained. Specimens in which the ratio Ca : P varied between 2.99 and 3.01 have been prepared by precipitating solutions of monocalcium phosphate with dilute ammonia, and the result of shaking these with water has been investigated. Equilibrium is established in less than 8 hrs. Warington's statement that the composition of the solution is a function of the relative amounts of solid and water has been confirmed. Calcium and phosphoric acid are not necessarily present in the solution in stoichiometric proportions. With very little water the  $\text{CaO}/\text{P}_2\text{O}_5$  ratio is 1 : 1; with 5 litres per g. of solid it is 2 : 1; and with 10 litres per g., 2.53 : 1, which last-named ratio is not changed by further dilution. It is considered probable that water decomposes tricalcium phosphate into tetracalcium phosphate, a salt  $\text{Ca}_5\text{H}_2(\text{P}_2\text{O}_8)_2$ , and monocalcium phosphate, and that these form a solid solution.

F. L. USHER.

**Solubility of some rare-earth nitrates in ether.** R. C. WELLS (J. Wash. Acad. Sci., 1930, 20, 146—148).—The solubilities of beryllium, yttrium, zirconium, lanthanum, cerium, praseodymium, erbium, and thorium nitrates in ether have been determined at about 20°. The solubility is greatly influenced by the degree of hydration of the salts.

C. W. GIBBY.

**Solubility of salvarsan in indifferent, detoxicating, and activating liquids.** G. L. DREYFUS (Münch. med. Woch., 1929, 76, 1285—1288; Chem. Zentr., 1929, ii, 2477).

**Physico-chemical investigations on amino-acids.** II. G. TAKAHASHI and T. YAGINUMA

(Proc. Imp. Acad. Tokyo, 1930, 6, 75—77; cf. A., 1929, 141).—The solubility curves for the  $\alpha$ - and  $\beta$ -hydrochlorides of the methyl (m. p. 118° and 148°), ethyl, and *n*-propyl (m. p. 110° and 136°) esters of *l*-leucine in the corresponding alcohols from -20° to 150° have been determined. The transition points  $\alpha \rightleftharpoons \beta$  are, respectively, 77.5°, 52.0°, and 2.5°, the corresponding salt concentrations being 82.3, 59.0, and 29.12%. At the ordinary temperature the  $\alpha$ -form of the methyl and ethyl ester salts and the  $\beta$ -form of the *n*-propyl ester salt are the stable polymorphs.

J. W. BAKER.

**Adsorption of electrolytes by activated carbon.** A. FRUMKIN (Kolloid-Z., 1930, 51, 123—129).—Ash-free sugar carbon activated by heating at 1000° in a stream of carbon dioxide was used in the experiments. When the carbon was outgassed by heating at a high temperature it did not adsorb electrolytes, but the adsorptive power returned in presence of air. Under such conditions the amount of hydrochloric acid adsorbed by the charcoal is equivalent to the content of oxygen in the charcoal and it is inferred that hydroxyl ions are sent into solution from the adsorption layer, according to the process  $\text{C}_x\text{O} + \text{H}_2\text{O} \rightarrow \text{C}_x + 2\text{OH}^+$ . Platinised carbon (prepared by moistening with chloroplatinic acid solution and heating in hydrogen) adsorbs hydrochloric acid from aqueous solution in the presence of air more strongly than pure carbon, the capacity increasing with the percentage of platinum. Small quantities of mercuric chloride poison the platinum and the adsorption value then falls to that for unplatinised carbon. When the carbon contains hydrogen its behaviour is entirely opposite; it does not adsorb acid but adsorbs alkali. This is represented by the scheme  $\text{C}_x + \text{H}_2 \rightarrow \text{C}_x + 2\text{OH}^+$ . To be effective, the carbon must contain a trace of platinum and the amount of alkali adsorbed increases with the content of platinum.

E. S. HEDGES.

**Heat of adsorption of carbon dioxide on charcoal calculated by means of Póányi's theory of adsorption.** J. K. DIXON (J. Physical Chem., 1930, 34, 870—874).—The heats of adsorption of carbon dioxide calculated by means of Póányi's theory are compared with the experimental values obtained by Magnus and Kälberer (A., 1927, 928). The differences range between 2700 and 3000 g.-cal./g.-mol. for charcoal outgassed at 100° and represent the heat of condensation of the carbon dioxide. The data now considered together with those of Lowry and Olmstead (A., 1928, 12) show that the theory is in satisfactory agreement with experiment.

L. S. THEOBALD.

**Heat of adsorption of (a) oxygen and (b) alcohol vapours on charcoal.** H. K. CAMERON (Trans. Faraday Soc., 1930, 26, 239—248).—The method previously described (McKie, A., 1929, 25) has been modified, and the results obtained for oxygen have been confirmed. Results for *n*-propyl and isoamyl alcohols confirm those of other workers, average values obtained being 16,400 and 17,700 g.-cal./mol., respectively. There is no marked variation in the heat of adsorption down to concentrations of  $10^{-5}$  mol. per g. of charcoal.

J. GRANT.

**Relation between gas content and adsorption of electrolytes by activated charcoal. III. Platinised charcoal as a hydrogen electrode.** B. BRUNS and A. FRUMKIN (*Z. physikal. Chem.*, 1930, **147**, 125—146; cf. A., 1929, 640).—The effect of adding electrolytes to an aqueous suspension of platinised activated carbon in equilibrium with gaseous hydrogen on the amount of gas adsorbed by the carbon has been investigated. When sodium hydroxide is added, the carbon, acting as a hydrogen electrode, acquires an increased negative charge by giving off hydrogen ions, and at the same time sodium ions are adsorbed by being attracted into the electrostatic double layer. The hydrogen liberated is derived partly from ions present as such in the outer part of the double layer and partly from the non-ionised gas adsorbed on the carbon, which consequently adsorbs a further quantity of gas. If the mixture is now made acid, the whole of this additional adsorbed hydrogen is given off again. Addition of a large amount of acid to carbon in equilibrium with pure water and hydrogen results in the evolution of hydrogen, suggesting a reversal of the sign of the charge on the carbon. Platinised carbon in equilibrium with carbon monoxide adsorbs sodium ions from a sodium hydroxide solution, an equivalent amount of carbon dioxide being formed at the same time, probably by some reaction such as  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ .

R. CUTHILL.

**Adsorption on the crystal lattice of cellulose.** J. STRACHAN (*Nature*, 1930, **125**, 671).—A summary of the optical results obtained with iodine adsorbed on cellulose.

L. S. THEOBALD.

**Adsorption at crystal-solution interfaces. IV. Macroscopic ammonium, caesium, and potassium alum crystals grown in the presence of dyes and other foreign materials.** M. E. LASH and W. G. FRANCE (*J. Physical Chem.*, 1930, **34**, 724—736; cf. A., 1928, 1318).—The growth of ammonium alum from cubic seed crystals in the presence and absence of foreign substances has been studied. Only four out of eighteen dyes investigated had any effect on the crystal habit of ammonium alum, whilst thirty-nine organic compounds containing the groups  $\text{NH}_2$ ,  $\text{OH}$ ,  $\text{SO}_3\text{Na}$ , and  $\text{CO}_2\text{H}$  had no effect. The effects of certain dyes on the crystal habit of ammonium, potassium, and caesium alums have been compared and the interfacial angles of a crystal of ammonium alum on which dye had been adsorbed were measured.

L. S. THEOBALD.

**Simultaneous adsorption of salts by colloidal aluminium hydroxide.** B. H. PETERSON (*Proc. Iowa Acad. Sci.*, 1928, **35**, 201—204).—The effect of sulphate on the adsorption of ferricyanide follows the Freundlich adsorption isotherm within the range of complete coagulation, the constants of the equation being changed. The curves obtained by plotting  $\log C$  against  $\log (X/M)$ , where  $C$  is the concentration of potassium ferricyanide remaining,  $X$  the amount adsorbed, and  $M$  the mass of the colloid as  $\text{Al}_2\text{O}_3$ , are fairly representative of the adsorption isotherms of salts by hydrous oxides. If the adsorption values of uncoagulated sol are included the curve exhibits a sharp break. Since the slope of the curve varies

with the sulphate content the effect may depend on the concentration of the ferricyanide.

CHEMICAL ABSTRACTS.

**Measurement of the adsorption of ions by silver iodide by means of potentiometric precipitation titration.** E. LANGE and R. BERGER (*Z. Elektrochem.*, 1930, **36**, 171—179).—The precipitation method has been applied to the measurement of the adsorption by silver iodide of silver and iodine ions. Adsorption in the systems  $\text{AgI}$  solid/ $\text{AgNO}_3$  solution and  $\text{AgI}$  solid/ $\text{NH}_4\text{I}$  solution exhibits a proportionality between the quantity of ions adsorbed and the potential change; if the adsorbed ions are regarded as entirely responsible for the electric charge of the double layer the calculated capacity characteristic of the layer is about 60 microfarads per  $\text{cm}^2$ , and is practically independent of the temperature.

H. F. GILBE.

**Adsorption of water by wood.** L. M. PIDGEON and O. MAASS (*J. Amer. Chem. Soc.*, 1930, **52**, 1053—1069).—The adsorption of water by wood of spruce and pine and by cotton cellulose has been measured by determining the change in weight of samples suspended by a quartz-fibre spiral in an evacuated tube. Adsorption isothermals for temperatures between  $12^\circ$  and  $42^\circ$  and a complete range of pressures have been determined. Heartwood and sapwood give identical values. Weathered wood gives identical values at low vapour pressures, but adsorption is less than that of green wood at higher pressures. Adsorption isosteres (curves of temperature against vapour pressures corresponding with a given amount of adsorption) obey the relation  $\log a/c = B + AT$  when adsorption exceeds 2%.

The S-shaped form of the adsorption curve shows that wood may be classed as a swelling gel. The first part of the adsorption curve is due to surface adsorption, the rest to the filling up of the sub-microscopic spaces. The similarity in the adsorption isothermals of different species of wood at low pressures shows that the fine structure of the cellulose is fundamentally the same. Cotton cellulose, however, differs from wood cellulose, for the adsorption curves do not coincide over any portion.

A hysteresis effect between gain and loss of water is found; the higher value attained by loss of water is considered to be the true equilibrium value.

The results are discussed in relation to modern theories of gels and found to be in accord.

R. K. CALLOW.

**Inner adsorption in crystalline salts.** D. BALAREV (*Kolloidchem. Beih.*, 1930, **30**, 249—296).—The problem studied is the contamination of precipitates by foreign substances present in the reacting solutions, and in accord with the inner adsorption theory the inclusions are due to adsorption at the large specific surface of conglomerate precipitates or of skeletal crystals. The importance of this in gravimetric analysis is indicated. The results of the author's and other work on this subject are gathered together and reviewed from this point of view, the examples studied being the precipitation of barium sulphate, copper sulphide, some phosphates, and the system ammonium chloride-ferric chloride-water.



It is stated that no case is known where barium sulphate is precipitated in a pure form and the most usual impurities are discussed. Some of these are more readily adsorbed than others, and methods of removing the adsorbed material in certain instances are given. The other salt in the presence of which barium sulphate is precipitated has a strong influence on the habit of the crystals. Older theories of the contamination of barium sulphate precipitates, based mainly on the formation of complex salts, are reviewed. The processes of formation and growth of crystals nuclei and subsequent aggregation of the crystallites are discussed in some detail, especially in relation to the relative rates of growth of the faces, edges, and solid angles and the production of mosaic patterns. Precipitates of barium sulphate dried in the air were found to contain water generally in a direct ratio to the amount of adsorbed salt. Experiments on the colouring of barium sulphate precipitates by means of potassium permanganate are described and it appears that all preparations of barium sulphate lose their ability to be stained by permanganate when they are calcined; this is doubtless because in the process of calcination the fine capillaries of the conglomerate precipitate and consequently the adsorbing surface also are destroyed. Experiments on the dehydration and rehydration of freshly-precipitated barium sulphate indicate a bivalent process similar to the dehydration of a gel; this phenomenon cannot be due to the adsorption of water at the outer boundary of the crystallites, but at inner surfaces. This property also is lost by heating the precipitate. The idea of inner adsorption is applied to the precipitation of metallic sulphides, and the well-known co-precipitation of zinc sulphide with copper sulphide in acid solution is explained in these terms. The inclusions in magnesium ammonium phosphate and zinc ammonium phosphate are treated from the point of view of inner adsorption. The system ammonium chloride-ferrous chloride-water has been variously treated as a mixed crystal system and an abnormal mixed crystal system, and is now shown to be a system characterised by inner adsorption.

E. S. HEDGES.

**Transformations effected by adsorption.** R. DUBRISAY, R. ARDITTI, and C. ASTIER (Compt. rend., 1930, 190, 929—931; cf. A., 1922, ii, 428; B., 1928, 36).—To  $x$  c.c. of a 0.05*N*-solution of phosphoric acid were added (100— $x$ ) c.c. of an equivalent solution of potassium hydroxide, ammonia, or calcium hydroxide, and the electrical resistance,  $\rho_n$ , and temperature of complete miscibility with phenol of the resulting solutions were compared with the corresponding values determined after the solutions had been in contact with 5 g. per 100 c.c. of kaolin, kieselguhr, or animal charcoal. In the case of calcium hydroxide animal charcoal had a very markedly, and kaolin a slightly greater, effect than kieselguhr in withdrawing phosphoric acid from solution.

C. A. SILBERRAD.

**Static friction and adsorption.** W. B. HARDY (Kolloid-Z., 1930, 51, 6—9).—The form of the friction-temperature curve for oils is altered by contact with solid surfaces as in the filtration of the oil through

glass beads, and over a wide range the friction may then be independent of temperature. The cause of this phenomenon is the adsorption of polar molecules in the oil by the solid surfaces. Commercial lubricating oils contain about 5% of such active material. When paraffin wax is dissolved in paraffin oil the curve connecting the coefficient of friction (between two steel surfaces) with the temperature shows a break which coincides with the m. p. of the wax. It is evident that above the m. p. the molecules of the wax are adsorbed by the solid surface, but not at lower temperatures, and it is suggested that below the m. p. the wax molecules are associated. Some anomalies are indicated.

E. S. HEDGES.

**Theory of electrical adsorption.** K. C. KAR and A. GANGULI (Z. Physik, 1930, 61, 411—415).—The method previously applied to the chemical adsorption of ions is used for polar adsorption, and an equation is derived connecting the amount of adsorption with the valency, mobility, and mass of the ion. This equation is essentially the same as that derived by Rinde, and indicates that there is no difference between chemical and electrical adsorption. The theoretical work cannot be tested quantitatively owing to lack of data, but it agrees with the observed phenomena qualitatively.

A. J. MEE.

**Complex nature of dielectric absorption and dielectric loss. Influence of ions adsorbed on inner surfaces.** E. J. MURPHY and H. H. LOWRY (J. Physical Chem., 1930, 34, 598—620).—Interstitial conduction, the electrical properties of an interstitial conduction system, dielectric absorption and loss are discussed. The main conclusions are as follows. In most solid dielectrics conduction takes place, not uniformly, but through a system of conducting paths of sub-microscopic dimensions dispersed in the insulating medium. In such systems ions are adsorbed by the interface between the conducting medium and the insulating units, and this has an important effect on the electrical properties of the dielectric. The application of an electric field produces a polarised distribution of the ions adsorbed on the surface of each structural unit. Free ions, adsorbed ions, and neutral molecules may each contribute to the total dielectric absorption and dielectric loss in a manner depending on the type of dielectric, the temperature, and other factors. The characteristics of dielectric absorption and loss are discussed on these lines.

L. S. THEOBALD.

**Adherence of microscopic particles to walls of the same nature.** A. VON BUZAGH (Kolloid-Z., 1930, 51, 105—112).—A method for determining the number of microscopic particles which adhere to a wall of the same material under given conditions is described. There is a close relation between adherence and particle size and this is connected with a definite attractive force, which is counteracted by gravity and by the Brownian movement. Consequently, particles of large size and those of particularly small size fail to adhere to the wall and there is an optimal particle size which, for quartz particles in distilled water, is 3  $\mu$ . The attractive force between the particle and the wall is in this case estimated to be 0.3 dyne/cm.<sup>2</sup>

E. S. HEDGES.

**Adherence of microscopic particles to walls of the same nature.** II. A. VON BUZÁGH (Kolloid-Z., 1930, 51, 230—239; cf. preceding abstract).—A quartz suspension containing particles of diameter about  $12\mu$  was examined with the object of comparing the property of adhesion of the quartz particles to a quartz surface with the electrokinetic potential of the particles. For this purpose the cataphoretic migration velocity of the particles in different electrolytes was measured. In general, no parallelism of this nature was found, although there was a relation between the discharging effect of small concentrations of the multivalent alkaline-earth, aluminium, and thorium ions and the adherence value. In dilute solutions of alkali hydroxides a relation between adherence number and electrokinetic potential appeared as an equilibrium phenomenon, due to chemical reaction of the alkali at the surface of the quartz. Some experiments with the addition of gelatin showed that the adherence of the quartz particles passes through a minimum with increasing concentration of gelatin. On the other hand, the adherence of glass particles rises with the gelatin concentration, whilst the electrokinetic potential falls. Greater amounts of gelatin have a protective action. It is considered that the electrokinetic potential is not the only factor determining the adherence of the particles, but that the thickness of the double layer and the degree of solvation of the particle are also of importance. E. S. HEDGES.

**Contact of solids.** W. STONE (Phil. Mag., 1930, [vii], 9, 610—620).—The phenomena observed on contact have been studied by means of glass beads. Adhesion is due to the presence of entangled water molecules in the surface of the glass and in dried air it practically disappears. Water molecules entangled in the region of contact of two glass beads cannot be removed by ordinary drying, unless the beads are first separated. Otherwise adhesion persists even when the beads are heated until they fuse together. Adhesion may or may not be accompanied by electrical effects. The latter are shown by Jena combustion glass but not by German soft soda glass. There is no adhesion between beads immersed entirely in water. Surfaces of contact are not injured so long as the only forces acting are those of natural adhesion. M. S. BURR.

**Nature of friction.** P. E. SHAW (Phil. Mag., 1930, [vii], 9, 628—639).—Theoretical. Since the parting of solid surfaces gives rise to electrical separation, even when the two materials are identical insulators or metals, it is assumed that solid combination takes place on contact, and charging of both surfaces on separation. In friction the work done is the equivalent of the work performed in total electric separation, plus any work performed in deformation of the surface structure. The laws of friction are deduced by considering a sphere in rolling and sliding contact, respectively, with a plane surface. M. S. BURR.

**Jamin effect in cylindrical tubes.** W. O. SMITH and M. D. CRANE (J. Amer. Chem. Soc., 1930, 52, 1345—1349).—A series of bubbles of air and water in a perfectly clean cylindrical capillary tube

is incapable of supporting a pressure, unless a drop covers the end. If the tube contains a series of constrictions, or is contaminated with grease, a pressure is supported. An equation is given for the greatest pressure which can be sustained.

J. G. A. GRIFFITHS.

**Angles of floating lenses.** C. G. LYONS (J.C.S., 1930, 623—634).—The shapes and angles of liquid lenses floating on the surface of a different liquid have been studied by a photomicrographic method. For lenses of oleic acid on aqueous solutions of various  $p_H$ , of ethylene dibromide, carbon tetrachloride, and nujol (medicinal paraffin) on water, and of water on the preceding three liquids the shape is controlled chiefly by the interfacial tension between the two liquids. For example, in the oleic acid series, as the alkalinity of the underlying solution increases, the lens sinks steadily into it and the interfacial tension decreases, whilst the individual surface tensions of the two liquids (against air) remain practically constant. The increased submergence of the lens as the interfacial tension decreases follows from considerations of the free energy of the system. The values of the angles calculated on the basis of Neumann's triangle do not agree with the observed values, and are modified by forces other than the surface tensions to an extent which is not in general negligible. For very large drops, however, when the lens surfaces approach segments of spheres, Neumann's triangular relation is obeyed. The contact angles at a junction of three liquids have been investigated in the case of lenses of aniline floating in a petroleum-soap solution interface. The theory of emulsification is discussed and it is suggested that emulsification by soap may be determined by the existence of a bimolecular soap leaflet at the oil-water interface. O. J. WALKER.

**Thermodynamic study of surface tension. Affinity and rate of adsorption.** R. DEFAV (Bull. Acad. roy. Belg., 1929, 15, [v], 849—866).—A generalised thermodynamical treatment of problems of surface tension and adsorption. Generalised equations are given for the affinity of adsorption of a surface phase, for the superficial internal energy, free energy, and entropy, and for Gibbs' equation. F. G. TRYHORN.

**Surface tension of solutions. V. Surface tension, surface concentration, and activity.** S. PALITZSCH (Z. physikal. Chem., 1930, 147, 51—68; cf. this vol., 153).—The surface concentrations in the system urethane-sodium chloride-water calculated by means of Gibbs' adsorption equation are in good agreement with Schofield and Rideal's equation (A., 1925, ii, 960)  $FA/RT = BF/RT + x$ , where  $F$  is the difference between the surface tension of the solution and that of the pure solvent,  $A$  is the area occupied on the surface by 1 g.-mol. of solute,  $B$  and  $x$  are constants, and  $R$  and  $T$  have their usual significance. If  $FA/RT$ , which may be shown to represent an osmotic coefficient, is graphed against  $F$ , the same straight line is obtained independent of the salt concentration, except at high values of  $F$ . The experimental data cannot, however, be reconciled with the view, open to serious

objection in any case, that the surface of a solution is comparable with a thin film of oil. It is suggested that the force measured in the usual type of surface tension determination is as effective within the body of the liquid as on its surface. In support of this view it is pointed out that the surface tension is of the same order of magnitude as the internal pressure provided that the basis of comparison is the same, *e.g.*, if both quantities are referred to unit area. There is, however, a pressure which is essentially distinct from the surface tension as normally measured and is due to forces acting from one phase to the other, mainly at right angles to the interface. It is this quantity, for which the term "surface pressure" is proposed, which is the "surface tension" of Gibbs' equation.

R. CUT HILL.

**Unimolecular films.** J. PERRIN (Kolloid-Z., 1930, 51, 1—6).—The optical properties of thin films of sodium and potassium oleate are described. By a photometric reflexion method the thickness of the films has been obtained, using the formula  $J = J_M \cdot \sin^2(2\pi h/\lambda)$ , where  $J_M$  is the maximal intensity of reflected light, of wave-length  $\lambda$ , and  $J$  is the intensity for the thickness  $h$ . The molecules of the thin films are oriented and have the optical properties of crystalline liquids.

E. S. HEDGES.

**Spatial asymmetry of polar molecules and the electrical double layer.** B. KAMIENSKI (Z. physikal. Chem., 1930, 147, 288—292).—The formation of an electrical double layer at the boundary of two phases, which have different dielectric constants and one of which contains polar molecules, is connected with the spatial asymmetry of the polar molecule. If the spatial symmetry of the molecule coincides with the electrical symmetry the formation of a double layer is not to be expected. This view is supported by electro-osmotic data. O. J. WALKER.

**Dependence of boundary surface activity and orientation of polar molecules on temperature and on the nature of the surface of separation.**

**VI. Boundary surface properties of aromatic amines and their salts.** P. REHBINDER and A. TAUBMANN (Z. physikal. Chem., 1930, 147, 188—205; cf. A., 1926, 674; 1927, 930, 1136).—By a method previously described the surface tension of aqueous solutions of *p*-toluidine has been determined at different temperatures and concentrations and the temperature coefficient, the total surface energy, the boundary surface activity, and the adsorption have thence been calculated. *p*-Toluidine behaves similarly to other strongly active aromatic substances. For certain ranges of temperature and concentration the temperature coefficient of surface tension is positive. The molecular constants of *p*-toluidine have been obtained from the limiting adsorption. The axial length of the oriented molecule is 6.9 Å. at the surface of separation water/air, and the minimum surface area occupied by the molecule is approximately 26 Å.<sup>2</sup> The latter quantity is characteristic of the polar group  $-C_6H_4 \cdot NH_2$ . Comparison with aniline indicates that the group  $CH_3$  represents an increase in axial length of 1.5 Å., the value obtained by X-ray methods being 1.2—1.3 Å. The molecular constants depend on the nature of the surface of

separation. Measurements of the surface activity for different  $p_H$  values indicate that the molecules only, and not the ions, of aromatic bases are active. The influence of the active aliphatic acid, *n*-valeric acid, on the surface activity of *p*-toluidine has been investigated. The activity of an equimolecular mixture or "salt" solution is slightly greater than that of *p*-toluidine alone at higher concentrations, but appreciably greater than that of the acid, *i.e.*, the more feebly active acid is driven from the surface, but helps to increase the concentration of the *p*-toluidine in the surface layer. At lower concentrations the relationships are reversed.

M. S. BURR.

**Surface forces and chemical equilibrium.** H. FREUNDLICH (J.C.S., 1930, 164—179).—The Liversidge lecture delivered on Dec. 12th, 1929. Previously recorded experiments are discussed in support of Thomson's view that the displacement of chemical equilibrium in a surface takes place in a direction favouring the formation of those substances which lower the surface tension and are therefore adsorbed positively. Such substances are said to exert "capillary action." Thus, the amount of anions adsorbed from certain salt solutions by very pure charcoal runs parallel with the adsorbability of the acids from a pure solution (cf. Bartell and Miller, A., 1923, ii, 464). Adsorption here causes a hydrolysis, the production of more strongly adsorbed substances (acids) being favoured. The presence of gases in the charcoal markedly modifies the reaction, particularly in the case of strong electrolytes (Burstein and Frumkin, A., 1929, 640). Again, solutions of indicators near the turning point change colour when shaken with an indifferent fluid (gas or liquid), the change becoming deeper the greater is the emulsification of the fluid and being reversed when the phases separate (Deutsch, A., 1928, 1183). Probably the formation of undissociated or less dissociated molecules is favoured at the interface (cf., however, Thiel, A., 1929, 782). Other instances are cited. Finally, the velocities of the reactions: (i)  $CH_3Br \cdot CH_3 \cdot NH_2 + NaOH = (CH_3)_2NH + NaBr + H_2O$  and (ii)  $(CH_3)_2NH + HBr = CH_3Br \cdot CH_3 \cdot NH_2$  have been measured in solutions containing animal charcoal. Bromoethylamine, which has a stronger capillary activity than the imine, would be expected to be more stable on the surface of the charcoal than in homogeneous solution, so that charcoal should retard (i) and accelerate (ii). Experiment confirms this; the reactants are entirely in the adsorbing layer. The biological significance of interface activity is briefly referred to.

S. K. TWEEDY.

**New method of examination of surface films.** J. H. SCHULMAN (Proc. Camb. Phil. Soc., 1930, 26, 273—277).—A method for the examination of surface films depending on the determination of the interphase potential is described (cf. Frumkin, A., 1925, ii, 873). It consists essentially in measuring the *P.D.* between a platinum wire, on which a little polonium has been electro-deposited, situated above the surface of a glass Langmuir trough and a calomel electrode in contact with the liquid in the trough. The air-liquid *P.D.* for a clean surface and for one covered with the film under investigation are deter-

mined and the difference ( $\Delta V$ ) is plotted against the area in  $\text{\AA}^2$  per molecule. The method is exemplified by data for palmitic and myristic acids. Further, if the number of molecules each contributing a vertical component of electric moment  $\mu$  is  $n$  per  $\text{cm}^2$ , Helmholtz's equation gives the relation  $\Delta V = \frac{1}{2}n\mu$ , whence  $\mu$  can be plotted against the mean molecular area. This in the case of myristic acid leads to the conclusion that until the solid condensed phase is reached (when there appears to be mutual action between the head groups) the change in  $\mu$  on compression is caused merely by change in the tilt of the molecules. C. A. SILBERRAD.

**Rate of a reaction at the interface between two solutions.** G. M. SCHWAB and H. KNOELL (Z. physikal. Chem., 1930, 147, 38—50; cf. Jablezynski, Wiecekowsky, and Klein, A., 1925, ii, 410).—The rate of reaction at the interface between an aqueous solution of sodium thiosulphate and a solution of iodine in carbon tetrachloride at  $20^\circ$  is given by the equation  $dx/dt = k[I_2]$ . When the iodine is present in excess,  $k$  is proportional to  $[S_2O_3^{2-}]$ , but if the thiosulphate is present in excess the value of  $dk/d[S_2O_3^{2-}]$  is constant only at very small thiosulphate concentrations and decreases to zero as the concentration increases, the rate of reaction being independent of  $[S_2O_3^{2-}]$  when this exceeds about  $0.2N$ . This is interpreted as meaning that the measured rate of reaction when the thiosulphate is in excess represents either the rate of actual reaction at the interface or the rate of diffusion of iodine to the interface according as the excess is small or large, respectively. The temperature coefficient of the velocity coefficient is only about 1.2. R. CUTHILL.

**Influence of reaction on the oxidation of amino-acids by animal charcoal.** M. GRADWOHL (Biochem. Z., 1930, 219, 136—144).—Considerable increase in the oxidation of amino-acids by animal charcoal was obtained with increasing alkalinity. The adsorption of glycine by animal charcoal was, however, almost independent of the reaction and its oxidation at  $p_H$  8.23—8.62 was decreased by 45—50% with  $0.0001N$ -, by about 70% with  $0.001N$ -, and completely by  $0.002N$ -hydrogen cyanide. The oxygen utilisation of an animal charcoal-glycine suspension was considerably greater in alkaline than in acid solution, but the amount of amino-acid disappearing as determined by "formol" titration was practically the same. The oxidation quotient of the reaction as determined by Warburg's method was 0.81 in acid and 2.27 in alkaline solution.

P. W. CLUTTERBUCK.

**Kinetics of step-reactions and their relation to the mass law of gel- and surface-dissociation.** E. VALKÓ (Kolloid-Z., 1930, 51, 130—134).—Theoretical. E. S. HEDGES.

**Effect of velocity on diffusion rates.** A. E. MURRAY (Trans. Nova Scotian Inst. Sci., 1930, 17, 168—171).—When salt solutions are enclosed in colloidal thimbles and allowed to diffuse into distilled water which is either circulated or constantly replaced, a small osmotic pressure is developed, and this is usually complete in 60—90 min. Experiments with solutions of sodium chloride and disodium

phosphate show that the osmotic effect is influenced by the velocity of the diffusate, but no simple relation is indicated. J. W. SMITH.

**Collodion membranes. VI. Sieve effect of membranes on homodisperse dissolved substances.** E. MANEGOLD and R. HOFMANN (Kolloid-Z., 1930, 51, 220—230; cf. this vol., 539).—The relations between filtration and dialysis are discussed and the hindering of the diffusion of molecularly-dissolved substances through the membrane can be expressed by a "sieve constant." Methods of determining this sieve constant are discussed. Measurements made with  $N$ -hydrochloric acid and with  $0.5M$ -sucrose show that so long as the radius of the capillaries of the diaphragm is greater than  $10$ — $12 \mu$  the free diffusion constants of these solutes can be calculated from their dialysis constants. With decreasing size of pores, the diffusion constants fall rapidly and continuously and reach one half their original value at a capillary radius of about  $5 \mu$ .

E. S. HEDGES.

**Membrane and osmosis. V.** F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1—9).—A discussion of the currents of diffusion set up when binary liquids are separated by a permeable membrane. F. G. TRYHORN.

**Membrane and osmosis. VI.** F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 119—127).—The properties of complex membranes, formed by uniting two or more homogeneous membranes of different properties, are discussed with the view of deducing the properties of naturally occurring heterogeneous membranes.

M. S. BURR.

**Structure in very permeable collodion gel films and its significance in filtration problems.** H. J. ELFORD (Proc. Roy. Soc., 1930, B, 106, 216—228).—Collodion films for ultrafiltration may be prepared either from ether-alcohol mixtures, in which case the gel is allowed just to set by evaporation of the solvent and is then washed with water, or from acetic acid solution, in which case the collodion when immersed in water is not in the gel state. The former (ultragel films) have permeability from  $100 \mu$  downwards, the latter (microgel films) from  $1$ — $5 \mu$  downwards, and they show other differences. Films of the two types have been examined with the aid of the slit ultramicroscope. Acetic acid collodion films vary with increasing concentration of collodion in solution from an irregular structure through the microgel structure to a granular ultragel. The thicker is the film the greater is the microgel development; the slower is the formation the more permeable is the film. The same transitions can be produced by varying the time of evaporation of ether-alcohol collodion films, but there is a sharp transition from microgel to ultragel with the "setting" of the film. The structure of ultragel films was further examined by ultra-violet light microscopy. Evidence of structure was obtained, but there is far greater uniformity than with acetic acid collodion films. C. IRWIN.

**Abnormal osmosis at non-swelling membranes. II.** K. SÖLLNER (Z. Elektrochem., 1930, 36, 234—241).—Theoretical. The examination of

systems consisting of two solutions of an electrolyte differing in concentration and communicating with each other through two membranes the dynamic potentials at which are unequal (this vol., 288) has been extended to include cases in which diffusion potentials are present. If the more mobile ion is the one which constitutes the mobile part of the double layer in the pores of the membrane, abnormal positive osmosis, but not abnormal negative osmosis, will occur at the membrane. If, on the other hand, the mobile part of the double layer consists of the less mobile ion, either type of abnormal osmosis may take place. When the two ions have the same mobility, the only possible abnormal osmosis at a membrane, either positive or negative, separating two solutions of different concentrations is of the positive type. Abnormal osmosis at a single pore even under the influence of the pore wall is possible only in the unlikely event of the material of the membrane being a sufficiently good electrolytic conductor. There is no possibility of a current circulating in a single pore apart from the action of the membrane, and no motion of liquid can occur within a pore without the intervention of some external force.

R. CUTHILL.

**Donnan's membrane equilibrium.** K. SHIKI (Kyōtō J. Med., 1929, 26, 57—67).—In the solution prepared by the addition of egg-white to 0.1—3.0*N*-hydrochloric acid or 0.01—1.77*N*-potassium hydroxide the time required for the attainment of equilibrium of the acid or alkali on both sides of the collodion membrane is much greater than in absence of egg-white, the difference increasing with increase in concentration of the electrolyte. The membrane potential also varies slightly with the concentration of the electrolyte.

CHEMICAL ABSTRACTS.

**Rhythmic evaporation rings of orange II and fast-red B.** E. C. H. DAVIES, K. TAYLOR, and E. W. RIBLETT (J. Physical Chem., 1930, 34, 842—854).—The conditions controlling the formation and the number of evaporation rings have been investigated. Pure orange II solutions give no rhythmic rings when the containing vessels are chemically clean. Rings are not due to air or vapours adsorbed by the containers from the laboratory. A surface skin of a foreign substance may give rise to evaporation rings when the film is not too volatile and can aid in promoting the adhesion of the rings to the surface of the container. A thin film of abietic acid on the surface of the evaporation vessel gives rise consistently to the formation of rhythmic rings in the case of orange II. Under such conditions the number of rings formed from a given volume of the dye solution increases with an increase in concentration of the dye, with a rise in the temperature of evaporation, and with a decrease in the radius of curvature of the evaporation vessel. With fast-red B no foundation film is necessary; the number of rings decreases slightly at higher temperatures, but the effects of concentration and curvature are the same as in the case of orange II. *n*-Butyric acid lowers the surface tension of fast-red B and produces an increase in the number of evaporation rings.

L. S. THEOBALD.

**Ebullioscopic determination of the molecular equilibria of pyrocatechol in solutions of potassium and sodium chlorides.** F. BOURION and (Mlle.) O. HUN (Compt. rend., 1930, 190, 871—873).—Equilibria between simple and triple or quadruple molecules of pyrocatechol are said to exist in solutions of sodium and potassium chloride (cf. this vol., 409). The association of pyrocatechol, which is greater than that of resorcinol (*loc. cit.*), increases with change of solvent in the order water, potassium chloride, sodium chloride, and increases with the salt concentration in both cases.

J. GRANT.

**Thermal method of measuring the vapour pressure of an aqueous solution.** A. V. HILL (Proc. Roy. Soc., 1930, A, 127, 9—19).—The principle of the method is that of a differential wet-bulb thermometer of high sensitivity. The apparatus consists of a thermopile which can be immersed in a glass chamber, the whole being submerged in a thermostat. On one face, *A*, of the thermopile is laid a small strip of filter-paper which has been dipped in solution *a*; on the other face, *B*, a similar strip dipped in solution *b*. The chamber is kept moist by covering its walls with a large strip of filter-paper which has been dipped in any solution *c*. Let  $p_a$ ,  $p_b$ , and  $p_c$  be the vapour pressures of the three solutions. As the solution *c* is in excess, the water-vapour pressure in the chamber will approximate to  $p_c$ , except in the neighbourhood of the faces *A* and *B*. The rate of condensation of moisture on these two faces is different, and this different rate of condensation tends to raise the temperature of *A* and *B* an unequal amount above that of the surroundings. It is shown that the final difference of temperature between *A* and *B* is  $k(p_b - p_a)$ , and is independent of the vapour pressure of the solution *c*. Thus the *E.M.F.* developed in the thermopile is  $K(p_b - p_a)$ , where *K* is a constant which can be determined for any given instrument with solutions of known vapour pressure, but depends on temperature and pressure. With this apparatus a reading can be obtained in 30—45 min., and the average error of a single observation is of the order of 1.5% of the difference read. Possible errors in the method are discussed.

L. L. BIRCHUMSHAW.

**Viscosity of solutions of cobalt chloride containing hydrochloric acid.** G. MATSUO, S. OGURI, S. TAKEDA, and B. URAKAWA (Bull. Waseda Coll. Eng., 1929, 9, 1—6).—The difference between the viscosity of the solution and that of a corresponding solution of hydrochloric acid, when plotted against the concentration of the hydrochloric acid solution, shows a minimum at 3.1*N*-acid and a maximum at 6*N*-acid. This suggests that the cobalt is present as  $[\text{Co}(\text{H}_2\text{O})]^{++}$  or  $[\text{CoCl}_4]^{--}$  ions according as the acid concentration is low or high; the maximum difference in viscosity occurs when the ions are present in equimolecular quantities.

CHEMICAL ABSTRACTS.

**Spectral properties of a benzoate as a function of the concentration of neutral salts.** F. VLÈS and N. KYVELOS (Compt. rend., 1930, 190, 932—934; cf. A., 1928, 14, 36).—The methods previously described are now shown to apply to an ordinary organic substance, not an indicator, such as sodium benzoate, dissolved in fixed amounts in solutions of

potassium chloride of various concentrations. The absorption was determined for  $\lambda_1=256$  and  $\lambda_2=273 \mu\mu$ , special precautions being taken to avoid the photolytic action of the ultra-violet light. The curve connecting the variation of the absorption ratio with the concentration of the potassium chloride shows five sinuities which are interpreted as indicating five different states, of which four are considered to be the dissociated and undissociated benzoate, and the complexes  $\text{NaOBz}_2\cdot 2\text{KCl}$  and  $\text{NaOBz}_2\cdot 3\text{KCl}$ .

C. A. SILBERRAD.

**Refraction of electrolytes.** XIV. K. FAJANS and H. KOHNER (Z. physikal. Chem., 1930, 147, 241—262; cf. this vol., 410).—A comparison of the authors' method of determining the refraction of electrolytes with the earlier methods of Chéneveau and of Heydweiller. The latter's values of the absolute refraction show good agreement with those of the authors, but are not considered to give sufficiently accurately the variation of the refraction with the concentration. The authors' improved weight-dilution method is indeed not trustworthy for dilute solutions below about 1 or 2*N*. Taking barium chlorate as an example, it is shown that the determination of the dependence of the refraction on the concentration is affected mainly by the accuracy of measurement of the relative concentrations of the various solutions.

O. J. WALKER.

**Refraction of electrolytes.** A. HANTZSCH and F. DÜRIGEN (Z. physikal. Chem., 1930, 147, 263—265).—The accuracy of the refraction data obtained by Fajans and Kohner (cf. preceding abstract) is recognised. The recently published conclusions (A., 1928, 834) must therefore be modified.

O. J. WALKER.

**Swelling pressure and osmotic pressure.** H. HULSHOF (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 165—175).—Theoretical. The forces at the two limiting surfaces between a liquid and solid in contact, and the thermodynamic potential of a limiting surface, are discussed. The nature of swelling pressure is considered and the conclusion is reached that osmotic pressure is the same as swelling pressure. Osmotically active particles are swelling centres in the solvent medium. For proof of this the conception of the anisotropy of the pressure, as a result of molecular attraction, is necessary. The relationship of swelling pressure to the properties of Perrin's particles is discussed, and also the effect of swelling pressure on diffusion.

M. S. BURR.

**Argillaceous suspensions.** R. DUBRISAY and J. J. TRILLAT (Rev. gén. Colloid., 1930, 8, 1—9).—Suspensions of kaolin in pure water, dilute acids, or in alkali solutions more concentrated than *N*/30 clarify rapidly and completely when kept. In alkaline solutions of concentration less than *N*/30 these suspensions do not settle completely and both microscopic and ultramicroscopic particles remain in the solution. Analysis shows that some of the alkali is fixed by the suspended particles. In alkaline solutions the volume of the deposit decreases at first with rising concentration of the alkali, passes through a minimum, and finally increases. This difference is caused mainly by the method of packing of particles

of the precipitate, for a constant volume is obtained after centrifuging. It is suggested that either the ultramicroscopic particles in suspension in the feebly alkaline solutions can exert an osmotic pressure which tends to compress the deposit, or that the particles of small dimensions arrange themselves in less space than the larger particles. The latter supposition is supported by X-ray spectrographic examination, which also shows that the fixation of alkali is not due to chemical combination, but to surface adsorption.

E. S. HEDGES.

**Influence of electrolytes on the dispersion of clays.** F. ALLAM (Chem. Erde, 1930, 5, 276—318).—The results are given of a number of experiments on the permeability and flocculation of a clay from Silesia with various salt solutions.

L. J. SPENCER.

**Sedimentry.** A. V. BLOM (Kolloid-Z., 1930, 51, 186—190).—In a discussion on sedimentation curves and the final volume of the sediment it is shown that these may be of use in characterising powders.

E. S. HEDGES.

**Preparation of negative colloidal ferric oxide by hydrolysis of Prussian-blue.** F. HAZEL and C. H. SORUM (J. Amer. Chem. Soc., 1930, 52, 1337—1340).—Negative colloidal ferric oxide is prepared by adding dropwise, during 5 hrs., 1 litre of a suspension of Prussian-blue (2 g.) to boiling water (5 litres). Hydrolysis should start after 10 drops have been added. The sol is kept for 14 hrs. and is then dialysed at 80—90° for 24 hrs. The diameter of the particles is 89  $\mu\mu$ . Flocculation values are given for the chlorides of sodium, barium, aluminium, and thallium. The last, in high concentrations, gives a non-flocculating zone where the charge on the sol is positive.

J. G. A. GRIFFITHS.

**Formation and particle structure of multi-coloured silver sols.** II. E. WIEGEL (Kolloid-Z., 1930, 51, 112—123; cf. A., 1929, 643).—When a silver hydrosol is added drop by drop to hydrogen peroxide the first small amounts of silver dissolve and the saturation point is indicated by a colour change which occurs when a slight excess of colloidal silver has been added. Multi-coloured silver sols can be obtained by the addition of nuclear dextrin silver sols to hydrogen peroxide and the differently coloured sols are characterised by different particle size. Such sols are formed by the primary dissolution of some of the particles in the form of silver peroxide. When the catalytic decomposition of the hydrogen peroxide starts, this dissolved silver is precipitated on existing particles of silver in the sol which act as nuclei. The size to which the particles grow depends on the relation of the number of nuclei to the concentration of dissolved silver and consequently numerous sols of different particle size and colour may be obtained. If a very small quantity of the nuclear sol is added, the particles grow so that they can be seen in the ordinary microscope. By counting the number of particles in the ultra-microscope and also by measurement of sedimentation velocity it was found that with increasing particle size the colour of the sols in transmitted light changes in the order yellow, red, violet, blue, greyish-green, grey, and by reflected



light, in the order blue, green, olive-yellow, brownish-red. The submicroscopic silver crystallites are often disc-shaped.  
E. S. HEDGES.

**Colloidal solutions of naphthalene.** N. VON WEIMARN (Kolloid-Z., 1930, 51, 100—104).—Colloidal solutions of naphthalene obtained formerly were stable for only 15 min., but the stability can be increased by forming the colloid in a sugar solution at low temperatures. The method consists in adding rapidly 0.5 c.c. of alcoholic naphthalene solution (about 1%) to 19.5 c.c. of 69% sucrose solution, shaking well, and cooling at  $-80^{\circ}$ . The mass sets to a glass which is stable for at least 24 hrs. More highly disperse and more stable systems are obtained by heating the mixture in boiling water until the naphthalene dissolves and then suddenly chilling to  $-80^{\circ}$ . When warmed, such glasses liquefy to a naphthalene sol which is stable at the ordinary temperature for several hours. By similar methods colloidal solutions of papaverine, camphor, salol, and benzophenone have been made. Sols of anthracene, phenanthrene, and anthraquinone have been made by pouring 1 c.c. of a dilute alcoholic solution into a large volume of water at the ordinary temperature. The anthracene sols are stable for some months. Anthracene and phenanthrene form unidimensional colloid systems, the particles being lamellæ of colloid thickness, and anthraquinone forms a bidimensional system of needles of colloid thickness.

E. S. HEDGES.

**Effect of multivalent hydroxy-compounds in the synthesis of hydrosols. I. Multivalent alcohols: glycerol and mannitol.** A. DUMANSKI and V. M. SEMONOVA (Kolloid-Z., 1930, 51, 210—220).—The influence of glycerol and of mannitol on the formation of colloidal ferric hydroxide by the action of sodium hydroxide or of ammonia on ferric chloride has been studied and the results are treated diagrammatically as a three-component phase-rule system and three-dimensional models have been constructed. Electronegative sols are formed under the peptising influence of these substances and the region of stability of the sols for a constant amount of alkali is greater in the mannitol system than in the glycerol system. For a given concentration of mannitol the region of stability is greater when sodium hydroxide is the reagent than when ammonia is used. The concentration of the original solutions has a great influence, the colloid stability region increasing with concentration. The degree of dispersion of the sol is highest when either small or very large amounts of alkali are present and may approximate to molecular dispersity.

E. S. HEDGES.

**Formation of colloids by light. I. Copper.** S. HORIBA and S. ISHII (J. Phys. Chem., Japan, 1929, 2, 118—131).—Colloidal cuprous hydroxide, formed by boiling cuprous chloride or bromide with aqueous gelatin, is photosensitive in the presence of acid.  
CHEMICAL ABSTRACTS.

**Effect of light on some colloids.** S. HORIBA and H. BABA (J. Phys. Chem., Japan, 1929, 3, 1—15).—On illumination, arsenious sulphide and Congo-

red, but not ferric or chromic hydroxide, exhibit increased osmotic pressure. CHEMICAL ABSTRACTS.

**Variation of physico-chemical properties in the region between colloiddally and molecularly disperse systems. III.** WO. OSTWALD and A. QUAST (Kolloid-Z., 1930, 51, 273—282; cf. A., 1929, 760, 878).—Previous measurements of the diffusion coefficients of a number of dyes are recalculated, using a new formula.  
E. S. HEDGES.

**Condition of sparingly soluble substances when formed in presence of a gel; silver bromide, silver iodide, and silver cyanide in gelatin.** A. C. CHATTERJEE and J. M. DHAR (J. Indian Chem. Soc., 1930, 7, 177—190; cf. A., 1928, 708).—The electrical conductivities of silver bromide, iodide, and cyanide, prepared from dilute aqueous solutions (0.00125—0.01*N*) in presence of 0.5% of gelatin, have been measured at  $20^{\circ}$ . The results indicate that the salts when prepared in this way are practically non-ionised, and probably exist in the colloidal state. Similar conclusions follow from the *E.M.F.* of cells of the type  $\text{Ag}|\text{0.1N-AgNO}_3||\text{N-KNO}_3|\text{silver salt in gelatin}|\text{Ag}$ . The statement by Bolam (Trans. Faraday Soc., 1924, 24, 461) that lead iodide in agar remains in a supersaturated condition is criticised, and it is suggested that this salt is not completely ionised in such circumstances.

J. R. I. HEPBURN.

**Electric moment of the colloid particle.** J. ERRERA (Kolloid-Z., 1930, 51, 104—105).—The electric moment of the rod-like particles of vanadium pentoxide in an aged sol is calculated to be  $415 \times 10^{-18}$ .

E. S. HEDGES.

**Influence of hydrated colloids on depression of f. p.** H. R. KRUYT and K. C. WINKLER (Z. anorg. Chem., 1930, 188, 200—204).—Gortner's observation, that the depression of the f. p. of solutions of sucrose is increased in the presence of hydrated colloids even after the depression due to the latter has been taken into account, has been confirmed by experiments in which starch was used as the hydrated colloid. When the dispersed starch is dehydrated by the addition of tannic acid the Gortner effect is not observed. The hydration of starch calculated from the f.-p. results is 0.8 : 1 by weight. The difference between this figure and the much higher one deduced from the relative viscosity according to Einstein's equation is attributed to the fact that in the f.-p. experiments only the fully oriented water molecules forming the inner hydration layer are effective, whilst the viscosity is also influenced by the more extensive diffuse layer.  
F. L. USHER.

**Ultra-violet Tyndall cone of pure water.** H. SCHADE and H. LOHFERT (Kolloid-Z., 1930, 51, 65—71).—The purest water, when sufficiently strongly illuminated by the Tyndall cone, does not appear to be optically void and the path of the light is recorded even more clearly by a photographic film. The effect can be intensified by using a source of ultra-violet light and condensing it through a quartz lens, when the Tyndall cone produced in the purest water can readily be photographed. There seems to be no doubt that the phenomenon is due to the scattering of light by the water itself and not from impurities

derived from the containing vessel. By repeated distillation of the water a constant end-value for the intensity of the light-cone is reached. The intensity of the scattered light was measured by means of a photo-electric cell and was found to increase as the temperature is lowered. The rate of change is greater below 20° than over the range 20—90°, and the temperature change is reversible. The addition of minute quantities of pure electrolytes diminishes the amount of light scattered. The curve connecting the intensity of scattered ultra-violet light with temperature agrees closely with the viscosity-temperature curve. An explanation based on the polymerisation of a fraction of the water molecules to large aggregates is suggested. E. S. HEDGES.

**Scattering of light in sols and gels.** F. G. DONNAN and K. KRISHNAMURTI (Coll. Symp. Ann., 1930, 7, 1—16).—For 1% agar gels the light scattering is more marked than for the sol at the same temperature. The effects of change of concentration and temperature are discussed. CHEMICAL ABSTRACTS.

**Viscosity of dilute lyophilic dispersions.** E. O. KRAEMER and G. R. SEARS (J. Rheology, 1930, 1, 231—239).—The viscosity of solutions of cellulose nitrate increases linearly with the concentration when the increment is less than 6—8%. These sols show little or no deviation from Poiseuille's law. The results are discussed in reference to a modified form of Einstein's equation,  $\eta/\eta_0 = 1 + 2.5cV$ , where  $c$  is the concentration (g./c.c.) and  $V$  is the "equivalent specific hydrodynamic volume." Values of  $V$  are recorded for two cellulose nitrates dispersed in acetone, ethyl acetate, ethylene glycol monoethyl ether and its acetate. Whilst  $V$  is somewhat variable, the ratio of the values obtained for the two cellulose nitrates is nearly constant over the whole range of solvents. T. H. MORTON.

**Viscosity of emulsions.** A. W. PORTER (Trans. Faraday Soc., 1930, 26, 233—235).—A more complete mathematical analysis of the results of Sibree (this vol., 290). Two possible equations are deduced, and it is shown that a simple power law, fractional or otherwise, is inadequate to represent the variation of the viscosity for all possible rates of shear (cf. Porter and Rao, A., 1927, 826). J. GRANT.

**Systems soaps-cresol-water.** E. ANGELESCO and D. M. POPESCU (Kolloid-Z., 1930, 51, 247—257).—Measurements of the viscosity and surface tension of mixtures of soap solutions of various concentrations with different amounts of *o*-cresol have been made, using the Ostwald viscosimeter and Traube's stalagmometer, and the results are tabulated for aqueous solutions of the sodium, potassium, lithium, and ammonium salts of stearic, oleic, and palmitic acids, and also for sodium hydroxide. The solubilities of *o*-cresol in sodium stearate, oleate, palmitate, and hydroxide have also been measured for different concentrations of the soaps. Conclusions are reserved for a future paper. E. S. HEDGES.

**Effect of non-electrolytes on the precipitation of thorium hydroxide from its salt solution in presence of alkali.** A. M. PATEL and B. N. DESAI (J. Indian Chem. Soc., 1930, 7, 161—166).—The

inhibition by sucrose and by glycerol of the precipitation of thorium hydroxide, prepared from sodium hydroxide and thorium nitrate at low concentrations (0.0003—0.0018 molal), has been studied. The limiting concentrations of sucrose or of glycerol required to prevent precipitation, using excess of sodium hydroxide, were found to increase with the initial concentration of the metal ion, and to decrease either with increase in dilution or with increase in the concentration of sodium hydroxide.

J. R. I. HEPBURN.

**Coagulation of mastic sol.** R. ISHIWARA (Hokkaido J. Med., 1929, 7, 284—286).—The threshold values of precipitation with potassium sulphate, ferricyanide, or ferrocyanide, or silver nitrate, but not with potassium chloride, vary with the concentration of colloid. CHEMICAL ABSTRACTS.

**Mechanism of coagulation of colloids by electrolytes.** Y. KAWAMURA (Hokkaido J. Med., 1929, 7, 287—296).—The threshold values for the coagulation of ethyl-alcoholic sols of Prussian-blue and of copper ferrocyanide are decreased in presence of potassium, magnesium, or hydrogen chloride, but not in presence of silver nitrate or ferric chloride, when the sol is diluted with ethyl alcohol. The former electrolytes are assumed to alter the medium, and the latter only to discharge the colloids. CHEMICAL ABSTRACTS.

**So-called "slow" coagulation.** H. R. KRUXT [with E. F. DE HAAN] (Kolloid-Z., 1930, 51, 61—65).—The process of coagulation is discussed on the view that the electrical charges are not evenly distributed over the total surface of the particle, but are confined to certain localities. In flocculation, the particles adhere at places which are unprotected by the charge. Protected places then form on the outside of the growing particles, so that the probability of adhesion gradually lessens throughout the course of the coagulation. Experiments on the slow coagulation of sols of selenium and of silver iodide by very dilute barium chloride solutions show that the cataphoretic migration velocity steadily increases during the process in accordance with the decrease in coagulation rate. Such an increase in migration velocity was not observed in the exceedingly slow coagulation of silver iodide sols in the absence of added electrolytes.

E. S. HEDGES.

**Flocculation produced on mixing two colloidal solutions of the same nature, but having oppositely charged particles.** A. BOUTARIO and (Mlle.) G. PERREAU (Compt. rend., 1930, 190, 868—870).—The limits of the zone of flocculation which are observed when a positive ferric hydroxide sol is mixed with a similar sol having the same concentration of  $\text{Fe}_2\text{O}_3$ , but rendered negative by the addition of sodium phosphate or citrate solution, are determined by the concentration of phosphate (or citrate) in the final mixture. Two zones of flocculation were obtained when sodium phosphate solution alone was added in increasing quantities to the positive sol.

J. GRANT.

**Effect of temperature on the stability of copper colloidal solutions.** B. R. DEACON (J. Physical Chem., 1930, 34, 1105—1112; cf. A., 1928, 476).—

Previous results have been confirmed by a more extended investigation. Kruyt's conception of the mechanism of coagulation is supported. For each copper colloid there is a certain temperature below which it remains stable for an indefinite time.

L. S. THEOBALD.

**Influence of hydrolysis temperature on some properties of colloidal ferric oxide. I. Particle size.** G. H. AYRES and C. H. SORUM (*J. Physical Chem.*, 1930, **34**, 875—884).—Ferric oxide sols have been prepared by the hydrolysis of ferric chloride solutions in an autoclave at temperatures between 100° and 145°. The particle size, determined by direct counts, varied between 52 and 76  $\mu\mu$ , with a mean size of 60  $\mu\mu$ , and is independent of the temperature of preparation and of concentration (0.5—4*M*-ferric chloride).

L. S. THEOBALD.

**Influence of physical state of a soap solution on the rate of saponification of triglycerides and the differing degrees of emulsification for neighbouring triglycerides.** J. W. McBAIN and Y. KAWAKAMI (*J. Physical Chem.*, 1930, **34**, 580—592).—A study of the rate of saponification of an homologous series of triglycerides shows that neighbouring members of a series exhibit different degrees of emulsification under the same conditions, thus revealing a highly specific effect of the length of long hydrocarbon chains. The emulsifying power of ordinary soap solutions on addition of sodium chloride passes through a maximum, as does the viscosity. The rate of saponification of coconut oil at 90° in the presence of fixed amounts of sodium palmitate and hydroxide and increasing amounts of sodium chloride has been measured and it is shown that the best emulsifying agent is neat soap in the presence of the maximum amount of sodium chloride which can be added without graining the soap.

L. S. THEOBALD.

**Influence of ageing on inorganic hydrophile colloids, cells, and colloids in the animal body.** N. R. DHAR (*J. Physical Chem.*, 1930, **34**, 549—553).—Theoretical.

L. S. THEOBALD.

**Structure of gelatin gels from studies of diffusion.** L. FRIEDMAN and E. O. KRAEMER (*J. Amer. Chem. Soc.*, 1930, **52**, 1295—1304).—The rates of diffusion at 5° of carbamide, glycerol, sucrose, and lactose from their aqueous solutions into 2—30% pure aqueous gelatin gels and of these substances from the gels to water have been computed from refractometric data. The diffusion constants decrease linearly with increasing concentration of gelatin, but at concentrations corresponding with zero diffusion (by extrapolation) some diffusion occurs. From the two-phase solid-liquid theory, a relation between diffusion constant and pore radius is developed. Gels containing 5, 10, and 15% of gelatin have pore radii of 4.7—5.7, 1.4—1.7, and 0.5—1.0  $\mu\mu$ , respectively.

J. G. A. GRIFFITHS.

**Structure of agar gels from studies of diffusion.** L. FRIEDMAN (*J. Amer. Chem. Soc.*, 1930, **52**, 1311—1314).—The diffusion constants in 0.8—6.0% agar gels have been determined for eight non-electrolytes. The constant decreases linearly with increasing concentration of the gel. Foreign sub-

stances produce marked specific effects; glycerol, trimethylene glycol, and sucrose greatly increase the rates of diffusion. The radii of the pores in 2% and 5% agar gels are 2.9 and 0.74  $\mu\mu$ , respectively.

J. G. A. GRIFFITHS.

**Diffusion of non-electrolytes in gelatin gels.** L. FRIEDMAN (*J. Amer. Chem. Soc.*, 1930, **52**, 1305—1310).—The diffusion constants of 11 non-electrolytes ( $M=32$ —342) have been determined in 3.8% and 5% gelatin gels, and bear an approximately linear relation to  $1/\sqrt{M}$ . In general, the velocity of diffusion is increased by lowering the temperature of setting. Non-electrolytes in the gel have specific effects on the diffusion constant; sucrose causes a large increase and methyl alcohol produces a marked decrease.

J. G. A. GRIFFITHS.

**Camphorylphenylthiosemicarbazide gel.** E. HATSCHKE (*Kolloid-Z.*, 1930, **51**, 44—49).—Camphorylphenylthiosemicarbazide dissolves readily at the ordinary temperature in hexane, benzene, acetone, and benzyl alcohol, the solubility rising with increasing temperature. On cooling, the substance crystallises without formation of a gel. Gels are formed when hot solutions of the substance in toluene or in carbon tetrachloride are allowed to cool, whether rapidly or slowly. Gels containing up to 2% of the compound are clear, but at higher concentrations the excess crystallises in the gel. Such gels in contact with the crystalline phase are stable for months. When solutions in benzene, toluene, or carbon tetrachloride are diluted with a non-solvent hydrocarbon (such as petroleum) unstable gels are formed, which eventually break up into macroscopic crystals. Gel formation in petroleum is still observable at a concentration of 0.2%. The mechanism of gel formation in these systems is discussed.

F. S. HEDGES.

**Isoelectric point of gelatin in relation to minimum physical properties of gelatin.** J. M. JOHNS (*J. Biol. Chem.*, 1930, **86**, 231—243).—Between  $p_H$  5.26 and 4.68 the viscosity of gelatin is increased by the presence of *N*/32-sodium chloride; outside this range it is depressed, whilst at the two points mentioned it is not affected by the salt. These two points therefore both represent apparent isoelectric points of the gelatin. The alkaline portion of the titration curve of gelatin is shifted to the acid side in presence of sodium chloride, whilst the acid portion is inconsistently affected; curves (showing many inflexions) are given for the effects of varying concentrations of sodium chloride on the viscosity and  $p_H$  of gelatin solutions. The minimum values shown by certain properties of gelatin solutions are regarded as appertaining to pure gelatin, for which  $p_H=4.95$ , and not to isoelectric gelatin. Assuming the existence of associated gelatin molecules between the two apparent isoelectric points, part of the effect of neutral salts may be explained by their compensation of the charges existing on ionised gelatin; in the absence of salt these charges tend to compensate one another intermolecularly.

C. R. HARRINGTON.

**Behaviour of certain lyophilic colloids in liquid ammonia.** R. TAFT (*Trans. Kansas Acad. Sci.*, 1929, **32**, 38—41).—Gelatin, glue, and albumin

swell slightly, starch yields a thick paste, glutenin disperses fairly readily, whilst pectin, cellulose acetate and penta- and tetra-nitrates, gliadin, rosin, dextrin, gamboge, Congo-red, and benzopurpurin disperse readily. Rubber, soaps, agar, silk, gum tragacanth, gum arabic, commercial sodium silicate, cotton cellulose, and filter-paper do not disperse. Evidence of the existence of a lyotropic series in liquid ammonia is adduced.

#### CHEMICAL ABSTRACTS.

**Theory of equilibrium distribution of ions in a gel system with variable distribution of micelles.** F. G. DONNAN (Kolloid-Z., 1930, 51, 24—27).—Theoretical. An application of the theory of membrane equilibrium to gel systems characterised by variable distribution of micelles.

E. S. HEDGES.

**Heat of swelling of raw caoutchouc.** L. HOCK (Kolloid-Z., 1930, 51, 190—191).—Polemical (cf. Stamberger and Blow, this vol., 541).

E. S. HEDGES.

**Colloid-chemical colour changes in organic dyes.** W. OSTWALD and H. RUDOLPH (Kolloid-chem. Beih., 1930, 30, 416—473).—The colour changes of dyes on addition of neutral salts has been studied especially for Erika B, sulphoncyanine, and Congorubin. Erika and Congorubin change to a bluish-violet colour on addition of almost any neutral salt and the change was followed kinetically in relation to the influence of the concentration of the neutral salt and of the dye. The resulting curves resemble those for the acid coagulation of a negative hydrosol; further, the Hardy-Schulze rule is observed in respect of the cations of the salts, the velocity of the colour change being far greater for bivalent than for univalent cations. Multivalent cations of easily hydrolysable salts liberate the free acid of the dye and interfere with the colour change. The absorption spectra of these two dyes are very similar, both in the pure state and in the technical form (containing salts); the absorption is weakened by purification. By the addition of salts of univalent cations an absorption curve with two peaks is obtained, in accordance with the mixed colour violet; after the addition of salts of bivalent cations the colour change is to an intense blue and the absorption curve has only one peak. The tendency for these colour changes to occur in Congorubin is reduced by treatment with alcohol or by ageing. Sulphoncyanine changes from bluish-violet to red on addition of neutral salts or alkalis. Acid salts liberate the free acid. The solutions are optically empty both before and after the colour change. Bivalent cations or high concentrations of univalent cations coagulate the dye, but this is sharply distinguished from the colour change. The colour change may also be brought about reversibly by raising the temperature. Contrary to that with other dyes examined, the absorption increases in intensity with purification of the dye in aqueous solution, but the alcoholic solution is not affected thereby. No essential difference is to be observed in the effects of salts of uni- and bi-valent cations, but there is a general weakening of the absorption spectrum and a displacement of the position of the absorption maximum towards the shorter wave-lengths. By

addition of acids the absorption maximum is first displaced in the direction of greater wave-length and later in the opposite direction; the accompanying colour changes are violet→blue→red. The colour change of Erika and of Congorubin is due to a diminution of the degree of dispersion of the sol. On the other hand, the colour change with sulphoncyanine is probably due to a peptisation or dissolution effect of the neutral salt.

E. S. HEDGES.

**Physico-chemical study of proteins.** T. SHITO (Hokkaido J. Med., 1929, 7, 187—215).—The  $p_H$  of a gelatin solution containing different amounts of hydrochloric acid has been determined. For gelatin as an acid,  $K=10^{-3.8}$  and the maximum viscosity is at  $p_H$  2.9—3.0. The average mol. wt. of gelatin is 1553.

#### CHEMICAL ABSTRACTS.

**Ultracentrifugal dispersity determinations with protein solutions.** T. SVEDBERG (Kolloid-Z., 1930, 51, 10—23).—Proteins have resisted colloid-chemical investigations, not only because of their unfavourable optical properties, but also because sedimentation methods of investigation have been difficult on account of the high dispersity and low density of the material. Refined centrifugal methods, using high speeds of revolution, have been applied to this problem, especially to the determination of the distribution of particle size. The methods of experimentation and the theory involved are discussed in some detail. Milk can be studied in the ultracentrifuge by measurement of the light absorption; the casein is contained as a polydisperse system of relatively low degree of dispersion, the absorption of light varying greatly with the particle size. The particles range between 10 and 70  $\mu\mu$ . With hæmogoblin the sedimentation in the ultracentrifuge is very little and particle size determinations gave the unexpected result that the system is monodisperse, the particles having a mol. wt. of 68,000 and thus containing 4 iron atoms to the molecule. Experiments with serum-globulin point to a mol. wt. of 103,800 and for purified egg-albumin 34,400. The hæmocyanin of the snail is found to give a monodisperse system although the mol. wt. is about 5,000,000. The mol. wt. indicated for serum-albumin is 67,500; this does not agree with Sørensen's value of 45,000, but it is pointed out that in osmotic methods of determination the materials often suffer chemical degradation. Gelatin is an example of a polydisperse protein system, the particle weight varying between 10,000 and 70,000. The centrifugal method is further useful in following the change of mol. wt. with the hydrogen-ion concentration of the medium. The hæmocyanin of the snail is stable between  $p_H$  7.3 and 4.3, but outside this region the mol. wt. falls from 5,000,000 to 100,000. The monodisperse proteins include egg-albumin, Bence-Jones protein, hæmoglobin, serum-albumin, serum globulin, amandin, edestin, excelsin, legumin, C-phycoeyan, R-phycoeyan, R-phycoerythrin, H-hæmocyanin, L-hæmocyanin, and the polydisperse proteins include euglobulin, fibrinogen, gelatin, gliadin, globin, glutenin, histone, casein, lactalbumin, legumelin, leucosin, muscle-globulin, ovoglobulin, and pseudoglobulin. Members of the latter class are unstable and their dispersity changes with time. A

table is given showing the mol. wt., sedimentation constant, molecular friction coefficient, dissymmetry number, and molecular radius of the monodisperse proteins in the isoelectric state and it is found that these can be grouped into two classes, having mol. wts. of 35,000—210,000 and of several millions, respectively. The hæmocyans form the latter class. The first class can be divided into 4 groups, the mol. wts. of which are respectively approximately 1, 2, 3, and  $6 \times 34,500$ . This regularity cannot be explained at present, but a simple aggregation hypothesis is ruled out. When the more complex proteins are degraded chemically they break up into particles of mol. wt. 34,500 or a small multiple of that value. The coefficient of light absorption and the isoelectric point are specific for the different proteins, the latter being particularly characteristic, but the specific volume at 20° has throughout practically the same value of 0.747.

E. S. HEDGES.

**Electrochemical constitutive relations of proteins and dyes.** W. PAULI (Kolloid-Z., 1930, 51, 27—30).—Some unexpected similarities between proteins and sulpho-dyes are pointed out. Aqueous solutions of proteins are coagulated by heat and by addition of alcohol; Congo-red and Congorubin undergo a colour change under the same treatment. The constitutions of the blue and red forms of these dyes are discussed and it is shown that both these and the proteins are characterised by the formation of "Zwitter-ions."

E. S. HEDGES.

**Highly-polymerised compounds. Viscosity measurements on molecular colloids.** H. STAUDINGER (Kolloid-Z., 1930, 51, 71—89).—A review of work on the polymerisation of organic products, the study of the constitution of natural complex organic colloids by observations on the properties of artificial polymerisation products such as polystyrene, polyhydroxymethylene, polyvinylacetate, etc., the relations between viscosity and mol. wt., the dependence of viscosity on concentration, quantitative relations between the mol. wt. and viscosity-concentration curves, variation of viscosity with temperature, and deviations from the Hagen-Poiseuille law.

E. S. HEDGES.

**Swelling phenomena in cellulose fibres.** K. RESS, C. TROGUS, N. LJUBITSCH, and L. AKIM (Kolloid-Z., 1930, 51, 89—96).—The swelling of cellulose in a mixture of cuprammonium hydroxide and sodium hydroxide is considerably greater than in sodium hydroxide alone. Microscopic measurements on single ramie fibres showed an increase in the thickness of the fibre amounting to 18 times the original thickness, accompanied by a shortening of the long axis to one third or one quarter of the original length. These changes are connected with the spiral formation of the structural units of the thread. Similar experiments were carried out on the swelling of the *p*-toluenesulphonic ester of ramie. Trinitroramie does not swell perceptibly in methyl alcohol, but does so in cyclohexanone, and particularly in mixtures of acetone and cyclohexanone or acetone and camphor.

E. S. HEDGES.

**Influence of hydrogen-ion concentration on the coagulation of hydrosols of Prussian-blue.**

R. A. KUGEL (Kolloid-Z., 1930, 51, 240—247).—The coagulation of dialysed sols of Prussian-blue by hydrochloric acid and by sulphuric acid at different concentrations has been studied, the hydrogen-ion concentration of the solutions being measured. The curves obtained for the two acids are similar, but equal hydrogen-ion concentration does not correspond with equal coagulating power. The amount of adsorption of hydrogen ions from different concentrations of the acids was also determined and the curves for hydrochloric and sulphuric acids were again similar, but the amount adsorbed was not determined by the hydrogen-ion concentration alone.

E. S. HEDGES.

**Hydrogen[ion] activity in dispersions and colloid disperse systems.** H. PALLMANN (Kolloidchem. Beih., 1930, 30, 334—405).—Determinations of the hydrogen-ion concentrations of suspensions have been made by the electropotentiometric method and by measurement of the rate of inversion of sucrose. Suspensions in acid systems have a stronger acid reaction than the dispersion medium, and in alkaline systems the suspension is more alkaline than the disperse phase. There is a simple linear relation between the apparent hydrogen-ion concentration,  $C^1_H$ , of an acid disperse system of medium concentration and the concentration  $x$  of disperse phase, which is expressed by the formula  $C^1_H = C^0_H + Kx$ , where  $C^0_H$  is the hydrogen-ion concentration of the dispersion medium and  $K$  is a constant. A similar relation holds for the hydroxyl-ion concentration of alkaline disperse systems. At higher concentrations of the disperse phase the  $C^1_H/x$  curve falls towards the  $x$  axis. The acidity of the dispersion medium remains constant and is independent of the amount of the disperse phase. The difference between the acidity of the suspension and that of the dispersion medium is ascribed to adsorption of hydrogen ions, and for a given weight of disperse phase the "suspension effect" increases with the degree of dispersion. Hydrogen ions adsorbed on clay particles exert only half their usual activity. Although good agreement was obtained between the measurements made by the electrometric ( $C^1_H$ ) and the inversometric ( $C^1_{HI}$ ) methods, in coagulated systems the ratio  $C^1_{HI}/C^1_H$  falls because the hydrogen ions adsorbed on the inner surfaces of conglomerate particles are active in the inversion process; the ratio is not affected by the size of the particles. Exchange adsorption of the anions is exhibited by positively-charged micelles and of cations by negative micelles, and hydrogen-ion exchange can be observed in most negatively-charged systems. Hydroxyl-ion exchange is less usual, but occurs in some positive micelles. The formation of the double layer is discussed and the micelle is regarded as composed of three parts, an ultramicroon surrounded by an intimate ionic layer and this in its turn by an outer diffuse swarm of ions. Both of these ionic layers are assumed to be completely dissociated, but their activity is diminished by interionic forces and the attractive force of the lattice of the micelle. In general, the hydrogen-ion activity of a disperse system ( $a_i$ ) is the sum of the mean hydrogen-ion activities of the disperse phase ( $a_d$ ) and that of the dispersion medium

( $\alpha_0$ ). The relation between the concentration of the suspension and the mean hydrogen-ion activity of the disperse system is given by the equation  $\alpha_i = \alpha_0 + n \cdot \bar{H}_d \bar{F}_n^i$ , where  $\bar{H}_d$  is the mean hydrogen-ion concentration of the micelles,  $\bar{F}_n^i$  the mean activity coefficient of these hydrogen ions, and  $n$  the number of micelles in unit volume. The  $\bar{F}_n^i$  value is nearly constant for small concentrations of suspension and the hydrogen-ion activity is proportional to the concentration. At higher concentrations the  $\bar{F}_n^i$  value decreases under the action of intermicellar forces and the  $\alpha_i/x$  curve falls towards the  $x$  axis. Exchange adsorption of ions seems to be concerned only with the outer ionic layer and is the stronger the greater is the lowering of potential of the particles by the incoming ions.

E. S. HEDGES.

**Hydrogen and hydroxyl ions in the ion-swarms surrounding suspended particles and dispersed ultramicros.** G. WIEGNER (*Kolloid-Z.*, 1930, 51, 49—60).—The micelle is regarded as an ultramicros surrounded by an intimate ionic layer which in its turn is encompassed by a looser "swarm" of ions. When hydrogen ions form part of a micelle or suspended particle, whether in the inner layer or the outer swarm, the hydrogen-ion concentration of the colloid system or suspension is greater than that of the dispersion medium. This difference is termed the "suspension or dispersion effect" and can be measured either electropotentiometrically or by the rate of inversion of sucrose; it is especially noticeable in clay suspensions. The hydrogen-ion concentration of the dispersion medium from which the particles have been removed is constant and independent of the concentration of the suspension. Similar relations hold throughout for hydroxyl-ion concentrations in alkaline suspensions. The apparent increase in hydrogen- or hydroxyl-ion concentration is proportional to the number of particles, except for high values of the latter. With spherical or disc-like particles, whether large or small, the suspension effect is the same whether measured electrometrically or by sucrose inversion, but the latter method gives a higher value when the particles in suspension are secondary aggregates. Observations on exchange adsorption of ions are recorded. In the study of soils, a system is not completely characterised by hydrogen-ion concentration measurements made on the dispersion medium or the suspension alone, but the increase due to the presence of the disperse phase is the important factor.

E. S. HEDGES.

**Problems of present-day colloid chemistry. IV. Constitution of the double layer during peptisation.** H. R. KRUYT (*Chem. Weekblad*, 1930, 27, 114—116).—The manner in which the electrical double layer is built up during the process of peptisation is discussed.

H. F. GILLER.

**Solvated colloids.** M. H. FISCHER and M. O. HOOKER (*Kolloid-Z.*, 1930, 51, 39—44).—The importance of electrical phenomena in determining the stability and other properties of colloids is considered to be over-estimated and emphasis is laid on the solvation of the colloid particles. The solvated type of colloid is described as having a considerable

solubility for its own dispersion medium and differs in this respect from the suspensoid type. Soaps of the heavy metals were prepared by double decomposition with the potassium soaps. Such soaps in various organic media give stable, clear gels. The formation of gels is especially marked in the case of aluminium and magnesium soaps and the best liquid media are benzene, toluene, xylene, chloroform, carbon tetrachloride, ethylene dichloride, hexane, heptane, and decane. Pentane, aniline, pyridine, cresol, *o*-toluidine, and benzyl benzoate are unsatisfactory. Cadmium stearate in toluene gives a clear solution at 100°, and on cooling to 60° forms a dense white gel. When cooled further to 6° crystallisation takes place and a liquid phase is exuded. The process is reversible and occurs also in the system strontium stearate-toluene, and with solutions of aluminium stearate in benzene, pyridine, or ethylene dichloride. It is suggested that the gel is a very viscous liquid-liquid system and that on further cooling it changes to a less viscous solid-liquid system.

E. S. HEDGES.

**Charge of colloid particles and their influencing [factors].** A. LOTTERMOSER and W. RIEDEL (*Kolloid-Z.*, 1930, 51, 30—39).—The difference between electrolytic and electrokinetic potential is emphasised. The electrokinetic potential of positively-charged sols of chromium is reduced by dilution to zero, and by further dilution the particles become negatively charged. This cannot be explained by replacement of adsorbed hydrogen ions by hydroxyl ions, for measurements of hydrogen-ion concentration show that the sol does not become alkaline on dilution. The original positive charge is due to adsorption of various cations, but with progressive dilution these are gradually desorbed and the particles acquire their natural negative charge, which they preserve in contact with a liquid of higher dielectric constant (water). The ultimate value of the negative charge acquired by this means is designated the "specific potential" (*Eigenpotential*). At the isoelectric point the specific potential and the positive potential due to adsorbed cations are balanced. Similar phenomena were observed in sols of ferric oxide, alumina, and thorium oxide. A method for measuring the specific potential is described. The influence of various kinds of anions on the positively-charged sol was examined electrokinetically. The originally adsorbed cations are neutralised by multivalent anions until the specific potential is reached and at higher concentrations further adsorption of cations occurs and the potential is again displaced in the positive direction. Only the adsorption of hydroxyl ions can make the particles more negative than the specific potential. Acclimatisation phenomena were observed in these experiments, the result depending on the method of adding the electrolyte. Oxygen displaces the electrokinetic potential of the chromium particles in the negative direction.

E. S. HEDGES.

**Possible multiplicity of electrokinetic potentials.** N. THON (*Z. physikal. Chem.*, 1930, 147, 147—150).—In view of the fact that the cataphoresis potential of a substance dispersed in an aqueous solution of an electrolyte passes through a maximum



or minimum with increasing electrolyte concentration and that the critical concentration is, for analogous electrolytes, always of about the same order of magnitude, is also largely independent of the nature of the disperse phase, and about a thousand times as great as the usual critical concentrations for streaming potentials, it is suggested that the two potentials are perhaps not the same.

R. CUTHILL.

**Variability of electrokinetic potential.** G. ETRISCH and A. ZWANZIG (*Z. physikal. Chem.*, 1930, **147**, 151—154).—A preliminary investigation of the influence of pressure and the presence of substances with surface activity on streaming potentials has been made with  $10^{-5}N$  aqueous solutions of sodium chloride containing varying amounts of methyl alcohol and flowing through glass capillaries. In the absence of alcohol the  $\zeta$  potential is independent of the pressure causing the flow, but the  $\zeta$  potential of alcoholic solutions increases, apparently tending towards a limit, as the pressure increases, and for a given pressure the potential first falls and then rises again as the alcohol concentration is increased. Similar results have been obtained using ethyl and propyl alcohols instead of methyl alcohol; with propyl alcohol the  $\zeta$  potential even reverses at high pressure and alcohol concentrations. These results are considered to show that more than one stratum is involved in the phenomena at the interface.

R. CUTHILL.

**Physical processes in the so-called electrical purification. I. Maximum charge of suspended particles.** R. LADENBURG and H. SACHSSE (*Ann. Physik*, 1930, [v], **4**, 863—897).—In connexion with the "electrostatic" wire and plate method of separating suspended particles from gases the dependence of the charge of the particle on its size and nature and on the external conditions has been examined. The maximum charge on small particles is found theoretically and also by experiment. From the maximum charge, the time taken by the particles to wander to the earthed electrode can be calculated. The formula derived for the charge on suspended particles of radii  $10^{-3}$  to  $10^{-5}$  cm. in the corona discharge is  $ne = \pi \rho^2 X$ , where  $X$  is the mean field strength in the discharge space,  $n$  is the number of elementary charges,  $\rho$  is the radius of the particles, and  $x$  is a constant depending on  $\delta$ , the dielectric constant of the particles, and equal to  $1 + 2(\delta - 1)/(\delta + 2)$ . For small currents, and correspondingly small field strength the charge on the smaller particles (radius less than  $10^{-4}$  cm.) is larger than that given by the formula, and is expressed approximately by the formula  $n = 20\rho \times 10^5$ .

A. J. MEE.

**Relation between hydrogen-ion concentration and the electric double layer.** T. YAMATORI (*Hokkaido J. Med.*, 1929, **7**, 217—228).—When a solution containing ferric hydroxide sol and acetate buffer mixtures of various  $p_H$  values is used as the inner solution and a buffer solution of the same concentration as the outer solution, ferric ions dialyse completely at  $p_H$  3.7—3.9; above this value there was no change in the electric charge. Measurements of the threshold value with potassium sulphate, and of gold and potassium ferriyanide sols with sodium

chloride show that  $\rho_0 = K(p_{H0} - p_H) = K \log_e (h_0/h)$ , where  $K$  is a constant and  $h_0$  and  $h$  are the actual hydrogen-ion concentrations.

CHEMICAL ABSTRACTS.

**Positive and negative photophoresis of colloidal particles in aqueous solution.** W. W. BARKAS (*Phil. Mag.*, 1930, [vii], **9**, 505—519).—Previous evidence of the photophoresis of colloidal particles in aqueous solutions (A., 1927, 17) has been confirmed. Ultra-microscopic measurements on gamboge, gold, and silver in aqueous suspension show that these move towards the source of illumination, whilst paraffin oil suspended in water moves from the source of illumination. The calculated photophoretic force on silver in water is of the same order of magnitude but opposite in direction to that on silver in nitrogen as determined by Ehrenhaft (*Physikal. Z.*, 1917, **18**, 352).

A. E. MITCHELL.

**Magnetophotophoresis and electrophotophoresis.** F. EHREHAFT, M. REISS, and E. WASSER (*Z. Physik*, 1930, **60**, 754—758).—Magnetic and electric fields change the temperature distribution around submicroscopic particles subjected to an intense beam of light, and so change their motion.

A. B. D. CASSIE.

**Third law of thermostatics.** D. MACGILLAVRY (*Rec. trav. chim.*, 1930, **49**, 348—356).—It is postulated that the absolute zero of temperature cannot be attained. The combination of this postulate with the conservation of energy and the entropy axiom is made the basis of a general proof of Nernst's theory. It is shown that in using Pfaff's expression  $CdT + \sum X_1 dx_1 \dots$  the dependent differentials must be eliminated by making use of the equation of state and the equilibrium conditions. By an extension of the considerations given by Lorentz (*Chem. Weekblad*, 1913, **10**, 621) Nernst's theorem is shown to be true for all systems of pure condensed phases of which the specific heats decrease with fall of temperature at least as rapidly as is supposed by Lorentz. The discrepancies shown by hydrogen in regard to the heat theorem are possibly due to the difficulty of defining strictly the equilibrium state inasmuch as the equilibrium mixture of the forms of hydrogen is a function of temperature, and in the virtual change of a system in the region of the equilibrium point the regenerated hydrogen may differ from the reactant hydrogen in its internal equilibrium.

F. G. TRYHORN.

**Thermodynamics of binary systems.** K. F. HERZFELD (*Prob. Mod. Phys.*, Sommerfeld-Fest., 1928, 143—148; *Chem. Zentr.*, 1929, ii, 2541).

**Thermodynamics of systems with several equilibria. II.** N. VON RASCHEVSKY (*Z. Physik*, 1930, **61**, 511—524; cf. this vol., 420).—A more rigorous treatment is given of the previously considered case of a reversible reaction between two substances which conform to the van der Waals equation of state. Confirmation is obtained of the conclusion that the system possesses two states of equilibrium and that therefore certain hysteresis effects are actually possible. The theory is extended to a system with two coexisting phases. Colloidal solutions in which the individual particles are associated with two equilibrium states are considered, and

possible effects (of importance in physiology) connected with the coagulation of the system by electrolytes are discussed. Work on the physiological aspect is in progress. H. A. JAHN.

**Gibbs-Helmholtz equation and the concept of affinity.** J. PALACIOS (Anal. Fis. Quim., 1930, 28, 223—246).—A simple derivation of the Gibbs-Helmholtz equation is given, and the concept of affinity is discussed in relation to heat effect and maximum work. H. F. GILLBE.

**Time effect in thermodynamic processes and the hysteresis phenomena arising therefrom.** N. VON RASCHESKY (Z. Physik, 1930, 60, 237—242).—Theoretical. R. A. MORTON.

**Influence on the ideal solution laws of the distribution of polarity within the molecule.** J. M. HILDEBRAND and J. M. CARTER (Proc. Nat. Acad. Sci., 1930, 16, 285—288).—Differences in the degree of polarity between two molecular species tend to produce, in their solutions, deviations from the ideal solution laws. The deviations caused by solutions of nitrobenzene, *o*-, *m*-, and *p*-dinitrobenzene, and *s*-trinitrobenzene in benzene are considered. There is a marked difference in the electric moments of the three dinitrobenzenes, but no significant difference in their behaviour in benzene. The substitution of one nitro-group causes a deviation represented by 320 g.-cal.; the corresponding numbers for two and three nitro-groups are 580 and 1200 g.-cal., respectively. It is inferred that deviation from Raoult's law is determined by the number and polarity of the substituent groups rather than by the electric moment of the molecule. W. R. ANGUS.

**Vapour-phase esterification of acetic acid by ethyl alcohol.** P. K. FROLICH, G. B. CARPENTER, and W. J. KNOX, jun. (J. Amer. Chem. Soc., 1930, 52, 1565—1570).—The esterification of acetic acid by an equimolecular quantity of alcohol in presence of a pumice-zirconium oxide catalyst has been studied at 250—300°, using a flow method. Under the conditions used, reaction proceeds too slowly at 250° to reach the equilibrium point. At 280°, 87.5% of ethyl acetate is produced, corresponding with an equilibrium constant of 49; the corresponding values at 300° are 88.8% and 63, respectively. Olefine formation occurs above 300°. The equilibrium constant for the hydrolysis of ethyl acetate by water under the same conditions at 280° is also found to be about 49. Comparison of the results with those recorded in the literature shows that the equilibrium concentration of the ester is almost constant over the range 75—300°. H. BURTON.

**Inner equilibria in the solid phase.** I. A. SMITS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 74—85, and Physikal. Z., 1930, 31, 376—382).—The relation between heat capacities and inner equilibrium is discussed, and from an analysis of recent measurements by various workers of the molecular heats at low temperatures of the ammonium halides, of hydrogen bromide and iodide, and of methane it is inferred that inner equilibria among different types of molecules occur in these compounds.

F. G. TRYHORN.

**Confusion in the expression of the so-called "hydrogen-ion concentration" of a solution and a review of Brönsted's conception of acidity and basicity.** I. M. KOLTHOFF (Rec. trav. chim., 1930, 49, 401—414).—In order to avoid the confusion which exists in expressing the hydrogen-ion concentration of a solution it is proposed to restrict the symbols  $[H^+]$  and  $p_H$  to represent the actual hydrogen-ion (proton) concentration as defined by the modern theory of strong electrolytes. The corresponding activity values are represented by  $[aH^+]$  and  $pa_H$ . Values derived on the basis of Sørensen's original work should be indicated by the symbols  $[sH^+]$  and  $ps_H$ . The acidity of a solution in water should be expressed by the hydroxonium-ion concentration or activity, and not by the hydrogen-ion concentration, since free protons do not occur to any measurable extent. Brönsted's conceptions regarding the nature of acidity and basicity are reviewed and some of the consequences discussed. O. J. WALKER.

**Dissociation of monochloroacetic acid in aqueous solution.** C. GROVE (J. Amer. Chem. Soc., 1930, 52, 1404—1407).—The hydrogen-ion concentrations of 0.003—0.3*M*-aqueous solutions of monochloroacetic acid have been determined by acid hydrolysis of dimethyl acetal and ethylene acetal. The dissociation constant of monochloroacetic acid,  $K_c$ , is given by  $\log K_c = 3.150 + \sqrt{\mu} - 3.2 \mu$ , where  $\mu$  is the ionic strength. J. G. A. GRIFFITHS.

**Electrometric determination of the two dissociation constants of dibasic acids.** V. SIHVONEN (Z. Elektrochem., 1930, 36, 165—171).—A method for the potentiometric determination of the two ionisation constants of dibasic acids has been developed wherein the two half elements concerned are brought to the same ionic concentration by the addition of a neutral salt. By extrapolation of experimentally determined values of the concentration dissociation constants of the acid and application of the square root relationship between activity coefficient and ionic strength a series of equations has been derived whereby the relationship between the exponent of the concentration constant and the ionic strength may be calculated. The results obtained with succinic, fumaric, and maleic acids are in close agreement with those obtained by other methods. The influence of bivalent anions on the ionisation of dibasic acids has been studied; the influence of the strongly ionised ethylenedisulphonic acid on the concentration constants of succinic acid differs from that of the chloride ion to a smaller extent than the influence of the calcium ion differs from that of the sodium ion. H. F. GILLBE.

**Effect of sulphate and chloride ions on solutions of aluminium salts.** A. W. THOMAS and T. H. WHITEHEAD (J. Amer. Leather Chem. Assoc., 1930, 25, 127—133).—The  $p_H$  values of solutions of aluminium sulphate or chloride are increased by the addition of 0.01—0.05*N*-solutions of sodium chloride, and of potassium chloride or sulphate. The addition of the sulphate is more effective than that of the chloride. The  $p_H$  is increased by dilution, but not so much as by the addition of the salt solutions. It is decreased by the addition of solid sodium chloride

but increased by the addition of solid sodium sulphate. The results are attributed partly to the effect of the chloride ion on the basic aluminium salt formed by hydrolysis, in forming penta-aquohydroxyaluminium chloride and hydrochloric acid from a hexa-aquoaluminium chloride, and partly to the removal of solvent by the hydration of the sodium and chloride ions. The effect of the sulphate ions is attributed to the tendency of the sulphate ion to replace hydroxyl groups in the Werner complex, the possible formation of hydrogen sulphate ions from the sulphate ions, and the hydration of the ions with a corresponding decrease in  $p_H$ . D. WOODROFFE.

**Electron affinity of free radicals. I. Electron affinity of triphenylmethyl.** H. E. BENT (J. Amer. Chem. Soc., 1930, 52, 1498—1504).—The equilibrium at 25° between sodium and triphenylmethyl in ethereal solution has been investigated. The free energy changes of the reactions involved have been determined, and the electron affinity of gaseous triphenylmethyl is computed to be  $59 \pm 5$  kg.-cal.

J. G. A. GRIFFITHS.

**Activity coefficient of silver acetate.** F. H. MACDOUGALL (J. Amer. Chem. Soc., 1930, 52, 1390—1393).—Solubilities at 25° of silver acetate in water and aqueous solutions of potassium nitrate up to 3*M* are recorded, and the activity coefficients of silver acetate in these solutions are calculated. The Debye equation for the activity coefficient reproduces the results for ionic strengths up to 1.2, the ionic diameter being taken as  $4.35 \times 10^{-8}$  cm.

J. G. A. GRIFFITHS.

**Dissociation from the point of view of the phase rule.** M. CENTNERSZWER (J. Chim. phys., 1930, 27, 9—28).—A review of the author's work on this subject.

F. J. WILKINS.

**P-T Diagrams for definite phase numbers.** P. NIGGLI (Chem. Erde, 1930, 5, 201—224).—Fifty pressure-temperature diagrams are given for one- to five-phase systems.

L. J. SPENCER.

**Possibility of the [diagrammatic] representation of a function of four variables, with practical application to four-component phase diagrams.** F. H. VON HÖNIGSBERG (Z. anorg. Chem., 1930, 189, 215—233).—By combining co-ordinates and numbers in a "diagram-table" or co-ordinates and colours which may be represented by numbers, it is possible to increase the number of variables which can be represented by a phase diagram to four. By making each colour in its different gradations represent a variable the method might be made applicable to more than four dimensions.

M. S. BURR.

**M. p. of calcium and the system calcium-calcium nitride.** A. VON ANTROPOFF and E. FALK (Z. anorg. Chem., 1930, 187, 405—416).—The system calcium-calcium nitride has been investigated by the determination of cooling curves in an atmosphere of argon. The eutectic mixture corresponds with 3—4% of nitride, but the cooling curve shows halts at 780° and 809°, and it is not known which corresponds with the calcium-calcium nitride eutectic. Sublimed calcium has m. p.  $848 \pm 0.5^\circ$ . Taking into account the m. p. lowering due to 0.3—0.4% of calcium nitride,

chemically pure calcium has m. p.  $851 \pm 1^\circ$ . This is much higher than the values previously given, but the latter are probably to be accounted for by the presence of nitride and other impurities. The m. p. of calcium nitride is  $1195 \pm 1^\circ$ . M. S. BURR.

**Palladium-hydrogen and chromium-nitrogen.** G. TAMMANN (Z. anorg. Chem., 1930, 188, 396—408).—Theoretical. Equilibria in the above systems are compared and discussed from the point of view of the phase rule. The two systems are distinguished by the existence in chromium-nitrogen of one solid phase more than is found in palladium-hydrogen under comparable conditions. A diagram constructed by plotting pressure against volume of gas in the solid phase shows a complete analogy with the  $p$ - $v$  diagram of carbon dioxide in the case of chromium-nitrogen, and with that of a mixture of carbon dioxide and sulphur dioxide in the case of palladium-hydrogen. The two last-named systems do not exhibit equilibria with fewer than two degrees of freedom. The heat of formation of palladium-hydrogen is not reconcilable with the relative instability of the complex, and it is inferred that molecular hydrogen is concerned in its production. The proportionality between the amount of hydrogen absorbed by palladium in the early stages and the square root of the pressure does not necessarily imply the dissolution of hydrogen in the metal in the atomic form, since the process in question is not reversible. The observed deviation from Henry's law can be ascribed to the work done in expanding the palladium lattice. From considerations of the crystal structure of palladium and of chromium it is suggested that the complexes formed may be represented as  $\text{Pd}_4(\text{H}_2)_2$  and as  $\text{Cr}_4(\text{N}_2)$  and  $\text{Cr}_2(\text{N}_2)$ , rather than as ordinary atomic compounds. F. L. USHER.

**Dissociation pressure of  $\text{Fe}_4\text{N}$ .** P. H. EMMETT, S. B. HENDRICKS, and S. BRUNAUER (J. Amer. Chem. Soc., 1930, 52, 1456—1464).—The equilibrium constant,  $K = P_{\text{NH}_3}^2 / P_{\text{H}_2}^3$  for the system  $2\text{Fe}_4\text{N} + 3\text{H}_2 = 2\text{NH}_3 + 8\text{Fe}$  decreases from 0.495 to 0.051 between 420° and 525°, whence  $\Delta H = -24,100$  g.-cal. The X-ray powder method shows that the only solid phases are  $\text{Fe}_4\text{N}$  and iron. Dissolution of nitrogen in the iron probably does not occur. In conjunction with Haber's data (A., 1915, ii, 532), the dissociation pressure of  $\text{Fe}_4\text{N}$  is computed to be 4250 and 5600 atm. at 420° and 525°, respectively.

J. G. A. GRIFFITHS.

**Behaviour of vanadium and of vanadium-iron alloys towards hydrogen.** L. KIRSCHFELD and A. SIEVERTS (Z. Elektrochem., 1930, 36, 123—129).—The influence of pressure on the solubility of hydrogen in vanadium of various degrees of purity has been determined at temperatures from 300° to 1000°, and isotherms and isobars have been obtained for the absorption of hydrogen by three vanadium-iron alloys, containing 9.1, 22.0, and 70.9% of vanadium, respectively. The isobars of the two alloys poorer in vanadium resemble at low temperatures those of pure vanadium, but at higher temperatures the influence of the iron in increasing the solubility of hydrogen becomes more marked; with the third alloy the presence of the iron has but little influence

on the form of the isobars. At all temperatures the solubility is less than that calculated additively from the composition of the alloy. H. F. GILLBE.

**Determination of the dissociation pressures of hydrated salts by a dynamical method. III.** J. R. PARTINGTON and R. J. WINTERTON (J.C.S., 1930, 635—643; cf. *ibid.*, 1923, 123, 160).—The dissociation pressures of sodium arsenate and sodium phosphate hydrates have been determined by the method previously described. The results recorded are:  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O} + 5\text{H}_2\text{O}$ , 5.24 mm. at 14.90° and 7.36 mm. at 20°;  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HAsO}_4 + 7\text{H}_2\text{O}$ , 9.98 mm. at 24.92°, 14.39 mm. at 30°, and 20.73 mm. at 35°;  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} + 5\text{H}_2\text{O}$ , 8.93 mm. at 14.90°, 12.93 mm. at 20°, 19.10 mm. at 24.92°, and 27.05 mm. at 30°. The pressure-temperature curves for sodium arsenate show a transition at about 22° between the hepta- and the dodeca-hydrate. The heats of hydration have been calculated from the Clapeyron-Clausius and the Nernst equations. The specific heats of the sodium arsenate hydrates over the range 16° to -12° are 0.414 and 0.350 for the dodeca- and the hepta-hydrate, respectively.

O. J. WALKER.

**Decomposition of solids in liquids. II. Different modifications of zinc hydroxide.** W. FEITKNECHT (Helv. Chim. Acta, 1930, 13, 314—345; cf. this vol., 436).—In the system zinc oxide-water there are seven possible solid phases at the ordinary temperature, viz., the oxide, and one amorphous and five crystalline modifications of the hydroxide (rhombic,  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -forms). Zinc oxide is deposited from alkaline zincate solutions of medium concentration (0.5—0.05*N*). The most stable form of the hydroxide is the rhombic, which crystallises in well-shaped irregular double pyramids from super-saturated zincate solutions having an alkali concentration up to *N*. All the other forms change more or less rapidly in presence of alkalis to the rhombic form. The  $\beta$ -form crystallises from very dilute alkali solutions (less than 0.05*N*), which are super-saturated with respect to zincate, as variously-shaped somatoids. The characteristic form of the  $\gamma$ -hydroxide is probably that of long needles obtained by the transformation of the  $\alpha$ -hydroxide in 0.1—0.4*N*-alkali solutions, but other forms are produced by crystallisation from strongly supersaturated zincate solutions containing 0.1—0.8*N*-alkali. The  $\delta$ -hydroxide is formed by the slow hydrolysis of zincate solutions of medium concentrations, and consists of small rhombic leaflets or, more usually, of large irregular aggregates. It is transformed very rapidly into the stable form. The  $\alpha$ -hydroxide is never formed as well-defined crystals, but always in a highly-dispersed, gelatinous, or pseudomorphous form. It is obtained by the lixiviation of basic zinc salts or by the precipitation of zinc halide solutions with alkali. By rapid precipitation from solutions of zinc salts and alkalis the amorphous hydroxide is obtained. It can also be obtained electrolytically and by hydrolysis of concentrated zincate solutions. In general, it may be said that the conditions which determine the formation of any particular modifi-

cation of zinc hydroxide are concentration of alkali, degree of supersaturation, and velocity of hydrolysis. It is probable that there are different molecular structures in solution corresponding with the different solid modifications. O. J. WALKER.

**Oxide hydrates. XXIV. System nickelous oxide-water. XXV. System nickelic oxide-water.** G. F. HÜTTIG and A. PETER (Z. anorg. Chem., 1930, 189, 183—189, 190—195).—XXIV. Preparations of hydrated nickelous oxide have been obtained by different methods, their X-ray diagrams compared, and their isobaric dehydration curves determined. The decomposition temperature of the monohydrate,  $\text{NiO} \cdot \text{H}_2\text{O}$ , is 230° under a pressure of water vapour of 10 mm., but to remove the last 0.2—0.3 $\text{H}_2\text{O}$  at the same pressure requires a temperature of about 360°. This water probably enters into the lattice structure (cf. Hüttig and Zörner, this vol., 723). The reaction  $\text{NiO} \cdot \text{H}_2\text{O}(\text{cryst.}) \rightarrow \text{NiO}(\text{cryst.}) + \text{H}_2\text{O}$  appears to be irreversible, so that, if the monohydrate has a temperature range of stable existence, it must be very small.

XXV. The system nickelic oxide-water behaves similarly to the system cobaltic oxide-water (this vol., 162). The existence of a definite monohydrate has been established. Its decomposition temperature is 138° at a pressure of 10 mm. This pressure consists of the sum of the partial pressures of water vapour and oxygen. The monohydrate breaks up irreversibly as follows:  $2(\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}) \rightarrow 4\text{NiO} + 2\text{H}_2\text{O} + \text{O}_2$ . At a higher water content than that corresponding with the monohydrate the dehydration process is reversible. There is no proof of the existence of a trihydrate. The results are confirmed by the appearance of the X-ray spectrograms of different preparations of hydrated oxide. M. S. BURR.

**Cristobalite liquidus in alkali oxide-silica systems and heat of fusion of cristobalite.** F. C. KRACEK (J. Amer. Chem. Soc., 1930, 52, 1436—1442).—The liquidus curves for silica containing small quantities of the oxides of the alkali metals have been determined between 1470° and 1713°. There is no evidence of immiscibility, but lithium and sodium give the reverse S-type of m.-p. curve which persists to some extent with potassium. Rubidium and caesium give almost ideal m.-p. curves, from which the latent heat of fusion of cristobalite is computed to be 30.5 g.-cal./per g. J. G. A. GRIFFITHS.

**Phase diagram for the system sulphur-naphthalene and its relation to introfaction.** H. P. MUNGER, M. DARRIN, and G. STEGEMAN (J. Physical Chem., 1930, 34, 593—595).—The f.-p. diagram has been determined. The extent of introfaction (impregnation) appears to be related to the depression of the f. p. L. S. THEOBALD.

**Phase-rule studies on the proteins. I. Determination of solid compounds with hydrogen chloride or ammonia.** W. D. BANCROFT and C. E. BARNETT (J. Physical Chem., 1930, 34, 449—498).—The pressure-concentration curves for ammonia or hydrogen chloride in contact with solid acids or bases have been determined and are used to show when the formation of a compound takes place. Small amounts

of impurities do not affect the general nature of the curves obtained, whilst the presence of moderate amounts of water only displaces the curve but does not change its type. With tartaric acid and ammonia the different dissociation pressures of the two ammonium salts can be measured at the ordinary temperature, but with succinic acid a higher temperature (107°) is necessary. Owing to the slight solubility of aniline hydrochloride in aniline the method can be applied to aniline and hydrogen chloride. Benzoquinone and tribromoaniline form definite compounds with 1 mol. of hydrogen chloride and with the latter substance the same compound is formed in aqueous solution when the concentration of hydrogen chloride is sufficiently high. Hexamethylenetetramine reacts with four molecules of hydrogen chloride giving a curve with four distinct steps. Aminoacetic acid takes up little or no ammonia, but forms a compound with hydrogen chloride. Glutamic acid reacts with 1 mol. of ammonia, as does *p*-aminobenzoic acid. Casein, zein, arachin, fibrin, and gliadin absorb ammonia readily, but there is no evidence of the formation of chemical compounds in any case. Compounds are formed, however, between hydrogen chloride and casein, arachin, fibrin, gliadin, or edestin and the equivalent weights obtained are 450, 280, 365, 250, and 300 or 405, respectively. These values are consistently lower than those obtained by other observers. The number of nitrogen atoms in the gliadin molecule which react with hydrogen chloride is a multiple of nine. Zein is unaffected by contact with hydrogen chloride, but the other proteins are discoloured to an extent which appears to depend on the partial pressure of and the time of contact with the gas and on the nature of the protein. The controversial nature of the system protein-water is discussed.

L. S. THEOBALD.

**Ternary system iron-carbon-oxygen.** E. SCHILL and E. H. SCHULZ (Z. anorg. Chem., 1930, 188, 290—308; cf. Schenck, B., 1928, 369).—A detailed examination of the phase diagrams of the above system, based on the measurements by Schenck of the gas equilibria over the solid phases (excluding ferric oxide), indicates the necessity of assuming the existence of a fifth solid of undetermined composition. Since the equilibria in which metal or oxide phases are involved do not vary with the gas pressure (the total number of gas molecules remaining unchanged), whereas the gas equilibrium over the new phase with either  $\gamma$ -iron or ferrous oxide is dependent on the pressure, it must be concluded that the former is a carbide other than  $\text{Fe}_3\text{C}$ . This conclusion receives support from the observations of Hofmann (A., 1928, 853) on the X-ray interference patterns of the reduction products of iron oxide.

F. L. USHER.

**System  $\text{NaOH}\text{--}\text{NaNO}_3\text{--}\text{H}_2\text{O}$ .** E. JÄNECKE (Z. anorg. Chem., 1930, 188, 72—89; cf. Kurnakov and Nikolaiev, A., 1928, 20).—Solubility data for the above system have been supplemented by determining the isotherms at 100° and 125°. It is shown from cooling curves that two anhydrous compounds are formed, viz.,  $\text{NaOH}\cdot\text{NaNO}_3$  and  $2\text{NaOH}\cdot\text{NaNO}_3$ , both with m. p. 272°. There is a ternary eutectic consisting of  $\text{NaOH}$ ,  $\text{NaOH}\cdot\text{H}_2\text{O}$ , and  $2\text{NaOH}\cdot\text{NaNO}_3$  at 61.8°.

In a triangular b.-p. diagram there are two regions, one of which lies wholly in the field of saturation of the nitrate and the other in that of the double salt,  $\text{NaOH}\cdot\text{NaNO}_3$ , where boiling is possible only at pressures higher than the atmospheric. Vapour pressures of the saturated solutions, for which a complete diagram is given, have also been determined.

F. L. USHER.

**System  $\text{CuSO}_4\text{--}\text{H}_2\text{SO}_4\text{--}\text{H}_2\text{O}$ .** H. D. CROCKFORD and L. E. WARWICK (J. Physical Chem., 1930, 34, 1064—1070).—The isotherms at 0°, 20°, 40°, and 55° have been determined. The solubility of copper sulphate is decreased by increasing the percentage of sulphuric acid and is increased by a rise in temperature.

L. S. THEOBALD.

**System  $\text{HgO}\text{--}\text{SO}_3\text{--}\text{H}_2\text{O}$ .** M. PAIC (Compt. rend., 1930, 190, 1014—1015).—The crystalline solid phases of the system have been examined by the powder method. The results confirm the existence at 25° of the four phases:  $3\text{HgO}\cdot\text{SO}_3$  (turpeth mineral),  $3\text{HgO}\cdot 2\text{SO}_3\cdot 2\text{H}_2\text{O}$ ,  $\text{HgSO}_4\cdot\text{H}_2\text{O}$ , and  $\text{HgSO}_4$  (cf. Hoitsemma, A., 1896, ii, 15). Ray's results relating to the two alleged hemihydrates  $\alpha$ - and  $\beta$ - $3\text{HgO}\cdot\text{SO}_3\cdot 0.5\text{H}_2\text{O}$  (J.C.S., 1897, 71, 1097) are not confirmed, and Athanasco's supposed  $4\text{HgO}\cdot\text{SO}_3$  (A., 1886, 981) is shown to be turpeth mineral. This last is also obtainable by grinding dry mercuric oxide with  $\text{HgSO}_4$  or  $3\text{HgO}\cdot 2\text{SO}_3\cdot 2\text{H}_2\text{O}$ . It consists solely of  $3\text{HgO}\cdot\text{SO}_3$ , the colour depending on the conditions of formation.

C. A. SILBERRAD.

**Ternary system zinc oxide-zinc chloride-water.** H. C. HOLLAND (J.C.S., 1930, 643—648).—The data for 25° and 50° show that the most important solid phase is the oxychloride  $\text{ZnCl}_2\cdot 5\text{ZnO}\cdot 8\text{H}_2\text{O}$  which exists in equilibrium with solutions over a wide range of concentration. The oxychlorides  $\text{ZnCl}_2\cdot\text{ZnO}\cdot 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2\cdot\text{ZnO}\cdot\text{H}_2\text{O}$  exist in contact with the very concentrated solutions. These solid phases are found at both temperatures. Many of the supposed oxychlorides mentioned in the literature are undoubtedly mixtures.

O. J. WALKER.

**Equilibrium in the molten state between potassium, sodium, and their fluorides.** E. RINCK (Compt. rend., 1930, 190, 1053—1054; cf. A., 1927, 939; 1929, 649).—The equilibrium constant  $[\text{Na}]/[\text{KF}]/[\text{K}]/[\text{NaF}]$  of the reaction  $\text{Na} + \text{KF} = \text{K} + \text{NaF}$  at 1000° has an average value of 0.29.

C. W. GIBBY.

**Equilibrium of thallium and lead with molten thallous chloride and lead chloride.** R. LORENZ and H. SCHMITT (Z. anorg. Chem., 1930, 187, 129—154; cf. A., 1924, ii, 258, 761).—The composition of the metal and salt phases in the system  $2\text{Tl} + \text{PbCl}_2 = \text{Pb} + 2\text{TlCl}$  has been determined at different temperatures and for varying molecular proportions, equilibrium being approached from both sides. Rise of temperature or dilution of the metal with antimony (which does not act on the molten chlorides) causes a displacement of the equilibrium in consequence of the change  $\text{Tl}_2 \rightarrow 2\text{Tl}$ , whilst the opposite effect is produced by dilution of the salt with potassium and sodium chlorides. The results are discussed with reference to Lorenz's law of mass action for condensed

systems, which gives values agreeing with the experimental isotherms. F. L. USHER.

**System potassium sulphate-magnesium sulphate-water.** B. A. STARRS and L. CLARKE (J. Physical Chem., 1930, **34**, 1058—1063).—The solubility data for 30° are recorded. Potassium sulphate, schönite, and magnesium sulphate heptahydrate are the stable phases at this temperature. The existence of mixed crystals reported by Weston (J.C.S., 1922, **121**, 1223) is disproved.

L. S. THEOBALD.

**Polytherms of the ternary systems containing water, alkali sulphate, and a sulphate of the vitriol type.** II. A. BENRATH [with L. CREMIERS] (Z. anorg. Chem., 1930, **189**, 82—90; cf. A., 1929, 1238).—The isotherms indicated, as well as various two-salt points, have been determined for the following systems:  $\text{MnSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$  at 50°, 80°, and 97°;  $\text{ZnSO}_4\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$  at 80°;  $\text{ZnSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$  at 80° and 97°. Combining the results with existing data, the isotherms for these systems between 0° and 100° have been constructed. The field of existence of the incongruently soluble salt  $\text{MnSO}_4\text{,K}_2\text{SO}_4\text{,4H}_2\text{O}$  extends up to 40°, and that of the salt  $\text{MnSO}_4\text{,K}_2\text{SO}_4\text{,2H}_2\text{O}$  from 34° to about 74°.

R. CUTHILL.

**Reciprocal salt pair  $\text{MgSO}_4 + 2\text{KNO}_3 \rightleftharpoons \text{Mg}(\text{NO}_3)_2 + \text{K}_2\text{SO}_4$ .** II. A. BENRATH and H. BENRATH [with H. WAZELLE] (Z. anorg. Chem., 1930, **189**, 72—81; cf. this vol., 163).—From the data for the ternary systems  $\text{MgSO}_4\text{--Mg}(\text{NO}_3)_2\text{--H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2\text{--KNO}_3\text{--H}_2\text{O}$ , and  $\text{MgSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$  and the two-salt curves for the quaternary system at 0° and 99.5° the complete equilibrium diagrams for the salt pair at these temperatures have been constructed. At 99.5° the magnesium nitrate field has vanished and the potassium nitrate field has become very small, the kieserite, langbeinite, and potassium sulphate fields occupying almost the whole area.

R. CUTHILL.

**Reciprocal salt pair  $\text{MgCl}_2$ ,  $\text{Na}_2(\text{NO}_3)_2$ ,  $\text{H}_2\text{O}$ .** I. A. SIEVERTS and H. MÜLLER (Z. anorg. Chem., 1930, **189**, 241—257).—The four ternary systems and the quaternary system have been investigated at 15°, 25°, and 50° and, where possible, the results have been compared with those of earlier investigators. Data for the quaternary system have never been obtained. Diagrams are also given. M. S. BURR.

**Equilibrium in the quaternary system  $\text{Na}_2\text{Cr}_2\text{O}_7\text{--NH}_4\text{Cl--H}_2\text{O}$ .** I. GERASIMOV (Z. anorg. Chem., 1930, **187**, 321—333).—The quaternary system  $\text{Na}_2\text{Cr}_2\text{O}_7\text{--NH}_4\text{Cl--H}_2\text{O}$  has been investigated at 0°, 20°, 50°, and 75° with the view of determining the conditions favourable for the preparation of ammonium dichromate by double decomposition. By mixing saturated solutions of sodium dichromate and ammonium chloride the yield of ammonium dichromate should amount to 64.8% at 0° and 45.9% at 20°.

M. S. BURR.

**Hexamminecobaltic sulphate.** I. P. B. SARKAR and T. P. BARAT (J. Indian Chem. Soc., 1930, **7**, 119—124).—A phase-rule study at 35° of the ternary system potassium sulphate, hexamminecobaltic sulphate, water indicates that a double salt

$[\text{Co}(\text{NH}_3)_6](\text{SO}_4)_3\text{,K}_2\text{SO}_4\text{,4H}_2\text{O}$ , is formed which is stable only between the concentration limits 28—46.8% of hexamminecobaltic sulphate, whilst the pure double salt is obtained only between the limits 33—37.5% of hexamminecobaltic sulphate. The pure double salt may also be prepared by dissolving 5.5 g. of potassium sulphate and 4.4 g. of pentahydrated hexamminecobaltic sulphate in the smallest quantity of water at 60° and allowing to crystallise.

J. R. I. HEPBURN.

**Application of the phase rule to soap boiling.** **System sodium palmitate-water-sodium chloride.** J. W. MCBAIN, L. H. LAZARUS, and A. V. PITTER (Z. physikal. Chem., 1930, **147**, 87—117).—The results of the previous investigation of the above system (A., 1926, 672) have been verified and supplemented by new determinations, and equilibrium data for systems containing 0—100% of soap from 0° to above 200° are recorded. The principal points of the equilibrium diagram for the system consisting of water and an equimolecular mixture of potassium oleate and laurate have also been obtained.

R. CUTHILL.

**Calorimetric researches. IV. Necessity of adopting a second calorimetric standard for bomb calorimetry.** Heat of combustion of the proposed standard: salicylic acid. L. J. P. KEFFLER (Rec. trav. chim., 1930, **49**, 428—440).—A further plea is made for the adoption of a second standard substance in bomb calorimetry (cf. Verkade and Coops, recent papers). The suitability of salicylic acid as a second standard is confirmed. The heat of combustion is found to be 5233.6 g.-cal./g. (weighed in a vacuum).

O. J. WALKER.

**Heat of dissociation of oxygen and of the C-H linking.** R. MECKE (Nature, 1930, **125**, 526—527).—The method used by Henri (this vol., 272) for determining the heat of dissociation of oxygen has been previously employed (this vol., 124). It can also be applied to the C-H linkings in hydrocarbons; in methane the energy of the C-H linking is 115 kg.-cal.; those of the C-C, C=C, and C≡C linkings in hydrocarbon compounds are 110—115, 200, and 300 kg.-cal., respectively.

L. S. THEOBALD.

**Heat capacities in some aqueous solutions.** F. D. ROSSINI (Bur. Stand. J. Res., 1930, **4**, 313—327).—Methods of calculating, from specific heat data, the apparent molal heat capacity of a solute in aqueous solution, the partial molal heat capacity of the solute, and the partial molal heat capacity of the water are discussed.

C. J. SMITHELLS.

**f. p. and heat capacities of aqueous solutions of potassium chloride.** W. H. BARNES and O. MAASS (Canadian J. Res., 1930, **2**, 218—229).—The f. p. of aqueous solutions of potassium chloride have been determined for concentrations which extend to the eutectic (−10.72°, 19.93% KCl). The heat changes associated with the cooling of a 19.8% solution from 25° to temperatures between −78.5° and 0° and of a 12.95% solution of potassium chloride to temperatures between −78.5° and −37° are recorded. In the latter case measurements were made when the solution was rapidly (r) or slowly (s) cooled, the mean values obtained being, respectively,



128.86 (*r*), 129.27 (*s*); and 114.31 (*r*), 114.83 (*s*). The small differences, although only of the order of the experimental error, are in the direction which would be expected if colloidal solutions (with which a larger amount of surface energy must be associated) result from the process of rapid freezing (cf. McIntosh and Edson, *A.*, 1916, ii, 230). J. W. BAKER.

**Heat of dilution of sulphuric acid.** R. GRAU and W. A. ROTH (*Z. anorg. Chem.*, 1930, **188**, 186—199; cf. Brönsted, *A.*, 1910, ii, 112; Naudé, *A.*, 1928, 1097).—Heats of dilution at 18° for 0–10,000 mols. of water per mol. of sulphuric acid have been redetermined, as well as the temperature coefficient of this quantity between 8° and 18°. Full data are given. The results, where comparison is possible, agree well with those of Brönsted and less well with those of Naudé. F. L. USHER.

**Heats of dissolution of certain alkali halides and the specific heat of their solutions.** H. R. CHIPMAN, F. M. G. JOHNSON, and O. MAASS (*Trans. Nova Scotian Inst. Sci.*, 1930, **17**, 149–167).—New methods for the determination of the specific heats of solutions of sodium chloride, potassium chloride, sodium bromide, and potassium bromide and also of the heats of dissolution are described and the results tabulated. The sign of the heat of dissolution changes at a concentration of about 0.486*M*, being negative at lower concentrations and positive at higher. The potassium salts show a temperature coefficient which varies with the concentration, approaching zero at zero concentration. This is discussed.

J. W. SMITH.

**Heat of formation of mixed crystals of the series KCl-KBr.** M. M. POROV, A. BUNDEL, and W. CHOLLER (*Z. physikal. Chem.*, 1930, **147**, 302–318).—The heats of dissolution of mixed crystals of the series KCl-KBr obtained by different methods have been determined and the corresponding heats of formation calculated. The mixed crystals were prepared by (*a*) grinding the components together in a mortar, (*b*) heating a mixture of the components at 600° for periods varying from 24 to 72 hrs., (*c*) rapid and slow crystallisation from the molten state, and (*d*) slow crystallisation followed by tempering. In general the heat of formation varies with the method of preparation of the crystals and is largest in the case of crystals obtained by method (*d*). Crystals prepared by methods (*b*) and (*c*), however, have equal heats of formation when their composition is approximately that of the mixture of minimum *m. p.* The mixed crystals do not decompose on keeping.

O. J. WALKER.

**Thermochemical researches on geometrical isomerides. II. Structure of oleic and elaidic acids.** L. J. P. KEFFLER (*Rec. trav. chim.*, 1930, **49**, 415–424).—The preparation of pure oleic and elaidic acids is described, and their heats of combustion are found to be 9450 and 9342 g.-cal./g., respectively. Hence oleic and elaidic acids should be considered as geometrical isomerides having respectively the *cis*- and *trans*-forms. O. J. WALKER.

**Hydrocarbons. III. Conductivity measurements with strong binary salts in ionising media with very small dielectric constants.**

**The Nernst-Thomson rule.** P. WALDEN (*Z. physikal. Chem.*, 1930, **147**, 1–37; cf. this vol., 37).—The conductivities of the following solutions at various dilutions have been measured at either 25°, or 72°, or both: tetra-amylammonium picrate in benzene, toluene, trichloroethylene, and pentachloroethane, the thiocyanate, perchlorate, and iodide in benzene, and silver perchlorate in benzene and toluene. For all these solutions, the equivalent conductivity,  $\Lambda$ , increases in a normal manner with rise in temperature, but decreases continuously with increase in the dilution,  $v$ , the product  $\Lambda v$  remaining approximately constant. For solutions of tetra-amylammonium picrate in pentachloroethane, however,  $\Lambda$  passes through a minimum at high dilution and then commences to rise. Measurements of the conductivity of solutions of tetraethylammonium chloride and picrate in chloroform and tetra-amylammonium picrate in ether at dilutions of about 5000–150,000, *i.e.*, beyond the dilution of minimum conductivity, show that even at these dilutions the ionisation is very small. Combination of the new material with existing data for the degree of ionisation of tetraethylammonium and tetra-amylammonium picrates at 25° and dilutions of 1000 and 10,000 in various solvents affords a very satisfactory confirmation of the Nernst-Thomson rule, and there is also good agreement with the formula  $\epsilon v^{1/3} = \text{constant}$ , where  $\epsilon$  is the dielectric constant, for the values 0.976 and 0.882 of  $\alpha$ , the degree of dissociation. Values of  $\alpha$  calculated from the data for  $\epsilon$ , and  $\Lambda_\infty \eta$ , where  $\eta$  is the viscosity, by means of the equation  $\alpha = 1 - 65.7 / \epsilon \Lambda_\infty \eta v^{1/3}$  (*A.*, 1921, ii, 423) agree with the experimental figures as closely as those calculated from the Onsager equation  $\alpha = 1 - [0.818 \times 10^6 / (\epsilon T)^{3/2} + 82.0 / (\epsilon T)^{1/2} \Lambda_\infty \eta] c^{1/2}$  (*A.*, 1927, 517). R. CUTHILL.

**Conductivity of thiocyanates in methyl alcohol.** (MISS) A. UNMACK, D. M. MURRAY-RUST, and (SIR) H. HARTLEY (*Proc. Roy. Soc.*, 1930, **A**, 127, 228–240).—The electrical conductivities in methyl alcohol at 25° of solutions of lithium, sodium, potassium, rubidium, caesium, ammonium, barium, strontium, calcium, zinc, magnesium, and cadmium thiocyanates have been measured over the concentration range 0.0001–0.002*N*. The results with the univalent cations are in general agreement with the Debye-Hückel-Onsager theory (cf. Onsager, *A.*, 1927, 1031), and with the exception of lithium they confirm the values for the mobilities of the ions found by Frazer and Hartley (*A.*, 1925, ii, 1163). Comparing the present results with those found by Frazer and Hartley for the chlorides and nitrates of the alkali metals, it is found that in each series the value of  $\alpha$  the slope of the straight-line graph obtained by plotting  $\Lambda_c$  against  $N_c$ , is slightly less for the lithium salt than the theoretical value, and that the difference between the observed and calculated values of  $\alpha$  increases with the atomic weight of the metal, showing a greater tendency to ionic association in the case of the heavier cations. It is suggested that in dilute solutions the size of the solvated ion is the factor which determines the ionic association, in accordance with Bjerrum's hypothesis (cf. *A.*, 1927, 314). The thiocyanates of the bivalent metals show much greater

deviations from theory, and it is clear that a considerable amount of association occurs even in very dilute solutions of the alkaline-earth metals, whilst the thiocyanates of zinc and cadmium behave as weak electrolytes in methyl alcohol. The mean value of the mobility of the thiocyanate ion is calculated to be 60.9. The addition of small quantities of water to the cell lowers the conductivity of the uni-univalent salts, although to a smaller extent than would be accounted for by the change in viscosity. With magnesium and calcium thiocyanates, however, the conductivity is considerably raised, indicating that the degree of association is diminished by the presence of a small amount of water. L. L. BIRCUMSHAW.

**New formula for determination of the limiting conductivities of uni-univalent electrolytes.** A. SALITÓWNA (Rocz. Chem., 1930, 10, 230—239).—Müller's formula, viz.,  $\lambda_{\infty} = \lambda_0 + 62.15/v^{0.415}$ , is given a more general form,  $\lambda_{\infty} = \lambda_0 + 31.46/E\eta v^{0.415}$ , where  $E$  is the dielectric constant of the solvent and  $\eta$  its coefficient of viscosity. The above modified formula gives accurate results for solutions of electrolytes giving univalent ions even in such cases where Kohlrausch's formula cannot be applied.

R. TRUSZKOWSKI.

**Coefficient of conductivity of strong electrolytes in aqueous solution.** B. GARB and M. HŁASKO (Rocz. Chem., 1930, 10, 248—252).—The molecular conductivities and the coefficients of conductivity of mixtures containing 0.002*N*- and 0.01*N*-lithium iodide, ammonium bromide, potassium thiocyanate, sodium nitrate, and rubidium chloride are respectively 129.5 and 0.94, and 121.46 and 0.883; these values are within the limits of experimental error identical with the mean of the corresponding values obtained for each salt separately at concentrations respectively of 0.01*N* and 0.05*N*. The same is the case for mixtures of salts with a common ion, viz., 0.002*N*- and 0.01*N*-potassium thiocyanate, chloride, bromide, iodide, and nitrate; here the respective values are 139.4 and 0.937, and 130.8 and 0.880. The conductivity coefficient is thus independent of the nature of the strong electrolyte used, but depends only on the number of ions in solution. R. TRUSZKOWSKI.

**Electrochemical investigation of the system  $\text{AlBr}_3\text{-KBr}$  in ethylene bromide.** W. A. PLOTNIKOV and W. A. KIKEZ (Z. physikal. Chem., 1930, 147, 215—226).—The conductivity of a solution containing 7.3% of potassium bromide, 39% of aluminium bromide, and 53.7% of ethylene bromide is  $4.63 \times 10^{-3}$ . Cryoscopic investigation of solutions of aluminium bromide in ethylene bromide show that 50% of the aluminium bromide molecules combine to form double molecules. By the addition of potassium bromide to these solutions the f. p. is raised, indicating the formation of complex molecules,  $\text{Al}_2\text{Br}_6 \cdot 2\text{KBr}$ . Electrolysis with platinum electrodes results in the separation of ethylene at the cathode and bromine at the anode. The decomposition voltage is 0.58, which is in approximate agreement with the value 0.64 derived from Berthelot's thermochemical data. The nature of the solvates probably formed is discussed. Taking into consideration the higher viscosity of the solution the electrical conductivity indicates that there must

be a considerable degree of ionisation in spite of the low dielectric constant of ethylene bromide.

M. S. BURR.

**Electrochemical investigation of the system  $\text{AlBr}_3\text{-KBr}$  in toluene and xylene.** V. A. PLOTNIKOV and (MISS) S. JAKUBSON (Z. physikal. Chem., 1930, 147, 227—230).—The conductivity of a toluene solution containing 41.94% of aluminium bromide and 6.54% of potassium bromide is  $4.22 \times 10^{-3}$ . The conductivity increases with the concentration of potassium bromide. By electrolysis of solutions of these two salts in toluene and in *o*-, *p*-, and commercial xylene with an aluminium anode and a platinum cathode, aluminium is dissolved from the anode and deposited at the cathode, but not in the proportions required by Faraday's law. With a silver or copper anode in the toluene solution these two metals go into solution in amounts in accordance with Faraday's law, provided that copper forms a univalent ion. The decomposition potential at 17.6° is 2.05 volts in toluene and 1.65 in *p*-xylene. From thermochemical data the value of the latter is 1.78 volt.

M. S. BURR.

**Electrical conductivities of some polysaccharides as a function of time and of spontaneous precipitation.** (MME.) Z. GRUZEWKA (J. Chim. phys., 1930, 27, 163—167).—The electrical conductivity of unstable colloidal solutions of polysaccharides varies with time as the result of the opposite effects of increasing viscosity due to coagulation and the liberation of electrolytes. The conductivities of sterile solutions do not vary.

C. W. GIBBY.

**Comparative measurements of the surface conductivity of solutions of various electrolytes at a boundary of pyrex.** J. W. MCBAIN and C. R. PEAKER (J. Physical Chem., 1930, 34, 1033—1040).—The surface conductivities of aqueous solutions of potassium chloride, barium chloride, potassium sulphate, aluminium chloride, and of potassium ferrocyanide at  $25^\circ \pm 0.01$  have been determined by the method previously used (this vol., 37) with the parallel plates replaced by concentric tubes of pyrex. The results confirm the observations previously made (*loc. cit.*) with optically-polished surfaces that the conductivities are greater in capillaries than in bulk and the relative increase in conductivity is greater the more dilute is the solution. The specific surface conductance decreases as the concentration decreases. In the case of potassium chloride, the present values are about 2.25 times as great as those previously obtained.

L. S. THEOBALD.

**Mechanism of electrical conduction in solid salts.** C. A. GOETHALS (Rec. trav. chim., 1930, 49, 357—362).—The electrical conductivity has been measured of pastilles of potassium nitrate made by rapid crystallisation of the molten salt, with and without the addition of finely-divided sand, and by compression of the powdered crystals. In the temperature range 220—320° the conductivities of pastilles formed from the salt crystallised with sand are distinctly lower than those of the other types. The conductivities are satisfactorily represented by the formula  $\log x = a + bT$ . The decrease in conductance of the nitrate crystallised on the sand particles is attributed to the distortion of the crystal lattice,

since in this condition the surface of the  $1.6 \times 10^5$  crystallites containing 1 c.c. of the salt was 400 cm.<sup>2</sup>

F. G. TRYHORN.

**Temperature-conductivity curves of solid salts. III. Lithium halides.** D. C. GINNINGS and T. E. PHIPPS (J. Amer. Chem. Soc., 1930, 52, 1340—1345).—The conductivities,  $\kappa$ , of lithium chloride, bromide, and iodide have been determined between the ordinary temperature and the respective m. p. The curve connecting  $\log \kappa$  with  $1/T$  consists of two intersecting straight lines, from which the "heats of liberation,"  $H$ , of the ions are calculated;  $H$  is a linear function of the m. p.

In conjunction with previous results (A., 1929, 753), it is shown that for a series of alkali halides with a common halogen, the lighter is the alkali metal the less is  $H$  for either ion in the lattice. For alkali halides with a common alkali metal, the lighter is the halide ion the greater is  $H$  for either ion in the lattice.

J. G. A. GRIFFITHS.

**Promotion of crystal formation by electrical action.** K. SCHAUM and E. A. SCHEIDT (Z. anorg. Chem., 1930, 188, 52—59; cf. Volmer, A., 1929, 1399).—The influence of various types of electrical excitation on the production of crystals in supercooled liquids has been examined. The substances studied were nitrobenzene, benzene, urethane, salol, acetophenone, and benzophenone. Fields produced by the town supply (440 volts D.C.) or by an influence machine giving 10—15 kilovolts were ineffective, but the higher potentials furnished by an induction coil (50—80 kilovolts), or a Tesla discharge, brought about crystallisation in every case in a short time, of the order of 1 or 2 min. The substances were maintained above the mean temperature of spontaneous crystallisation, and it was proved that the effects were not due to mechanical disturbance. Spark discharge in the liquids themselves caused immediate crystallisation. The action is probably due to the orientation of dipoles.

F. L. USHER.

**Electrochemical behaviour and rate of dissolution of single zinc crystals in sulphuric acid.** M. STRAUMANTIS (Z. physikal. Chem., 1930, 147, 161—187; cf. A., 1929, 989).—The potential of single zinc crystals, prepared by a method which is described, and placed in neutral zinc sulphate solution, is the same at all the different crystallographic faces, and agrees also with that of a polycrystalline piece of the metal. On the addition of a small quantity of sulphuric acid to the zinc sulphate solution the potential falls, but reaches a minimum at concentrations less than 0.01*N*-sulphuric acid. It then increases to an approximately constant value at about 2*N*-sulphuric acid. By saturation of the solution with hydrogen the potential in both acid and neutral solutions increases. By saturation with oxygen, however, the potential falls in neutral solution, but increases in acid solution to a smaller extent than for hydrogen. The values found depend on whether the solution is stirred or not. The observed potential changes may be explained on the assumption that the potential is a function of the rate of dissolution of the zinc. For higher velocities the relationship is linear such that  $\epsilon_1' = \epsilon - k \cdot \Delta v / \Delta t$ , where  $\epsilon_1'$  is the potential of the

dissolving zinc and  $\epsilon'$  the potential at the beginning of dissolution. In sulphuric acid of the same concentration the relationship is the same for all the different crystal faces. The coefficient  $k$  increases with dilution of the acid. The most electronegative and reproducible values for the zinc potential are obtained if dissolution is prevented, as with very pure zinc. Dissolution is brought about at a measurable rate when metallic impurities are present. The impurities occur in the crystal in parallel layers (A., 1929, 631). The different surfaces of a single zinc crystal dissolve in 2*N*-sulphuric acid at different rates in the order  $(1120) > (1010) = (1011) > (0001)$ . There is an induction period the length of which, for each face, is in the inverse order. These differences are explained by the difference in the orientation of the layers of impurities with respect to the different crystal faces, and not to differences in the crystal faces themselves. The etching of the different crystal faces by 2*N*-sulphuric acid has been studied microscopically.

M. S. BURR.

***E.M.F.* of zinc amalgams.** J. L. CRENSHAW (J. Physical Chem., 1930, 34, 863—869).—The measurements of the *E.M.F.* of zinc amalgams by Richards and Forbes (A., 1907, ii, 424), Pearce and Eversole (A., 1928, 309), and the author (A., 1910, ii, 258) when compared by a method which gives no undue weight to the most dilute amalgams, for which the experimental error is greatest, are in good agreement. The observations agree more closely with each other than with Hildebrand's equation.

L. S. THEOBALD.

**Mercurous ion.** A. E. BRODSKY (Z. Elektrochem., 1930, 36, 268).—There is an unexplained discrepancy between the value for the normal electrode potential of the mercurous ion previously recorded (this vol., 35) and the value calculated from Drucker's data (A., 1912, ii, 424).

R. CUTHILL.

**Potential [at metallic electrodes] in electrolytes with foreign ions.** I. A. SCHMID and W. WINKELMANN (Helv. Chim. Acta, 1930, 13, 304—310).—The potential of a copper rod placed in solutions of various sodium and potassium salts is reproducible, and varies with the concentration of the salt and with the nature of the anion. Measurements have also been made of the potential of the metallic electrode in the primary cell amalgamated zinc|electrolyte|carbon which was short-circuited through a resistance, using different sodium and potassium salts and acids as electrolytes. The slope of the current-potential curve is dependent on the concentration of the electrolyte and on the nature of the anion. The acids, however, give curves different from those of the corresponding neutral salts.

O. J. WALKER.

**Electrolytic reduction potentials of organic compounds. V, VI. Reduction potentials of ketones and their relation to their molecular constitutions.** M. SHIKATA and I. TACHI (Mem. Coll. Agric. Kyōtō, 1930, 8, 1—19, 21—46; cf. A., 1928, 136, 648, 958).—V. The electrolytic reduction potentials of acetone, methyl ethyl ketone, acetophenone, acetoin, benzophenone, and benzoin have been measured with a dropping mercury cathode and a polarograph. Mono-substitution of Me by Et in-

creases the reduction potential by 100–160 millivolts; di-substitution doubles the effect. Substitution of hydrogen in the  $\alpha$ -position to a carbonyl group increases the reduction potential. The solubilities of benzophenone and benzoin in water at 25°, determined polarographically, are  $1.51 \times 10^{-4}$  and  $4.41 \times 10^{-4}$  mols. per litre.

VI. The electrolytic reduction potentials of diacetyl, benzil, acetylacetone, benzoylacetone, dibenzoylmethane, acetonylacetone, and diphenyl triketone ( $\alpha\gamma$ -diphenylpropanetrione) have been determined. The solubility of benzil in water at 25° is estimated to be  $8.86 \times 10^{-5}$  mol. per litre. Introduction of a carbonyl group in the  $\alpha$ -position in a monoketone makes the reduction potential positive by a greater amount than that found for the  $\beta$ - or  $\gamma$ -position. C. W. GIBBY.

Diphenylamine and diphenylbenzidine as reduction-oxidation indicators. I. M. KOLTHOFF and L. A. SARVER (Z. Elektrochem., 1930, 36, 139–141).—The intensity of the blue coloration produced with equivalent quantities of dichromate and diphenylamine or diphenylbenzidine in acid solution increases with the acid concentration up to about 10*N*, and thereafter diminishes. The catalytic influence of the ferrous ion is ascribed to the formation of some higher oxidation product, since the ferric ion is without effect. Potassium permanganate causes the production of the blue colour with both indicators even in 0.01*N*-sulphuric acid and in acetic acid, but not in sodium acetate solution: the formation of the colour thus appears to depend more on the oxidation potential of the oxidising material than on the  $p_H$  of the solution. The solubility of diphenylbenzidine, determined nephelometrically, is 0.06 mg. per litre, and its ionisation constant at 25° is about  $10^{-13}$ ; the solubility increases slowly with increase of  $p_H$ . On account of this slight solubility and of the instability of the blue substance the potentiometric study of the oxidation of diphenylamine by dichromate is very difficult, but appears to indicate that the reactions involved follow the sequence diphenylamine  $\rightarrow$  diphenylbenzidine  $\rightarrow$  blue quinonoid substance; the blue substance then combines with a further quantity of diphenylbenzidine to form a green, insoluble compound. The corrections necessary when diphenylamine or diphenylbenzidine is employed as a reduction-oxidation indicator are described. H. F. GILLBE.

Oxidation-reduction potentials of hæmin and related substances. I. Potentials of various hæmins and hæmatins in presence and absence of pyridine. J. B. CONANT and C. O. TONGBERG (J. Biol. Chem., 1930, 86, 733–741).—The normal potential of the hæmin-reduced hæmin system at  $2 \times 10^{-4}$  molar concentration in a mixture of equal volumes of 0.1*M*-borax and 0.2*M*-sodium tartrate ( $p_H$  9.15) and  $22^\circ \pm 2^\circ$  is  $-0.230$  volt, and that of the hæmatin-reduced hæmatin system under similar conditions  $-0.242$  volt. Increase in  $p_H$  makes the potential more negative, whilst increasing dilution and the presence of pyridine or of cyanide make it more positive; the cyanide effect is destroyed by preliminary heating of the borax solution of hæmin or hæmatin. C. R. HARRINGTON.

Active dextrose. C. E. CLIFTON and J. M. ORT (J. Physical Chem., 1930, 34, 855–862).—The determination of the oxidation potentials of dextrose solutions in sodium hydroxide-sodium phosphate buffers at  $p_H$  10 yields further evidence of a small but definite amount of a powerful reducing agent or an active dextrose (cf. A., 1929, 889), which alone is responsible for the reduction intensities developed in these solutions. The active form is quickly destroyed by a mild oxidising agent, and it exists in equilibrium with the main bulk of inactive or ordinary dextrose. The concentration of the active constituent is of the order of 1 in 266,000. L. S. THEOBALD.

Polarographic studies with the dropping mercury cathode. X. Reduction of sulphurous acid. B. GOSMAN (Coll. Czech. Chem. Comm., 1930, 2, 185–197).—A polarographic investigation of solutions of sulphurous acid and of sulphites has been made, using the dropping mercury cathode. Solutions of normal sulphites show no electro-reduction up to the voltage of deposition of sodium ions. In acidic solutions undissociated sulphurous acid molecules are reduced at about  $-0.2$  volt, the reduction potential depending on the concentration of sulphurous acid and of hydrogen ions, yielding hyposulphurous acid thus  $2SO_2 + 2e \rightarrow S_2O_4^{2-}$ . In neutral solution a second reduction stage potential is observed at  $-1.2$  volt and is supposed to yield sulphonylic acid. The polarographic method is convenient for the study of negative catalysis in the reaction between oxygen and sulphites. J. W. SMITH.

Study of complex salts by means of the polarograph. E. SHIKATA and Y. KIDA (J. Phys. Chem., Japan, 1929, 2, 75–90).—The anodic potential, decomposition voltage, and saturation current were measured for the addition of ammonium or sodium nitrate or nitric acid to copper nitrate solution. The complexes differ in stability according to the concentration of hydrogen and nitrate ions, and when alkali is added they are decomposed to form hydrated complexes. CHEMICAL ABSTRACTS.

Electrometric study of the precipitation of copper ions by alkalis. A. J. HOPKINS and R. A. BEEBE (J. Physical Chem., 1930, 34, 570–579).—Using the quinhydrone electrode, electrometric titrations of solutions of copper sulphate, nitrate, or chloride with sodium hydroxide have been carried out under various conditions. In the case of the sulphate, the single sharp inflexion at  $p_H$  7 of the electrometric titration curve in all cases indicates the precipitation of only one definite basic salt of the composition  $CuSO_4 \cdot 3Cu(OH)_2 \cdot xH_2O$ . When the precipitate is heated in the presence of excess of copper sulphate a slow conversion of the 1 : 3 salt into a salt of higher sulphate content, possibly the 1 : 2 salt, is indicated. The amount of alkali required for complete precipitation of copper from a sulphate solution depends on concentration and stirring to some extent; in the case of the nitrate, the effect of a change in the conditions of precipitation is more marked, but in the case of the chloride, this effect practically disappears. The precipitate from nitrate solutions is a mixture of copper hydroxide and the basic salt

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ ; that from chloride solutions has the composition  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ .

L. S. THEOBALD.

**Electrolytic deposition of copper [from copper sulphate] in the presence of amino-acids.** C. MARIE and GÉRARD (Compt. rend., 1930, 190, 864—866).—In the presence of glycine at 24° the overvoltage decreases with decrease in current density and glycine content (cf. Fuseya and Nagano, B., 1927, 632). It is not influenced by the concentration of the copper sulphate solution ( $N-2N$ ), although for dilute solutions the deposits are more fragile and less adherent. The precipitated copper entrains copper sulphate and glycine in approximately molecular proportions (cf. A., 1927, 840). Similar results, with higher overvoltages, were obtained in the presence of leucine.

J. GRANT.

**Decomposition potential of alumina in molten cryolite-alumina mixtures.** P. DROSSBACH (Z. Elektrochem., 1930, 36, 179—181).—The decomposition potential of alumina in cryolite-alumina mixtures at 1200°, calculated from the heat effect, is 2.16 volts.

H. F. GILLBE.

**Deposition potential of copper from solutions of its simple salts containing the corresponding free acid.** F. FOERSTER and K. GÄBLER (Z. Elektrochem., 1930, 36, 197—206).—The increase of potential necessary for the cathodic deposition of copper from solutions of cupric sulphate and perchlorate when free sulphuric or perchloric acid is present is due to the influence of the anions on the crystallisation processes at the electrode, and not to the variation of activity of the copper ions in the solution.

H. F. GILLBE.

**Significance of the anomalous behaviour of palladium anodes in solutions containing chlorides.** F. MÜLLER and A. RIEFKOHL (Z. Elektrochem., 1930, 36, 181—183).—The following solubilities have been determined in g./100 c.c.: palladous and platinous chlorides in 2*N*-sodium chloride solution, 28 and 0.84, respectively; palladous sulphate in *N*-sodium sulphate solution, 0.4; palladous oxide in *N*-sodium nitrate solution, very small. These figures tend to confirm the suggestion that the primary product of the anodic polarisation of palladium in sodium chloride solutions is palladous chloride, the high solubility of which permits the metal to retain its activity up to a certain critical current density, platinum under the same conditions remaining passive. The passivity of palladium in solutions of sulphate and nitrate is, in the same way, due to the slight solubility of the sulphate and oxide films which are formed.

H. F. GILLBE.

**Production of a current by motion of an electrode in an electrolyte solution.** M. O. CHARMANDARIAN and B. J. PERWUSCHIN (Z. Elektrochem., 1930, 36, 248—252; cf. Procopiu, A., 1922, ii, 112).—If in an apparatus consisting of two platinum electrodes in contact with an aqueous solution of an acid one electrode is set in motion, an *E.M.F.* is set up, the moving electrode being negative. The intensity of the resulting current depends on the acid used, and by previously electrolysing the solution for some time the current is increased or in some cases reversed.

In an acid solution previously saturated with hydrogen the moving electrode is at first negative but soon becomes positive. Electrodes wrapped in filter-paper, or charged with oxygen or chlorine, or treated with chromic acid give very feeble currents, but except in the first case the current soon becomes normal again. Contamination of the electrode surface reduces the current, but ignition of the electrode restores its activity.

R. CUTHILL.

**Mechanism of a simple voltaic cell.** R. T. LATTEY and M. W. PERRIN (Trans. Faraday Soc., 1930, 26, 227—233).—Voltaic cells of the type  $\text{Zn}|\text{ZnSO}_4|\text{M}$ , where M is Cu, Pt, Au, Ag, Hg, Pb, or Fe, show, on open circuit, a deposit of the anode metal on the cathode. In the case of copper at the ordinary temperature it consists of hydrated zinc oxide with a small proportion of metallic zinc, but metallic zinc only is deposited from boiling solutions. *E.M.F.* measurements made with these and similar cells, with electrodes of varying areas, and in the presence and absence of dissolved oxygen, support the view that metallic ions from solution are discharged on and alloy with the cathode. Dissolved oxygen (e.g., in cold solutions) acts as a depolariser by oxidising the deposit to an oxide film which is porous both to gas and to electrolyte.

J. GRANT.

**Mercury-basic mercury sulphate voltaic cell.** W. C. VOSBURGH and O. N. LACKEY (J. Amer. Chem. Soc., 1930, 52, 1407—1410).—The *E.M.F.* of the cell  $\text{Hg}|\text{HgSO}_4 \cdot x\text{M} \cdot \text{H}_2\text{SO}_4|x\text{M} \cdot \text{H}_2\text{SO}_4, \text{Hg}_2\text{SO}_4 \cdot 3\text{HgO} \cdot \text{SO}_3|\text{Au}$  has been determined for the range 20—35°. The *E.M.F.* is reproducible, decreases linearly with rise of temperature, but falls slowly with time. Solubilities of basic mercuric sulphate in dilute sulphuric acid are recorded.

J. G. A. GRIFFITHS.

**Cells with liquid-liquid junctions.** E. A. GUGGENHEIM (J. Amer. Chem. Soc., 1930, 52, 1315—1337).—The calculation of diffusion potentials for different types of liquid-liquid junctions between two electrolytes is discussed. Measurements have been made with the cell  $\text{Hg}|\text{HgCl}|0.1N\text{-HCl}||c\text{-KCl}|0.1N\text{-KCl}|\text{HgCl}|\text{Hg}$  at 18° ( $c=0.1-3.5\text{ }N$ ). The "continuous mixture layer" type (Henderson, A., 1908, ii, 655) is theoretically unstable, but is reproducible to 0.2 millivolt. Taylor's calculation of the "free diffusion junction" potential (A., 1927, 1144) is criticised, but the results almost coincide, in reproducibility and magnitude, with those of the first type. The conditions of the Planck formula are approximately satisfied by the "constrained diffusion junction," which is realised by means of a collodion membrane. The potentials are less reproducible. The instability and non-reproducibility of "sharp" junctions are attributed to the absence of cylindrical symmetry.

J. G. A. GRIFFITHS.

**Pyrochemical Daniell cells with a sharp zone.** F. OPPENHEIMER (Z. anorg. Chem., 1930, 189, 297—304).—Measurements of the *E.M.F.* of the fused salt cell  $\text{Pb}|\text{PbCl}_2|\text{CdCl}_2|\text{Cd}$  at 600°, 650°, and 700° give 122.8, 124.3, and 126.5 millivolts, respectively; of the cell  $\text{Pb}|\text{PbCl}_2|\text{ZnCl}_2|\text{Zn}$  at 550° and 600°, 291.9 and 285.7 millivolts; and of the cell  $\text{Cd}|\text{CdCl}_2|\text{ZnCl}_2|\text{Zn}$  at 600° and 650°, 155.3 and 150.4 millivolts. These results obtained under conditions which prevent diffu-

sion differ from those recorded by Lorenz and others (A., 1927, 523; 1928, 1331; 1929, 1241). They are also much more reproducible. They confirm Lorenz's views that the *E.M.F.* of the pyrochemical Daniell cell is simply the difference of the two *E.M.F.* of the single electrodes and that the chlorine ion only, and not the metal ion, migrates. M. S. BURR.

**Quantum state of molecules active from the point of view of reaction kinetics.** A. ÖLANDER (Z. physikal. Chem., 1930, B, 7, 311—318).—By consideration of the experimentally determined energies of activation of certain reactions, and the energies associated with the various vibrational quantum states of reacting molecules, an attempt has been made to identify the active molecule of reaction kinetics with certain states of vibrational excitation of the molecule. In the decomposition of hydrogen iodide, the collision between molecules with vibrational quantum numbers of 3 and 4 respectively appears to produce reaction. At a gold surface 4 quanta altogether suffice, and at a platinum surface 2 quanta. A selection rule appears to exist for energy transition in reactions between molecules of exactly similar type to the spectroscopic selection rules. The decomposition of ozone probably occurs between molecules with vibrational quantum numbers of 4 and 5. J. W. SMITH.

**Critical pressures of ignition of dry and "wet" mixtures of carbon monoxide and oxygen.** V. E. COSSLETT and W. E. GARNER (Trans. Faraday Soc., 1930, 26, 190—195).—The lower critical pressure for ignition of mixtures of carbon monoxide and oxygen was determined for wet and dry mixtures. The presence of water vapour has very little effect on the critical pressure. The residual pressure of gas was found to depend very largely on the state of the walls of the silica reaction vessel. In wet gas mixtures the residual pressure is independent of the initial pressure, in agreement with the results of Kopp and co-workers (cf. this vol., 299) on the ignition of mixtures of hydrogen and oxygen.

C. J. SMITHELLS.

**Propagation of detonation across a gas gap between two cartridges of explosive.** G. ST. J. PERROTT and D. B. GAWTHORP.—See B., 1930, 487.

**Explosion regions of gas mixtures in which one or two of the gases are endothermic.** K. POSTHUMUS (Rec. trav. chim., 1930, 49, 309—347).—A review of theories of gaseous explosions is given and the explosion regions of several binary and ternary gas systems have been determined.

For the system hydrogen-nitrous oxide a limit was found at 5.2%  $H_2$  and 94.8%  $N_2O$ . An accurate determination of the limit with excess of hydrogen was impossible. The value given is  $N_2O$  25.0,  $H_2$  75.0%. For the ternary systems  $H_2$ - $N_2O$ -He,  $H_2$ - $N_2O$ -A,  $H_2$ - $N_2O$ - $N_2$ ,  $H_2$ - $N_2O$ - $CO_2$  the upper limits of explosion occur at the respective percentages He 49—50, A 71.6, N 60.8, and  $CO_2$  54.3%.

For the system acetylene-nitrous oxide the limits found were  $C_2H_2$  2.2,  $N_2O$  97.8, and  $C_2H_2$  67.0,  $N_2O$  33.0%. The upper limits of the inert gas in explosive mixtures of the systems  $C_2H_2$ - $N_2O$ -He and  $C_2H_2$ - $N_2O$ -A are respectively He 50 and A 69—70%. The importance of the nature and strength of the means

of ignition in determining the position and magnitude of the explosion region is indicated.

F. G. TRYHORN.

**Decomposition of nitrogen pentoxide at low pressures.** H. J. SCHUMACHER and G. SPRENGER (Proc. Nat. Acad. Sci., 1930, 16, 129—135).—There is no marked diminution in the velocity coefficients in the decomposition of nitrogen pentoxide at 35° in the pressure range 0.2—0.004 mm. until a pressure of 0.06 mm. is reached. Below this value the fall becomes considerable. The value  $7.9 \times 10^{-3}$  was found for the higher pressures. F. G. TRYHORN.

**Thermal decomposition of chlorine dioxide.** H. J. SCHUMACHER and G. STIEGER (Z. physikal. Chem., 1930, B, 7, 363—386).—Investigation of the thermal decomposition of chlorine dioxide at 35—55° has shown that the rate of reaction rises at the start to a maximum, then begins to fall, becoming approximately proportional to the total pressure and to the square root of the dioxide pressure. If, however, the rate is above a certain critical value it rises continuously until explosion occurs. The velocity is dependent in large measure on the nature of the surface of the containing vessel and on the ratio of the surface area to the volume, and the temperature coefficient, too, is influenced by the containing vessel, the value at 40° for a glass bulb being about 5. These results are regarded as indicating that the decomposition consists of a chain of reactions initiated by the wall reaction  $ClO_2 = ClO + O$ , and largely terminating with other wall reactions. The oxide  $ClO_3$  is probably one of the intermediate products. The effect of the addition of carbon dioxide, oxygen, or chlorine is only what would be expected from the resulting change in pressure, but chlorine monoxide takes part in the reaction and markedly retards it. Carbon monoxide, also, retards the reaction, although to a smaller extent, and if it is present when explosion occurs at 45° slow formation of carbon dioxide starts and goes on until either all the oxygen or all the monoxide has combined. R. CUTHILL.

**Ignition and combustion of carbon disulphide.** M. PRETTE and P. LAFFITTE (Compt. rend., 1930, 190, 796—798).—The ignition temperature at 0.001 mm. pressure of carbon disulphide-air mixtures varies linearly with the proportion (1.3—34.0%) of the former, and in all cases there is a period of induction of 2—6 sec. An intense violet flame is always obtained, which for mixtures containing more than 10%  $CS_2$  appears a few degrees below the ignition point (cf. A., 1929, 1215), the temperature of which is unaffected by fairly large amounts of carbon dioxide, small amounts of methane, and less than 3% of water vapour. The fine brown deposit accumulating on the cooler parts of the apparatus during combustion at 300° was shown to be carbon monosulphide (cf. Dixon, A., 1926, 10). J. GRANT.

**Propagation of flame in gaseous explosions.** W. M. THORNTON (Phil. Mag., 1930, [vii], 9, 260—272).—Experiments on a 7% mixture of methane in air show that at all pressures at and below atmospheric flame travels faster in a transverse electric field. This may be a consequence of the increase of kinetic energy of the gas, either in or just beyond the wave front,



due to the ionic velocity added by the electric field, which has the same result as raising the temperature. However, Baly has supposed that the propagation of flame is affected by means of molecular complexes,  $A^+B^+$ , having a momentary excess of rotational energy,  $B$  being a molecule which has gained its critical quantum of activity at the expense of  $A$ , and since an electric field modifies the spin of the electrons in the orbit (as is disclosed by its influence on the radiation from a flame, the spectrum lines of the Stark effect being widened) it may be that this change of energy of spin is the additional rotational energy required by Baly's complexes, and so the velocity of explosion is accelerated. Further evidence of activation by radiation is afforded by the fact that, for a constant tube diameter, the velocity of explosion is proportional to the fourth power of the flame temperature (cf. Stefan's law). The idea of combining molecules being the source of radiation is investigated; it is suggested that the two "steam lines" observed in the radiation from the explosion of wet electrolytic gas, or from steady flames, are caused by the spin induced by combining collisions of hydrogen and oxygen molecules (a heavy and a light molecule), the combination obviously giving rise to strong oscillatory motion and momentarily reduced translational motion. Numerous experimental facts are cited in support of this idea in a generalised form. The correlation of explosions initiated by compression and ignition is briefly discussed; the velocity of flame at any point in a tube is proportional to the volume of gas burnt.

S. K. TWEEDY.

**Kinetics of the thermal dissociation of propane and [*n*- and *iso*]-butanes.** R. N. PEASE and E. S. DUGAN (J. Amer. Chem. Soc., 1930, 52, 1262—1267).—For each hydrocarbon the reaction is only about 1% heterogeneous. Dilution of the hydrocarbon with nitrogen causes the liberation of slightly larger amounts of hydrogen. The first order velocity coefficient falls as the reaction proceeds, perhaps owing to rehydrogenation of the dissociation products. The coefficient also falls slightly at very low pressures, but there is no indication of a second order reaction. The temperature coefficient of the reaction velocity is about 2.75 per 25° for each hydrocarbon.

S. K. TWEEDY.

**Extinction of ethylene flames by carbon dioxide and nitrogen.** G. W. JONES and R. E. KENNEDY (Anæsth. and Analg., 1930, 9, 6—10).—The limits of inflammability of mixtures of ethylene and air or oxygen at the ordinary temperature and pressure in 2-in. tubes with upward propagation of flame were 3.05, 28.60, and 3.10, 79.9%, respectively. To impart non-inflammability to ethylene at least 9 vols. of carbon dioxide or 15.3 vols. of nitrogen were required.

CHEMICAL ABSTRACTS.

**Non-catalytic polymerisation and hydrogenation of ethylene.** R. N. PEASE (J. Amer. Chem. Soc., 1930, 52, 1158—1164).—The behaviour of ethylene at 450—600°, and of ethylene and hydrogen or nitrogen at 550—600° when passed through a heated pyrex tube has been studied. The polymerisation reaction which takes place probably first produces butylene; above 525°, ethane, methane, a little

hydrogen, and liquid products begin to appear. It seems to be a homogeneous chain reaction; investigation of the effect of packing in static experiments revealed a depressing action on the reaction. The hydrogenation reaction appears to be closely coupled with the polymerisation; its rate is of the same order. It is suggested that ethylene is activated by hydrogen, and then activated ethylene which would have polymerised is largely converted into ethane (cf. Frey and Smith, A., 1928, 1211).

R. K. CALLOW.

**"Uniform movement" of flame in mixtures of ethylene, propylene, or butylene with air.** (MISS) E. H. M. GEORGEON and F. J. HARTWELL (J.C.S., 1930, 733—737; cf. A., 1927, 211).—The rate of "uniform movement" of flame in these mixtures has been determined in a horizontal quartz tube 2.5 cm. in diameter and 150 cm. long. The maximum velocities, 166, 101, and 98 cm. per sec., were obtained with mixtures containing 7.3—7.7% of ethylene, 5.0—5.3% of propylene, and 3.9—4.1% of butylene, respectively. The velocity was unaffected by the length of the tube, was only slightly decreased by saturating the mixture with water vapour, but was considerably retarded by mechanical disturbance; this probably accounts for the smaller values obtained by Chapman (J.C.S., 1921, 119, 1677). In a glass tube, similar to that of quartz, the lower and upper limits of explosive mixtures were 3.3 and 18.25% of ethylene, 2.58 and 7.5% of propylene, and 1.93 and 6.0% of butylene.

J. G. A. GRIFFITHS.

#### Kinetics of the oxidation of gaseous benzene.

R. FORT and C. N. HINSHELWOOD (Proc. Roy. Soc., 1930, A, 127, 218—227).—The principle of the experimental method has been previously described in detail (Hinshelwood and Topley, A., 1924, ii, 251); it consists of admitting pure benzene and oxygen at known pressures to a porcelain or silica bulb maintained at a convenient uniform temperature and measuring the fall in pressure as the reaction proceeds. The final products of oxidation are steam and carbon monoxide with a smaller amount of carbon dioxide. The induction period observed is due to the fact that the first oxygenated products (partial pressure up to about 5 mm.) are formed without any pressure increase. For a given ratio of oxygen to benzene the rate of oxidation increases with the total pressure; it also increases rapidly with the partial pressure of benzene. The influence of oxygen is more complex and depends on the benzene pressure, but with high ratios of oxygen to benzene there is a steady increase of rate with oxygen pressure. The rate of reaction is nearly the same in porcelain and silica bulbs, and also in a silica bulb packed with silica tubes giving several times the original surface, but with a bulb packed with small silica spheres giving a very large surface the results are erratic. The mechanism of the oxidation is considered to be similar to that of ethylene or acetylene to glyoxal, formaldehyde, and formic acid. From a study of the temperature coefficient over different stages of the reaction the values of the heat of activation  $E$  over these stages are calculated, and it is shown that a bi- or ter-molecular reaction which could proceed at the speed of the benzene

oxidation in the same region of temperature would have a heat of activation not greater than 50,000 g.-cal., unless it depended on a chain mechanism. This is the value of  $E$  for the induction period, and the much greater value, 82,000 g.-cal., found for the later stages of the reaction is considered to be due to the increase of chain length as well as to the increase in the primary rate of reaction. The chains are probably not of great length, since an increase in the surface-area has only a small influence on the rate of reaction; it is concluded that they are propagated more readily when the initial oxygenated product encounters another molecule of hydrocarbon than when it is further oxidised to oxygen.

L. L. BIRCUMSHAW.

**Decomposition of nitrogen pentoxide in inert solvents.** H. EYRING and F. DANIELS (J. Amer. Chem. Soc., 1930, **52**, 1472—1486).—The rate of decomposition of nitrogen pentoxide at 0.1—1.8M concentrations in nitrogen peroxide, ethylidene chloride, chloroform, ethylene chloride, carbon tetrachloride, pentachloroethane, bromine, as vapour alone, and in nitromethane, has been determined at temperatures between 15° and 45°. The solvents have specific effects. The velocity coefficient  $k$  decreases for the solvents in the order named, and is about twice as great for nitrogen peroxide as for the vapour of the reactant alone. The value of  $k$  is higher for concentrated solutions, but the reaction is unimolecular in all cases. The critical increment,  $E=24,000$ — $25,000$  g.-cal., calculated from the temperature coefficient, is unaffected by moisture. It is concluded that the variation of  $k$  is due to changes of  $E$  rather than  $s$  in the Arrhenius equation  $k=se^{-E/RT}$ ;  $s$  is identified with the infra-red frequency of the valency linking about to break. The velocity coefficients for saturated solutions of nitrogen pentoxide do not accord with the activity theory, and a solvent-reactant complex is assumed. J. G. A. GRIFFITHS.

**Decomposition of nitrogen pentoxide in chemically active solvents.** H. EYRING and F. DANIELS (J. Amer. Chem. Soc., 1930, **52**, 1486—1492).—The velocity coefficient for the decomposition of nitrogen pentoxide in increasing concentrations of nitric acid decreases to about 0.05 of the value for pure nitrogen pentoxide. The critical increments calculated from the temperature coefficients are 28,300 g.-cal. and about 28,000 g.-cal. when the solvents are nitric acid and propylene chloride, respectively.

Nitrogen pentoxide oxidises carbon disulphide (this reaction is accelerated by water), and precipitates iodine pentoxide from solutions of iodine in carbon tetrachloride. Carbon dioxide, nitrous oxide, water, and acetic acid are produced in an approximately bimolecular reaction between acetone and nitrogen pentoxide. The effects are attributed to the solvation of the nitrogen pentoxide and the subsequent decomposition of the complex. J. G. A. GRIFFITHS.

**Velocity of reaction between sodium nitrite and potassium iodide in acetic acid solution in presence or absence of added substances.** M. BOBTELSKI and D. KAPLAN (Z. anorg. Chem., 1930, **189**, 234—240).—The reaction between sodium nitrite and potassium iodide is bimolecular (unimolecular

with respect to either reactant). Hydrogen ions have such a powerful catalytic effect that their influence can be investigated only in acetic acid buffered with sodium acetate. In these circumstances the reaction velocity is proportional to the hydrogen-ion concentration. The reaction is delayed by alkali chlorides, nitrates, and sulphates, with the exception of sodium and ammonium chlorides. The alkaline-earth, magnesium, and zinc salts accelerate the reaction to a moderate extent, but the cadmium ion has a marked inhibiting action. Bivalent manganese, cobalt, and nickel are strong accelerators. The relative change in catalytic effect from chloride to nitrate or sulphate varies with the cation. In general, the catalytic effect diminishes in the order chloride>nitrate>sulphate, except in the case of zinc, for which the order is nitrate>chloride>sulphate. The differences between the three salts are the greater the stronger is the action of the cation. M. S. BURR.

**Velocity of reaction in mixed solvents. II. Velocity of reaction between sodium thiosulphate and alkyl iodides in organic solvents-water mixtures.** M. PRASAD and R. D. GODBOLE (J. Indian Chem. Soc., 1930, **7**, 127—135).—The solvents employed were mixtures of water with methyl, ethyl, *n*- and *iso*-propyl alcohols, glycerol, and glycol; the reactions studied were those between methyl or ethyl iodide and sodium thiosulphate. In water-methyl alcohol mixtures the velocity coefficient increased steadily with methyl alcohol content, whilst each of the other alcohols showed a maximum at a point which corresponded with the composition of a molecular hydrate. No connexion was found between velocity of reaction and either viscosity or dielectric constant. J. R. I. HEPBURN.

**Velocity of esterification with alcohol, ethylene glycol, and glycerol containing hydrochloric acid.** A. KAILAN and A. OSTERMANN (Monatsh., 1930, **55**, 98—131).—The velocities of esterification of  $\beta$ -phenylpropionic acid in ethylene glycol and glycerol, *n*-valeric, *n*- and *iso*-butyric acids, and 2:4- and 3:5-dinitrobenzoic acids in glycerol, and 3:5-dinitrobenzoic acid in alcohol, have been determined in absence and presence of water with hydrogen chloride as a catalyst at 25°. With glycerol and the various acids used, the velocity coefficients are found to be proportional to the concentration of hydrogen chloride, both in the absolute and moist alcohol; the same is also true for  $\beta$ -phenylpropionic acid in ethylene glycol when the concentration of the catalyst is  $N/12$ — $N/3$ . For 3:5-dinitrobenzoic acid and alcohol the velocity is proportional to the concentration of the catalyst only when alcohol containing a small amount of water is used. The coefficients for *n*-butyric acid in anhydrous and moist glycerol, and in ethylene glycol containing only a small amount of water, are the same as those for  $\beta$ -phenylpropionic acid under the same conditions. In wet ethylene glycol,  $\beta$ -phenylpropionic acid is esterified more slowly than *n*-butyric acid, whilst in alcohol it is esterified about 20% more rapidly. The coefficients for *iso*-butyric acid are about 82, 70, and 55% of those for *n*-butyric acid in glycerol, ethylene glycol, and alcohol, respectively. The dinitrobenzoic acids are esterified

more rapidly in glycerol than in alcohol, the alcohols containing 0.03 mol. of water per litre.

H. BURTON.

**Kinetic determination of hydrogen-ion concentrations in aqueous solution.** J. N. BRÖNSTED and C. GROVE (J. Amer. Chem. Soc., 1930, **52**, 1394—1403; cf. A., 1929, 273).—The velocity of hydrolysis at 20° of dimethyl acetal in 0.001—0.005*M*-solutions of perchloric acid depends only on, and is directly proportional to, the hydrogen-ion concentration. The molar velocity coefficient is given by  $0.434 k_{H^+} = 3.92$ . In the hydrolysis of ethylene acetal in 0.005—0.1*M*-solutions of perchloric acid, a small acid catalysis, additional to that due to hydrogen ions, occurs. The value of  $k_{H^+}$  is given by  $0.434 k_{H^+} = 0.180 + 0.19c$ , where  $c$  is the molarity of the acid producing the additional effect.

Salts have specific accelerating effects on these hydrolyses, linearly proportional to their concentrations up to 0.2*M*.

J. G. A. GRIFFITHS.

**Velocity of reaction of halogeno-carboxylic acids and sulphites. II.** H. J. BACKER and W. H. VAN MEELS (Rec. trav. chim., 1930, **49**, 363—380; cf. this vol., 426).—A determination of the velocity coefficients of the reaction between potassium sulphite and potassium salts and ethyl esters of monochloro- and monobromo-acetic acids shows that the reactions with the esters are much more rapid than with the potassium salts. The equation  $CO_2Na \cdot CH_2Br + Na_2S_2O_3 = CO_2Na \cdot CH_2 \cdot S_2O_3Na + NaBr$ , suggested for the reaction between sodium thiosulphate and sodium bromoacetate, is confirmed by a study of the oxidation of the products by bromine, and the velocity coefficients of the reactions between sodium thiosulphate and the potassium salts of chloro-, bromo-, and iodo-acetic acids have been measured. Among other velocity coefficients measured, in most cases at 25°, 35°, and 45°, are those of the reactions between alkali sulphites and the alkali salts or ethyl esters of  $\alpha$ - and  $\beta$ -chloro-, -bromo-, and -iodo-propionic,  $\alpha$ -bromobutyric,  $\alpha$ -bromo-*n*-valeric,  $\alpha$ -bromohexonic, bromosulphoacetic, and  $\alpha\beta$ -dibromosuccinic acids. The influence of the presence of a number of inorganic salts on these velocity coefficients has been investigated.

F. G. TRYHORN.

**Velocity of reaction of halogeno-carboxylic acids with sulphites. III.** H. J. BACKER and W. H. VAN MEELS (Rec. trav. chim., 1930, **49**, 457—470; cf. preceding abstract).—The reactions of halogeno-carboxylic acids with sulphites to form sulphonie acids are governed by the following conditions: iodo-acids react somewhat faster than bromo-acids, which react about a hundred times as fast as chloro-acids. Addition of an iodide to the chloro-acid accelerates the reaction. In the case of acids which undergo secondary reactions (hydrolysis, reduction, loss of hydrogen halide) a slight rise of temperature is favourable; too strong heating, however, favours the secondary reactions. The velocity coefficient increases with the concentration and with the addition of other salts. In dilute solution the water should be replaced partly by alcohol. Alkyl sulphites react about twenty times as fast as the metallic salts.

O. J. WALKER.

**Rate of decomposition of monobromosuccinic acid.** (FRAU) W. WYCZAŁKOWSKA (Z. physikal. Chem., 1930, **A**, **147**, 231—232).—Polemical against Ölander (A., 1929, 1384).

M. S. BURR.

**Bromosuccinic acid.** A. ÖLANDER (Z. physikal. Chem., 1930, **A**, **147**, 233—235).—A reply to Wyczałkowska (preceding abstract).

M. S. BURR.

**Rate of coupling of diazonium salts with phenols in buffer solutions.** J. B. CONANT and W. D. PETERSON (J. Amer. Chem. Soc., 1930, **52**, 1220—1232).—The rate of coupling of diazotised sulphanilic acid, *p*-bromoaniline, aniline, *p*-toluidine, and *o*-anisidine with salts of  $\alpha$ -naphthol-4-sulphonic,  $\alpha$ -naphthol-3 : 8-disulphonic,  $\beta$ -naphthol-3 : 6-disulphonic,  $\beta$ -naphthol-6 : 8-disulphonic, and phenol-*p*-sulphonic acids in buffer solutions of constant ionic strength ( $\mu=0.24$ ) has been measured colorimetrically by comparison with solutions in which reaction is complete. Over a wide range of concentration the rate of reaction corresponds with that calculated by means of the usual bimolecular equation. The rate of coupling is a simple function of the  $p_H$  of the solution;  $\log k = \log k_0 + p_H$ . Each pair of components may be characterised (at a given temperature and salt concentration) by a "coupling value," defined as the  $p_H$  at which  $\log k=1$ . In the case of the twenty pairs studied, it is found possible to assign empirical coefficients to each amine and phenol such that the sum is approximately equal to the coupling value. The temperature coefficient has been measured between 15° and 25°; the average value of  $E$  is 15,000. Preliminary experiments indicate that the salt effect between the ranges  $\sqrt{\mu}=0.5$  and 0.9 may be neglected, but from  $\sqrt{\mu}=0.2$  to 0.5 there may be considerable decrease in the velocity coefficient. Attempts to interpret the data in terms of Brönsted's theory have not yet been successful.

R. K. CALLOW.

**Tervalent carbon. X. Velocity of dissociation of hexaphenylethane.** K. ZIEGLER, L. EWALD, and P. ORTH (Annalen, 1930, **479**, 277—303).—An attempt has been made to determine the velocity of dissociation of hexaphenylethane by addition of a reagent, susceptible to determination, which reacts instantly at low temperatures with triphenylmethyl, but does not itself cause dissociation of hexaphenylethane, and, in this connexion, the reactions with oxygen, iodine, and bromine have been studied kinetically. The required conditions are not fulfilled in the case of oxygen, since the unimolecular coefficient ( $k$ , time in minutes) for the absorption of oxygen by hexaphenylethane in toluene solution at 0° is dependent on the concentration of the ethane and, in agreement with Mithoff and Branch (this vol., 301), on the partial pressure of the oxygen, its value varying from 0.6 to 0.7 at the highest concentration studied to 0.14 in 0.0015*M*-solution. Reduction of the partial pressure of oxygen from 1 to 0.2 atm. (0.007*M*) reduces the value of  $k$  in the ratio 1.4 : 1. Although  $k$  does not seem to approach a limiting value, it is approximately constant throughout the reaction in very dilute solution (0.0015*M*) at low partial pressures of oxygen (0.04 atm.). Consideration of the theoretical kinetics shows that the

results cannot be explained either on the assumption that hexaphenylethane is also attacked, or that the reaction with oxygen is not sufficiently rapid, and it is suggested that an intermediate active, labile, easily-dissociated peroxide is formed by attack of the ethane linking by oxygen. The value of  $k$  is also dependent on temperature and from measurements in dilute solution at  $0^\circ$  and  $-21^\circ$  the value of  $-Q = R[T_1T_2/(T_2 - T_1)] \log_e k_2/k_1$  is 11–14 kg.-cal. (cf. heat of dissociation, 10.5–12 kg.-cal., A., 1929, 1010). Contrary to Mithoff and Branch (*loc. cit.*) this is independent of temperature. The reaction of triphenylmethyl with iodine in chloroform solution in the presence of pyridine (as its hydriodide) and alcohol,  $2CPh_3 + I_2 + 2EtOH + 2C_5H_5N = 2CPh_3 \cdot OEt + 2C_5H_5N \cdot HI$  (the formation of periodides necessitating the addition of all these reagents), fulfils the necessary conditions and is followed by spectrophotometric measurements. At  $0^\circ$  the value of  $k$  (0.25), when the initial concentration of iodine is 0.04*N* and of the hexaphenylethane 0.018*M* is constant throughout the reaction, and has almost the same value when iodine is present in excess (0.08*N*). The half-change period for the dissociation of hexaphenylethane at  $0^\circ$  is, therefore,  $2.75 \pm 0.1$  min. The reaction velocity at  $-23^\circ$  is too slow for measurement, probably owing to the increased stability of pyridine hydriodide periodide superimposed on the ordinary temperature effect, whilst at  $10^\circ$  the heat of reaction introduces a 20% error into the temperature control, the value of  $k$  being 0.6–0.88, and the half-change period approximately 1 min. at this temperature. The value of the heat of activation calculated from these measurements at  $0^\circ$  and  $10^\circ$  is 13.4 kg.-cal., in fair agreement with the value given above. Bromine under similar conditions reacts almost instantaneously with the undissociated hexaphenylethane, thus supplying a reaction of the undissociated molecule which can be isolated kinetically from reactions of the free radical.

J. W. BAKER.

**Theory of metallic corrosion in the light of quantitative measurements.** III. G. D. BENGOUGH, J. M. STUART, and A. R. LEE (Proc. Roy. Soc., 1930, A, 127, 42–70; cf. A., 1928, 250, 1333).—Previous work on the corrosion of zinc in dilute potassium chloride solutions (*loc. cit.*) has been extended up to 4*N*-solution, and to a series of potassium sulphate solutions ranging from 0.0001*N* to *N*. A detailed investigation has been made of the degree of reproducibility obtainable by the oxygen absorption method of measuring corrosion; when adequate control is kept over the temperature, pressure, mechanical stability, and chemical purity of the system, the corrosion rates of horizontally supported annealed zinc specimens with a total area of 14.9 cm.<sup>2</sup> are reproducible to  $\pm 1.0\%$  throughout the whole range of chloride and sulphate solutions. A comparison between the oxygen absorption and loss of weight methods of measuring corrosion indicated a difference of not more than  $\pm 1.0\%$  between the two, except when very small amounts were measured. Corrosion-time curves for true oxygen absorption and total corrosion are given for the two series of solutions; in each case, the curves are exponential

for very dilute solutions. The different slopes of the straight-line curves obtained by plotting the rate of corrosion against the concentration for the two series are due to the different rates at which oxygen reaches the metal owing to changes in oxygen solubility and available cathodic area. The relation between oxygen solubility and corrosion rate is considered in detail. Within the range 0.2–2*N*-potassium chloride the curve showing the relation between true oxygen  $y$  and oxygen solubility  $x$  is a parabola for which the equation is  $y = K(x + A)^2 + B$ , where  $K = 0.08$ ,  $A = 1.56$ , and  $B = 0.39$ . The parabolic relation is obtained only when the main source of oxygen supply is the slow convection due to the slight density changes caused by surface dissolution of oxygen. If major convection currents due to changes in temperature, pressure, liquid flow, and evaporation are not eliminated, the curves tend to become a straight line. Hydrogen is evolved during the corrosion of electrolytic zinc in all the solutions more concentrated than 0.00005*N*. The proportion of total corrosion due to this evolution increases with concentration, reaching 17.4% of the total corrosion in 2*N*-potassium chloride and 7.7% in *N*-potassium sulphate. The gas is evolved from the pits which form the anodes of the oxygen absorption process. The rate of evolution is dependent on the presence of films of metallic impurities and of roughened metal. From spectroscopically pure zinc hydrogen evolution is greatly reduced, becoming zero in 0.0001*N*-potassium chloride.

L. L. BIRCUMSHAW.

**Dissolution velocity of metals.** M. TARELÉ (Bull. Chem. Soc. Japan, 1930, 5, 57–64).—Measurements of the rate of dissolution of magnesium in 0.02*N*-solutions of hydrochloric, tricarballic, 2:5- and 2:4-dihydroxybenzoic, and acetic acids indicates that the dissolution velocity increases with increase of the dissociation constant of the acid; there is, however, no direct proportionality, and the same is true of 0.1*N*- and 0.05*N*-solutions. Change of the dissolution velocity with the concentration is ascribed to variation of the influence of the resulting salt, which acts in three ways, viz., by altering the ionisation of the acid, by influencing the solubility of the salt, and by its solvent action on the metal. The unimolecular velocity coefficient of the dissociation of zinc in 0.01*N*-hydrochloric acid is about 2.5–3.0 times as great when the metal is in contact with platinum, whereas with magnesium the influence of platinum is negligible. Neutral salts, however, which have but little influence on the zinc-platinum couple, produce large variations in the dissolution velocity of magnesium, their influence diminishing in the order  $Br^-$ ,  $I^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $OAc^-$ .

H. F. GILLBE.

**Velocity of dissolution of aluminium in alkali solutions.** M. CENTNERSZWER and W. WITTANDT (Bull. Acad. Polonaise, 1930, A, 50–61).—In agreement with Jablczynski and Hermanowicz (A., 1929, 657), it is found that the rate of dissolution of aluminium in sodium hydroxide solution is proportional to the free surface area of the metal and to the square root of the sodium hydroxide concentration. Potassium, lithium, barium, and calcium hydroxide solutions all

show the same order of reaction as the sodium hydroxide solution. Calcium hydroxide shows a slower velocity of reaction than the corresponding concentrations of the other hydroxides, but this is probably due to the formation of a protective film of the insoluble calcium aluminate.

With weak bases such as ammonia, ethylamine, diethylamine, and triethylamine the reaction velocity is more closely proportional to the fourth root of the base concentration, but this is proportional to the square root of the hydroxyl-ion concentration for weak bases. It is concluded that the velocity of dissolution of aluminium depends only on the hydroxyl-ion concentration, and this is supported by the fact that for different bases the rate of dissolution is approximately proportional to the hydroxyl-ion concentration of the solutions. This yields a convenient method of determining the hydrolysis constants of sodium and potassium carbonates, which are both about  $1.4 \times 10^{-4}$ . The reaction velocities have a temperature coefficient of about 2 for  $10^\circ$  and are independent of the rate of stirring of the solution; hence it is a true reaction velocity which is measured and not a rate of diffusion.

J. W. SMITH.

**Passivity of metals. IV. Influence of acids in passivity and corrosion.** U. R. EVANS.—See B., 1930, 462.

**Reproducibility in corrosion work.** U. R. EVANS.—See B., 1930, 463.

**Electrochemical study of the radioactive elements.** F. JOLIOT (J. Chim. phys., 1930, 27, 119—162).—The kinetics of the deposition of polonium on polarised gold electrodes have been investigated. The rapidity of fixation depends on the velocity of diffusion of polonium through the liquid layer adhering to the electrode. In nitric acid solution the deposition potentials of cation and anion are 0.37 and 1.12 volts, respectively, measured against a *N*-calomel electrode, independently of the concentration of polonium between  $10^{-11}$  and  $10^{-8}N$ . The rates of deposition on gold, copper, and nickel electrodes in solutions  $0.1N$  in nitric acid are of the same order as for gold electrodes. Except for platinum, the potential has more influence than the nature of the electrode on the conditions of deposition. Two active cations of different degrees of oxidation can be distinguished, one in nitric, sulphuric, acetic, and (probably) hydrochloric acid solutions, having a deposition potential of 0.37 volt, and the other, in reducing solutions, having a deposition potential of 0.02 volt. Anodic deposition is practically complete in a strongly oxidising solution, and is impeded in reducing solutions. The natures of the ions cannot be stated exactly. The normal potential of bismuth is  $-0.05 \pm 0.01$  volt at  $18^\circ$ . The deposition potential of tellurium in an acid solution  $10^{-3}N$  is  $-0.011$  volt at  $19^\circ$ .

C. W. GIBBY.

**Negative induced reactions.** S. MIYAMOTO (Bull. Chem. Soc. Japan, 1930, 5, 54—57).—Various types of negative induced reactions, previously described, are discussed.

H. F. GILLBE.

**Catalytic oxidation of nitric oxide.** L. SZEGÖ (Gazzetta, 1930, 60, 212—229).—To minimise the

effect of surface adsorption of reaction products in dynamic measurements of the oxidation of nitric oxide by catalysts of large specific surface an interferometric method of analysis has been adopted. At  $30^\circ$  glass wool was without influence on the kinetics of the reaction  $2NO + O_2 = 2NO_2$ , but silica gel has a marked effect as a positive catalyst, causing approximately a twentyfold increase in the velocity coefficient. The coefficient is a linear function of the quantity of the gel. The coefficient falls with rising temperature, but this is not due to any variation of the adsorptive power of the gel; it is interpreted in terms of the theory of active centres.

F. G. TRYHORN.

**Autocatalytic reduction of bromate [ions] by hydrogen peroxide in acid solution.** W. C. BRAY and P. R. DAVIS (J. Amer. Chem. Soc., 1930, 52, 1427—1435).—The autocatalytic reduction of  $0.005$ — $0.01M$ -potassium bromate in  $0.1$ — $0.4N$ -sulphuric acid by  $0.036$ — $0.08M$ -hydrogen peroxide has been investigated in the dark at  $25^\circ$ . The equation  $BrO_3' + 3H_2O_2 = Br' + 3H_2O + 3O_2$  represents the net reaction which probably occurs in two independent reactions:  $d[BrO_3']/dt = k_1[BrO_3'][(H_2O_2)][H'] + k_2[BrO_3']([Br'])([H'])^2$ . Values of  $k_1$  and  $k_2$  are evaluated, and the mechanism of the reaction is discussed. The decomposition of hydrogen peroxide catalysed by bromide ions is appreciable only at the end of the reaction.

J. G. A. GRIFFITHS.

**Silver ion catalysis of persulphate oxidations. V. Quantitative study of the oxidation of ammonia.** C. V. KING and F. L. GRISWOLD (J. Amer. Chem. Soc., 1930, 52, 1493—1498).—The oxidation of ammonia by persulphate and silver ions to nitrogen is quantitative only within a limited range of low silver ion and high ammonium hydroxide concentrations. In general, the oxidation to nitrogen and nitrate ions proceeds simultaneously (cf. Yost, A., 1926, 365; King, A., 1928, 27). Some nitrogen is evolved when there is insufficient ammonia for the formation of the  $Ag(NH_3)_2$  ion. The yield of nitrogen is increased by ammonium nitrate and decreased by sodium hydroxide or potassium nitrate.

J. G. A. GRIFFITHS.

**Catalysis in the hydration of propionic anhydride.** M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1930, 52, 1410—1418; cf. A., 1929, 51).—The velocity coefficient of hydration of propionic anhydride in  $0.046M$ -solution at  $0^\circ$  is independent of the concentration of sodium chloride, increases linearly with the concentration of hydrochloric acid, and decreases approximately linearly with increasing concentrations of acetic and propionic acids. The accelerating influence of the ions increases in the order: propionate,  $H_3O^+$ , acetate, and formate. Butyric acid and the butyrate ion retard the reaction.

J. G. A. GRIFFITHS.

**Primary neutral salt effect in the catalytic hydrolysis of ethyl acetate.** R. A. ROBINSON (Trans. Faraday Soc., 1930, 26, 217—226).—The influence of neutral salts on the hydrolysis of ethyl acetate in acid solutions may be separated into a primary effect due to the influence of neutral salts on the activities of the various participating species, and

a secondary effect apparent when a weak acid is used as catalyst and accompanied by a change in  $p_H$  value. The reaction velocities ( $k$ ) at 25° for the hydrolysis of ethyl acetate in 1M to saturated aqueous solutions of dextrose, lithium, sodium, and potassium chlorides and bromides, sodium potassium, and calcium nitrates, barium chloride, and lithium iodide were measured with 0.1N-hydrochloric acid as catalyst. The relation  $k \propto \sqrt{\gamma}$ , where  $\gamma$  is the activity coefficient, was substantiated, and lithium chloride shown to be the only salt which raises the solubility of ethyl acetate in water. The activity coefficients of mono- and di-chloroacetic acids were calculated from the data obtained and shown to conform to the rules postulated by Harned and Robinson (A., 1929, 140).

J. GRANT.

**Catalysis in the hydration of acetopropionic anhydride.** M. KILPATRICK, jun., and (Miss) M. L. KILPATRICK (J. Amer. Chem. Soc., 1930, 52, 1418—1427).—The rate of hydration of acetopropionic anhydride at 0° is unaffected by sodium chloride up to 0.2M, but is accelerated by  $H_3O^+$ , acetate, and formate ions in this order of increasing effect. Butyrate and propionate ions retard the reaction.

In conjunction with previous results (A., 1929, 151; this vol., 713), it is concluded that an anion accelerates the reaction if the anhydride which might be formed hydrates more rapidly than the original anhydride, and conversely. The rate-determining complex is not the mixed anhydride. Deviations from the unimolecular law in the reactions retarded by buffer solutions are taken to indicate the formation of intermediate anhydrides. J. G. A. GRIFFITHS.

**Organic catalysts. IV. Decarboxylation of phenylglyoxylic acid and pyruvic acid.** W. LANGENBECK and R. HUTSCHENREUTER (Z. anorg. Chem., 1930, 188, 1—13; cf. A., 1929, 432).—Although phenylglyoxylic acid in the absence of catalysts does not decompose below 200°, small amounts of primary amines or of amino-acids bring about its conversion into benzaldehyde and carbon dioxide at 137°. The reaction ceases before completion in consequence of side reactions. Imino-derivatives of phenylglyoxylic acid are formed as intermediate products. The most active catalysts are  $\alpha$ -amino-acids, and the reaction is accelerated by the addition of hydroxyl-containing substances. Benzaldehyde exercises a retarding effect due to its reacting with the intermediate product. Pyruvic acid undergoes a similar decomposition in the presence of amino-acids, this reaction being strongly inhibited by water.

F. L. USHER.

**Allotropic modifications of sulphur. II. Catalytic effects.** C. R. PLATZMANN (Bull. Chem. Soc. Japan, 1930, 5, 43—47).—Smith's observations (A., 1903, ii, 139) on the influence of ammonia and of sulphur dioxide on the rate of establishment of the m. p. of crystalline sulphur and on the formation of  $S_8$  from the molten substance have been confirmed. Neutral or weakly acid substances such as diphenyl and thiophen-2-carboxylic acid have an influence similar to that of sulphur dioxide, whilst weakly basic substances such as pyridine, quinoline, and aniline resemble ammonia in their behaviour.

Addition of such substances does not alter the cryoscopic constant, and the conclusion is reached that the  $S_\mu$  is formed from  $S_\pi$ , which is the initial product. H. F. GILLBE.

**Potential and catalytic activity of a platinum surface.** A. RIUS (Z. Elektrochem., 1930, 36, 149—156).—A close relation exists between the potential of a platinum surface and its catalytic influence on the decomposition of hydrogen peroxide. When the former is altered, e.g., by thermal treatment or by poisoning, the catalytic activity exhibits a corresponding change. The optimum  $p_H$  for the decomposition of hydrogen peroxide in aqueous solution is 12.2—12.7, but in solutions of the same  $p_H$  the velocity is influenced by the salts present.

H. F. GILLBE.

**Production of chlorine from concentrated hydrochloric acid in presence of complex catalysts. Potassium chromate as oxidising agent.** I. M. BOBTELSKI (Z. anorg. Chem., 1930, 189, 196—214).—At the ordinary temperature no chlorine is evolved by the action of chromic acid on hydrochloric acid solution until the concentration of the latter reaches about 25%. In general, added chlorides, with the exception of those containing cations of variable valency, exert a small accelerating action only. Zinc chloride has no influence and cadmium chloride has a slight retarding action. Sulphates have a still smaller accelerating influence than chlorides. Chlorides of variable valency, except ferric chloride, have an appreciable accelerating action in the order  $Ag^+ > Mn^{2+} > Pb^{2+} > Co^{2+} > Cu^+$ . The accelerating effect of the copper ion is exactly proportional to the concentration. The cobalt ion is active only in highly concentrated hydrochloric acid solution. The activity of the lead ion is approximately proportional to the concentration and is independent of the chromate concentration over a wide range. The most powerful catalyst investigated is the complex formed by dissolving silver chloride in concentrated hydrochloric acid solution. A concentration of silver ion of  $0.5 \times 10^{-4}N$  in a 25% hydrochloric acid solution increases the velocity fourfold, but above a certain limiting concentration of silver there is no further effect. Its catalytic effect is not influenced by the presence of other chlorides with the exception of manganous chloride. The accelerating action of the latter has a concentration optimum which depends on the concentration of hydrochloric acid, becoming smaller as the latter increases. A rise of temperature of 10° doubles the chlorine evolution in the presence of manganese or silver. The relationship between the ability of a metallic ion to form complexes and its catalytic power is discussed. M. S. BURR.

**Effect of X-radiation on a platinum catalyst in the synthesis of water.** P. H. EMMETT and E. J. JONES (J. Physical Chem., 1930, 34, 1102—1104).—Irradiation of a platinum catalyst for 3 hrs. by the X-rays produced by a Coolidge tube with a molybdenum target has no effect on the synthesis of water from a mixture of hydrogen with excess of oxygen. L. S. THEOBALD.



**Impulse processes on heterogeneous catalysts and the possibility of detecting chain reactions.** K. BENNEWITZ and W. NEUMANN (*Z. physikal. Chem.*, 1930, B, 7, 247—275).—When active and inactive platinum surfaces are arranged alternately in the form of a radiometer and suspended by a quartz fibre in a mixture of ethylene and hydrogen, a turning moment would be expected theoretically, on account of the suction effect produced by the reaction on the active surface. Simultaneous measurements of the reaction velocity and turning moment, however, show that when this moment is present at all it amounts to only about 0.001 of the theoretically predicted value. It is concluded that only a vanishingly small fraction of the reaction takes place on the surface of the catalyst itself, the remainder occurring as a chain reaction in the gaseous phase. A chain mechanism for the reaction between ethylene and hydrogen is suggested. J. W. SMITH.

**Decomposition of methane at various temperatures at various catalysts.** F. FISCHER and H. BAHR (*Ges. Abh. Kennt. Kohle*, 1928, 8, 274—279; *Chem. Zentr.*, 1930, i, 31).—When natural gas containing 92.5% CH<sub>4</sub> was passed through a heated porcelain or silica tube, decomposition commenced at 850° with formation of hydrogen and separation of carbon, tar, and naphthalene. The production of hydrogen was almost doubled by the use of moist methane. When finely-divided graphite was used as catalyst no tar and little naphthalene were formed; with barium sulphate at 630—650° water, hydrogen sulphide, and traces of an unsaturated hydrocarbon were formed. The decomposition of methane when only 15% was present was observed; traces of benzene were detected. With zinc oxide containing potassium carbonate (1% as K<sub>2</sub>O) decomposition commenced at 700°. A. A. ELDRIDGE.

**Reaction of methane and lower homologues with carbon monoxide and carbon dioxide at various catalysts.** F. FISCHER and H. BAHR (*Ges. Abh. Kennt. Kohle*, 1928, 8, 279—281; *Chem. Zentr.*, 1930, i, 31).—Methane and carbon monoxide (2:1 vols.) were passed over various catalysts at different temperatures; carbon dioxide was formed from the monoxide, and methane was partly decomposed into carbon and hydrogen, but no reaction between carbon monoxide and methane was observed. A. A. ELDRIDGE.

**Equilibrium  $6\text{CO}_2 + \text{C}_6\text{H}_6 \rightleftharpoons 12\text{CO} + 3\text{H}_2$ .** H. BAHR (*Ges. Abh. Kennt. Kohle*, 1928, 8, 217—219; *Chem. Zentr.*, 1929, ii, 3263).—When a mixture of carbon dioxide and benzene vapour is heated in the presence of various metallic catalysts at 550—750°, only traces of carbon monoxide are produced. The mixture  $4\text{CO} + \text{H}_2$ , when passed over the same catalysts at 200—800°, was unaffected except for the formation of 24% of carbon monoxide by fission of carbon monoxide by the iron from a catalyst composed of zinc oxide containing 0.5% of ferric oxide. A. A. ELDRIDGE.

**Ammonia-oxygen gas cell. Formation of nitrates and nitrites in presence of alkalis.** C. MARIE and C. HAENNY (*Compt. rend.*, 1930, 190, 967—968; cf. A., 1929, 1015).—The reactions  $\text{NH}_3 +$

$\text{KOH} + 2\text{O}_2 = \text{KNO}_3 + 2\text{H}_2\text{O}$  ( $Q = +120,000$  g.-cal.) and  $\text{NH}_3 + \text{NaOH} + 2\text{O}_2 = \text{NaNO}_3 + 2\text{H}_2\text{O}$  ( $Q = 113,000$  g.-cal.) have been realised by the system  $\text{O}_2|\text{Pt}|\text{KOH} + \text{NaOH}(\text{fused})|\text{Pt}|\text{NH}_3$  (either hydroxide may also be used alone). At 250° nitrate and at 350° nitrite is readily detectable. The temperature coefficient between 200° and 250° is  $1.1 \times 10^{-4}$  volt per 1°. At 243° the *E.M.F.* is 0.665 volt, agreeing well with the thermochemical data. If the platinum at the cathode is replaced by gold the reaction is considerably, although temporarily, retarded. It is accelerated by traces of a metallic oxide (e.g., nickel or cupric oxide), an alkali nitrate, or water. The *E.M.F.* does not vanish on solidification; with a mixture containing 60% of potassium hydroxide there is an increase thereon of 0.2 volt. C. A. SILBERRAD.

**Electrolytic preparation of arsine and stibine.** M. HŁASKO and M. MASŁOWSKI (*Rocz. Chem.*, 1930, 10, 240—247).—At constant *P.D.*, the yield per coulomb of arsine or of stibine from arsenic or antimony cathodes in sodium acetate solution, acidified with acetic acid, rises with increasing density of current at the cathode. With constant density of current, the yield per coulomb of electricity used diminishes with increasing *P.D.* The best yields are obtained using concentrated acetate solutions, applying a current of 4 amp., with a *P.D.* of 55 volts and a density of current at the cathode equal to 14 units per cm.<sup>2</sup> Under identical conditions of current the yield of arsine is considerably greater than is that of stibine. The electrolytic method of preparation of these hydrides is greatly inferior to the usual method of acting on alloys of the metals in question with dilute acids. R. TRUSZKOWSKI.

**Preparation of thallium by electrolysis.** L. ANDRIEUX (*Compt. rend.*, 1930, 190, 925—927).—Various mixtures obtained by dissolving thallous oxide (brown hydrated thallic oxide was actually used; this affords thallous oxide when heated) in boric oxide or an alkali pyroborate with or without addition of oxide and/or fluoride of sodium, lithium, magnesium, calcium, barium, or zinc, were electrolysed at about 900°, using carbon electrodes (cf. this vol., 305). The best results (yields of 53—69% of metal) were obtained with an alkali pyroborate, sodium pyroborate and fluoride, or boric oxide with lithium oxide and fluoride. With calcium or barium, borides (CaB<sub>6</sub> or BaB<sub>6</sub>) were also obtained; with zinc, a zinc-thallium alloy was produced. Under no conditions was any boride of thallium formed. C. A. SILBERRAD.

**Electrochemistry of chromium.** A. V. PAM FILOV and G. F. FILIPITSHEV.—See B., 1930, 425.

**Photolysis of aqueous hydrogen peroxide solutions.** I. Methods. II. Results. A. J. ALLMAND and D. W. G. STYLE (*J.C.S.*, 1930, 596—606, 606—623).—I. Details of quantum efficiency measurements of the photolysis of hydrogen peroxide in concentrated and dilute aqueous solutions are given. The extinction coefficients for light of wave-lengths between 365 and 254  $\mu$  differ from those of Urey (A., 1929, 864). Corrections for the pronounced thermal decomposition are applied.

II. The photolysis of perhydrol and pure hydrogen peroxide in solutions between 0.02 and 13.5*M* has been investigated. The velocity of decomposition is directly proportional to the incident light flux,  $I_0$ , at high and low concentrations, and at low light intensities, but in solutions between 11.5 and 0.48*M* the velocity is proportional to  $\sqrt{I_0}$ . At constant light intensity, the velocity, and sometimes the quantum efficiency  $\gamma$ , pass through a maximum as the concentration is increased. The purely thermal reaction shows a similar maximum,  $\gamma$  has values between 20 and 500, and experiments with intermittent illumination show that the postulated catalytic chain has a mean life of about 1 sec., and this decreases with increasing concentration. Both  $\gamma$  and the temperature coefficient, which is independent of concentration, decrease as the frequency of the light is increased. Hydrogen peroxide, in dilute solution containing an inhibitor, decomposes with a velocity which rises with increase in concentration at a rate proportional to the square root of the light flux absorbed. It is suggested that the reaction chains are initiated by hydroxyl groups or oxygen atoms.

J. G. A. GRIFFITHS.

**Action of X-rays on Eder's solution.** R. W. G. WYCKOFF and L. E. BAKER (Amer. J. Roentgenol., 1929, 22, 551—554).—The measurement of radiation by precipitation of mercurous chloride from a solution of mercuric chloride and ammonium oxalate is described.

CHEMICAL ABSTRACTS.

**Decomposition of cobalt trinitrotri-amine in acid solution in the light and in the dark.** R. LUTHER and H. FRIESER (Z. Elektrochem., 1930, 36, 141—146).—Cobalt trinitrotri-amine in acid solution decomposes completely to cobaltous salt both in the dark and in the light. In the dark the reaction takes place in two stages, both of which are uni-molecular, the velocity coefficients at 55° and 65° being  $K_1=0.039$  and 0.17 and  $K_2=0.0025$  and 0.0088, respectively; the temperature coefficients of  $K_1$  and  $K_2$  are thus 4.4 and 3.5, respectively. The intermediate product is light-sensitive, and decomposes with a quantum yield of 0.37 at 366  $\mu$ ; the velocity of the total dark reaction increases with increase of the acid concentration of the solution. The decomposition in light appears to take place in one stage and its velocity is independent of the acid concentration; the quantum yield is 0.2 at 366  $\mu$  and the temperature coefficient of the velocity 1.03. The adsorption curves of cobalt trinitrotri-amine and its intermediate and final decomposition products have been photographed and the molar extinction coefficients at 366 and 500  $\mu$  have been determined.

H. F. GILLBE.

**Decomposition of solid barium azide under the influence of X-rays.** P. GÜNTHER, L. LEPIN, and K. ANDREEV (Z. Elektrochem., 1930, 36, 218—220).—Barium azide is slowly decomposed on exposure to soft X-rays, more than half the amount decomposed being converted into nitride, which is formed, however, directly, and not by the secondary reaction which occurs in the thermal decomposition (cf. this vol., 719). It is suggested that this reaction may also be brought about locally by mechanical

shock, the sensitivity of the azide to shock thus being explained.

R. CUTHILL.

**Dissolution of copper in solutions of potassium cyanide accelerated by X-rays.** K. PESTRECOV (Coll. Czech Chem. Comm., 1930, 2, 198—200).—In view of the resemblance between the chemical effects of alternating currents and of X-rays a study has been made of the rate of dissolution of copper in electrolyte solutions while exposed to the action of X-rays. Copper immersed in an aqueous solution of potassium cyanide shows always a 30% increase in the rate of dissolution when exposed to X-radiation, but after a certain period of irradiation exhibits a pronounced fatigue effect. Copper in 10% copper sulphate solution shows no increased rate of dissolution. Zinc, platinum, and cadmium show no change in rate of dissolution under the action of X-rays, but the two last are not dissolved during alternating-current electrolysis.

J. W. SMITH.

**Photomicrography of silver halide grains with ultra-violet radiation.** A. P. H. TRIVELLI and R. P. LOVELAND (J. Opt. Soc. Amer., 1930, 20, 97—105).—The possibility of using the mercury line 3650 Å. for photomicrography has been investigated. Photomicrographs of silver bromide grains in gelatin have been taken, using a glass lens system, and present no difficulties if the microscope is corrected for the wave-length used.

C. W. GIBBY.

**Photochemical properties of silver bromide in presence of dilute aqueous solutions of gelatin or gum arabic.** A. REYCHLER (Bull. Soc. chim. Belg., 1930, 39, 125—131).—The changes which occur in exposure and development of the photographic plate are reproduced by dilute aqueous suspensions of silver bromide, prepared from 0.1*N*-silver nitrate and potassium bromide, and protected by the addition of a few drops of a solution of gelatin or gum arabic. In a theoretical discussion it is suggested that exposure to light disrupts the crystal lattice of silver bromide, liberating nuclei of silver, which act as centres of reduction in the subsequent process of development.

J. R. I. HEPBURN.

**Blackening of photographic plates by electron rays.** M. J. NACKEN (Physikal. Z., 1930, 31, 296—306).—A quantitative investigation has been made of the blackening of photographic plates by electron rays under a series of voltages and of various intensities from a heated cathode. Precautions were taken to protect the plate from the light from the cathode and from secondary rays, and the apparatus, which is described in detail, was shielded from the earth's magnetic field. The Roscoe-Bunsen law that the blackening under a constant voltage depends only on the product of the intensity and the time of exposure is shown to be obeyed at all voltages. The blackening as ordinate is plotted against the logarithm of the above product ( $\log It$ ) as abscissa for each of the applied voltages 0.7, 1.5, 3.75, 5.5, and 8.7 kilovolts. Starting at small values of  $It$ , the curves rise at first slowly, then linearly, and then become nearly horizontal and remain so over a definite region. Following this, a further steep and nearly linear rise of the curves takes place up to the highest values of the blackening investigated. With the faster electrons,

whilst the horizontal regions become less pronounced and occur at greater values of  $It$  and for higher values of the blackening, the initial linear rise is more pronounced and the curves resemble those obtained with visible light. The value for the blackening at the horizontal region is shown to be connected with the depth of penetration of the electrons, and it is shown that the final increase in the blackening with long exposures cannot be due to the action of the electrons themselves.

H. A. JAHN.

**Herschel effect.** A. P. H. TRIVELLI (J. Franklin Inst., 1929, 207, 765—797).—The effect originally observed by Herschel was a visible or print-out effect; what is ordinarily understood to-day is the latent Herschel effect, which is considered here. The effect is analysed for a pure silver bromide emulsion (H. and D. speed 63) by the method of cross-exposures, using a non-intermittent sensitometer with 26 steps of  $\sqrt{2}$  ratio; the tungsten source was screened by Wratten filters nos. 49 and 87 respectively for the blue and red exposures. Various expressions for the magnitude of the effect are compared, the ordinary percentage one, viz.,  $100(D_b - D_r)/D_b$ , being regarded as the most useful. The effect shows a maximum at a certain blue-light exposure and with a given development. The parallelism between the action of light and of chemical agents (e.g., hydrogen peroxide) is elaborated, and the view expressed that desensitisers for the ordinary photographic effect are sensitisers for the Herschel effect and *vice versa*.

L. V. CHILTON.

**Herschel effect and failure of reciprocity law.** A. P. H. TRIVELLI and V. C. HALL (J. Franklin Inst., 1929, 208, 483—506).—The reciprocity failure is studied over a range of intensities of 2,000,000:1 for emulsions of pure silver bromide and of silver bromide. The pure bromide emulsion behaves abnormally, in a manner indicating that in its case the normal relation between grain size-frequency distribution and sensitivity is reversed. The Herschel effects obtained with these emulsions, employing (i) exposures to white light of high, medium, and low-intensity, and (ii) cross-exposures to infra-red light (Wratten filter no. 87), were studied in detail. Contrary to the results of Leszynski (B., 1927, 174) strong Herschel effects are obtained with very low-intensity white-light exposures; the effect varies with the intensity of the latter and is a maximum at a particular density, which density is lower the lower is the white-light intensity. The general behaviour of the two emulsions is the same, the magnitude of the Herschel effect depending on the density and the intensity of the first exposure and on the time of the infra-red exposure.

L. V. CHILTON.

**Quantum theory of X-ray exposures on photographic emulsions.** L. SILBERSTEIN and A. P. H. TRIVELLI (Phil. Mag., 1930, [vii], 9, 787—800).—One-grain-layer plates were prepared from an emulsion of silver bromide, exposed to X-rays and developed; the undeveloped grains were counted and classified. The results were in good agreement with the probability formula for a grain being affected by the exposure, each light-quantum hitting a silver halide grain making it developable. N. M. BLIGH.

**Photography of bodies radiating heat as a basis for photothermometry.** K. HENCKY and P. NEUBERT (Naturwiss., 1930, 18, 392—393).—The use of neocyanine as a sensitiser for photographic plates has made them so sensitive to the infra-red that it is now possible to photograph a body heated at 300—400° when visible light is excluded. It is therefore possible to determine the complete temperature fields of surfaces. The method is described. A. J. MEE.

**Photolysis of organic iodides; influence of temperature.** G. Emschwiller (Compt. rend., 1930, 190, 866—868).—The absorption constants (this vol., 554) increase with rise of temperature, the absorption curve of ethyl iodide being translated towards the longer wave-lengths by about 12 Å. per 10°. These variations do not explain completely the increased rates of photolysis at high temperatures, and it is shown that the coefficient of utilisation of light (*loc. cit.*) also increases with rise in temperature. The temperature coefficient is also influenced by the nature of the radiation and consequently by the material of which the apparatus is made.

J. GRANT.

**Absorption of hydrogen bromide by cinnamic acid in presence of ultra-violet light.** G. M. Woods and T. C. Poulter (Proc. Iowa Acad. Sci., 1928, 35, 217).—Some  $\alpha$ -bromophenylpropionic acid appeared to be formed. Hence the polarity of the double linking was slightly altered by the ultra-violet light.

CHEMICAL ABSTRACTS.

**Effect of X-irradiation on certain compounds.** W. STENSTROM (Radiol., 1929, 13, 437—440).—The phenol group of tyrosine in dilute aqueous or hydrochloric acid solution is affected; cystine is unchanged in 96 hrs. Changes in cholesterol depend on the solvent. Acetylene and propane are unchanged.

CHEMICAL ABSTRACTS.

**Photochemical preparation of optically active materials.** W. KUHN and E. KNOFF (Z. physikal. Chem., 1930, B, 7, 292—310; cf. A., 1929, 522).— $\alpha$ -Azidopropiondimethylamide shows an absorption band in the ultra-violet region at about 2900 Å. with a strong anisotropic factor of 0.02—0.03. When this compound in hexane solution is acted on by circularly polarised light of this wave-length, it undergoes decomposition of the azido-group, but one stereoisomeride is decomposed to a greater extent than the other. From the amount of nitrogen liberated it has been shown that the reaction approximately obeys Einstein's equivalence law. The reaction products are inactive, and the unchanged dimethylamide can be separated from them by distillation. When 40% of the original *r*-dimethylamide was decomposed, the remainder showed in a 10-cm. tube a rotation of +0.78° when it had been illuminated with *d*-circularly polarised light, and -1.04° when *l*-circularly polarised light was used. The order of magnitude of these effects is in agreement with those calculated theoretically. Only, however, at complete decomposition will the remaining dimethylamide consist of one active component only. The biological significance of these observations is discussed.

J. W. SMITH.

**Reactions between bromine and organic hydroxy acids.** I. Dark reaction. II. Photochemical

**reaction.** R. M. PURKAYASTHA and J. C. GHOSH (Z. physikal. Chem., 1930, B, 7, 276—284, 285—291).—I. The dark reactions between bromine and phenyl-lactic, lactic, and mandelic acids alone, or in the presence of sodium hydroxide, bromine ions, or an inorganic salt have been investigated. The experimental data are explainable on the supposition that bromine molecules are continuously activated and deactivated even in the dark by collision with solvent molecules, and that the concentration of active bromine molecules is proportional to the total bromine concentration. The anions of the organic hydroxy-acids are supposed to combine with the active bromine molecules.

II. The effects of acid and bromine concentrations and light intensity on the velocity of the photochemical reactions between bromine and organic hydroxy-acids have been investigated, and the quantum yields under various conditions calculated. The mechanisms of the dark and photochemical reactions appear to differ only in that active bromine molecules are responsible for the initiation of reaction chains in the former, whilst bromine atoms are principally responsible for them in the latter. J. W. SMITH.

**Photobromination of organic compounds having an ethylenic double linking.** A. BERTHOUD (Helv. Chim. Acta, 1930, 13, 385—391; cf. A., 1927, 528).—Photobromination experiments with cinnamic acid show that the intermediate substance ABr (where A is the acceptor) reacts, not only to form molecules of  $A_2Br_2$ , but also in the following ways:  $2ABr \rightarrow ABr_2 + A$  and  $2ABr \rightarrow 2A + Br_2$ . One of the products of the action of light on bromine and  $\alpha$ -phenylcinnamitrile dissolved in carbon tetrachloride is a substance having the composition and mol. wt. corresponding with  $C_{30}H_{11}N_2Br$ . The formation of this compound can be accounted for if it is assumed that the substances  $C_{15}H_{11}NBr$  and  $(C_{15}H_{11}NBr)_2$  are intermediate products.

O. J. WALKER.

**Action of irradiated substances.** O. RIED (Wien. klin. Woch., 1929, 42, 1105—1107; Chem. Zentr., 1930, i, 93).—The photo-activity of fats is increased if certain metals or metallic compounds are added before irradiation. The effect is parallel with the biological action. Certain organic substances such as trypanflavine and quinine also have an activating effect.

A. A. ELDRIDGE.

**Irradiation reaction of albumin.** B. RAJEWSKY (Strahlenther., 1929, 33, 362—374; Chem. Zentr., 1929, ii, 2978).—The mechanism of the coagulating effect of X-rays differs from that of ultra-violet light; the mechanisms are discussed.

A. A. ELDRIDGE.

**Magnesium carbonates. II. Normal magnesium carbonate.** H. MENZEL [with A. BRÜCKNER and H. SCHULZ (Z. Elektrochem., 1930, 36, 188—196)].—Normal magnesium carbonate pentahydrate when desiccated at the ordinary temperature loses water continuously, no carbon dioxide being lost even when only 1 mol. of water remains; the dehydration-time curve gives no indication of the formation of the trihydrate, and the X-ray diagram shows the gradual disappearance of the pentahydrate lattice, but no appearance of that of the trihydrate.

The trihydrate loses water more slowly, and its final composition approaches that of the basic carbonate,  $5MgO \cdot 4CO_2$ , but if the desiccation be conducted more rapidly by the aid of phosphorus pentoxide, its composition approaches that of a monohydrated normal carbonate, and simultaneously a new type of lattice structure appears. Thermal dehydration of the trihydrate in a current of air results in the formation of the monohydrate, which in turn decomposes with loss of carbon dioxide. By heating the trihydrate at  $320^\circ$  in an atmosphere of carbon dioxide nearly all the water is driven off, leaving the nearly pure anhydrous normal carbonate, which, however, is not a single substance physically. The monohydrated normal carbonate has been prepared in a pure state by dehydration of the trihydrate with boiling xylene.

H. F. GILLBE.

**Absorption of hydrogen by calcium and its alloys.** G. KASSNER and B. STEMPEL (Z. anorg. Chem., 1929, 181, 83—94).—At  $250^\circ$ , calcium filings quickly absorb hydrogen in amounts corresponding with the formula  $CaH_2$ . At higher temperatures absorption is slower probably owing to sintering of the hydride formed and at  $500^\circ$  conversion into the hydride is complete in 2—3 hrs. At  $800^\circ$ , the velocity of absorption becomes large again. The solubility of hydrogen in calcium hydride is small. The vapour-pressure curve between  $755^\circ$  and  $920^\circ$  can be represented by the equation  $\log p = -3475 + 0.005322/T$ . The vapour pressure is considerably higher than that measured by previous investigators and corresponds with the equation  $2CaH_2 \rightleftharpoons 2CaH + H_2$  and not with the equation  $2CaH \rightleftharpoons 2Ca + H_2$ . The heat of reaction calculated according to van't Hoff's equation has the value 24.8 kg.-cal. rising to 31.5 kg.-cal. at  $755^\circ$  and  $920^\circ$ , respectively, whilst the Nernst formula gives the value 22.6 kg.-cal. Calcium hydride in the form of water-clear, hexagonal prisms with superimposed rhombohedra has been prepared. The classification of the metal hydrides on the basis of the electromotive series is discussed.

L. S. THEOBALD.

**Hydrates of calcium carbonate.** F. KRAUSS and W. SCHRIEVER (Z. anorg. Chem., 1930, 188, 259—273).—Previous work on hydrates of calcium carbonate is fully reviewed. The hexahydrate may be prepared by adding 0.1N-sodium carbonate slowly to 0.1N-calcium chloride solution, both at  $0^\circ$ . The subsequent washing, drying, and examination of the compound must be carried out at a low temperature, since it decomposes at  $8^\circ$ . From experiments on the isobaric dehydration of the hexahydrate it is evident that a monohydrate also exists, and this compound has been prepared and examined. The monohydrate is very unstable, even when kept under water at  $0^\circ$ , and on decomposition yields calcite. Densities have been determined as follows: hexahydrate,  $d_4^{20}$  1.77; monohydrate,  $d_4^{20}$  1.99.

F. L. USHER.

**Dehydration of heulandite.** P. GAUBERT (Compt. rend., 1930, 190, 802—804).—Heulandite and Rinne's metaheulandite-I, which are identical in structure, lose water continuously on application of heat, and crystallographic examination of the changes in structure indicates that at least one other hydrate

(heulandite-*B*, identical with Rinne's metaheulandite-*II*) distinguished by definite physical properties and containing 2 mols. of water is produced. Heating at 245° for several days removes 9–10% of water from heulandite-*A* and destroys its power of adsorbing liquids in which it is immersed. Heulandite-*B* (*n*, in molten state, 1.508) also loses water if heated, and although its lattice-structure is not changed, it contracts to a greater extent than heulandite-*A*, and therefore loses its powers of immediate absorption of liquids. J. GRANT.

**Reactions occurring in thermal decomposition of solid barium azide.** P. GÜNTHER, K. ANDREEW, and A. RINGBOM (Z. Elektrochem., 1930, 36, 211–218).—The thermal decomposition of barium azide starts by the reaction  $\text{BaN}_6 = \text{Ba} + 3\text{N}_2$ , the metal formed then reacting with unchanged azide to give nitride,  $\text{Ba} + 2\text{BaN}_6 = \text{Ba}_3\text{N}_2 + 5\text{N}_2$ . It is this latter reaction which is responsible for the explosive character of the decomposition, the former reaction being only feebly exothermic. The final product of decomposition seems to be mixed crystals of nitride with 25% or more of free metal, although there is some evidence of the formation, as an intermediate product, of a nitrogen compound of barium of the hydrazide type. If the azide is decomposed slowly in presence of oxygen the metal nuclei are oxidised and little nitride is formed; in explosive decomposition, too, there is a comparatively low yield of nitride, the reaction with the metal nuclei being partly prevented by the violent dispersal of the reactants. R. CUTHILL.

**Action of silver nitrate on solutions of mercuric and potassium iodides.** J. GOLSE (Compt. rend., 1930, 190, 873–875).—The reaction of solid silver nitrate with an excess of a solution of potassium iodide saturated with mercuric iodide follows the equations  $\text{HgI}_2 \cdot 2\text{KI} + 2\text{AgNO}_3 = \text{HgI}_2 \cdot 2\text{AgI} + 2\text{KNO}_3$ , and  $2(\text{HgI}_2 \cdot \text{KI}) + 2\text{AgNO}_3 = \text{HgI}_2 \cdot 2\text{AgI} + \text{HgI}_2 + 2\text{KNO}_3$ , according as the iodo-mercuric reagent contains less or more than 7.50 g. of potassium iodide per 100 c.c., respectively. The bright yellow colloidal precipitate of silver mercuric iodide is decomposed in both cases as follows if the silver nitrate is present in excess:  $\text{HgI}_2 \cdot 2\text{AgI} + 2\text{AgNO}_3 = 4\text{AgI} + \text{Hg}(\text{NO}_3)_2$ . In addition, the reaction  $\text{HgI}_2 + 2\text{AgNO}_3 = 2\text{AgI} + \text{Hg}(\text{NO}_3)_2$ , which does not normally take place, occurs in the latter case owing to the state of fine division of the mercuric iodide. J. GRANT.

**Ammonia compounds of mercury.** E. WEITZ, K. BLASBERG, and E. WERNICKE (Z. anorg. Chem., 1930, 188, 344–356).—The conditions under which the mercury atom in different mercuric salts can take up more than 2 mols. of ammonia are discussed theoretically. The mercuric salts of oxyacids are able under suitable conditions to form tetrammine compounds, whereas the halides can take up only 2 mols. The absence of capacity to form tetrammine compounds is attributable to the same cause as inability to ionise. The following new compounds are described: tetramminomercuric nitrate, rhombic or hexagonal; tetramminomercuric perchlorate, needles; tetramminomercuric sulphate; diamminomercuric thiosulphate, needles; tetramminomercuric sulphite, needles; diamminomercuric sulphite. F. L. USHER.

**Compounds of mercury and of bismuth with 8-hydroxyquinoline.** L. DEDE and W. HESSLER (Z. anorg. Chem., 1930, 188, 325–343; cf. Berg, A., 1928, 39).—Whereas 8-hydroxyquinoline forms with most bi- and ter-valent metals inner complex phenoxides by co-ordinative saturation of the nitrogen, mercury and bismuth behave differently. By the interaction of equimolecular quantities of 8-hydroxyquinoline and mercuric chloride the compound  $(\text{C}_9\text{H}_6\text{ON})\text{Hg}_2\text{Cl}_2(\text{C}_9\text{H}_7\text{ON})$  is formed with the elimination of 1 mol. of hydrogen chloride. The production of an analogous compound from 8-methoxyquinoline shows that the metal in the former case is not linked through the hydroxylic oxygen. By the action of dilute hydrochloric acid on each of these compounds crystalline substances  $[\text{HgCl}_2(\text{C}_9\text{H}_8\text{ON})]\text{Cl}$  and  $[\text{HgCl}_2(\text{C}_{10}\text{H}_{10}\text{ON})]\text{Cl}$  are produced, in which the mercury is attached at the 5:7 positions. Bismuth trichloride reacts in an analogous manner, although bismuth nitrate in a solution of mannitol forms a complex phenoxide, and does not react with 8-methoxyquinoline. The following have been prepared in addition to the compounds specified above: dichloro-8-hydroxyquinoline mercuric chloride, m. p. 215°; dichloro-8-methoxyquinoline mercuric chloride, m. p. 224°; dichloro-8-hydroxyquinoline mercuric sulphate, m. p. 185°; dichloro-8-methoxyquinoline mercuric sulphate, m. p. 192°; trichlorodi-8-hydroxyquinolinium bismuth chloride;  $\text{BiCl}_3(\text{C}_9\text{H}_7\text{ON}, \text{HCl})_2 \cdot \text{EtOH}$ , m. p. 208°; trichlorodi-8-methoxyquinolinium bismuth chloride;  $\text{BiCl}_3(\text{C}_{10}\text{H}_9\text{ON}, \text{HCl})_2 \cdot \text{EtOH}$ , m. p. 112°; trichloro-8-hydroxyquinolinium bismuth sulphate, m. p. 201°; bismuth mononitrate-di-8-hydroxyquinolinolate, decomp. 246°. F. L. USHER.

**Behaviour of silver and of silver-copper alloys on ignition in oxygen and air.** J. A. A. LEROUX and E. RAUB (Z. anorg. Chem., 1930, 188, 205–231; cf. Steacie and Johnson, A., 1926, 1089).—When alloys of silver and copper are maintained at 600° or 750° in air or oxygen the copper is gradually oxidised and the silver acts as an oxygen carrier. The diffusion of oxygen is retarded at the crystal boundaries and by inter-granular accumulation of oxides. The product of oxidation is chiefly cuprous oxide in alloys poor in silver, but cupric oxide is formed as the main product when the silver content exceeds 75%. The rate of oxidation is dependent on the partial pressure of the oxygen. Microscopical examination of alloys with 10–80% Ag shows the presence of two oxidation layers, the outer of which is homogeneous and very impermeable to oxygen, the inner one being inhomogeneous. Loss of silver by heating is greater in oxygen than in air, and is due to the formation of a volatile oxide stable at high temperatures, probably  $\text{Ag}_2\text{O}$ . Figures showing the loss per cm.<sup>2</sup> at 600° and at 750° are given. F. L. USHER.

**Preparation of definitely oriented single crystals of metals.** R. GLOCKER and L. GRAF (Z. anorg. Chem., 1930, 188, 232–239).—A detailed description is given of a method of obtaining copper, silver, or gold, and mixed crystals of silver and gold, in single crystals 6 cm. long and 0.75 cm. in diameter. The direction of growth can be controlled by placing in the bottom of the crucible in which the fusion is

conducted a small single crystal having the required orientation and arranging that this crystal shall not be completely melted, although the rest of the contents are liquid. The resulting crystal has then the same orientation as the nucleus. Further proof has been afforded by this process that in one and the same temperature gradient growth is possible in all directions.

F. L. USHER.

**Introduction of hydrogen into the gold atom and similar experiments.** A. GASCHLER (Z. Elektrochem., 1930, 36, 257—259).—The formation of gold from mercury under the influence of positive rays from a hydrogen discharge tube (A., 1926, 656) has been confirmed, and the formation of xenon from iodine under similar conditions has been observed.

R. CUTHILL.

**Preparation of boron hydride.** XIII. A. STOCK, E. WIBERG, and H. MARTINI (Z. anorg. Chem., 1930, 188, 32—36; cf. A., 1929, 279).—Whilst technical iron boride and nickel boride do not react with hydrochloric acid, manganese boride does so and yields boron hydride corresponding with at most 3% of the boron present. Beryllium boride prepared from very pure metal is readily attacked by acid and possesses the advantage over magnesium boride of furnishing a gas free from silanes which are troublesome to remove. The yield of  $B_4H_{10}$  is the same as with the magnesium compound.

F. L. USHER.

**Anhydrous aluminium alums.** N. SCHISCHKIN (Z. anorg. Chem., 1930, 189, 289—296).—Anhydrous sodium, potassium, and ammonium alums, of the general formula  $MAI(SO_4)_2$ , have been obtained by adding hot concentrated sulphuric acid to a hot concentrated solution of aluminium and alkali sulphates. A crystalline precipitate separated out at 190—200°. This was filtered, washed with ice-cold water, and dried in a vacuum over sulphuric acid. The salts have  $d_4^{20}$  as follows: sodium 2.85, potassium 2.75, and ammonium 2.45. The potassium and ammonium salts form hexagonal plates which are probably short hexagonal prisms. The sodium salt forms plates of doubtful shape which display, in polarised light, the properties of biaxial crystals. The salts dissolve in water with great difficulty, but the process is hastened by heat or by the presence of acid, and the ordinary alums crystallise out from the solutions. The properties of anhydrous alums suggest that they are best represented by the formula  $M[Al(SO_4)_2]$ .

M. S. BURR.

**Acid clays of Japan.** T. OKUNO (Mem. Coll. Eng. Kyushu, 1930, 5, 171—225).—The acidity produced in solutions of various salts on shaking with Japanese acid clays has been investigated and adsorption isotherms have been determined for the latter. The author concludes that the acidity is due mainly to the hydrolysis of iron and aluminium salts. A classification of the clays on the basis of their adsorbing powers is given, and their compositions as found by spectral analysis are recorded. Applications to the purification of sugar and molasses are discussed.

C. W. GIBBY.

**Gallium sulphide.** A. BRUKL and G. ORTNER (Naturwiss., 1930, 18, 393).—If sulphur vapour is passed over metallic gallium heated at 1300° gallium

trisulphide,  $Ga_2S_3$ , is formed. It is yellow, and has m. p. about 1250°. By reduction with hydrogen at 400° a lower sulphide is formed: this can be separated from unchanged trisulphide by sublimation in hydrogen at 800°. The lower sulphide forms yellow crystals and has the formula  $GaS$ , m. p. 960°. By heating in a high vacuum to 700°, further decomposition takes place, and an easily volatile sublimate is formed on the cold part of the tube. This has the composition  $Ga_2S$ . It is greyish, and easily oxidised. Still further heating in a vacuum causes decomposition into metallic gallium and gallium trisulphide. The statement made by Nilson and Pettersson that gallium may sometimes be univalent is justified by these analyses.

A. J. MEE.

**Reaction of hydrogen bromide with silicon.** W. C. SCHUMB and R. C. YOUNG (J. Amer. Chem. Soc., 1930, 52, 1464—1469).—The reaction between powdered silicon and hydrogen bromide has been studied by a dynamic method at temperatures between 340° and 700°. At 360°, the product is a mixture of di-, tri-, and tetra-bromosilane, the respective b. p. being 64.0°, 111.8°, and 153.4°. Tri-bromosilane has f. p.  $-73 \pm 1^\circ$ . The reaction was very slow below 340° and the proportion of silicon tetrabromide increased with rise of temperature. The reaction probably involves the primary formation of silicon tetrabromide followed by reduction. Tri-bromosilane is decomposed into silicon tetrabromide, silicon, and hydrogen at 700°. J. G. A. GRIFFITHS.

**Higher and lower silicic acids of definite composition.** P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1930, 189, 168—173).—Vapour pressure-composition curves have been obtained for silica hydrates in a coarse state of division prepared by the slow hydrolysis of ethyl orthosilicate (cf. A., 1929, 1154). At 11° the existence of the compound  $2SiO_2 \cdot 5H_2O$  is indicated. By isothermal dehydration of metasilicic acid at higher temperatures a marked halt in pressure indicates the presence of the compound  $2SiO_2 \cdot H_2O$ , but isothermal dehydration of this compound at different temperatures gives no polysilicic acids still richer in silica. M. S. BURR.

**Silicic acids of definite composition. (Isolation,  $p$ - $t$  and  $t$ - $x$  diagrams).** P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1930, 189, 174—182).—With the help of  $p$ - $x$  curves (cf. preceding abstract) the conditions for the preparation of the following pure silica hydrates have been determined:  $SiO_2 \cdot 2H_2O$ ,  $2SiO_2 \cdot 3H_2O$ ,  $SiO_2 \cdot H_2O$ , and  $2SiO_2 \cdot H_2O$ . The  $p$ - $t$  curves of these compounds have been determined between 10° and 70° and are found to be reversible over a wide range of temperature, indicating that the hydrates possess a considerable degree of stability. On dehydrating, by rise of temperature at constant pressure, silica hydrate prepared as before (*loc. cit.*), the  $t$ - $x$  curve confirms the existence of the hydrates  $2SiO_2 \cdot 5H_2O$ ,  $SiO_2 \cdot 2H_2O$ ,  $2SiO_2 \cdot 3H_2O$ ,  $SiO_2 \cdot H_2O$ , and  $2SiO_2 \cdot H_2O$  previously indicated by the  $p$ - $x$  curve.

M. S. BURR.

**Germanium. III. Sulpho- and per-germanates.** R. SCHWARZ and H. GIESE (Ber., 1930, 63, [B], 778—782; cf. A., 1929, 1407).—The salts,



$K_2GeS_7 \cdot 9H_2O$  and  $Na_4GeS_7 \cdot 9H_2O$ , are prepared by adding freshly-precipitated germanium sulphide, washed successively with alcohol and ether saturated with hydrogen sulphide, to a concentrated aqueous solution of the necessary alkali sulphide and pouring the mixture into acetone; the oil which is precipitated becomes crystalline when preserved over phosphoric oxide in an atmosphere of hydrogen sulphide. The alkali sulphogermanates rapidly decompose when exposed to air. The silver salt, obtained from the solution of germanium sulphide in sodium sulphide, has the composition  $GeS_2 \cdot 4Ag_2S$ .

Addition of 30% hydrogen peroxide to a concentrated solution of potassium metagermanate at 0° causes slow precipitation of the *potassium* salt,  $K_2Ge_2O_7 \cdot 4H_2O$ . The *sodium* compound,  $Na_2Ge_2O_7 \cdot 4H_2O$ , is analogously prepared; addition of much alcohol to the filtrate from this compound precipitates a second salt,  $Na_2GeO_5 \cdot 4H_2O$ . The substances decompose slowly at the ordinary temperature. Similar attempts to obtain per-plumbates were unsuccessful. The tendency of germanium to form per-salts appears more pronounced than that of other members of its group and to ally it more closely to the elements of the fourth sub-group.

H. WREN.

**Germanium. IV. Systems  $Na_2GeO_3$ - $Na_2SiO_3$  and  $K_2GeO_3$ - $GeO_2$ .** R. SCHWARZ and M. LEWINSOHN (Ber., 1930, 63, [B], 783—787; cf. preceding abstract).—Sodium metagermanate, m. p. 1078°, and sodium metasilicate m. p. 1087°, appear to form a continuous series of mixed crystals the m. p. of which differ little from those of the individual salts. Although the determination of the solidus curve involves a little uncertainty, the two graphs appear to meet at a point corresponding with the molar composition  $Na_2GeO_3 : Na_2SiO_3$ .

Contrary to observations with germanium oxide and sodium or lithium oxide, mixtures of germanium oxide with potassium oxide crystallise readily except in the region corresponding with the digermanate so that thermal analysis is readily effected. The existence of *potassium metagermanate*, m. p. 823°, *digermanate*, m. p. 783°, and *tetragermanate*, m. p. 1033°, is established; a trigermanate does not appear to exist, but the di- and tetra-germanates probably form mixed crystals. Germanium oxide has m. p. 1126°. The results of thermal analysis are confirmed by measurements of density.

The alkali germanates show very close resemblance to the alkali silicates; the relationships are still obvious when the oxygen is replaced by the NH group, although the germanium compounds are marked by greater instability. With the sulphur compounds the relationship of germanium to silicon disappears and is replaced by that to tin.

H. WREN.

[Lead hydride.] F. PANETH (Z. physikal. Chem., 1930, B, 7, 155—156; cf. A., 1929, 788).—The conclusions of Schultze and Müller (this vol., 302), regarding the non-existence of free methyl are not considered to be justified by their experiments and are not in agreement with the positive evidence already recorded.

F. L. USHER.

**Preparation of pure paranitrogen.** E. JUSTI (Naturwiss., 1930, 18, 393—394).—The effect noticed in the preparation of paranitrogen does not occur if the nitrogen is subjected to double fractional distillation and is specially purified (cf. this vol., 524).

A. J. MEE.

**Colour of arsenic trisulphide.** H. B. WEISER (J. Physical Chem., 1930, 34, 1021—1032).—Precipitated and dried arsenic trisulphide varies in colour continuously from yellow through orange to red, according to the conditions of precipitation. The lighter shades are obtained when hydrogen sulphide acts on a solution of arsenious oxide or an arsenite containing sufficient hydrochloric acid or other electrolyte to bring about immediate precipitation. The darker shades result when arsenic trisulphide sol is subsequently coagulated by excess of an electrolyte. The red colour of the sulphide is not due to allotropy (Winter, A., 1905, ii, 245), to the presence of a red thioarsenite (Semler, A., 1924, ii, 532), or to the sulphide  $As_2S_2$  (Bhatnagar and Rao, A., 1923, ii, 756). The changes in colour are due to changes in the physical nature of the precipitated salt. Precipitation in the presence of foreign electrolytes yields a flocculent precipitate of large particles or loose aggregates which disintegrate on drying to an impalpable yellow or orange-yellow powder. Coagulation of the sol gives a gelatinous precipitate consisting of aggregates of ultramicroscopic particles which, on drying, coagulate to a red glass. The differences in structure are illustrated by photomicrographs. Disintegration of the red glassy mass by grinding or by heating below the sintering temperature gives the yellow colour, whilst heating the yellow sulphide at about 175° causes sintering, contraction, and a change in colour to orange or brown, according to the temperature and to the time of heating. The red sulphide is stable in the dark and when dry. Light and moisture together cause a superficial chemical disintegration, coating the red sulphide with a yellow film of sulphur and sulphide.

L. S. THEOBALD.

**Action of hydrogen sulphide on solutions of arsenic acid.** F. FOERSTER [with G. PRESSRICH and W. REUSS] (Z. anorg. Chem., 1930, 188, 90—113; cf. McCay and Foster, A., 1904, ii, 253).—Sufficiently rapid introduction of hydrogen sulphide into pure arsenic acid solutions always gives rise to arsenic pentasulphide, as stated by McCay and Foster. The precipitation of the pentasulphide is progressively inhibited by hydrochloric acid at concentrations from  $N$  to  $4N$ , but is promoted when the concentration exceeds  $6N$ . If the addition of hydrogen sulphide is interrupted before all the arsenic acid is precipitated the solution contains monothioarsenic acid in amount corresponding with the incompleteness of precipitation, and this acid is the primary product of the reaction whether hydrochloric acid is present or not. From solutions of pure arsenic acid the pentasulphide separates in a highly disperse form which adsorbs arsenic acid so strongly that the last traces of the latter react with great difficulty at the ordinary temperature, although this is not the case at 40°. In the presence of salts of multivalent cations which by hydrolysis yield colloidal hydroxides the arsenic

pentasulphide is flocculated, but the completion of the reaction is greatly delayed owing to adsorption of the arsenic acid, especially at low temperatures.

F. L. USHER.

**Purity of oxygen from electrolytic source.** L. J. P. KEFFLER (Rec. trav. chim., 1930, 49, 425—427).—Electrolytic oxygen supplied by the British Oxygen Co. can be used without any preliminary treatment in bomb calorimetry when an accuracy of 0.1% is sufficient. When higher accuracy is required combustible impurities in the oxygen should be removed by preheating it before each experiment, or the exact impurity content determined in preliminary experiments.

O. J. WALKER.

**Laboratory preparation of hydrogen sulphide.** M. ABBAD (Anal. Fis. Quim., 1930, 28, 264—269).—For reasons of convenience, economy, and purity of the product, the reaction between aluminium sulphide and water is recommended for the preparation of hydrogen sulphide on the laboratory scale. A convenient form of apparatus, and the preparation of the aluminium sulphide by Moissan's method, are described.

H. F. GILLBE.

**Oxidation of thiocyanic acid and ammonium thiocyanate to hydrocyanic acid by atmospheric oxygen.** W. GLUUD, K. KELLER, and W. KLEMP (Z. anorg. Chem., 1930, 188, 37—46).—Thiocyanic acid and ammonium thiocyanate are volatilised unchanged when their aqueous solutions are dropped into a vessel preheated at 350°, or when sprayed with hot air or superheated steam. Both substances are readily oxidised in the vapour phase by atmospheric oxygen at 450—750° to hydrocyanic acid and sulphur dioxide, the reaction occurring at the lower temperature in the presence of contact materials such as porcelain or aluminium. The yield is about 80% of the theoretical. Gaseous hydrogen cyanide is fairly stable in excess of air up to 750°, and its stability is increased in the presence of sulphur dioxide.

F. L. USHER.

**Action of sulphur dioxide on natural phosphates.** G. CALCAGNI.—See B., 1930, 458.

**Isomorphism between hexacarbamidochromic permanganate, perchlorate, fluoborate, fluoro-sulphonate, and iodide.** E. WILKE-DÖRFURT and R. PFAU (Z. Elektrochem., 1930, 36, 118—122).—By adding a solution containing permanganate and perchlorate ions or permanganate and fluoborate ions in various proportions to a saturated aqueous solution of hexacarbamidochromic chloride a range of mixed crystals of the complex permanganate and perchlorate and permanganate and fluoborate, respectively, have been prepared. Mixed crystals of hexacarbamidochromic iodide and perchlorate have been prepared both by precipitation and by simultaneous crystallisation, the solution-solid composition curves being of the same form, irrespective of the method employed; the crystals obtained by precipitation, however, contain less iodide than those formed by crystallisation from a solution of the same composition. Mixed crystals of fluoborate and iodide, fluosulphonate and iodide, and fluoborate and fluoro-sulphonate have also been prepared.

H. F. GILLBE.

**Sodium tungstates stable in aqueous solution.** A. LOTTERMOSER, W. RIEDEL, and O. BRETSCHNEIDER (Z. Elektrochem., 1930, 36, 183—187).—Conductimetric titration of aqueous solutions of sodium tungstate with hydrochloric acid demonstrates the existence of normal, meta-, and para-tungstates, whilst comparative conductivity measurements with solutions of mixtures having the theoretical composition of the three salts indicate that other types of tungstate do not exist. The salts  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$  (or  $3\text{Na}_2\text{O} \cdot 7\text{WO}_3 \cdot 16\text{H}_2\text{O}$ ), and  $\text{Na}_2\text{O} \cdot 4\text{WO}_3 \cdot 10\text{H}_2\text{O}$  have been prepared by evaporation of solutions of the appropriate composition, but neither the di- nor the tri-tungstate could be obtained.

H. F. GILLBE.

**Oxidations with fluorine. XV. Rôle of the labile peroxide from sulphuric acid in the preparation of persulphate by means of fluorine.** F. FICHTER and A. GOLDACH (Helv. Chim. Acta, 1930, 13, 378—385; cf. this vol., 435).—In the action of fluorine on saturated potassium hydrogen sulphate solution the first product is sulphur tetroxide  $\text{SO}_4$  (cf. A., 1927, 741), which is obtained in appreciable concentration only when the temperature is low. The tetroxide then oxidises the hydrogen sulphate to persulphate:  $2\text{KHSO}_4 + \text{SO}_4 = \text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{SO}_4$ . This reaction is favoured by rise of temperature. A maximum yield of persulphate is obtained at about 40°. Measurements of the oxidation potential in solutions of sulphur tetroxide are given.

O. J. WALKER.

**Manganites, manganates, and permanganates. II.** A. S. COCȘINISCHI (Z. anorg. Chem., 1930, 189, 283—286; cf. this vol., 439).—By heating sodium permanganate,  $\text{NaMnO}_4 \cdot 3\text{H}_2\text{O}$ , a residue of the approximate composition  $2\text{MnO}_2 \cdot \text{Na}_2\text{O}$  is obtained. By fusing together sodium manganate and sodium chloride at 600—1100° manganites are obtained of which the sodium content decreases linearly with rise in temperature. By treatment with water, alkali is removed and water takes its place. This water can be removed at 200° and its presence may be due to the formation of polymanganic acids.

M. S. BURR.

**Recovery of iodine as sodium iodide from waste iodine solutions.** W. D. BONNER and K. MASAKI (J. Chem. Educ., 1930, 7, 616—617).—The iodine, precipitated with chlorine, is repeatedly dissolved in sulphurous acid and reprecipitated with chlorine; the solution in sulphurous acid is then neutralised with calcium hydroxide (with long stirring), filtered, and alkalinity (determined by addition of iodate and titration with acid) removed by addition of a further quantity of the original solution. After addition of barium iodide until no further turbidity is produced the total iodide is determined; a calculated quantity of sodium or potassium carbonate is added, the solution being then filtered and evaporated.

CHEMICAL ABSTRACTS.

**Formation of iodates from iodides by molecular oxygen.** F. A. HENGLEIN and L. TEICHMANN (Z. anorg. Chem., 1930, 188, 138—142).—Potassium iodide when heated with oxygen undergoes no change at pressures below 5 atm., although at and above 10 atm. partial transformation into iodate occurs. Equal

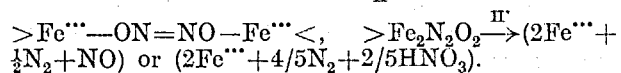
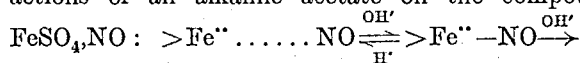
weights of potassium iodide and potassium hydroxide heated for 3 hrs. at temperatures between 300° and 500° give rise to good yields of iodate accompanied by periodate. With excess (3:1) of potassium hydroxide the oxidation is still further promoted. complete transformation having been observed in several experiments. The pressures used varied from 1 to 20 atm. The yield of periodate falls with rising temperature. The significance of the reaction in biological processes is discussed. F. L. USHER.

**Formation of the yellow hydrated iron oxide from iron sulphides.** V. RÖDT (Rec. trav. chim., 1930, 49, 441—456).—Both ferrous and ferric sulphides undergo atmospheric oxidation in the moist state and give the yellow  $\gamma$ -form of hydrated ferric oxide,  $\text{FeO}_2\text{H}$ . If particular care is taken in the preparation of the sulphides the whole of the sulphur separates as such during the oxidation. The dehydration curves of the yellow hydrated oxide show a sharp break at 210° with rapid and at 180° with slow rise of temperature, and at these temperatures magnetic  $\gamma$ -ferric oxide is formed; this has a great tendency to adsorb water. It is difficult, therefore, to obtain the yellow basic oxide with its theoretical water content. O. J. WALKER.

**Oxide hydrates. XXIII. Mode of combination of water in naturally occurring and artificially prepared hydrated ferric oxides.** G. F. HÜTTIG and A. ZÖRNER (Z. Elektrochem., 1930, 36, 259—268; cf. this vol., 543).—The isobaric dehydration of various naturally occurring and artificially prepared ferric oxides has been carried out, and some of the products of dehydration have been examined by X-ray methods. The results show that as amorphous hydrated ferric oxide loses water it passes by a continuous transition through hydrohæmatite to hæmatite. The free energy appears to be minimal, however, for a hydrohæmatite of the approximate composition  $\text{Fe}_2\text{O}_3 \cdot 0.7\text{H}_2\text{O}$ , so that hæmatite, as well as the amorphous hydrated oxide, which has the greatest free energy content of all the hydrates, tend by ageing to pass spontaneously into this hydrate. Hydrohæmatites apparently consist of the hæmatite lattice with a variable water content. In respect of their free energy content the limonites are intermediate between the above hydrohæmatite and goethite, which has the least free energy of all the hydrates. In the dehydration of limonites, water in excess of the amount required by the formula  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  is given off without the appearance of a second solid phase, apparently being combined zeolitically, but on further dehydration hydrohæmatite starts to be formed, and when the composition corresponds approximately with the formula  $\text{Fe}_2\text{O}_3 \cdot 0.4\text{H}_2\text{O}$  all the  $\alpha$ -monohydrate has disappeared. Atmospheric oxidation of the precipitate obtained by adding alkali to a ferrous salt solution gives limonite directly. R. CUTHILL.

**Reactions between ferrous salts and nitric oxide. II.** L. CAMBI and A. CAGNASSO (Atti R. Accad. Lincei, 1930, [vi], 11, 133—139; cf. A., 1929, 780).—The action of nitric oxide at 0° on aqueous suspensions of ferrous carbonate, ferrous hydrogen phosphate, and ferrous acetate indicates that this

gas is able to combine with easily oxidisable ferrous salts possessing anions of low electroaffinity. The chief products are nitroso-salts containing an NO-radical with properties analogous to a halogen atom. Its properties differ from those of a hyponitrite, into which it is transformed by decomposition with a silver salt in neutral or slightly acid solution. The following scheme is suggested for the successive actions of an alkaline acetate on the compound



F. G. TRYHORN.

**Derivatives of iron carbonyl.** V. W. HIEBER, F. SONNENKALB, and E. BECKER (Ber., 1930, 63, [B], 973—986; cf. A., 1929, 412).—Prolonged action of ammonia on iron pentacarbonyl at 65° leads to the production, without more marked evolution of carbon monoxide than in a blank experiment, of the compound  $\text{Fe}(\text{CO})_5\text{NH}_3$ , decomposed by dilute sulphuric acid into tetracarbonyl and ferrous salt. Under similar conditions except that a little pyridine is present and the reaction is less prolonged, the substance  $\text{Fe}(\text{CO})_3\text{NH}_3$  results, whereas in presence of a greater proportion of the organic bases the product approximates more or less closely to the composition,  $\text{Fe}_2(\text{CO})_{4-2} \cdot 4\text{NH}_3 \cdot \text{C}_5\text{H}_5\text{N}$ . Iron pentacarbonyl and pyridine at 80—85° evolve 2—2.2 mols. of carbon monoxide and yield the compound  $\text{Fe}_2(\text{CO})_{4-3}\text{C}_5\text{H}_5\text{N}$ , which decomposes above 100° with loss of carbon monoxide and pyridine. The substance is decomposed by ammonia at 80° into a compound which cannot be freed completely from pyridine, but appears to have essentially the composition  $\text{Fe}(\text{CO})_2\text{NH}_3$ , whereas with hydrazine it yields the substance  $\text{Fe}_2(\text{CO})_{4-5} \cdot 5-6\text{N}_2\text{H}_4$ . Vigorous reaction occurs with nitric oxide, which first substitutes the carbon monoxide and subsequently oxidises the iron. Bromine vigorously attacks the pyridine carbonyl with quantitative evolution of carbon monoxide, whereas iodine at -21° gives iron dicarbonyl dipyridine iodide, which loses carbon monoxide quantitatively at a higher temperature. Cyanogen at 60—65° gives the substance  $\text{Fe}(\text{CO})_2(\text{CN})_2 \cdot \text{C}_5\text{H}_5\text{N}$ .

The compound  $\text{Fe}_2(\text{CO})_5\text{en}_2$  evolves carbon monoxide quantitatively when treated with a large excess of bromine. In an indifferent medium iodine liberates about 2 mols. of carbon monoxide as a maximum, whereas in pyridine all the carbon monoxide is ultimately displaced. The compound  $\text{Fe}(\text{CO})_3\text{NH}_3$  is decomposed by warm, dilute sulphuric acid with evolution of carbon monoxide and hydrogen, whereas the substance  $\text{Fe}_2(\text{CO})_{4-3}\text{C}_5\text{H}_5\text{N}$  yields carbon monoxide and dioxide and hydrogen; with cold, dilute sulphuric acid the last-named substance yields the compound  $\text{Fe}_3(\text{CO})_7 \cdot \text{C}_5\text{H}_5\text{N} \cdot 3\text{H}_2\text{O}$ , whilst concentrated hydrochloric acid causes evolution of hydrogen. With hydrogen chloride, concentrated or dilute sulphuric, acid and saturated hydrochloric acid, the amounts of carbon monoxide and hydrogen evolved from the substance  $\text{Fe}_2(\text{CO})_5\text{en}_2$  vary greatly with the experimental conditions. Thermal decomposition of the pyridine and ethylenediamine carbonyls does not

lead to quantitative evolution of carbon monoxide on account of the catalytically accelerated action  $2\text{CO}=\text{C}+\text{CO}_2$  and the subsequent changes,  $3\text{Fe}+2\text{CO}=\text{Fe}_3\text{C}+\text{CO}_2$  and  $\text{Fe}+\text{CO}_2=\text{FeO}+\text{CO}$ . The experiments afford further evidence of the presence of true carbonyl compounds containing the iron-carbon linking.

H. WREN.

**Occurrence of iron pentacarbonyl in coal gas stored under pressure for 30 years.** J. A. N. FRIEND and R. H. VALLANCE (J.C.S., 1930, 718—720).—Coal gas, originally free from iron carbonyl, was stored under 50—80 atm. pressure at the ordinary temperature in a steel cylinder for 30 years. Considerable quantities of iron pentacarbonyl have now been isolated from the gas, which still contains carbon monoxide.

J. G. A. GRIFFITHS.

**Quantitative analysis by X-ray spectroscopy.** C. E. EDDY and T. H. LABY (Proc. Roy. Soc., 1930, A, 127, 20—42; cf. Eddy, Laby, and Turner, A., 1929, 867).—Previous work (*loc. cit.*) on the X-ray emission spectra method has been extended and developed as a method of quantitative analysis. Details are given of the experimental arrangements, the X-ray tube, and the method of calibration of the photographic films. A number of factors, *e.g.*, line intensity and applied potential, non-homogeneous targets, comparison of lines of different wave-length, are discussed and tested by experiment. The method has been applied to several alloys of copper and zinc, tin-cadmium, lead-bismuth, zinc-copper-tin, and tin-zinc. With alloys of nearly equal atomic number the method has an accuracy of 0.5%; successful preliminary experiments have also been made with alloys of elements of unequal atomic number. The results obtained are not in agreement with those of Coster and Nishina (A., 1925, ii, 324), who found that the presence of a third element affected the values, or with those of Günther and Stranski (cf. A., 1926, 111), who found that the ratio of the intensities of two lines of a given element was dependent on their absolute intensities. A comparison of the X-ray emission method with other methods of spectral analysis is made. The former is extremely useful in testing the purity of metals to be used for the accurate determination of their physical properties.

L. L. BIRUMSHAW.

**Application of the Tyndall effect to analysis.** J. ERDÖS (Z. anal. Chem., 1930, 80, 122—127).—A review of recent literature describing the use of nephelometry in organic analysis with a description of the chromophotometer of Plesch as modified by Rusznyák (Biochem. Z., 1922, 133, 365; A., 1923, ii, 891).

A. R. POWELL.

**Application of gravimetric titrations to micro-analytical determinations.** B. ORMONT (Z. anal. Chem., 1930, 80, 200—203; cf. A., 1929, 41).—The subject is discussed, and the necessity for further work is emphasised.

H. F. HARWOOD.

**Evaluation of complex and catalytic reactions in analytical chemistry.** F. FEIGL (Chem. Weekblad., 1930, 27, 110—114).—A description is given of various analytical processes which involve the formation of complex compounds such as the double

cyanides and the compounds of metals with oximes. The application of catalytic reactions, *e.g.*, the catalytic acceleration by sulphides of the reaction between iodine and sodium azide, to the detection of small quantities of substances is also described.

H. F. GILLBE.

**Application of azeotropism to chemical analysis.** M. LECAT (Bull. Acad. Roy. Belg., 1929, [v], 15, 1073—1091, and Ann. Soc. Sci. Bruxelles, 1930, 50, 18—21).—A volatile organic substance of known properties is added to the substance to be identified. The degree of azeotropism is measured by the difference between the b. p. of the binary azeotropic mixture and of one of the components; tables are given by which the type of unknown substance can be identified. The tables contain data for the most suitable substances to be added, the unknown substance having b. p. approximately 80°, 100°, 125°, 150°, 175°, 200°, and 225°; the limits of the degree of azeotropism to be expected with different types of compounds (hydrocarbon, alcohol, ester, ketone) are recorded. Under the most unfavourable conditions it is necessary to examine three separate binary systems before identification is complete. The method is limited to substances volatile without decomposition under ordinary pressure. Only 5—20 g. of the unknown substance are needed, and the maximum time necessary for examination is 4—5 hrs. Although it is desirable to use pure substances, the presence of minor impurities does not seriously interfere with the method.

J. O. CUTTER.

**Couples in the titration of acids and bases.** M. L. HOLT and L. KAHLBERG (Amer. Electrochem. Soc., May, 1930. Advance copy, 19 pp.; cf. A., 1929, 1255).—Of a number of metals examined, platinised platinum, tungsten, antimony, and molybdenum give the greatest and most abrupt changes of single potential at the end-point in the titration of 0.1N-hydrochloric acid with 0.1N-sodium hydroxide. The end-point can be accurately determined from measurements of the *E.M.F.* developed between such an "indicator" electrode and a reference electrode consisting of a metal which is unattacked by the solution and exhibits only a very small change of potential at the end-point. The most satisfactory couples were found to be tungsten-graphite, antimony-graphite, and tungsten-silver. These couples also give good results in the titration of hydrochloric acid with ammonia and the alkylamines, for which the hydrogen electrode is not very trustworthy. The tungsten-graphite couple, which is probably the best combination of all, can also be used for the titration of formic, acetic, and nitric acids with sodium hydroxide. Numerous titration curves are given, including some obtained with the hydrogen electrode for comparison. The method of preparing and setting up the electrodes and of carrying out the titrations is explained, and the significance of the observed potential changes is discussed. It is found that addition of a little quinhydrone to the solution increases the sensitivity of the tungsten-graphite couple.

H. J. T. ELLINGHAM.

**Analysis by means of specific gravity and refractivity determinations.** II. Solutions of

**hydrogen peroxide in water.** N. SCHOORL (Pharm. Weekblad, 1930, 67, 390—392).—Data are given for these physical constants and their temperature moduli. Both constants are linear functions of the hydrogen peroxide content between 0 and 30%;  $d_4^{20}$  increases by 0.0037 and  $n_D^{20}$  by 0.00065 for 1% increase; the latter is difficult to determine because of evolution of oxygen, and the variation with temperature is greater.

S. I. LEVY.

**Chlorometric, bromometric, and iodometric determination of available chlorine in hypochlorite solutions and bleaching powder.** II. H. DRTZ and R. MAY.—See B., 1930, 417.

**Determinations of chlorides in salt brines.** S. L. NEAVE.—See B., 1930, 417.

**Volumetric determination of iodine in soluble iodides.** H. SZANCER (Arch. Pharm., 1930, 268, 263—264).—The iodide is decomposed by dilute sulphuric acid and potassium nitrite in a closed vessel. Excess of sodium hydrogen carbonate is added and the iodine titrated with thiosulphate in presence of potassium iodide. Accurate results are obtained in presence of chloride or bromide. H. E. F. NOTTON.

**Volumetric determination of fluorine by the use of ferric chloride.** J. G. FAIRCHILD (J. Wash. Acad. Sci., 1930, 20, 141—146).—In the volumetric determination of fluorine by means of the reaction  $\text{FeCl}_3 + 3\text{NaF} = \text{FeF}_3 + 3\text{NaCl}$ , the excess of ferric chloride being titrated with iodine, the conditions for determining 0.005—0.060 g. of fluorine are: potassium iodide 0.5 g., sodium chloride 2 g., zinc chloride equivalent to 0.05 g. of zinc oxide; time before titration 30 min., during which the solution should be kept within 1° of 38°. As little as 0.005 g. can be determined accurately. The ferric chloride should contain hydrochloric acid in the ratio of 1 mol. to 0.32 mol. of ferric chloride. The application of the method to phosphate rock is described.

C. W. GIBBY.

**Rôle of silica in the decomposition of fluorides.** P. FUCHS (Chem. Erde, 1930, 5, 99—105).—In the Berzelius method for the decomposition of insoluble fluorides, e.g., fluor spar, by fusion with alkali carbonate mixed with silica, the part played by the silica is in the formation of a double sodium calcium silicate. The carbonate and silica may be fused beforehand to avoid frothing in the actual analysis, and the addition of sodium hydroxide is advantageous.

L. J. SPENCER.

**Iodometric analysis of a mixture of hypsulphite, sulphite, and thiosulphate.** R. WOLLAK.—See B., 1930, 417.

**Decomposition products of sodium thiosulphate solution.** E. SCHULEK (Z. anal. Chem., 1930, 80, 190—191; cf. A., 1926, 1017).—The author claims to have proved experimentally the formation of hydrogen sulphide as a result of bacterial action in sodium thiosulphate solutions on preservation.

H. F. HARWOOD.

**Potentiometric studies of reduction. I. Determination of selenium, tellurium, and gold.** K. SOMEYA (Sci. Rep. Tôhoku, 1930, 19, 123—153).—Potassium iodide and sodium thiosulphate are feeble

reducing agents which are reasonably stable in air, thereby possessing an advantage over stronger agents which are unstable in air. The titration apparatus can be simpler; with selenium, tellurium, and gold the accuracy of determination is at least as good as that of more complicated methods.

W. E. DOWNEY.

**Electrometric analysis of nitrating acid.** E. MÜLLER and H. KOGERT (Z. anorg. Chem., 1930, 188, 60—71).—Technical nitrating acid can be analysed rapidly by conductometric titration of the diluted acid with a solution of lead nitrate. A second method has also been devised in which first one portion of the diluted acid is treated with lead carbonate in excess, and the amount of lead in solution (equivalent to the nitric acid) is determined potentiometrically by titration with ferrocyanide. In a second portion the sulphuric acid is determined by adding lead nitrate solution in excess and titrating the excess of lead as before.

F. L. USHER.

**Detection of certain anions.** P. AGOSTINI and R. ABBATE (Annali Chim. Appl., 1930, 20, 112—117).—The tests given, which make use largely of organic reagents and are based on reactions not commonly employed, allow of the detection of the principal anions. In particular, ready methods are given for detecting nitrates in presence of nitrites, ferrocyanides in presence of thiocyanates, phosphates in presence of arsenates, and sulphites, thiosulphates, and sulphides when present together. T. H. PORE.

**Determination of nitrates by the Kjeldahl method.** P. H. CARTER (Chemist-Analyst, 1930, 19, No. 2, 15).—In modifying the Kjeldahl method to include nitrates 5 c.c. of sulphuric acid are added with the salicylic acid, the remainder of the sulphuric acid being added after some time.

CHEMICAL ABSTRACTS.

**Micro-colorimetry. II. Determination of phosphorus: molybdic acid-stannous chloride reagent.** T. KUTTNER and L. LICHTENSTEIN (J. Biol. Chem., 1930, 86, 671—676).—Further technical notes on the method already described (A., 1928, 336) are given.

C. R. HARRINGTON.

**Determination of hypophosphorous, phosphoric, and glycerophosphoric acids in pharmaceutical mixtures of their salts.** F. E. RAURICH.—See B., 1930, 440.

**Colorimetric determination of phosphoric and arsenic acids.** R. ZINZADZE (Z. Pflanz. Düng., 1930, 16A, 129—184).—The intensity of the blue colour produced by the reduction of phosphomolybdate solutions depends on the proportion of reducing agent present, reaching a maximum and subsequently declining with excess of reducing agent. A solution of pure molybdenum blue is prepared by dissolving 3 g. of pure molybdenum trioxide in 50 c.c. of concentrated sulphuric acid heated to fuming point. When cool the solution is poured into 50 c.c. of distilled water and without further cooling is reduced by the addition of 0.15 g. of finely powdered molybdenum. Complete reduction is indicated after a few minutes' heating when 2.5 c.c. of the reagent are required for the

decolorisation of 0.2 c.c. of *N*-potassium permanganate solution. The reagent so prepared is decolorised by dilution with approximately five times its volume of water. Similar dilution in the presence of phosphoric or arsenic acids results in a blue coloration proportional, in intensity, to the amounts of these acids present, and utilisable for their determination in solutions containing 0.001—1.0 mg./c.c. The reagent retains its colour intensity indefinitely and the test colour with phosphates is constant for 7—10 days. The same colour intensity is produced by equivalent amounts of phosphoric and arsenic acids and analyses of mixed solutions are thus possible. The accuracy of the method is influenced by the presence of other substances (including silica) in quantities averaging 500 times that of the phosphate. Details for the preparation of solutions for the analysis of soils, organic material, plant ash, etc. are given. Oxidising and reducing agents must be eliminated before analysis.

A. G. POLLARD.

**Sources of error in organic elementary analysis. IV. Copper oxide and lead chromate.** J. LINDNER [with F. HERNLER] (Ber., 1930, 63, [B], 949—959; cf. A., 1927, 66, 166, 269).—The possibility of absorption of carbon dioxide by traces of alkali present in copper oxide can be obviated by soaking the material in a solution of chromium tri-oxide to which sufficient ammonia has been added to form ammonium chromate. Thorough penetration of the solution into the oxide is effected by repeated evacuation of the containing vessel. The product is subsequently dried and strongly ignited. Almost complete removal of carbon dioxide from copper oxide or lead chromate is most rapidly effected by ignition of the material in a crucible, but the method is subject to the danger of absorption of carbon from reducing gases; copper oxide coated with molten lead chromate is particularly liable to this change. The minimum weight of carbon dioxide evolved from 100 g. of copper oxide per hour is 0.001 mg.; with lead chromate the minimum is appreciably greater. The period of ignition necessary to attain this value varies very greatly. Apparently, therefore, a platinum contact is superior to copper oxide or lead chromate, but the errors involved with the last-named substances are outweighed by those incident to the measurement of the products of combustion and, further, subsidiary aids are required with the platinum process which themselves introduce similar sources of error.

H. WREN.

**Potentiometric determination of alkali sulphides.** G. SCAGLIARINI and P. PRATESI (Atti R. Accad. Lincei, 1930, [vi], 11, 193—196).—Electrometric titrations of alkali sulphide solutions with 0.1*N*-sodium nitroprusside solutions have been made, using cells of the type  $\text{Ag}, \text{Ag}_2\text{S} | \text{Na}_2\text{S} - \text{KCl} - \text{Hg}_2\text{Cl}_2, \text{Hg}$ . A sharp fall of potential is observed at the point of equivalence of the sulphide and nitroprusside solutions. The results agree excellently with those obtained by the iodometric method, and have the advantage of being uninfluenced by the presence of alkaline chlorides, sulphates, nitrates, silicates, and hydrogen carbonates, provided too high a degree of alkalinity is avoided.

F. G. TRYHORN.

**Sodium oxalate as a standard in volumetric analysis.** ANON. (U.S. Bur. Stand., 1930, Circ. 381, 9 pp.).—Sodium oxalate is very suitable as a primary volumetric standard as the salt is readily obtained pure, is stable and non-hygroscopic, and may be heated at 240—250° without decomposition. It should not be employed in the form of a stock solution, as this attacks glass on preservation, but with suitable apparatus an absolute accuracy of 0.1% is attainable in the results. A description is given of the methods of testing the salt for impurities.

H. F. HARWOOD.

**Volumetric determination of sodium.** E. R. CALEY (J. Amer. Chem. Soc., 1930, 52, 1349—1353).—In a rapid method for the volumetric determination of sodium the precipitate of sodium magnesium uranyl acetate obtained as previously described (A., 1929, 900) is dissolved in acetic acid and the solution is titrated at 90° with sodium phosphate, potassium ferrocyanide being the external indicator. J. G. A. GRIFFITHS.

**Determination of sodium by the uranyl [magnesium acetate] method.** E. KAHANE (Bull. Soc. chim., 1930, [iv], 47, 382—404).—The crystalline triple salt of sodium acetate, uranyl acetate, and the acetate of a metal of the magnesium group contains 6 and not 9 mols. of water of crystallisation per mol. of salt. None of this water is lost at 110° or in a vacuum, but the results obtained by using Blanchetière's method, which are based on the supposition that the salt becomes anhydrous at 105°, are not incorrect by the 7.77% to be expected owing to the fact that precipitation is incomplete in the 30 min. allowed by this worker. Complete precipitation requires several days. However, an aqueous reagent containing per litre 500 c.c. of 90% alcohol, 20 c.c. of acetic acid, 100 g. of magnesium acetate, and 32 g. of crystalline uranyl acetate completely precipitates the *octahydrate* in the cold in 30 min. as a dense, granular, non-hygroscopic precipitate, which may be weighed directly either before or after ignition, or its weight may be ascertained by colorimetric determination, or by reducing with copper or aluminium in presence of sulphuric acid and titrating with potassium permanganate. About 2.5 c.c. of the reagent are required per mg. of sodium and per c.c. of sodium solution. Ammonium, lithium, magnesium, and calcium ions may be present, as well as potassium to an extent not exceeding ten times the quantity of sodium present. Phosphates must be removed, although their presence does not give rise to a very serious error.

S. K. TWEEDY.

**Quantitative precipitation of calcium oxalate in the presence of the phosphate ion.** J. T. DOBBINS and W. M. MEBANE (J. Amer. Chem. Soc., 1930, 52, 1469—1472).—Optimal conditions for the quantitative precipitation and filtration of calcium oxalate in the presence of phosphate ions have been determined. The solution (50 c.c.), at 20—25°, is made alkaline with 5 c.c. in excess of concentrated ammonia solution. Excess of saturated ammonium oxalate is added and the liquid is filtered after 1 hr.

J. G. A. GRIFFITHS.

**Determination of beryllium in aluminium-free steel.** F. SPINDECK.—See B., 1930, 463.



**Luminescence analysis.** E. BEUTEL and A. KUTZELNIGG (*Monatsh.*, 1930, **55**, 158—166).—Zinc and the following zinc compounds show no luminescence when irradiated with ultra-violet light: sulphate, nitrate, carbonate, oxalate, phosphate, chromate, chloride, silicate, and zinc green. The following show varying degrees of luminescence according to their method of preparation, physical state, and origin: zinc oxide, hydroxide, sulphide, carbonate (basic), cyanide, smithsonite, hydrozincite, and potassium zinc cyanide. Colloidal solutions of zinc, zinc oxide, cyanide, and sulphide show indefinite luminescence. H. BURTON.

**Spectrographic determination of cadmium, lead, and iron in zinc.** D. M. SMITH.—See B., 1930, 425.

**Rapid volumetric determination of lead.** R. C. WILEY.—See B., 1930, 425.

**Optical method for measuring the mercury content of air.** K. MÜLLER and P. PRINGSHEIM (*Naturwiss.*, 1930, **18**, 364—367).—A more rapid method than that of Stock (*A.*, 1926, 703) has been devised, based on the extent of absorption of the mercury resonance line (2537 Å.). A quartz mercury lamp is employed as a source of light, the beam being allowed to impinge on a resonance lamp whereby the line 2537 Å. is rendered sharper. The emitted light then traverses a tube containing the air under examination, the extent of absorption resulting being measured by means of a photo-electric cell. The apparatus must be previously calibrated for known concentrations of mercury vapour. The vapour of some organic substances, *e.g.*, benzene, also causes absorption, but the presence of such compounds may be detected by examining the degree of absorption of the self-reversed mercury line; in the case of mercury vapour this absorption in a particular experiment was only 5% as compared with 50% for the original resonance line, whilst with benzene vapour it was about 55% in both cases. Although the apparatus is costly and somewhat complex, 10 to 20 determinations may be made hourly, with concentrations of mercury ranging from 5 to 500  $\gamma$  per m.<sup>3</sup> of air. H. F. HARWOOD.

**Applications of ceric sulphate in volumetric analysis.** VII. Oxidation of quinol by ceric sulphate. N. H. FURMAN and J. H. WALLACE, jun. (*J. Amer. Chem. Soc.*, 1930, **52**, 1443—1447).—The oxidation of 0.1*N*-solutions of quinol to quinone by ceric sulphate is rapid and stoichiometric at the ordinary temperature. The end-point can be determined electrometrically, by means of diphenylamine, which turns blue and requires a slight end correction, or by methyl-red, the colour change of which is less satisfactory. The electrometric end-point only can be used when quinol is added to ceric sulphate.

J. G. A. GRIFFITHS.

**Gravimetric determination of aluminium in presence of iron by means of hydrazine carbonate.** J. LUKAS and A. JÍLEK (*Coll. Czech. Chem. Comm.*, 1930, **2**, 161—168).—Aluminium may be separated quantitatively from iron by means of hydrazine carbonate if the solution containing the two cations

be first reduced in acid medium by a non-precipitating hydrazine salt (sulphate or chloride). The aluminium separates as a basic carbonate, whilst the iron passes into the filtrate. The carbonate precipitate should be redissolved in hydrochloric acid and reprecipitated. The iron may be determined directly by precipitation with ammonia after destroying hydrazine salts with bromine. J. W. SMITH.

**Gravimetric determination of aluminium as oxide.** R. FRICKE and K. MEYRING (*Z. anorg. Chem.*, 1930, **188**, 127—137; cf. *A.*, 1920, ii, 387).—The precipitation of aluminium hydroxide from its alkaline solution by carbon dioxide provides a convenient and accurate method for the gravimetric determination of the metal, since the precipitate is easily washed and filtered. It is important to avoid an excess of alkali before passing in carbon dioxide, to carry out the precipitation slowly, and, when the specimen to be analysed is neutral or acid, to use alkali hydroxide free from silica. The method cannot be employed in the presence of lithium or of alkaline-earth metals. Full details of procedure are given. F. L. USHER.

**Separation and determination of nickel and cobalt.** F. G. GERMUTH (*Chemist-Analyst*, 1930, **19**, No. 2, 4—9).—For the determination of small quantities of nickel the  $\alpha$ -benzildioxime method is recommended; the acetyldioxime method is as good when not more than 0.1 g. of cobalt is present. For the determination of small quantities of cobalt the 1-nitroso- $\beta$ -naphthol method is preferred.

CHEMICAL ABSTRACTS.

**Perchloric acid as an oxidising agent in the determination of chromium.** J. J. LICHTIN.—See B., 1930, 417.

**Determination of molybdenum in steels and in ferromolybdenum.** W. WERZ.—See B., 1930, 463.

**Light reactions of tin halides and their analytical application.** E. SCHRÖER and A. BALANDIN (*Z. anorg. Chem.*, 1930, **189**, 258—262).—An attempt has been made to determine the causes of the following light reaction which is employed for the detection of tin. A vessel containing cold water is dipped in a solution of tin in hydrochloric acid and a Bunsen flame allowed to play on it. An intense blue light is obtained. Experiment shows that this cannot be ascribed to thermoluminescence. It is suggested that it may be due to excitation by free electrons. Since the colour varies with the halogen present the method may also be used for the detection of the halogens. A method of employing it for the detection of organically bound chlorine is described. M. S. BURR.

**Determination and separation of rare metals from other metals.** XIX. Separation of titanium from other elements. L. MOSER, K. NEUMAYER, and K. WINTER (*Monatsh.*, 1930, **55**, 85—97).—Details are given for the separation of titanium from uranium, chromium, alkaline-earth metals, beryllium, zinc, nickel, or cobalt by the chloride-bromate method previously described (*A.*, 1923, ii, 438). Titanium can also be separated from uranium, chromium, zinc, nickel, cobalt, or manganese by the sulphosalicylic acid method (*loc. cit.*). A method is

also described for the separation of titanium from iron, aluminium, chromium, manganese, nickel, cobalt, or zinc, and silicic or phosphoric acids, involving the use of tannic acid and antipyrine in sulphuric acid solution. The principle of the method is as follows: the sulphuric acid solution of the two metals is diluted with 10% tannic acid solution and water until the acidity is about *N*; a 20% solution of antipyrine is then added with stirring in the cold or in the hot (in presence of ammonium sulphate), when the whole of the titanium is precipitated as an orange-red tannic acid complex. This is filtered, washed with a solution containing sulphuric acid, ammonium sulphate, and antipyrine, dried, and ignited.

H. BURTON.

**Spectrographic determination [of minute amounts of gold].** P. URBAIN (Compt. rend., 1930, 190, 940—942).—A series of solutions is prepared containing 1, 2, 5, 10, 20, 50 . . .  $\times 10^{-3}$  mg. of gold in solution as potassium aurocyanide. To each is added potassium argentocyanide in quantity containing 0.1 mg. of silver, and enough water and potassium cyanide to make up 2 c.c. of solution 0.1*N* as regards potassium cyanide. This solution is electrolysed using as cathode a small rod of carbon, which is then used to make a spark spectrum. This is photographed and the ratios of the intensities of the following pairs of lines are determined: Au 2676—Ag 2660, Au 2428—Ag 2438, and Au 3123—Ag 3281. In this way a standard curve for each pair of lines is prepared. The solution for analysis is treated similarly, and comparison of the ratios of the intensities of the pairs of lines with the standard gives the amount of gold. The method is applicable to amounts of gold as small as 0.001 mg.

C. A. SILBERRAD.

**Potentiometric determination of platinum with titanous chloride and with stannous chloride.** E. MÜLLER and W. STEIN (Z. Elektrochem., 1930, 36, 220—234).—Platinum in an approximately 0.008*N* solution of hydrochloroplatinic acid may be determined by adding 0.5 c.c. of concentrated hydrochloric acid and 6—8 drops of chlorine water to 20 c.c. of solution and titrating in a current of nitrogen with 0.04*N*-titanous chloride solution. When the potential of a platinum electrode immersed in the solution undergoes a first abrupt change, indicating that all the chlorine has reacted, the temperature is slowly raised to about 60° and the addition of titanous chloride is continued gradually and with constant stirring until a second "jump" in potential shows reduction to the platinous state to be complete. The titration of platinum in dilute solution with stannous chloride is found, contrary to previous results (A., 1929, 532), to be unsatisfactory.

R. CUTHILL.

**Physical methods in chemical laboratories.** XI. Technique and application of rotation dispersion to the solution of chemical problems. G. KORTÜM (Z. angew. Chem., 1930, 43, 341—348).—A review describing methods of determining the rotation dispersion of organic compounds and the value of the study of this property in the elucidation of the structure of optically active compounds.

A. R. POWELL.

**Photo-electric recording of daylight.** T. H. HARRISON (Nature, 1930, 125, 704—705).—An apparatus used at the National Physical Laboratory is described.

L. S. THEOBALD.

**Reflexion factor of magnesium oxide.** J. S. PRESTON (Trans. Opt. Soc., 1930, 31, 15—35).—A small integrating reflectometer for determining reflexion coefficients is described. The total reflexion factor of magnesium oxide for diffused light is 0.974.

C. W. GIBBY.

**Preparation of graded series of ultra-filters and measurement of their pore sizes.** A. P. KRUEGER and R. C. RITTER (J. Gen. Physiol., 1930, 13, 409—419).—A simplification of Bechhold's procedure (A., 1908, ii, 24) for making a series of membranes of graded pore sizes is presented, together with data for permeability of the membrane series to water and to colloid sols of known particle sizes. A convenient ultrafiltration apparatus for operation under aseptic conditions is described.

T. R. SESHADRI.

**Membranes for high-pressure ultra-filtration.** J. W. McBAIN and S. S. KISTLER (Trans. Faraday Soc., 1930, 26, 157—162).—Cellophane is advocated as a membrane for ultrafiltration, and its properties are described with reference to this application. It has been adapted for use with non-aqueous solutions. Membranes of suitable density for use as molecular sieves have been made, and used to determine the degree of hydration of sucrose in dilute solution.

C. J. SMITHELLS.

**Microcalorimeter.** A. F. H. WARD (Proc. Camb. Phil. Soc., 1930, 26, 278—284).—The instrument was devised to measure the heat of adsorption of minute quantities of gas (e.g., 0.01 c.c.), and is capable of measuring with an accuracy of 10% a heat evolution of 0.0005 g.-cal. It is a modification of one described by Tian (cf. A., 1924, ii, 240), and depends on measuring the rise in temperature by means of a series of iron-constantan couples, one set of junctions being in contact with a copper tube in which the heat is evolved, the other connected to a copper ring in a thermostat capable of being maintained constant within 0.0000017°. An alternative method depends on passing a current through another set of couples so that the Peltier effect exactly compensates the heat to be measured (cf. Berenger-Calvet, A., 1927, 629).

C. A. SILBERRAD.

**New type of Dewar flask for use as a calorimeter.** W. L. WATTON (Proc. Physical Soc., 1930, 42, 226—238).—The water equivalent of a new type of Dewar flask, of which the inner vessel was of thin copper, was measured at laboratory temperatures with special attention to stirring, and was found to be more constant than for the usual type. The necessary precautions are fully discussed.

N. M. BLIGH.

**Adiabatic calorimeter for low-temperature measurements.** D. LE B. COOPER and D. McINTOSH (Trans. Nova Scotian Inst. Sci., 1930, 17, 197—198).—A calorimeter of the Richards type, with an outer vacuum jacket of copper, is described. The calorimeter liquid used is a mixture of chloroform and carbon tetrachloride and the inner and outer liquids are kept at the same temperature by the addition of

small amounts of solid carbon dioxide to the outer container. The apparatus is designed to measure the heat evolved in reactions with organic substances at a temperature at which substitution does not take place.

J. W. SMITH.

**Electrical calibration of a calorimeter with the aid of a titration coulometer.** W. A. ROTH and H. TROITZSCH (*Z. Elektrochem.*, 1930, 36, 242—244).—The water equivalent of a calorimeter can be determined with an error of about 0.1% by observing the rise of temperature produced when a current is passed for a suitable time through a resistance within the calorimeter, the total quantity of electricity passing being determined with a silver titration coulometer. The current density at the anode in the coulometer should not exceed 0.15 amp./cm.<sup>2</sup>

R. CUTHILL.

**Calibration of calorimeters.** H. VON WARTENBERG and H. SCHÜTZ (Z. Elektrochem., 1930, 36, 256—257).—A modification of the electrical method for determining the water equivalent of a calorimeter is described. The heat generated by passing a current at a steady voltage through a known resistance is obtained by measuring the total amount of electricity passing by means of a voltmeter.

R. CUTHILL.

**Thermoregulators.** II. J. WING (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 196—197).—The regulator previously described (*A.*, 1926, 141) has been modified; it is made entirely of pyrex glass and is suspended so that it is continuously shaken by the vibration of the stirrer. The current-carrying capacity of the relay is greatly increased by the substitution of flat plates of pure silver for the ordinary contact points and, if a 0.5 microfarad condenser is used in parallel, currents up to 2 amp. at 110 volts can be easily handled. The contact leads are made of tungsten, which is not wetted by mercury, and the contact chamber is filled with hydrogen; thus the current which may be used in the regulator is limited only by the volatilisation of the mercury at the contact points and not by oxidation of the mercury. Currents up to 0.5 amp. may be used with a condenser in parallel. In operation, the regulator is entirely closed and may be used to control temperatures above the b. p. of mercury. A regulator, intermediate in sensitivity between the above and the bimetallic regulator, in which the expansion of the regulator liquid directly opens the heating circuit, is described. It has a sensitivity of  $\pm 0.5^\circ$  and will make and break a current of 0.5 amp. and 110 volts.

E. H. SHARPLES.

**Electrically-heated thermostats.** P. VAN CAMPEN (*Z. Elektrochem.*, 1930, 36, 268).—A reply to Hock and Nottebohm (*A.*, 1929, 1034).

R. CUTHILL.

**Automatic low-temperature thermostat (cryostat).** A. C. EGERTON and A. R. UBBELOHDE (*Trans. Faraday Soc.*, 1930, 26, 236—239).—Liquid air blown from a Dewar flask into a metal vessel with double walls, immersed in the liquid (dry petroleum), of the lagged, Dewar flask cryostat serves to keep the latter at the desired temperature, the rate of flow of heat between the liquid air and petrol being regulated

by control of the pressure of the dry hydrogen or air in the walls of the metal vessel. The level of the air is kept constant by means of a tambour, the splayed end of which rests on the surface, whilst the other is connected to a straw lever which alters a resistance in series with an electrically-driven blower. This enables temperatures of  $-120^\circ$  to  $-160^\circ \pm 0.5^\circ$  to be maintained, but an accuracy of  $\pm 0.1^\circ$  is obtainable if a thermoregulator is used to operate a solenoid-controlled electric relay which connects the gas-space between the walls of the metal vessel with a source of low or high vacuum, according as the temperature of the bath is too high or too low, respectively. A bath of 500 c.c. capacity requires 200 c.c. of liquid air per hr.

J. GRANT.

**Dielectric constants of liquids. I. Measuring apparatus.** G. DEVOTO and M. STEVENSON (*Gazzetta*, 1930, 60, 199—207).—Details are given of a valve apparatus which is based essentially on Drude's method but gives undamped oscillations of variable frequency. Values of the dielectric constants of sugar solutions obtained with this apparatus are in good agreement with, and of greater uniformity than, those obtained by other workers.

F. G. TRYHORN.

**Measurement of the dielectric constants of organic liquids.** A. O. BALL (*J.C.S.*, 1930, 570—596).—The determination of the dielectric constants,  $\epsilon$ , of liquids is discussed, and a low-frequency alternating bridge is described for weak insulators. Condensers have been designed which require only small quantities of liquid and yield absolute values of  $\epsilon$ . Capacities are determined by complete substitution, a carbon film resistance being the compensator. Errors due to polarisation capacities and series resistances in the cells have been investigated. It is claimed that dielectric constants as high as 40 can be determined between  $0^\circ$  and  $80^\circ$  with an error of less than 0.2%. Results are recorded for benzene ( $\epsilon$  at  $25^\circ = 2.274$ ; cf. Hartshorn, *A.*, 1929, 628), benzonitrile, chloroform, and nitrobenzene; those of the last two are not affected by the variation of frequencies between 500 and 2500.

J. G. A. GRIFFITHS.

**Lag in a thermometer when the temperature of the external medium is varying.** A. T. STARR (*Phil. Mag.*, 1930, [vii], 9, 901—912).—Mathematical.

N. M. BLYTH.

**Support for m.-p. tubes.** E. V. ZAPPI (*Anal. Asoc. Quím. Argentina*, 1929, 17, 239—240).—A platinum or gold clip is described. R. K. CALLOW.

**Device for fastening m.-p. tubes to thermometers.** H. L. LOCHTE (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 200).—A glass rod, 3—5 mm. in diameter, is fastened to the thermometer and the m.-p. tube is placed in the angle so formed. E. H. SHARPLES.

**Modified Thiele m.-p. apparatus.** E. CONTE (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 200).—A Thiele tube is fitted with a 4 mm. (o. d.) side tube which has an orifice, 0.5 mm. diam., about 12 mm. in the bottom side-arm of the Thiele tube. Air is either pumped or drawn through the side tube at such a rate that it is just possible to count the bubbles. Under

these conditions the temperature variation throughout the tube is greatly reduced. E. H. SHARPLES.

**Simple method of removing water in drying processes in the laboratory.** B. REWALD and SCHWIEGER (*Chem.-Ztg.*, 1930, **54**, 281).—To prevent foaming and the formation of skins in the removal of water from solutions containing proteins in the Aufhäuser apparatus small quantities of benzene are added occasionally to the contents of the distillation flask whereby the water distils with the benzene at 69.2°. A. R. POWELL.

**Improved laboratory condenser and its use in the construction of apparatus.** E. S. WEST (*Ind. Eng. Chem. [Anal.]*, 1930, **2**, 199).—The efficiency of the condenser originally described (A., 1928, 984) has been increased by indenting the walls of the inner tube. The use of these condensers for the construction of all-glass distillation apparatus of various kinds is described. E. H. SHARPLES.

**Condenser for extraction and distillation apparatus.** R. ZINZADZE (*Chem. Fabr.*, 1930, 113—114).—The condenser is divided into two chambers by means of a cone-shaped glass dome with an opening in the side just below the flattened apex of the cone. In the upper chamber is a worm-shaped cooler surrounding and terminating in a vertical cooling tube with its lower end just above the dome. The space round the dome thus acts as a collecting chamber for the condensed liquid, which may be withdrawn therefrom by a side tube provided with a three-way cock connected with a tube entering the lower part of the condenser below the dome and with a tube for removing the liquid from the apparatus at the end of the extraction operation. Various modifications of the apparatus are described and illustrated. A. R. POWELL.

**Continuous feeding of distillation apparatus by means of a siphon.** R. BOITEUX (*Bull. Soc. Chim. biol.*, 1930, **12**, 241—243).—A convenient apparatus for the continuous distillation of water is described and illustrated. W. O. KERMACK.

**Continuous extractor for solids.** J. H. GARDNER and E. B. W. KERONE (*J. Chem. Educ.*, 1930, **7**, 593).—A wide glass tube is sealed to the neck of a 1 litre flask and bent downwards; into it is sealed (slightly above the level of the centre of the flask) a small tube sealed also to the bottom of the flask. The flask, charged with solid, is connected to a reflux condenser and to another flask (in which the solvent is boiled) by means of the large tube. The flow of solution is regulated by means of a plug of glass wool inserted in the inlet of the small tube.

CHEMICAL ABSTRACTS.

**Safety device to protect heating units.** F. H. FISH (*Ind. Eng. Chem. [Anal.]*, 1930, **2**, 197—198).—To prevent water-bath electric heating coils burning out a small float is used; this, on sinking with the level of the water, actuates a short-circuiting device across a fuse. E. H. SHARPLES.

**Modified Peterson-Palmquist apparatus for the determination of carbon dioxide in air.** E. P. JONES (*Ind. Eng. Chem. [Anal.]*, 1930, **2**, 195—196).—The apparatus consists essentially of a bulb of

known volume terminating in a uniform calibrated glass tube which is connected to a mercury levelling reservoir, a manometer, and an absorption pipette. The main advantages are that there are no rubber connexions in that part of the apparatus which is in contact with the sample and the number of stopcocks in contact with the sample has been reduced.

E. H. SHARPLES.

**Glass valve not requiring grease.** M. BODENSTEIN (*Z. physikal. Chem.*, 1930, **B**, **7**, 387—389).—An all-glass valve of the needle-valve type is described. The needle is fused into the body of the valve, which is, however, sufficiently elastic to permit the needle being sprung into its seat. R. CUTHILL.

**Magnetically-operated mercury float-valve for high-vacuum work.** H. RAMSER and E. WIBERG (*Z. Elektrochem.*, 1930, **36**, 253).—A description is given of a mercury valve with a float which contains a piece of iron enabling it to be moved by an electromagnet. R. CUTHILL.

**Improved Pirani gauge.** H. G. TANNER (*J. Physical Chem.*, 1930, **34**, 1113—1115).—An improved form of Pirani gauge suitable for the measurement of low pressures down to  $5 \times 10^{-5}$  mm. is described.

L. S. THEOBALD.

**Simple apparatus for demonstration of Gay-Lussac's law and determination of the coefficient of expansion of air.** W. WIDDER (*Physikal. Z.*, 1930, **31**, 334—335).—With a simple apparatus consisting of a capillary tube closed at one end and sealed to a bulb at the other and containing a mercury pellet separating the air in the bulb from that in the capillary, values for the coefficient of expansion of air can be obtained with an error of less than 1%. The bulb is heated at various temperatures and the corresponding pressures are deduced from the volume of the air enclosed in the capillary by the mercury pellet. H. A. JAHN.

**Improved calomel electrode vessel.** S. E. HILL (*Science*, 1930, **71**, 193).—A modified electrode vessel with attached cup for the string salt bridge to replace beakers is described. L. S. THEOBALD.

**Model to explain the mechanism of electrolysis.** M. DE K. THOMPSON (*Amer. Electrochem. Soc.*, May, 1930. Advance copy, 4 pp.).—A mechanical model is described which illustrates the mechanism of electrolysis for three different relative velocities of anions and cations and thus indicates how the transport numbers are related to the losses of electrolyte from the anolyte and catholyte.

H. J. T. ELLINGHAM.

**The chromoionometer, an adaptation of the Duboscq colorimeter for the determination of  $p_H$  without use of standard solutions.** M. G. ART (*Bull. Soc. Chim. biol.*, 1930, **12**, 25—33).

P. W. CLUTTERBUCK.

**Self-registering drop counter (stalagmograph).** R. FISCHER (*Biochem. Z.*, 1930, **219**, 248—251).

P. W. CLUTTERBUCK.

**Surface tension hydrometer.** J. E. CALTHROP (*J. Sci. Instr.*, 1930, **17**, 128—130).—A simple hydrometer, having an accuracy of 1.5%, is described. C. W. GIBBY.

**Simple dilatometer.** R. C. GALE (J. Sci. Instr., 1930, 17, 131).—A robust apparatus, particularly suitable for measuring the linear expansion of steels, is described. The expansion of a test piece is transmitted to a graduated dial by a piece of silica tubing, and its temperature is measured by means of a thermocouple inserted in an axial hole.

C. W. GIBBY.

**Phthaleinoscopic apparatus for acidimetry in coloured media.** P. BRUÈRE (Ann. Falsif., 1930, 23, 68—79).—Coloured solutions may be titrated, using bromothymol-blue, phenol-red, and phenolphthalein as indicators, by observing the appearance of particular absorption bands with a small spectroscope. Calibration of the indicators is essential. Applications to the titration of red wines, other

alcoholic beverages, molasses, and vinegar, are described.  
C. W. GIBBY.

**Silver voltameter.** H. VON WARTENBERG and H. SCHÜTZA (Z. Elektrochem., 1930, 36, 254—256).—A voltameter consisting of two silver anodes and a platinum or silver cathode in a mixed aqueous solution of fluoboric acid and silver fluoborate, 0.5N in respect of the free acid, is described. The cathode deposit is smooth and coherent and does not change in weight in contact with air and the solution, and the accuracy for current densities at the cathode up to 1.5 amp./dm.<sup>2</sup> is equal to that of the usual voltameter with silver nitrate as electrolyte. With the aid of a microbalance currents as low as 10<sup>-5</sup> amp. may be measured.  
R. CUTHILL.

## Geochemistry.

**Transparency of the lower atmosphere.** H. BUISSON, G. JAUSSEAN, and P. ROUARD (Compt. rend., 1930, 190, 808—810).—The optical density of 1900 m. of air is obtainable from the logarithm of the ratio of the microphotometric degree of illumination of two portions of the same photographic plate, exposed under identical conditions at 2500 and 600 m., respectively, from the source, which is a mercury arc placed on the straight line joining the two plates. It is shown that after allowing for molecular diffusion, the absorption increases slowly with decrease in wavelength from  $\lambda$  5780 to  $\lambda$  2900, and then rapidly between  $\lambda$  2900 and  $\lambda$  2482 Å. (cf. following abstract). This is attributed to the large oxygen band rather than to ozone.  
J. GRANT.

**Direct measurement of atmospheric absorption.** LINK and HUGON (Compt. rend., 1930, 190, 810—813).—Atmospheric absorption was measured from the variation with distance (900—31,000 m.) of the photometric degree of illumination due to a 1000-watt lamp, allowance being made for the diminution due solely to an increase in distance between the photographic plate and the source. Absorption decreases with increase in wave-length for the rays 0.63, 0.525, and 0.46  $\mu$ , but the results (the error of which is 10%) vary considerably with changes in visibility. The minimum values are in good agreement with those calculated by an astronomical method and from the Rayleigh-Cabannes formula (cf. preceding abstract).  
J. GRANT.

**Sea-water at Puget Sound Biological Station from September 1927 to September 1928.** M. W. JOHNSON and T. G. THOMPSON (Pub. Puget Sound Biol. Sta., 1929, 7, 119—128).—Determinations of  $p_{\text{H}}$ , chlorine, and dissolved oxygen are recorded.  
CHEMICAL ABSTRACTS.

**Sea-water near Puget Sound Biological Station during the summer of 1927.** T. G. THOMPSON, R. C. MILLER, G. H. HITCHINGS, and S. P. TODD (Pub. Puget Sound Biol. Sta., 1929, 7, 65—99).—Data are recorded. Titrimetric methods are not applicable to the determination of carbon dioxide in sea-water.  
CHEMICAL ABSTRACTS.

**Manganese content of the Mississippi river water at Fairport, Iowa.** A. H. WIEBE (Science, 1930, 71, 248).—Data are recorded.  
L. S. THEOBALD.

**Iodine in water-supplies of the Argentine Republic.** A. A. BADO and R. A. TRELLES (Anal. Asoc. Quim. Argentina, 1929, 17, 209—215).—Analyses of public water-supplies are tabulated. Iodine is generally absent when the ratio  $\text{Na}_2\text{O}/(\text{CaO} + \text{MgO})$  is less than unity. The incidence of goitre seems to decrease with improvement of hygienic conditions, in spite of lack of iodine.  
R. K. CALLOW.

**Chemico-physical data and chemical analysis of the water of Vanzone d'Ossola.** R. NASINI and E. BOVALINI (Annali Chim. Appl., 1930, 20, 91—112).—The water of this spring, which is at an altitude of 1450 m., contains about 3.38 g. of ferric sulphate and 0.8 g. of aluminium sulphate per litre, together with other salts and appreciable proportions of zinc, arsenic, nickel, cobalt, manganese, and copper. It exhibits marked catalytic and oxidising activity.  
T. H. POPE.

**Germanium and arsenic in meteorites.** J. PAPISH and Z. M. HANFORD (Science, 1930, 71, 269—271).—Traces of germanium have been identified in certain meteorites, viz., siderites from Mexico and Ontario, siderolites from Kansas and Chile, and aerolites from Texas and Michigan. Germanium and arsenic have been separated from the first two siderites.  
L. S. THEOBALD.

**Presence of nesquehonite in the serpentine of Viù in Val di Lanzo.** M. FENOGLIO (Atti R. Accad. Lincei, 1930, [vi], 11, 310—316).—In places the serpentine at Fubina, to the east of Viù, is covered with a white incrustation of nesquehonite,  $d^{15}$  1.824, containing MgO 29.20, CO<sub>2</sub> 31.69, H<sub>2</sub>O 39.30%. The crystallographic properties agree moderately well with those given by Genth and Penfield (A., 1890, 571) and by Cesáro (A., 1911, ii, 209). Genetic connexion between nesquehonite and the other hydrated magnesium carbonates is considered unlikely, the first-named being formed at the ordinary

temperature and pressure and the last two most probably at higher temperatures and pressures.

T. H. POPE.

**Origin of talc in the Göpfersgrün-Thiersheim stratum in the Fichtel Mts.** E. ENK (Kolloid-Z., 1930, 51, 257—273).—The possible mechanism of the formation of talc from minerals of the olivine type is discussed from a colloid-chemical point of view.

E. S. HEDGES.

**Tungsten ores of Galicia. II. Analyses of scheelite from Carbia and Villar de Cervos.** I. P. PONDAL and J. V. GARRIGA (Anal. Fis. Quim., 1930, 28, 262—263).—Two specimens of Galician scheelite had  $d$  6.02, 6.08, and contained  $\text{WO}_3$  80.41, 80.21,  $\text{CaO}$  19.24, 19.43%, respectively; neither contained even traces of iron, tantalum, niobium, rare earths, or molybdenum.

H. F. GILLBE.

**Mineralogical and chemical behaviour of the alteration products formed from the gneiss of the central French massif before the establishment of the oligocene sedimentary deposits.** J. DE LAPARENT (Compt. rend., 1930, 190, 1062—1064).—A description of a ferruginous siliceous clay found in the central French massif is given. It contains some of the quartz and all the white mica, but none of the feldspar or black mica, of the gneiss from which it was formed.

C. W. GIBBY.

**Structure of the micas and related minerals.** L. PAULING (Proc. Nat. Acad. Sci., 1930, 16, 123—129).—General principles governing the structures of complex ionic crystals (A., 1929, 748) have been applied in formulating a structure for talc, pyrophyllite, the micas, and the brittle micas which is substantiated by the X-ray examination of these minerals, explains their remarkable physical properties, and leads to a general chemical formula unifying the widely varying analyses reported for different specimens.

The structure leads to a general formula for the micas,  $\text{KX}_n\text{Y}_4\text{O}_{10}(\text{OH},\text{F})_2$ , with  $2 \leq n \leq 3$ , in which X represents cations of co-ordination number 6 ( $\text{Al}^{+++}$ ,  $\text{Mg}^{++}$ ,  $\text{Fe}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Ti}^{+++}$ ,  $\text{Li}^+$ , etc.) and Y cations of co-ordination number 4 ( $\text{Si}^{++++}$ ,  $\text{Al}^{+++}$ , etc.). The subscript  $n$  can have any value between 2 (hydrargillite layer) and 3 (complete octahedral layer). Potassium can be partly replaced by sodium and possibly to some extent by calcium. This formula represents satisfactorily the numerous recently published mica analyses almost without exception. The distribution of the various ions X and Y must be such as to give agreement with the electrostatic valency rule. The clintonites or brittle micas have a similar structure, the layers having twice the electrical charge of those in mica and being held together by calcium instead of potassium ions. The correspondingly stronger forces bring the layers closer together, the separation of adjacent layers being 9.5—9.6 Å. in place of the value 9.9—10.1 Å. for the micas. The general formula  $\text{CaX}_n\text{Y}_4\text{O}_{10}(\text{OH},\text{F})_2$  with  $2 \leq n \leq 3$  holds for these minerals.

F. G. TRYHORN.

**Formulae of monoclinic amphiboles and pyroxenes.** F. MACHATSCHKI (Z. Krist., 1929, 71, 219—236; Chem. Zentr., 1929, ii, 2990).

**Formation of minerals in the phosphate deposits of Drachenhöhle near Mixnitz (Styria).** F. MACHATSCHKI (Zentr. Min. Geol., 1929, A, 321—332; Chem. Zentr., 1929, ii, 3119).—The occurrence of tricalcium phosphate, collophane, is described. The light veins are of variscite. Variscite, amorphous  $2\text{AlPO}_4 \cdot 4\text{H}_2\text{O}$ , loses  $1\text{H}_2\text{O}$  below  $100^\circ$ ,  $2\text{H}_2\text{O}$  between  $100^\circ$  and  $120^\circ$ , and  $1\text{H}_2\text{O}$  above  $120^\circ$ .

A. A. ELDRIDGE.

**Relative hydration of the anhydride molecule in natural metallic salt hydrates as a criterion of classification; weathering and limits of existence.** M. RAKUSIN (Zentr. Min. Geol., 1929, A, 332—350; Chem. Zentr., 1929, ii, 3117).

**Action of organic acids on limestone.** A. N. MURRAY and W. W. LOVE (Bull. Amer. Assoc. Petr. Geol., 1929, 13, 1467—1476).—Organic acids derived from the bacterial decomposition of plants may be the most effective solvents of limestone, especially in the development of porosity.

CHEMICAL ABSTRACTS.

**Halloysite from Elbingerode [Harz].** O. H. ERDMANNSDÖRFFER (Chem. Erde, 1930, 5, 96—98).—Nodules of greyish-green halloysite (anal. I) coated with a white powdery material (anal. II) occur in limonite in the "Grosse Graben," which has been worked for iron and manganese ores and pyrite. Both are optically isotropic with  $n=1.515$ — $1.528$ . II gives the ratios  $\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{H}_2\text{O} = 2.20 : 1 : 4.90$ . Between  $105^\circ$  and  $400^\circ$  very little water is lost and the material then behaves like kaolin. An X-ray powder photograph shows a few faint lines coinciding with those of kaolin. The ignited material gives no X-ray spectrum.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$ ( $105^\circ$ )	$\text{H}_2\text{O}$ (ign.)	Total
I	36.27	29.53	5.31	0.10	0.02	0.23	1.60	0.64	14.19	12.70	100.53
II	39.00	30.07	2.98	0.01	0.04	0.40	1.31	1.24	12.70	15.15	101.09

Also traces of  $\text{P}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{MnO}$ .

L. J. SPENCER.

**Steatite from the Münchberg gneiss area.** F. DEUBEL (Chem. Erde, 1930, 5, 87—95).—A new occurrence of steatite has been found near Schwarzenbach a. d. Saale on the south-east border of the Münchberg gneiss area in Bavaria. It is shown to be a replacement of quartzite, no doubt by hydrothermal action. Analysis of the material gave:  $\text{SiO}_2$  61.95,  $\text{Al}_2\text{O}_3$  0.87,  $\text{FeO}$  0.57,  $\text{MgO}$  32.16, loss on ignition 4.99, total 100.54%.

L. J. SPENCER.

**Basalt from the Atlantic Ocean.** C. W. CORRENS (Chem. Erde, 1930, 5, 76—86).—A description with chemical analysis is given of a fragment (62.7 g.) of basalt raised from the floor of the Atlantic at a depth of 2000 m. in lat.  $1^\circ 56' \text{S.}$ , long.  $12^\circ 40' \text{W.}$  It has a glassy crust which has been acted on by seawater.

L. J. SPENCER.

**Spectrum analysis of Mansfield copper shale.** A. CISSARZ (Chem. Erde, 1930, 5, 48—75).—To the long list of elements previously detected by ordinary analytical methods the following are now added: tin, tungsten, platinum, iridium, palladium, and yttrium, bringing the total up to 42.

L. J. SPENCER.

**"Terra rossa" as solution residue of marine limestones.** E. BLANCK (Chem. Erde, 1930, 5, 43—



47).—The analyses by Leiningen (A., 1929, 905) support the view first expressed by the author in 1915.

L. J. SPENCER.

**Optical data for some rare minerals.** T. BARTH and H. BERMAN (Chem. Erde, 1930, 5, 22—42).—Mention is made of various media of high refraction and of the dispersion method for determining under the microscope the refractive indices of immersed mineral particles. Optical data are given for some thirty minerals.

L. J. SPENCER.

**Phonolites and trachytes of the Laacher See district.** W. AHRENS (Chem. Erde, 1930, 5, 1—21).—Trachytoid phonolitic tuffs at Burgbrohl, belonging to the alluvial period, are of later age than the main mass of trachytes of the Laacher See district. The contained blocks of trachytoid phonolite lava are described petrographically with chemical analyses. The analyses are compared with published analyses of the trachytes and plotted on diagrams, showing that at this later period the magma became more acid.

L. J. SPENCER.

**Geological and petrographical examination of the granites quarried in Silesia.** W. BECKER and F. MACHT (Chem. Erde, 1930, 5, 412—436).—Details are given of the stone from several quarries in the neighbourhood of Strehlen, including the jointing of the rock, the size of grain of each constituent mineral, and the relative proportions of each mineral. These are points of importance in the quarrying of the stone and in its suitability for various purposes.

L. J. SPENCER.

**Mineralogy and petrography of the Rhön Mts.** F. HEIDE (Chem. Erde, 1930, 5, 396—411).—Petrographical descriptions are given of phonolite rocks, with one chemical analysis.

L. J. SPENCER.

**Lead-zinc and pyrites ores of the Deutsch-Bleischarley mine, Upper Silesia.** H. SCHNEIDER-HÖHN (Chem. Erde, 1930, 5, 385—395).—These ores are known to contain arsenic, and they were examined by the metallographic method for arsenic minerals. In the lead-zinc ore, shelly blende surrounds cores of galena and jordanite ( $Pb_4As_2S_7$ ), but in the pyrites ore, consisting of a mixture of pyrite, marcasite, and shelly blende, no arsenic mineral could be detected. Chemical tests showed that much arsenic is present in the pure pyrite (no doubt in isomorphous mixture) and only traces in the marcasite and blende.

L. J. SPENCER.

**Nontronite.** W. NOLL (Chem. Erde, 1930, 5, 373—384).—Weinschenk (A., 1897, ii, 413) regarded nontronite as analogous to kaolin and he gave the formula as  $H_4Fe_3Si_2O_9$ , but very few analyses agree with such a formula. Dehydration curves and X-ray powder photographs also show no relation to kaolin. The water is "zeolitic." A new analysis of green greasy nontronite from Tachau, Bavaria, gave  $SiO_2$  40.02,  $Al_2O_3$  10.55,  $Fe_2O_3$  26.16,  $FeO$  1.37,  $H_2O$  21.83, total 99.93%, corresponding with the ratios  $R_2O_3 : SiO_2 : H_2O = 1 : 2.49 : 4.53$ .

L. J. SPENCER.

**Basalt of the StöfFel, Westerwald [Nassau].** E. LEHMANN (Chem. Erde, 1930, 5, 319—372).—From this hill of Miocene basalt 600,000 tons of stone are quarried annually. The basalt is penetrated by dykes of essexite-porphry, which is a product of differen-

tiation of the basaltic magma. Detailed petrographical descriptions with chemical analyses are given of these rocks.

L. J. SPENCER.

**Desert guano in Chile.** W. WETZEL (Chem. Erde, 1930, 5, 260—275).—Desert guano is found in the Toco desert, central Atacama, at spots which were formerly the breeding grounds of sea-birds. It contains the mummified remains of birds and of lower organisms. The material is humus-like and is largely soluble in ammonia solution; sandy impurities and salts ( $P_2O_5$  3.89%) are present in smaller amount. The organic (mummy) substance contains C 41.2, H 5.2, O 37.1, N 16.2%, and the chitinous material insoluble in ammonia solution contains C 38.4, H 5.7, O 37.9, N 20.1%.

L. J. SPENCER.

**Analytical determination of the isomorphous variation in rock-forming minerals.** H. VON PHILIPSBORN (Chem. Erde, 1930, 5, 233—253).—The powdered rock, a pyroxene-granulite from Hartmannsdorf, Saxony, was separated into different fractions with Clerici's solution and an electromagnet. Analysis Ia is of the heavier and darker fraction ( $d$  3.55—3.58,  $n = \frac{1}{2}(\alpha + \gamma)$ ] 1.715) of the hypersthene and lb of the lighter and paler fraction ( $d$  3.49—3.55,  $n$  1.706), IIa of the heavier fraction ( $d$  3.40—3.42,  $n$  1.708) and IIb of the lighter fraction ( $d$  3.37—3.40,  $n$  1.698) of the monoclinic pyroxene. Analysis III is of the heavier fraction ( $d$  2.69—2.71,  $n$  1.555—1.560) of the plagioclase, corresponding with  $Ab_{47}An_{53}$ ; the lightest fraction with  $n$  1.549 corresponds with  $Ab_{70}An_{30}$ . Analysis IV is of the garnet ( $d$  3.92,  $n_{Na}$  1.766) and V is ilmenite. From optical data on the still lighter and heavier fractions of the pyroxenes their composition is arrived at by extrapolation. VI is the bulk composition of the rock ( $d$  3.181), corresponding with hypersthene 28.53, monoclinic pyroxene 29.60, plagioclase 32.59, orthoclase 0.44, garnet 3.31, ilmenite 4.35, magnetite 0.35, apatite 0.83%.

	$SiO_2$	$TiO_2$	$Al_2O_3$	$Fe_2O_3$	$FeO$	$MnO$	$MgO$	$CaO$	$Na_2O$	$K_2O$	Total
Ia	49.42	0.54	2.64	3.42	23.15	0.26	18.17	0.94	1.23	0.19	99.96
lb	50.30	0.53	3.26	3.26	20.09	0.26	20.14	1.41	1.28	0.22	100.75
IIa	49.50	0.69	4.39	2.81	9.90	0.24	11.87	19.34	1.47	0.16	109.37
IIb	50.12	0.65	4.74	2.01	8.57	0.24	12.87	19.84	1.60	0.14	109.78
III	55.41	—	29.42	0.40	—	—	—	11.11	n.d.	n.d.	96.34
IV	35.50	0.88	21.77	1.47	19.64	0.72	8.75	8.50	—	—	104.23
V	—	48.3	—	10.3	38.3	0.3	1.7	—	—	—	100.4
VI	48.61	2.45	12.33	3.22	9.64	0.17	10.12	10.37	2.92	0.18	100.47

V, also insoluble silicates 1.5; VI, also  $P_2O_5$  0.36,  $Cr_2O_3$  0.10%.

L. J. SPENCER.

**Distribution of foreign substances in crystals.** J. NOTHHAFT and H. STEINMETZ (Chem. Erde, 1930, 5, 225—232).—The distribution of colour and inclusions in various minerals and in crystals of lead nitrate grown from solutions containing various colouring matters is described. In fluorite the bands of colour parallel to the cube faces are built up of minute fibres perpendicular to the cube faces, and there are diagonal areas in the crystal free from inclusions. The observations are discussed in connexion with the growth of crystals.

L. J. SPENCER.

**Thuringite from Schmiedefeld, Thuringia.** H. JUNG and E. KÖHLER (Chem. Erde, 1930, 5, 182—200).—Olive-green material consisting of a compact aggregate of fine scales with  $d$  3.187 gave on analysis:  $SiO_2$  20.82,  $TiO_2$  trace,  $Al_2O_3$  17.64,  $Fe_2O_3$  8.70,  $FeO$

37-96, MgO 4.15, H<sub>2</sub>O+ 10.31, H<sub>2</sub>O— 0.07, total 99.65%, agreeing with the formula 14(Fe,Mg)O<sub>5</sub>(Al,Fe)<sub>2</sub>O<sub>3</sub>·12H<sub>2</sub>O·7SiO<sub>2</sub>. Most of the water is expelled at about 420°, and the dehydration curve is very similar to that of kaolin. X-Ray powder photographs of thuringite have been compared with those of quartz, magnetite, and kaolin; some of the magnetite and kaolin lines correspond, but those of quartz are absent. Magnetite has a unit cube of edge 8.393 Å. containing eight molecules.

L. J. SPENCER.

**Weathering of shell limestone and soil formation near Jena.** W. HORPPE (Chem. Erde, 1930, 5, 165—181).—Several chemical analyses are given of limestones from different strata in the "Muschelkalk," of the weathered rocks, and of the overlying soils. These show a gradual removal of lime and an accumulation of the residual constituents of the limestone.

L. J. SPENCER.

**Bleaching processes [in rocks].** H. HARRAS-SOWITZ (Chem. Erde, 1930, 5, 146—164).—Many different geological processes may give rise to much the same result. Exogene bleaching and endogene bleaching are distinguished; the former is due to ordinary weathering at the surface, and the latter to fumarole and hydrothermal actions. By the removal of certain constituents the rocks may be altered to kaolin, bauxite, alunite, etc., or even to a pure quartz sand.

L. J. SPENCER.

**Minerals from the Adamello Mts. [Trentino].** C. GOTTFRIED (Chem. Erde, 1930, 5, 106—112).—The minerals described are from marble (metamorphic limestone) at contact with tonalite. Garnet as reddish-brown rhombic-dodecahedra, with  $d$  3.512 and  $n_{540}$  1.7585, gave analysis I, corresponding with grossular 80.55, andradite 8.13, almandine 4.48, pyrope 6.85%. Idocrase as olive-green crystals, with  $a:c=1:0.5391$ ,  $d$  3.336,  $\omega$  1.719,  $\varepsilon$  1.715, gave analysis II, agreeing with Tschermak's formula Si<sub>17</sub>Al<sub>10</sub>Ca<sub>18</sub>Mg<sub>3</sub>H<sub>6</sub>O<sub>72</sub>. X-Ray rotation photographs gave a unit cell of dimensions  $a$  22.03,  $c$  11.89 Å., containing 2.3 such molecules, i.e., 168 oxygen atoms. The space-group is  $D_{4h}^1$ .

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	H <sub>2</sub> O
I	39.66	0.46	18.77	2.52	1.92	0.07	2.06	34.79	0.07
II	37.03	0.75	16.25	3.13	1.00	0.04	2.45	36.39	2.29

II, also ZnO 0.29, Na<sub>2</sub>O 0.28, K<sub>2</sub>O 0.03, F 0.31, total less O for F 100.15%.

L. J. SPENCER.

**Tellurium minerals of Hungary.** S. KOCH (Bán. Koh. Lapok, 1929, 62, 425—429, 449—452; Chem. Zentr., 1929, ii, 2872—2873).—Native tellurium contained 0.15—2.78% Au. Tetradymite (Bi<sub>2</sub>Te<sub>2</sub>S) contained Te 35.56—36.67, S 4.11—4.47, Bi 59.00—60.34, Fe 0—0.19, Cu 0—0.03%. Wharlite contained Te 35.47, Bi 59.47, Fe 0.29, Ag 4.37%. Hessite contained Ag 61.52—61.55, Au 0.69—1.01, Te 37.76—37.77%, Fe, Pb, S, traces. Pezrite contained Ag 46.76, Au 18.26, Te 34.98%, Fe, Pb, S, traces. Muthmannite contained Au 22.90, Ag 26.36, Pb 2.58, Te 46.44%. Krennerite, (Au,Ag)Te<sub>2</sub>, contained Au 34.77,

Ag 5.87, Cu 0.34, Fe 0.59, Te 58.60, S 0.65%. Sylvanite contained Au 25.87—26.08, Ag 11.57—11.90, Cu 0.09—0.10, Fe 0.30—0.40, Te 61.98—62.45%, Pb traces. Nagyágite contained Au 8.11—9.47, Pb 51.18—53.55, Sb 0—6.05, Te 29.88—18.99, S 10.83—11.90%. Tellurite and stützite were also found.

A. A. ELDRIDGE.

**Analyses of minerals from Recsk, Hungary.** G. VAVRINECZ (Magyar chem. Fol., 1929, 35, 4—9; Chem. Zentr., 1929, ii, 2991).—The following data are recorded: chalkanthite,  $d$  2.292, CuO 29.64, FeO 0.13, SO<sub>3</sub> 30.18, rock 5.27, H<sub>2</sub>O (diff.) 34.78%; melanterite, FeO 24.15, CuO 0.14, Al<sub>2</sub>O<sub>3</sub> 0.65, SO<sub>3</sub> 28.81, rock 3.05, H<sub>2</sub>O (diff.) 43.20%; pisanite,  $d$  1.910—1.937, CuO 4.60—11.50, FeO 15.12—21.24, SO<sub>3</sub> 28.17—28.53, rock 0.16—1.67%; halotrichite,  $d$  1.84—1.86, FeO 7.45, CuO 0.27, CaO trace, Al<sub>2</sub>O<sub>3</sub> 10.46, Fe<sub>2</sub>O<sub>3</sub> 1.17, SO<sub>3</sub> 34.32, H<sub>2</sub>O (diff.) 46.33%; brochantite, CuO 56.1, FeO 1.3, CaO 1.9, Al<sub>2</sub>O<sub>3</sub> 2.8, SO<sub>3</sub> 17.1, SiO<sub>2</sub> 0.3, H<sub>2</sub>O (diff.) 20.5%.

A. A. ELDRIDGE.

**Lava of the 1928 eruption of Etna.** S. DI FRANCO (Atti R. Accad. Lincei, 1930, [vi], 11, 212—218).—Comparisons have been made of the lavas of the eruptions of 1669, 1910, and 1928. An analysis of the last-named gives SiO<sub>2</sub> 48.52, TiO<sub>2</sub> 1.96, Al<sub>2</sub>O<sub>3</sub> 16.86, Fe<sub>2</sub>O<sub>3</sub> 2.97, FeO 7.54, MnO 0.09, MgO 4.93, CaO 10.03, Na<sub>2</sub>O 4.88, K<sub>2</sub>O 1.83, P<sub>2</sub>O<sub>5</sub> 0.53, H<sub>2</sub>O 0.05, total 100.19%.

The magmatic formulae of Löwinson-Lessing and Osann, and the Osann and Niggli parameters are tabulated and compared.

F. G. TRYHORN.

**Composition of the melilite group.** H. BERMAN (Amer. Min., 1929, 14, 389—407).—The general formula is (Ca+Na)<sub>20-x</sub>Mg<sub>y</sub>Al<sub>2</sub>Si<sub>30-(y+z)</sub>O<sub>70</sub>, where  $x=0-3$ ,  $y=0-10$ , and  $z=0-20$ . Analyses are tabulated, and the members are defined in terms of molecular percentage.

CHEMICAL ABSTRACTS.

**Age of the earth.** A. P. COLEMAN (Nature, 1930, 125, 668—669).—The Grenville rocks of Ontario and Quebec require a longer time than the  $2 \times 10^9$  years allotted by Jeans if the earth began in a gaseous form.

L. S. THEOBALD.

**Equation of state for soil-nitrogen.** H. JENNY (J. Physical Chem., 1930, 34, 1053—1057).—Average soil-nitrogen contents for various regions of the United States can, as a first approximation, be represented by the equation  $N=0.55e^{-0.087T}(1-e^{-0.005H})$  where  $T$  varies between 0° and 22° and  $H$ , the humidity factor, varies between 0 and 400. Calculated and observed values for many regions of the United States are compared.

L. S. THEOBALD.

**Staining method for the determination of rocks.** A. GABRIEL and E. P. COX (Amer. Min., 1929, 14, 290—292).—The polished surface or section is etched with hydrogen fluoride and treated with a concentrated solution of sodium cobaltinitrite for the detection of potash feldspars.

CHEMICAL ABSTRACTS.

## Organic Chemistry.

**Pyrogenic decomposition of methane.** A. VYSOKÝ (Paliva a Top., 1929, 11, 53—59; Chem. Zentr., 1929, ii, 2992).—Benzene is formed at 800—850°. The formation of benzene is not greatly affected by partial oxidation of the methane by oxygen in presence or absence of a copper catalyst.

A. A. ELDRIDGE.

**Oxidation of methane by sulphuric acid in presence of catalysts.** F. FISCHER and H. BAHR (Ges. Abh. Kennt. Kohle, 1928, 8, 281—282; Chem. Zentr., 1930, i, 31).—When a slow stream of methane is passed into warm concentrated sulphuric acid containing mercury (0.5 g. per 100 c.c.) sulphur dioxide is evolved at 180°, the methane content of the gas diminishes, the carbon dioxide content increases, and a pleasant ester odour is developed. The reaction is apparently  $\text{CH}_4 + 4\text{SO}_3 = \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{SO}_2$ .

A. A. ELDRIDGE.

**Preparation of free ethyl.** F. PANETH and W. LAUTSCH (Naturwiss., 1930, 18, 307, and Nature, 1930, 125, 564; cf. A., 1929, 788).—The ethyl radical in the free state has been prepared by the thermal decomposition of lead tetraethyl at reduced pressure in a stream of hydrogen. The free ethyl readily forms volatile compounds with zinc, antimony, cadmium, and lead. The zinc compound was studied in greater detail. The existence of ethyl groups in this compound was established by oxidation to the alcohol and application of the iodoform reaction. The zinc was found to be free from lead; the m. p. and b. p. were approximately equal to those of zinc diethyl. As zinc was placed at some distance from the source of decomposition of the lead tetraethyl, it is asserted that free ethyl must exist and be transported for some distance in the gas stream.

W. R. ANGUS.

**Polymerisation reactions under high pressure.**  
**I. Isoprene and butaldehyde.** J. B. CONANT and C. O. TONGBERG (J. Amer. Chem. Soc., 1930, 52, 1659—1669).—The rate of polymerisation of isoprene has been studied at pressures up to 12,000 atm. at 23—25° (cf. Bridgman and Conant, A., 1929, 1243). The rate is much slower with freshly-distilled isoprene than with the hydrocarbon which has been kept for some days in an atmosphere of nitrogen containing a small amount of oxygen. The rate is increased by using isoprene which has been shaken with oxygen or mixed with a small amount of pinene which has been shaken with oxygen. Quinol is a negative catalyst. Partial polymerisation can, however, be effected at a pressure of 12,000 atm. in absence of oxygen. Although the reaction is of a high order, the rate approximates to one of the first order, presumably because of an autocatalytic effect. The temperature and pressure coefficients of the rate have also been determined. The polymerised product is a colourless, rubber-like solid. Vinyl acetate is polymerised at a much slower rate than isoprene; the rate is increased by quinol and decreased by oxidised pinene. The rate of polymerisation of *n*-butaldehyde is markedly increased by first treating the aldehyde with ozone. The solid polymeride which is formed passes into the

original aldehyde after keeping for about 24 hrs. at 25°.

H. BURTON.

**Aliphatic diolefines. III. Behaviour of  $\Delta^{\alpha\alpha}$ - and  $\Delta^{\beta\beta}$ -hexadienes toward hydrochloric acid.** F. CORTESE (J. Amer. Chem. Soc., 1930, 52, 1519—1521).—Prolonged shaking of  $\Delta^{\alpha\alpha}$ -hexadiene with hydrochloric acid affords 57% of  $\alpha\alpha$ -dichlorohexanes, b. p. 176—178°/760 mm., 23% of  $\varepsilon$ -chloro- $\Delta^{\alpha\alpha}$ -hexene, b. p. 121—125°/760 mm.,  $d_4^{20}$  0.9141,  $n_D^{20}$  1.4305, diallyl oxide, and a small amount of its polymerisation products. Similar treatment of  $\Delta^{\beta\beta}$ -hexadiene gives a mixture of chlorohexenes and polymerised hydrocarbon. When the above dichlorohexane fraction is cooled to -50°, meso- $\alpha\alpha$ -dichlorohexane, b. p. 177.8—178.2° (corr.)/751.8 mm., m. p. 18.7°,  $d_4^{25}$  1.0459, crystallises.

H. BURTON.

**Preparation of methylene iodide.** G. PANOPOULOS and A. PETZETAKIS (Chem.-Ztg., 1930, 54, 310).—When potassium persulphate and iodoacetic acid (cf. Kaufler and Herzog, A., 1909, i, 870) in aqueous solution are gradually warmed to 85° and maintained at this temperature for 6 hrs., an almost theoretical yield of methylene iodide is obtained. Hydrogen peroxide, perborates, perchlorates, and peroxides do not give this product. The reaction forms a delicate test for persulphates.

H. E. F. NOTTON.

**Catalytic decomposition of pentachloroethane.** A. MAILHE and SABRON (Bull. Soc. chim., 1930, [iv], 47, 349—350).—Hydrogenation of pentachloroethane vapours in presence of nickel at 270° yields trichloroethylene and hydrogen chloride, the trichloroethylene being unchanged by further treatment with hydrogen in presence of nickel at 300—330°. In presence of nickel chloride at 330° pentachloroethane is converted into tetrachloroethylene, b. p. 120—122°,  $d_4^{20}$  1.623,  $n_D^{20}$  1.5008, which also is not hydrogenated when passed over nickel at 300—350° in presence of hydrogen.

R. BRIGHTMAN.

**$\beta$ - and  $\gamma$ -Ethylenic alcohols and chlorides.** C. COURTOT and J. PIERRON (Compt. rend., 1930, 190, 1057—1059).—Treatment of  $\Delta^{\alpha}$ -hexen- $\varepsilon$ -ol with boiling hydrochloric acid (cf. Norris, A., 1907, i, 1034) gives 2 : 5-dimethyltetrahydrofuran instead of the corresponding chloride.  $\varepsilon$ -Chloro- $\Delta^{\alpha}$ -hexene, b. p. 120—124°,  $d_4^{12}$  0.91025,  $n_D^{12}$  1.4350, prepared in 30% yield from the hexenol and phosphorus pentachloride in dry chloroform, when oxidised with a mixture of chromic and sulphuric acids (cf. A., 1929, 796, 802) does not yield allylacetone; oxidation occurs at the double linking.  $\delta$ -Chloro- $\Delta^{\alpha}$ -hexene is oxidised to formic acid,  $\beta$ -phenylethyl chloride is unaffected, and  $\omega$ -bromostyrene gives some formic acid. None of the above chlorides is hydrolysed to any appreciable extent by water at about 95°. The halogen atom in an ethylenic chloride is activated by a double linking only in the  $\alpha$ -series.

H. BURTON.

**Abnormal reaction of dihalogenated propylenes.** A. KIRRMANN and J. GRARD (Compt. rend., 1930, 190, 876—878; cf. A., 1926, 817).— $\alpha\alpha$ -Dichloro- $\Delta^{\beta}$ -propene (I),  $d^{21}$  1.169,  $n_D^{21}$  1.450, reacts

with magnesium propyl bromide to give hexane, chlorohexene, b. p. 121—121.5°,  $d_{25}^{25}$  0.8872,  $n_D^{25}$  1.4300 (dibromide, b. p. 107°/13 mm.,  $d_{25}^{25}$  1.664,  $n_D^{25}$  1.515, yielding a hexene, b. p. 64°,  $d_{25}^{25}$  0.672,  $n_D^{25}$  1.388, with sodium),  $\Delta^3$ -nonene, b. p. 44—46°/12 mm., and dodecadiene (mixture of isomerides), b. p. 79—84°/11 mm.,  $d_{25}^{25}$  0.779,  $n_D^{25}$  1.444 (tetrabromide).  $\alpha\gamma$ -Dichloropropene (II), b. p. 109—110°,  $d_{25}^{25}$  1.222,  $n_D^{25}$  1.4735, yields similar results, but with I the chlorohexene and with II, and also with  $\alpha\gamma$ -dibromopropene, the nonene predominates. An interpretation of these results involving the intermediate formation of  $\dot{\text{C}}\text{HCl}\cdot\text{CH}\cdot\dot{\text{C}}\text{H}_2$  and  $\dot{\text{C}}\text{I}$  from both I and II followed by addition and isomerisation, is given. A. I. VOGEL.

**Allene and methylacetylene tetrabromides.** C. D. HURD, R. N. MEINERT, and L. U. SPENCE (J. Amer. Chem. Soc., 1930, 52, 1138—1146).— $\Delta^2$ -Propinene is prepared in a high state of purity from methyl iodide and sodium acetylide in liquid ammonia (cf. Lebeau and Picon, A., 1913, i, 438). Preparation by dehalogenation of propylidene chloride gives poor yields, whilst similar preparation from propylene bromide invariably yields allene as well. Such a mixture cannot be readily separated by fractional distillation, although the percentage of allene may be lowered from 5.5 to 1.2% by this means.  $\alpha\alpha\beta\beta$ -Tetrabromopropane is prepared by passing methylacetylene into a solution of bromine in carbon tetrachloride. The purest material has b. p. 105—107°/9 mm.,  $d_4^{20}$  2.687,  $n_D^{20}$  1.6166.

Allene tetrabromide is prepared by the addition of bromine to allene prepared from  $\beta\gamma$ -dibromo- $\Delta^2$ -propene, or to the latter compound directly. Attainment of a high degree of purity requires several crystallisations as well as fractional distillation. It has m. p. 10.7°, b. p. 115.5°/9 mm.,  $d_4^{20}$  2.703,  $n_D^{20}$  1.6200. Values of  $d_4$  and  $n_D$  for other temperatures are given for each substance, and the figures are compared with those recorded in the literature.

R. K. CALLOW.

**Reaction of various Grignard reagents with epichlorohydrin. Preparation of some new chlorohydrins.** C. F. KOELSCH and S. M. McELVAIN (J. Amer. Chem. Soc., 1930, 52, 1164—1169; cf. this vol., 59; Fourneau and Tiffeneau, A., 1908, i, 163).—The following chlorohydrins have been obtained, generally from the chloride, in the yields indicated in parentheses:  $\alpha$ -chlorohexan- $\beta$ -ol, b. p. 72—74°/12 mm. (from the iodide; 19%); 3:5-dinitrobenzoate, m. p. 65—66°;  $\alpha$ -chloroheptan- $\beta$ -ol, b. p. 92—94°/13 mm.,  $d_{25}^{25}$  0.9931,  $n_D^{25}$  1.4474 (from the iodide; 16%); 3:5-dinitrobenzoate, m. p. 59°;  $\alpha$ -chloro-8-methylhexan- $\beta$ -ol, b. p. 82—84°/13 mm.,  $d_{25}^{25}$  0.9915,  $n_D^{25}$  1.4503 (9%); 3:5-dinitrobenzoate, m. p. 49—50°;  $\alpha$ -chlorooctan- $\beta$ -ol, b. p. 104—107°/13 mm.,  $d_{25}^{25}$  0.9715,  $n_D^{25}$  1.4485 (30%); 3:5-dinitrobenzoate, m. p. 55°;  $\alpha$ -chloro-8-ethylhexan- $\beta$ -ol, b. p. 103—104°/15 mm.,  $d_{25}^{25}$  0.9828,  $n_D^{25}$  1.4528 (11%); 3:5-dinitrobenzoate, an oil;  $\alpha$ -chloro- $\gamma$ -cyclohexylpropan- $\beta$ -ol, b. p. 122—124°/11 mm.,  $d_{25}^{25}$  1.0533,  $n_D^{25}$  1.4854 (15%); 3:5-dinitrobenzoate, m. p. 95—96°;  $\alpha$ -chloro- $\delta$ -cyclohexylbutan- $\beta$ -ol, b. p. 142—144°/12 mm.,  $d_{25}^{25}$  1.0305,  $n_D^{25}$  1.4832 (30%); 3:5-dinitrobenzoate, m. p. 107—108°;  $\alpha$ -chloro- $\gamma$ -phenylpropan- $\beta$ -ol, b. p. 142—

144°/23 mm.,  $d_{25}^{25}$  1.1528,  $n_D^{25}$  1.5470 (18%); 3:5-dinitrobenzoate, m. p. 120—121°;  $\alpha$ -chloro- $\delta$ -phenylbutan- $\beta$ -ol, b. p. 158—160°/23 mm.,  $d_{25}^{25}$  1.1203,  $n_D^{25}$  1.5375 (32%); 3:5-dinitrobenzoate, an oil;  $\alpha$ -chloro- $\epsilon$ -phenylpentan- $\beta$ -ol, b. p. 152—154°/8 mm.,  $d_{25}^{25}$  1.0895,  $n_D^{25}$  1.5320 (13%); 3:5-dinitrobenzoate, m. p. 106—107°;  $\alpha$ -chloro- $\zeta$ -phenylhexan- $\beta$ -ol, b. p. 147—148°/2.5 mm.,  $d_{25}^{25}$  1.0710,  $n_D^{25}$  1.5262 (25%); 3:5-dinitrobenzoate, an oil).

The analogous structure of all the compounds prepared is assumed from the known structures in the case of the products from magnesium ethyl,  $n$ -butyl, and phenyl halides, and  $\alpha$ -chloro- $\gamma$ -cyclohexylpropan- $\beta$ -ol is also obtainable by the interaction of  $\gamma$ -cyclohexyl- $\Delta^2$ -propene with hypochlorous acid. Treatment of  $\alpha$ -chloro- $\gamma$ -cyclohexylpropan- $\beta$ -ol with powdered sodium hydroxide in dry ether yields  $\gamma$ -cyclohexylpropylene  $\alpha\beta$ -oxide, b. p. 197—200°/740 mm.,  $d_{25}^{25}$  0.9357,  $n_D^{25}$  1.4572 (cf. Rességuier, A., 1914, i, 528).  $\alpha$ -Chloro- $\delta$ -phenylbutan- $\beta$ -ol yields benzoic acid when oxidised with permanganate.

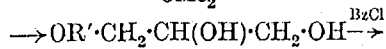
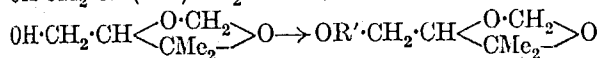
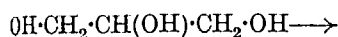
The constants for the following compounds differ considerably from those recorded in the literature:  $\gamma$ -chloropentane (from the alcohol and hydrogen chloride), b. p. 96—97°/729 mm.,  $d_{25}^{25}$  0.8724,  $n_D^{25}$  1.4073; chloromethylcyclohexane [cyclohexylmethyl chloride] (from the carbinol and thionyl chloride), b. p. 67—68°/20 mm.,  $d_{25}^{25}$  0.9812,  $n_D^{25}$  1.4630.

In general, Grignard reagents derived from primary alkyl halides give higher yields than those from secondary, whilst no product could be isolated from tertiary compounds. The yield increases with the mol. wt. of the alkyl group. The effect of aryl groups is irregular. Iodides appear to give smaller yields. R. K. CALLOW.

[Preparation of] lauryl alcohol. S. G. FORD and C. S. MARVEL (Organic Syntheses, 1930, 10, 62—64).

[Preparation of] *l*-propylene glycol. P. A. LEVENE and A. WALT (Organic Syntheses, 1930, 10, 84—86).

**Acyl wandering and racemisation of glycerides.** B. SUZUKI and Y. INOUE (Proc. Imp. Acad. Tokyo, 1930, 6, 71—74).—The di-*p*-nitrobenzoate of glyceryl methyl ether prepared in accordance with the scheme  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{CH}_2\text{Cl}\cdot\text{CH}(\text{OR})\cdot\text{CH}_2\cdot\text{OR}$   $\xrightarrow[\text{EtOH}]{\text{AgNO}_3}$   $\text{OR}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OR} \xrightarrow[\text{Ag}_2\text{O}]{\text{MeI}}$   $\text{OR}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{OR}$  ( $\text{R}=\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ -*p*) is the  $\alpha\alpha'$ -derivative, wandering of the *p*-nitrobenzoyl group occurring, since the product is identical with glyceryl  $\beta$ -methyl ether  $\alpha\alpha'$ -di-*p*-nitrobenzoate, m. p. 69°, obtained thus:  $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{\text{HOCl}}$   $\text{OH}\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{\text{NaOMe}}$   $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{OR}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{OR}$ , but is different from glyceryl  $\alpha$ -methyl ether  $\alpha\beta$ -di-*p*-nitrobenzoate, m. p. 73°, prepared thus:  $\text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{\text{NaOMe}}$   $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{\text{NaOMe}}$   $\text{OMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH} \rightarrow \text{OMe}\cdot\text{CH}_2\cdot\text{CH}(\text{OR})\cdot\text{CH}_2\cdot\text{OR}$ .  $\alpha$ -Phthaloylglyceryl  $\alpha'\beta'$ -dibenzoate, prepared thus:



$\text{OR}'\cdot\text{CH}_2\cdot\text{CHBz}\cdot\text{CH}_2\cdot\text{OBz}$  ( $\text{R}'=\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ ), is resolved by fractional precipitation of its *strychnine* salt from chloroform solution, the free acid ester regenerated from the extreme fractions having  $[\alpha]_D^{25} -21.21^\circ$  and  $+23.25^\circ$ , respectively, which, however, racemise fairly rapidly in solution [*strychnine* salt  $-25.1^\circ$  to  $-8.87^\circ$  (constant) in 98 hrs.]. This racemisation is not considered to be due to wandering of the acyl groups. Similar racemisation of the *strychnine* salt of *isopropylideneglycerol*  $\alpha$ -phthalate occurs ( $-20.77^\circ$  to  $-10.35^\circ$  in 12 days) and hence it is suggested that glycerides of fatty acids found in natural products do not necessarily exist in the racemic state, but may be readily racemised during isolation. In support of this view, specimens of castor bean and pea-nut oils rapidly isolated from the seeds by maceration with cold ether exhibit optical rotations the magnitude of which is double that usually found, but decrease to this normal value on keeping.

J. W. BAKER.

**Reactions relating to carbohydrates and polysaccharides. XXVI. Structure of acetone glycerol [*isopropylideneglycerol*].** H. HIBBERT and J. G. MORAZAIN (Canad. J. Res., 1930, 2, 35—41).—When condensation of glycerol with acetone in presence of anhydrous copper sulphate is carried out at  $56^\circ$  (17 hrs.) or at  $20^\circ$  (123 hrs.), in each case  $\alpha$ -*isopropylideneglycerol*, b. p.  $82.5\text{--}83^\circ/13\text{ mm.}$ , is obtained in good yield, although the conditions in the second method would be expected to favour the formation of a six-membered ring. The homogeneity of the product is demonstrated by the uniformity of properties of the fractions obtained by distillation. It is readily hydrolysed by heating with water. The constitution is proved by the preparation, by careful treatment with methyl sulphate and a constant excess of sodium hydroxide solution, of the  $\gamma$ -methyl ether, b. p.  $57^\circ/14\text{ mm.}$ ,  $154^\circ/774\text{ mm.}$ , which yields on hydrolysis glyceryl  $\alpha$ -methyl ether. Moreover, a homogeneous benzoate, m. p.  $42^\circ$ , is formed when the  $\alpha$ -*isopropylideneglycerol* is treated with benzoyl chloride in pyridine.

R. K. CALLOW.

**Reactions relating to carbohydrates and polysaccharides. XXVIII. Structure of *isopropylideneglycerol*.** H. HIBBERT and J. G. MORAZAIN (Canad. J. Res., 1930, 2, 214—216).—Methylation of *isopropylideneglycerol* (see above) with methyl iodide and silver oxide at  $40^\circ$  gives a 76% yield of the  $\alpha$ -methyl ether, b. p.  $58\text{--}60^\circ/14\text{ mm.}$ ,  $154^\circ/774\text{ mm.}$ ,  $n_D^{20} 1.4150$ , which is hydrolysed by acidified water at  $60^\circ$ , exclusively to glyceryl  $\alpha$ -methyl ether, b. p.  $110^\circ/13\text{ mm.}$ ,  $221^\circ/754\text{ mm.}$ ,  $d_4^{25} 1.1169$ ,  $n_D^{25} 1.4430$ . Since no indication of the presence of glyceryl  $\beta$ -methyl ether, b. p.  $122\text{--}123^\circ/13\text{ mm.}$ ,  $d_4^{25} 1.1273$ ,  $n_D^{25} 1.4485$ , could be detected it follows that condensation of acetone and glycerol in either neutral or acid medium gives only the five-membered cyclic ketal.

J. W. BAKER.

**Reactions relating to carbohydrates and polysaccharides. XXVII. Synthesis and structure of trichloroethylideneglycerol.** H. HIBBERT, J. G. MORAZAIN, and A. PAQUET (Canad. J. Res., 1930, 2, 131—143; cf. preceding abstract).—Attempts under varying conditions, both with and without catalysts, to cause glycerol and chloral to condense to the semi-acetal were unsuccessful. The cyclic acetal,  $\alpha\beta$ -trichloroethylideneglycerol, b. p.  $132\text{--}133^\circ/10\text{ mm.}$ , obtained either by Böcsken's (A., 1927, 646) or Yoder's (A., 1923, i, 309) method, is very stable to hydrolysis and is proved to possess a five-ring structure by methylation with methyl sulphate and sodium hydroxide to a *methyl ether*, b. p.  $108^\circ/10\text{ mm.}$ , m. p.  $15\text{--}16^\circ$ ,  $d_4^{20} 1.4228$ ,  $n_D^{20} 1.4806$ , identical with that obtained by condensation of glyceryl  $\alpha$ -methyl ether with chloral hydrate in the presence of concentrated sulphuric acid at  $65^\circ$ . All attempts to isolate an isomeric six-ring cyclic acetal, or to convert the five- into a six-ring compound, were unsuccessful. Moreover, the above carbinol is converted by the action of the appropriate acid chloride and pyridine into a mixture of *cis*-(?), m. p.  $73^\circ$ , and *trans*-, m. p.  $83^\circ$ , *benzoates*, and *cis*- and *trans*-*p*-nitrobenzoates, m. p.  $102^\circ$  and  $102.5^\circ$  (mixed m. p.  $92^\circ$ ), which, because of the proximity of their m. p., are assumed to be geometrical and not structural isomerides. The mechanism of cyclic acetal formation and the effect of the polar character of the aldehyde are discussed. Hydroxytrichloroethylideneglycol (De Forcrand, A., 1889, 689), has m. p.  $50\text{--}51^\circ$  (*loc. cit.* m. p.  $42^\circ$ ).

J. W. BAKER.

**Isomeric nitrobenzylideneglycerols.** H. HIBBERT (Canad. J. Res., 1930, 2, 117).—Tanasescu and Macovski (this vol., 213) erroneously state that Hibbert and others (A., 1929, 47, 170) obtained only a five-membered ring acetal by condensation of *p*-nitrobenzaldehyde with glycerol, whereas actually both the 5- and 6-membered ring compounds were isolated.

J. W. BAKER.

**Glycidol. I. Preparation from glycerol chlorohydrin. II. Reactions with secondary amines.** T. H. RIDER and A. J. HILL (J. Amer. Chem. Soc., 1930, 52, 1521—1527, 1528—1530).—I. Glycerol  $\alpha$ -chlorohydrin is prepared in good yield by heating a mixture of glycerol (1 part), hydrochloric acid ( $d 1.19$ ; 3.75 parts), and acetic acid (0.1 part) for 10 hrs. at  $100^\circ$  and then distilling. The *phenylcarbimide* derivatives of glycerol  $\alpha$ - and  $\beta$ -chlorohydrins have m. p.  $128\text{--}129^\circ$  and  $131\text{--}133^\circ$ , respectively; a mixture of them can be separated by crystallisation from high-boiling petroleum. Treatment of glycerol  $\alpha$ -chlorohydrin (1 mol.) with sodium wire (0.7 mol.) in ether at  $10\text{--}12^\circ$  gives a 90% yield (on the chlorohydrin used) of glycidol (hydroxymethylethylene oxide), b. p.  $41^\circ/1\text{ mm.}$ ,  $d_4^{25} 1.1143$ ,  $n_D^{25} 1.4302$  (*phenylcarbimide* derivative, m. p.  $60^\circ$ ;  $\alpha$ -*naphthylcarbimide* derivative, m. p.  $102^\circ$ ). Pure glycidol does not reduce Fehling's solution or ammoniacal silver nitrate. It is polymerised by treatment with pyridine or calcium chloride. Glycidol is also obtained in 60—68% yield from the  $\alpha$ -chlorohydrin and alcoholic potassium hydroxide or sodium ethoxide; the use of alcohol is, however, undesirable, since it leads to the formation of glyceryl ethyl ether

and it is impossible to isolate the whole of the glycidol from its alcoholic solution.

II. Slow addition of glycidol to a secondary amine, maintained below its b. p., affords 82–96% yields of  $\gamma$ -dialkylaminopropane- $\alpha\beta$ -diols. The following are described: dimethylamino-, b. p. 111°/15 mm. [picrate, m. p. 126–128° (lit. 160°)]; diethylamino-, b. p. 106°/3 mm.; di-*n*-propylamino-, b. p. 143°/9 mm.; diisobutylamino-, b. p. 122°/2 mm.; di-*n*-amylamino-, b. p. 149°/2 mm., and piperidino-, m. p. 83°.

H. BURTON.

**Manufacture of ethyl ether.** K. E. STÄRBLÖM. See B., 1930, 409.

**Ether and ester.** J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 492–500).—By the action of ethyl ether on nitric acid (*d* 1.5) or nitrogen pentoxide at –15° ethyl nitrate is formed;  $\text{Et}_2\text{O} + \text{HNO}_3 = \text{EtNO}_3 + \text{EtOH}$ . The action is autocatalytic, the catalyst being oxides of nitrogen, and the observed period of induction is lengthened by pre-addition of carbamide nitrate. An attempt to increase the yield of ethyl nitrate by addition of sulphuric acid was unsuccessful, the mixture being violently explosive above –15°, ethyl nitrate being decomposed into nitrogen peroxide, carbon monoxide, and water under these conditions. Ether interacts with many acids, both inorganic and organic, to yield esters, and examples from the literature are summarised and discussed (cf. Underwood and Wakeman, this vol., 320). The reaction  $\text{Et}_2\text{O} + (\text{R}\cdot\text{CO})_2\text{O} \rightleftharpoons 2\text{R}\cdot\text{CO}_2\text{Et}$  is shown to be reversible and is catalysed in both directions by anhydrous ferric chloride. Thus when ether and benzoic or phthalic anhydride is heated with anhydrous ferric chloride at 150° small yields of ethyl benzoate and phthalate, respectively, are obtained. Conversely, when ethyl formate, carbonate, oxalate, malonate, succinate, or phthalate is heated in a sealed tube with anhydrous ferric chloride, small quantities of ether are formed. The position of the equilibrium varies greatly from case to case. Thus ethyl acetate gives no trace of ether even when the temperature is raised to 200°, whilst ethyl orthoformate, which, when heated alone, distils unchanged at 144–146°, distils completely below 60° when a small quantity of ferric chloride is added, and the distillate is readily fractionated into ether and ethyl formate. The conversion of ethyl malonate into ethyl acetate by boiling with zinc chloride (Underwood and Wakeman, *loc. cit.*) could not be repeated. When ethyl malonate is refluxed with anhydrous zinc chloride for 3 hrs. the only products are carbon dioxide and only traces of ethylene, ethyl chloride, and ethyl acetate, whilst when heated with slightly moist zinc chloride at 150°, a small quantity of ether is the sole product.

J. W. BAKER.

**Esters of halogenated alcohols. II. Reactions of esters containing the trichloromethoxyl group.** V. NEKRASSOV and N. MELNIKOV (J. pr. Chem., 1930, [iii], 126, 81–96; cf. A., 1929, 1269).—The interaction of trichloromethyl chloroformate (diphosgene) and primary aliphatic alcohols leads first to alkyl trichloromethyl carbonates, which react further with the alcohol only when heated to give alkyl carbonates. The alkyl trichloromethyl carbonates are partly

decomposed by heat into carbonyl chloride and alkyl chloroformate. Aniline reacts vigorously with them to give diphenylcarbamide, aniline hydrochloride, and phenylalkylurethanes; and sodium phenoxide yields phenyl and the phenyl alkyl carbonates. The reactions of sodium phenoxide with trichloromethyl chloroformate are similar to those of the aliphatic alcohols, but the intermediate phenyl trichloromethyl carbonate is much more readily decomposed. Hexachlorodimethyl carbonate (triphosgene) reacts with aniline to yield diphenylcarbamide and aniline hydrochloride, with alcohols to form initially alkyl trichloromethyl carbonate and alkyl chloroformate, and with sodium phenoxide to yield phenyl carbonate, and, if there is a deficit of phenoxide, a little phenyl trichloromethyl carbonate. The reactions of the alkyl or aryl trichloromethyl carbonates with alcohols, aniline, etc. are regarded as occurring according to the scheme:  $\text{OR}\cdot\text{CO}_2\text{CCl}_3 + \text{R}\cdot\text{OH} \rightarrow \text{CO}(\text{OR})_2 + \text{CCl}_3\cdot\text{OH}$ ;  $\text{CCl}_3\cdot\text{OH} \rightarrow \text{HCl} + \text{COCl}_2$ . The following are described: trichloromethyl ethyl carbonate, b. p. 78°/19 mm.,  $d_4^{20}$  1.4205,  $n_D^{20}$  1.4450; trichloromethyl isooctyl carbonate, b. p. 120°/23 mm.,  $d_4^{20}$  1.2644,  $n_D^{20}$  1.4466; phenyl trichloromethyl carbonate, m. p. 70.5° (prepared but not analysed by Kling and collaborators, A., 1920, i, 139; m. p. 66°); isooctyl-*N*-phenylurethane, m. p. 55–56°, b. p. 174°/17 mm. H. A. PIGGOTT.

**Silicic acids and esters.** L. SOLANO and E. MOLES (Anal. Fis. Quím., 1930, 28, 171–176).—Pure ethyl orthosilicate does not appear to undergo appreciable hydrolysis at the ordinary temperature when in contact with water containing 1% of ethyl alcohol even after 3–4 weeks; the impure material, containing pyrosilicate and silicon tetrafluoride, rapidly hydrolyses as reported by Thiessen and Koerner (A., 1929, 1154).

H. F. GILLBE.

**Complexes of gold chlorides with organic sulphides.** P. C. RAY and D. C. SEN (J. Indian Chem. Soc., 1930, 7, 67–77).—By addition of the appropriate organic sulphide, with cooling, to auric chloride in the presence of aqua regia (nitric acid *d* 1.4; hydrochloric acid *d* 1.2) compounds of the type  $\text{AuCl}_3\cdot\text{R}_2\text{S}$  are formed, for which the name aurichloride dialkyl sulphide is suggested. These are non-conducting and unimolecular and are therefore assumed to be compounds of quadricovalent gold. They react with potassium thiocyanate and thio-carbamide thus:  $\text{AuCl}_3\cdot\text{R}_2\text{S} + 4\text{KSCN} = \text{KAu}(\text{SCN})_4 + 3\text{KCl} + \text{R}_2\text{S}$ ;  $\text{AuCl}_3\cdot\text{R}_2\text{S} + 2\text{CS}(\text{NH}_2)_2 = \text{AuCl}[\text{S}\cdot\text{C}(\text{NH})\cdot\text{NH}_2]_2 + 2\text{HCl} + \text{R}_2\text{S}$ , and are converted into aurochloride dialkyl sulphides,  $\text{AuCl}\cdot\text{R}_2\text{S}$  (cf. Phillips, A., 1901, i, 444), by warming with alcohol, this conversion occurring more readily with derivatives of methyl (or substituted methyl) sulphides, and these derivatives are also obtained as by-products in the initial reaction. The aurochloride dialkyl sulphide is reconverted into the auri-compound by the action of dilute aqua regia or chlorine water. Thus from the appropriate sulphide are obtained: aurichloride dimethyl, m. p. 160°; diethyl, m. p. 95° (most unstable of the series); di-*n*-propyl, m. p. 80°; diisobutyl, m. p. 83°; methyl *n*-propyl, m. p. 85°; and dibenzyl, m. p. 118°, sulphide; aurochloride dimethyl (Phillips, *loc. cit.*) [converted by warm pyridine into the compound



$\text{AuCl} \cdot \text{C}_5\text{H}_5\text{N}$ , m. p. 250—252° (decomp.); dibenzyl, m. p. 125° (Herrmann, A., 1905, i, 733, gives 122°); and methyl *n*-propyl, m. p. 100—101°, sulphide. The compound  $\text{Au}_2\text{Cl}_4 \cdot 2(\text{CH}_2\text{Ph})_2\text{S}$ , m. p. 133°, obtained by Herrmann (*loc. cit.*; who gives m. p. 127°), is found to possess a mol. wt. of 944 corresponding with the bimolecular formula, and is considered to be auroaurichloride dibenzyl sulphide,  $[\text{AuCl}_3(\text{CH}_2\text{Ph})_2\text{S} \cdot \text{AuCl}(\text{CH}_2\text{Ph})_2\text{S}]$ , since it may be synthesised from the auro- and auri-chloride dibenzyl sulphides and may be separated into its components by the action of cold potassium thiocyanate, which gives aurochloride dibenzyl sulphide (not acted on by this reagent) and potassium aurithiocyanate and benzyl sulphide, the products of its action on the auri-chloride portion. J. W. BAKER.

[Preparation of] sodium  $\beta$ -bromoethanesulphonate. C. S. MARVEL and M. S. SPARBERG (Organic Syntheses, 1930, 10, 96—97).

Influence of poles and polar linkings on course pursued by elimination reactions. VII. Generalised form of olefinic degradation of sulphones. G. W. FENTON and C. K. INGOLD (J.C.S., 1930, 705—708).—The degradation of sulphones in the presence of concentrated potassium hydroxide solution although undoubtedly based on a mechanism similar to that previously advanced for the decompositions of quaternary ammonium hydroxides is, when expressed in terms of this mechanism, far from general, since an electron source which is stronger than methyl seriously inhibits the sulphone decomposition. Since this mechanism ultimately considers the activation or de-activation of the  $\beta$ -hydrogen atom attacked by hydroxyl it has been possible to generalise the sulphone degradation by employing anions more basic (greater proton affinity) than hydroxyl.

Thus phenyl- $\beta$ -phenylethyl-, diethyl-, ethyl-*n*-propyl-, ethylisoamyl-, ethyl-*n*-octyl-, diisopropyl-, di-*n*-butyl-, di-*n*-octyl-, diisoamyl-, and diisobutylsulphones were heated with alcoholic sodium ethoxide at temperatures not above 235° and underwent degradation with formation of respectively styrene, ethylene, ethylene, ethylene, propylene, propylene,  $\Delta^{\alpha}$ -*n*-butene,  $\Delta^{\alpha}$ -*n*-octene,  $\Delta^{\alpha}$ -isoamylene, and isobutene.  $\alpha\beta$ -Dibromo-*n*-octane has b. p. 240—242°.

R. J. W. LE FÈVRE.

Ethaneseleninic acid. H. J. BACKER and W. VAN DAM (Rec. trav. chim., 1930, 49, 479—481).—Dropwise addition of ethyl sulphate to an aqueous solution of potassium diselenide gives diethyl diselenide, b. p. 85°/21 mm. (Rathke, Annalen, 1869, 152, 216), which is oxidised by nitric acid (*d* 1.4) at 100° to the nitrate,  $\text{EtSe}(\text{ONO}_2)(\text{OH})_2$ , of ethaneseleninic acid [hydrochloride, m. p. 106° (decomp.)], from which the lead salt of ethaneseleninic acid, m. p. 47°, is obtained, the free acid being liberated by decomposition with the theoretical quantity of sulphuric acid. The acid is a much weaker acid than the carboxylic acids ( $k_{25}$   $5.29 \times 10^{-6}$ ).

J. W. BAKER.

Preparation of fatty acids from their higher homologues. F. ROCHUSSEN (Ber. Schimmel & Co., 1929, 181—186).—The preparation, by a modification of Crossley and Le Sueur's method, of lauric from

$\alpha$ -bromomyristic, decoic and undecoic from  $\alpha$ -bromolauric, octoic, nonoic, and decoic from  $\alpha$ -chloro-undecoic, and hexoic and heptoic from  $\alpha$ -bromo-octoic acid is described. CHEMICAL ABSTRACTS.

Ethyl difluoroacetoacetate. Y. DÉSIRANT (Bull. Soc. chim. Belg., 1930, 39, 143—156).—Ethyl difluoroacetoacetate, b. p. 70—70.5°/28 mm.,  $d_4^{20}$  1.2418,  $n_D^{20}$  1.40590 [copper, m. p. 179.5—180.5° (decomp.)], and sodium salts, was prepared as follows.  $\alpha$ -Bromo- $\beta$ -difluoroethane when heated with mercuric oxide in the presence of water at 150° in a bronze autoclave gives  $\beta$ -difluoroethanol, oxidised by chromic acid or by nitric acid (*d* 1.29) to difluoroacetic acid. Interaction of ethyl difluoroacetate with anhydrous sodium ethoxide in dry ether gives an additive compound, which on heating with ethyl acetate during 5 hrs., followed by decomposition with 10% sulphuric acid at 0°, keeping of the ethereal extract over anhydrous calcium chloride for 2 days (to decompose the ethyl difluoroacetoacetate-water additive compound), and distillation affords ethyl difluoroacetoacetate, b. p. 160° (slight decomp.). Titration by a modified Kurt Meyer method indicated an enolic content of 1—2%. The ketonic modification probably forms a monohydrate. By dissolution in ether, followed by precipitation with water, the enolic content, as shown by the immediate precipitation of the cupric salt, is considerably increased: distillation over sodium yielded an ester containing 80% of the enolic form. Fractional crystallisation of the ester at low temperatures (solid carbon dioxide and ether) gave the almost pure enol (98.9—99.1%), m. p. —45.5°. The enolic form gradually passes into the ketonic form, the enolic content after 4 days, 4 months, and 1 year being 67.3%, 16%, and 9%, respectively. In the presence of phthalic acid the final equilibrium mixture contained 14% of the enolic form. The equilibrium is considerably influenced by alcohol at —15° (cf. ethyl acetoacetate, which is unaffected), a sample initially containing 58% of the enol containing 98% of the ketonic form after 90 min. At the ordinary temperature an alcoholate is probably formed. Conductivity and hydrogen-ion concentration measurements indicated that the enolic form behaved as a strong acid. A slight increase in potential with time was observed with the quinhydrone electrode.

When ethyl difluoroacetoacetate is heated with 10% sulphuric acid difluoroacetone, b. p. 46.5—46.7°/757 mm.,  $d_4^{20}$  1.1644,  $n_D^{20}$  1.32802, is formed.

A. I. VOGEL.

Coloured iodine compounds of basic salts of rare earths. Starch iodide problem. II. D. KRÜGER and E. TSCHIRCH (Ber., 1930, 63, [B], 826—836; cf. this vol., 62).—Under suitable conditions, all the colorations developed by starch-iodine mixtures are observed when ammonia is added to solutions of the nitrates of certain rare earths in the presence of iodine and the alkali salts of organic acids; the colorations are very intense and sometimes persistent. The conditions for the formation of yellow, brown, red, or violet in place of blue colours are (1) the addition of definite organic ions to a lanthanum nitrate solution containing iodine and acetate previous to that of ammonia (potassium

iodide of a large excess of acetate may cause transformation of the blue colour into brown or yellow) and (2) replacement of the acetate ion by certain other organic ions. Under (1), the influence of propionate, *n*- and *iso*-butyrate, *n*- and *iso*-valerate, iodo-, monochloro-, dichloro-, trichloro-, and tribromo-acetate and *p*-toluenesulphonate is described in detail. Under (2), only acetate and propionate ions give blue solutions; the higher fatty acids (up to octoic) afford yellow to yellowish-brown solutions or white precipitates. At certain concentrations, benzoate ions cause a bluish-black tone, whereas the isomeric toluic acids give dark brown to lemon-yellow solutions in the sequence *p* → *m* → *o*; phenylacetic acid gives almost colourless to pale yellow precipitates.

Contrary to previous observations (*loc. cit.*), praseodymium does not give dark blue solutions; this is the case also with neodymium, samarium, europium, yttrium, and erbium. The ability of the basic acetates to form blue or coloured iodine compounds appears restricted to lanthanum. Basic propionates of neodymium, praseodymium, and samarium are not coloured by iodine. The ability to give coloured iodine compounds of basic benzoates is not confined to lanthanum.

The presence of other rare-earth metals in relatively small concentration considerably affects the blue coloration of basic lanthanum acetate, the action increasing in the sequence Pr → Nd → Sm. Smaller amounts retard greatly the development of the colour without appreciably affecting its ultimate intensity.

The relationship of the observations to the starch-iodine problem is discussed in detail. The most significant feature is the very marked influence on the iodine reaction exerted by chemical changes so slight that they can scarcely be appreciated by the customary analytical methods. H. WREN.

**Hydrogenation of liquid acid anhydrides.** C. MANNICH and A. H. NADELMANN (Ber., 1930, 63, [B], 796—799).—Acetic anhydride at the atmospheric temperature and pressure is slowly hydrogenated in the presence of palladium-black, giving acetaldehyde with a little ethyl acetate. At 40°/3.75 atm., reduction occurs more readily, but not more than 20% of the possible hydrogen is absorbed. Reaction is much more rapid and complete after addition of hydrogen chloride (optimum 2%) or acetyl chloride. The change consists in the production of acetyl chloride, which suffers reduction; the acetic anhydride behaves as acceptor for the liberated hydrogen chloride. Acetaldehyde with a little paracetaldehyde and ethyl acetate is produced. Hydrogenation of propionic anhydride takes place similarly. Lauric anhydride is reduced with greater difficulty and addition of hydrogen chloride is not helpful to the same extent. In presence of decahydronaphthalene at 40°/3.75 atm., the main products are *lauraldehyde*, b. p. 124—126°/11 mm. (*semicarbazone*, m. p. 102.5—103.5°; *p*-nitrophenylhydrazone, m. p. 90°; *oxime*, m. p. 76—77°), *polymeric lauraldehyde*, m. p. 57°, characterised by very difficult depolymerisation, *dilauryl ether*, m. p. 32.5°, b. p. about 175°/0.15 mm.,

converted by hydrogen bromide in glacial acetic acid into  $\alpha$ -bromododecane, and an unidentified substance, C<sub>24</sub>H<sub>48</sub>O, m. p. 69°. H. WREN.

**Differentiation between *cis*- and *trans*-ethylenic compounds by catalytic hydrogenation.** C. PAAL and H. SCHIEDEWITZ (Ber., 1930, 63, [B], 766—778; cf. A., 1927, 646).—The observation that *cis*-forms are more readily and smoothly converted by catalytic hydrogenation than are *trans*-varieties into the corresponding saturated substances has been extended to further examples. *iso*Crotonic acid is much more readily reduced than is crotonic acid to *n*-butyric acid, thus confirming its *cis*-configuration. Differences in the rates of hydrogenation of erucic and brassidic acids to behenic acid are less marked than in the cases of oleic and elaidic acids, but are sufficient to establish them as the *cis*- and *trans*-varieties of the acid CH<sub>3</sub>·[CH<sub>2</sub>]<sub>17</sub>·CH:CH·[CH<sub>2</sub>]<sub>11</sub>·CO<sub>2</sub>H. The behaviour of *cis*- and *trans*-*o*-hydroxy- and -*o*-ethoxy-cinnamic acids and of stilbene and *iso*-stilbene is in accordance with expectation.

The preparation of *isocrotonic* acid by partial hydrogenation of tetrolic acid is described. Similar treatment of stearolic and behenolic acids does not give similar results, since mixtures of oleic and elaidic or erucic and brassidic acids are formed. Catalytic reduction of tolane in presence of very small amounts of palladium in the dark affords *isostilbene*, apparently free from stilbene and dibenzyl.

H. WREN.

**Polymorphism of crystals and microcrystalline orientations of fatty acids as a function of temperature.** J. THIBAUD and F. D. LA TOUR (Compt. rend., 1930, 190, 945—947; cf. Thibaud, A., 1927, 645; de Boer, *ibid.*, 503).—The phenomenon of polymorphism is a general one for the even series of saturated fatty acids C<sub>12</sub>—C<sub>32</sub>. By evaporation of a solution of an acid microcrystalline orientations, form *B*, or crystals, form *B*, are obtained, which exhibit a definite transition temperature at which irreversible conversion into microcrystalline orientations, form *C*, or into crystals, form *C*, occurs; the transformation can be brought about only by heat. The appearance of the third form *A* is extremely rare.

The spacings of the *B*-forms are always greater than those of the *C*-forms, the following values being observed (in Å., that of the *B*-form given first): lauric acid, 30.6, 27.4; myristic acid, 35, 31.2; palmitic acid, 39.3, 35.6; stearic acid, 43.95, 39.9; cerotic acid, 69, 64.

The transition temperatures of the change form *B* → form *C* relating to microcrystalline orientations vary from acid to acid in a manner similar to the m. p., and are: lauric acid, 6.5°; myristic acid, 24—25°; palmitic acid, 40°; stearic acid, 54—55°; cerotic acid, 82.5°. The transition temperatures for the transformation *B* → *C* relating to true crystals rise with increasing mol. wt., tending to a constant value of 48°. In the case of myristic acid exhibiting both crystal form *A* (spacing 37 Å.) and form *B*, the change *B* → *C* occurs at 33°, and *A* → *C* at 43°. The transition temperature is independent of the surface (gold or aluminium) on which the acid is deposited, but films on ebonite show small divergences

from the above values probably due to parasitic action. Preparations on mica tend to furnish form *C* at temperatures (below the transition point) at which use of gold or aluminium surfaces always affords *B*.

An equimolecular mixture of palmitic and stearic acids gives both crystals and microcrystalline orientations and exhibits a definite transition temperature at which form *B* (spacing 41.6 Å.) passes into form *C* (spacing 37.6 Å.).

C. W. SHOPPEE.

Certain dialkylacetic acids containing 12, 13, and 14 carbon atoms and their bactericidal action towards *B. lepre*. XVIII. B. F. ARMENDT and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 1289—1291).—The dialkylacetic acids have been prepared by standard methods. The following are described: *ethyl dialkyl-malonates*: isopropyl-*n*-heptyl-, b. p. 137—140°/4 mm.,  $d_4^{25}$  0.9249,  $n_D^{25}$  1.4375; di-*n*-amyl-, b. p. 147—149°/4.5 mm.,  $d_4^{25}$  0.9334,  $n_D^{25}$  1.4343; *n*-butyl-*n*-hexyl-, b. p. 143—147°/4 mm.,  $d_4^{25}$  0.9333,  $n_D^{25}$  1.4347; *n*-butyl-*n*-heptyl-, b. p. 138—140°/3.5 mm.,  $d_4^{25}$  0.9288,  $n_D^{25}$  1.4365; *n*-amyl-*n*-hexyl-, b. p. 146—149°/4 mm.,  $d_4^{25}$  0.9300,  $n_D^{25}$  1.4361; *n*-butyl-*n*-octyl-, b. p. 156—159°/4 mm.,  $d_4^{25}$  0.9263,  $n_D^{25}$  1.4360; *n*-amyl-*n*-heptyl-, b. p. 163.5—165°/5 mm.,  $d_4^{25}$  0.9239,  $n_D^{25}$  1.4371; di-*n*-hexyl-, b. p. 155—158°/4 mm.,  $d_4^{25}$  0.9249,  $n_D^{25}$  1.4373, and *dialkyl-acetic acids*: isopropyl-*n*-heptyl-, b. p. 133—134°/4 mm.,  $d_4^{25}$  0.9429,  $n_D^{25}$  1.4399; di-*n*-amyl-, b. p. 141—143°/4 mm.,  $d_4^{25}$  0.8900,  $n_D^{25}$  1.4381; *n*-butyl-*n*-hexyl-, b. p. 134—135°/4 mm.,  $d_4^{25}$  0.8945,  $n_D^{25}$  1.4391; *n*-butyl-*n*-heptyl-, b. p. 148—149°/4 mm.,  $d_4^{25}$  0.8911,  $n_D^{25}$  1.4409 (cf. Levene and Taylor, A., 1923, i, 81); *n*-amyl-*n*-hexyl-, b. p. 149—150°/4 mm.,  $d_4^{25}$  0.8850,  $n_D^{25}$  1.4410; *n*-butyl-*n*-octyl-, b. p. 160—161°/4 mm.,  $d_4^{25}$  0.8873,  $n_D^{25}$  1.4435; *n*-amyl-*n*-heptyl-, b. p. 155.5—157°/4 mm.,  $d_4^{25}$  0.8900,  $n_D^{25}$  1.4430; di-*n*-hexyl-, b. p. 159—160°/4 mm.,  $d_4^{25}$  0.8895,  $n_D^{25}$  1.4421.

The dodecoic acids have no bactericidal action, the tridecoic acids practically no action, and the tetradecoic acids have slight bactericidal action. This indicates, as in previous researches, that the mol. wt. of the acid plays an important rôle.

R. K. CALLOW.

Preparation and bacteriological action towards *B. lepre* of certain olefinic acids. XVII. E. BROWNING, H. W. WOODROW, and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 1281—1283).—Series of allyl- and undecenyl-alkylacetic acids and certain  $\alpha\beta$ -unsaturated dialkylacetic acids have been prepared by standard methods. The  $\alpha\beta$ -unsaturated acids are prepared from the saturated acids by treatment with red phosphorus and bromine, esterification, and treatment with methyl-alcoholic potassium hydroxide. The following are described: *ethyl alkyl-alkyl-malonates*: -*n*-nonyl-, b. p. 144—146°/2 mm.,  $d_4^{25}$  0.9469,  $n_D^{25}$  1.4465; -*n*-decyl-, b. p. 154—155°/2.5 mm.,  $d_4^{25}$  0.9392,  $n_D^{25}$  1.4471; -*n*-undecyl-, b. p. 168—169°/5 mm.,  $d_4^{25}$  0.9345,  $n_D^{25}$  1.4478; -*n*-dodecyl-, b. p. 166—168°/2.5 mm.,  $d_4^{25}$  0.9305,  $n_D^{25}$  1.4484; -*n*-tridecyl-, b. p. 178—182°/5 mm.,  $d_4^{25}$  0.9276,  $n_D^{25}$  1.4499; -*n*-tetradecyl-, b. p. 184—186°/1.5 mm.,  $d_4^{25}$  0.9239,  $n_D^{25}$  1.4502; *ethyl undecenyl-alkyl-malonates*: -*n*-butyl-, b. p. 158—190°/4 mm.,  $d_4^{25}$  0.9206,  $n_D^{25}$  1.4501; -*n*-amyl-, b. p. 190—194°/

4 mm.,  $d_4^{25}$  0.9344,  $n_D^{25}$  1.4530; -*n*-hexyl-, b. p. 207—209°/4 mm.,  $d_4^{25}$  0.9258,  $n_D^{25}$  1.4514; -*n*-heptyl-, b. p. 208—211°/4 mm.,  $d_4^{25}$  0.9225,  $n_D^{25}$  1.4518; *allyl-alkyl-acetic acids*: -*n*-nonyl-, b. p. 148—150°/3 mm.,  $d_4^{25}$  0.9015,  $n_D^{25}$  1.4510; -*n*-decyl-, b. p. 149—151°/1—1.5 mm.,  $d_4^{25}$  0.8989,  $n_D^{25}$  1.4520; -*n*-undecyl-, b. p. 167—169°/4 mm.,  $d_4^{25}$  0.8953,  $n_D^{25}$  1.4530; -*n*-dodecyl-, b. p. 164—166°/1—2 mm.,  $d_4^{25}$  0.8933,  $n_D^{25}$  1.4540; -*n*-tridecyl-, b. p. 179—183°/5 mm.,  $d_4^{25}$  0.8879,  $n_D^{25}$  1.4556; -*n*-tetradecyl-, m. p. 24°, b. p. 187—188°/2.5 mm.,  $d_4^{25}$  0.8865,  $n_D^{25}$  1.4538; *undecenyl-alkyl-acetic acids*: -*n*-butyl-, b. p. 175—180°/3 mm.,  $d_4^{25}$  0.8929,  $n_D^{25}$  1.4566; -*n*-amyl-, b. p. 186—190°/3 mm.,  $d_4^{25}$  0.8956,  $n_D^{25}$  1.4575; -*n*-hexyl-, b. p. 200—204°/3 mm.,  $d_4^{25}$  0.8915,  $n_D^{25}$  1.4564; -*n*-heptyl-, b. p. 205—209°/5 mm.,  $d_4^{25}$  0.8870,  $n_D^{25}$  1.4572; *alkylidene-alkyl-acetic acids*: *n*-butylidene-*n*-butyl-, b. p. 121—123°/2 mm.,  $d_4^{25}$  0.9456,  $n_D^{25}$  1.4484; *n*-heptylidene-*n*-heptyl-, b. p. 180—182°/2 mm.,  $d_4^{25}$  0.8993,  $n_D^{25}$  1.4566; *n*-octylidene-*n*-octyl-, b. p. 185—186°/1 mm.,  $d_4^{25}$  0.8983,  $n_D^{25}$  1.4625.

The unsaturated acids have about the same bactericidal value as the corresponding saturated acids (A., 1929, 676).

R. K. CALLOW.

Isolation of additive products of thiocyanogen and unsaturated fatty acids. H. P. KAUFMANN (Chem. Umschau, 1930, 37, 113—117).—Thiocyanates of various fatty acids have been prepared, in many cases by the use of nascent thiocyanogen. The insolubility of the products in pentane is of assistance in the purification. The dithiocyanates of oleic and erucic acids (pale yellow non-crystallisable oils) and of elaidic acid, m. p. 79°, were similar to those obtained by Kimura (B., 1930, 429), but greater purity of the preparations is claimed. Further, *petroselinic dithiocyanate* (a pale yellow oil) and a *hexathiocyanate* of (freshly prepared)  $\beta$ -*elaeostearic glyceride* (an unstable viscous yellow oil, which readily absorbs bromine and darkens on keeping) were isolated. Preliminary notes are given of other sulpho-derivatives (mercapto-acids etc.) obtainable from the fatty acid thiocyanates.

E. LEWKOWITSCH.

Structure of oleic and elaidic acids. L. J. P. KEFFLER. See this vol., 703.

[Preparation of] erucic acid. C. R. NOLLER and R. H. TALBOT (Organic Syntheses, 1930, 10, 44—46).

Polymerisation of the methyl esters of the higher unsaturated acids of train oil. II. Polymerised product. K. KINO (J. Soc. Chem. Ind. Japan, 1930, 33, 153—154b; cf. this vol., 577).—Distillation of the polymerised product furnishes fractions possessing single, double, quadruple, and sextuple mol. wt. The relation between the mol. wt. and the iodine value indicates the intramolecular formation of cyclobutane rings, which are probably produced more readily from the higher unsaturated esters. Each fraction possesses a fish-like odour, and the variation of odour with composition has been observed.

C. W. SHOPPEE.

[Preparation of] isopropyl lactate. F. A. McDERMOTT (Organic Syntheses, 1930, 10, 88—89).

Ether-esters of lactic acid. S. SABETAY (Bull. Soc. chim., 1930, [iv], 47, 436).—The following have

been prepared by acylation of ethyl lactate (or the appropriate alcohol) in chloroform solution in presence of pyridine: *ethyl  $\alpha$ -phenylacetoxypionate*, b. p. 144.5—145.5°/6 mm.,  $d^{20}_4$  1.096,  $n^{20}_D$  1.4880; *ethyl  $\alpha$ -cinnamylloxypionate*, b. p. 172.5—173°/6 mm.,  $d^{20}_4$  1.106,  $n^{20}_D$  1.5374; *phenylethyl  $\alpha$ -acetoxypionate*, b. p. 144—147°/6 mm.,  $d^{20}_4$  1.099,  $n^{20}_D$  1.4913; *citronellyl  $\alpha$ -acetoxypionate*, b. p. 153°/8 mm.,  $d^{20}_4$  0.9647,  $n^{20}_D$  1.4479.

R. BRIGHTMAN.

**Epoxy-acids [oxido-acids] from oleic and elaidic acids.** B. H. NICOLET and T. C. POULTER (J. Amer. Chem. Soc., 1930, 52, 1186—1191).—The chlorohydrins of oleic and elaidic acids are obtained as an oil and a semi-solid, respectively, by passing chlorine into the cooled solutions of the potassium salts containing potassium carbonate. The oxido-acids, each m. p. 53.8°, are obtained when the chlorohydrins are boiled with sodium ethoxide solution. The action of perbenzoic acid (Pigulevski and Petrova, A., 1927, 447) or of peracetic acid (Hilditch and Lea, A., 1928, 868) on oleic or elaidic acids yields dihydroxystearic acids as the only solid product. The oxido-acids react quantitatively with hydrogen chloride in ether, and may be determined in this way by titration of the excess of acid. Oxido-oleic acid yields (?) *1-chloro-9-hydroxystearic acid*, m. p. 35°, and elaidic acid yields an isomeric acid, m. p. 50°. *Methyl oxido-oleate*, m. p. 18°; *methyl oxidoelaidate*, m. p. 25°; the isomeric methyl dihydroxystearates, and methyl  $\alpha$ -ketostearate, m. p. 43°, are obtained by adding phosphoric oxide to solutions of the acids in methyl alcohol. When a solution of oxido-oleic acid in the appropriate alcohol containing 1% of sulphuric acid is kept for 2 days, *monoethyl*, m. p. 87°, *mono-n-propyl*, m. p. 87—88°, and *mono-n-butyl*, m. p. 90°, ethers of low-melting 9,10-dihydroxystearic acid are formed. Elaidic acid yields only dihydroxystearic acid, m. p. 133°, under these conditions. Hydrolysis of oxido-oleic acid to dihydroxystearic acid, m. p. 96°, or of oxido-elaidic acid to dihydroxystearic acid, m. p. 133°, takes place slowly with 1% hydrochloric or sulphuric acid and somewhat more rapidly with 2% potassium hydroxide solution. Investigation of the products obtained by heating the oxido-acids shows that at 114° and 150° the main reaction is a condensation in which the oxido-group disappears and the carboxyl group disappears to the extent of 50—75%, possibly with hydroxy-ester formation. Distillation of the oxido-acids at about 290°/10 mm. yields  $\alpha$ -ketostearic acid and a (?) hydroxyoleic acid. In all the reactions investigated oxido-oleic acid is the less stable and reacts in general from two to four times as rapidly as oxidoelaidic acid.

R. K. CALLOW.

**Enolic structure of pyruvic acid and its aliphatic derivatives.** I. S. NEUBERG (Biochem. Z., 1930, 219, 165—170).—When pyruvic acid is treated with sufficient sodium hydroxide to make the solution neutral or faintly acid and warmed with sodium chlorate, no reaction occurs, but if osmium tetroxide is also added, pyruvic acid is oxidised to oxalic acid. The significance of the reaction in respect to the hydroxy-acrylic structure of pyruvic acid is discussed.

P. W. CLUTTERBUCK.

**Reduction of semicarbazones and thiosemicarbazones of  $\alpha$ -ketonic acids and of the thiodiketotriazines.** J. BOUGAULT and L. POPOVICI (Compt. rend., 1930, 190, 1019—1020; cf. A., 1929, 1068).—Reduction with sodium amalgam of the semicarbazones of pyruvic and benzylpyruvic acids yield, respectively, the corresponding *semicarbazide acids*,  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 181°, and  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 172°. In the same way, the thiosemicarbazones of phenylglyoxylic, phenylpyruvic, benzylpyruvic, and pyruvic acids yield on reduction the *thiosemicarbazide acids*,  $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , m. p. 168°,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , m. p. 198°,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , m. p. 164°, and  $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$ , m. p. 145°. The above substances are all oxidised by iodine and sodium carbonate to the semicarbazones or thiosemicarbazones of the decarboxylated aldehydes. The thiodiketotriazines formed by ring closure of the thiosemicarbazones yield the same reduction products as the thiosemicarbazones themselves. T. H. MORTON.

**Synthesis of certain higher aliphatic compounds. III. Variation of keto-acid synthesis; improved method for the extension of normal carbon chains.** (MRS.) G. M. ROBINSON (J.C.S., 1930, 745—751).—Better yields of keto-acids are obtained by hydrolysis of the complexes derived from the condensation of fatty acid chlorides and ethyl sodio- $\alpha$ -acetylsuccinate (and homologues related to higher dibasic acids) than from the hydrolysis of the isomeric substances derived from the condensation of ester chlorides of dibasic acids and ethyl sodioalkyl-acetoacetates. The following syntheses are illustrative.

Interaction of the product obtained by treating ethyl acetosuccinate with granulated sodium under ether with undecoyl chloride gave, after successive treatment with 4% aqueous potassium hydroxide, boiling 5% sulphuric acid, and 8% sodium hydroxide solution,  $\gamma$ -ketomyristic acid, m. p. 87°. This keto-acid, by reduction with sodium and ethyl alcohol, afforded  $\gamma$ -*n*-decylbutyrolactone, m. p. 30—31°.

From sodium, ether, ethyl  $\alpha$ -acetylglutarate, and lauryl chloride, etc.,  $\delta$ -ketopalmitic acid, m. p. 88°, was obtained, giving by reduction (as above),  $\delta$ -undecylaleralactone, m. p. 29.5—30.0°. Ethyl sodio- $\alpha$ -aceto-decoate and  $\epsilon$ -carbethoxyhexoyl chloride in ethereal solution formed, after three-stage hydrolysis,  $\zeta$ -ketopalmitic acid, m. p. 78°. Similarly, ethyl sodio- $\alpha$ -acetonoate and  $\zeta$ -carbethoxyheptoyl chloride gave  $\eta$ -ketopalmitic acid, m. p. 77—78°; ethyl sodioacetosuccinate and undecenoyl chloride yielded  $\gamma$ -keto- $\Delta^4$ -tetradecenoic acid, m. p. 79.5° (reduction gave  $\gamma$ - $\Delta^6$ -decenylbutyrolactone, m. p. 26—27°); elaidyl chloride and ethyl sodioacetosuccinate formed trans- $\gamma$ -keto- $\Delta^7$ -heptacosenoic acid, m. p. 82.5° (corresponding  $\gamma$ - $\Delta^7$ -heptadecenylbutyrolactone, m. p. 42°); ethyl sodio- $\alpha$ -acetobutyrate and  $\theta$ -carbethoxynonyl chloride afforded  $\alpha$ -ketotridecoic acid, m. p. 63°, from the acid chloride of which, by interaction with ethyl sodioacetosuccinate,  $\gamma$ - $\mu$ -diketopalmitic acid, m. p. 101°, was obtained. Lastly,  $\beta$ -benzoylpropionic acid was prepared from ethyl sodioacetosuccinate and benzoyl chloride.

R. J. W. LE FÈVRE.

[Preparation of] anhydrous oxalic acid. E. BOWDEN (Organic Syntheses, 1930, 10, 78—79).

[Preparation of] methyl oxalate. E. BOWDEN (Organic Syntheses, 1930, 10, 70—72).

Action of phenylcarbamazide on ethyl malonate. T. CURTIUS and H. MEIER (J. pr. Chem., 1930, [ii], 125, 458—463).—Ethyl mono- and diphenylcarbamidomalonates are not formed from ethyl malonate and phenylcarbamazide at 130° (cf. A., 1923, i, 850); at 110° *s*-diphenylcarbamide results. Digestion of the reaction product (130°) with dilute sodium hydroxide and acidification of the extract gives a substance, m. p. 115° after softening at 75—90°. Neutralisation of the acid solution affords a further compound, m. p. 140° after sintering at 110—120° (silver salt), probably a diphenylurazole.

H. BURTON.

[Preparation of] glutaric acid. T. J. OTTERBACHER (Organic Syntheses, 1930, 10, 58—59).

Preparation of maleic anhydride. F. A. MASON (J.C.S., 1930, 700—701).—Excellent yields are obtained by distillation of maleic acid with neutral high-boiling solvents (e.g., xylene or tetrachloroethane). The water formed distils with the solvent and fractionation leaves only 10% of the acid as fumaric acid. It has b. p. 197—199° (uncorr.) and setting point 52° (lit. 196° and 60°, respectively).

R. J. W. LE FÈVRE.

[Preparation of] ethyl fumarate. B. B. CORSON, (Miss) E. ADAMS, and R. W. SCOTT (Organic Syntheses, 1930, 10, 48—52).

[Preparation of] ethyl mesoxalate. B. B. CORSON and R. K. HAZEN (Organic Syntheses, 1930, 10, 54—57).

Complex compounds of organic acids with aluminium hydroxide. O. QUADRAT and J. KORECKÝ (Coll. Czech. Chem. Comm., 1930, 2, 169—184).—By observation of the change in the rotatory power of solutions of optically active organic acids with the aluminium content of the solutions, and by determination of the number of hydroxyl groups saturated by the aluminium hydroxide it has been established that the aluminium ion gives only one complex compound with tartaric acid in acid medium, 1 mol. of the acid being associated with each aluminium atom. In the case of malic acid there are probably two compounds, two molecules of the acid being associated with three and four atoms of aluminium, respectively. The presence of the grouping

$\begin{array}{c} \text{CH.O} \\ \diagup \\ \text{O.CO} \end{array} \text{Al.O}$  postulated by Hanuš and Quadrat (Compt. rend. Acad. Tchèque Sci., 1909, 8, No. 25) for the case of the tartaric acid complex is assumed in the malic acid complex.

J. W. SMITH.

Determination of tartaric acid by precipitation as potassium hydrogen tartrate. K. TÄUFEL and B. W. MARLOTH (Z. anal. Chem., 1930, 80, 161—185).—The solution (100 c.c.) which must contain between 0.3 and 1.0% of tartaric acid is evaporated to half its volume and its  $p_H$  value adjusted to 3.27 by a colorimetric or potentiometric method; 20 c.c. of *N*-formic acid, 5 c.c. of *N*-potassium hydroxide, and 10 g. of powdered potassium chloride are added, and the

mixture is well stirred and diluted to 100 c.c. The sides of the beaker are rubbed with a glass rod and the solution is left over-night. The resulting precipitate is filtered and washed with 30 c.c. of 66% alcohol, dissolved in 40—50 c.c. of hot water, and the solution titrated with 0.2*N*-sodium hydroxide. A correction of 1.1 c.c. of the alkali must be added to the titration figure to allow for the solubility of the potassium hydrogen tartrate in the original solution. With solutions poor in tartaric acid 0.3 g. of this substance per 100 c.c. should be added. H. F. HARWOOD.

Condensations producing esters of acetyl-propenecarboxylic acids. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1930, 5, 109—115).—Condensations between ethoxymethylene compounds  $\text{CX}:\text{CH}:\text{OEt}$  and sodiomethylene derivatives (this vol., 461) have been extended to derivatives in which an acetyl group replaces the nitrile group of the earlier investigations. Products of the same four types are obtained although differentiation between types I and II is less clearly defined. In the following summary the numbers in parentheses refer to the types of condensation products (*loc. cit.*). Ethyl ethoxymethyleneacetate and methyl sodioacetate give only  $\alpha$ -methyl  $\gamma$ -ethyl  $\alpha\gamma$ -diacetylglutaconate (I) (Feist, A., 1927, 151). Methyl ethoxymethyleneacetate and ethyl sodioacetate give  $\gamma$ -methyl  $\alpha$ -ethyl  $\alpha\gamma$ -diacetylglutaconate (I); ethyl ethoxymethylenemalonate and ethyl sodioacetate give a substance,  $\text{C}_{12}\text{H}_{14}\text{O}_6$ , m. p. 77°, probably ethyl resorcinol-4 : 6-dicarboxylate obtained by elimination of 1 mol. of alcohol from ethyl acetylcarbethoxyglutaconate (I or II), together with ethyl  $\alpha\gamma$ -diacetylglutaconate and ethyl  $\alpha\gamma$ -dicarboethoxyglutaconate. Ethyl ethoxymethyleneacetate and ethyl sodiomalonate give ethyl diacetylglutaconate (IV), the above resorcinol derivative (from the product of type I or II), and ethyl  $\alpha\gamma$ -dicarboethoxyglutaconate. The products of types III and IV are also obtained when the condensation is effected in alcohol instead of in ether. Sodioacetylacetone with ethyl ethoxymethylenemalonate gives ethyl  $\alpha\alpha$ -(or  $\gamma\gamma$ )-diacetylpropene- $\gamma\gamma$ -(or  $\alpha\alpha$ )-dicarboxylate (I or II) and ethyl dicarboethoxyglutaconate (IV), whilst with ethyl ethoxymethyleneacetate the sole product is ethyl  $\alpha\gamma$ -diacetylglutaconate (IV). Ethoxymethyleneacetylacetone and ethyl sodioacetate give ethyl  $\alpha\gamma$ -diacetylglutaconate (III).

J. W. BAKER.

Determination of citric acid in the presence of some other organic acids. A. I. KOGAN (Z. anal. Chem., 1930, 80, 112—122).—The citric acid solution (60 c.c.) is boiled with 1 c.c. of 80% acetic acid, and a 1.5% solution of permanganate is added drop by drop (5—8 drops in 5 min.) to the boiling solution until a permanent precipitate of manganese dioxide remains; distillation is then continued until 25 c.c. remain and 25 c.c. of water are added slowly while the liquid is again distilled to 25 c.c. The distillate is diluted to 200 c.c. and 100 c.c. are treated with 10 c.c. of 10% sodium hydroxide and the acetone is converted into iodoform by addition of a 50% excess of 0.1*N*-iodine-potassium iodide solution. The liquid is acidified after 5 min. and the excess of iodine titrated with thiosulphate. Substances (e.g., lactic, malic, and

tartaric acids) which yield acetaldehyde on oxidation with permanganate interfere, but the aldehyde may be oxidised to acetic acid by treatment of the acidified distillate with sulphuric acid and permanganate until the solution above the manganese dioxide precipitate is pink. The higher manganese compounds are then destroyed by addition of a slight excess of 35% hydrogen peroxide and the solution is treated with sodium hydroxide and manganese sulphate to destroy hydrogen peroxide, filtered, and treated with iodine as above. Whichever method is used correct results are obtained only by following exactly the stated conditions and by using the empirical factor: 1 c.c. of 0.1*N*-iodine = 0.00392 g. of citric acid.

A. R. POWELL.

**Structure of ferric citrates.** G. SIBONI (Boll. chim. farm., 1930, 69, 227—234, 275—282).—A discussion of Belloni's work (A., 1920, i, 814). T. H. POPE.

**Rotatory power and structure in the sugar group.** The two crystalline lactones of *l*-rhamnonic acid. E. L. JACKSON and C. S. HUDSON (J. Amer. Chem. Soc., 1930, 52, 1270—1275).—The oxidation of *l*-rhamnose with bromine water containing barium benzoate as a buffer yields a second crystalline lactone of *l*-rhamnonic acid, m. p. 172—181°,  $[\alpha]_D^{20}$  -98° in water, falling to -30° (cf. Votoček and Beneš, A., 1928, 1356). It mutarotates rapidly and therefore probably possesses the  $\delta$ -structure. The well-known first rhamnonolactone, m. p. 148—150°,  $[\alpha]_D^{20}$  -40°, is of the stable type, showing very slow mutarotation, and it therefore probably possesses the  $\gamma$ -structure. Will and Peters (A., 1888, 933; 1889, 952) describe the first lactone, but give a crystallographic description of the second (cf. following abstract).

The stable lactone is obtained by oxidation of rhamnose in presence of free hydrobromic acid and by evaporation of the labile lactone with dilute hydrochloric acid. The labile lactone is obtained from the stable lactone by conversion into lead rhamnonate and decomposition with hydrogen sulphide. This behaviour is analogous to that of *d*-mannonolactone (Nef, A., 1914, i, 497). Comparison of the rotations of the *d*-mannonolactones and the *l*-rhamnonolactones shows that after reversing the sign of the rotation of the latter the replacement of  $\text{CH}_2\cdot\text{OH}$  by Me in both  $\gamma$ - and  $\delta$ -lactones causes a decrease of 12—13°. With ammonia in alcohol both rhamnonolactones yield *l*-rhamnonamide, m. p. 134—134.5°,  $[\alpha]_D^{20}$  +27.7° in water, the rotation of which is in agreement with the amide rule.

R. K. CALLOW.

**$\gamma$ - and  $\delta$ -Rhamnonolactones.** Crystallographic and optical properties. F. E. WRIGHT (J. Amer. Chem. Soc., 1930, 52, 1276—1281; cf. preceding abstract).—The data given show that the two lactones are distinct, whilst the measurements of Will and Peters (A., 1889, 952) refer to the  $\delta$ -lactone.

R. K. CALLOW.

***d*-Galacturonic acid from lemon pectic acid.** K. P. LINK and A. D. DICKSON (J. Biol. Chem., 1930, 86, 491—497).—Commercial lemon pectin is hydrolysed with 2.5% sulphuric acid, and the solution is neutralised with barium carbonate and cleared with charcoal. The filtrate is concentrated in a vacuum and poured into alcohol, the precipitated barium

galacturonate being collected, reprecipitated, and dehydrated, first with alcohol and ether and then in a desiccator; 80 g. of the pectin yield 40 g. of barium salt. The latter may be converted into the acid by decomposition with sulphuric acid (slightly less than the theoretical amount), concentration of the filtrate, removal of residual barium salt by alcohol precipitation, and finally concentration to crystallisation. The galacturonic acid so obtained has m. p. 159° (decomp.),  $[\alpha]_D^{20}$  +53.59° in water after 24 hrs.

C. R. HARINGTON.

**$\alpha$ -Ketogluconic acid. II.** H. OHLE and R. WOLTER [with R. WOHINZ] (Ber., 1930, 63, [B], 843—852; cf. A., 1927, 647).—Powdered sucrose, suspended in acetone, is mixed with concentrated sulphuric acid and the mixture is agitated until homogeneous at a temperature not exceeding 15—16°; the solution, cooled to 0°, is neutralised by sodium hydroxide and the acetone is removed. The residue is treated with 0.05*N*-sulphuric acid, whereby diisopropylidene-glucose is transformed into a mixture of dextrose and isopropylidene-glucose without hydrolysing the diisopropylidene-fructose. Oxidation by permanganate (*loc. cit.*) effects the conversion of the last-named compound into potassium  $\alpha$ -ketodiisopropylidene-gluconate, from which  $\alpha$ -ketodiisopropylidene-gluconic acid, m. p. 99—100°,  $[\alpha]_D^{20}$  -49.35° in chloroform, is obtained by acidification and extraction with ether. The acid is transformed into the following salts: potassium, sodium, ammonium (?+0.5H<sub>2</sub>O), m. p. 204—205° (decomp.), and monohydrated brucine, m. p. 175° (decomp.) after softening at 163°,  $[\alpha]_D^{20}$  -36.28° in water. Treatment of an ethereal solution of the acid with phosphorus pentachloride affords an additive compound of the acid chloride and phosphoryl chloride, which is converted into methyl  $\alpha$ -ketodiisopropylidene-gluconate, b. p. 128—129°/0.15 mm., m. p. 52°,  $[\alpha]_D^{20}$  -44.70° in chloroform,  $[\alpha]_D^{20}$  -54.56° in methyl alcohol;  $\alpha$ -ketodiisopropylidene-gluconamide, m. p. 98—99°,  $[\alpha]_D^{20}$  -50.58° in chloroform,  $\alpha$ -ketodiisopropylidene-gluconmethylethylamide, m. p. 123—124°, and  $\alpha$ -ketodiisopropylidene-gluconanilide, m. p. 107—107.5°,  $[\alpha]_D^{20}$  -16.15° in chloroform. The preparation of free  $\alpha$ -ketogluconic acid or its lactone could not be effected, whereas its salts are obtainable either from free  $\alpha$ -ketodiisopropylidene-gluconic acid or its previously isolated salts; the sodium compound, anhydrous,  $[\alpha]_D^{20}$  -81.72° in water, and monohydrate, and ammonium salt, decomp. 160—161° when rapidly heated, are described.  $\alpha$ -Ketogluconic acid undergoes complex change in the presence of alkali hydroxide, probably involving the formation of structural isomerides and degradation products, since the final optical activity of the solutions is not materially affected by neutralisation. Esterification of the acid is effected with unusual ease. Methyl  $\alpha$ -ketogluconate, m. p. 173° (decomp.),  $[\alpha]_D^{20}$  -82.08° to -77.44° in water [tetra-acetate, b. p. 199—203°/0.3 mm. (bath temperature); phenylhydrazine, m. p. 163°,  $[\alpha]_D^{20}$  -124.1° to -220° to -40°], and ethyl  $\alpha$ -ketogluconate, m. p. 123—124° after softening at 105°, are described. Sodium  $\alpha$ -ketogluconate is converted by acetic anhydride in presence of pyridine into  $\alpha$ -ketotriacetylgluconolactone, m. p. 154°,  $[\alpha]_D^{20}$  -60.4° in chloroform.

H. WREN.



**Sulphur analogue of glyceric acid.**  $\beta$ -Thioglyceric acid. C. F. KOELSCH (J. Amer. Chem. Soc., 1930, 52, 1105—1108).— $\beta$ -Chloro- $\alpha$ -hydroxypropionic acid (ammonium salt, m. p. 141°) is prepared by the oxidation of aqueous glycerol  $\alpha$ -monochlorohydrin by very slowly running a layer of nitric acid into the bottom of the vessel and allowing admixture to take place by diffusion. Interaction of the sodium salt with sodium hydrogen sulphide or potassium xanthate does not yield the  $\beta$ -thiol acid. Ethyl  $\alpha$ -hydroxy- $\beta$ -thiolpropionate, b. p. 113—115°/19 mm.,  $d_4^{20}$  1.1779,  $n_D^{20}$  1.4754, is obtained by the interaction of ethyl  $\beta$ -chloro- $\alpha$ -hydroxypropionate and potassium hydrogen sulphide in aqueous alcohol at 70°.  $\alpha$ -Hydroxy- $\beta$ -thiolpropionic acid, a syrup (S-2:4-dinitrophenyl derivative, m. p. 167—168°), is obtained by hydrolysis and purified by way of its barium salt. R. K. CALLOW.

**Simple seleninocarboxylic acids.** H. J. BACKER and W. VAN DAM (Rec. trav. chim., 1930, 49, 482—491; cf. this vol., 194).—A series of seleninofatty acids has been prepared by the interaction of potassium diselenide and an aqueous solution of the alkali salt of the requisite halogeno-acid and oxidation of the resulting diselenodicarboxylic acid with nitric acid ( $d$  1.4) at 40—45°;  $[\text{CO}_2\text{H}\cdot\text{CHR}\cdot\text{Se}]_2 + 3\text{O} + \text{H}_2\text{O} = 2\text{SeO}_2\text{H}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ . Their dissociation constants have been measured and their resolution has been effected. Thus from the appropriate halogeno-acid are obtained:  $\alpha$ -diselenodiacetic, m. p. 97—98° (Behaghel and Rollmann, this vol., 73, give m. p. 101°) [quinine salt (+4H<sub>2</sub>O), m. p. 147° (decomp.)];  $\alpha$ -diselenodibutyric (Fredga, A., 1929, 1285) [quinine salt (+1.5H<sub>2</sub>O), m. p. 128° (decomp.)];  $\alpha$ -diselenodivaleric, m. p. 74° [quinine salt (+H<sub>2</sub>O), m. p. 171° (decomp.)] (from  $\alpha$ -bromo- $n$ -valeric acid, b. p. 125—127°/16 mm., obtained by the action of bromine on valeric acid in the presence of phosphoric oxide);  $\beta$ -diselenodipropionic, m. p. 137—138°; seleninoacetic, isolated as its barium (+2H<sub>2</sub>O) salt (crystallographic data by TERPSTRA) [quinine salt (+7H<sub>2</sub>O), m. p. 122° (decomp.), +H<sub>2</sub>O, and anhydrous];  $\alpha$ -seleninobutyric, isolated as its lead salt [barium salt (+2H<sub>2</sub>O), and quinine salt (+5H<sub>2</sub>O), m. p. 112° (decomp.)];  $\alpha$ -seleninovaleric (Fredga, loc. cit.) [lead, dihydrated barium, and quinine, m. p. 120° (decomp.), salts], and  $\beta$ -seleninopropionic, m. p. 109—110° (decomp.), acid. The values of  $k_1$  for  $\alpha$ -seleninoacetic, -propionic, -butyric, -valeric, and  $\beta$ -seleninopropionic acids are 2.50, 3.36, 2.95, 2.75, and 0.336 ( $\times 10^{-3}$ ), and for  $k_2$  3.74, 3.28, 3.28, 3.30, and 1.02 ( $\times 10^{-6}$ ), respectively. By fractional crystallisation of the appropriate quinine salts (above) are obtained  $d$ - $\alpha$ -seleninobutyric,  $[n]_D + 25^\circ$  (barium salt,  $[M]_D + 82^\circ$ ), and  $l$ - $\alpha$ -seleninovaleric acid  $[M]_D - 11.5^\circ$  (barium salt,  $[M]_D - 12.5^\circ$ ). The rotatory dispersions of these acids and their barium salts have been determined for light of various wavelengths. J. W. BAKER.

**Employment of optically active acylhydrazines in the resolution of racemic aldehydes and ketones.** S. SABETAY (Compt. rend., 1930, 190, 1016—1018).—When equivalent proportions of  $d$ -citronellal and hydrazine are heated under

reflux  $d$ - $d$ -citronellylhydrazine, m. p. 139—140°, is obtained. If, however, 2 mols. of hydrazine are used, then  $mono$ - $d$ -citronellylhydrazine, m. p. 83°, is formed. These compounds are optically active, and the condensation seems to have been effected without racemisation of the citronellal acid. The monohydrazide will condense with aldehydes, and it is suggested that by this means racemic aldehydes and ketones might be resolved. With hydratropaldehyde in alcoholic solution hydratropaldehydemono- $d$ -citronellylhydrazone, m. p. 69°, is produced. The aldehyde and the citronellylhydrazine are regenerated by treatment with dilute acid or alkali.

T. H. MORTON.

**Preparation of acetals.** J. A. NIEUWLAND, R. R. VOGT, and W. L. FOOHEY (J. Amer. Chem. Soc., 1930, 52, 1018—1024).—Solutions of boron or silicon fluorides in alcohols with mercuric oxide catalyse the formation of ethylidene compounds from glycols or hydroxy-acids and acetylene, and are in this respect superior to sulphuric acid. These solutions possess high electrical conductivity, and hydrofluoboric and hydrofluosilicic acids are probably the active constituents. The compound  $\text{BF}_3\cdot\text{Et}_2\text{O}$ , b. p. 123°, formed by dissolving boron trifluoride in ether, may also be used as a catalyst.

The ethylidene compound of ethylene glycol is obtained by mixing 5 g. of a 60% solution of boron trifluoride in methyl alcohol with 1 g. of mercuric oxide, adding 102 g. ethylene glycol, and passing acetylene. By similar methods are prepared ethylidene compounds of the following: trimethylene glycol; pinacol; methylethylpinacol (mixture of isomerides), b. p. 150—180°; ethylene glycol methyl and ethyl ethers; ethylene glycol butyl ether, b. p. 142—146°/14 mm.,  $d_4^{20}$  0.9072,  $n_D^{20}$  1.4263; diethylene glycol, b. p. 250°/14 mm.; diethylene glycol ethyl ether, b. p. 140—145°/14 mm.; glycerol (78% of  $\alpha\beta$ - and 22% of  $\alpha\gamma$ -acetal); glyceryl methyl ether, b. p. 145—147°,  $d_4^{20}$  1.0098,  $n_D^{20}$  1.4145; glyceryl ethyl ether, b. p. 170—171°; glyceryl phenyl ether, m. p. 29°, b. p. 142—144°; ethylene chlorohydrin; trimethylene chlorohydrin, b. p. 127—129°/14 mm.; glycerol chlorohydrin; glycerol monoacetin, b. p. 91.5—92°/14 mm., 200—201°/760 mm.,  $d_4^{20}$  1.1110,  $n_D^{20}$  1.4323; lactic acid;  $\alpha$ -hydroxyisobutyric acid, b. p. 147.7—150.3°/745 mm.,  $d_4^{20}$  1.0226,  $n_D^{20}$  1.4034; methyl tartrate, b. p. 136.8—137.2°/16 mm.,  $d_4^{20}$  1.2306,  $n_D^{20}$  1.4426; ethyl tartrate, b. p. 146.5—147.5°/18 mm.,  $d_4^{20}$  1.1408,  $n_D^{20}$  1.1438; methyl hydrogen malate, b. p. 121—122°/15 mm.,  $d_4^{20}$  1.1975,  $n_D^{20}$  1.4397; ethyl hydrogen malonate, b. p. 125—130°/17 mm.,  $d_4^{20}$  1.1215,  $n_D^{20}$  1.4402; methyl citrate, m. p. 73°; mandelic acid, b. p. 142—144°/14 mm.,  $d_4^{20}$  1.1681,  $n_D^{20}$  1.4145; benzoic acid, m. p. 77°, b. p. 127—129°/14 mm.; and the following compounds: terethylidenebisglycerol; bisethylidene-pentaerythritol, m. p. 40°, b. p. 113°/14 mm.; terethylidenemannitol; bisethylidene tartrate.  $\alpha\beta$ -Diphenyl glycol gives an unstable compound, m. p. 107—115°, b. p. 203—206°. Diethylene glycol ethyl ether and glycerol dichlorohydrin give compounds of high b. p. Glycerol bromohydrin and glycollic acid do not react.  $\beta$ -Hydroxy- $\beta\beta$ -diphenylpropionic acid and ethyl citrate react, but the products could not be isolated. Ethyl dextrosecycloacetate yields a compound, b. p. 195°/5—6 mm. R. K. CALLOW.

**Resinification. I. Condensation of formaldehyde with urethane.** M. GIUA and G. RACCIU (Atti R. Accad. Sci. Torino, 1929, 64, 300—304; Chem. Zentr., 1930, i, 40—41).—Condensation of aqueous formaldehyde with urethane in presence of hydrochloric acid affords methyleneurethane,  $\text{CH}_2\text{N}\cdot\text{CO}_2\text{Et}$ , which when boiled with dilute acetic acid gives trimeric methyleneurethane. If the oily reaction product is heated with acetic acid until all of the latter has been removed, resinous tetrameric methyleneurethane remains. A. A. ELDRIDGE.

**Catalytic decomposition of formaldehyde acetals by metallic oxides.** M. CABANAC (Compt. rend., 1930, 190, 881—882).—The decomposition of acetals in the presence of thoria at  $400^\circ$  has been studied. The diethyl acetal yields 22% of acetaldehyde, 13% of ethyl vinyl ether, 30% of alcohol, 8% of water, and a gas containing 30% of ethylene, 42% of hydrogen, 6% of carbon monoxide, 14% of carbon dioxide, and 8% of methane. The dimethyl and dipropyl acetals decompose similarly. Small quantities of the corresponding vinyl ethers were isolated from the dibutyl, diisobutyl, and diisoamyl acetals. Alumina, blue tungstic oxide, and manganous oxide give similar results but the yields are smaller and the gaseous products different. A. I. VOGEL.

**Chloral compounds.** E. FOURNEAU and G. FLORENCE (Bull. Soc. chim., 1930, [iv], 47, 350—356).—In view of the ready hydrolysis of the hypnotics previously obtained (A., 1928, 1228) from chloral and aminohydroxy-esters, the condensation products of chloral alkoxydes with acetic esters and of chloral with hydroxy-acids and their ethyl esters have been prepared. All the compounds obtained were inactive, even those containing branched chains, such as the derivatives of  $\alpha$ -hydroxyisobutyric and  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acids, and the narcotic action of the compounds previously prepared is accordingly attributed to the presence of the amino-group, which facilitates the liberation of chloral in the system. The following are described:  $\beta\beta\beta$ -trichloro- $\alpha$ -acetoxy- $\alpha$ -propoxyethane, b. p.  $114$ — $116^\circ$ ;  $\beta\beta\beta$ -trichloro- $\alpha$ -acetoxy- $\alpha$ -butoxyethane, b. p.  $129$ — $131^\circ$  (yield 78%);  $\beta\beta\beta$ -trichloro- $\alpha$ -acetoxy- $\alpha$ -isobutoxyethane, b. p.  $128^\circ/20$  mm. (yield 72%);  $\beta\beta\beta$ -trichloro- $\alpha$ -acetoxy- $\alpha$ -sec.-butoxyethane, b. p.  $126^\circ/20$  mm. (yield 65%);  $\beta\beta\beta$ -trichloro- $\alpha$ -acetoxy- $\alpha$ -isoamylloxyethane, b. p.  $138^\circ/20$  mm. (yield 74%), and  $\beta\beta\beta$ -trichloro- $\alpha$ -isovaleroxy- $\alpha$ -ethoxyethane, b. p.  $143^\circ/20$  mm. (yield 41%), are obtained in the yields indicated from the chloral alcoholate and acid chloride in ethereal solution in presence of pyridine. *n*-Butylchloral has m. p.  $49$ — $50^\circ$ , b. p.  $129$ — $130^\circ$ ; isobutylchloral, b. p.  $122^\circ$ ; sec.-butylchloral, b. p.  $120$ — $121^\circ$ , isoamylchloral, m. p.  $56^\circ$ . Anhydrous chloral and ethyl lactate yield a condensation product,  $\text{C}_7\text{H}_{11}\text{O}_4\text{Cl}_3$ , which does not crystallise at  $-18^\circ$  and decomposes on distillation. Ethyl  $\alpha$ -hydroxy- $\alpha$ -ethylbutyrate yields a similar product. Both these products were toxic towards dogs and fish, although devoid of hypnotic powers.  $\alpha$ -Hydroxyisobutyric acid and anhydrous chloral when heated in a sealed tube at  $100^\circ$  for 6 hrs. yield  $\alpha$ -hydroxyisobutyric chloralide,  $\text{CCl}_3\cdot\text{CH}(\text{O})\text{CMe}_2$ ,

m. p.  $70$ — $71^\circ$ .  $\alpha$ -Hydroxy- $\alpha$ -methylbutyric chloralide, similarly prepared, has m. p.  $74$ — $75^\circ$ .

R. BRIGHTMAN.

**Heats of formation of the alcoholates of chloral.** S. CHECHIK (J. Amer. Pharm. Assoc., 1930, 19, 320—325).—The heats of formation of the additive compounds of chloral and sixteen aliphatic alcohols have been determined but no generalisations are possible from the results. Additive compounds of chloral with the following alcohols are described: *sec*.-propyl, m. p.  $49^\circ$ , *n*-butyl, m. p.  $58.5^\circ$ , isobutyl, liquid, *sec*.-butyl, liquid, *tert*.-butyl, m. p.  $52^\circ$ , *n*-amyl, liquid, isoamyl, m. p.  $55^\circ$ , *tert*.-amyl, m. p.  $68^\circ$ , *n*-hexyl, liquid, also with methyl-*n*-propylcarbinol, liquid, and diethylcarbinol, liquid. E. H. SHARPLES.

**[Preparation of] bromoacetone.** P. A. LEVENE (Organic Syntheses, 1930, 10, 12—13).

**[Preparation of] acetol.** P. A. LEVENE and A. WALTI (Organic Syntheses, 1930, 10, 1—2).

**Hydroxyketones and carbohydrate structure.** W. H. LINNELL and B. W. MELHUISH (Quart. J. Pharm., 1930, 3, 40—51).—The properties of  $\delta$ -keto-*n*-amyl alcohol and  $\epsilon$ -keto-*n*-hexyl alcohol (cf. Lipp, A., 1889, 843) have been compared with those of the  $\gamma$ - and normal aldose sugars. The alcohols reduce Fehling's and ammoniacal silver solutions and are converted by 1% methyl-alcoholic hydrogen chloride in 48 hrs. into the cyclic ethers, 2-methoxy-2-methyl-tetrahydrofuran, b. p.  $115$ — $117^\circ$ , and 2-methoxy-2-methyltetrahydropyran, b. p.  $116$ — $117^\circ$ , respectively. These are stable to hydrolysis by *N*-hydrochloric acid and to oxidation by permanganate. Attempts to separate optically active forms from them by partial hydrolysis with emulsin or maltase were unsuccessful.  $\epsilon$ -Keto-*n*-hexyl alcohol is more readily dehydrated to the cyclic anhydride than is the lower homologue. H. E. F. NOTTON.

**[Preparation of] dimethylglyoxime.** W. L. SEMON and V. R. DAMERELL (Organic Syntheses, 1930, 10, 22—27).

**Pentose and uronic acid content of orange albedo, and an arabinogalacturonic acid derived from orange pectin.** J. R. BOWMAN and R. B. MCKINNIS (J. Amer. Chem. Soc., 1930, 52, 1209—1215).—A method has been devised for determining simultaneously the furfuraldehyde and carbon dioxide formed by boiling material with dilute hydrochloric acid. Extraction of orange albedo by alcohol yields no pentoses, and the residue yields twice the ratio of furfuraldehyde to carbon dioxide obtainable from digalacturonic acid; it is, therefore, concluded that it contains an equal proportion of combined pentose and uronic acid. An arabinogalacturonic acid has been prepared from the albedo by extraction with dilute sodium hydroxide and subsequent alternate precipitation with acid and dissolution in alkali. It yields the same ratio of furfuraldehyde to carbon dioxide as the albedo. Hydrolysis by 2% sulphuric acid leaves the galacturonic acid unattacked, and it can be separated and identified; the pentose is partly attacked, but arabinose can be separated and characterised as the phenylhydrazone. Arabinogalacturonic acid or a polymeride is probably the nuclear

unit of orange albedo pectin. Apple pectin, on the other hand, contains digalacturonic acid (McKinnis, A., 1928, 1016). It is suggested that in nature a transition takes place from digalacturonic acid to arabinogalacturonic acid and finally, perhaps, to arabinose. It is possible that some pectins contain both uronic acids in varying proportions, and that this is the cause of the confusion which exists concerning their constitution.

R. K. CALLOW.

**Derivatives of lyxofuranose.** H. G. BOTT, E. L. HIRST, and J. A. B. SMITH (J.C.S., 1930, 658—669).—Lyxose, on treatment with cold 1% methyl-alcoholic hydrogen chloride at 20° for 10 hrs., gave a syrup containing methyl-lyxofuranoside, methyl-lyxopyranoside, and free lyxose; when this reaction was stopped at the point of maximum specific rotation the product consisted mainly of the former, but at equilibrium the solution contained mainly the latter. Methylation of the mixture (lyxose 15%, methyl-lyxopyranoside 10%, and methyl-lyxofuranoside 75%) with methyl sulphate and alkali completed by Purdie's reagents gave a mixture of *trimethylmethyl-lyxofuranoside* (90%) with *trimethylmethyl-lyxopyranoside* (10%) from which by heating with *N*/15-hydrochloric acid, *trimethyl-lyxofuranose*, b. p. about 95°/0.04 mm.,  $n_D^{20}$  1.4580,  $[\alpha]_D^{20} +39^\circ$  in water, was obtained.

Slow distillation of *trimethyl-lyxofuranose* caused some decomposition with formation of a *hexamethyl-dipentose*, b. p. about 160°/0.05 mm., m. p. 77°,  $[\alpha]_D^{20} +114^\circ$ .

Bromination of an aqueous solution of *trimethyl-lyxofuranose* at 35—40° led to *trimethyl-γ-lyxonolactone*, m. p. 37—40° (also obtained by methylation of *lyxonolactone* with Purdie's reagents).

Oxidation at 90° of *trimethylmethyl-lyxofuranoside* with nitric acid (*d* 1.42) yielded methyl *meso*-dimethoxysuccinate, m. p. 68°.

The mixture (methyl-lyxofuranoside and -lyxopyranoside and lyxose) when six times methylated with silver oxide and methyl iodide gave, along with the chief product, *trimethylmethyl-lyxoside*, a *methyl ester*,  $C_4H_5O_2(OMe)_2 \cdot CO_2Me$ , m. p. 127—128°,  $[\alpha]_D^{20} +175^\circ$  in water.

Lyxose, contrary to previous statements made in the literature, falls into line with the other aldoses and ketoses examined in giving a series of normal derivatives which are pyranose in type and a series of more labile *γ*-derivatives which have the furanose structure.

R. J. W. LE FÈVRE.

**Relations between rotatory power and structure in the sugar group. XXV. Ring structures of various monosaccharides. XXVI. Ring structures of various compound sugars.** C. S. HUDSON (J. Amer. Chem. Soc., 1930, 52, 1680—1700, 1707—1718; cf. A., 1926, 714).—XXV. The measurements of Brauns (A., 1923, i, 441; 1927, 93) on the halogenoacetyl derivatives of cellobiose and 4-glucosidomannose, taken in conjunction with the proof that normal tetramethylglucose and normal tetramethylmannose are true epimerides (Wolf from and Lewis, A., 1928, 509), disprove Haworth's assumption that ring change does not occur during methylation. Using the evidence available in the literature,

the ring structures of various monosaccharides are disclosed through the application of the rules of optical superposition and isorotation.

XXVI. Application of the isorotation rules to compound sugars (in conjunction with published data regarding their structure) has resulted in new constitutions being assigned to maltose, melibiose, sucrose, gentianose, and raffinose. H. BURTON.

**Precipitation of sugars and polyhydroxy-compounds as cuprobarium complex compounds.** P. FLEURY and P. AMBERT (Bull. Soc. chim., 1930, [iv], 47, 420—435).—A more detailed account of work already published (this vol., 196).

**Sugar oxidations and decompositions. VIII. Formation of lactic acid from sugars and related materials.** K. BERNHAUER and H. WOLF (Biochem. Z., 1930, 219, 232—240).—By the action of calcium hydroxide on various sugars under pressure, only sucrose gives a high yield of lactic acid, whereas invert-sugar, dextrose, lævulose, galactose, maltose, and lactose give only two fifths of the yield with sucrose. Similarly *γ*-methylglucoside yields 2.5 times as much lactic acid as the *α*- or the *β*-glucoside. The formation of lactic acid from dihydroxyacetone, methylglyoxal, and isosaccharic acid was also investigated.

P. W. CLUTTERBUCK.

**Sugar activation by alkali. I. Formation of lactic and saccharic acids.** P. A. SHAFFER and T. E. FRIEDEMANN (J. Biol. Chem., 1930, 86, 345—374).—Various sugars were kept in alkaline solution at 37—40° for 2 months or until the reducing value had reached a minimum. Provided that excess of total alkali were present the total acid produced was independent of the alkalinity. The amounts of total acid from dextrose, lævulose, and mannose (1 mol.) and from dihydroxyacetone and glyceraldehyde (2 mols.) were approximately the same, whilst that from galactose and pentoses was less. The proportion of the total acid represented by lactic acid was, at equal alkalinity, the same for dextrose, lævulose, and mannose, and considerably less for galactose; this proportion was, however, raised by increase in alkalinity, and lowered by rise in temperature or increase in concentration of sugar. At low alkalinities 1 mol. of dextrose yields more lactic acid than 2 mols. of triose, but at high alkalinity the conversion of triose into lactic acid is almost quantitative. The yield of lactic acid is associated with the proportion of the sugar which is present in the ionised condition, the action of alkali being therefore in the first instance salt formation.

C. R. HARRINGTON.

**Sugars containing nitrogen. I. Azido-derivatives of dextrose.** A. BERTHO [with H. NÜSSEL] (Ber., 1930, 63, [B], 836—843).—*β*-Azidoacetoglucose, m. p. 129° (decomp.),  $[\alpha]_D^{20} -33.0^\circ$  in chloroform,  $[\alpha]_D^{20} -41.7^\circ$  in methyl alcohol, is obtained by long preservation of mixtures of acetobromoglucose and technical sodium azide at 30—40° or, preferably, from the components in boiling acetonitrile. Removal of the acetyl groups by methyl-alcoholic ammonia leads to the non-crystalline *β*-azidoglucose. Similarly, *α*-1:6-dibromoacetoglucose and sodium azide in ethyl alcohol or acetonitrile afford *β*-6-bromo-

1-azidoacetoglucose, m. p. 137—138° (decomp.),  $[\alpha]_D^{25}$  -15.2° in chloroform; prolongation of the reaction causes the production of mixed crystals of this compound with 1:6-diazidoacetoglucose. Replacement of the 6-bromine atom in triacetylmethylglucoside 6-bromohydrin or  $\beta$ -methylglucoside 6-bromohydrin by the azido-group could not be effected by sodium azide or the corresponding acid.

The applicability of Hudson's rules to these compounds is discussed. H. WREN.

**Structure of methylated sugars. II.** C. H. WHITNAH and J. E. MILBERY (J. Amer. Chem. Soc., 1930, 52, 1627—1633; cf. this vol., 69).—Methylation of mannose with methyl sulphate and sodium hydroxide solution at 30° and  $p_H$  7.0—8.5 gives a product which is probably a trimethyl- $\gamma$ -methylmannoside. Similar treatment at 35° affords a product which is a mixture of methylated compounds and has no  $\gamma$ -properties. Stable and unstable forms of sugars show a large difference in their behaviour towards potassium permanganate in an acid phosphate buffer (cf. Kuhn and Wagner-Jauregg, A., 1925, i, 1241); the unstable forms are oxidised much more rapidly.

H. BURTON.

**Crystalline  $\alpha$ -methylmannofuranoside ( $\gamma$ -methylmannoside).** I. W. N. HAWORTH and C. R. PORTER (J.C.S., 1930, 649—651).—Methylation of mannose dicarbonate (mannofuranose dicarbonate) with either diazomethane or methyl iodide and silver oxide yielded crystalline *methylmannofuranoside dicarbonate*, m. p. 172—173° (decomp.),  $[\alpha]_D^{25}$  +98° in acetone, from which, by warming in acetone solution with barium hydroxide,  *$\alpha$ -methylmannofuranoside*, m. p. 118—119°,  $[\alpha]_D^{25}$  +113° in water,  $[\alpha]_D^{25}$  +117° in methyl alcohol, was obtained. It underwent hydrolysis with much greater rapidity than normal  $\alpha$ -methylmannopyranoside, although it was slightly more stable towards 0.01*N*-hydrochloric acid than the corresponding glucofuranoside.

R. J. W. LE FÈVRE.

**Crystalline  $\alpha$ -methylmannofuranoside ( $\gamma$ -methylmannoside).** II. W. N. HAWORTH, E. L. HIRST, and J. I. WEBB (J.C.S., 1930, 651—658).—By the direct condensation of mannose with methyl alcohol in the presence of 1% hydrogen chloride at 20° yields of about 30% of  $\alpha$ -methylmannofuranoside were obtained. It was hydrolysed completely to mannose when heated at 100° for 2 hrs. with 0.01*N*-hydrochloric acid, the velocity coefficient being  $k = 0.015$  (min. and decimal logs.); it was stable in the presence of 15% aqueous sodium hydroxide for 90 min. at 60°; by acetylation (acetic anhydride and pyridine) it yielded *tetra-acetyl- $\alpha$ -methylmannofuranoside*, m. p. 63°,  $[\alpha]_D^{19}$  +107° in chloroform; treatment of its acetone solution with methyl sulphate and aqueous sodium hydroxide gave *tetramethyl- $\alpha$ -methylfuranoside*, m. p. 24°, b. p. 120°/0.23 mm.,  $[\alpha]_D^{19}$  +98.6° in water, which was very slightly more stable than the initial unmethylated mannoside and when heated at 100° for 8 hrs. with 0.01*N*-hydrochloric acid, was transformed into *tetramethylmannofuranose*, b. p. 124°/0.1 mm.,  $n_D^{15}$  1.4532,  $[\alpha]_D^{15}$  +39° in water changing to  $[\alpha]_D^{20}$  +43° after 10 min. The last-named compound condensed readily with cold methyl

alcohol containing 0.25% of hydrogen chloride with formation of the equilibrium mixture of the  $\alpha$ - and  $\beta$ -forms of tetramethylmethylmannofuranoside. Oxidation of tetramethylmannofuranose with bromine water gave crystalline tetramethyl- $\gamma$ -mannonolactone, thus proving the presence of a 5-membered ring in the new  $\alpha$ -methylmannofuranoside. The work of Irvine and Burt (A., 1924, i, 944) on the isolation of a liquid  $\gamma$ -methylmannoside is criticised adversely.

Acetylation of the syrup obtained when the mother-liquors from the crystallisation of  $\alpha$ -methylmannofuranoside were evaporated under diminished pressure afforded tetra-acetyl- $\beta$ -methylmannopyranoside, m. p. 156°, along with (?) tetra-acetyl- $\beta$ -methylmannofuranoside. R. J. W. LE FÈVRE.

**Unsaturated derivatives of gentiobiose and cellobiose.** B. HELFERICH, E. BOHN, and S. WINKLER (Ber., 1930, 63, [B], 989—998).— $\beta$ -Hepta-acetylgentiobiose 6'-bromohydrin is prepared in 52% yield by shaking acetodibromoglucose with tetra-acetylglucose in chloroform with silver carbonate in presence of finely-divided calcium chloride and a little iodine. It is transformed by sodium iodide in acetone at 100° into  $\beta$ -hepta-acetylgentiobiose 6'-iodohydrin, m. p. 250—252° (decomp.),  $[\alpha]_D^{25}$  -3.6° in pyridine. With silver fluoride in pyridine the 6'-bromohydrin into  $\beta$ -hepta-acetylgentiobiose  $C_{26}H_{34}O_{17}$ , m. p. (indef.) 139—143°,  $[\alpha]_D^{25}$  -9.1° in chloroform, hydrolysed by Zemplén's method to *gentiobiose*, m. p. 175° (corr.),  $[\alpha]_D^{25}$  +2.1° to  $[\alpha]_D^{25}$  -18.7° in water.

$\beta$ -Methylcellobioside and triphenylmethyl chloride in pyridine at 100° yield 6:6'-ditriphenylmethyl- $\beta$ -methylcellobioside,  $[\alpha]_D^{25}$  -12.1° in chloroform, converted by acetic anhydride in cold pyridine into 2:3:4:2':3'-penta-acetyl-6:6'-ditriphenylmethyl- $\beta$ -methylcellobioside,  $[\alpha]_D^{25}$  +19.0° in chloroform; 2:3:4:2':3'-penta-acetyl- $\beta$ -methylcellobioside has m. p. (indef.) 191—196°,  $[\alpha]_D^{25}$  -37.9° in chloroform. 6:6'-Di-*p*-toluenesulphonyl-2:3:4:2':3'-penta-acetyl- $\beta$ -methylcellobioside, m. p. 160—162° (corr.),  $[\alpha]_D^{25}$  -2.9° in chloroform, is converted by sodium iodide in acetone at 100° into 6:6'-di-iodo-2:3:4:2':3'-penta-acetyl- $\beta$ -methylcellobioside, m. p. 216—219°,  $[\alpha]_D^{25}$  -7.4° in chloroform, transformed by silver fluoride in pyridine into 2:3:4:2':3'-penta-acetyl- $\beta$ -methylcellobiosedienide, m. p. 99—102° (corr.),  $[\alpha]_D^{25}$  -90.4° in chloroform; the compound combines immediately with bromine, but does not reduce Fehling's solution until it has been hydrolysed by dilute acid.

H. WREN.

**Constitution of trehalose.** H. BREDERECK (Ber., 1930, 63, [B], 959—965).—Anhydrous trehalose is converted by triphenylmethyl chloride in anhydrous pyridine into 6:6'-ditriphenylmethyltrehalose, m. p. 278—281° (corr.),  $[\alpha]_D^{25}$  +62.8° in pyridine (also +2.5EtOH), transformed by acetic anhydride in pyridine into hexa-acetylditriphenylmethyltrehalose, m. p. 245—247° (corr.),  $[\alpha]_D^{25}$  +115.7° in chloroform. Hydrolysis of the last-named compound by hydrogen bromide in glacial acetic acid gives 2:3:4:2':3':4'-hexa-acetyltrehalose, m. p. 93—96° (corr.),  $[\alpha]_D^{25}$  +159.3° in chloroform, and an apparently crystalline-isomeric form, m. p. 118—121° (corr.),  $[\alpha]_D^{25}$  +155.6° in chloroform; from the hexa-acetate the octa-acetate, m. p.

100—102° (corr.), is prepared and the ditriphenylmethyl compound may be regenerated. 6:6'-*Di-p-toluene-sulphonylhexa-acetylthrehalose*, m. p. 170—172° (corr.),  $[\alpha]_D^{25} +136.1^\circ$  in chloroform, is converted by sodium iodide in acetone at 130° into *hexa-acetylthrehalose* 6:6'-*di-iodohydrin*, m. p. 191—193° (corr.),  $[\alpha]_D^{25} +92.3^\circ$  in chloroform, which with silver fluoride in pyridine gives *hexa-acetylthrehalosediene*, m. p. 205—207° (corr.),  $[\alpha]_D^{25} +107.5^\circ$  in chloroform. Hydrolysis of the last-named compound by Zemplén's method gives the non-crystalline *threhalosediene* which does not reduce boiling Fehling's solution; it is readily hydrolysed by cold dilute acids to *isorhamnose*, identified as the di-*p*-nitrophenylhydrazone. The production of a ditriphenylmethylthrehalose establishes the presence of two terminal hydroxyl groups in the sugar and the absence of reducing power in threhalosediene proves the presence of pyran rings.

H. WREN.

**Melibiose.** P. A. LEVENE and E. JORPES (J. Biol. Chem., 1930, **86**, 403—415).—Acetobromomelibiose gave, with zinc dust and acetic acid, *melibial hexa-acetate*, m. p. 113°,  $[\alpha]_D^{25} +87.0^\circ$  in chloroform, which was deacetylated with methyl-alcoholic ammonia to give *melibial*,  $[\alpha]_D^{25} +142.3^\circ$  in water; this compound gave a positive pine splinter reaction. With methyl alcohol and silver carbonate, acetobromomelibiose yielded  $\beta$ -*methylmelibioside hepta-acetate*, m. p. 150°,  $[\alpha]_D^{25} +90.5^\circ$  in chloroform, which was deacetylated with barium hydroxide to give  $\beta$ -*methylmelibioside*,  $[\alpha]_D^{25} +75.0^\circ$  in water; a second *methylmelibioside*,  $[\alpha]_D^{25} +107.0^\circ$  in water, was obtained by treatment of melibiose with methyl-alcoholic hydrogen chloride; the respective rates of hydrolysis indicated that the former glucoside had the 1:5- and the latter the 1:4-ring structure. The previous failure of Levene and Wintersteiner (A., 1927, 1171) to observe 1:4-lactone formation with melibiononic acid was due to the slowness of the reaction. The results confirm the theory that melibiose is 6- $\alpha$ -galactosidoglucose.

C. R. HARRINGTON.

**Non-tannin materials from *Badan* (*Saxifraga crassifolia*).** II. Arbutin. A. E. TSCHITSCHIBABIN, A. V. KIRSANOV, and M. G. RUDENKO (Annalen, 1930, **479**, 303—306).—Extraction of the dried leaves of *S. crassifolia* with boiling water and concentration of the filtered, aqueous extract at 20 mm. affords the glucoside arbutin, purified by crystallisation from ethyl acetate, in 12% yield. This substance is identical with the second crystalline product, isolated in quantity too small for investigation, from the roots of the same plant (A., 1929, 574). It is not accompanied by methylarbutin.

J. W. BAKER.

**Digitalis glucosides. IV. Correlation of gitoxigenin with digitoxigenin.** W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1930, **86**, 199—216).—*isoGitoxigenin*, with hydrochloric acid at 0°, gave *chloroisogitoxigenin*,  $C_{23}H_{33}O_4Cl$ , m. p. 167°; at 20° it yielded *anhydroisogitoxigenin*,  $C_{23}H_{32}O_4$ , m. p. 212°. *isoGitoxigenin* acid gave, with hydrochloric acid at 20°, *chloroisogitoxigenic acid*,  $C_{23}H_{33}O_5Cl$ , m. p. 255°,  $[\alpha]_D^{25} -101^\circ$  in 95% alcohol (*methyl ester*, m. p. 155°), which was converted by dilute ammonia into *γ-isogitoxigenic acid*, m. p. 260°,  $[\alpha]_D^{25} -27^\circ$  in 95%

alcohol (compare isomerisation of  $\alpha$ -*isostrophanthic acid*, A., 1927, 1194), and with alcoholic sodium hydroxide into *anhydro-γ-isogitoxigenic acid*,  $C_{23}H_{32}O_5$ , m. p. 210°,  $[\alpha]_D^{25} +61^\circ$  in 95% alcohol (cf. A., 1929, 798) (*methyl ester*, m. p. 151°). The latter ester absorbed 2 mols. of hydrogen to give *γ-digitoxanol-diacid monomethyl ester*,  $C_{24}H_{38}O_5$ , m. p. 191—192°, which was readily hydrolysed to the *diacid*,  $C_{23}H_{36}O_5$ , m. p. 207°,  $[\alpha]_D^{25} +5.0^\circ$  in 95% alcohol; this gave a *methyl ester*, m. p. 156—157°,  $[\alpha]_D^{25} +6.5^\circ$  in chloroform, which, with sodium hydroxide, yielded the more stable *monomethyl ester*, m. p. 218°. The hydrogenation of methyl *anhydro-γ-isogitoxigenate* must therefore have involved simultaneous saturation of a double linking and opening of a lactone ring to form the corresponding deoxy-acid. *Methyl isodigitoxigenate*, m. p. 174°, could not be hydrogenated; *γ-isodigitoxigenic acid*,  $C_{23}H_{34}O_5 \cdot H_2O$ , m. p. 118°,  $[\alpha]_D^{25} +60^\circ$  in 95% alcohol (*methyl ester*, m. p. 168°), was obtained from *isodigitoxigenic acid* with hydrochloric acid, and yielded, when heated with acetic anhydride and acetyl chloride, the *acetate of digitoxenol diacid anhydride*,  $C_{25}H_{34}O_5$ , m. p. 182—184°; this, with methyl-alcoholic hydrogen chloride, gave the *monomethyl ester*,  $C_{26}H_{38}O_6$ , m. p. 89°, which was hydrogenated to the *acetate of γ-digitoxanol diacid monomethyl ester*,  $C_{26}H_{40}O_6$ , m. p. 80° and 182°,  $[\alpha]_D^{25} +4^\circ$  in methyl alcohol. The acid obtained by hydrolysis of the latter compound with methyl-alcoholic sodium hydroxide was identified directly and through its methyl esters with the *γ-digitoxanol-diacid* derived, as described above, from *γ-isogitoxigenic acid*. It follows that gitoxigenin is a hydroxy-derivative of digitoxigenin.

C. R. HARRINGTON.

**Cellulose chemistry.** W. WELTZEN (Kolloid-Z., 1930, **51**, 172—176).—Previously published work on cellulose is discussed from the point of view of "corrosion," by which is understood the dissolution or chemical attack of cellulose in presence of small quantities of impurities. Substantive dyeing is also discussed.

E. S. HEDGES.

**Acetolysis of cellulose and isolation of two crystalline forms of glucose penta-acetate.** C. S. WEBBER, C. J. STAUD, and H. LEB. GRAY (J. Amer. Chem. Soc., 1930, **52**, 1542—1547).—Treatment of cellulose (unsized rag paper) with acetic anhydride and sulphuric acid at 109° and addition of the product to dilute sodium hydroxide solution gives a precipitate of cellobiose octa-acetate and glucose penta-acetate, separable by crystallising the former ester from alcohol. The residue from the chloroform extract of the aqueous filtrate deposits a new crystalline form (plates) of  $\alpha$ -glucose penta-acetate in addition to the usual variety (needles).

H. BURTON.

**Action of sodium hydroxide on cellulose.** J. S. RUMBOLD (J. Amer. Chem. Soc., 1930, **52**, 1013—1018).—The absorption of sodium hydroxide from aqueous solution (2—8%) by cotton has been shown to take place very rapidly, and then to change only slightly over a period of 2 or 3 days. Previous treatment of the cotton with sodium hydroxide solutions of concentration greater than 5% increases its power of absorption. The maximum effect is produced by concentrations of 20% and over. The absorption

curves indicate that in 4–5% solutions the compounds  $12\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{NaOH}$  and  $6\text{C}_6\text{H}_{10}\text{O}_5\cdot\text{NaOH}$  are formed from native and mercerised cotton, respectively. R. K. CALLOW.

**Optical rotation of cellulosic materials. I. Optical rotation of soluble cellulose in alkali.** T. F. MURRAY, jun., C. J. STAUD, and H. LEB. GRAY (J. Amer. Chem. Soc., 1930, 52, 1508–1519).—Treatment of "Eastman filtration cotton" with 3*N*-phosphoric, -sulphuric, and -hydrochloric acids for 24 and 48 hrs. at 54° gives extracts which are dextrorotatory (probably due to dextrose formation), except for phosphoric acid (inactive). The product from the hydrochloric acid treatment is highly degraded. The resulting hydrocelluloses, when extracted with 17.5% sodium hydroxide solution at the ordinary temperature, give levorotatory solutions containing about 3, 6–10, and 34–48%, respectively (for the above order of the acids), of extracted material. Oxidation of the cellulose with potassium dichromate (available oxygen=0.5 and 2 atoms per  $\text{C}_6\text{H}_{10}\text{O}_5$  unit) in *N*-phosphoric acid at 23–25° and 54° causes a loss in weight of less than 0.4%. With potassium permanganate under similar conditions the loss varies from 0.56 to 25.4%. The oxidised celluloses also give levorotatory alkaline extracts; the specific rotations of these increase to a maximum and then diminish, and are higher with more drastic oxidation. Photomicrographs showing degradation of the variously treated fibres are given. H. BURTON.

**X-Ray investigations of cellulose derivatives. VI. Lattice changes of nitrocellulose.** C. TROGUS, K. HESS, and J. R. KATZ (Z. physikal. Chem., 1930, B, 7, 17–24).—When cellulose nitrate in the fibrous state is allowed to swell in organic liquids, it undergoes a reversible change of lattice structure which is much more extensive than that of cellulose triacetate (cf. following abstract, and A., 1929, 1222). Mixtures of cyclohexanone and methyl alcohol are especially suitable for the purpose. The character of the change depends, not only on the solvent, but also on the degree of nitration of the cellulose and on the previous treatment of the original cellulose. It is probable that new chemical compounds of the nature of co-ordination compounds (cf. this vol., 21) may be formed. In the cyclohexanone-methyl alcohol mixtures it is the cyclohexanone and not the alcohol which is active, and other ketones, including camphor, are found to have a similar influence. The subject is of importance in connexion with celluloid and cellulose lacquers. M. S. BURR.

**X-Ray investigations of cellulose derivatives. V. Connexion between cellulose triacetates I and II and the reversion of cellulose.** K. HESS, C. TROGUS, W. OSSWALD, and K. DZIENGEL (Z. physikal. Chem., 1930, B, 7, 1–16).—If either the fibrous cellulose triacetate I or the crystalline triacetate II (cf. A., 1929, 1222) is dissolved in pyridine and the solution evaporated at different temperatures, the products give identical X-ray diagrams between approximately 35° and 75°. This behaviour is also observed with other solvents, but the temperatures vary. The transformation of triacetate I into triacetate II is therefore reversible and is characterised

by an equilibrium which depends on temperature and solvent. By the acetylation of ramie fibres, whether mercerised or not, fibrous bundles of either triacetate, or mixtures of both, can be obtained, the nature of the product depending on the temperature of acetylation, triacetate I preponderating at low temperatures and triacetate II at high. Since, by hydrolysis, triacetate I gives natural cellulose and triacetate II cellulose hydrate, the two celluloses can also be changed reversibly into one another through their acetates, the extent, under similar conditions of hydrolysis, depending on the position of equilibrium of the two acetates. The influence of variations in the conditions of hydrolysis on the composition of the product is unknown.

M. S. BURR.

**Crystalline product from cellulose cinnamate.** G. VON FRANK and H. MENDRZYK (Ber., 1930, 63, [B], 875–887).—Cellulose tricinnamate,  $\text{C}_6\text{H}_7\text{O}_5(\text{CO}\cdot\text{CH}\cdot\text{CHPh})_3$ , softening at 180° and becoming transparent at 200°,  $[\alpha]_D^{25} +176.5^\circ$  in chloroform, is readily prepared from cellulose, cinnamyl chloride, and pyridine in nitrobenzene at 100–120°; it yields a hexabromide, decomp. about 210°. It has great thermal stability and is hydrolysed with difficulty. Partial hydrolysis by means of phenol or the chloroacetic acids (particularly trichloroacetic acid) yields secondary cinnamates, characterised by solubility in cold benzene or hot acetone. If the last-mentioned solutions are cooled, a portion of the material (20% if trichloroacetic acid is used) separates as minute crystals. Purification of the crystalline and amorphous fractions leads to products of a similar degree of esterification (between 2 and 3) and approximately the same specific rotation, but varying softening points and reducing powers. Hydrolysis of the crystalline cinnamate yields a product resembling Hess's cellulose A, insoluble in water and organic media, soluble in sodium hydroxide, and giving the Röntgen diagram of hydrocellulose. It is converted exclusively into dextrose by concentrated hydrochloric acid. The triacetate obtained from it by acetic anhydride and pyridine shows no tendency to crystallise. Its insolubility in hot benzene-alcohol or methyl alcohol, its rotation  $[\alpha]_D^{25} -20.69^\circ$  in chloroform, and high m. p. appear to ally it more closely to cellulose triacetate than to the degradation products of cellulose obtained by Hess and Bergmann. Cryoscopic experiments with the cinnamate and acetate, mainly in phenol, indicate the presence of a tetrosan. Measurements of the rate of diffusion of solutions of the crystalline cinnamate in pyridine and *m*-cresol and of the acetate in pyridine and glacial acetic acid show the presence of particles of very considerable size and of very marked heterodispersivity so that trustworthy conclusions with regard to the mol. wt. are not afforded. The presence of particles with 25–50 glucose residues is determined, whereas, on the basis of reducing power, particles with about 100 glucose residues are probable. Re-esterification of the crystalline secondary cinnamate appears to yield the tri-cinnamate. H. WREN.

**More complex intermediate products of the acetolysis of cellulose.** K. H. MEYER and H. HOPFF (Ber., 1930, 63, [B], 790–791).—The product,



m. p. 261—262°, obtained by Hess and Friese (A., 1927, 44) by the acetolysis of cellulose is not homogeneous, since it can be separated by fractional precipitation of its solution in acetone with methyl alcohol into portions, m. p. 275°, 270°, 255°, and 229°, respectively. Determinations of mol. wt. in freezing glacial acetic acid gave values of about 600 (in agreement with Hess) or about 1000 if traces of water were rigidly excluded. In the boiling solvent, slight depressions were observed due to the production of an azeotropic mixture with minute amounts of water. In freezing bromoform constant values of about 3000 are obtained. The complex character of the product is confirmed by measurements of viscosity in ethylene chlorohydrin (cf. Freudenberg, this vol., 457).

H. WREN.

**Cellulose xanthate.** I. E. GEIGER (Helv. Chim. Acta, 1930, 13, 281—303).—The reaction between carbon disulphide and sodium hydroxide solution is shown to be  $6\text{NaOH} + 3\text{CS}_2 = \text{Na}_2\text{CO}_3 + 2\text{Na}_2\text{CS}_3 + 3\text{H}_2\text{O}$  (cf. Bernhard, Kunstseide, 1925, 7, 169; Leuchs, *ibid.*, 286); sodium sulphide is not formed. During the decomposition of cellulose xanthate in aqueous solution some sodium trithiocarbonate is formed from the liberated carbon disulphide (by the above reaction); this can be determined by acidification of the solution with sulphuric acid and titrating with iodine. Contrary to the statement of Bernhard (*ibid.*, 1927, 7, 316) no sulphide is produced. Treatment of a solution of cellulose xanthate, which has been allowed to ripen (decompose) for 24 hrs., with carbon disulphide affords a further sulphurised xanthate which is not precipitable by saturated sodium chloride solution or 96% methyl alcohol (see below). Sulphurisation of a xanthate (low S content) may also be effected by another xanthate (high S content), presumably through intermediately formed carbon disulphide. Determinations of the amounts of sodium trithiocarbonate and cellulose xanthate formed by the action of carbon disulphide on viscose solutions containing varying amounts of free sodium hydroxide (about 3.25—13.4%) show that xanthate formation proceeds with about the same velocity as trithiocarbonate production. The amount of trithiocarbonate formed increases with rise in the concentration of alkali.

Treatment of cellulose xanthate solutions of varying degrees of ripeness with iodine in dilute acetic acid gives disulphides containing 9.13—16.84% S; the amount of sulphur decreases with length of ripening. Successive treatment of the xanthate solution, from which the disulphide with 16.84% S is obtained, with carbon disulphide (yielding solution A) and iodine affords a disulphide containing 32.1% S. Addition of A to 96% methyl alcohol gives a solution which gelatinises after about 1 hr.; addition of a small amount of ether to the methyl-alcoholic solution causes the separation of a sodium cellulose xanthate. This salt has the approximate composition  $\text{C}_{12}\text{H}_{17}\text{O}_{10}(\text{CS}_2\text{Na})_3$ , is easily soluble in water, and decomposes when kept to a water- and alkali-insoluble product. Carbon disulphide is eliminated during the decomposition and the product formed contains cellulose, sodium carbonate, and sodium trithio-

carbonate. Methylation of A with methyl sulphate and dilute sodium hydroxide gives a methyl ester,  $\text{C}_{12}\text{H}_{19}\text{O}_{10}\cdot\text{CS}_2\text{Me}$ ; elimination of half of the originally combined sulphur occurs.

Treatment of a solution of a disulphide (17.7% S) in 8% sodium hydroxide solution with carbon disulphide, and addition of the resulting red solution to iodine in dilute acid affords an unstable disulphide containing 29.66% S. The viscosity of solutions of the disulphides in sodium hydroxide decreases, whilst the ease of dissolution and depth of colour increase with rise in the sulphur content.

H. BURTON.

**Constitution of pine lignin. X. and XI. Synthesis of  $\alpha$ -coniferaldehyde or its polymeric forms.** P. KLASON (Ber., 1930, 63, [B], 792—795, 912—914; cf. A., 1929, 1428).—X. The view of Freudenberg and others (A., 1929, 1046) that  $\alpha$ -vanillylglycerol and not vanillylglyceraldehyde is the fundamental substance of lignin is at variance with the author's experience with the ligninsulphonic acids which contain one aldehydic group for 30 carbon atoms or by energetic sulphite treatment one group for about 10 carbon atoms.

The previous assumption that  $\beta$ -naphthylamine lignosulphonate,  $3\text{C}_{10}\text{H}_{10}\text{O}_3 + \text{H}_2\text{SO}_3 + \text{C}_{10}\text{H}_9\text{N} - \text{H}_2\text{O}$ , contains aliphatic hydroxyl, since it retains 5% of water after desiccation over phosphoric oxide, is untenable, since the water content sinks to below 2% after very prolonged drying and the methoxyl content of the methylated salt is the same when air-dried material or that dried at 130° is employed. Lignin in wood does not therefore contain double linkings; these are developed as the aliphatic hydroxyl groups are lost and render the addition of sulphurous acid possible.

Addition of benzenesulphonyl chloride in toluene to a warm solution of sodium  $\alpha$ -lignosulphonate yields the compound  $3\text{C}_{10}\text{H}_{10}\text{O}_3 + \text{H}_2\text{SO}_3 + \text{Ph}\cdot\text{SO}_2 - \text{H}$  ( $\beta$ -naphthylamine salt), which, when treated with anhydrous hydrazine in pyridine, gives benzenesulphinic acid, identified by reduction to thiophenol. The presence of a phenolic hydroxyl group is therefore established. In the absence of toluene, sodium  $\alpha$ -lignosulphonate acquires two benzenesulphonyl residues. Since  $\beta$ -naphthylamine  $\alpha$ -lignosulphonate does not contain aliphatic hydroxyl groups, the enhanced methoxyl content observed after methylation must be ascribed exclusively to phenolic hydroxyl groups. Although Freudenberg's lignin (*loc. cit.*) appears not to contain phenolic hydroxyl, this is not necessarily true of lignin in wood.

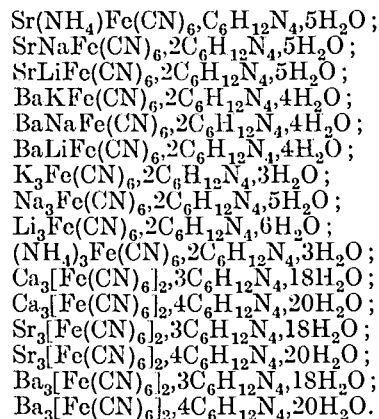
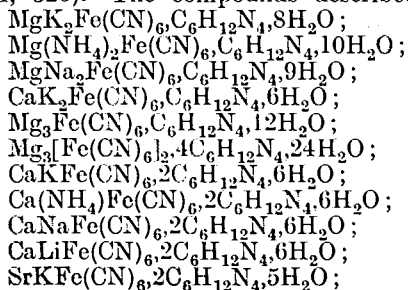
The observation that  $\alpha$ -lignin after very mild treatment with calcium hydroxide loses its ability to become converted into  $\alpha$ -lignosulphonic acid is confirmed (cf. A., 1923, i, 187); if the treatment is protracted, the product loses completely the reactions of lignin.

XI. Repetition of the work of Pauly and Feuerstein (A., 1929, 446) confirms the existence of two isomeric coniferaldehydes, one of which ( $\alpha$ -form) is labile and combines with sulphurous acid yielding a hydro-sulphonic acid affording an insoluble naphthylamine salt, whereas the other ( $\beta$ -variety) is stable. The compounds are probably *cis*- and *trans*-forms.

The only practicable method of oxidising coniferyl alcohol to the aldehyde is by means of air in presence of platinum; the trimeric form of  $\alpha$ -coniferaldehyde is produced. Preservation of solid coniferyl alcohol is accompanied by auto-oxidation to a dimeric aldehyde. A dimeric aldehyde is also obtained by the action of air on coniferin in glacial acetic acid in presence of platinised asbestos. H. WREN.

**Relationship between optical rotatory power and refraction of simple amines and alcohols.** W. LEITHE (Ber., 1930, 63, [B], 800—805; cf. A., 1929, 1079).—Examination of *d*-sec.-butylamine and *d*- $\alpha$ -pipecoline and their methyl and ethyl derivatives shows that the increase of refractive power in the series primary  $\rightarrow$  secondary  $\rightarrow$  tertiary amine is accompanied by a very pronounced increase in molecular rotation. Cyclic amines have a greater rotatory power than the corresponding aliphatic bases. Parallel therewith, a markedly greater  $R(N)$  value exists in the cyclic amine than in the aminoparaffins. Similarly for oxygenated compounds the parallelism between rotation and refraction is traced qualitatively from Pickard and Kenyon's observations on sec.-butyl alcohol and its derivatives. The following data are recorded: *d*-sec.-butylamine, b. p. 63°,  $d_4^{15}$  0.7308,  $n_D$  1.39626,  $[\alpha]_D^{15} +7.80^\circ$ ; *d*-ethyl-sec.-butylamine, b. p. 98°,  $d_4^{15}$  0.7396,  $n_D$  1.40428,  $[\alpha]_D^{15} +18.0^\circ$  (hydrogen oxalate, m. p. 155—156°); *d*-diethyl-sec.-butylamine, b. p. 131°,  $d_4^{15}$  0.7567,  $n_D$  1.41534,  $[\alpha]_D^{15} +89.3^\circ$  (picrate, m. p. 117°); *d*-*N*-methyl- $\alpha$ -pipecoline, b. p. 127°,  $d_4^{15}$  0.8233,  $n_D$  1.44306,  $[\alpha]_D^{15} +68.8^\circ$  [picrate, m. p. 240° (decomp.)]; *d*-*N*-ethyl- $\alpha$ -pipecoline, b. p. 148°,  $d_4^{15}$  0.8365,  $n_D$  1.45038. H. WREN.

**Compounds of hexamethylenetetramine with hydrated salts. VIII. Ferro- and ferricyanides.** G. A. BARBIERI (Gazzetta, 1930, 60, 229—243; cf. A., 1928, 159).—Study of the additive compounds formed by hexamethylenetetramine with a number of ferro- and ferricyanides shows that the former combine with only 1 mol. of the base, whereas ferricyanides containing a single anion  $[\text{Fe}'''(\text{CN})_6]^-$  unite with 2 mols., and those containing two such anions with 3 or 4 mols. of the base. Comparison of the behaviour of simple and mixed ferro- and ferricyanides with respect to their ability to combine with hexamethylenetetramine indicates that the latter does not enter into direct combination with either the anion or the cation, but that it unites with the hydrated salts by means of indirect secondary valencies as defined by Werner ("Neuere Anschauungen auf dem Gebiet der anorganischen Chemie," 1913, 311) and by Weinland ("Einführung in die Chemie der Komplexverbindungen," 1924, 326). The compounds described are:



T. H. POPE.

**Determination of choline and some physico-chemical data of choline and its salts.** W. ROMAN (Biochem. Z., 1930, 219, 218—231).—A chemical method for the determination of 5  $\gamma$  to 5 mg. of choline with an error of  $\pm 5\%$  is described, the method depending on the precipitation of choline periodide and subsequent titration of the iodine with thiosulphate. The solubilities of choline and choline chloride in various solvents and of choline periodide in various salt solutions especially at low temperatures are given. The barium ion inhibits the blueing of starch by iodine solutions. Evaporation of solutions of choline results in a loss which with larger amounts of choline (0.3 mg., and upwards) may amount to 10% but with smaller quantities may amount to 100%. The losses are smaller on evaporating in a vacuum. Choline and choline chloride solutions at 70° are not, but pure dry choline at 40° is, decomposed. Choline and choline chloride solutions are not affected by white nor by ultra-violet light. P. W. CLUTTERBUCK.

**[Preparation of] taurine.** C. S. MARVEL and C. F. BAILEY (Organic Syntheses, 1930, 10, 98—99).

**Formylation of amino-acids.** R. E. STEIGER (J. Biol. Chem., 1930, 86, 695—702).—The amino-acid is boiled for 2 hrs. under reflux with excess of anhydrous formic acid in a special apparatus. Toluene is then gradually introduced into the reaction flask, the boiling being continued; the water formed in the reaction together with the excess of formic acid distils over with the toluene. The formyl derivatives of *dl*-valine, *dl*-leucine, and *dl*-phenylalanine have thus been prepared in yields of 95—97%.

C. R. HARRINGTON.

**Transformation of alkylated malonic acids into  $\alpha$ -amino-acids.** T. CURTIUS. I. Ester hydrazides of malonic acid [with K. HOCHSCHWENDER]. II. Intermediate products in the synthesis of glycine and  $\alpha$ -alanine from malon- and methyl-malon-azidic acids [with H. MEIER]. III. Synthesis of  $\alpha$ -amino-*n*-valeric acid from *n*-propyl-malonazidic acid and *n*-butaldehyde from *n*-propylmalonylazide [with W. LEHMANN]. IV. *iso*Butyl- and *isopropyl*-malonamic acids and synthesis of  $\alpha$ -aminoisovaleric acid from *iso*-propylmalonazidic acid [with (FRL.) A. BENCKISER]. V. Synthesis of  $\alpha$ -aminoisohexanoic acid from *isobutyl*malonazidic acid [with M. SCHENCK].

VI. Synthesis of  $\alpha$ -amino- $\delta$ -methylhexoic acid from isoamylmalonazidic acid [with W. WIRBATSZ]. VII. Synthesis of *m*-tolylalanine from *m*-methylbenzylmalonazidic acid [with J. GALER]. VIII. Synthesis of *p*-nitrophenylalanine from *p*-nitrobenzylmalonazidic acid [with W. MÜHLHAÜSSER] (J. pr. Chem., 1930, [ii], 125, 211—302).—I. Gradual addition of alcoholic hydrazine hydrate to a warm solution of ethyl malonate in alcohol affords a mixture of the dihydrazide and ethyl malonhydrazide,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , m. p. 70° (benzylidene derivative, m. p. 112°). When heated at 150—160° this gives the *sec*-malonylhydrazide of Bülow and Bozenhardt (A., 1910, i, 102), which is also formed together with the *sec*-hydrazide,  $(\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH})_2$ , m. p. 133—134°, when ethyl malonate is heated with alcoholic hydrazine hydrate at 120—130°.

II. When an ethereal solution of malonazidic acid (A., 1921, i, 653) is distilled, glycine-*N*-carboxylic anhydride is obtained from the residue; decomposition in ethereal chloroform solution gives a mixture of the same anhydride and polymeric glycine anhydride,  $(\text{CH}_2\text{C}(\text{NH})\text{CO})_x$ . This anhydride is also formed when the azidic acid is decomposed with boiling methyl alcohol, and when glycine-*N*-carboxylic anhydride is treated with aniline. Methylmalonazidic acid (*loc. cit.*) is decomposed by boiling with methyl alcohol to the normal urethane, which on hydrolysis with hydrochloric acid at 90° gives  $\alpha$ -alanine.  $\alpha$ -Alanine-*N*-carboxylic anhydride is not obtained by decomposing this azidic acid in indifferent solvents.

III. Potassium *n*-propylmalonhydrazide, m. p. about 120° [free acid, m. p. 139° (decomp.)], is prepared by the general method (A., 1922, i, 721) and converted by nitrous acid into *n*-propylmalonazidic acid. Decomposition of this in boiling carbon tetrachloride gives a mixture of anhydrides, hydrolysed by hydrochloric acid at 120° to  $\alpha$ -amino-*n*-valeric acid hydrochloride. Ethyl  $\alpha$ -amino-*n*-valerate hydrochloride, m. p. 65°, and sodium nitrite give ethyl  $\alpha$ -diazon-valerate.

*n*-Propylmalonhydrazide, m. p. 158° [dihydrochloride, m. p. 180° after frothing at 160° and sintering at 119°; dibenzylidene derivative, m. p. 224° (decomp.); disalicylidene derivative, m. p. 203°; diacetophenone condensation product, m. p. 235°], is converted into *n*-propylmalonylazide, which reacts with aniline in ether forming mainly *n*-propylmalonanilide, m. p. 198° (*p*-toluidide, m. p. 186°). The diazide decomposes in boiling ether into  $\alpha\alpha$ -dicarbimidobutane; with alcohol the ester,  $\text{CO}(\text{NH}\cdot\text{CHPr}\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$ , m. p. 86° after softening at 82°, results. This ester is hydrolysed by 5% sulphuric acid, yielding *n*-butaldehyde (*m*-nitrobenzoylhydrazone, m. p. 131°).

IV. Ethyl sodiocyanoacetate condenses with iso-butyl bromide, forming a mixture of ethyl mono- and di-isobutylcyanoacetates. These are hydrolysed by sulphuric acid at 100° mainly to isobutylmalonamic acid, m. p. 140—146° (ethyl ester, m. p. 85°), and diisobutylmalonamic acid, m. p. 142° (ethyl ester, m. p. 76°). Potassium isobutylmalonamate, m. p. 203°, reacts with anhydrous hydrazine at 140°, yielding 1-amino-2:5-diisoamyl-1:3:4-triazole, m. p. 178°, and unidentified products; potassium diisobutyl-

malonamate, m. p. 93°, is unaffected by hydrazine hydrate at 100°. The potassium salt, m. p. 215°, of isopropylmalonamic acid, m. p. 158°, and anhydrous hydrazine at 120° afford 1-amino-2:5-diisobutyl-1:3:4-triazole, m. p. 202°, and a small amount of impure isopropylmalonyldihydrazide (dibenzylidene derivative, m. p. 254°); at 145—150° the triazole is the sole product.

Potassium ethyl isopropylmalonate, m. p. 92—93°, is converted into potassium isopropylmalonhydrazide, m. p. 87° (the benzylidene derivative of the free acid has m. p. 162°), and thence into isopropylmalonazidic acid. Decomposition of this in boiling ether gives  $\alpha$ -aminoisovaleric-*N*-carboxylic anhydride and a small amount of polymeric  $\alpha$ -aminoisovaleric anhydride, m. p. above 300°. The former anhydride, when heated, evolves carbon dioxide yielding the latter. Hydrolysis of these anhydrides with hydrochloric acid affords  $\alpha$ -aminoisovaleric acid (ethyl ester hydrochloride, m. p. 76°). Ethyl  $\alpha$ -diazoisovalerate is described.

V. isoButylmalonazidic acid is prepared from potassium isobutylmalonhydrazide [free acid, m. p. 154—155° (decomp.) (hydrochloride; benzylidene derivative, m. p. 138°)], and converted by treatment with hydrochloric acid into  $\alpha$ -aminoisohexoic acid [nitrate, m. p. 179—180° (decomp.)]. When the azidic acid is decomposed by boiling with ether and then with alcohol, polymeric  $\alpha$ -aminoisohexoic anhydride, not melted at 305° after sintering and colouring at 290°, is obtained. When isobutylmalonhydrazidic acid is treated with nitrous acid in the absence of ether, isobutylmalonamicazide, m. p. 87° (decomp.), is formed. This is unaffected by cold hydrochloric acid (decomposition occurs in the hot) or by boiling with ether; when boiled with methyl alcohol  $\alpha$ -*N*-carbomethoxy-aminoisohexoamide (?), m. p. 60°, is obtained.

VI. Ethyl isoamylcyanoacetate, b. p. 120—140°/11 mm., is hydrolysed with warm sulphuric acid to isoamylmalonamic acid, m. p. 136° (decomp.) (ethyl ester, m. p. 97°), the potassium salt, m. p. 207° (decomp.), of which reacts with anhydrous hydrazine at 140° forming 1-amino-2:5-diisohexyl-1:3:4-triazole, m. p. 135°. isoAmylmalonazidic acid is prepared from the potassium salt of isoamylmalonhydrazidic acid, m. p. 149° (decomp.) [benzylidene derivative, m. p. 143° (decomp.)], and converted by warming with hydrochloric acid into  $\alpha$ -amino- $\delta$ -methylhexoic acid, m. p. 280° (partial sublimation) [hydrochloride, m. p. 255° (decomp.)]; ethyl ester hydrochloride, m. p. 93°. The azidic acid decomposes in boiling ether yielding  $\alpha$ -amino- $\delta$ -methylhexoic-*N*-carboxylic anhydride, m. p. 68° (decomp.), which when heated with alcohol gives polymeric  $\alpha$ -amino- $\delta$ -methylhexoic anhydride, darkens at 250°. The amino-acid is also prepared from these anhydrides by heating with hydrochloric acid.

VII. Potassium ethyl 3-methylbenzylmalonate affords the potassium salt of 3-methylbenzylmalonhydrazidic acid, m. p. 143.5—144° (decomp.) (benzylidene derivative, m. p. 132°), convertible into 3-methylbenzylmalonazidic acid. This decomposes in boiling ethereal solution forming an amorphous product and a small amount of 2:5-diketo-3:6-di-(3-methylbenzyl)-piperazine, m. p. 212.5°; in boiling chloroform, the polymeric *m*-tolylalanine anhydride, decomp. 221—224° after darkening at 212° and sintering at 185°.

results. When an ethereal solution of the azidic acid is kept for some weeks *m*-tolylalanine-*N*-carboxylic anhydride, m. p. about 135° (decomp.), is formed. Hydrolysis of the polymeric anhydride with hydrochloric acid at 125° gives *m*-tolylalanine [ $\alpha$ -amino- $\beta$ -*m*-tolylpropionic acid], m. p. about 208° [hydrochloride, m. p. 218.5° (decomp.); nitrate, m. p. 153° (decomp.); ethyl ester hydrochloride, m. p. 203° (decomp.) after darkening]. Ethyl  $\alpha$ -diazo- $\beta$ -*m*-tolylpropionate is an oil.

VIII. Potassium ethyl *p*-nitrobenzylmalonate (the diethyl ester is prepared from *p*-nitrobenzyl chloride and ethyl sodiomalonate) is converted into *p*-nitrobenzylmalonhydrazidic acid, m. p. 137° [potassium salt, m. p. 190° (decomp.) after darkening at 175°; hydrochloride, m. p. 171° (decomp.); benzylidene derivative, m. p. 149° (decomp.); isopropylidene derivative, m. p. 142° (decomp.); acetophenone condensation product, m. p. 154° (decomp.)], and thence into *p*-nitrobenzylmalonazidic acid. This is converted by aniline in ethereal solution into the monoanilide, m. p. 149°, of *p*-nitrobenzylmalonic acid. The azidic acid decomposes in boiling ethereal solution, forming polymeric *p*-nitrophenylalanine anhydride, hydrolysed by hydrochloric acid at 130° to  $\alpha$ -amino- $\beta$ -*p*-nitrophenylpropionic acid.

When ethyl di-*p*-nitrobenzylmalonate is heated with hydrazine di-*p*-aminobenzylmalon-sec.-hydrazide,  $\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$ , m. p. 288° (decomp.) after darkening at 280° [dihydrochloride, m. p. about 300° (decomp.); dibenzylidene derivative, m. p. 271° (decomp.)], is produced. This is hydrolysed by hydrochloric acid at 140° to  $\alpha$ -di-*p*-aminophenylpropane- $\beta$ -carboxylic acid [dihydrochloride, m. p. 251° (decomp.); monobenzoyl derivative, m. p. 250°].

H. BURTON.

O-Alkyl-substituted hydroxylamino-acids, -esters, and -alcohols. L. W. JONES and R. T. MAJOR (J. Amer. Chem. Soc., 1930, 52, 1078—1085).—Interaction of ethyl bromoacetate and *ON*-dimethylhydroxylamine in dry ether yields *ON*-dimethylhydroxylammonium bromide, m. p. 143°, which separates, and ethyl methoxymethylaminoacetate,  $\text{OMe}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p. 164—166°, which is isolated by way of the hydrochloride, m. p. 90—91°. Ethyl bromoacetate and *ON*-diethylhydroxylamine yield similarly *ON*-diethylhydroxylammonium bromide, an oil, and ethyl ethoxyethylaminoacetate, b. p. 82°/19 mm., which reacts slowly with methyl iodide to give acetaldehyde and ethyl methylethylaminoacetate, an oil, isolated as the hydrochloride, m. p. 132°, and also obtained from ethyl bromoacetate and methyl-ethylamine. Ethyl bromoacetate and *O*-methylhydroxylamine yield *O*-methylhydroxylammonium bromide, m. p. 164°, and ethyl methoxyaminoacetate, b. p. 112°/116 mm. and 167—170° with some decomposition [chloroplatinate, m. p. 141° (decomp.)], the oily hydrochloride of which reacts with potassium cyanate to give ethyl *N*-methoxyhydantoate,  $\text{NH}_2\cdot\text{CO}\cdot\text{N}(\text{OMe})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , m. p. 112° (acid, decomp. 164°, obtained by evaporation with hydrochloric acid), with phenylcarbimide to give ethyl *N'*-phenyl-*N*-methoxyhydantoate, m. p. 91°, and with phenylthiocarbimide to give ethyl *N'*-phenyl-*N*-

methoxythiohydantoate, m. p. 110°. These hydroxylamino derivatives show a general resemblance to the corresponding ammonium derivatives.

Treatment of dimethylaminoethanol with 3% hydrogen peroxide solution yields dimethylhydroxyethylamine oxide (hydrochloride, m. p. 48—49°; chloroplatinate, decomp. 191°; picrate, m. p. 124°). Diethylhydroxyethylamine oxide picrate has m. p. 125—126° with darkening. No product could be isolated in an attempt to prepare methoxydimethylhydroxyethylammonium iodide by the action of methyl iodide on the amine oxide. The presence of a trace of moisture is necessary in the preparation of *ON*-dimethyl-*N*-hydroxyethylhydroxylamine (A., 1927, 754) and of the *ON*-diethyl compound (A., 1926, 155).

The formation of formaldehyde and dimethylaminoethanol by heating methoxydimethylhydroxyethylammonium hydroxide (A., 1927, 754) is confirmed.

R. K. CALLOW.

Condensations with dimethyldithiocarbamic acid. K. BODENDORF (Arch. Pharm., 1930, 268, 264—267).—Dimethylamine dimethyldithiocarbamate (I), m. p. 134—136° (decomp.), does not behave like other dimethylamine salts (cf. Mannich and Heilner, A., 1922, i, 351) when condensed with ketones and formaldehyde. With acetophenone and formaldehyde in alcohol it gives the compound,  $\text{COPh}\cdot\text{CH}(\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NMe}_2)_2$ , m. p. 141°, and with larger and smaller proportions of acetone, the corresponding methyl ketone, m. p. 101°, and the compound  $\text{CO}[\text{CH}(\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NMe}_2)_2]_2$ , m. p. 146—147°, respectively. The salt, I, reacts similarly with *p*-nitrobenzyl chloride giving *p*-nitrobenzyl *N*-dimethyldithiourethane, m. p. 108—109°, and with ethyl chloroacetate, giving carbethoxymethyl *N*-dimethyldithiourethane, m. p. 63—64°, hydrolysed by boiling 0.5*N*-potassium hydroxide to carboxymethyl dimethyldithiourethane, m. p. 147—148°.

H. E. F. NOTTON.

Catalytic hydrogenation of *L*-cystine to *L*-cysteine. M. BERGMANN and G. MICHALIS (Ber., 1930, 63, [B], 987—989).—Proteins can be smoothly reduced by hydrogen in presence of spongy palladium, but not of platinum catalysts, to the corresponding thiol compounds. Thus *L*-cystine yields *L*-cysteine, decomp. about 240°,  $[\alpha]_D^{20}$  -10.14° in water, identified also as the hydrochloride and methyl ester hydrochloride. Dialanylecystine is quantitatively converted into alanylcysteine as shown by titration with iodine, whilst di- $\beta$ -aminoethyl disulphide affords  $\beta$ -thioethylamine.

H. WREN.

Behaviour of cystine with silver salts. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1930, 86, 129—143).—Treatment of a solution of cystine in dilute sulphuric acid with silver sulphate, followed by neutralisation to  $pH$  5—6, causes precipitation of 70—85% of the total nitrogen in the form of a compound,  $(\text{C}_3\text{H}_5\text{O}_2\text{NSAg})_2\cdot\text{Ag}_2\text{SO}_4$ . Decomposition of this compound with hydrochloric acid yields a solution containing more than 90% of its nitrogen in the form of cysteine. The reduction of the greater part of the cystine to cysteine is accompanied by oxidation of a small fraction, as indicated by the

presence of ammonia and of cysteic acid in the mother-liquor from the precipitation. The silver compound fails to give characteristic reactions for cysteine until after decomposition with hydrochloric acid; it is therefore regarded as a silver mercaptide, thus differing from the apparently normal silver salt of cystine described by Neuberg and Mayer (A., 1905, i, 567). The latter compound also has a tendency to change spontaneously into a mercaptide.

C. R. HARRINGTON.

**Determination of arginine.** C. J. WEBER (J. Biol. Chem., 1930, 86, 217—222).—The red colour produced by arginine with  $\alpha$ -naphthol and sodium hypochlorite observed by Sakaguchi (J. Biochem., Japan, 1925, 5, 25) has been made the basis of a colorimetric method for the determination of arginine, which is caused to react with  $\alpha$ -naphthol and sodium hypobromite, excess of the latter being destroyed by addition of carbamide.

C. R. HARRINGTON.

**Jaffé's reaction for creatinine.** V. Compound of picric acid with two mols. of creatinine. Its combinations with acid and alkali. I. GREENWALD (J. Biol. Chem., 1930, 86, 333—343).—A solution of creatinine picrate in sodium hydroxide in presence of excess of creatinine yields, with slight excess of hydrochloric acid, a compound,

$(C_4H_7ON_3)_2, C_6H_3O_7N_3, H_2O$ ; with excess of acetic acid and alcohol a compound,

$(C_4H_7ON_3)_2, C_6H_3O_7N_3, (NaOH)_{2.5}, 2H_2O$ , and with excess of hydrobromic acid a compound,

$(C_4H_7ON_3)_2, C_6H_3O_7N_3, HBr, 5H_2O$ . None of these three compounds gives the Jaffé reaction until after decomposition with acetic acid or sodium acetate.

The formula proposed by Anslow and King (A., 1929, 938) for the red compound responsible for the Jaffé reaction is criticised on the ground that it fails to explain why dihydroxymethylcreatinine does not give the reaction, or why the compound of 2 mols. of creatinine with 1 mol. of picric acid reacts only after decomposition with acetic acid.

C. R. HARRINGTON.

**Photochemical preparation of optically active materials [azidopropiondimethylamide].** W. KUHN and E. KNORR.—See this vol., 717.

**Interpretation of the dehydration of acetylglutamic acid by means of glutamylthiohydantoin derivatives.** B. H. NICOLET (J. Amer. Chem. Soc., 1930, 52, 1192—1195).—*Acetylglutamic acid*, m. p. 193—194°, is readily obtained by shaking sodium glutamate solution with acetic anhydride. It is converted by boiling with acetic anhydride into acetylglutamic anhydride, an oil. The proof that the product has the structure assigned to it and is not a lactimide (cf. the work of Bergmann, Stern, and White, A., 1926, 1236, on aspartic acid) is furnished by converting it into *acetylglutamanilide* (not isolated) by treatment with aniline, which is then heated with ammonium thiocyanate and acetic anhydride and yields 1-acetyl-2-thiohydantoin-5- $\beta$ -propionanilide, m. p. 197°, hydrolysed to 2-thiohydantoin-5- $\beta$ -propionanilide, m. p. 216° (decomp.; darkens 200°). Similarly, treatment of acetylglutamic anhydride with ammonia and condensation of the product with ammonium thiocyanate yields 1-acetyl-2-thiohydantoin-5- $\beta$ -propionamide (Thierfelder, A., 1922, i, 326),

hydrolysed ultimately to glutamylthiohydantoin (Johnson and Guest, A., 1912, i, 316). R. K. CALLOW.

**Direct synthetic urea process.** H. J. KRASE, V. L. GADDY, and K. G. CLARK.—See B., 1930, 408.

**Formation of carbamides from the azides of mono- and di-alkylacetic acids.** T. CURTIUS. I. Hydrazide and azide of  $\delta$ -methylhexoic acid [with W. SIEBER]. II. Hydrazide and azide of  $\gamma$ -methyl- $\alpha$ -ethylvaleric acid [with (FRL.) F. NADENHEIM]. III. Hydrazides and azides of isobutyric and isohexoic acids [with O. HAMBSCH]. IV. Hydrazide and azide of  $\delta$ -methyl- $\alpha$ -isobutylhexoic acid [with W. RITTER] (J. pr. Chem., 1930, [ii], 125, 152—210).—I. Ethyl  $\delta$ -methylhexoate and alcoholic hydrazine yield  *$\delta$ -methylhexoylhydrazine*, m. p. 37—40° [hydrochloride, m. p. 174° (decomp.) after sintering at about 115°; benzylidene derivative, m. p. 93°], oxidised by iodine in alcoholic solution to *s-di- $\delta$ -methylhexoylhydrazine*, m. p. 123°.  *$\delta$ -Methylhexoylazide* reacts with aniline, water, and alcohol forming a compound, m. p. 195° (decomp.) after darkening at 185—190°,  $\delta$ -methylhexoamide, and *ethyl isohexylcarbamate*, b. p. 122°/13 mm., respectively. When the last-named compound is distilled with calcium oxide only a small amount of isohexylamine is obtained; fission with 37% hydrochloric acid at 110—120° gives a quantitative yield of isohexylamine (*chloroplatinate*, blackens without melting above 200°; *mercurichloride*, m. p. 185—187°; *picrate*, m. p. 123—125°). Decomposition of the azide in boiling chloroform affords *isohexylcarbimide*, b. p. 50°/vac.(?), which with isohexylamine yields *disohexylcarbamide*, m. p. 44°. The carbimide reacts with ethyl aminoacetate forming *ethyl isohexylureidoacetate*, m. p. 48—50° (free acid, m. p. 121—123°), convertible into *isohexylureidoacetylhydrazine*, m. p. 115—116° (benzylidene derivative, m. p. 211°).

II. The ethyl ester of  $\gamma$ -methyl- $\alpha$ -ethylvaleric acid (*silver salt*) is prepared by way of *ethylisobutylmalonic acid*, m. p. 97—98° (ethyl ester, b. p. 121—124°/13 mm.), and converted by treatment with anhydrous hydrazine in alcohol at 125° into  *$\gamma$ -methyl- $\alpha$ -ethylvalerhydrazide*, m. p. 74° (hydrochloride, m. p. 105° after sintering at 90°; *picrate*, m. p. 79°; *benzylidene derivative*, m. p. 76° or 88°; *salicylidene derivative*, m. p. 117°; *acetyl derivative*, m. p. 124°; *benzoyl derivative*, m. p. 141°). *s-Di- $\gamma$ -methyl- $\alpha$ -ethylvalerylhydrazine* has m. p. 204° after previous sintering.  *$\gamma$ -Methyl- $\alpha$ -ethylvalerylazide* reacts with water, yielding a mixture of  *$\gamma$ -methyl- $\alpha$ -ethylvaleramide*, m. p. 88°, and two *di- $\alpha$ -ethylisoamylcarbamides*, m. p. 215° and 223°.  *$\alpha$ -Ethylisoamylcarbamide*, b. p. 165°/750 mm., affords by the usual methods *phenyl- $\alpha$ -ethylisoamylcarbamide*, m. p. 100°, and *ethyl  $\alpha$ -ethylisoamylcarbamate*, b. p. 128°/28 mm. The last-named compound is hydrolysed by 37% hydrochloric acid at 110° to  *$\alpha$ -ethylisoamylamine*, b. p. 130—134°/749 mm.,  $d^{20}_4$  0.7278,  $n^{20}_D$  1.4160 (hydrochloride, m. p. 185° with darkening after sintering at 177°; *chloroplatinate*, sinters at 180° and darkens above 200° without melting; *picrate*, m. p. 123°).

III. *isoButylhydrazide* (modified method of preparation given) (hydrochloride, m. p. 122°; *picrate*,

m. p. 114°; *salicylidene* derivative, m. p. 170°; acetophenone condensation product, m. p. 154°; *acetyl* derivative, m. p. 156°; *benzoyl* derivative, m. p. 178°) is converted by the usual method into *isobutyrylazide*, and thence, by decomposition in boiling ethereal solution, into *isopropylcarbimide*, b. p. 72°/756 mm. (lit. 67°). Decomposition of the azide with water gives *s*-diisopropylcarbamide and a small amount of *isobutyramide*. The carbimide reacts with hydrazine in ethereal solution, forming *diisopropylhydrazodicarboxylamide*, m. p. 212°, and with ethyl aminoacetate, yielding *ethyl isopropylureidoacetate*, m. p. 100°. The last-named compound is converted by the usual methods into *isopropylureidoacetylhydrazine*, m. p. 179° [*hydrochloride*; *benzylidene* derivative, m. p. 225° (decomp.)], and *isopropylureidoacetylazide*, m. p. about 100°.

*isoHexoylhydrazine*, m. p. 35–38° (*hydrochloride*, sinters at 90°, decomp. at higher temperatures; *picrate*, m. p. 117°; *benzylidene* derivative, m. p. 89°; *salicylidene* derivative, m. p. 153°; acetophenone condensation product, m. p. 89°; *acetyl* derivative, m. p. 87°; *benzoyl* derivative, m. p. 121°), is oxidised by alcoholic iodine to *s*-diisohexoylhydrazine, m. p. 138–139°. *isoHexoylazide* is decomposed by water to isohexoamide and a small amount of *diisoamylcarbamide*, m. p. 46° [formed also from *isoamylcarbimide*, b. p. 132° (lit. 134–135°), and water or *isoamylamine*]. During the preparation of *isoamylcarbamide* from the azide a small amount of *isoamylcarbamide*, m. p. 94° (lit. 89–91°), is produced. *Phenylisoamylcarbamide* has m. p. 116°. Treatment of the reaction product from *isoamylcarbamide* and ethyl aminoacetate with anhydrous hydrazine gives *isoamylureidoacetylhydrazine*, m. p. 114–116° (*benzylidene* derivative, m. p. 192°), convertible into *isoamylureidoacetylazide*.

IV. Ethyl  $\delta$ -methyl- $\alpha$ -isobutylhexoate (improved method of preparation by way of *isobutylisoamylmalonic acid* given) reacts with anhydrous hydrazine in alcohol at 125–130°, forming  $\delta$ -methyl- $\alpha$ -isobutylhexoylhydrazine, m. p. 35–40° (*hydrochloride*, m. p. 164° after previous sintering; *picrate*, m. p. 101–102°; *benzylidene* derivative, m. p. 112°; acetophenone condensation product, m. p. 100°; *acetyl* derivative, m. p. 120°; *benzoyl* derivative, m. p. 124°), oxidised by alcoholic iodine to *s*-di- $\delta$ -methyl- $\alpha$ -isobutylhexoylhydrazine, m. p. 225–227° with darkening after sintering at about 200°.  $\delta$ -Methyl- $\alpha$ -isobutylhexoylazide decomposes in boiling ethereal solution, yielding  $\alpha$ -isobutylisohexylcarbimide, b. p. 210–220°, from which are prepared *s*-di- $\alpha$ -isobutylisohexylcarbamide, m. p. 228–230°,  $\alpha$ -isobutylisohexylcarbamide, m. p. 103°, *phenyl- $\alpha$ -isobutylisohexylcarbamide*, m. p. 190°, and *ethyl  $\alpha$ -isobutylisohexylcarbamate*, b. p. 160–170°/18 mm. Hydrolysis of the first of these carbamides with hydrochloric acid at 170° gives  $\delta$ -amino- $\beta$ - $\gamma$ -dimethyloctane, b. p. 186–190°/744 mm.,  $n_D^{20}$  1.42323 (*hydrochloride*, m. p. 173–174°; *picrate*, m. p. 115–116°), which is probably the aminodimethyloctane described by Kononov (A., 1896, i, 673).

H. BURTON.

Action of carbamazide on ethyl fumarate. T. CURTIUS and W. DÖRR (J. pr. Chem., 1930, [ii], 125,

425–443).—When carbamazide is heated with ethyl fumarate (or maleate) at 100° (bath)/80–100 mm. nitrogen is evolved and a 40% yield (10–15% with the maleate) of *ethyl  $\alpha\alpha'$ -carbamidosuccinate* (I),  $\text{NH}_2\cdot\text{CO}\cdot\text{N}<\begin{smallmatrix} \text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CH}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ , m. p. 154°, is obtained. Di-

gestion of the oily residue from this, after removal of unchanged ester, with warm, dilute hydrochloric acid gives a small amount of *ethyl carbonyl- $\alpha\alpha'$ -diaminosuccinate* (II),  $\text{CO}<\begin{smallmatrix} \text{NH}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{NH}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$ , m. p. 93°, also formed by similar treatment of I. More prolonged treatment of I affords diaminosuccinic acid, and hydrolysis with rather more than 1.5 mols. of alcoholic potassium hydroxide furnishes the *potassium salt*, m. p. 180° (not sharp), of *ethyl hydrogen  $\alpha\alpha'$ -iminosuccinate* (III),  $\text{NH}<\begin{smallmatrix} \text{CH}\cdot\text{CO}_2\text{Et} \\ \text{CH}\cdot\text{CO}_2\text{H} \end{smallmatrix}$ , m. p. 73°

(cf. Lehrfeld, A., 1882, 163; Hell and Poliakov, A., 1892, 819). When III is kept in a desiccator it loses water yielding an *anhydride*, m. p. 93°, which on treatment with acidulated water regenerates III. Treatment of III or its anhydride with boiling alcoholic hydrazine affords the *hydrazine salt* of *iminosuccinhydrazidic acid*, chars when heated (*benzylidene* derivative), converted by nitrous acid into *iminosuccinazidic acid*, explodes when heated. When I is treated with alcoholic hydrazine hydrate a mixture of  *$\alpha\alpha'$ -carbamidosuccinhydrazide*, decomp. 350° (*dibenzylidene* derivative, m. p. about 330° with charring), and *carbonyl- $\alpha\alpha'$ -diaminosuccinhydrazide*, chars above 350° (*benzylidene* derivative, m. p. 310°) (obtained also from II), is obtained. The first-named hydrazide is converted by nitrous acid below –10° into  *$\alpha\alpha'$ -carbamidosuccinazide*, which reacts with aniline in ethereal solution forming  *$\alpha\alpha'$ -carbamidosuccinanilide*, chars above 360°.

H. BURTON.

Action of carbamazide on ethyl acetoacetate, ethylacetoacetate, acetonedicarboxylate, and azodicarboxylate. T. CURTIUS and W. SIEBER (J. pr. Chem., 1930, [ii], 125, 444–457).—When carbamazide is heated with ethyl acetoacetate at 100° (bath) for 50 hrs., nitrogen, carbon dioxide, azoimide, and ethyl allophanate are formed. A small amount of a substance, m. p. 68°, is obtained by distillation of the residue with steam. The reaction of ethyl allophanate is explained by the reactions: (i)  $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{NH}_2\cdot\text{CO}_2\text{Et}$ ; (ii)  $\text{NH}_2\cdot\text{CO}\cdot\text{N}_3 \rightarrow \text{N}_2\text{H} + \text{HNCO}$ ; (iii)  $\text{NH}_2\cdot\text{CO}_2\text{Et} + \text{HNCO} \rightarrow \text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ . With ethyl ethylacetoacetate and acetonedicarboxylate, nitrogen, carbon dioxide, azoimide, and a small amount of cyanuric acid are formed. A substance (or mixture),  $\text{C}_6\text{H}_{11}\text{O}_4\text{N}_3$ , m. p. 173°, is obtained from ethyl diazocarboxylate and carbamazide. Repeated crystallisation of this from alcohol gives ethyl allophanate (methyl allophanate is isolated when methyl diazocarboxylate is used), and treatment with silver nitrate affords a *silver salt*, probably  $\text{NAg}\cdot\text{C}\cdot\text{N}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ . Hydrolysis of the substance with cold hydrochloric acid furnishes cyanuric acid and ethyl allophanate.

H. BURTON.

Hydrazides and azides of phenyl- and ethylsuccinic acids. T. CURTIUS. See this vol., 766.



**Action of hydrazine on ethyl  $\gamma$ -butyrolactone- $\alpha$ -carboxylate.** T. CURTIUS and H. SAUERBERG (J. pr. Chem., 1930, [ii], 125, 139—151).—Ethyl  $\gamma$ -butyrolactone- $\alpha$ -carboxylate reacts with hydrazine hydrate, yielding ethyl  $\gamma$ -hydroxybutyrylhydrazine- $\alpha$ -carboxylate, m. p. 82°, and  $\beta$ -hydroxyethylmalondihydrazide, m. p. 144° (decomp.) [dihydrochloride, m. p. 153—154°; dibenzylidene derivative, m. p. 198° (decomp.); diacetophenone condensation product, m. p. 191° (decomp.)], according to the amount of hydrazine used. When these hydrazides are treated with nitrous acid the former regenerates the original lactonic ester, whilst the latter furnishes  $\gamma$ -butyrolactone- $\alpha$ -carboxazide. Treatment of this with aniline in ethereal solution gives  $\gamma$ -butyrolactone- $\alpha$ -carboxyanilide, m. p. 137°, but with *p*-toluidine  $\beta$ -hydroxyethylmalondi-*p*-toluidide, m. p. 248°, results. This is hydrolysed by warm ethereal hydrochloric acid to  $\gamma$ -butyrolactone- $\alpha$ -carboxy-*p*-toluidide, m. p. 127°. When a solution of the above azide in chloroform is heated, nitrogen is evolved, and a red product,  $C_{12}H_{16}O_9N_6$ , is formed. Treatment of this with water (or hydrochloric acid) gives carbon dioxide (cf. A., 1922, i, 721), ammonia, and indefinite substances. Treatment of an ethereal solution of the azide with alcohol affords a compound, m. p. 147°, which evolves carbon dioxide when heated with dilute sulphuric acid, and ammonia with dilute sodium hydroxide solution. H. BURTON.

**Formation of hydrazihydrazides and hydraziazides from unsymmetrical aliphatic tricarboxylic acids.** T. CURTIUS and W. SANDHAAS (J. pr. Chem., 1930, [ii], 125, 90—105).—Ethyl sodiobenzylmalonate and ethyl chloroacetate afford 73% of ethyl  $\alpha$ -phenylpropane- $\beta\beta\gamma$ -tricarboxylate, b. p. 195—201°/11 mm., which reacts slowly with anhydrous hydrazine at the ordinary temperature, forming the diammonium salt (+EtOH), m. p. 138—139°, m. p. (alcohol free) 144—145° (decomp.), of the amphoteric  $\alpha$ -phenylpropane- $\beta\beta\gamma$ -tricarboxyhydrazihydrazide,

$$\begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2,$$
 dimorphous, m. p. 148° and 172° (hydrochloride, m. p. 210°; benzylidene derivative, m. p. 215°; isopropylidene derivative, m. p. 141.5°). The hydrazihydrazide is converted by nitrous acid into  $\alpha$ -phenylpropane- $\beta\beta\gamma$ -tricarboxyhydraziazide, m. p. 202—203° (decomp.) after sintering at 190—195°, decomposed by heating with benzene to

the carbimide 
$$\begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{NCO},$$
 m. p. 203—204° (corresponding urethane, m. p. 232°, and phenylcarbamide derivative, m. p. 221°, obtained by the action of alcohol and aniline, respectively, on the carbimide or the hydraziazide). Hydrolysis of the hydraziazide with concentrated potassium hydroxide solution affords the hydrazicarboxylic acid,

$$\begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CO}_2\text{H},$$
 m. p. 200°, also formed together with the impure carbamide, 
$$\begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{NH} \quad \text{CO},$$
 when the azide is decomposed with water. When ethyl  $\alpha$ -phenylpropane- $\beta\beta\gamma$ -tricarboxylate is heated with hydrazine hydrate and alcohol, benzylsuccinyldihydrazide, m. p.

146° (dibenzylidene derivative, m. p. 186°; diisopropylidene derivative, m. p. 172°), is produced. This is converted by the usual method into benzylsuccinyldiazide. H. BURTON.

**Preparation of semicarbazide.** L. F. AUDRIETH (J. Amer. Chem. Soc., 1930, 52, 1250—1251).—Free semicarbazide may be prepared rapidly and conveniently by addition of the sulphate to liquid ammonia. The solution is decanted from the precipitated ammonium sulphate and evaporated. The action of barium hydroxide on the sulphate yields a solution which may be evaporated below 60°, but the yield is not so good. Preparation of guanidine and aminoguanidine by the action of ammonia on the sulphates is not successful, but methylhydrazine may be obtained in this way. R. K. CALLOW.

**[Preparation of] malononitrile.** B. B. CORSON, R. W. SCOTT, and C. E. VOSE (Organic Syntheses, 1930, 10, 66—69).

**Thermal decomposition of sodium and potassium methyls.** W. H. CAROTHERS and D. D. COFFMAN (J. Amer. Chem. Soc., 1930, 52, 1254—1259).—Sodium and potassium methyls are prepared analogously to sodium ethyl (A., 1929, 433). Thermal decomposition proceeds ultimately according to the equation  $8\text{MCH}_3 = 6\text{CH}_4 + \text{M}_2\text{C}_2 + 6\text{M}$ , since methane is evolved and the action of water on the residue yields chiefly acetylene and hydrogen. The decompositions are, however, gradual. The decomposition of sodium methyl becomes rapid at 200° and may be completed at a slightly higher temperature. The decomposition of potassium methyl first becomes rapid at 100°, but is not completed below 250°. In this behaviour evidence is found for the reactions  $\text{KCH}_3 \rightarrow \text{K}_2\text{CH}_2$  or  $\text{K}_3\text{CH} \rightarrow \text{K}_4\text{C}$ , followed by  $2\text{K}_4\text{C} \rightarrow \text{K}_2\text{C}_2 + 6\text{K}$ , the mechanism of which is discussed in terms of electronic reactions. R. K. CALLOW.

**Relative firmness of element-organic union.** E. KRAUSE (Ber., 1930, 63, [B], 999—1000).—In connexion with the work of Ipatiev (this vol., 463) it is pointed out that distinction must be drawn between (1) the absolute firmness of the element-organic union as such which can be judged solely on physico-chemical data for which sufficient material is not available and (2) the behaviour of the linking towards chemical reagents of differing type. In the latter case the affinity of the reagent towards both metal and alkyl group is involved. H. WREN.

**Thermal decomposition of metal alkyls in hydrogen-ethylene mixtures.** H. S. TAYLOR and W. H. JONES (J. Amer. Chem. Soc., 1930, 52, 1111—1121).—The decomposition of mercury diethyl and of lead tetraethyl in hydrogen-ethylene mixtures at 250—300° has been investigated. The decomposition of mercury dimethyl is slow, and only preliminary experiments are described. When mercury diethyl decomposes alone the reaction is complicated, resulting in a mixture of gaseous, mostly saturated, hydrocarbons, and liquid polymerides of ethylene. When ethylene is present, it is induced to polymerise. The presence of hydrogen causes hydrogenation only to a small extent. Increase of pressure causes a roughly proportional increase in the amount of poly-

merisation. The amount of polymerisation is increased also by increased concentration of the metal alkyl in each case. Experiments are described with static and with dynamic methods, and in the latter it is found that no appreciable surface effect exists. It is suggested that the initial reaction is between ethyl and ethylene:  $C_2H_5 + 2C_2H_4 = C_4H_9 + C_2H_4$ , followed by  $C_4H_9 + 2C_2H_4 = C_6H_{13} + C_2H_4$ , with the final elimination of the radicals by interaction or surface reaction. The end-products are comparable with those from excited mercury, hydrogen, and ethylene (this vol., 46; cf. also Lind, A., 1926, 769, 1077).

R. K. CALLOW.

**Preparation of cyclopropane.** W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1930, 19, 341—344).—A modification of Gustavson's method (A., 1899, i, 421) for the preparation of cyclopropane in substantial quantities is described. Fuming sulphuric acid absorbs 99.5—100% of the gas, which has no action on acidified potassium bromate solution. A yield of at least 80% is obtained. *cycloPropane* is not suitable for use as a general anæsthetic because of its low margin of safety.

E. H. SHARPLES.

**Principles underlying aromatic side-chain reactivity from the viewpoint of the electronic theory of valency.** C. K. INGOLD and C. S. PATEL (J. Indian Chem. Soc., 1930, 7, 95—110).—On the basis of Ingold and Rothstein's classification of aromatic side-chain reactions (A., 1928, 747) into two main categories: (A) those which require an influx of electrons from the nucleus to the side-chain and (B) those requiring a recession of electrons from the side-chain towards the nucleus, two classifications of nuclear substituents are given [(A), in which a +I effect involves  $op > m$  activation, -I  $op > m$  deactivation and +T  $op$ -activation (-T inoperative), and (B), in which +I involves  $op > m$  deactivation, -I  $op > m$  activation, and -T  $op$ -activation (+T inoperative)] permitting the deduction of the effect of the substituents on side-chain reactions of either type. The relation of this theory of side-chain reactivity to that of nuclear reactivity (Ingold, A., 1929, 1289) on the one hand, and that of free radical chemistry (Burton and Ingold, A., 1929, 1052) on the other, is discussed. The velocity of acid hydrolysis (type A reaction) and reduction (type B reaction) of a series of phenyl-substituted benzyl bromides has been determined. The mean values of the bimolecular velocity coefficient ( $k \times 10^6$ ;  $t$  in min.) for the hydrolysis of benzyl bromide, 3- and 4-bromomethyldiphenyl, 2- and 1-bromomethylnaphthalene with 90% alcohol at 24°, determined by titration of the liberated hydrobromic acid during the first 20—45% of the reaction, are, respectively, 78, 146, 165, 184, and 220, whilst the corresponding percentage reduction which occurs in 2 hrs. with hydriodic acid of constant b. p. at 100° is, respectively, 32, 43, 67, 99, and 99%. Thus in each type of reaction the velocity decreases in the order  $\alpha$ -naphthyl >  $\beta$ -naphthyl >  $p$ -diphenyl >  $m$ -diphenyl > phenyl. This order is identical with that established by Schlenk and by Gomberg (A., 1910, i, 236; 1917, i, 537) for the ability of these groups to promote dissociation of the hexarylethanes into free radicals. In the cases studied,

the inductive effect of the phenyl group is negligible and the observed order is in complete agreement with the authors' view that the duplex electrical readjustments ( $\pm T$  effects) of which the phenyl group is capable are the essential factor governing both the stability of free radicals and the enhancement of side-chain reactivity of both types A and B. The following are described in the course of the investigation: 3-bromomethyldiphenyl, b. p. 150°/15 mm. (not pure), converted into *m*-phenylbenzyltrimethylammonium picrate, m. p. 152°; 4-bromomethyldiphenyl, b. p. 130—140°/10 mm., m. p. 82° (*p*-phenylbenzyltrimethylammonium picrate, m. p. 179°), obtained together with a dibromo-4-methyldiphenyl, m. p. 129°, by bromination of 4-methyldiphenyl at 200°.

J. W. BAKER.

**[Preparation of] *n*-amylbenzene.** H. GILMAN and J. ROBINSON (Organic Syntheses, 1930, 10, 4—5).

**[Preparation of] 1:2:4:5-tetramethylbenzene (durene).** L. I. SMITH (Organic Syntheses, 1930, 10, 32—39).

Possible relation between the affinity of aryl radicals and the decomposition of aryl iodide dichlorides. I. Zappi and Deulofeu's work on the decomposition of phenyl iodide dichloride. L. C. GUGLIAMELLI, C. L. RUIZ, P. CHANUSSOT, and E. HERMITTE (Anal. Asoc. Quim. Argentina, 1929, 17, 291—307).—In connexion with the investigation of the instability of 2-iodofluorene dichloride (Chanussot, this vol., 202), the authors attack the theory advanced by Zappi and Deulofeu (*ibid.*, 79, 201) of the decomposition of phenyl iodide dichloride.

When heated in a sealed tube phenyl iodide dichloride yields a mixture of *o*- and *p*-chloriodobenzene with evolution of hydrogen chloride; all the liberated chlorine is consumed (cf. Caldwell and Werner, J.C.S., 1907, 91, 240, 528). Also, the whole of the chlorine of phenyl iodide dichloride reacts with magnesium methyl iodide in the Zerevitinov reaction. The interaction of phenyl iodide dichloride with allyl alcohol is a complex reaction in which the formation of acetaldehyde can be demonstrated, and the hydrogen chloride liberated (the determination of which is the only evidence on which the theory of Zappi and Deulofeu is based) is the result of this oxidation; moreover, only iodobenzene, and no chloriodobenzene, can be recognised in the product. Amylene, however, acts as a simple halogen acceptor, and no hydrogen chloride is formed.

In iodide dichlorides the equivalence of the two chlorine atoms, which are probably united to iodine by singlet linkings, is thus supported, and the suggestion of Zappi and Deulofeu that one is united by a covalency and one by an electrovalency is disproved.

R. K. CALLOW.

**Decomposition of phenyl iodide dichloride.** II. Action of allyl alcohol on phenyl iodide dichloride. E. V. ZAPPI and V. DEULOFEU (Anal. Asoc. Quim. Argentina, 1929, 17, 308—317).—Further examination of the interaction of allyl alcohol and phenyl iodide dichloride (this vol., 79, 201) shows that the reaction is not as formulated there, since (a) the disappearance of the ethylenic linking, as determined by titration with bromine, is more complete than the

theory requires, (b) only minimal amounts of dihalogenated benzene can be isolated, and (c) the formation of considerable amounts of acraldehyde is shown by Powick's reaction (A., 1923, ii, 191), and complex oxidation products of allyl alcohol are formed. It is concluded that the predominant reaction is  $\text{PhICl}_2 = \text{PhI} + \text{Cl}_2$ . R. K. CALLOW.

**Comparative reactivities of some chloro- and bromo-nitrobenzenes.** M. M. SPRUNG (J. Amer. Chem. Soc., 1930, 52, 1650—1654).—The (bimolecular) velocity coefficients for the reaction between the three chloronitrobenzenes and sodium sulphite in 50% aqueous alcohol at 30° are of the same degree of magnitude; the relative reactivities are in the order  $m > o > p$ . For the bromonitrobenzenes at 40°, the order is  $p > m > o$ . 1-Chloro- and 1-bromo-2:4-dinitrobenzenes are about 2000 times as reactive as the mononitro-derivatives, and picryl chloride is about 25 times as reactive as the dinitro-compounds.

H. BURTON.

[1:3:4:5-Tetranitrobenzene.] W. BORSCHÉ (Ber., 1930, 63, [B], 1007).—1:3:4:5-Tetranitrobenzene (cf. Holleman, this vol., 331) has been described previously by the author as 1:2:3:5-tetranitrobenzene (cf. A., 1923, i, 1091). H. WREN.

**Preparation of organic reagents in analytical laboratories. II. Cupferron.** K. H. SLOTTA and K. R. JACOBI (Z. anal. Chem., 1930, 80, 97—103).—Ammonia is passed into an ice-cold solution of 25 g. of nitrobenzene in 125 c.c. of 96% alcohol and 25 c.c. of water to complete saturation. The solution is then treated with a rapid stream of hydrogen sulphide while immersed in a freezing mixture until, after 2½—3 hrs., a pale yellow, pasty mass is obtained; 500 c.c. of ether are added, the solution is shaken vigorously and filtered, and the ethereal layer separated from the aqueous polysulphide layer and saturated with ammonia. After allowing the aqueous layer to settle the ethereal solution is withdrawn, cooled in ice, and treated with ethyl nitrite from 25 g. of sodium nitrite, 40 c.c. of water, 33 c.c. of 96% alcohol, and 90 c.c. of hydrochloric acid (1:1). The solution becomes dark red at first, but the colour slowly disappears and crystals of cupferron separate; they are collected, washed with ether, and dried over calcium chloride and ammonium carbonate. The yield is 80% of the theoretical.

A. R. POWELL.

**Comparative reactivities of some substituted benzyl halides.** M. M. SPRUNG (J. Amer. Chem. Soc., 1930, 52, 1640—1649).—The reaction between benzyl and substituted benzyl chlorides or bromides and sodium sulphite in 50% aqueous-alcoholic solution at 30—40° is bimolecular. In the case of benzyl chloride the velocity coefficient increases with diminishing initial concentration of the reactants, and decreases with added sodium hydrogen sulphite. Reaction is considered to occur between the halide and sulphite ion. Introduction of a nuclear chlorine or bromine atom into the molecule causes a diminution in the coefficient, except for *p*-bromobenzyl chloride (in this case there is an increase). Introduction of a nitro-group causes an increase in the coefficient. The order of reactivity of isomerides for all the cases studied is  $p > o > m$ .

H. BURTON.

**Action of sodamide on [ $\beta$ -phenyl- $\beta$ -alkylethyl] bromides.** (MILLÉ.) AMAGAT (Compt. rend., 1930, 190, 1055—1057).—When  $\beta$ -phenyl- $\beta$ -alkylethyl bromides are treated with sodamide in boiling xylene elimination of hydrogen bromide occurs, and the hydrocarbons formed are mainly the *s*-derivatives  $\text{CHPh:CHR}$  (cf. Ramart-Lucas and Amagat, A., 1927, 241); a small amount of the isomeride  $\text{CRPh:CH}_2$  is also produced. The following bromides are prepared from the appropriate alcohol and hydrobromic acid (*d* 1.47) by heating the mixture on the water-bath:  $\beta$ -phenylpropyl bromide, b. p. 115°/21 mm.;  $\beta$ -phenylbutyl bromide, b. p. 130—132°/28 mm.;  $\beta$ -phenylisobutyl bromide, b. p. 123—124°/13 mm., and  $\beta$ -phenyl- $\beta$ -ethylbutyl bromide, b. p. 128—130°/12 mm. Preparation of the above bromides by Norris' method (A., 1907, i, 1034) results in the formation of appreciable amounts of unsaturated hydrocarbons; similar results are noticed during the preparation of the corresponding chlorides by means of thionyl chloride and pyridine at low temperatures.

H. BURTON.

**Additive compounds of copper halides and silver nitrate with benzyl sulphide.** E. H. HUFFMAN [with G. MCP. SMITH] (J. Amer. Chem. Soc., 1930, 52, 1353—1356).—Cupric and cuprous halides give compounds  $\text{CuX}_2(\text{C}_7\text{H}_7)_2\text{S}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ) when boiled with benzyl sulphide in acetone. The compounds are insoluble in water and dissociate in acetone, but all of the copper is not precipitated by hydrogen sulphide. Silver and cadmium halides did not give similar compounds, but the substance  $\text{AgNO}_3, 2(\text{C}_7\text{H}_7)_2\text{S}$ , m. p. 105.5°, was prepared.

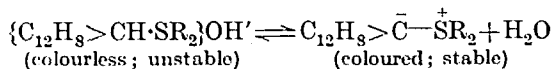
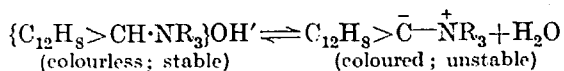
J. G. A. GRIFFITHS.

**Influence of poles and polar linkings on course pursued by elimination reactions. VIII. Methylenic and paraffinic degradations of sulphones. IX. Isolation of a substance believed to contain a semipolar double linking with participating carbon.** C. K. INGOLD and J. A. JESSOP (J.C.S., 1930, 708—713, 713—718).—VIII. When olefinic degradation of sulphones is inhibited, both methylenic decomposition (otherwise characteristic of ammonium hydroxides) and paraffinic degradation (otherwise characteristic of phosphonium hydroxides) occur side by side provided both are structurally possible. Thus sulphone sulphur shows simultaneously the tendency of phosphonium phosphorus to enlarge its valency group and the ability of ammonium nitrogen to deplete the valency group of an adjoining carbon atom. The experimental data relate to the decomposition by potassium hydroxide of sulphones containing methyl, phenyl, *p*-tolyl, benzyl, 9-fluorenyl, and 9-phenyl-9-fluorenyl groups. The order of facility of methylenic extrusion is 9-fluorenyl > benzyl > methyl, which is the order of anionic stability as the theory of the reaction demands. The same order obtains for paraffinic elimination, consistently with the results of thermal decompositions of phosphonium hydroxides.

The following substances are described incidentally: 9-fluorenyl-*p*-tolylsulphone, m. p. 226—227° (from 9-bromofluorene and alcoholic sodium *p*-toluenesulphinate dihydrate); 9-phenyl-9-fluorenyl-*p*-tolylsulphone, m. p. 211—212°; a hydrocarbon,  $(\text{C}_{19}\text{H}_{12})_4$ ,

decomp. above 300° (from the decomposition of 9-phenyl-9-fluorenyl-*p*-tolylsulphone); and *silver methanesulphinate*.

IX. With a reference to the earlier observations of the colour of fluorenylammonium hydroxide solutions it is concluded that since sulfoxides have a smaller tendency to hydrate than amine oxides therefore in the fluorenylsulphonium series the relative stabilities of the hydroxide and the anhydride should be reversed:



This has been verified; 9-bromofluorene and methyl sulphide condensed at the ordinary temperature in nitromethane solution, yielding *fluorenyl-9-dimethylsulphonium bromide*, m. p. 133° (corresponding *picrate*, m. p. 149—150°), treatment of which in aqueous solution with aqueous ammonia, barium hydroxide, or sodium hydroxide gave *dimethylsulphonium 9-fluorenylidide*, m. p. about 70—75° (decomp.). This compound was sufficiently stable for analysis and mol. wt. determinations in benzene solution. Evolution of methyl sulphide became perceptible after a few hours at the ordinary temperature and more rapid at higher temperatures. It did not form a sulphonium hydroxide by addition of water, but was more basic than a sulfoxide, since it reacted with dilute hydrochloric acid, giving immediately the corresponding fluorenyl-9-dimethylsulphonium salt; the 9-carbon atom thus appears to have conferred on it by its constitutional environment properties analogous to those of a nitrogen atom.

R. W. J. LE FÈVRE.

Decomposition of sulphonazides. T. CURTIUS.

I. *Benzenesulphonazide*. T. CURTIUS and J. RISSOM. II. *p*-Toluenesulphonazide. T. CURTIUS and G. KRAEMER. III. *p*-Chlorobenzenesulphonazide. T. CURTIUS and K. VORBACH. IV. *Benzene-1:3-disulphonazide*. T. CURTIUS and H. MEIER. V. *Naphthalene-1-sulphonazide*. T. CURTIUS, H. BOTTLE, and G. HASSE. VI. *Naphthalene-2-sulphonazide*. T. CURTIUS, H. BOTTLE, and W. RAUDENBUSCH. VII. *Naphthalene-1:5-disulphonazide*. T. CURTIUS and R. TÜXEN. VIII. *Anthraquinone-2-sulphonazide*. T. CURTIUS and H. DERLON (J. pr. Chem., 1930, [ii], 125, 303—311, 311—323, 323—340, 340—357, 358—366, 366—379, 380—401, 401—419, 420—424).—Aromatic sulphonazides are prepared either by treatment of the sulphonhydrazide with nitrous acid or, more conveniently, from the sulphonyl chloride and sodium azide. When a sulphonazide is heated with a large excess of an aromatic hydrocarbon or amine, 1 mol. of nitrogen is evolved and the residue,  $R \cdot SO_2 \cdot N <$ , which is formed, then reacts with the solvent ( $C_6H_5 \cdot R'$ ), yielding (usually) a mixture of the *o*- and *p*- (not *m*-) sulphonylarylamide,  $R \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot R'$ . Formation of the amide  $R \cdot SO_2 \cdot NH_2$  also occurs to some extent. With aniline, the reaction  $R \cdot SO_2 \cdot N_3 + NH_2Ph \rightarrow N_3H + R \cdot SO_2 \cdot NHPh$  also takes place. With methyl- and dimethyl-anilines, *pp'*-dimethyldiamino- and *pp'*-tetra-

methyldiamino-diphenylmethanes are usually formed as by-products. Previous work (A., 1921, i, 747; 1924, i, 998; 1926, 415) is reviewed.

I. When benzenesulphonazide is heated with benzene at 105°, benzenesulphonanilide is obtained. With boiling toluene, a mixture of benzenesulphonamide (I), and benzenesulphon-*o*- and -*p*-toluidides results. Methylaniline gives I, a benzenesulphonamidomethylaniline (*picrate*, m. p. 151—152°), and a small amount of *pp'*-dimethyldiaminodiphenylmethane; dimethylaniline affords I, 2- and 4-benzenesulphonamidodimethylanilines, and *pp'*-tetramethyldiaminodiphenylmethane. Treatment of the last-named compound with nitrous acid yields a mixture of the 2:2'-dinitro-derivative, m. p. 123°, and *p*-nitrodiphenylamine. The azide and diphenylamine at 140° furnish a *benzenesulphonamidodiphenylamine*, m. p. 130°, hydrolysed by hydrochloric acid at 110° to an *aminodiphenylamine hydrochloride*, m. p. 190—195°. With boiling pyridine, a *benzenesulphonamidopyridine*, m. p. 152° (*hydrochloride*, m. p. 202°), is obtained. Hydrolysis of this with hydrochloric acid at 150° gives the *benzenesulphonate*, m. p. 115°, of an aminopyridine (*mercurichloride*, m. p. 194°). When the azide is heated with ethyl malonate at 140—145°, I and a small amount of *ethyl benzenesulphonamidomalonate*, m. p. 69—70°, are formed.

II. *p*-Toluenesulphonhydrazide, m. p. 109—110° [decomp.; silver nitrate additive compound; *hydrochloride*, m. p. 164—165° (decomp.); *benzylidene* derivative, m. p. 127—128° (decomp.); *isopropylidene* derivative, m. p. 158—159° (decomp.)], is prepared from *p*-toluenesulphonyl chloride and aqueous hydrazine hydrate (1:2). *p*-Toluenesulphonazide, m. p. 22°, reacts with benzene and *p*-xylene, forming *p*-toluenesulphon-anilide and -*p*-xylidide, m. p. 120—121°, respectively. *p*-Xylidine *picrate* and *p*-toluenesulphonate have m. p. 171° (decomp.) and 232—233°, respectively. The reactions with aniline, methyl- and dimethyl-anilines are described; mixtures of the expected products are obtained. The *picrate*, m. p. 207°, of 3(or 4)-*p*-toluenesulphonamidopyridine, m. p. 210° (*hydrochloride*, m. p. 206°; *p*-toluenesulphonate, m. p. 180°), on hydrolysis with hydrochloric acid at 120° gives 3(or 4)-aminopyridine *picrate*, m. p. 138—139° (*p*-toluenesulphonate, m. p. 107—108°).

III. The decomposition of *p*-chlorobenzenesulphonazide, m. p. 39°, in presence of toluene, *p*-xylene, naphthalene, aniline, methyl- and dimethyl-anilines, pyridine, and quinoline at the b. p. or 130—140° was studied, and the following compounds were isolated: *p*-chlorobenzenesulphon-*p*-xylidide, m. p. 114°, and -*α*-naphthalide, m. p. 190° (the *β*-naphthalide, m. p. 134°, is also described); 2-*p*-chlorobenzenesulphon-amido-aniline, m. p. 116°, and -methylaniline, m. p. 178°; a *p*-chlorobenzenesulphonamidopyridine *picrate*, m. p. 191°, hydrolysed by hydrochloric acid at 120° to an unidentified *picrate*, m. p. 154°. *p*-Chlorobenzenesulphonhydrazide [*hydrochloride*, m. p. 158—159°; *picrate*, m. p. 83°; *benzylidene* derivative, m. p. 128—129° (decomp.); *isopropylidene* derivative, m. p. 140—143° (decomp.)] has m. p. 113—114°.

[With R. FINGADO.]—*p*-Chlorobenzenesulphonazide and ethyl malonate do not react at 110°/20—25 mm.: with ethyl sodiomalonate the sodium salt of ethyl

5-hydroxy-1-p-chlorobenzenesulphonyl-1:2:3-triazole-4-carboxylate, m. p. 95° (cf. A., 1924, i, 998), is obtained.

IV. Benzene-1:3-disulphonazide, m. p. 82°, and *p*-xylene give benzene-1:3-disulphon-*p*-xylidide, m. p. 156°; with dimethylaniline at 130—135°, a mixture of benzene-1:3-disulphonamide, *pp'*-tetramethyldiaminodiphenylmethane, and an impure compound, m. p. about 210° after previous softening, is formed. Benzene-1:3-disulphonhydrazide [silver nitrate additive compound; dibenzylidene derivative, m. p. 171°; diisopropylidene derivative (+0.5C<sub>3</sub>H<sub>6</sub>O), m. p. 149° (decomp.)] has m. p. 145° (decomp.).

*p*-Acetamidobenzenesulphonazide (A., 1926, 393) and *p*-xylene give a small amount of *p*-acetamidobenzenesulphon-*p*-xylidide, m. p. 230°.

V. Naphthalene-1-sulphonhydrazide, m. p. 123° (decomp.) [hydrochloride, m. p. 142°; benzylidene derivative, m. p. 153° (decomp.); isopropylidene derivative, m. p. 165°], and naphthalene-1-sulphonazide, m. p. 53°, are described. Naphthalene-1-sulphon-*p*-xylidide has m. p. 159°. The azide reacts with ethyl sodiomalonate, yielding the sodium salt, decomp. 178°, of ethyl 5-hydroxy-1-naphthalene-1-sulphonyl-1:2:3-triazole-4-carboxylate [ammonium, m. p. 158° (decomp.); hydrazine, m. p. 135° (decomp.), piperidine, m. p. 167° (decomp.), barium, m. p. 192° (decomp.), and silver salts]. The free ester isomerises rapidly to the corresponding triazolone or ethyl diazomalon-naphthalene-1-sulphonylamate, m. p. 140°, which is hydrolysed by aqueous-alcoholic sodium hydroxide to disodium 5-hydroxy-1-naphthalene-1-sulphonyl-1:2:3-triazole-4-carboxylate, decomp. 197°. Acidification of this salt affords diazomalon-naphthalene-1-sulphonylamic acid, which is decomposed by boiling with water to hydroxyacetnaphthalene-1-sulphonamide, m. p. 210°. Prolonged treatment of the above diazo-ester with concentrated aqueous ammonia gives the ammonium salt, m. p. 179° (decomp.), of 5-hydroxy-1-naphthalene-1-sulphonyl-1:2:3-triazole-4-carboxylamide; this hydroxy-compound rearranges to 5-hydroxy-1:2:3-triazole-4-carboxynaphthalene-1-sulphonamide, m. p. 177° (decomp.). Prolonged treatment of the diazo-ester with alcoholic hydrazine at the ordinary temperature affords the dihydrazine salt, decomp. 185°, of 1-amino-5-hydroxy-1:2:3-triazole-4-carboxynaphthalene-1-sulphonamide, m. p. 168° (decomp.) [benzylidene derivative, m. p. 203° (decomp.)]; with hydrazine hydrate alone at 95°, a mixture of  $\alpha$ -naphthalene-sulphonamide and the hydrazine salt, m. p. 210° (decomp.), of 1-amino-5-hydroxy-1:2:3-triazole-4-carboxylhydrazide, decomp. when heated without melting [dibenzylidene, m. p. 201° (decomp.), disilylidene, m. p. 207° (decomp.), and di-*o*-nitrobenzylidene derivatives, m. p. 211° (decomp.)], is formed.

VI. The reactions between naphthalene-2-sulphonazide and toluene, *p*-xylene, naphthalene, aniline, acetanilide, methyl- and dimethyl-anilines, pyridine, and quinoline are investigated. Di- $\beta$ -naphthyl disulphide is formed during the reaction with dimethylaniline. Naphthalene-2-sulphon-*p*-xylidide, m. p. 118°, and  $\alpha$ -naphthalide, m. p. 179°; 2-naphthalene-2-sulphonamidoaniline, m. p. 182° (hydrochloride, m. p. 224°); naphthalene-2-sulphonamidopyridine, m. p. 198° [hydrochloride, m. p. 193° (decomp.)]; nitrate,

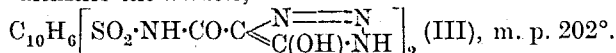
m. p. 156°; picrate, m. p. 192° (decomp.)], and an aminopyridine (picrates, m. p. 218° and 226°) are incidentally described.

Naphthalene-2-sulphonazide and ethyl sodiomalonate afford the sodium salt, m. p. 142° (decomp.), of ethyl 5-hydroxy-1-naphthalene-2-sulphonyl-1:2:3-triazole-4-carboxylate [ammonium, m. p. 153° (decomp.), hydrazine, m. p. 133°, barium, and silver salts], which on acidification yields ethyl diazomalon- $\beta$ -naphthalenesulphonylamate, m. p. 127° (the free acid, decomp. 132—137°, is decomposed by water at 50° to hydroxyacetnaphthalene-2-sulphonamide, m. p. 147°). Prolonged treatment of the diazo-ester with aqueous ammonia affords the ammonium salt, m. p. 178° (decomp.), of 5-hydroxy-1-naphthalene-2-sulphonyl-1:2:3-triazole-4-carboxylamide. This amide is unstable and rearranges into 5-hydroxy-1:2:3-triazole-4-carboxynaphthalene-2-sulphonamide, m. p. 169° (decomp.). Alcoholic hydrazine hydrate converts the diazo-ester into the dihydrazine salt, decomp. 198°, of 1-amino-5-hydroxy-1:2:3-triazole-4-carboxynaphthalene-2-sulphonamide, m. p. 171° (decomp.) [benzylidene derivative, m. p. 200° (decomp.); isopropylidene derivative, m. p. 184° (decomp.)], whilst with hydrazine hydrate alone at 100°, a mixture of naphthalene-2-sulphonamide, m. p. 217°, and the hydrazine salt of 1-amino-5-hydroxy-1:2:3-triazole-4-carboxylhydrazide (cf. V) is formed.

VII. Naphthalene-1:5-disulphonhydrazide, blackens about 240° without melting [dihydrochloride; disulphate; dinitrate; disodium salt (+3H<sub>2</sub>O); dibenzylidene derivative, decomp. 228°; diisopropylidene derivative, m. p. 201—202° (decomp.) after previous sintering], is prepared from the dichloride and alcoholic hydrazine hydrate. Treatment of naphthalene-1:5-disulphonazide, m. p. 177°, with hydrazine hydrate in alcoholic solution gives the dihydrazine salt, m. p. 194°, of naphthalene-1:5-disulphinic acid, m. p. 166—167° (ammonium and ferric salts). The acid is also obtained when the above disodium salt is decomposed with warm water (and subsequent acidification) and by reducing naphthalene-1:5-disulphonyl chloride with zinc dust and water. When the disulphonyl chloride is dissolved in boiling alcohol and the resulting solution cooled rapidly, ethyl hydrogen naphthalene-1:5-disulphonate, m. p. 147° (pyridine salt, m. p. 242°), separates. Attempts to prepare naphthalene-1:5-disulphonmonoazide chloride were unsuccessful. Naphthalene-1:5-disulphon-*p*-xylidide, not melted at 285°, is obtained from the azide and boiling *p*-xylene. The azide reacts with ethyl sodiomalonate in alcohol forming the disodium salt, decomp. 210—211° after previous sintering, of the triazole,

$$\text{C}_{10}\text{H}_6\left[\text{SO}_2\cdot\text{N}<\overset{\text{N}=\text{N}}{\text{C}}(\text{OH})\cdot\text{C}\cdot\text{CO}_2\text{Et}\right]_2$$
 (I) [dipotassium, diammonium, m. p. 181° (decomp.), and dipyridine salts, m. p. 188°], which on acidification affords the isomeric triazolone or diazo-ester,  $\text{C}_{10}\text{H}_6[\text{SO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{N}_2)\cdot\text{CO}_2\text{Et}]_2$ , (II) m. p. 216 (decomp.). Hydrolysis of II with dilute sodium hydroxide solution gives the unstable acid, which is decomposed by water at 70° to the amide,  $(\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{SO}_2)_2\text{C}_{10}\text{H}_6$ , m. p. 247—248° (decomp.). Treatment of II with aqueous ammonia at 90—100° affords a small amount of naphthalene-1:5-

disulphonamide together with the ammonium salt, m. p. 196—197°, of the above hydroxytriazolcarboxylamide (I where  $\text{CO}_2\text{Et}=\text{CO}\cdot\text{NH}_2$ ); acidification of the mother-liquors with dilute hydrochloric acid furnishes the triazole,



VIII. Anthraquinone- $\beta$ -sulphonazide, m. p. 153°, is prepared from the sulphonyl chloride and sodium azide in alcohol. When the chloride is treated with hydrazine hydrate, reduction and hydrazide formation occur simultaneously; the product formed is oxanthranol- $\beta$ -sulphonhydrazide, m. p. 222—223° (isopropylidene derivative, m. p. 165°). The azide and boiling *p*-xylene give a small amount of anthraquinone- $\beta$ -sulphon-*p*-xylidide, m. p. 200°. Acidification of the reaction product from the azide and ethyl sodiomalonate yields ethyl 1-anthraquinone- $\beta$ -sulphonyl-1 : 2 : 3-triazol-5-one-4-carboxylate (or ethyl diazomalon-anthraquinone- $\beta$ -sulphonylmalate), m. p. 183° (decomp.).

H. BURTON.

#### Stereoisomerism of diphenyl compounds.

IV. W. M. STANLEY and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 1200—1205).—Theoretical. The distances between the centres of nuclear carbon atoms of the benzene ring and the centres of the atoms of substituent groups have been calculated from X-ray data. In the case of 2 : 6 : 2' : 6'-substituted diphenyl compounds it is then possible to estimate the interference with free rotation by subtracting the distance between the 2 : 2'-carbon atoms from the sum of the distances of the 2 : 2'-groups from the nuclei. The resultant differences are tabulated for compounds with two different kinds of groups in the 2 : 6 : 2' : 6'-positions. Eight compounds with comparatively large differences have been resolved and are not readily racemised. The probable ease of racemisation of the other tetra-substituted compounds and of 2 : 6 : 2'-tri-substituted compounds is also discussed.

R. K. CALLOW.

Reduction of nitro-derivatives of diphenyl. L. GUGLIALMELLI and M. R. FRANCO (Anal. Asoc. Quim. Argentina, 1929, 17, 340—351).—Pure 4 : 4'-dinitrodiphenyl is conveniently prepared by nitrating diphenyl to 4-nitrodiphenyl and then further nitrating the purified product. The yields of 4-nitro-4'-aminodiphenyl obtainable by modifications of the process of reduction by sulphides have been compared. The most satisfactory method is reduction of 4 : 4'-dinitrodiphenyl suspended in 60 parts of a boiling mixture of acetone and water (1 : 5) with a solution of polysulphide prepared from 3 parts of sodium sulphide and 0.8 part of sulphur. 4-Nitro-4'-aminodiphenyl has m. p. 197—198°. A substance, m. p. 224°, is obtained by incomplete reduction.

R. K. CALLOW.

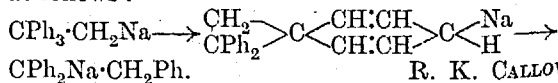
Tervalent carbon. IX. Triarylmethyls containing electro-positive and -negative substituents. K. ZIEGLER and W. MATHES (Annalen, 1930, 479, 111—122).—*p*-Nitrobenzophenone dichloride and benzene react in presence of aluminium chloride forming crude *p*-nitrotriphenylmethyl chloride. This is converted by boiling methyl alcohol into *p*-nitrotriphenylmethyl methyl ether, dimorphous, m. p. 104° and 116° (stable), which, on treatment with acetyl

chloride, gives the pure chloride ( $k=4.5\times 10^{-8}$ , in sulphur dioxide at a dilution of 100 litres per mol.). *pp'*-Dinitrotriphenylmethyl chloride, m. p. 141° ( $k=2-3\times 10^{-9}$ ) (corresponding methyl ether, m. p. 123—124°), is prepared similarly from 4 : 4'-dinitrobenzophenone dichloride, m. p. 143°. *p*-Nitro-*p'*-methoxytriphenylmethyl chloride, m. p. 106—108° (decomp.) ( $k=2\times 10^{-3}$ ), and *pp'*-dinitro-*p'*-methoxytriphenylmethyl chloride, m. p. 107—108° ( $k=3\times 10^{-6}$ ) (corresponding perchlorate), are obtained from the above dichlorides and anisole. Treatment of a mixture of anisole, *p*-nitrobenzaldehyde, and acetic acid with sulphuric acid at 0° and oxidation of the product formed with lead tetra-acetate in acetic acid give *p*-nitro-*p'* : *p'*-dimethoxytriphenylcarbinol, m. p. 104° [corresponding chloride, m. p. 111—117° (decomp.)], purified by way of the perchlorate. The solutions obtained by treatment of the above chlorides with molecular silver are green (red in higher concentration), they decompose on keeping even in the dark, and, generally speaking, contain little of the ethane derivative. It is not possible to measure the heat of dissociation of the ethanes by the optical method of Ziegler and Ewald (A., 1929, 1010). A simple relationship between the electrochemical character and the tendency for association of a radical does not appear to exist.

H. BURTON.

Action of sodium on  $\beta$ -chloro- $\alpha\alpha\alpha$ -triphenylethane in liquid ammonia. Rearrangement of an organo-alkali compound. C. B. WOOSTER and N. W. MITCHELL (J. Amer. Chem. Soc., 1930, 52, 1042—1048).— $\beta$ -Chloro- $\alpha\alpha\alpha$ -triphenylethane was added slowly to a solution of sodium in liquid ammonia, and further quantities of sodium added to complete the reaction. A red sodium compound was formed which yielded  $\alpha\beta$ -triphenylethane when decomposed with ammonium chloride. The structure of the sodium compound could not be determined; in a proposed synthesis of alkyl derivatives only the corresponding ethylene derivatives were obtained with thionyl chloride or hydrogen chloride and phenylethylcarbinol or diphenylbenzylcarbinol.

Two mechanisms for the rearrangement are discussed, viz., (a)  $\text{CPh}_3\cdot\text{CH}_2\text{Na}\rightarrow\text{CPh}_2\text{Na}\cdot\text{CH}_2\text{Ph}$ , and (b)  $\text{CPh}_3\cdot\text{CH}_2\text{Cl}\rightarrow\text{CPh}_3\cdot\text{CH}\cdot\rightarrow\text{CPh}_2\cdot\text{CHPh}\rightarrow\text{CPh}_2\text{Na}\cdot\text{CHPhNa}\rightarrow\text{CPh}_2\text{Na}\cdot\text{CH}_2\text{Ph}$ . Although certain evidence in favour of (b) can be adduced from analogy with other reactions, the difficulty of eliminating hydrogen chloride from the halogen compound favours mechanism (a). Interaction with sodium takes place to a negligible degree in ether and very slightly in boiling toluene. The action of boiling pyridine on the halogen compound is barely perceptible. In mechanism (a) rearrangement might take place as follows :



R. K. CALLOW.

Polarisation of the ethylenic linking. G. WITTIG and M. LEO (Ber., 1930, 63, [B], 943—949).— $\alpha\alpha\zeta\zeta$ -Tetraphenylhexane- $\alpha\zeta$ -diol dissolved in dioxan is converted by cold methyl-alcoholic hydrogen chloride into  $\alpha\zeta$ -dimethoxy- $\alpha\alpha\zeta\zeta$ -tetraphenylhexane, m. p. 229—231°, which, with potassium-sodium alloy,



gives the *dipotassium* compound, converted by alcohol into  $\alpha\alpha\zeta$ -tetraphenyl-*n*-hexane, m. p. 124–5–126°. With oxygen, the dipotassium derivative affords the cyclic *peroxide*,  $C_{34}H_{36}O_4$ , m. p. 186° (decomp).  $\alpha\alpha\zeta$ -Tetraphenyl- $\Delta^{\alpha}$ -hexadiene yields a potassium derivative, converted by alcohol into  $\alpha$ -diphenyl- $\Delta^{\alpha}$ -propene, by carbon dioxide into  $\beta\beta$ -diphenylacrylic acid, and by tetramethylethylene bromide into the original material. This previously unobserved loosening of the ethane linking is found also in the decomposition of tetraphenylhexadiene into  $\alpha$ -diphenyl- $\Delta^{\alpha}$ -propene and polymerised  $\alpha$ -diphenylallene when distilled under atmospheric pressure. Dibenzyl reacts feebly with alkali metals, probably owing to slight contamination with stilbene.  $\alpha\zeta$ -Diphenyl- $\Delta^{\alpha}$ -hexadiene is rapidly attacked, but the product yields ill-defined substances when acted on by ethyl alcohol or carbon dioxide. *Di-p-diphenyllethane*, m. p. 198–199°, prepared by reducing 1:4'-diphenylbenzil with hydriodic acid and red phosphorus, gives a *potassium* compound converted by alcohol into *p*-methyldiphenyl, but the compound is more stable than *s*-tetraphenylethane or tetraphenylhexadiene. It appears, therefore, that aryl groups can pass on their action through the ethylenic linking; the reason lies in the ready polarisability of the ethylenic linking.

[Preparation of] 1-bromonaphthalene. H. T. CLARKE and M. R. BRETHEN (Organic Syntheses, 1930, 10, 14–15).

1:4-Dibenzyl-naphthalene and its corresponding keto-derivatives. K. DZIEWOŃSKI, J. MOSZEWSKI, S. LEPIANKIEWICZ, and L. SUCHER (Bull. Acad. Polonaise, 1929, A, 650–657).—The dibenzyl-naphthalene, m. p. 88°, obtained as one of the products of the action of benzyl chloride on naphthalene in presence of aluminium chloride or fused zinc chloride ("β-dibenzyl-naphthalene" of Dziewoński and Moszewski, A., 1929, 56, 1054) is now shown to be 1:4-dibenzyl-naphthalene (picrate, m. p. 107°), also prepared by the reduction of 4-benzoyl-1-benzyl-naphthalene, m. p. 113° (phenylhydrazone, m. p. 155–156°; oxime, m. p. 202–203°). The latter is obtained by the interaction of 1-benzyl-naphthalene and benzoyl chloride in presence of fused zinc chloride. The orientation of both compounds is established by their oxidation with nitric acid to the known 1:4-dibenzoyl-naphthalene, m. p. 106° (Scholl and Neumann, A., 1922, i, 261) (dioxime, m. p. 261°).

Treatment of 1:4-dibenzyl-naphthalene with chlorosulphonic acid at the ordinary temperature affords 1:4-dibenzyl-naphthalenesulphonic acid, isolated as the sodium salt. Nitration of 4-benzoyl-1-benzyl-naphthalene yields a mononitro-derivative, m. p. 172–173°. A by-product of the reduction of the same compound is 1:4-dibenzyl-tetrahydronaphthalene, m. p. 92–93°.

R. CHILD.

Preparation of *N*-chloroacetanilide. C. D. BARNES and C. W. PORTER (J. Amer. Chem. Soc., 1930, 52, 1721–1722).—*N*-Chloroacetanilide (97% pure) is obtained in 70% yield when a solution of acetanilide in dilute sodium hydrogen carbonate is treated at 5° with the solution prepared from sodium carbonate and chlorine (until it contains

1.6–1.8 × 10<sup>-3</sup> equivalents of chlorine per c.c.). *N*-Chloroacetanilide crystallises either in plates or in needles.

H. BURTON.

Constitution of certain chloroiodo- and bromoiodo-anilines. F. B. DAINS and A. W. MAGERS (J. Amer. Chem. Soc., 1930, 52, 1572–1573).—Iodination of 4-bromo-2-iodoaniline by Wheeler's method (A., 1910, i, 662) gives 4-bromo-2:6-di-iodoaniline, m. p. 148°, convertible into 1-bromo-3:4:5-tri-iodobenzene, m. p. 153°. The compound obtained by iodination of *m*-bromoaniline is 3-bromo-4-iodoaniline (cf. A., 1918, i, 340), that from *p*-chloroaniline is 4-chloro-2-iodoaniline, and the di-iodo-derivative from *p*-chloro- or 4-chloro-2-iodo-aniline is 4-chloro-2:6-di-iodoaniline. The last-named compound is converted by the usual method into 1-chloro-3:4:5-tri-iodobenzene, m. p. 148°. The iodination product of *o*-anisidine is 6-iodo-*o*-anisidine (cf. loc. cit.).

H. BURTON.

Interaction of chlorosulphonic acid with substituted amides of malonic and methylmalonic acids. K. G. NAIK and C. H. SHAH (J. Indian Chem. Soc., 1930, 7, 111–118; cf. Naik and Amin, A., 1929, 57).—When symmetrical malonamides of the type  $CH_2(CO\cdot NHR)_2$  are treated with chlorosulphonic acid, preferably in dry chloroform, disulphonic acids are formed where R is phenyl, benzyl, *o*-, *m*-, or *p*-tolyl,  $\alpha$ - or  $\beta$ -naphthyl, or *as-m*-xylyl, of the general type  $(SO_3H)_2\cdot C(CO\cdot NHR)_2$ . A similar disulpho-derivative is formed from mono-*p*-tolylmalonamide. Corresponding arylamides of methylmalonic acid yield disulphonic acids of the type  $SO_3H\cdot CH_2\cdot C(SO_3H)(CO\cdot NHR)_2$  whilst dipropylmalonamide yields a monosulphonic acid only. Treatment of representative disulphonic acids with nitric acid leads to replacement of the sulphonyl by the nitro-group.

The following disulphomalonarylamides are described: *disulphomalon-anilide* ( $2H_2O$ ) [the calcium, barium, and ammonium salts are monohydrated, sodium salt ( $3H_2O$ ), potassium salt ( $9H_2O$ )]; nitration yields *dinitromalon-anilide*, m. p. 124°, which on hydrolysis gives dinitromalonic acid (potassium salt); *-benzylamide* ( $H_2O$ ) (sodium and potassium salts anhydrous, barium and ammonium salts +  $0.5H_2O$ ); *-p-toluidide*, on nitration gives *dinitromalon-p-toluidide*, m. p. 68°; *-o-toluidide* (potassium salt), *dinitromalon-o-toluidide*, m. p. 85°; *-m-toluidide* ( $H_2O$ ) (calcium salt); *-α-naphthylamide* ( $4H_2O$ ); *-β-naphthylamide* ( $6H_2O$ ); *-as-m-xylylidide*: *disulphomalonmono-p-tolylamide* ( $H_2O$ ). Sulphomalonpropylamide was not obtained crystalline [barium salt ( $3H_2O$ )]. *Sulphomethylsulphomalonanilide* [sodium salt anhydrous, potassium salt ( $H_2O$ )] on nitration gives a tetra-nitro-compound, m. p. 120°; other *sulphomethylsulphomalonarylamides* are: *-o-toluidide* ( $H_2O$ ), [potassium salt ( $2H_2O$ )]; *-m-toluidide*; *-p-toluidide* ( $H_2O$ ); *-α-naphthylamide* ( $5H_2O$ ), and the *-β-naphthylamide* ( $3H_2O$ ). The free sulphonic acids do not melt but generally decompose at about 280–300°. Malon- and methylmalon-*as-m*-xylylides and methylmalon- $\alpha$ - and  $\beta$ -naphthylamides are stated to have been prepared and to be new, but they are not described.

H. A. PIGGOTT.

**Interaction between thionyl chloride and substances containing the reactive methylene group.**  
**I. Formation of sulphoxides.** K. G. NAIK, R. D. DESAI, and M. M. PAREKH (J. Indian Chem. Soc., 1930, 7, 137—144).—Thionyl derivatives of the type  $(\text{NHR}\cdot\text{CO})_2\text{C}\cdot\text{SO}$  are obtained by the action of thionyl chloride on malonarylamides. The following are described: *thionylmalon-anilide*, m. p. 129° (decomp.); *-o-toluidide*, m. p. 129—130°; *-m-toluidide*, m. p. 142—143°; *-p-toluidide*, decomp. above 170°, "m. p." 215°; *-α-naphthylamide*, decomp. 165°, "m. p." 210°; *-β-naphthylamide*, decomp. above 170°, "m. p." 199°; *-1:4:5-xylidide*, m. p. 172—173°; also the *monophenylamide*, m. p. 150°; *-mono-p-tolyl*, m. p. 156—157°; *-mono-m-tolyl*, m. p. 140°; *-mono-o-tolyl*, m. p. 168°; *-mono-α-naphthyl*, m. p. 170°, and *mono-β-naphthylamide* m. p. 160°. All these sulphoxides are readily decomposed by water or alcohol with liberation of sulphur dioxide and regeneration of the original amide. Malonmethylamide with thionyl chloride yields *thionylbismalonmethylamide*,  $[(\text{NHMe}\cdot\text{CO})_2\text{CH}]_2\text{SO}$ , m. p. 208°; the *ethylamide* (?), m. p. 176°, is similarly obtained. Malonmethylamide and malon-o- and -p-tolylamides give liquid products, the amides of methylmalonic acid do not give definite products, and malonamide itself is unacted on. The preparation of the *mono-m-tolyl*, m. p. 165°; *-o-tolyl*, m. p. 162°; *-α-naphthyl*, m. p. 146°, and *-β-naphthyl*, m. p. 188°, *-malonamides*, is described.  
 H. A. PIGGOTT.

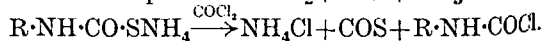
**Interaction between thionyl chloride and substances containing the reactive methylene group.**  
**II. Conversion of sulphoxides into sulphides.** K. G. NAIK and M. M. PAREKH (J. Indian Chem. Soc., 1930, 7, 145—150).—Continued heating of malonarylamides with thionyl chloride leads to the formation of sulphides of the type  $[(\text{NHR}\cdot\text{CO})_2\text{C}]_2\text{S}$ . The same change is brought about by heating the sulphoxides (preceding abstract) with thionyl chloride, hydrogen chloride, or iodine, and occurs apparently through the interaction of 2 mols. of sulphoxide with liberation of sulphur dioxide, the evolution of which is observed. In this way were prepared: *thiobismalon-anilide*, m. p. 196° (from malonanilide or its sulphoxide); *-o-toluidide*, m. p. 214°; *-m-toluidide*, m. p. 164°; *-p-toluidide*, m. p. 198°; *-α-naphthylamide*, m. p. 132°; *-β-naphthylamide*, m. p. 146°; *thiobismalonmonophenylamide*, m. p. 114°; *thiobismono-m-tolylamide*, m. p. 123°. In the preparation of the α- and β-naphthyl compounds, substances free from sulphur, m. p. 248° and 265°, respectively, were obtained.  
 H. A. PIGGOTT.

**Polymorphism. I. Polymorphism of o-nitroaniline.** J. F. J. DIPPY and N. H. HARTSHORNE (J.C.S., 1930, 725—732).—o-Nitroaniline exists in two polymorphous crystalline forms, one yellowish-green, triclinic or monoclinic, m. p. 68.1—68.3°, unstable between the ordinary temperature and its m. p. and changing spontaneously into the second, stable modification, m. p. 70.1—70.2°, which is dark orange and orthorhombic (microscopic crystallographic examination by A. STUART). The m. p. were determined on the microscope slide in a special

apparatus which is described. When o-nitroaniline is crystallised in thin films both forms are normally obtained, the quantity of the metastable form decreasing with increasing crystallisation temperature, until, just below the m. p., the stable form is the sole product. The rate of transformation into the stable form depends on (1) the rate at which the boundary between the two forms moves in a direction normal to itself, and (2) the length of the boundary, which, in turn, depends on the proportion of the stable form present in small grains. Ordinary "pure" o-nitroaniline (Schuchardt) has a very low stabilisation velocity, very little change occurring in 21 hrs., but crystallisation from absolute alcohol affords specimens in which the velocity is considerably increased, the change being complete in 24 hrs. Intermediate velocities were obtained with purified samples to which 1% of p-nitroaniline had been added, and hence it is suggested that the original sample contains some other impurity which exerts a retarding influence on the conversion of the unstable into the stable form.  
 J. W. BAKER.

**Carbimides. VII. Preparation of aromatic thiocarbimides and carbimides.** K. H. SLOTTA and H. DRESSLER (Ber., 1930, 63, [B], 888—898; cf. this vol., 329).—Arylthiocarbimides are obtained in 70—95% yield by the gradual addition of carbon disulphide to a solution of the requisite amine in well-cooled toluene through which ammonia is briskly passed. The ammonium salt of the dithiocarbamate separates and is decomposed by the gradual addition of carbonyl chloride dissolved in toluene:  $\text{NHR}\cdot\text{CS}_2\text{NH}_4 + \text{COCl}_2 = \text{HCl} + \text{NH}_4\text{Cl} + \text{COS} + \text{R}\cdot\text{N}\cdot\text{C}\cdot\text{S}$ . The ammonium chloride is removed and the filtrate distilled under diminished pressure. The following compounds are thus prepared: *phenylthiocarbimide*, b. p. 120—125°/15 mm.; *ammonium p-anisylthiocarbamate* and thence *p-anisylthiocarbimide*, b. p. 164°/37 mm.; *p-ethoxyphenylthiocarbimide*, m. p. 62°; *ammonium p-dimethylaminophenylthiocarbamate*, m. p. 170°, and thence *p-dimethylaminophenylthiocarbimide*, m. p. 70° after softening at 66°; *ammonium p-hydroxyphenylthiocarbamate* (in aqueous methyl-alcoholic solution), and thence *p-hydroxyphenylthiocarbimide*, b. p. 175—185°/11 mm., m. p. 43—44°. The last-named compound reacts with acetobromoglucose and potassium hydroxide in aqueous acetone to yield *p-tetra-acetylglucosidoxyphenylthiocarbimide*, m. p. 150—152°, hydrolysed by methyl-alcoholic ammonia to *p-glucosidoxyphenylthiocarbimide*, decomp. 190—192°. Di-p-hydroxyphenylthiocarbimide is converted by boiling acetic anhydride into p-acetoxyphenylthiocarbimide and p-acetoxyacetanilide.

The preparation of arylcarbimides is effected analogously, carbonyl sulphide being used in place of carbon disulphide:  $\text{R}\cdot\text{NH}_2 + \text{COS} + \text{NH}_3 \rightarrow$



The preparation of the ammonium salt proceeds satisfactorily provided that sufficient ammonia is always present to prevent the formation of aryl-ammonium thiocarbamate and a very rapid current of carbonyl sulphide is used. The product is treated with calcium oxide, the solvent is removed, and the

residue distilled. The new method is inferior to the customary process for the preparation of phenylcarbimide, but leads smoothly to the production of *p*-anisylcarbimide, b. p. 106–110°/16 mm., and *p*-phenetylcarbimide, b. p. 113–116°/16 mm. Ammonium phenylthiocarbamate, decomp. 80°, *p*-anisylthiocarbamate, decomp. 81°, and *p*-phenetylthiocarbamate, decomp. 85°, are described.

H. WREN.

**Mono- and poly-alkoxy- or halogeno-substituted derivatives of benzhydroxylamine and  $\alpha\beta$ -diphenylethylamine.** VALETTE (Bull. Soc. chim., 1930, [iv], 47, 289–300).—In continuation of earlier work (Torrès, A., 1926, 396, 609) a number of symmetrical *m*-disubstituted dialkoxy-, and mono-substituted *m*- and *p*-benzyloxy-, chloro- and bromo-derivatives of benzhydroxylamine and alkoxy-derivatives of  $\alpha\beta$ -diphenylethylamine have been prepared, and their anæsthetic action on the cornea of rabbits and the sciatic (motor) nerve has been examined. Monoalkoxy-groups exert a stronger anæsthetic action in the *para*- than in the *meta*-position, but the *para*-derivatives possess more marked irritant properties. 3:3'-Dialkoxy-derivatives are less active anæsthetics than the corresponding mono-substituted derivatives and are without irritant action on the mucous membrane, but are more toxic. The anæsthetic action in this series increases with the mol. wt. of the alkoxy-group, reaching a maximum with the propyl derivative, which is six times as active as cocaine. Introduction of halogen increases the anæsthetic power of benzhydroxylamines, but much less than the introduction of alkoxy-group, bromine, especially in the *m*-position, having a stronger effect than chlorine. There is no relation between the toxicity and the anæsthetic action of those benzhydroxylamine hydrochlorides.

The following are described: *m*-benzyloxybenzophenone, m. p. 62–63°, yielding on reduction of the oxime with 2.5% sodium amalgam in acid solution *m*-benzyloxybenzhydroxylamine (hydrochloride, m. p. 210–212°); *p*-benzyloxybenzophenone, m. p. 84–85° (oxime, m. p. 163–164°); *p*-benzyloxybenzhydroxylamine (hydrochloride, m. p. 213–214°); 3:3'-dimethoxybenzophenone, b. p. 230–235°/20 mm. (oxime, m. p. 86–87°), obtained by methylation of 3:3'-dihydroxybenzophenone, m. p. 174°, in presence of sodium ethoxide (3:3'-dinitrobenzophenone has m. p. 153°); 3:3'-diaminobenzophenone, m. p. 150°; 3:3'-dimethoxybenzhydroxylamine, m. p. 55°, b. p. 235–240°/35 mm. [hydrochloride, m. p. 235–236° (decomp.)]; 3:3'-diethoxybenzophenone, b. p. 210°/25 mm. (oxime, m. p. 70°); 3:3'-diethoxybenzhydroxylamine (hydrochloride, m. p. 241–242°); 3:3'-dipropoxybenzophenone, b. p. 220–225°/40 mm. (oxime, m. p. 90–92°); 3:3'-dipropoxybenzhydroxylamine (hydrochloride, m. p. 230–231°; lactate, m. p. 96–97°); 3:3'-dibutoxybenzophenone, oil (oxime, m. p. 74–75°?); 3:3'-dibutoxybenzhydroxylamine (hydrochloride, m. p. 186°; acetate, m. p. 105°; nitrate, m. p. 160°; lactate, m. p. 100–101°). 3:4:3':4'-tetramethoxybenzhydroxylamine [hydrochloride, m. p. 242° (decomp.)]. *p*-Propoxydeoxybenzoin, m. p. 65–66° (oxime, m. p. 85–86°). *p*-isopropoxydeoxybenzoin, m. p. 103–104° (oxime, m. p. 111–112°), *p*-butoxydeoxybenzoin,

m. p. 85–86° (oxime, m. p. 99–100°), *p*-isobutoxydeoxybenzoin, m. p. 62° (oxime, m. p. 96°), and *p*-isoamyloxydeoxybenzoin, m. p. 57–58° (oxime, m. p. 88–89°), are obtained by condensation of phenylacetyl chloride with the appropriate phenyl alkyl ether in carbon disulphide in presence of aluminium chloride. On reduction with sodium and alcohol the oximes give the corresponding  $\alpha$ -alkoxyphenyl- $\beta$ -phenylethylamine in 40–50% yield. The hydrochloride of  $\alpha$ -*p*-*n*-propoxyphenyl- $\beta$ -phenylethylamine has m. p. 174–175°; the hydrochloride of the corresponding isopropyl compound has m. p. 206°, butoxyhydrochloride, m. p. 181–182°, and isoamyloxyhydrochloride, m. p. 161°.  $\alpha$ -*p*-isoButoxyphenyl- $\beta$ -phenylethylamine has m. p. 48°, b. p. 235–240°/30 mm. (hydrochloride, m. p. 196–197°). 3-Chloro- (hydrochloride, m. p. 275–276°), 4-chloro- (hydrochloride, m. p. 268–269°), 3-bromo- (hydrochloride, m. p. 263–264°), and 4-bromo-benzhydroxylamine [hydrochloride, m. p. 261° (decomp.)] are similarly obtained. 4-Chlorobenzhydroxylamine has b. p. 245–250°/20 mm.

R. BRIGHTMAN.

**Complex compounds of cobalt with  $\alpha\beta$ -diphenylethylenediamine.** E. N. GAPON (Bull. Soc. chim., 1930, [iv], 47, 343–348).—When an alcoholic hydrochloric acid solution of cobalt chloride and  $\alpha\beta$ -diphenylethylenediamine is oxidised by a current of air, the dark red  $\alpha\beta$ -diphenylethylenediaminecobaltic tetrachloride,  $[(\text{CH}_2\text{NHPH})_2]\text{CoCl}_4 \cdot 6\text{H}_2\text{O}$ , is formed; in presence of larger amounts of hydrochloric acid the cis-dichlorodi- $\alpha\beta$ -diphenylethylenediaminecobaltic chloride, violet (annexed formula) is obtained. In aqueous  $[(\text{CH}_2\text{NHPH})_2]\text{CoCl}_2 \cdot \text{Cl}$  solution with concentrated hydrochloric acid the

hydrochloride-dihydrate,  $[\text{Co}(\text{CH}_2\text{NHPH})_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ , is obtained, whilst oxidation in aqueous alcohol (2 vols. water, 1 vol. alcohol) in presence of hydrochloric acid for 7 hrs. yields the trans-dichlorodi- $\alpha\beta$ -diphenylethylenediaminecobaltic chloride, green, which when repeatedly moistened with water and dried is converted into the cis-isomeride, probably through the intermediate formation of the diaquo-salt. R. BRIGHTMAN.

**Effect of organic bases on the extent and mechanism of the reducing action of sodium methoxide on nitrobenzene and azoxybenzene.** H. S. FRY and P. E. BOWMAN (J. Amer. Chem. Soc., 1930, 52, 1531–1536).—The reduction of nitrobenzene (0.2 mol.) and azoxybenzene (0.1 mol.) by an excess of methyl-alcoholic sodium methoxide solution in presence of 0.125–0.75 mol. of aniline, methyl- and dimethyl-anilines, quinoline, and isoamylamine has been studied by the method previously described (A., 1927, 454). With nitrobenzene there is a marked increase in the extent of the reduction (except with isoamylamine) as compared with that occurring in absence of a base; the extent of the reduction is calculated from the amount of sodium formate produced (cf. *loc. cit.*). The increase follows the order of increasing concentration and strength of the base, except with aniline and isoamylamine. Azoxybenzene is partly reduced to azobenzene: an increase in the concentration of the base also causes

a rise in the amount reduced, except with *isoamylamine*. The anomalous results with *isoamylamine* are due to the intermediate formation of formaldehyde, which combines with the base. The combined aldehyde is determined by extracting the reaction mixture with benzene, treating this with dilute sulphuric acid, saturating the acid extract with mercuric chloride, and then adding sodium hydroxide solution to precipitate the amine mercurichloride and the excess of chloride. The aldehyde content of the filtrate is then determined by the hydrogen peroxide method. The formaldehyde is produced by the change  $2\text{Ph}\cdot\text{NO}_2 + 3\text{NaOMe} \rightarrow 3\text{CH}_2\text{O} + (\text{NPh})_2\text{O} + 3\text{NaOH}$ , which occurs concurrently with Klinger's reaction (A., 1882, 1061; *loc. cit.*). The results afford further evidence for the previously proposed mechanism involving the acidic dissociation of sodium hydroxide.

H. BURTON.

**Preparation of *s*-diphenylsemicarbazide.** C. R. NOLLER (J. Amer. Chem. Soc., 1930, 52, 1132—1134).—*s*-Diphenylsemicarbazide prepared from carbamide and phenylhydrazine gives products of varying m. p. owing to the presence of an additive compound, m. p. 166—166.5° (corr.), with 1-phenylsemicarbazide (1 : 1), the existence of which is shown by a m.-p. curve. This probably explains the discrepant m. p. (151—171°) recorded in the literature. Pure *s*-diphenylsemicarbazide, m. p. 175—175.5° (corr.), is obtained by a modification of the method of Cazeneuve and Moreau (A., 1900, i, 196) by heating phenylhydrazine with guaiacol carbonate.

R. K. CALLOW.

**Hydrazides and azides of phenyl- and ethylsuccinic acids.** T. CURTIUS. I. **Hydrazide and azide of phenylsuccinic acid** [with G. von BRÜNING]. II. **Hydrazide and azide of ethylsuccinic acid** [with H. DERLON] (J. pr. Chem., 1930, [iii], 125, 63—89).—I. Ethyl phenylsuccinate reacts with hydrazine hydrate, forming only the normal *phenylsuccinhydrazide*, m. p. 174.5° (cf. A., 1915, i, 872) (*dihydrochloride*, m. p. 150°; *dibenzylidene derivative*; *diisopropylidene derivative*, m. p. 194°), converted by the usual method into *phenylsuccinazide*. Treatment of an ethereal solution of the azide with aniline gives *phenylsuccinanilide*. The azide is converted by heating with benzene into *phenylethylenedicarbimide*, from which *phenylethylenedicarbamate*,  $\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\text{—NH}\cdot\text{CO}$  (I), m. p. 68°,  $\alpha,\beta$ -di(*phenylcarbamido*)-*phenylethane*, m. p. 208°, and *ethyl phenylethylenedicarbamate* are prepared by the action of water, aniline, and alcohol, respectively. Hydrolysis of the dicarbamate with hydrochloric acid at 110° affords  $\alpha$ -phenylethylenediamine (*dihydrochloride*, m. p. 274°). Ethyl aminoacetate and the above azide react in ethereal solution, forming *ethyl phenylsuccinylidiamidoacetate*, m. p. 131°, convertible into the corresponding *dihydrazide*, m. p. 228° (*dibenzylidene derivative*, m. p. 204—206°), and *diazide*. Treatment of this azide with aniline, water, and alcohol gives *phenylsuccinylidiamidoacetanilide*, m. p. 215°, the cyclic carbamide,  $\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}$ , m. p. 195°, and the ester,

$\text{CO}_2\text{Et}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , m. p. 184° (decomp.), respectively.

II. Ethyl ethylsuccinate [the free acid is conveniently prepared by hydrolysing ethyl butane- $\alpha,\beta$ -tricarboxylate with a mixture (1 : 1) of 19% hydrochloric and acetic acids] and hydrazine hydrate react in boiling 90% alcohol, forming *ethylsuccinhydrazide*, m. p. 163° (*dihydrochloride*; *dipicrate*, m. p. 190°; *dibenzylidene*, m. p. 197°; *disalicylidene*, m. p. 193—194°; and *di-m-nitrobenzylidene derivatives*, m. p. 216°). Benzoylation of this in presence of sodium hydrogen carbonate gives the normal *dibenzoyl derivative*, m. p. 190°, but in presence of sodium hydroxide a *monobenzoyl derivative*, m. p. 235—237°, of either ethylsuccinhydrazidic acid or *N*-aminoethylsuccinimide is produced. *Ethylsuccinylazide* is converted by the usual methods into *ethylsuccin-anilide*, m. p. 199°, *p-toluidide*, m. p. 225—227°, and *ethyl ethylethylenedicarbamate*, m. p. 85°. The last-named compound is hydrolysed by hydrochloric acid at 120° to  $\alpha,\beta$ -diaminobutane (cadmium iodide compound). The diazide decomposes in boiling benzene, yielding impure *ethylethylenedicarbimide*, which with aniline gives a mixture of  $\alpha,\beta$ -di(*phenylcarbamido*)butane, m. p. 209°, and the compound,  $\begin{array}{c} \text{CHEt}\cdot\text{NH}\cdot\text{CO} \\ | \\ \text{CH}_2\text{—N}\cdot\text{C}\cdot\text{NHPH} \end{array}$ , m. p. 139°.

Hydrolysis of this mixture with hydrochloric acid at 120° also furnishes  $\alpha,\beta$ -diaminobutane.

When ethylsuccinic acid is treated with phosphorus pentachloride some elimination of the ethyl group occurs and a mixture of succinyl and *ethylsuccinyl chloride*, b. p. 115—120°/76 mm., is produced. The last-named chloride does not react with ethyl aminoacetate hydrochloride (cf. A., 1923, i, 1072). Ethylsuccinyl diazide and ethyl aminoacetate react in ether, forming a compound,  $\text{C}_{12}\text{H}_{20}\text{O}_6\text{N}_2$ , m. p. 127°, which with hydrazine hydrate gives a *hydrazide*,  $\text{C}_8\text{H}_{16}\text{O}_4\text{N}_6$ , m. p. 235°.

H. BURTON.

**Behaviour of *o*-carboxyphenoxyacetic and phenylglycine-*o*-carboxylic acids on azide rearrangement.** T. CURTIUS. I. **Hydrazides and azides of *o*-carboxyphenoxyacetic acid** [with K. MOLL]. II. **Hydrazides and azides of phenylglycine-*o*-carboxylic acid** [with R. FINGADO] (J. pr. Chem., 1930, [iii], 125, 106—138).—I. Ethyl *o*-carbethoxyphenoxyacetate (Meyer and Duczmal, A., 1913, i, 1344) is converted by hydrazine hydrate first into *o*-carbethoxyphenoxyacetylhydrazide, m. p. 222° (*hydrochloride*, m. p. 175°; *benzylidene derivative*, m. p. 133°; *isopropylidene derivative*, m. p. 107°), and then into *o*-carboxyphenoxyacetylhydrazide, m. p. 172° [*dihydrochloride*, m. p. 203° (decomp.); *dibenzylidene derivative*, m. p. 207°; *diisopropylidene derivative* (+2H<sub>2</sub>O), m. p. (anhydrous) 138°]. This dihydrazide is converted by nitrous acid into *o*-carboxyphenoxyacetyl diazide, m. p. 65°, which with aniline in cold ether gives *phenoxyacetanilide-*o*-carboxyazide* (I), m. p. 105° (decomp.). In boiling ethereal solution *o*-phenylcarbamidophenoxyacetanilide (II), m. p. 209°, is obtained, whilst with aniline alone, *phenoxyacetanilide-*o*-carboxyanilide*, m. p. 176°, results. Treatment of I with alcohol gives *o*-carbethoxyaminophenoxyacetanilide, m. p. 140°, hydrolysed by 1% hydro-

chloric acid to *o*-carbethoxyaminophenoxyacetic acid, m. p. 95°. The last-named acid and II are hydrolysed by hydrochloric acid at 120° to the lactam (III), m. p. 173° (lit. 166—167°), of *o*-aminophenoxyacetic acid. When the above diazide is heated with methyl, ethyl, or benzyl alcohol a mixture of III and the corresponding impure diurethanes is obtained. The diurethanes are hydrolysed by hydrochloric acid at 100° to III, ammonia, and a resinous product (probably formed from the intermediate *o*-aminophenol and formaldehyde). Treatment of *o*-carbethoxyphenoxyacethydrazide with nitrous acid gives, according to the conditions used, either the *sec.*-hydrazide, m. p. 167°, of *o*-carbethoxyphenoxyacetic acid or *o*-carbethoxyphenoxyacetazide, m. p. 43°. This azide reacts with aniline forming *o*-carbethoxyphenoxycetanilide, m. p. 93°, and when boiled with benzene decomposes to *o*-carbethoxyphenoxymethylcarbimide. Treatment of this with alcohol and aniline furnishes *ethyl o*-carbethoxyphenoxymethylcarbamate and *phenyl o*-carbethoxyphenoxymethylcarbamide, m. p. 204°, respectively.

II. When ethyl *o*-carbethoxyanilinoacetate (1 mol.) is heated with hydrazine hydrate (2 mols.) at 100°, *anilinoacethydrazide-o*-carboxyhydrazide, m. p. 161° (*dihydrochloride*, m. p. 201°; *dipicrate*, m. p. 185°; *dibenzylidene* derivative, m. p. 253°; *diisopropylidene* derivative, m. p. 205°), is obtained. This is converted by the usual method into *anilinoacetazide-o*-carboxyazide, m. p. 56° (decomp.), which with alcohol gives *ethyl o*-carbethoxyaminooanilinomethylcarbamate. When an ethereal solution of the diazide is first boiled and then treated with benzyl alcohol, *benzyl anilino-methylcarbamate-o*-carboxyazide, m. p. 112°, is formed. If the preliminary heating is carried out in chloroform the *carbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Ph})_2$ , m. p. 195° (decomp.), is isolated instead of the expected diurethane derivative. The diazide reacts with aniline forming the *azide*,  $\text{N}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , decomp. 156° [converted by boiling with alcohol into the *carbamide*,  $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh})_2$ , m. p. 232°], and the *dicarbamide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 182°; with *p*-toluidine the compound,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p. 195° (decomp.), which exists in two crystalline forms, results.

When ethyl *o*-carbethoxyanilinoacetate (4 parts) is heated with hydrazine hydrate (1 part) at 100°, *o*-carbethoxyanilinoacethydrazide, m. p. 125° (*hydrochloride*, m. p. 237°; *benzylidene* derivative, m. p. 182°; *isopropylidene* derivative, m. p. 162°), is formed; with 2 mols. of the ester and 1 mol. of hydrazine hydrate the *sec.*-hydrazide, m. p. 248°, of *o*-carbethoxyanilinoacetic acid results. Hydrolysis of the normal hydrazide with 10% sodium hydroxide solution below 60° gives *anilinoacethydrazide-o*-carboxylic acid, m. p. 200.5° (the m. p. falls to 189° after keeping) (*benzylidene* derivative, m. p. 260°; *isopropylidene* derivative, m. p. 237°). *o*-Carbethoxyanilinoacetazide and alcohol give *ethyl o*-carbethoxyanilinomethylcarbamate.

H. BURTON.

Diazo-hydrates, azoxy-compounds, and nitrones. Z. JOLLES and J. KRUGLIAKOFF (Atti R.

Accad. Lincei, 1930, [vi], 11, 197—202).—Not only normal diazo-hydrates (this vol., 467), but also  $\alpha$ - and  $\beta$ -azoxy-compounds, nitrosophenylhydroxylamine, and nitrones, which are of analogous chemical structure, exhibit marked oxidising properties, as they are converted by slight excess of alkaline ferrous sulphate solution into the corresponding compounds containing one oxygen atom less in the molecule. The compounds examined in this way were salicyl-*N*-phenylnitron,  $\alpha$ - and  $\beta$ -benzeneazoxybenzoic acids,  $\alpha$ - and  $\beta$ -benzeneazoxyphenols, hydroxyhelianthin, and nitrosophenylhydroxylamine. If present in excess, phthalin is oxidised to phenolphthalein by phenylazoxycarboxylamide in alkaline solution.

T. H. POPE.

Iodination of phenyl and tolyl ethers. F. B. DAINS, A. W. MAGERS, and W. L. STEINER (J. Amer. Chem. Soc., 1930, 52, 1570—1572).—Attempted iodination of phenols by Datta and Chatterjee's method (A., 1917, i, 327) gives nitro- rather than iodo-derivatives. The method is, however, applicable to tolyl ethers and nitroanisoles. The following are described: 5-iodo-2-methoxytoluene, m. p. 74°; 6-iodo-3-methoxytoluene, m. p. 75°; 3-iodo-4-methoxytoluene, b. p. 240°; 4-iodo-2-nitroanisole, m. p. 98° (lit. 73°); 2-iodo-4-nitroanisole, m. p. 96°; 4-iodo-3-nitroanisole, m. p. 62°. 6-Iodo-*m*-anisidine, an oil (*hydrochloride*, m. p. 155—156°), is obtained by iodination in presence of calcium carbonate and water. Phenyl-3-nitro-*p*-anisyl- and phenyl-5-nitro-*o*-anisyl-carbamides have m. p. 164° and 192°, respectively.

H. BURTON.

Derivatives of phenyl ether. I. Nitro-, amino-, and hydroxy-derivatives. G. LOCK (Monatsh., 1930, 55, 167—184).—Nitration of diphenyl ether with nitric (*d* 1.48) and acetic acids affords a mixture of 2- (24%) and 4-nitrodiphenyl ethers (44%); oxalic and picric acids are formed as by-products. When the amount of acetic acid used is less than 12 mols. per mol. of the ether, some dinitration occurs. The following derivatives of diphenyl ether have been prepared, generally from potassium phenoxides and bromobenzenes in absence or presence of copper-bronze: 2-, 3-, and 4-nitro-, m. p. 61° [lit. 56°]; the compound described by Jones and Cook (A., 1916, i, 644) as 4-nitrodiphenyl ether is *p*-bromonitrobenzene; 2-hydroxy- [*benzoate*, m. p. 48.5° (corr.)]; 3-hydroxy-, b. p. 320° (corr.)/743 mm., prepared by the usual method from the 3-amino-derivative or by demethylation of the 3-methoxy-derivative, b. p. 303° (corr.)/745 mm., and 4-hydroxy- [*benzoate*, m. p. 97—98° (corr.)]. Good yields of the aminodiphenyl ethers are obtained by reducing the nitro-derivatives with stannous chloride and alcoholic hydrochloric acid.

H. BURTON.

Derivatives of phenyl ether. L. C. RAIFORD, G. W. THIESSEN, and I. J. WERNERT (J. Amer. Chem. Soc., 1930, 52, 1205—1209).—The constitution of 2': 4-dibromo-4-nitrodiphenyl ether, m. p. 79°, obtained by bromination of *p*-nitrodiphenyl ether (Raiford and Colbert, A., 1926, 1242) has been determined by synthesis by condensing 4-chloronitrobenzene and potassium 2:4-dibromophenoxide at 150—170°. The same compound is also obtained by bromination of

2'-bromo-4-nitrodiphenyl ether, m. p. 82°, obtained analogously. The initial entrance of bromine into position 2 is indicated by the failure to brominate 4-bromo-4'-nitrodiphenyl ether. Similarly, 2'-bromo-2:4-dinitrodiphenyl ether, m. p. 88—89°, yields the 2':4'-dibromo-compound, m. p. 131°, also obtained synthetically; 4'-bromo-2:4-dinitrodiphenyl ether reacts with bromine only at 180° to give a tribromo-derivative, m. p. 140—141°.

Nitration of 4'-bromo-4-nitrodiphenyl ether yields 2:4:2':4'-tetranitrodiphenyl ether. 2':4'-Dibromo-4-nitrodiphenyl ether yields the same tetranitro-ether and a 2':4'-dibromotrinitro-compound, m. p. 139°. 2':4'-Dibromo-2:4:6-trinitrodiphenyl ether, m. p. 163—164°, is obtained synthetically.

The conversion of nitro-derivatives into halogen derivatives by way of the amines and diazonium compounds has also been studied. Diazotisation of 4-aminodiphenyl ether and treatment with cuprous bromide gives the 4-bromo-compound in 42% yield. The 4:4'-dibromo-ether is obtained similarly. Bromination of 4-acetamidodiphenyl ether, m. p. 128—129° (lit., 99°, 127°), yields the 4'-bromo-compound, m. p. 157°, which by hydrolysis, diazotisation, and decomposition of the diazonium perbromide, yields the 4:4'-dibromo-compound. 2':4'-Dibromo-4-aminodiphenyl ether, b. p. 225—230°/10 mm. (acetyl derivative, m. p. 158°), could not be diazotised and converted into a tribromo-compound. Reduction of 2':4'-dichloro-4-nitrodiphenyl ether, m. p. 71°, yields 2':4'-dichloro-4-aminodiphenyl ether, m. p. 62° (acetyl derivative, m. p. 144°), which gives 4:2':4'-trichlorodiphenyl ether, m. p. 51°, in only 17% yield. Increased substitution by halogen thus appears to interfere with diazotisation. 2':4'-Dichloro-2:4-dinitrodiphenyl ether has m. p. 118°.

R. K. CALLOW.

**1:3- and 1:4-cycloHexanediols.** Constitution of the halogen derivatives. L. PALFRAY and B. ROTHSTEIN (Compt. rend., 1930, 190, 942—945).—The *cis*- and *trans*-1:4-cyclohexanediol diacetates, m. p. 35° and 102°, and the liquid 1:3-cyclohexanediol diacetate by treatment with concentrated aqueous hydrochloric or hydrobromic acid furnish the same respective products as were previously obtained (A., 1929, 1441) from the corresponding glycols. The mechanism of the change 1:3-diacetate → 1:4-dibromide is discussed; since the same transformation occurs when a glacial acetic acid solution of hydrobromic acid is employed, preliminary hydrolysis is considered to be unlikely, and a pseudo-migrational process (cf. this vol., 463) is suggested; the latter involves elimination of R·CO<sub>2</sub>H between the 3- and 4-positions with subsequent addition, oriented by the electro-negative residue in the 1-position, of HHal to the double linking.

3-Chlorocyclohexanol, prepared by the same method as the 4-chloro-isomeride (A., 1929, 1441), has the same constants, gives the same phenylcarbimide derivative, by treatment with sodium in ether affords the same Δ<sup>3</sup>-cyclohexenol (A., 1928, 1130), and by oxidation with chromic acid yields the same 4-chloro-cyclohexanone (semicarbazone, m. p. 196°: cf. *loc. cit.*) as 4-chlorocyclohexanol.

*trans*-1:4-Dibromocyclohexane, m. p. 112°, by

treatment with silver acetate in glacial acetic acid at 100°, furnishes a diacetate, m. p. 102°, identical with that obtained by direct acetylation of quinitol, which by hydrolysis with aqueous-alcoholic potassium hydroxide gives *trans*-cyclohexane-1:4-diol, m. p. 139°. If the view of Lindemann and Baumann (this vol., 209) that the above dibromide, m. p. 112°, is *cis*-1:3-dibromocyclohexane is correct, the foregoing facts must involve either (a) pseudo-migration, or (b) an addition of acetic acid, or (c) a stereoisomeric change. Against (a), it is shown that the 1:2-dibromocyclohexane (probably *cis*), obtained from cyclohexane by bromine addition, treatment with silver acetate, and alkaline hydrolysis of the diacetate obtained, affords *cis*-pyrocatechol. Against (b), it is shown that no addition of acetic acid to cyclohexene occurs at 100° (cf. Brunel, A., 1905, i, 869), whilst (c) is rendered unlikely by the work described above as contrary to (a). C. W. SHOPPEE.

**Action of oxygen on 1:4-dimethylcyclohexane.** G. CHAVANNE and (MLE.) E. BODE (J. Amer. Chem. Soc., 1930, 52, 1609—1622).—The mixture of stereoisomeric 1:4-dimethylcyclohexanes obtained by catalytic reduction of *p*-xylene absorbs oxygen at the ordinary temperature in diffused light, but at a slower rate than 1:3-dimethylcyclohexane (A., 1927, 452). The rate of oxidation increases in sunlight or at 100° in diffused light. When a pure specimen of the hydrocarbon is used the initial absorption of oxygen is slow; absorption is catalysed by a small amount of oxidised material. The gaseous products formed during the oxidation are carbon monoxide, carbon dioxide, hydrogen, methane, and probably ethane. Separation of the remainder of the reaction product into (a) acid and (b) neutral parts gives (a) acetic, β-methylvaleric, and δ-acetyl-β-methylvaleric acid, b. p. 141.2°/2.5 mm. (semicarbazone, m. p. 153°) (prepared by oxidation of 1:4-dimethyl-Δ<sup>1</sup>-cyclohexene, b. p. 127.6—128.1°/753.4 mm., *d*<sub>4</sub><sup>20</sup> 0.8051, with 2% potassium permanganate solution), and (b) 1:4-dimethylcyclohexanol (main product), acetonylacetone, and two stereoisomeric 1:4-dimethylcyclohexane-1:4-diols, m. p. 193° and 165.5—166°. These are converted by hydrochloric acid into the corresponding 1:4-dichloro-1:4-dimethylcyclohexanes, m. p. 46—49° and 38.6—39.3°, respectively. H. BURTON.

**Behaviour of allyl derivatives of pyrocatechol and resorcinol towards heat.** C. D. HURD, H. GREENGARD, and F. D. PILGRIM (J. Amer. Chem. Soc., 1930, 52, 1700—1706).—Resorcinol monoallyl ether, b. p. 122°/2 mm., *n*<sub>D</sub><sup>20</sup> 1.5525, is prepared from resorcinol and allyl bromide in presence of acetone and potassium carbonate; a similar method is used for all the ethers mentioned in this paper, some of which undergo rearrangement when distilled. Rearrangement of the above ether occurs at 210—220°; 4-allylresorcinol, b. p. 144—146°/5 mm. (dimethyl ether, b. p. 82—85°/4 mm., *n*<sub>D</sub><sup>20</sup> 1.5318), is produced. Treatment of this with potassium hydroxide at 180°, and subsequent methylation and permanganate oxidation of the product formed gives 2:4-dimethoxybenzoic acid. Resorcinol diallyl ether, b. p. 149—153°/4 mm., rearranges at 210° into 4:6-diallylresorcinol, b. p. 160—163°/5 mm.; the diallyl ether



of this when distilled in a vacuum gives 3-allyloxy-2:4:6-triallylphenol, b. p. 182—184°/5 mm. (phenyl-carbimide derivative, m. p. 160—161°). Pyrocatechol diallyl ether rearranges at 180° into 3:6-di-allylpyrocatechol, b. p. 165—170°/25 mm. (lead salt), also formed during the distillation of 3-allylpyrocatechol monoallyl ether. Triallylpyrocatechol, b. p. 186—189°/22 mm. (lead salt), is obtained from 3:6-diallylpyrocatechol monoallyl ether or 3-allylpyrocatechol diallyl ether. 3:6-Diallylpyrocatechol diallyl ether at 180—200° gives tetra-allylpyrocatechol, b. p. 196—200°/22 mm. (lead salt). H. BURTON.

**Synthesis of some iodinated hydroxydiphenyl sulphides.** S. L. BASS and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 1146—1152; cf. Hilbert and Johnson, A., 1929, 806).—2:6-Di-iodo-4-nitrodiphenyl sulphide, which exists in two crystalline forms, each m. p. 155.5°, is obtained by condensing 3:4:5-tri-iodonitrobenzene with sodium phenyl sulphide in boiling alcohol. Reduction by stannous chloride in hydrochloric acid yields the 4-amino-compound, m. p. 146° [hydrochloride, m. p. 192° (decomp.)], which, when diazotised in acetic acid with butyl nitrite and the product decomposed with dilute sulphuric acid, yields 2:6-di-iodo-4-hydroxydiphenyl sulphide, m. p. 92—95° (+H<sub>2</sub>O), 139° (anhydrous). 2:6-Di-iodo-4-nitro-4'-methylidiphenyl sulphide, two crystalline forms, each m. p. 121—122°, the 4-amino-compound, m. p. 197—198° [hydrochloride, m. p. 182° (decomp.)], and the 4-hydroxy-compound, m. p. 154°, are obtained similarly.

An attempt to apply Ziegler's method (A., 1890, 1292) was unsuccessful. 2:5-Di-iodoanisole-4-diazonium chloride couples with thiophenol to give 3:5-di-iodo-4-methoxybenzenediazothiophenyl ether, m. p. 91°, from which no sulphide is obtainable. The required 3:5-di-iodo-4-hydroxydiphenyl sulphide, m. p. 84—85°, is prepared by iodination of *p*-hydroxydiphenyl sulphide in ammonia solution with iodine. 3:5-Di-iodo-4-hydroxy-4'-methylidiphenyl sulphide, m. p. 112—113°, is obtained similarly.

The following are also described: *p*-methoxy-*p*'-nitrodiphenyl sulphide, m. p. 71°; the *p*'-amino-compound, m. p. 96° (hydrochloride, m. p. 205—207°), and *p*'-iodo-compound, m. p. 102°, b. p. 202—205°/3—4 mm., and *p*-hydroxy-*p*'-iododiphenyl sulphide, m. p. 111—112°, b. p. 205—210°/3—4 mm.

All these phenols are extremely insoluble in water and therefore do not exhibit bactericidal activity when tested in the usual way. R. K. CALLOW.

**Conjugated systems. IV. Addition of hypochlorous and hypobromous acids to phenylbutadiene.** I. E. MUSKAT and L. B. GRIMSLEY (J. Amer. Chem. Soc., 1930, 52, 1574—1580).—Treatment of  $\alpha$ -phenylbutadiene with 1 mol. of dilute hypochlorous acid gives  $\delta$ -chloro- $\alpha$ -phenyl- $\Delta^a$ -buten- $\gamma$ -ol (corresponding dichloride, b. p. 164°/5 mm.), which on distillation in a vacuum eliminates water and hydrogen chloride forming some  $\delta$ -chloro- $\alpha$ -phenylbutadiene and a yellow hydrocarbon, C<sub>10</sub>H<sub>10</sub>, m. p. 235°. Treatment of the above chlorohydrin with phosphorus pentachloride in ether affords a mixture of  $\delta$ -chloro- $\alpha$ -phenylbutadiene and  $\gamma$ - $\delta$ -chloro- $\alpha$ -phenyl- $\Delta^a$ -butene, whilst with hypochlorous

acid a mixture of  $\beta\delta$ -dichloro- $\alpha$ -phenylbutan- $\alpha$ - $\gamma$ -diols is probably produced. The chlorohydrin and a large excess of hypochlorous acid afford a trichloro- $\alpha$ -phenylbutanol, b. p. 164—167°/5 mm.  $\delta$ -Bromo- $\alpha$ -phenyl- $\Delta^a$ -buten- $\gamma$ -ol is obtained similarly with hypobromous acid; this absorbs a second molecule of hypobromous acid. Treatment of the chloro- or bromo-hydrin with powdered potassium hydroxide in dry ether furnishes impure styrylethylene oxide, b. p. 94°/6 mm. H. BURTON.

**Substitution and addition. III. Displacement [of the double linking] in the allyl group.** J. MEISENHEIMER and J. LINK (Annalen, 1930, 479, 211—277).—The isomerisation of derivatives of phenyl- and ethyl-substituted allyl alcohols under various conditions is described. The main results are as follows. Cinnamyl and  $\alpha$ -phenylallyl alcohols yield only cinnamyl halides when treated with the anhydrous hydrogen halide (the iodide being best obtained by the action of concentrated hydriodic acid on the ether, alcohol, chloride, or bromide in acetic acid). Hydrolysis of cinnamyl chloride with boiling 15% aqueous potassium hydroxide or cold sodium hydroxide solution gives mainly dicinnamyl ether together with small quantities of cinnamyl alcohol and  $\alpha$ -phenylallyl alcohol. Contrary to Braun and Köhler (A., 1918, i, 162), the ether is the main product when cinnamyl bromide is warmed with water. Contrary to Klages and Klenk (A., 1906, i, 638), the sole product of the action of absolute-alcoholic potassium hydroxide at the ordinary temperature on cinnamyl halides is cinnamyl ethyl ether. With 70% aqueous-alcoholic potassium hydroxide cinnamyl chloride gives 20—25%, and with silver oxide in absolute alcohol 35—45% (similar results with silver nitrate), of  $\alpha$ -phenylallyl ethyl ether, b. p. 86.5—87°/13 mm., reduced with hydrogen and platinum-black in acetic acid to  $\alpha$ -phenyl-*n*-propyl ethyl ether, which is synthesised by the action of ethyl iodide on the sodio-derivative of phenylethylcarbinol, prepared from the alcohol and molecular sodium in xylene, Straus and Berkow's method (A., 1913, i, 1317), giving mainly  $\beta$ -methylstyrene. Acetylation of cinnamyl or  $\alpha$ -phenylallyl alcohol with acetyl chloride and pyridine gives the corresponding acetates, hydrolysed to the original alcohol. Cinnamyl acetate is unchanged after heating with potassium acetate and acetic acid, but  $\alpha$ -phenylallyl acetate isomerises moderately rapidly under these conditions (30% in 1 hr.; 75% in 4 hrs.), and the proportions given in the following results are corrected accordingly. Cinnamyl chloride heated with acetic acid and excess of potassium acetate at 100° for 1 hr. gives 40—45% of  $\alpha$ -phenylallyl acetate, a residue of high b. p. being obtained. With silver acetate under similar conditions this residue amounts to 50% of the product, whilst only 12—15% of isomerisation occurs. With silver acetate at 75—95° and 50—55°, the proportions of  $\alpha$ -phenylallyl acetate are 30—35 and 37%, the residue being reduced to 25 and 10%, respectively. Ethylaniline converts cinnamyl chloride exclusively into cinnamylethylaniline, m. p. 50° (picrate, m. p. 121°), reduced by hydrogen and platinum-black in ether to  $\gamma$ -phenyl-*n*-propylethylaniline, b. p. 140—145°/0.5—1 mm. (converted in the usual manner into phenyl-

( $\gamma$ -phenyl- $n$ -propyl)methylethylammonium picrate, m. p. 111–112°), also synthesised from  $\gamma$ -phenyl- $n$ -propyl iodide and ethylaniline. Other reducing agents cause fission of the molecule. Dry hydrogen chloride converts  $\Delta^{\alpha}$ -penten- $\gamma$ -ol ( $\alpha$ -ethylallyl alcohol) into a mixture of the corresponding chloride (40%) and  $\alpha$ -chloro- $\Delta^{\beta}$ -pentene (60%). A similar mixture (30 and 70%, respectively) is obtained from  $\Delta^{\beta}$ -penten- $\alpha$ -ol. Phosphorus trichloride acts on  $\Delta^{\alpha}$ -penten- $\gamma$ -ol in accordance with the scheme  $3\text{ROH} + \text{PCl}_3 \longrightarrow \text{P(OR)}_3 + 3\text{HCl} \longrightarrow \text{P(OH)}_3 + 3\text{RCl}$  (Milobendski and Sachnowski, A., 1918, i, 477), since addition of pyridine removes the hydrogen chloride formed and *dipentenyl hydrogen phosphite* (?), b. p. 81–83°/1 mm., can be isolated after pouring the product into water, whilst saturation of the pyridine reaction mixture with dry hydrogen chloride prior to pouring into water raises the proportion of  $\gamma$ -chloro- $\Delta^{\alpha}$ -pentene to 55–59%. The interaction of  $\Delta^{\alpha}$ -penten- $\gamma$ -ol with 1 mol. of thionyl chloride follows a similar course, yielding 24–26% of the corresponding chloride either in ether or without solvent, but addition of 1 mol. of diethylaniline increases the proportion of  $\gamma$ -chloro- $\Delta^{\alpha}$ -pentene to 45%.  $\Delta^{\beta}$ -Penten- $\alpha$ -ol is converted by thionyl chloride in ether into a mixture containing 80% of the secondary chloride. In boiling acetic acid the  $\alpha$ -chloro-compound is only slightly isomerised in 2.5 hrs., but 20% of the  $\gamma$ -chloro-compound isomerises in 8 hrs. Contrary to Prévost (A., 1928, 1211), a mixture of bromo-compounds results from the action of either hydrogen bromide or phosphorus tribromide on  $\Delta^{\alpha}$ -penten- $\gamma$ -ol. Each alcohol is converted by acetyl chloride and pyridine into the corresponding acetate, which hydrolyses to the original alcohol. When heated in glacial acetic acid with potassium acetate  $\alpha$ -chloro- $\Delta^{\beta}$ -pentene gives 7–8% (in 4.5–5 hrs.) and  $\gamma$ -chloro- $\Delta^{\alpha}$ -pentene 57–58% (in 24 hrs.) of the  $\gamma$ -acetate, the corresponding proportions when silver acetate is used being 40–45% (in 5 hrs.) and 46–47% (in 6 hrs.). Although no isomerisation of the chloro-compounds occurs when they are boiled with diethylaniline, both are converted by heating with methylaniline into *phenyl- $\Delta^{\beta}$ -pentenylmethylamine*, b. p. 130–131°/15 mm. (*picrate*, m. p. 89–90°), reduced by hydrogen and platinum-black in ether to *n-amylmethylaniline*, b. p. 129–131°/15 mm. (*picrate*, m. p. 97.5°), identical with a synthetic specimen. Similarly with diethylamine, the sole product from either chloride is *diethyl- $\Delta^{\beta}$ -pentenylamine*, b. p. 156–158°/735 mm. (*picrate*, m. p. 39–41°) (erroneously described throughout as the dimethyl compound), reduced to *diethyl- $n$ -amylamine*, b. p. 50–51°/15 mm., 155–158°/735 mm. (*picrate*, m. p. 55–56.5°), identical with a synthetic specimen. When  $\alpha$ -chloro- $\Delta^{\beta}$ -pentene is heated with potassium phthalimide in a sealed tube at 190–200° it gives a mixture of  $\alpha$ -*phthalimido- $\Delta^{\beta}$ -pentene*, m. p. 69–70°, b. p. 180°/14 mm., and a small amount (10%) of  $\gamma$ -*phthalimido- $\Delta^{\alpha}$ -pentene*, m. p. 78–79°, the former being reduced catalytically to *n-amyl-phthalimide*, b. p. 175°/14 mm., m. p. 16–17° (also synthesised from *n*-amyl bromide and potassium phthalimide). By hydrolysis of the  $\alpha$ - and  $\gamma$ -phthalimido-derivatives with alkali to the corresponding amic acids and subsequent hydrolysis of these with

concentrated hydrochloric acid are obtained  $\alpha$ -amino- $\Delta^{\beta}$ -pentene, b. p. not sharp about 110–113° (*picrate*, m. p. 169°), and  $\gamma$ -amino- $\Delta^{\alpha}$ -pentene, isolated only as its *picrate*, m. p. 154°. Diazotisation of  $\alpha$ -amino- $\Delta^{\beta}$ -pentene in acetic acid gives a mixture of  $\Delta^{\beta}$ -pentenyl acetate (75%) and  $\alpha$ -ethylallyl acetate (25%). Similar diazotisation of  $\gamma$ -amino- $\Delta^{\alpha}$ -pentene occurs much less readily, isomerisation occurring, but quantitative results could not be obtained. Both  $\alpha$ -chloro- $\Delta^{\beta}$ - and  $\gamma$ -chloro- $\Delta^{\alpha}$ -pentene are hydrolysed by water, the former more readily than the latter. By long shaking with aqueous sodium carbonate the former gives a mixture of  $\Delta^{\beta}$ -penten- $\alpha$ -ol (45%) and  $\Delta^{\alpha}$ -penten- $\gamma$ -ol (55%), the corresponding proportions when  $\gamma$ -chloro- $\Delta^{\alpha}$ -pentene is similarly hydrolysed being 31.5 and 68.5%, respectively, 33% of the chloro-compound remaining unattacked in each case.  $\alpha$ -Chloro- $\Delta^{\beta}$ -pentene is converted by absolute or aqueous-alcoholic potassium hydroxide, or by silver oxide in absolute alcohol, mainly into ethyl  $\Delta^{\beta}$ -pentenyl ether. The results are discussed on the basis of various theories of the mechanism of such isomeric changes, and it is considered that they cannot be explained on the assumption that either the original substance or the reaction product undergoes spontaneous rearrangement, nor on Moureu and Gallagher's theory (A., 1922, i, 34) of water elimination subsequent to addition, on Prévost's "synionie" theory (A., 1928, 1111) or the related theory of anionotropic changes due to Burton and Ingold (A., 1928, 634; 880). A theory is summarised, which is based essentially on an extension of that already developed (A., 1927, 957), preliminary formation of an additive product by means of auxiliary valencies being postulated.

J. W. BAKER.

**Synthetic experiments with *l*- $\gamma$ -phenylbutyl alcohol.** H. RUPE and F. VAN WALRAVEN (Helv. Chim. Acta, 1930, 13, 361–377).—Ethyl  $\beta$ -phenyl- $\Delta^{\alpha}$ -butenoate is reduced rapidly (the free acid only slowly) by hydrogen in presence of dilute alcohol and a nickel catalyst to ethyl  $\beta$ -phenylbutyrate, which on further reduction with sodium and alcohol gives a 66% yield of *r*- $\gamma$ -phenylbutyl alcohol. Decomposition of the Grignard reagent from  $\gamma$ -phenylbutyl bromide with ammonium chloride solution affords 65% of  $\beta$ -phenylbutane and 20–25% of  $\beta\eta$ -*diphenyl- $n$ -octane*, b. p. 190–191°/11 mm., whilst treatment with acetone, methyl ethyl ketone, and *d*-3- and 4-methylcyclohexanones furnishes *γ*-phenylbutyldimethylcarbinol, b. p. 127°/10 mm., *γ*-phenylbutylmethylcarbinol, b. p. 141–143°/11 mm., *d*-1-*γ*-phenylbutyl-3-methylcyclohexan-1-ol, b. p. 85°/0.01 mm.,  $d_n^{20}$  0.9695,  $[\alpha]_D^{20} +29.97^\circ$ , and 1-*γ*-phenylbutyl-4-methylcyclohexan-1-ol, b. p. 172–173°/10 mm., respectively.  $\gamma$ -Phenylbutyl bromide and sodium *d*-oxymethylcneamphor react in alcohol, yielding *γ*-phenylbutoxymethylene-camphor, b. p. 110.5–111°/0.003 mm.,  $d_n^{20}$  1.0263,  $[\alpha]_D^{20} +131.05^\circ$ .

Treatment of a solution of  $\beta$ -phenylbutyryl chloride in benzene with menthol dissolved in pyridine, subsequent removal of volatile products with steam, and twofold crystallisation of the residual solid (freed from oil by filtration) from alcohol gives menthyl  $\beta$ -phenylbutyrate, m. p. 47°, reduced by sodium and alcohol to *l*- $\gamma$ -phenylbutyl alcohol, b. p. 117.5°/10

mm.,  $d_4^{25}$  0.9858,  $[\alpha]_D^{25}$   $-39.56^\circ$  (cf. Cohen, J.C.S., 1915, 107, 901). Magnesium *l*- $\gamma$ -phenylbutyl bromide reacts with 4- and *d*-3-methylcyclohexanones forming 1- $\gamma$ -phenylbutyl-4-methylcyclohexan-1-ol, b. p.  $172-173^\circ/10$  mm.,  $d_4^{25}$  0.9712,  $[\alpha]_D^{25}$   $-11.2^\circ$ , and 1- $\gamma$ -phenylbutyl-3-methylcyclohexan-1-ol, b. p.  $173^\circ/10.5$  mm.,  $d_4^{25}$  0.9696,  $[\alpha]_D^{25}$   $+5.12^\circ$ , respectively.  $\gamma$ -Phenylbutoxymethylenecamphor, prepared from the active bromide, has b. p.  $110.5-111^\circ/0.001-0.002$  mm.,  $d_4^{25}$  1.0297,  $[\alpha]_D^{25}$   $+40.34^\circ$ . All the above optically active compounds show normal dispersion.

Reduction of the oily residue from the preparation of the solid menthyl ester with sodium and alcohol gives an alcohol,  $\alpha_D +8.26^\circ$ , which could not be purified through the hydrogen phthalate. H. BURTON.

$\beta$ -Benzyl-*n*-hexyl and  $\gamma$ -phenyl- $\beta$ -benzyl-*n*-propyl alcohols and isomeric  $\beta$ -benzyl-*n*-hexan- $\beta$ -ol and  $\alpha$ -phenyl- $\beta$ -benzylpropan- $\beta$ -ol. R. DOLIQUE (Compt. rend., 1930, 190, 878-880).—Ethyl benzyl-*n*-butylmalonate, b. p.  $187^\circ/15$  mm.,  $d_4^{25}$  1.028, prepared by successive butylation (60% yield) and benzylation (45-50% yield) of ethyl malonate, is hydrolysed to the acid, m. p.  $104^\circ$ , with alcoholic sodium hydroxide, and further converted by heating into benzyl-*n*-butylacetic acid, b. p.  $179^\circ/10$  mm.,  $d_4^{25}$  1.001 (ethyl ester, b. p.  $155-156^\circ/16$  mm. or  $274^\circ/756$  mm.,  $d_4^{25}$  0.959; benzyl ester, b. p.  $223^\circ/16$  mm., from acid chloride and benzyl alcohol). Reduction of ethyl benzyl-*n*-butylacetate with sodium and alcohol gives  $\beta$ -benzyl-*n*-hexyl alcohol, b. p.  $170-171^\circ/27$  mm.,  $d_4^{25}$  0.943 (phenylurethane, m. p.  $55.5^\circ$ ), in 60% yield. The isomeric  $\beta$ -benzyl-*n*-hexan- $\beta$ -ol, b. p.  $155^\circ/27$  mm.,  $d_4^{25}$  0.947, is obtained from benzyl methyl ketone and magnesium *n*-butyl bromide.  $\gamma$ -Phenyl- $\beta$ -benzyl-*n*-propyl alcohol, m. p.  $27-28^\circ$ , b. p.  $197^\circ/10$  mm.,  $d_4^{25}$  1.046 (phenylurethane, m. p.  $94^\circ$ ), accompanied by a little  $\gamma$ -phenyl- $\beta$ -benzylpropylamine (benzoyl derivative, m. p.  $102.5-103^\circ$ ), is obtained in 55% yield by reduction of the corresponding amide. The interaction between ethyl acetate and magnesium benzyl chloride affords  $\alpha$ -phenyl- $\beta$ -benzylpropan- $\beta$ -ol, b. p.  $182^\circ/15$  mm.,  $d_4^{25}$  1.026, decomposed into diphenylpropylene on distillation at the ordinary pressure. Benzyl dibenzylacetate, from dibenzylacetyl chloride and benzyl alcohol, has m. p.  $81^\circ$ . A. I. VOGEL.

Action of sulphur on organic compounds. L. SZPERL [with R. GOLDFLAMÓWNA and M. ZAWADZKI] (Rocz. Chem., 1930, 10, 253-258).—Phenyl- $\alpha$ -naphthylcarbinol when heated with traces of sulphur at  $195-205^\circ$  yields phenyl- $\alpha$ -naphthylcarbinyl ether. Prolonged heating at  $240^\circ$  of mixtures containing 1 atom of sulphur per mol. of carbinol yields phenyl- $\alpha$ -naphthyl ketone (oxime, m. p.  $152.5-154^\circ$ ), and 1-benzyl-naphthalene, produced by reduction of the ketone by hydrogen sulphide. The m. p. and the properties of the above oxime are different from those given by Kegel (A., 1888, 1307) and by Spiegler (A., 1884, 1182). R. TRUSZKOWSKI.

Action of diazomethane on aromatic acyl chlorides. V. Mechanism of the reaction. T. MALKIN and M. NIERENSTEIN (J. Amer. Chem. Soc., 1930, 52, 1504-1508).—The reaction between diazomethane and benzoyl chloride is considered to occur as postulated by Lewis, Nierenstein, and Rich (A.,

1925, i, 935). The diazo-compound, when formed, is considered to be a cyclic diazo-anhydride. The mechanism put forward by Bradley and Robinson (A., 1928, 759, 1009) is held to be unfounded on these authors' experimental data (cf. Bradley and Schwarzenbach, A., 1929, 68). H. BURTON.

Action of diazomethane on benzoic and succinic anhydrides, and a reply to Malkin and Nierenstein. W. BRADLEY and R. ROBINSON (J. Amer. Chem. Soc., 1930, 52, 1558-1565).—Benzoic anhydride (1 mol.) and diazomethane (2.5 mols.) react in cold ethereal solution, forming methyl benzoate and diazoacetophenone. Under similar conditions succinic anhydride gives a 73% yield of methyl succinate, but when moisture or alcohols are rigidly excluded, methyl succinate, a diazo-compound, and unidentified products are obtained. Succinic anhydride and diazomethane apparently form a complex which is abnormally reactive towards water.

The authors reaffirm their previously proposed mechanism (A., 1928, 759) of the reaction between diazomethane and benzoyl chloride.  $\alpha$ -Chloroacetophenone is formed by the action of hydrogen chloride on diazoacetophenone; the conditions described by Malkin and Nierenstein (preceding abstract) favour this process. Diazoacetophenone is readily decomposed by cold solutions of hydrogen chloride, and it is unlikely that it possesses a diazo-anhydride structure as suggested by Malkin and Nierenstein (*loc. cit.*). H. BURTON.

[Preparation of] *o*-chlorobenzoic acid. H. T. CLARKE and E. R. TAYLOR (Organic Syntheses, 1930, 10, 20-21).

Nitration of *o*-fluorobenzoic acid. F. GOVAERT (Bull. Soc. chim. Belg., 1930, 39, 101-124).—Nitration of *o*-fluorobenzoic acid, prepared in 75% yield by the oxidation of *o*-fluorotoluene with solid potassium permanganate, with nitric acid alone, or in the presence of sulphuric acid, gives as main product 2-fluoro-5-nitrobenzoic acid (sodium,  $+H_2O$ , barium,  $+4H_2O$ , and silver salts) (I) (95%), m. p.  $139^\circ$ , together with an acid (II), m. p.  $115^\circ$ , the latter being isolated by ether extraction of the mother-liquors. I is converted by sodium ethoxide into 5-nitro-2-ethoxybenzoic acid, m. p.  $160^\circ$  (ethyl ester, m. p.  $88^\circ$ ; lit.  $68^\circ$  and  $98^\circ$ ), and further by aqueous hydrobromic acid into 5-nitrosalicylic acid, m. p.  $228^\circ$  (anilide, m. p.  $224^\circ$ ). II is a compound of 2 mols. of I and 1 mol. of 2-fluoro-3-nitrobenzoic acid, since treatment with sodium ethoxide yields a mixture of 5-nitro-2-ethoxybenzoic acid and impure 3-nitro-2-ethoxybenzoic acid, m. p.  $76-80^\circ$ , and aqueous sodium hydroxide gives a mixture of 3- and 5-nitrosalicylic acids, the relative proportions of which were determined by thermal analysis.

The conductivity of 2-fluoro-5-nitrobenzoic acid and of its sodium salt has been measured over a range of dilutions and the dissociation constant  $K_1 = 1.88 \times 10^{-3}$  (decreasing slightly at high dilutions) evaluated.

Attempts to prepare 2-fluoro-3-nitrotoluene from 2-iodo-*m*-nitrotoluene and from 3-nitro-*o*-toluidine were unsuccessful. A. I. VOGEL.

**2-Iodo-5-nitrobenzoic acid.** H. GOLDSTEIN and A. V. GRAMPOLOV (Helv. Chim. Acta, 1930, 13, 310—314).—Nitration of *o*-iodobenzoic acid with a mixture of nitric (*d* 1.52) and sulphuric acids at 130—135° gives 2-iodo-5-nitrobenzoic acid (I), m. p. 194° [methyl ester (II), m. p. 123°; ethyl ester, m. p. 98°; acid chloride, m. p. 83°; amide, m. p. 231°; anilide, m. p. 203°], also prepared by the usual method from 5-nitroanthranilic acid. The 2-iodonitrobenzoic acid described by Gumbel (A., 1894, i, 32) and the methyl 2-iodonitrobenzoate of Reverdin (A., 1898, i, 180) are identical with I and II, respectively.

[With E. CORNAMUSAZ.]—Treatment of 2-iodo-5-nitrobenzoic acid with 20% potassium hydroxide solution and a small amount of copper-bronze at 110—120° affords 5-nitrosalicylic acid. 4-Nitrodiphenylamine-2-carboxylic acid is obtained by the action of boiling aniline.

H. BURTON.

**Salts of nitriles. III. Sodiophenylacetone-nitrile.** M. M. RISING and G. BRAUN (J. Amer. Chem. Soc., 1930, 52, 1069—1074).—The preparation and isolation of pure sodiophenylacetone-nitrile (cf. A., 1928, 881; 1929, 312) are described in detail. It is established that the reaction by which it is formed with simultaneous production of toluene is:  $2\text{CH}_2\text{Ph}\cdot\text{CN} + 2\text{Na} = 2[\text{CHPh}\cdot\text{CN}]\text{Na} + 2\text{H}$ ;  $[\text{CHPh}\cdot\text{CN}]\text{Na} + 2\text{H} = \text{PhMe} + \text{NaCN}$ . Sodiophenylacetone-nitrile yields phenylacetone-nitrile quantitatively when treated with acids, and treatment of the ethereal solution of the salt with ethyl iodide yields  $\alpha$ -phenylbutyronitrile. Reduction of the salt with sodium in alcohol yields toluene and sodium cyanide.

R. K. CALLOW.

**Peptide-like substances. XXX. Peptides of dehydro-amino-acids, their behaviour towards pancreatic enzymes, and their use in peptide synthesis.** M. BERGMANN, V. SCHMITT, and A. MIEKELEY (Z. physiol. Chem., 1930, 187, 264—276).—The azlactone of chloroacetyldehydrophenylalanine (2-chloromethyl-4-benzylidene-5-oxazolone), m. p. 114° (corr.), obtained by warming chloroacetylserine with acetic anhydride, on ring hydrolysis gives chloroacetyldehydrophenylalanine, m. p. 207° (corr.) [amide, m. p. about 189° (corr.)]. With ammonia, the halogenated peptide yields glycyldehydrophenylalanine, m. p. 277° (corr., decomp.). It is hydrolysed by Merck's pancreatin, unlike the chloroacetyl compound. The azlactone with glycine yields chloroacetyldehydrophenylalanylglycine, darkens at 185°, m. p. above 200° (decomp.). Methyl-alcoholic ammonia gives glycyldehydrophenylalanylglycine, darkens at 215°, decomp. 224°. Catalytic hydrogenation yields glycyl-dl-phenylalanylglycine. With *d*-glutamic acid the azlactone yields chloroacetyldehydrophenylalanyl-*d*-glutamic acid, m. p. 91—92° (decomp.), which with methyl-alcoholic ammonia gives glycyldehydrophenylalanyl-*d*-glutamic acid, darkens 170°, decomp. 174° (corr.). It is hydrolysed by pancreatin. Hydrogenation gives a mixture of glycyl-*d*-phenylalanyl-*d*-glutamic acid, decomp. 199—200°,  $[\alpha]_D^{20} -10.8$ , and glycyl-*l*-phenylalanyl-*d*-glutamic acid, m. p. 204° (corr.),  $[\alpha]_D^{20} -4.7$ .

J. H. BIRKINSHAW.

**Photobromination of organic compounds having an ethylenic double linking.** A. BERTHOUD.—See this vol., 718.

**cycloButylalkylalkylacetic** [ $\beta$ -cyclobutyl- $\alpha$ -alkylpropionic] acids and their bactericidal action towards *B. lepræ*. XVI. S. G. FORD and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 1259—1261).—A series of cyclobutylmethylalkylacetic acids,  $\text{C}_4\text{H}_7\cdot\text{CH}_2\cdot\text{CHR}\cdot\text{CO}_2\text{H}$ , has been prepared by the malonic ester synthesis from cyclobutylmethyl bromide and the appropriate ethyl alkylmalonates. Ethyl cyclobutane-1:1-dicarboxylate is reduced by sodium and alcohol in toluene to cyclobutylcarbinol, from which the bromide is obtained by treatment with phosphorus tribromide in ether-pyridine solution. The following ethyl cyclobutylmethyl-alkyl-malonates are described: -*n*-octyl-, b. p. 160—163°/3 mm.,  $d_4^{25} 0.9558$ ,  $n_D^{25} 1.4558$ ; -*n*-nonyl-, b. p. 168—171°/2.8 mm.,  $d_4^{25} 0.9552$ ,  $n_D^{25} 1.4569$ ; -*n*-decyl-, b. p. 177—181°/3 mm.,  $d_4^{25} 0.9466$ ,  $n_D^{25} 1.4578$ ; -*n*-undecyl-, b. p. 188—191°/3.2 mm.,  $d_4^{25} 0.9458$ ,  $n_D^{25} 1.4582$ ; -*n*-dodecyl-, b. p. 196—199°/3 mm.,  $d_4^{25} 0.9393$ ,  $n_D^{25} 1.4590$ , and  $\alpha$ -cyclobutylmethyl derivatives of the following acids: -*n*-decanoic, b. p. 150—152°/2 mm.,  $d_4^{25} 0.9154$ ,  $n_D^{25} 1.4615$ ; -*n*-undecanoic, b. p. 177—181°/3.5 mm.,  $d_4^{25} 0.9124$ ,  $n_D^{25} 1.4622$ ; -*n*-dodecanoic, b. p. 176—179°/2.7 mm.,  $d_4^{25} 0.9095$ ,  $n_D^{25} 1.4628$ ; -*n*-tridecanoic, b. p. 188—192°/2.5 mm.,  $d_4^{25} 0.9080$ ,  $n_D^{25} 1.4635$ ; -*n*-tetradecanoic, b. p. 204—205°/2.5 mm.,  $d_4^{25} 0.9046$ ,  $n_D^{25} 1.4642$ .

The acids containing 16 to 18 carbon atoms show the greatest bactericidal action, comparable with that of other ring acids of the same mol. wt. R. K. CALLOW.

**Phenylation of oleic acid.** E. G. SCHMIDT (J. Amer. Chem. Soc., 1930, 52, 1172—1174).—Phenylation of oleic acid with the production of phenylstearic acid proceeds with great speed in the presence of approximately equimolecular quantities of oleic acid and aluminium chloride with an excess of benzene. A considerable excess of aluminium chloride or prolonged boiling of the reaction mixture produces compounds having lower neutralisation equivalents than that of phenylstearic acid. R. K. CALLOW.

**Ethyl esters of chaulmoogric acid.** M. LORA Y TAMAYO (Anal. Fis. Quim., 1930, 28, 177—178).—Ethyl chaulmoograte, prepared by Perkins' method, conforms to the specification of the United States Pharmacopœia. H. F. GILLBE.

**Hydrazide and azide of *p*-ethoxybenzoic acid.** T. CURTIUS and W. ULMER (J. pr. Chem., 1930, [ii], 125, 54—62).—Ethyl *p*-ethoxybenzoate, b. p. 142°/11 mm., and hydrazine hydrate afford *p*-ethoxybenzhydrazide, m. p. 124° (hydrochloride, m. p. 216°; benzylidene, m. p. 197°; salicylidene, m. p. 192°; *m*-methoxybenzylidene, m. p. 190°; *m*-nitrobenzylidene, m. p. 174°; *p*-nitrobenzylidene, m. p. 206°; isopropylidene, m. p. 130°; *N*-phenylisatin, m. p. 185°, and acetyl, m. p. 172°, derivatives), which when treated with dilute sodium hydroxide in alcoholic solution gives *p*-ethoxybenzaldehyde-*p*-ethoxybenzoylhydrazone, m. p. 207° (hydrolysis products hydrazine, *p*-ethoxybenzaldehyde, and *p*-ethoxybenzoic acid). The hydrazide is converted by the usual method into *p*-ethoxybenzazide, m. p. 31°, which on treatment with ammonia and aniline furnishes *p*-ethoxybenzamide and *p*-ethoxybenzanilide, respectively. When the azide is heated in carbon tetrachloride solution *p*-ethoxyphenylcarbimide, b. p. 110°/11 mm., is obtained.

*s*-Di-*p*-ethoxyphenylcarbamide, m. p. 226°, *s*-phenyl-*p*-ethoxyphenylcarbamide, m. p. 186°, and *ethyl p*-ethoxyphenylcarbamate, m. p. 94°, are prepared from the carbimide. Treatment of the above carbamate with hydrochloric acid at 120° gives *p*-aminophenol [hydrochloride, m. p. 230° (decomp.)].

H. BURTON.

**Benzoylformic acid.** B. B. CORSON, N. E. SANBORN, and P. R. VAN ESS (J. Amer. Chem. Soc., 1930, 52, 1623—1626).—Exposure of a 0.1*N*-aqueous solution of benzoylformic acid, f.p. 64.85±0.05° (corr.) [thiosemicarbazone, m. p. 188—189° (corr.; decomp.); 2:4-dinitrophenylhydrazine, m. p. 196—197° (corr.; decomp.)], to sunlight causes a rapid decomposition to benzaldehyde. Benzoylformic acid phenylhydrazine is formed in 98.1±0.2% yield when an aqueous solution of the acid is treated with phenylhydrazine hydrochloride in presence of a small amount of hydrochloric acid; the acid can be determined gravimetrically by this procedure. The solubilities of the acid in water at 0° and carbon tetrachloride at 0—52° are given.

H. BURTON.

**Catalysts in the preparation of *o*-benzoylbenzoic acid and ethylbenzenes by the Friedel and Crafts reaction.** W. GALLAY and G. S. WHITBY (Canad. J. Res., 1930, 2, 31—34).—In a series of comparative experiments it is shown that in the preparation of *o*-benzoylbenzoic acid from benzene and phthalic anhydride, ferric chloride is a much poorer catalyst than aluminium chloride, but an equimolecular mixture of the two chlorides, although less active than aluminium chloride, has an activity greater than the sum of the activities of its components separately. Ferric chloride is not a catalyst for the combination of benzene and ethylene. Amalgamated aluminium is a better catalyst than aluminium chloride for both reactions.

R. K. CALLOW.

**Organic catalysts. IV. Decarboxylation of phenylglyoxylic and pyruvic acids.** W. LANGENBECK and R. HÜTSCHENREUTER.—See this vol., 714.

**[Preparation of]  $\alpha$ -phenyl- $\beta$ -benzoylpropiononitrile.** C. F. H. ALLEN and R. K. KIMBALL (Organic Syntheses, 1930, 10, 80—81).

**Problem of preparing optically active free radicals.** E. S. WALLIS (Proc. Nat. Acad. Sci., 1930, 16, 215—218).—Various attempts have been made to prepare an optically active derivative of a triarylcarbinol for the purpose indicated in the title. The following method was found to be successful. Phenyl-diphenyl- $\alpha$ -naphthylmethyl chloride reacts with thioglycolic acid in boiling xylene forming *dl*-phenyl-diphenyl- $\alpha$ -naphthylthioglycolic acid, m. p. 116—116.5°, resolved by means of brucine into the *l*-acid, m. p. 109—110°,  $[\alpha]_D^{25}$  -12.93° in ether (the brucine salt, m. p. 215°,  $[\alpha]_D^{25}$  -16.91° in chloroform, is prepared in acetone solution, and purified by crystallisation from chloroform—light petroleum).

H. BURTON.

**Manufacture of halogenoarylthioglycolic acids.** I. G. FARBENIND. A.-G.—See B., 1930, 410.

**[Preparation of] piperonylic acid.** R. L. SHRINER and E. C. KLEIDERER (Organic Syntheses, 1930, 10, 82—83).

**[Preparation of]  $\beta$ -resorcylic acid.** M. NIERENSTEIN and D. A. CLIBBENS (Organic Syntheses, 1930, 10, 94—95).

**Chemistry of the three-carbon system. XXIV. Regeneration of esters from their sodio-derivatives.** W. E. HUGH and G. A. R. KON (J.C.S., 1930, 775—782).—When ethyl cyclopentylidenemalonate (Kon and Speight, A., 1926, 1246, method of preparation improved) is converted by the action of dry sodium ethoxide in light petroleum into the sodio-derivative of the  $\beta\gamma$ -ester and the latter decomposed by benzoic acid in ethereal petroleum, a 30—50% yield of ethyl  $\Delta^1$ -cyclopentenylmalonate, b. p. 147—148°/19 mm.,  $d_4^{25}$  1.0511,  $n_D^{25}$  1.45743, iodine addition (Linstead and May, A., 1927, 1167) 38.4%, is obtained, since under these conditions only the more facile keto-enol change proceeds, whilst the three-carbon tautomeric change involved in the reconversion of the  $\beta\gamma$ -into the  $\alpha\beta$ -ester is largely inhibited. About 30% of the equilibrium ester (mixture of  $\alpha\beta$ - and  $\beta\gamma$ -forms) is also obtained. The  $\beta\gamma$ -ester is also obtained by esterification of the  $\alpha\beta$ -acid with 1% alcoholic hydrogen chloride at the ordinary temperature. Ozonolysis of the  $\beta\gamma$ -ester yields a product, b. p. 140—150°/11 mm., which is both an aldehyde and a  $\beta$ -ketonic ester and probably has the structure  $\text{CHO} \cdot [\text{CH}_2]_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , but on hydrolysis of the  $\beta\gamma$ -ester only the  $\alpha\beta$ -acid is obtained. Replacement of sodium ethoxide by sodium methoxide in the original reaction affords methyl ethyl  $\Delta^1$ -cyclopentenylmalonate, b. p. 137—138°/18 mm.,  $d_4^{25}$  1.09776,  $n_D^{25}$  1.46380, iodine addition 37%. The following are also described, but in none of these cases could similar conversion of the  $\alpha\beta$ - into the  $\beta\gamma$ -ester be accomplished. Condensation of propiophenone with ethyl sodiocyanoacetate in alcohol gives ethyl  $\alpha$ -cyano- $\beta$ -ethylcinnamate, b. p. 185°/15 mm.,  $d_4^{25}$  1.0695,  $n_D^{25}$  1.53803, ethylated through its sodio-derivative to ethyl  $\alpha$ -cyano- $\beta$ -phenyl- $\alpha$ -ethyl- $\Delta^2$ -pentenoate, b. p. 182—186°/16 mm.,  $d_4^{25}$  1.0545,  $n_D^{25}$  1.52175, which, in the presence of 1 mol. of sodium ethoxide at 35°, is converted into  $\beta$ -phenyl- $\alpha$ -ethyl- $\Delta^2$ -pentenonitrile, b. p. 142—146°/14 mm.,  $d_4^{25}$  1.0790,  $n_D^{25}$  1.54052. Condensation of benzyl methyl ketone with ethyl cyanoacetate in the presence of piperidine affords ethyl  $\alpha$ -cyano- $\gamma$ -phenyl- $\beta$ -methyl- $\Delta^2$ -butenoate, b. p. 182—184°/11 mm.,  $d_4^{25}$  1.0790,  $n_D^{25}$  1.53401, converted successively as above into ethyl  $\alpha$ -cyano- $\gamma$ -phenyl- $\beta$ -methyl- $\alpha$ -ethyl- $\Delta^2$ -butenoate, b. p. 190—192°/13 mm.,  $d_4^{25}$  1.0452,  $n_D^{25}$  1.51986, and  $\gamma$ -phenyl- $\beta$ -methyl- $\alpha$ -ethyl- $\Delta^2$ -butenonitrile, b. p. 159—161°/16 mm.,  $d_4^{25}$  0.97806,  $n_D^{25}$  1.52469. Condensation of benzyl methyl ketone with ethyl malonate yields an ester, b. p. 180—188°/14 mm., probably ethyl  $\alpha$ -carbethoxy- $\gamma$ -phenyl- $\beta$ -methyl- $\Delta^2$ -butenoate, hydrolysed to an acid,  $\text{C}_{12}\text{H}_{10}\text{O}_3$ . An attempt to convert ethyl  $\alpha$ -cyanocyclohexylidenemalonate into the corresponding  $\beta\gamma$ -ester was also unsuccessful.

J. W. BAKER.

**Constitution of salts of certain cyclic imides.** T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, 52, 1028—1029).—The additive compounds with alkali hydroxides (*i.e.*, hydrated salts) formed by cyclic imides when shaken in alcohol, acetonitrile, methyl ethyl ketone, or ether with the solid alkali may contain as many molecules of alkali hydroxide as there

are oxygen atoms in the imide. It is concluded that salt formation is dependent on the carbonyl or sulphonyl groups present, and that the metal is attached to oxygen. *Compounds* of sodium (A) and potassium (B) hydroxides with the following in the proportions indicated have been prepared: succinimide (2A); succinanil (A; B; 2A; 2B); phthalimide (2A; 2B); phthalanil (A; B; 2B); saccharin (2A; 2B; 3A; 3B); benzoylphthalimide (B; 2B); acetylphthalimide (B); *o*-toluenesulphonylphthalimide (2B).

R. K. CALLOW.

**Reaction between acid chlorides and nitrosylsulphuric acid.** W. J. DEVERALL and H. W. WEBB (J.C.S., 1930, 720—724).—In extension of previous work (A., 1926, 811) the interaction of *o*-, *m*-, and *p*-nitrobenzoyl and phthalyl chlorides with nitrosylsulphuric acid in carbon tetrachloride solution,  $\text{SO}_2(\text{OH})\cdot\text{O}\cdot\text{NO} + 2\text{R}\cdot\text{COCl} \longrightarrow \text{SO}_2(\text{O}\cdot\text{COR})_2 + \text{NOCl} + \text{HCl}$ , has been investigated. *o*- and *p*-Nitrobenzoyl chlorides readily react to give, respectively, *di-o*- and *di-p*-nitrobenzoylsulphuric acid, completely decomposed by water into sulphuric and nitrobenzoic acids, but converted by heating in boiling pentachloroethane (b. p. 161°) into a mixture of a sulphonic acid and a sulphone. *m*-Nitrobenzoyl chloride does not react with nitrosylsulphuric acid even at 65° without a diluent.

[With L. F. BARRON.]—Both forms of phthalyl chloride seem to react with nitrosylsulphuric acid in accordance with the scheme  $\text{C}_6\text{H}_2\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{O} + 2\text{OH}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO} \longrightarrow \text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\rangle\text{O} +$

$\text{OH}\cdot\text{SO}_2\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{NO} + \text{NOCl} + \text{HCl}$ , and only with the *s*-chloride could a small quantity of a substance,  $\text{C}_6\text{H}_4(\text{CO}_2)_2\text{O}\cdot\text{H}_2\text{S}_2\text{O}_7$ , be isolated.

[With C. K. WILLIAMS.]—It is thought that the reaction between acid chlorides and nitrosylsulphuric acid is preceded by the formation of an additive compound (*loc. cit.*) and, addition to a semipolar linking being unlikely, the action of *o*-, *m*-, and *p*-nitrobenzenesulphonyl (prepared by a modification of Limpricht's method, A., 1875, 1027), toluenesulphonyl, sulphuryl, and thionyl chlorides was investigated. No reaction occurs below 130°, at which temperature the *o*- and *p*-nitrobenzenesulphonyl chlorides react explosively, the *m*-compound still remaining unattacked. The chlorophenols react with nitrosylsulphuric acid to give products  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\cdot\text{OH}$ , which could not be purified, the relative reaction velocities as measured by the rate of evolution of nitrosyl chloride being *m*:*p*:*o*=6.5:4:3. These reactions are discussed on the basis of the relative orienting effects of the substituent groups in aromatic substitution (*cf.* Rule, A., 1924, ii, 645).

J. W. BAKER.

**Action of hydracids on phthalimide-epihydrin.** WEIZMANN and S. MALKOVA (Bull. Soc. chim., 1930, [iv], 47, 356—361).—Potassium phthalimide when heated with excess of epibromohydrin gives 75% of the theoretical yield of *phthalimide-epihydrin*, m. p. 93—94°, hydrolysed by dry hydrogen chloride or by dilute hydrochloric acid to *N*- $\gamma$ -chloro- $\beta$ -hydroxypropylphthalimide, m. p. 96—97°. On further hydrolysis with concentrated hydrochloric acid the latter is converted (yield 75%) into the *hydrochloride* of  $\gamma$ -chloro-

$\beta$ -hydroxypropylamine, the structure of which is shown by its condensation with benzaldehyde to 2-phenyl-5-chloromethyloxazolidine, m. p. 82—83°. Hydrolysis of the phthalimide-epihydrin with hydrogen bromide or with hydrobromic acid similarly yields *N*- $\gamma$ -bromo- $\beta$ -hydroxypropylphthalimide, m. p. 112.5°; refluxing with 48% hydrobromic acid hydrolyses the latter to  $\gamma$ -bromo- $\beta$ -hydroxypropylamine hydrobromide, m. p. 113—113.5°, which with benzaldehyde gives 2-phenyl-5-bromomethyloxazolidine, m. p. 80—81°. With hydrogen iodide or aqueous hydriodic acid the epihydrin gives  $\gamma$ -iodo- $\beta$ -hydroxypropylphthalimide, m. p. 124°, which does not give iodohydroxypropylamine by hydrolysis.

R. BRIGHTMAN.

**New cyclic azoxy-compound.** S. C. HUSSEY, C. S. MARVEL, and F. D. HAGER (J. Amer. Chem. Soc., 1930, 52, 1122—1127).— $\alpha$ -Diphenyl- $\Delta^2$ -propene is reduced by sodium and alcohol to  $\alpha$ -diphenylpropane, nitration of which in sulphuric acid yields  $\alpha$ -4:4'-dinitrodiphenylpropane, m. p. 143—144°. Oxidation of this with chromic acid yields *p*-nitrobenzoic acid, and catalytic reduction yields  $\alpha$ -4:4'-diaminodiphenylpropane hydrochloride, m. p. 232—235°. Nitration of the amino-compound yields  $\alpha$ -2:2'-dinitro-4:4'-diaminodiphenylpropane, m. p. 146.5—148°, which yields only a tar when reduced by King's method (J.C.S., 1920, 117, 988). Diazotisation of the amino-compound and a Sandmeyer reaction yields  $\alpha$ -4:4'-dicyanodiphenylpropane, which is hydrolysed to the 4:4'-dicarboxylic acid, m. p. 258—260°. The latter is nitrated with potassium nitrate in sulphuric acid to give  $\alpha$ -2:2'-dinitrodiphenylpropane-4:4'-dicarboxylic acid, m. p. 273—275°, which is reduced by boiling alcoholic sodium methoxide to give 2:2'-azoxydiphenylethylmethane-4:4'-dicarboxylic acid, a non-crystalline powder, darkening at 270°, decomp. 320—330°. An unsuccessful attempt to resolve this by way of its *brucine* salt (+H<sub>2</sub>O), m. p. 230—243°, [ $\alpha$ ]<sub>D</sub><sup>20</sup>—47.3°, is described.

R. K. CALLOW.

**[Preparation of] pyromellitic acid.** E. PHILIPPI and R. THELEN (Organic Syntheses, 1930, 10, 90—92).

**Constitution of isochondodendrine.** [3-*p*-Carboxyphenoxy-4:5-dimethoxyphthalic acid.] IV. F. FALTIS and H. FRAUENDORFER (Ber., 1930, 63, [B], 806—815; *cf.* A., 1929, 698).—4-Hydroxy-5-methoxyphthalic acid, m. p. 219° (slight decomp.), is prepared by heating metahemipinic acid with concentrated hydrochloric acid at 100° under strictly defined conditions; the corresponding *anhydride*, prepared by protracted heating of the acid at 180°, has m. p. 220°. The acid is transformed by bromine in glacial acetic acid into 3-bromo-4-hydroxy-5-methoxyphthalic acid, m. p. 230° (slight decomp.), which with diazomethane affords methyl bromohemipinate, m. p. 87—88.5°, hydrolysed to bromohemipinic acid, m. p. 175—176° (decomp.). Condensation of the methyl ester with the potassium salt of methyl *p*-hydroxybenzoate affords methyl 3-*p*-carboxymethoxyphenoxy-4:5-dimethoxyphthalate, m. p. 113—114° after softening at 111°, hydrolysed to 3-*p*-carboxyphenoxy-4:5-dimethoxyphthalic acid, m. p. 184—188° (decomp.) after softening at 175° (m. p. greatly dependent on mode



of heating). The acid is identical with that obtained from the product of the degradation of isochondrodendrinate (cf. A., 1922, i, 569; 1928, 433). H. WREN.

**Condensation of secondary amines with aldehydes and naphthols.** J. B. LITTMAN and W. R. BRODE (J. Amer. Chem. Soc., 1930, 52, 1655—1659).—When a mixture of benzaldehyde and  $\beta$ -naphthol in alcohol is treated with dimethylamine a 70.7% yield of 1- $\alpha$ -dimethylaminobenzyl- $\beta$ -naphthol, m. p. 164—164.5° (hydrochloride, decomp. 208—210°), is obtained. 1- $\alpha$ -Diethylaminobenzyl-, m. p. 117—118°, and 1- $\alpha$ -piperidinobenzyl- $\beta$ -naphthols, m. p. 198—198.5° (hydrochloride, decomp. 203—205°), are obtained similarly. The last-named compound is also formed when benzylidenedipiperidine is treated with  $\beta$ -naphthol in alcoholic solution. 1- $\alpha$ -Dimethylaminobenzyl- $\beta$ -naphthol reacts with  $\beta$ -naphthol in benzene forming phenyldi- $\alpha$ -2-hydroxynaphthylmethane (Hewitt and Turner, A., 1901, i, 207). The reactions occurring between benzaldehyde,  $\beta$ -naphthol, and a secondary amine are:  $\text{Ph}\cdot\text{CHO} + 2\text{NHR}_2 \longrightarrow \text{H}_2\text{O} + \text{CHPh}(\text{NR}_2)_2 \xrightarrow{\text{C}_{10}\text{H}_7\cdot\text{OH}} \text{C}_{10}\text{H}_6(\text{OH})\cdot\text{CHPh}\cdot\text{NR}_2 \xrightarrow{\text{C}_{10}\text{H}_7\cdot\text{OH}} \text{CHPh}(\text{C}_{10}\text{H}_6\cdot\text{OH})_2 + \text{NHR}_2$ . H. BURTON.

**Preparation of primary amines from aldehydes and monochloroamine.** C. R. HAUSER (J. Amer. Chem. Soc., 1930, 52, 1108—1111).—When shaken with an excess of cold, aqueous monochloroamine certain aldehydes yield the unstable chloroamines. Benzaldehyde yields an oil which gives benzylideneimine hydrochloride with hydrogen chloride in ether. *p*-Tolualdehyde yields an oil; *o*-chlorobenzaldehyde yields a solid. Reduction of the chloroamines by sodium amalgam in alcoholic acetic acid yields the corresponding amines in 44—68% yield. From *n*-propaldehyde and *n*-butaldehyde there are obtained very unstable chloroamines which give very small yields of the amines.

R. K. CALLOW.

**Intramolecular rearrangement in the isomeric tetrachloro-derivatives of *p*-tolylhydrazones.** F. D. CHATTAWAY and A. B. ADAMSON (J.C.S., 1930, 843—850).—Chlorination (with gaseous chlorine) of *o*-, *m*-, and *p*-nitrobenzaldehyde-*p*-tolylhydrazones in acetic acid at the ordinary temperature yields, initially, the  $\omega$ :3-dichloro-, and subsequently the  $\omega$ :3:5-trichloro-derivatives. Thus the *m*-compound gives  $\omega$ -chloro-*m*-nitrobenzaldehyde-3:5-dichloro-*p*-tolylhydrazone, m. p. 137°, converted by heating with acetic acid and anhydrous sodium acetate into *m*-nitrobenz- $\beta$ -acetyl-3:5-dichloro-*p*-tolylhydrazide,  $\text{C}_6\text{H}_2\text{Cl}_2\text{Me}\cdot\text{N}\cdot\text{Ac}\cdot\text{NH}\cdot\text{COR}$  ( $\text{R}=\text{C}_6\text{H}_4\cdot\text{NO}_2$ ), m. p. 173°. Similarly, the *o*- and *p*-compounds give, initially,  $\omega$ -chloro-*o*-, m. p. 163°, and *p*-, m. p. 163°, -nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone (the latter being converted by alcoholic ammonia into 3-chloro-*p*-tolyl-*p*-nitrobenzenylhydrazidine,  $\text{C}_6\text{H}_3\text{MeCl}\cdot\text{NH}\cdot\text{N}\cdot\text{CR}\cdot\text{NH}_2$ , m. p. 162°, and by acetic acid and sodium acetate into *p*-nitrobenz- $\beta$ -acetyl-3-chloro-*p*-tolylhydrazide, m. p. 164°) and, subsequently,  $\omega$ -chloro-*o*-, m. p. 87°, and *p*-, m. p. 139°, -nitrobenzaldehyde-3:5-dichloro-*p*-tolylhydrazone (the latter being similarly converted into

3:5-dichloro-*p*-tolyl-*p*-nitrobenzenylhydrazidine, m. p. 159°, and *p*-nitrobenz- $\beta$ -acetyl-3:5-dichloro-*p*-tolylhydrazide, m. p. 183°). Warm concentrated aqueous ammonia converts  $\omega$ -chloro-*o*-nitrobenzaldehyde-3-chloro- and -3:5-dichloro-*p*-tolylhydrazones, respectively, into 3-*keto*-1:2-endo-3'-chloro-, exploding at 134°, and -3':5'-dichloro-, exploding at 155°, -*p*-tolylimino-2:3-dihydro-1:2-benzisodiazole 1-oxide (of type  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{ON} \end{smallmatrix}\text{NR}$ ), reduced by stannous chloride and hydrochloric acid to 3-*keto*-1:2-endo-3'-chloro-, m. p. 173°, and 3':5'-dichloro-, m. p. 202°, -*p*-tolylimino-2:3-dihydro-1:2-benzisodiazole, respectively. When the temperature is allowed to rise during chlorination four atoms of chlorine are introduced to give substances for which the structure

$\text{C}_6\text{H}_2\text{Cl}_2\text{Me}\cdot\text{N}\cdot\text{NCl}\cdot\text{N}\cdot\text{CClR}$  is suggested. These do not react with boiling acetic anhydride or hot alcoholic ammonia; they liberate iodine from potassium iodide in dilute acetic acid, and are reduced by phenylhydrazine or tin and cold hydrochloric acid to the  $\omega$ :3:5-trichloro-compounds. Under the influence of hot acetic acid containing a little water they undergo an exothermic isomeric change into compounds for which the structure  $\text{C}_6\text{H}_2\text{Cl}_2\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{N}\cdot\text{CCl}_2\text{R}$  is proposed; these give none of the above reactions of the original compounds, but vigorous reduction with tin and hydrochloric acids gives only 3:5-dichloro-*p*-toluidine, whilst boiling with acetic acid converts them into viscid, amorphous solids which on hydrolysis give only *m*- or *p*-nitrobenzoic acid. Thus are obtained:  $\omega$ -chloro-*m*-, m. p. 95°, and *p*-, m. p. 97°, -nitrobenzaldehyde-3:5-*N*-trichloro-*p*-tolylhydrazone, isomerising to 3:5-dichloro-*p*-tolueneazo-*m*-, m. p. 165°, and *p*-, m. p. 188°, -nitrophenyldichloromethane. Similarly, by chlorination of  $\omega$ -bromo-*m*-nitrobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone is obtained  $\omega$ -bromo-*m*-nitrobenzaldehyde-*N*-chloro-3:5-dibromo-*p*-tolylhydrazone, m. p. 77°, isomerised to 3:5-dibromo-*p*-tolueneazo-*m*-nitrophenylchlorobromomethane, m. p. 157°. J. W. BAKER.

**Reduction of *m*-nitrobenzaldehyde with sodium arsenite.** H. E. BIGELOW and J. H. PHILP (Trans. Nova Scotian Inst. Sci., 1928—9, 17, 193—196).—Reduction of *m*-nitrobenzaldehyde with aqueous sodium arsenite (25% excess of the quantity required for reduction of both nitro- and aldehyde groups) with mechanical stirring at 105—106°, and dilution of the reaction mixture precipitates *m*-azoxybenzyl alcohol, m. p. 86°, in 25% yield. Acidification of the aqueous mother-liquor yields gelatinous *m*-azoxybenzoic acid, decomp. above 300°, which is purified by precipitation of its solution in ammonia with hydrochloric acid, washing with water, and extracting the residual inorganic salts with 90% alcohol in a Soxhlet extractor. J. W. BAKER.

**"Oxidising" action of alkalis. IV. Nitrobenzaldehydes, nitro- and halogeno-benzyl alcohols.** G. LOCK (Ber., 1930, 63, [B], 855—869; cf. this vol., 597).—When *o*-nitrobenzaldehyde is shaken with 35% sodium hydroxide, the mixture becomes warm and completely solidifies suddenly at about 45°; if the change is interrupted at this stage by addition of water, *o*-nitrobenzyl alcohol and *o*-nitro-

benzoic acid are obtained in 91% yield. Disproportionation of *m*- and *p*-nitrobenzaldehyde takes place similarly under like conditions. If the reaction with *o*-nitrobenzaldehyde is not interrupted the temperature rises further; at about 85° a violent change occurs leading, if the temperature is not allowed to exceed 100°, to azotoluene, ammonia, *o*-nitrobenzyl alcohol, *o*-nitrobenzoic acid, and *o*-azobenzoic acid, m. p. 236° (corr., decomp.) [*silver salt*; methyl ester, m. p. 105—106° (corr.)]. *m*-Nitrobenzaldehyde suffers further change rather below 80°, yielding *m*-nitrobenzoic acid and *m*-azoxybenzoic acid, identified as the methyl ester, m. p. 136.5° (corr.), and also by conversion into methyl *m*-azobenzoate, m. p. 161° (corr.). *p*-Nitrobenzaldehyde yields *p*-nitrobenzoic acid and *p*-azoxybenzoic acid [*silver salt*; methyl ester, m. p. 204.5—205° (corr.)].

*o*-Nitrobenzyl alcohol with 35% or 25% sodium hydroxide gives ammonia, hydrocyanic acid, and *o*-azobenzoic acid, whereas *m*- and *p*-nitrobenzyl alcohols afford the corresponding azoxybenzoic acids. With 25% sodium hydroxide, the production of *m*-azoxybenzyl alcohol, m. p. 86°, is also observed.

Disproportionation of halogenobenzaldehyde is not conveniently effected with solid potassium hydroxide, since the reaction is liable to be too violent. The most suitable method consists in the addition of the aldehyde to 50% potassium hydroxide, followed by warming on the water-bath, if necessary with addition of alcohol. The preparation of the corresponding halogenated benzyl alcohols and benzoic acids from *m*-chloro-, *m*-bromo-, *o*-iodo-, and *p*-iodo-benzaldehyde in good yield is recorded. Dehydrogenation of *m*-chloro-, *m*-bromo-, and *p*-iodo-benzyl alcohol with molten potassium hydroxide follows the same lines as that of the hydroxybenzyl alcohol, but the amount of hydrogen liberated is much less (28—42%) and the acids formed are not homogeneous, the production of benzoic acid being established. The halogenobenzaldehydes behave completely analogously to the halogenobenzyl alcohols and hence suffer first disproportionation to the alcohols, which react further with the molten alkali.

H. WREN.

**Reduction of di-*p*-dimethylaminobenzaldazine, benzald-*p*-dimethylaminobenzaldazine, and di-*m*-nitrobenzaldazine in alkaline and acid solution.** T. CURTIUS and A. BERTHO (J. pr. Chem., 1930, [ii], 125, 23—39; cf. A., 1912, i, 137, 307, 505).—Reduction of di-*p*-dimethylaminobenzaldazine, m. p. 256—258° (decomp.; lit. 250—253°) [*dihydrochloride*, m. p. 228—229° (decomp.) after previous softening; *picrate*, m. p. 215° (decomp.)], with sodium amalgam and boiling alcohol gives a 65—67% yield of *s*-pp'-tetramethyldiaminodibenzylhydrazine, m. p. 150—151° (decomp.) (*dibenzoyl derivative*, m. p. 153°). This is readily oxidised to the original azine in presence of acids, since attempted preparation of its hydrochloride and *picrate* results in the formation of the above salts. Acetylation of the hydrazine with acetic anhydride affords the *N*-acetyl derivative, m. p. 127°, of *p*-dimethylaminobenzaldehyde-*p*-dimethylaminobenzylhydrazine, which on hydrolysis with dilute acid yields *p*-dimethylaminobenzaldehyde as the only recognisable product. Reduction of the azine with

zinc dust and alcoholic acetic acid gives impure pp'-tetramethyldiaminodibenzylamine (*picrate*, m. p. 192° with darkening). Benzaldehyde and *p*-dimethylaminobenzaldehydehydrazine afford benzald-*p*-dimethylaminobenzaldazine, m. p. 134°, reduced by sodium amalgam and alcohol to *s*-benzyl-*p*-dimethylaminobenzylhydrazine, m. p. 140—141°. Reduction of di-*m*-nitrobenzaldazine with sodium amalgam and amyl alcohol, hydrazine, or zinc dust and acetic acid gives indefinite products; with tin and hydrochloric acid, *m*-aminobenzaldehyde is obtained.

H. BURTON.

**Resolution of racemic aldehydes into their optical antipodes.** M. BETTI [with P. PRATESI] (Ber., 1930, 63, [B], 874—875).—*r*-*p*-Methoxyhydratropaldehyde, b. p. 255°/760 mm., is converted by optically active phenyl-2-hydroxy- $\alpha$ -naphthylmethylamine in alcoholic solution into the corresponding *aldimino*-compounds, C<sub>27</sub>H<sub>25</sub>O<sub>2</sub>N, m. p. 120°, [ $\alpha$ ]<sub>D</sub> +43.1° in benzene, and m. p. 120°, [ $\alpha$ ]<sub>D</sub> +40.3° in benzene (separated from one another by treatment with alcohol), from which 1-*p*-methoxyhydratropaldehyde, [ $\alpha$ ]<sub>D</sub> -2.45° in chloroform, and *d*-*p*-methoxyhydratropaldehyde, [ $\alpha$ ]<sub>D</sub> +2.52° in chloroform, are obtained.

H. WREN.

**Constitution of cyclanones.** II. R. CORNUBERT and C. BORREL (Bull. Soc. chim., 1930, [iv], 47, 301—322; cf. this vol., 347).—Partly a recapitulation of published work (A., 1929, 560). 2-Methyl-5-ethyl cyclopentanone, b. p. 164—165°/750 mm., *d*<sub>4</sub><sup>20</sup> 0.900, *n*<sub>D</sub><sup>20</sup> 1.436, is obtained in 87% yield from ethyl  $\alpha$ -methyl- $\alpha'$ -ethyladipate, b. p. 136—137°/15 mm., *n*<sub>D</sub><sup>20</sup> 1.429 (yield 95% from ethyl 2-methylcyclopentanone-5-carboxylate). 2-Methyl-5-isopropylcyclopentanone, b. p. 178°, *d*<sub>4</sub><sup>15</sup> 0.891, *n*<sub>D</sub><sup>15</sup> 1.449, similarly obtained from ethyl  $\alpha$ -methyl- $\alpha'$ -isopropyladipate, b. p. 126—127°/14 mm., *n*<sub>D</sub><sup>15</sup> 1.445, and by hydrogenation of 2-methyl-5-isopropylidenecyclopentanone, b. p. 98—99°/25 mm., *n*<sub>D</sub><sup>15</sup> 1.4865, in presence of nickel, with benzaldehyde yields, in addition to the "tetrahydropyrone" compound, a benzylidene derivative, m. p. 61.5°, a considerable proportion of the ketone being unchanged. 2-Methyl-5-butylcyclopentanone from ethyl 2-methyl 5-*n*-butylcyclopentanone-5-carboxylate, b. p. 142—144°/17 mm., or from  $\alpha$ -methyl- $\alpha'$ -*n*-butyladipic acid with acetic anhydride, has b. p. 93—94°/16 mm., *d*<sub>4</sub><sup>15</sup> 0.889, *n*<sub>D</sub><sup>15</sup> 1.4466; 2-methyl-5-isobutylcyclopentanone, b. p. 82—83°/13 mm., *d*<sub>4</sub><sup>15</sup> 0.882, *n*<sub>D</sub><sup>15</sup> 1.447 (from  $\alpha$ -methyl- $\alpha'$ -isobutyladipic acid); 5-benzyl-2-methylcyclopentanone, b. p. 150°/16 mm., *d*<sub>4</sub><sup>15</sup> 1.010, *n*<sub>D</sub><sup>15</sup> 1.5212, obtained by hydrogenation of 5-benzylidene-2-methylcyclopentanone, m. p. 57°, b. p. 187—188°/23 mm. (*semicarbazone*, m. p. 205°), by decarboxylating ethyl 5-benzyl-2-methylcyclopentanone-5-carboxylate, b. p. 193°/20 mm., *d*<sub>4</sub><sup>18</sup> 1.068, *n*<sub>D</sub><sup>18</sup> 1.5050, or heating  $\alpha'$ -benzyl- $\alpha$ -methyladipic acid with acetic anhydride. 2-Methyl-5-propylcyclopentanone, b. p. 78—79°/18 mm., *d*<sub>4</sub><sup>18</sup> 0.889, *n*<sub>D</sub><sup>18</sup> 1.4405, is obtained in 87% yield by decarboxylating ethyl 2-methyl-5-propylcyclopentanone-5-carboxylate, b. p. 135°/21 mm., *d*<sub>4</sub><sup>22</sup> 0.9912, *n*<sub>D</sub><sup>22</sup> 1.4472, with barium hydroxide; the latter is obtained (yield 81%) by hydrogenation of ethyl 2-methyl-5-allylcyclopentanone-5-carboxylate, b. p. 134°/22 mm., *d*<sub>4</sub><sup>23</sup> 1.0047, *n*<sub>D</sub><sup>23</sup> 1.4565.

Ethyl adipate, b. p. 137°/21 mm., heated with sodium in toluene at 60—80° and finally at 120—130°, gives ethyl cyclopentanone-2-carboxylate, b. p. 114°/20 mm., in 80% yield, which with methyl iodide in presence of sodium ethoxide at -15° gives a 95% yield of ethyl 2:5-dimethylcyclopentanone-5-carboxylate, converted by boiling with sodium ethoxide for 1½ hrs. into ethyl  $\alpha$ -methyladipate, b. p. 133—134°/18 mm. (yield 83%). This when heated with sodium in toluene gives ethyl 2-methylcyclopentanone-5-carboxylate in 70% yield.

The nickel formate catalyst used in hydrogenation is obtained by dissolving nickel hydrogen carbonate (from sodium hydrogen carbonate and a nickel salt) in 78% formic acid, distilling off excess of acid at 120°, drying in a vacuum at 170°, and finally decomposing the powdered mass at 300°.

R. BRIGHTMAN.

**Synthesis of cyclic compounds. VI. 3- and 4-Methylcyclohexanones.** A. I. VOGEL and M. P. GOMMEN (J.C.S., 1930, 768—774).—Reduction of unsaturated cyano-esters of the type

$\text{CR'R''C(CN)CO}_2\text{Et}$  (which, contrary to the view of Haworth and others, J.C.S., 1908, 93, 1943; 1910, 97, 486, possess the  $\alpha\beta$ -structure) with moist aluminium amalgam in ether (Vogel, A., 1928, 1116), where CR'R'' is 3- or 4-methylcyclohexylidene, affords, respectively, 83 and 87% of the corresponding saturated ester and 6 and 4%, respectively, of the bimolecular cyano-ester,  $[\text{CR'R''CH(CN)CO}_2\text{Et}]_2$ .

The close similarity of these results with those obtained when CR'R'' is cyclopentylidene or cyclohexylidene suggests that there is no essential difference in behaviour between unsubstituted and methyl-substituted cyclohexane rings (cf. Birch and Thorpe, J.C.S., 1922, 121, 1821). Prolonged hydrolysis of the reduced cyano-esters with alcoholic potassium hydroxide affords the corresponding malonic acids, identical with specimens synthesised from the appropriate cyclohexyl iodide and ethyl sodiomalonate. The following compounds are thus obtained: ethyl 3-, b. p. 163°/16 mm.,  $d_4^{19}$  1.0288,  $n_D^{19}$  1.4914, and ethyl 4-, b. p. 172°/21 mm.,  $d_4^{21}$  1.0227,  $n_D^{21}$  1.4882; -methylcyclohexylidenecyanoacetate, reduced to ethyl *r*-3-, b. p. 152°/15 mm.,  $d_4^{24}$  1.0022,  $n_D^{24}$  1.4586, and ethyl *r*-4-, b. p. 162°/20 mm.,  $d_4^{22}$  1.0018,  $n_D^{22}$  1.4585; -methylcyclohexylcyanoacetate, together with the bimolecular cyano-esters, m. p. 76° and 75°, respectively. By hydrolysis of the saturated cyano-esters are obtained: 3-, m. p. 115—116°, and 4-, m. p. 182—183° (Hope and Perkin, J.C.S., 1909, 95, 1367, give m. p. 177—178°) -methylcyclohexyl-1-malonic acid, the latter being synthesised from 4-methylcyclohexyl iodide, b. p. 63°/3.5 mm.,  $d_4^{20}$  1.5086,  $n_D^{20}$  1.5325 (obtained by the action of iodine and red phosphorus on the alcohol, which, in turn, was obtained by reduction of 4-methylcyclohexanone, b. p. 171°/747 mm.,  $d_4^{20}$  0.9159,  $n_D^{20}$  1.4455,  $\gamma^{20}$  31.04,  $[P]$  289.6). Similar synthesis of 3-methylcyclohexyl-1-malonic acid from pure 3-methylcyclohexanone, b. p. 169°/747.5 mm.,  $d_4^{17}$  0.9151,  $n_D^{17}$  1.4463,  $\gamma^{20}$  31.23,  $[P]$  290.9, affords a mixture of *r*-3-, and *r*-4-acids, possibly due to elimination of water and subsequent addition of hydrogen iodide during the conversion of the cyclohexanol into the iodide. 2-Methylcyclohexanone has b. p. 165°/757 mm.,  $n_D^{19}$  1.4484,  $d_4^{19}$  0.9255,  $\gamma^{20}$  31.99,  $[P]$  288.2.

3 F

The value of  $[P_1/n]$  for the contribution of each  $\text{CH}_2$  group to the parachor of cyclohexane calculated from the above data for the 2-, 3-, and 4-methyl derivatives is in close agreement with that obtained from the observed parachor of the simple cyclohexane ring and further supports the view that there is no essential difference between the substituted and unsubstituted 6-ring.

J. W. BAKER.

**Formation of phenols from dibromides of cyclohexenones.** A. D. PETROV [with (in part) A. O. SAVELJEV] (Ber., 1930, 63, [B], 898—903; cf. A., 1929, 551).—Addition of bromine and formation of phenols do not occur with cyclohexenones containing highly tenacious groups in positions 3 and 5. If a tenacious group is present at 5 and a less tenacious radical at 3, addition of bromine takes place, but phenols are not produced. The last-named compounds are formed through the dibromides from those cyclohexenones which contain mobile groups in positions 3 and 5; a heavy group of little tenacity in position 4 offers no obstacle.

Phenyl *p*-methoxystyryl ketone, m. p. 77—78°, is converted by ethyl acetoacetate in presence of alcoholic sodium ethoxide into ethyl 4-phenyl-6-*p*-anisyl- $\Delta^3$ -cyclohexen-2-one-1-carboxylate, m. p. 106—107°, transformed by alcoholic potassium hydroxide or hydrochloric acid under pressure into 3-phenyl-5-*p*-anisyl- $\Delta^2$ -cyclohexenone, m. p. 98°, which yields an abnormal compound, m. p. 173°, with hydroxylamine. The ketone does not add bromine. Similarly, *p*-methylacetophenone and anisaldehyde afford *p*-tolyl *p*-methoxystyryl ketone, m. p. 97—98°, transformed into ethyl 3-*p*-tolyl-6-*p*-anisyl- $\Delta^3$ -cyclohexen-2-one-1-carboxylate, m. p. 156—157°, and thence into 3-*p*-tolyl-5-*p*-anisyl- $\Delta^2$ -cyclohexenone, m. p. 86—87° (oxime, m. p. 170°), which does not add bromine. 5-Phenyl-3-methylcyclohexenone gives a dibromide, m. p. 69°, which passes into a tar at the atmospheric temperature. 5-Anisyl-3-methylcyclohexenone yields an analogous, liquid dibromide. Phenylacetaldehyde and ethyl acetoacetate afford ethyl  $\beta$ -phenylethylidenediacetoacetate, m. p. 136° [whence ethyl 6-oximino-2-benzyl-4-methyl- $\Delta^4$ -cyclohexene-1:3-dicarboxylate, m. p. 172° (decomp.)], hydrolysed to 5-benzyl-3-methylcyclohexenone, b. p. 200—201°/20 mm.; the corresponding bromide passes into 5-benzyl-3-methyl-phenol, identified as the tribromide, m. p. 121—122°.

H. WREN.

**Identification of nitriles. Preparation of phenyl alkyl ketones.** R. L. SHRINER and T. A. TURNER (J. Amer. Chem. Soc., 1930, 52, 1267—1269).—Aliphatic nitriles react simply with an excess of magnesium phenyl bromide (4 mols. is the optimum proportion with acetonitrile) to give products from which ketones are obtained in good yield on hydrolysis; few by-products are formed under these conditions (cf. Baerts, A., 1922, i, 817). The following have been obtained in the yields given in parentheses and the semicarbazones [m. p. (corr.) given in parentheses] prepared: acetophenone (70%; 198—199°); propiophenone (91%; 173—174°); butyrophenone (77%; 184—184.5°); valerophenone (79%; 157—157.5°); hexophenone (83%; 127—128°); isohexophenone (50%; 145—146°).

R. K. CALLOW.

**Constitution of acetyl-*m*-cymene.** A. LACOURT (Bull. Soc. chim. Belg., 1930, 39, 132—142).—*m*-Cymene is prepared in 77% yield by heating fenchone with 1.5 parts of phosphoric oxide for 1.5 hrs. at 110—170°, followed by cooling, further addition of 1.5 parts of phosphoric oxide and reheating at 130° for 0.5 hr. With acetyl chloride, and aluminium chloride (equimolecular proportions) in carbon disulphide solution at 20° it gives a 90% yield of acetyl-*m*-cymene (I), b. p. 125.2—125.4°/12 mm.,  $d_{20}^{20}$  0.9694,  $n_D^{20}$  1.52459 (semicarbazone, m. p. 171—172°; oxime, m. p. 92—92.6°; the ketone regenerated from the semi-carbazone with phthalic acid had  $d_{20}^{20}$  0.9679,  $n_D^{20}$  1.5228). This substance has not the 1:3:5 constitution (Reyes, Diss., Paris, 1903), but is 6-acetyl-3-isopropyltoluene, since oxidation with nitric acid ( $d$  1.19) gives methylterephthalic acid, m. p. 326—330° (dimethyl ester, m. p. 72—73°; barium salt), identical with the acid obtained by oxidation of 2:4-dimethylbenzoic acid, m. p. 123.5° (lit. 126°) (prepared in 70% yield from magnesium *m*-4-xylyl bromide and carbon monoxide), with potassium permanganate. Nitration of I with fuming nitric acid and fuming sulphuric acid (60% SO<sub>3</sub>) gives an impure dinitro-compound, m. p. 178—186°, further oxidised by nitric acid ( $d$  1.15) to 2:4-dinitro-3-isopropyl-1-methylbenzoic acid, m. p. 182—183°.

A. I. VOGEL.

**[Preparation of] benzophenone oxime.** A. LACHMAN (Organic Syntheses, 1930, 10, 10—11).

**[Preparation of] *m*-nitroacetophenone.** B. B. CORSON and R. K. HAZEN (Organic Syntheses, 1930, 10, 74—77).

**Reduction of benzophenone to benzpinacol by means of magnesium amalgam and some observations concerning magnesiumous chloride [magnesium subchloride].** H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, 52, 1128—1131).—In connexion with the supposed formation of magnesium subchloride in the reduction of benzophenone by magnesium triphenylmethyl chloride, the reduction of benzophenone by magnesium under various conditions has been investigated. No reduction is observed when it is heated with magnesium and magnesium chloride or fluoride, or with activated magnesium for long periods, but some reduction takes place with magnesium and mercury or mercuric chloride. No definite evidence is thus obtained for the formation of magnesium subchloride (Gilman and Fothergill, A., 1929, 1432). R. K. CALLOW.

**Delicate colour test for Michler's ketone and a less sensitive test for carbonyl chloride and dialkylanilines.** H. GILMAN, O. R. SWEENEY, and L. L. HECK (J. Amer. Chem. Soc., 1930, 52, 1604—1607).—The colour test previously described for Grignard reagents (A., 1925, ii, 1011; 1928, 160; 1929, 303) is positive for 1 c.c. of a 0.00001 *M*-solution of Michler's ketone in benzene when 1 c.c. of a 2.25 *M*-magnesium phenyl bromide solution is used. A positive test is also obtained when 1 c.c. of a 0.202 *M*-solution of carbonyl chloride in benzene is shaken with 1 c.c. of dimethylaniline and the product treated with the magnesium phenyl bromide. When the carbonyl

chloride and dimethylaniline are first heated at 118°, the test is more sensitive. H. BURTON.

**Elimination of the amino-group from tertiary amino-alcohols. VIII. Migratory tendency of the *p*-tolyl group.** A. MCKENZIE, A. K. MILLS, and J. R. MYLES (Ber., 1930, 63, [B], 904—911; cf. A., 1929, 1066).—Ethyl *r*-alanine hydrochloride is converted by magnesium *p*-tolyl bromide and treatment of the product with hydrogen chloride in ether into  $\beta$ -amino- $\alpha$ -di-*p*-tolylpropanol hydrochloride, decomp. 242—243°;  $d$ - $\beta$ -amino- $\alpha$ -di-*p*-tolylpropanol hydrochloride, from ethyl *d*-alanine hydrochloride, decomposes at 257.5—258.5° and has  $[\alpha]_D^{25} +40.7^\circ$  in alcohol. Treatment of the racemic amino-alcohol with nitrous acid causes wandering of the *p*-tolyl group with production of *r*-*p*-tolyl  $\alpha$ -*p*-tolylethyl ketone, b. p. 175°/2 mm. (oxime, m. p. 85.5—86.5°), whilst the active amino-alcohol yields *d*-*p*-tolyl  $\alpha$ -*p*-tolylethyl ketone, b. p. 178—179°/1.5 mm.,  $[\alpha]_D^{25} +75.3^\circ$  in benzene (oxime, m. p. 83—84°,  $[\alpha]_D^{25} +62.1^\circ$  in benzene). *r*- $\beta$ -Amino- $\alpha$ -phenyl- $\alpha$ -*p*-tolylethanol, m. p. 108—109° (hydrochloride, m. p. 183—184°), from  $\omega$ -aminoacetophenone hydrochloride and magnesium *p*-tolyl bromide, is converted by nitrous acid into  $\omega$ -*p*-tolylacetophenone, m. p. 95—96°. *r*-Desylamine hydrochloride is transformed by magnesium *p*-tolyl bromide into *r*- $\beta$ -amino- $\alpha$ - $\beta$ -diphenyl- $\alpha$ -*p*-tolylethanol, m. p. 149—150° (hydrochloride, m. p. 231—232°). Resolution of the amino-alcohol with *l*-camphor-10-sulphonic acid in aqueous alcohol affords *d*- $\beta$ -amino- $\alpha$ - $\beta$ -diphenyl- $\alpha$ -*p*-tolylethanol *l*-camphor-10-sulphonate,  $[\alpha]_D^{20} +80^\circ$  in alcohol, whence *d*- $\beta$ -amino- $\alpha$ - $\beta$ -diphenyl- $\alpha$ -*p*-tolylethanol, m. p. 124—125°,  $[\alpha]_D^{20} +286^\circ$  (among other data). Similarly, with *d*-camphor-10-sulphonic acid under similar conditions the *r*-alcohol yields *l*- $\beta$ -amino- $\alpha$ - $\beta$ -diphenyl- $\alpha$ -*p*-tolylethanol *d*-camphor-10-sulphonate, whence *l*- $\beta$ -amino- $\alpha$ - $\beta$ -diphenyl- $\alpha$ -*p*-tolylethanol,  $[\alpha]_D^{20} -284^\circ$  in alcohol (also prepared from *d*-desylamine hydrochloride and magnesium *p*-tolyl bromide). De-amination of the racemic amino-alcohol yields *p*-tolyl benzhydryl ketone, m. p. 98.5—99.5° (also prepared from diphenylacetyl chloride, toluene, and aluminium chloride), which does not yield an oxime or a semicarbazone, but is converted by magnesium phenyl bromide into  $\alpha\beta$ -triphenyl- $\alpha$ -*p*-tolylethanol, m. p. 180—181°. Similar treatment of the *d*-amino-alcohol shows almost exclusive wandering of the phenyl group, yielding the inactive *p*-tolyl benzhydryl ketone with a little active *p*-tolyldeoxybenzoin. The production of *p*-tolyl benzhydryl ketone by the action of cold, concentrated sulphuric acid on *r*-*p*-tolylhydrobenzoin is recorded.

The relative tendencies of the phenyl and *p*-tolyl groups towards wandering appear to vary from case to case. H. WREN.

**Condensation of ketones with resorcinol. I. Condensation by addition.** R. N. SEN and M. QUDRAT-I-KHUDA (J. Indian Chem. Soc., 1930, 7, 167—175).—Acetone, heated with hydrochloric acid and resorcinol, is first converted into mesityl oxide, which then condenses with the resorcinol. Methyl ethyl ketone, acetophenone, and cyclohexanone behave similarly. The products, in which the entering

group appears to be in the 4-position, form coloured quinonoid monopotassium salts, faintly coloured monobenzyl and colourless diacetyl derivatives. The structure  $\cdot\text{CO}\cdot\text{C}\cdot$  seems necessary for reaction with resorcinol; isatin, phenyl styryl ketone, and benzoyl-acetone all condense readily, whereas benzophenone and trihydroxybenzophenone do not, although Michler's ketone does so with the formation of di-hydroxymalachite-green. The following were prepared:  $\delta$ -hydroxy- $\delta$ -2 : 4-dihydroxyphenyl- $\beta$ -methyl- $\Delta^{\beta}$ -pentene, from acetone or mesityl oxide, m. p. 153° (potassium salt; benzoyl derivative, m. p. 145°; acetyl compound, m. p. 162°; dibromo-compound, m. p. 146—147°; tribromo-compound, m. p. 136°);  $\epsilon$ -hydroxy- $\epsilon$ -2 : 4-dihydroxyphenyl- $\gamma$ -methyl- $\Delta^{\gamma}$ -heptene, from methyl ethyl ketone, m. p. 118° (benzoyl compound, m. p. 126°; acetyl compound, m. p. 108°); 2 : 4-dihydroxydiphenyl- $\beta$ -methylstyrylcarbinol, from acetophenone, m. p. 132—134° (potassium salt; benzoyl derivative, m. p. 141°; acetyl derivative, m. p. 133°); 1-hydroxy-2-cyclohexylidene-1-(2' : 4'-dihydroxyphenyl)-cyclohexane from cyclohexanone, m. p. 140° (benzoyl derivative, m. p. 150°; acetyl compound, m. p. 155°); 2 : 3-dihydroxy-3-(2' : 4'-dihydroxyphenyl)indolenine, from isatin, decomposes without melting (dipotassium salt; dibenzoyl derivative, no m. p.; triacetyl derivative, no m. p.); 2 : 4-dihydroxydiphenylstyrylcarbinol from phenyl styryl ketone, m. p. about 190° (potassium salt; benzoyl compound, m. p. 128—130°; acetyl compound, m. p. 153°);  $\beta$ - $\delta$ -dihydroxy- $\delta$ -2 : 4-dihydroxydiphenyl- $\Delta^{\beta}$ -butene, from benzoylacetone, no m. p.; 4 : 4'-tetramethyl-diamino-2'' : 4''-dihydroxytri-phenylcarbinol, m. p. about 168°. Acetone condenses with pyrogallol under similar conditions to give  $\delta$ -hydroxy- $\delta$ -trihydroxyphenyl- $\beta$ -methyl- $\Delta^{\beta}$ -pentene, which decomposes at a high temperature without melting.

H. A. PIGGOTT.

**Benzoylfluorenes.** P. PFEIFFER and E. LÜBBE (Ber., 1930, 63, [B], 762—766).—The action of ethyl benzoate and sodium on fluorene affords 9-benzoyl-fluorene, m. p. 136° after softening at 133° [Werner (A., 1906, i, 436) records m. p. 138°]. The lithium derivative of fluorene is converted by benzoyl chloride into the compound, m. p. 180.5° after softening at 176°, now shown by analysis and quantitative hydrolysis to be a *dibenzoylfluorene* ( $\alpha$ -form). Treatment of monobenzoylfluorene with benzoyl chloride in pyridine or in alcohol containing sodium or lithium alkoxide gives  $\beta$ -*dibenzoylfluorene*, m. p. 191° after softening at 188°, distinguished from the  $\alpha$ -form also by crystalline form, by stability towards glacial acetic acid, and more ready oxidation by potassium permanganate. The  $\alpha$ -variety passes smoothly into the  $\beta$ -form when heated at 260°. The structures  $\text{C}_6\text{H}_4 > \text{C}:\text{CBz}\cdot\text{Oph}$  and  $\text{C}_6\text{H}_4 > \text{CBz}_2$  are assigned to the isomerides.

H. WREN.

**Conversion of  $\alpha$ -benzilmonoxime into the  $\beta$ -oxime by animal charcoal.** T. W. J. TAYLOR and S. MARKS (Nature, 1930, 125, 636).—When a benzene solution of the  $\alpha$ -oxime is boiled with animal charcoal the change to the  $\beta$ -oxime is complete in a short time. Soft-wood charcoal, powdered silica gel, finely-divided calcium phosphate, or the solvent

obtained by boiling animal charcoal with benzene are unable to affect this change. L. S. THEOBALD.

**New synthesis of dicinnamoylmethane.** K. VENKATARAMAN (J. Indian Chem. Soc., 1930, 7, 157—160).—Dicinnamoylmethane (cf. Lampe and Milobendzki, A., 1913, i, 876) is synthesised by the condensation of malonyl chloride with styrene in presence of stannic chloride. The yield is small and is not appreciably affected by use of malonyl bromide in the place of the chloride. In the preparation of malonyl bromide by the method of Mayes and Partington (A., 1926, 1219) a substance,  $\text{C}_3\text{H}_5\text{O}_3\text{Br}$ , a bright orange liquid that partly solidifies on keeping, b. p. 110—120°/10 mm., probably the hemi-chloride, was isolated.

H. A. PIGGOTT.

**Indones. X. New reactions of 3-phenyl-2-ethyl- and 3-phenyl-2-methyl-indone.** R. DE FAZI and F. PIRRONE (Atti R. Accad. Lincei, 1930, [vi], 11, 70—74).—Passage of chlorine through an anhydrous carbon tetrachloride solution of 3-phenyl-2-ethylindone at 5° yields almost solely 2 : 3-dichloro-3-phenyl-2-ethylhydrindone, m. p. 96—97°, whilst at 20—25° it gives two of the possible dichloro-3 : 3'-diphenyl-2 : 2'-diethyldiketodi-indanyls, m. p. 141—142° and 148—149°, respectively, of the probable structures  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CPhCl} \\ \text{CO} \end{smallmatrix} > \text{CET}:\text{CET} < \begin{smallmatrix} \text{CPhCl} \\ \text{CO} \end{smallmatrix} > \text{C}_6\text{H}_4$  and  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CPhCl} \\ \text{CO} \end{smallmatrix} > \text{CET}:\text{CET} < \begin{smallmatrix} \text{CO} \\ \text{CPhCl} \end{smallmatrix} > \text{C}_6\text{H}_4$ . The

analogous compounds, 2 : 3-dichloro-3-phenyl-2-methylhydrindone, m. p. 92—93°, and the two isomeric dichloro-3 : 3'-diphenyl-2 : 2'-dimethyldiketodi-indanyls, m. p. 126—127° and 131—132°, were also prepared. On the other hand, the action of bromine, at either 5° or 20—25°, on 3-phenyl-2-ethylindone gives two isomeric 3 : 3'-dibromo-3 : 3'-diphenyl-2 : 2'-diethyldiketodi-indanyls, m. p. 107—108° and 149—150°, respectively, whilst from 3-phenyl-2-methylindone under similar conditions only one 3 : 3'-dibromo-3 : 3'-diphenyl-2 : 2'-dimethyldiketodi-indanyl, m. p. 143—144°, is obtained.

The action of copper or sodium sulphide on 2 : 3-dichloro-3-phenyl-2-ethylhydrindone gives, not diphenyldiethyltruxones, but 3 : 3'-dichloro-3 : 3'-diphenyl-2 : 2'-diethyldiketodi-indanyl and 3-phenyl-2-ethylindone, whilst the latter compound alone is obtained under similar conditions from 3 : 3'-dichloro-3 : 3'-diphenyl-2 : 2'-diethyldiketodi-indanyl. The methyl homologues behave in this respect similarly to the ethyl compounds.

T. H. POPE.

**[Preparation of] duroquinone.** L. I. SMITH (Organic Syntheses, 1930, 10, 40—42).

**[Preparation of] diphenylmethylenimine hydrochloride.** A. LACHMAN (Organic Syntheses, 1930, 10, 28—30).

**Manufacture of derivatives of naphthalene [from *p*-benzoquinones and  $\alpha\gamma$ -butadienes.]** I. G. FARBENIND. A. G.—See B., 1930, 452.

**Theory of dyeing.** P. PFEIFFER, O. ANGERN, L. WANG, R. SEYDEL, and K. QUEHL (J. pr. Chem., 1930, [ii], 126, 97—145).—Previous work (A., 1927, 676) on the possibility of formation of molecular compounds (detected by mixed m.-p. curves or by

actual isolation) between sarcosine anhydride (1:4-dimethyl-2:5-diketopiperazine) or the amino-acids, glycine, glycyglycine, and phenylalanine, is summarised and extended to include a variety of bases, phenols, acids, and dyes containing either a chromophoric or an auxochromic group. The results indicate that molecular compound or salt formation occurs with components containing an auxochrome group (with the exception of hydroxyl and amino-groups in the *o*-position to a chromophoric group, in which case intramolecular co-ordination occurs), but never with those containing only a chromophoric group, and hence the latter type of group is unimportant in connexion with the dyeing of wool and silk. The following new results are recorded. Sarcosine anhydride (A) forms compounds with the following substances (B): acetic AB<sub>2</sub>, *n*-butyric AB<sub>2</sub>, m. p. indefinite, tartaric AB<sub>2</sub>, m. p. 156°, citric AB, m. p. 179°, benzoic, AB<sub>2</sub>, m. p. 97.5°, *p*-toluic AB, m. p. 108°, *o*-, AB<sub>2</sub>, m. p. 91° and *p*-, AB<sub>n</sub> (not isolated) -anisic, and *p*-hydroxybenzoic AB, m. p. 175.5—176° (softens at 150°) and AB<sub>2</sub>, m. p. 187.5°, acids: also with sodium benzoate AB<sub>2</sub>, *p*-toluate AB<sub>2</sub>, and *p*-nitrobenzoate AB, EtOH; with *p*-tolyl methyl ether-AB+6H<sub>2</sub>O, m. p. 62°, +5H<sub>2</sub>O, m. p. 101°, and anhydrous, and AB<sub>2</sub>+6H<sub>2</sub>O, m. p. 78°, naphthalene-2-AB+2H<sub>2</sub>O, m. p. 110°, and AB<sub>2</sub>+0.5H<sub>2</sub>O, m. p. 200°, β-naphthol-6- A<sub>2</sub>B+2H<sub>2</sub>O, m. p. 78°, -sulphonic acids; with the free acids of the dyes β-naphthol-orange AB+4H<sub>2</sub>O, and ponceau-2R A<sub>2</sub>B<sub>3</sub>+10H<sub>2</sub>O; also with aniline AB (no compound with dimethylaniline), perchloric acid AB, calcium chloride AB+2H<sub>2</sub>O, and calcium bromide A<sub>3</sub>B+4H<sub>2</sub>O (no compound with 6-amino-3:4'-dimethylazobenzene). The following substances also form compounds (A=first and B, the second component mentioned): naphthalene-2-sulphonic acid with glycine AB, m. p. 193°, sarcosine AB, m. p. 186°, and glycyglycine AB, m. p. 225°; β-naphthol-6-sulphonic acid with glycine AB, m. p. 238°, sarcosine A<sub>2</sub>B<sub>3</sub>+H<sub>2</sub>O, m. p. 205—210°, and glycyglycine AB+0.33H<sub>2</sub>O, m. p. 231°; ammonia with resacetophenone A<sub>2</sub>B, 2:4-dihydroxybenzophenone AB, 1- and 2-hydroxyanthraquinone AB, alizarin and its β-methyl ether AB, and quinizarin AB (no compound formation with azobenzene, anthraquinone, 1-hydroxy-4-methoxyacetophenone, or 2-hydroxy-4-methoxybenzophenone); piperidine with resacetophenone AB, 1- and 2-hydroxyanthraquinone (unstable), alizarin AB, alizarin β-methyl ether (unstable), and quinizarin (composition uncertain), (no compound with azobenzene, anthraquinone, and 1-hydroxy-4-methylacetophenone); β-naphthylamine with 1-methoxyanthraquinone AB<sub>2</sub>; *m*-cresol with sarcosine AB<sub>2</sub> (no compound with azobenzene or phenyl methyl ketone). No evidence of compound formation is obtained with the following pairs: acetic or *n*-butyric acid and azobenzene, anthraquinone; *p*-toluic acid with azobenzene, α-methoxyanthraquinone or phenyl methyl ketone.

J. W. BAKER.

**Dehydration of derivatives of *o*-benzoylbenzoic acid.** G. DOUGHERTY and A. H. GLEASON (J. Amer. Chem. Soc., 1930, 52, 1024—1027; cf. A., 1929, 318).—The yields of anthraquinone derivatives obtained by heating derivatives of *o*-benzoylbenzoic acids with

sulphuric acid have been compared. The following gave unsatisfactory results owing to sulphonation or formation of tar: 2'-hydroxy-4'-methyl- and -4'-ethylbenzoylbenzoic acids, mesityloylbenzoic acid, benzoylbenzamide, propyl and butyl *o*-benzoylbenzoates, and benzophenone-2:4'-dicarboxylic acid. The yields obtained from the following after heating for certain periods were determined: 4'-chloro-, 4'-bromo-, 4'-methyl-, 6(or 3)-chloro- (m. p. 233.5°, prepared from 3-chlorophthalic anhydride and benzene), 2':5'-dichloro-, 3:6-dichloro-, 3':4'-dimethyl-, 2':4'-dimethyl-, and 5'(2')-chloro-2'(5')-methylbenzoylbenzoic acids. In general substitution by halogen has a depressing effect. The 4'-methyl compound also gives a low yield, but two methyl groups or methyl in presence of chlorine accelerate the reaction. Measurements of rate of reaction show that the reaction is not unimolecular in these cases, and this difference from the unsubstituted acid may be explained by the comparatively slow velocity of formation of the sulphate in the first phase of the reaction (cf. *loc. cit.*).

R. K. CALLOW.

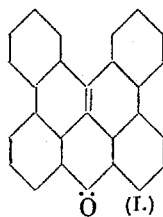
**Decomposition of sulphonazides. VIII. Anthraquinone-2-sulphonazide.** T. CURTIUS and H. DERLON.—See this vol., 760.

**Condensation products of anthrafuchsone.** E. CLAR and W. MÜLLER (Ber., 1930, 63, [B], 869—873).—Anthrafuchsone [*ms*-diphenylmethylenanthrone], m. p. 208° (cf. Padova, A., 1909, i, 167), is converted by aluminium chloride in boiling benzene into 1:10-benzoylene-9-phenylphenanthrene, m. p. 228—229° (if a large excess of aluminium chloride is employed or reaction is effected in boiling xylene, anthraquinone and resinous matter are produced). The compound is preferably prepared by irradiation of a solution of anthrafuchsone in xylene. It is oxidised by chromic acid in glacial acetic acid to 1-*o'*-benzoylphenylanthraquinone, m. p. 178—179°, whereas anthrafuchsone is transformed into benzophenone and anthraquinone under like conditions. Treatment of anthrafuchsone with aluminium chloride at 140—160° gives the ketone I, m. p. 305°, in poor yield. Particularly when a large excess of aluminium chloride is used, the production of (?) 1:10-benzoylene-9:10-phenanthrone, m. p. 231° after darkening at 223°, is observed.

Anthrone and 9:9:10:10-tetrahalo-9:10-dihydroanthracene in boiling xylene yield dianthrone and 9:10-dichloroanthracene.

H. WREN.

**Plant colouring matters. XX. Colouring matter from saffron.** VI. P. KARRER and A. HELFENSTEIN (Helv. Chim. Acta, 1930, 13, 392—397).—A simplified method for the extraction of α-crocin from saffron is given. Under the conditions previously described (A., 1927, 571; 1928, 644), mono- and di-ethyl esters of α-crocin are produced; esterification occurs during the process of extraction. When methyl alcohol is used some mono- and dimethyl esters of α-crocin are formed. The purest specimens of β- and γ-crocins so far obtained have m. p. 218° and 215—216°, respectively. A specimen of the monomethyl ester of α-crocin, prepared by the

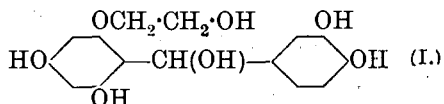




action of methyl sulphate and sodium hydroxide, has m. p. 218°. The *dimethyl*, m. p. 96°, and *diethyl*, m. p. 62°, esters of dihydro- $\alpha$ -crocetin (A., 1929, 49) are prepared by the action of ethereal diazo-methane and -ethane, respectively.

H. BURTON.

**Constitution of catechin. X.** M. NIERENSTEIN (J. Amer. Chem. Soc., 1930, 52, 1672—1676).—Extraction of the young twigs of *Acacia catechu*, Willd., with water affords 1-leucomaclurin glycol ether (I), m. p. 198°,  $[\alpha]_D^{25}$  —62.57° in water. Methylation of



this with diazomethane gives a *tetramethyl ether*, m. p. 147°,  $[\alpha]_D^{25}$  —36.4° in alcohol (contains no phenolic hydroxyl group), methylated further with methyl iodide and silver oxide to the *hexamethyl ether*, m. p. 97°,  $[\alpha]_D^{25}$  —63.4° in alcohol. This is hydrolysed by methyl-alcoholic sodium methoxide to glycol monomethyl ether and pentamethyl-leucomaclurin; the last-named compound is not isolated but is methylated by diazomethane to hexamethyl-leucomaclurin, m. p. 103° (lit. 94—96°). When I is heated with acetic anhydride *penta-acetyl-1-acacatechin*, m. p. 151°,  $[\alpha]_D^{25}$  —12.0° in tetrachloroethane, is obtained. This is identical with the product formed by acetylation of acacatechin from the heart wood of *A. catechu*, Willd.

H. BURTON.

**Constitution of orotic acid. M.** BACHSTEZ (Ber., 1930, 63, [B], 1000—1007; cf. Biscaro and Belloni, A., 1905, i, 672).—Orotic acid, m. p. 345—346° (corr. decomp.) [*lithium salt*], is shown to be identical with uracil-6-carboxylic acid prepared through the ethyl ester obtained from carbamide and ethyl oxalacetate. Treatment of the potassium salt with phosphoryl chloride and phosphorus pentachloride gives *dichloro-orotic acid*,  $C_4H_4O_4N_2Cl_2$ , m. p. 117° (corr., decomp.). Treatment of orotic acid with bromine in excess gives 5:5-dibromobarbituric acid. With nitric and sulphuric acids orotic acid affords nitrouracil-6-carboxylic acid, isolated as the *potassium salt*. With methyl- or ethyl-alcoholic hydrogen chloride, orotic acid gives the corresponding *O-methyl*, m. p. 298—300° (corr. decomp.), and *O-ethyl*, m. p. 325—327°, derivatives. *N-Methyl*, m. p. 251° (corr.), and *N-ethyl*, m. p. 211—213° (corr.), compounds are derived from alkyl iodide and the silver salt.

H. WREN.

**Constituents of resins. II. Dehydrogenation of boswellic acid.** K. BEAUCOURT (Monatsh., 1930, 55, 185—200).—Dehydrogenation of boswellic acid (A., 1929, 1457) with selenium at 300—360° for 36 hrs. gives liquid products, b. p. (mainly) 195—235°/0.03 mm., which after separation of a small amount of a hydrocarbon,  $C_{30}H_{34}$ , m. p. 216—218°, and further treatment with selenium at 350—360° afford indefinite liquid products. When dehydrogenation is carried out at 320—350° for 60 hrs. or with palladised charcoal (cf. Diels and Gädke, A., 1927, 241) at 270—350°, a hydrocarbon,  $C_{30}H_{22}$ , m. p. 306—307° (corr.; block), and liquid products are formed. Purification of the latter through their picrates furnishes three fractions:

(a) b. p. 137—139°/9 mm. (*picrate*, m. p. 128—129°); (b) b. p. 141—143°/9 mm. (*picrate*, m. p. 131—131.5°), and (c) b. p. 145—150°/9 mm. [*picrate*, m. p. 132—133.5°; *stypnate*, m. p. 158—161° (decomp.)]. The picrates from (a) and (b) are probably identical with sapotalin picrate and give mainly a *product*, b. p. 142—144°/10 mm.,  $d_4^{20}$  1.0087,  $n_D^{20}$  1.60967 (*stypnate*, m. p. 156—157.5°), corresponding with a trimethylnaphthalene. Fraction (c) corresponds with a tetramethylnaphthalene.

H. BURTON.

**Rotenone. II. Derivatives of derritol. III. Dehydrorotenone.** F. B. LA FORGE and L. E. SMITH.

**IV. Constitution of rotenone.** F. B. LA FORGE (J. Amer. Chem. Soc., 1930, 52, 1088—1091, 1091—1098, 1102—1104).—II. The reduction of rotenone (a) catalytically, with the formation of dihydro-rotenone and rotenonic acid (A., 1929, 1181), and (b) by zinc and potassium hydroxide, with the formation of derritol and rotenol (Butenandt, A., 1928, 1017), is shown to involve different groups, for derritol and rotenone each yield two products, one an acid, when they are reduced catalytically.

*Derritol methyl ether*, m. p. 122° (*oxime*, m. p. 172—173°), obtained from derritol by treatment with methyl sulphate and alkali, is hydrogenated in presence of platinum oxide-platinum-black, giving *dihydro-derritol methyl ether*, m. p. 107°, and *methyl derritolic acid*, m. p. 154—156°. Similarly, rotenol yields dihydrorotenol and rotenolic acid (not isolated), which is further reduced to *dihydrorotenolic acid*, m. p. 76—80°.

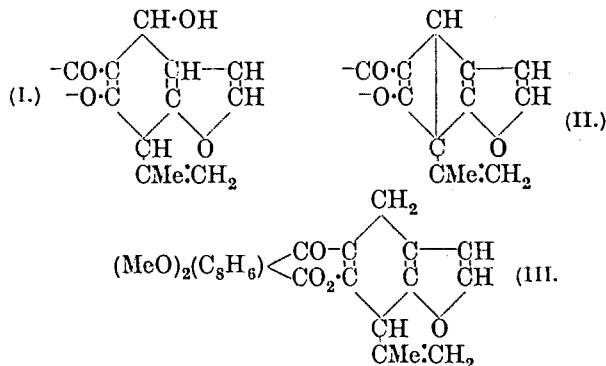
III. Dehydrorotenone (Butenandt, *loc. cit.*) and other compounds of the “dehydro-series” have been prepared, and it is shown that the series of diketones such as rotenonone prepared by vigorous oxidation are derivatives of the dehydro-compounds, since they are formed from these as well as from the rotenone series.

Dehydrorotenone is best prepared from rotenone by the action of iodine and potassium acetate. The bulk of the product is *acetylotenolone*, m. p. 184°, which is hydrolysed to *rotenolone*,  $C_{23}H_{22}O_7$ , m. p. 140—141°. Both compounds yield dehydrorotenone with boiling 5% sulphuric acid. Similarly, dihydrorotenone yields *dehydrodihydrorotenone*, m. p. 228—230°, and *dihydrorotenolone acetate*, m. p. 189°; *isorothenone* yields *dehydroisorothenone*, m. p. 195°. Catalytic hydrogenation of dehydrorotenone yields as the main product *dehydrodihydrorotenonic acid*, m. p. 223°. *Acetylotenolone* is converted by zinc dust in boiling alcoholic potassium hydroxide into rotenol and derritol.

Treatment of dihydrorotenone with *amyl nitrite* and hydrochloric acid in acetic acid yields *dihydro-rotenonone*, m. p. 272—275°. This is converted by boiling alcoholic potassium hydroxide into *dihydro-dehydrohydroxyrotenononic acid*,  $C_{23}H_{24}O_8$  or  $C_{23}H_{22}O_8$ , m. p. 257°. Dihydrorotenonone (dehydrodihydrorotenonone) is also obtained from dehydrodihydrorotenone and *amyl nitrite*. Similarly, *isorothenone* yields *isorothenone* (*dehydroisorothenone*),  $C_{23}H_{20}O_7$  or  $C_{23}H_{18}O_7$ , and *dehydrodihydrorotenononic acid*, m. p. very high, is obtained from dihydrorotenonic acid. *Dehydrodihydroxyrotenonic acid*,  $C_{23}H_{24}O_8$ , m. p.

157° (Butenandt's hydroxyketo-acid, m. p. 152°), is best prepared from dehydrorotenone by treatment with zinc dust in boiling alcoholic potassium hydroxide. It is converted by oxidation with hydrogen peroxide in alkaline solution into *derric acid*,  $C_{12}H_{14}O_7$ , m. p. 169°, derived from the portion of the original molecule containing the methoxyl groups.

The annexed formulæ are suggested for rotenolone (I) and dehydrorotenone (II).



IV. Formula (III) is proposed for rotenone on the basis of Takei's formula for tubaic acid (A., 1929, 933). It appears to afford an explanation of the typical reactions of rotenone, and, in particular, it satisfies the requirements postulated by Butenandt (*loc. cit.*). The constitution of *isorotenone*, which remains to be accounted for, is discussed.

R. K. CALLOW.

**Precipitation of saponins by sterols.** L. KOELER and H. RAUM (Biochem. Z., 1930, 219, 335—340).—Most saponins are not precipitated from alcoholic or other solutions by cholesterol, but by the method of Kofler and others (B., 1930, 166) it can be shown that the saponins form loose compounds with cholesterol, which are broken up even by ether. There is no parallelism between the capability of saponins to combine with cholesterol and the extent of their hæmolytic action. Saponins behave towards ergosterol in the same way as towards cholesterol.

W. MCCARTNEY.

**Isoprene and caoutchouc. XX. Colloidal nature of caoutchouc, gutta-percha, and balata.** H. STAUDINGER (Ber., 1930, 63, [B], 921—934; cf. this vol., 609).—The relationship between the viscosity-concentration constant  $K_c$  and mol. wt. is expressed by the formula  $M = K_c \times 10^4$  [ $K_c$  has been termed the "specific viscosity" by Duclaux (A., 1920, i, 534)]. To the term  $K_m$  (*loc. cit.*) the designation viscosity-mol. wt. constant is now applied. The values of  $K_c$  for hemicolloidal degradation products of gutta-percha and caoutchouc are calculated from previous observations (*loc. cit.*). In these cases, as with the polystyrenes,  $K_c$  is approximately proportional to the mol. wt. and the expression  $M = K_c \times 10^4$  is therefore applicable to eucolloidal caoutchouc and balata as a first approximation. The mol. wts. of more and less soluble caoutchouc, balata from latex, crêpe, and rolled caoutchouc are of the same order of magnitude when calculated from  $K_c$  and  $K_m$  and harmonise with the values obtained by osmotic measurements.

The differences between caoutchouc, gutta-percha, and balata do not depend essentially on differing size of the molecules and persist in their degradation products. It appears that caoutchouc is the *trans*-modification and gutta-percha and balata are the *cis*-forms of polyrenes. Hydrogenation of the double linking removes the difference between the two series. The conception of balata and gutta-percha as *cis*-compounds is based on higher density and, particularly, on the ability to crystallise.

The molecules of balata, gutta-percha, and caoutchouc are regarded as similarly composed of long stiff threads, the stability of which decreases with increasing length.

The hypothesis that simple substances, hemicolloids, and eucolloids have the same structural principle in the sense of Kekulé's theory appears inconsistent with the physical differences in properties of their solutions, but these differences are explained by the great divergence of the spheres of influence of small molecules and macromolecules in solution. The assumption is made that the sphere of influence is proportional, not to the volume, but to the square of the length. Calculation shows that the limiting concentration at which the region of influence fills the whole available space is reached by crude caoutchouc in 0.2% solution, by balata in 0.68% solution, whilst hemicolloidal polyrenes afford true solutions of 6.8% concentration.

H. WREN.

**Hydrogenation and dehydrogenation through catalysis by alkali metals.** G. CUSMANO (Gazzetta, 1930, 60, 105—112).—Aromatic products, among which are 2:3-dihydroxycymene and tetrahydrocarvone, are obtained by heating at 240° monosodio-buchu-camphor, or buchu-camphor containing a small amount of the sodio-derivative. The formation of these substances results from a simultaneous dehydrogenation and hydrogenation.

At the same temperature the sodio-derivative of buchu-camphor methyl ether, or the ether itself in the presence of small amounts of the former compound, gives methyl alcohol and thymol as a result of intramolecular rearrangement. A similar reaction is shown by the sodium thymoxide. Since at 300° the sodium derivatives of menthol and menthone give hydrogen and, respectively, menthone and thymol, it appears that the course of dehydrogenation, hydrogenation, and intramolecular change in the above reactions is determined by the presence of the combined sodium atoms, which thus exert a catalytic action analogous to that of nickel, copper, and platinum in the metallic state.

F. G. TRYHORN.

**Potassium  $\Delta^{1:4}$ -terpadiene-3:6-dione-2(or 5)-sulphonate (Carstanjen's compound).** H. G. HEWITT (J. Amer. Pharm. Assoc., 1930, 19, 217—220).—An account of attempts to determine the optimum conditions for the preparation of the above compound (Carstanjen, A., 1877, 892) from thymoquinone and potassium sulphite.

H. E. F. NOTTON.

**Conversion of menthone into citronellol.** J. DÈUVRE (Bull. Soc. chim., 1930, [iv], 47, 323—326).—In alcoholic solution at 0°, persulphuric acid converts *l*-menthone, b. p. 90—91°/15 mm.,  $[\alpha]_D^{25}$   $-9.5^\circ$  (ob-

tained by sulphuric-chromic acid oxidation of menthol, which was prepared by hydrogenating isopulegol into ethyl  $\epsilon$ -hydroxydihydrocitronellate, b. p. 145—148°/13 mm.,  $[\alpha]_D^{25}$  -10.67°. This substance, with phosphorus tribromide in benzene, in presence of pyridine, gives ethyl *d*-citronellate, b. p. 113—115°/12 mm.,  $[\alpha]_D^{25}$  +0.3°, probably containing a large proportion of the isopropylidene form, and a fraction, b. p. 135°/12 mm. Reduction of the ethyl *d*-citronellate with sodium and alcohol gives a *d*-citronellol, b. p. 112—113°/12 mm.,  $d_4^{25}$  0.854,  $n_D^{25}$  1.4557,  $[\alpha]_D^{25}$  +1.3° in benzene (allophanate, m. p. 105—106°), which on quantitative ozonisation yields 5% of formaldehyde, 18% of formic acid, and 75% of acetone, indicating the presence of 75% of the isopropylidene ( $\beta$ ) form and 23% of the propenyl ( $\alpha$ ) form.

R. BRIGHTMAN.

**Camphoreins. I. Phenolcamphorein and its derivatives.** V. DEULOFEU (Anal. Asoc. Quím. Argentina, 1929, 17, 318—328).—Phenolcamphorein (Singh, Rai, and Lal, J.C.S., 1922, 121, 1421) yields sodium and disodium salts which are deeply coloured, and it is suggested that the salts, the parent compound, and its tetrabromo-derivative (Krishna, *ibid.*, 253) all contain a quinonoid nucleus in the solid state. The diacetyl derivative, m. p. 71° (decomp.), and the dibenzoyl derivative, m. p. 174—175° (decomp.), of tetrabromophenolcamphorein are yellow in colour and are probably lactones. As an indicator, phenolcamphorein changes colour over the range  $pH=6.7-7.2$ . Lead lakes of phenolcamphorein and its tetrabromo-derivative are described.

Phenolcamphorein anhydride (Singh, Rai, and Lal, *loc. cit.*) yields successively a dibromo-derivative, m. p. 128—129°, and a tetrabromo-derivative, m. p. 132—133°, which are not fluorescent and are less deeply coloured than is the parent compound. The deep colour of these compounds indicates that they are internal xanthonium salts.

R. K. CALLOW.

[Tricyclene series.] G. KOMPPA (Ber., 1930, 63, [B], 1007; cf. A., 1929, 821).—The conversion of tricyclenic acid into tricyclene has been accomplished previously by Lipp (A., 1920, i, 491).

H. WREN.

**Caryophyllin and urson.** F. D. DODGE (J. Amer. Chem. Soc., 1930, 52, 1722—1723; cf. A., 1919, i, 91).—A criticism of van der Haar's conclusions (A., 1928, 68, 644) regarding caryophyllin and urson.

H. BURTON.

**Aldehyde syntheses in the furan series.** T. REICHSTEIN (Helv. Chim. Acta, 1930, 13, 345—349).—Furfuraldehyde is obtained when a mixture of furan and anhydrous hydrocyanic acid in ether is saturated with dry hydrogen chloride at -15°, the solution then warmed to the ordinary temperature, and the resulting product decomposed with water. Similarly, 2-methyl- and 2-ethyl-furan afford 5-methyl- and 5-ethyl-furfuraldehyde [*semicarbazone*, m. p. 176—177° (corr.)]. Reduction of *s*-di-2-furylthylene with sodium and alcohol gives *s*-di-2-furylthane, b. p. 5—88°/12 mm., converted as above into di-2-furylthane-5:5'-dialdehyde, m. p. 119.5—121° (corr.). 2-Acetylfuran, ethyl pyromucate, and coumarone are unaffected; furfuryl methyl and difurfuryl ethers

give resinous products, and 2:5-dimethylfuran undergoes fission to acetylacetone (*disemicarbazone*).

H. BURTON.

**Ketone syntheses in the furan series.** T. REICHSTEIN (Helv. Chim. Acta, 1930, 13, 356—360).—Acetyl chloride reacts with furan in presence of benzene and stannic chloride (cf. Stadnikov and Goldfarb, A., 1929, 74) at about 0°, forming 2-acetylfuran. 2-Acetyl-5-methylfuran, b. p. 74°/12 mm., m. p. about -2° [*semicarbazone*, m. p. 190—191° (corr.)], is prepared similarly but in poor yield. A better yield (34%) is obtained by using zinc chloride and ether. Furan and pyromucyl chloride condense in presence of benzene and stannic chloride giving a small amount of di-2-furyl ketone, b. p. about 102°/1 mm., m. p. 33—34° [*semicarbazone*, m. p. 144—145.5° (corr.)], also prepared in small amount by the dry distillation of silver furilate at 70 mm.

H. BURTON.

**Preparation of 5-bromofurfuraldehyde and some of its derivatives.** H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1930, 52, 1170—1172).—5-Bromofurfuraldehyde, m. p. 82°, b. p. about 90—95°/8 mm. (*oxime*, m. p. 150—152°; *diacetate*, m. p. 51—52°, b. p. 128—130°/5—6 mm.), is obtained by brominating furfuraldehyde diacetate (cf. Iowa State Coll. J. Sci., 1929, 4, 35) in carbon disulphide, best by adding bromine (2 mols.) to the cooled solution, followed by distilling the solvent from the filtered mixture and distilling the residue in steam. Methods in which acid is removed by calcium carbonate or by reaction in presence of pyridine are also described. When excess of bromine is used a compound, m. p. 134—135°, may be isolated in small amount.

R. K. CALLOW.

**Rearrangement of the  $\alpha$ -furfuryl group. 2-Furylacetic acid and 5-methylfuroic acid.** M. M. RUNDE, E. W. SCOTT, and J. R. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 1284—1289).—2-Furylacetaldoxime, obtained by condensation of furfuraldehyde with nitromethane and reduction of the product, is converted by boiling acetic anhydride into 2-furylacetonitrile, b. p. 78—80°/20 mm.,  $d_4^{25}$  1.0854,  $n_D^{25}$  1.4715, which is hydrolysed by boiling aqueous alkali to 2-furylacetic acid, m. p. 67.3—67.5° (*anilide*, m. p. 79—80°). This loses carbon dioxide at 250° to give 2-methylfuran. The nitrile and acid differ from those described by Kirner and Richter (A., 1929, 1458), and it is evident that molecular rearrangement must have occurred in the series of reactions used by these authors, most probably in the reaction of  $\alpha$ -furfuryl chloride with sodium cyanide, yielding 5-methylfuronitrile and finally 5-methylfuroic acid. This is confirmed by the preparation of 5-methylfuroic acid, m. p. 108.3—109.5° (corr.), identical with the product obtained by the method of Kirner and Richter, by distillation of rhamnose with 10% hydrochloric acid and oxidation of the resulting aldehyde with silver oxide in presence of barium hydroxide.

R. K. CALLOW.

**Ammono-furfuraldehydes.** H. H. STRAIN (J. Amer. Chem. Soc., 1930, 52, 1216—1219).—Hydrofuramide, formed from furfuraldehyde and aqueous ammonia, and the hypothetical furfurylideneimide which would be expected to result by its reaction with liquid ammonia, may be regarded as nitrogen ana-

logues of aldehydes ("ammono-aldehydes," cf. A., 1927, 767), and to undergo analogous reactions. Actually, hydrofuramide and liquid ammonia yield furine, analogous to amarine: the attempt to "ammonate" hydrofuramide by means of ammonium chloride in liquid ammonia yields only furine, and attempted "nitridation" by means of iodine in liquid ammonia yields tars.

Furine nitrate, m. p. 94° (lit., 154°), yields when kept for a long time, when heated above its m. p., or when crystallised from alcohol-ether, a (?) crystalline modification, decomp. 180—182°. Attempted "nitridation" of furine yields tars and a little of a substance, m. p. 239°. Furine and potassamide in liquid ammonia yield tar and hydrogen; none of the expected analogues of lophine can be isolated.

R. K. CALLOW.

**Derivatives of coumarin.** II. F. D. DODGE (J. Amer. Chem. Soc., 1930, 52, 1724—1725).—When coumarin is treated with sodium hydrogen sulphite solution, sodium dihydrocoumarin-3-sulphonate is formed (cf. A., 1916, i, 413). Treatment with sodium sulphite solution and subsequent acidification affords sodium dihydrocoumaric acid- $\beta$ -sulphonate (+3H<sub>2</sub>O) (cf. Dey and Row, A., 1924, i, 538). H. BURTON.

**Constitution of primetin.** W. NAGAI and S. HATTORI (Acta Phytochim., 1930, 5, 1—8).—The crude material obtained from *Primula modesta* is purified by extraction with light petroleum and crystallisation of the residue from methyl alcohol. Primetin is 5:6-dihydroxyflavone, m. p. 230—231°. It gives a green colour with ferric chloride and yields small amounts of benzoic acid when heated with methyl-alcoholic potassium hydroxide. Acetic anhydride and sodium acetate yield diacetylprimetin, m. p. 189°; diazomethane yields methylprimetin, m. p. 211—212°. The latter with acetic anhydride and pyridine gives acetylmethylprimetin, m. p. 166—167°, which shows almost the same absorption spectrum as 6-hydroxyflavone.

J. H. BIRKINSHAW.

**Occurrence and physiological significance of daphnin in *Daphne odora*.** T. ASAI (Acta Phytochim., 1930, 5, 9—21).—The following derivatives of daphnetin (7:8-dihydroxycoumarin) were prepared: diacetyldaphnetin, m. p. 137°, dibenzoyldaphnetin, m. p. 152°, daphnetin monoethyl ether, m. p. 155°, daphnetin diethyl ether, m. p. 72°.

The daphnin content of the organs of *D. odora* changes with the time of year. Large amounts are present in the leaf-buds in the early stages of development. It has absorption bands at 3200 and 3900 Å., and in this respect resembles flavone. Coumarin and hydroxycoumarin glucosides show the same absorption spectrum and localisation in the plant organs as hydroxyflavone and probably subserve the same physiological function.

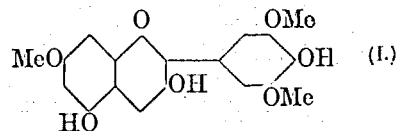
J. H. BIRKINSHAW.

**Synthesis of pyrylium salts of anthocyanidin type.** XIX. Synthesis of delphinidin chloride not involving demethylation, and syntheses of hirsutidin chloride and of delphinidin chloride 3'-methyl ether, possibly identical with petunidin chloride. W. BRADLEY, R. ROBINSON, and G. SCHWARZENBACH (J.C.S., 1930, 793—817).— $\omega$ -Diazo-

3:4:5-triacetoxyacetophenone, m. p. 125—126° (decomp.), was prepared from triacetylalloyl chloride and diazomethane at -10°, and converted by heating with glacial acetic acid into  $\omega$ :3:4:5-tetra-acetoxyacetophenone, m. p. 122—123°. This, when condensed with 2-O-benzoylphloroglucinaldehyde in alcohol-ethyl acetate under the influence of hydrogen chloride gave 5-O-benzoyldelphinidin chloride, which on alkaline hydrolysis, followed by treatment with acid, gave delphinidin chloride, identical in every respect with the natural product. The principal method of comparison in this and later cases was based on the colour reactions in alkaline solutions of definite  $p_H$  value (cf. Robertson and Robinson, A., 1929, 477). The mixture of solvents appeared to be necessary in this condensation, but it could also be carried out in ethyl alcohol under the influence of hydrogen chloride and acetyl chloride.

O-Benzoylphloroglucinaldehyde with methyl iodide and silver oxide in acetone yielded 6-hydroxy-2-benzoyloxy-4-methoxybenzaldehyde, m. p. 109°, and the dimethyl ether; on alkaline hydrolysis, the former gave phloroglucinaldehyde 4-methyl ether (Karrer and Bloch, A., 1927, 564). Benzoylation by a similar process gave 6-hydroxy-2-benzoyloxy-4-benzoyloxybenzaldehyde, m. p. 202—203°. Acetylation of 2-O-methylphloroglucinaldehyde under special conditions gave 4:6-diacetoxy-2-methoxybenzaldehyde, m. p. 107°, also obtained by methylation of O-diacetylphloroglucinaldehyde (cf. Robertson and Robinson, A., 1927, 974).

In the presence of hydrogen chloride, a solution of 4-O-methylphloroglucinaldehyde rapidly became red and deposited a coloured, amorphous substance, possibly axanthylum salt; hence its benzoyl derivative was used for the synthesis of the flavylum salt. The 2-O-methylisomeride behaved similarly, but special conditions for condensation which eliminated the formation of by-product were evolved. 2-O-Benzoyl-4-O-methylphloroglucinaldehyde and  $\omega$ -acetoxy-4-benzoyloxy-3:5-dimethoxyacetophenone in ethyl acetate condensed under the influence of hydrogen chloride to 5-O-benzoyl-7:3':5'-O-trimethyldelphinidin chloride; this needed aqueous methyl-alcoholic potassium hydroxide for hydrolysis, after which, conversion into chloride gave 7:3':5'-trimethyldelphinidin chloride (I) identical in all respects with



hirsutidin chloride. The isomeric 5:3':5'-O-trimethyldelphinidin chloride was obtained directly by the condensation of 2-O-methylphloroglucinaldehyde with  $\omega$ -acetoxy-4-benzoyloxy-3:5-dimethoxyacetophenone in formic acid saturated with dry hydrogen chloride, the benzyl group being eliminated during the reaction as in the previous case.

The action of 8% aqueous sodium hydroxide and copper-bronze on 5-bromovanillin gave, not 3-O-methylgallic acid as stated by Shriner and McCutchan (A., 1929, 1069), but 4:5-dihydroxy-3-methoxybenzaldehyde [the 2:4-dinitrophenylhydrazones begins to decomp. at 230°; diacetyl derivative (lit. 98—99° for

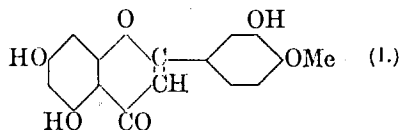
substance  $+H_2O$ ]. On methylation (methyl sulphate) this gave the known 3:4:5-trimethoxybenzaldehyde, m. p. 74–75°. The following route to 3-O-methylgallic acid is more convenient than earlier ones. The interaction of methyl gallate and diphenyl-dichloromethane under special conditions gave methyl 3-hydroxy-4:5-diphenylmethylenedioxybenzoate ( $+1/2 C_6H_6$ , detected by reaction with formaldehyde and sulphuric acid), m. p. 165°, and this on methylation (methyl iodide and sodium ethoxide) gave methyl 3-methoxy-4:5-diphenylmethylenedioxybenzoate, m. p. 134.5°, which on acid hydrolysis gave 3-O-methylgallic acid. Hydrolysis with sodium hydroxide, however, yielded 3-methoxy-4:5-diphenylmethylenedioxybenzoic acid, m. p. 217°, the chloride (m. p. 109°) of which with diazomethane gave  $\omega$ -diazo-3-methoxy-4:5-diphenylmethylenedioxyacetophenone, decomp. about 160–170° according to the rate of heating; converted by acetic acid into the corresponding  $\omega$ -acetoxy-compound, m. p. 126–127°.

The diacetyl derivative (m. p. 170–171°) of 3-O-methylgallic acid was converted through its chloride, m. p. 109°, into  $\omega$ -diazo-4:5-diacetoxy-3-methoxyacetophenone, m. p. 90–91°, and  $\omega$ -4:5-triacetoxy-3-methoxyacetophenone, m. p. 138.5°. When either this or, better,  $\omega$ -acetoxy-3-methoxy-4:5-diphenylmethylenedioxyacetophenone was condensed with 2-O-benzoylphloroglucinaldehyde by hydrogen chloride in ethyl acetate, 5-O-benzoyl-3'-O-methyldephinidin chloride ( $+2H_2O$ ) was formed. Hydrolysis in the usual way gave 3'-O-methyldephinidin chloride [ $H_2O$  and  $1/2 H_2O$  (?)]. This closely resembled natural petunidin chloride in general appearance and properties, but showed a marked difference in some of its colour reactions in alkaline solution. It is considered that although petunidin is not identical with this in a pure state, it may still be essentially this 3'-O-methyl ether with some of its properties altered by small amounts of impurities.

H. A. PIGGOTT.

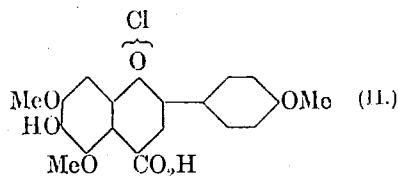
**Anthoxanthins. XI. Synthesis of diosmetin and luteolin 3'-methyl ether.** A. LOVECY, R. ROBINSON, and S. SUGASAWA. **XII. Transition from a flavylum salt to a flavone, illustrated by a new synthesis of scutellarein tetramethyl ether.** R. ROBINSON and G. SCHWARZENBACH (J.C.S., 1930, 817–822, 822–830, cf. A., 1929, 326).—XI. *iso*-Vanillic acid, prepared by heating veratric acid with hydrobromic acid, was converted into its methyl ester, which on benzylation gave methyl O-benzylisovanillate, m. p. 124°. This was hydrolysed to O-benzylisovanillic acid, m. p. 177°, prepared less conveniently by benzylation of isovanillin to O-benzylisovanillin, m. p. 63°, and subsequent oxidation with permanganate in acetone. O-Benzylisovanillic anhydride, m. p. 156° (from the acid and thionyl chloride in presence of pyridine), when condensed with phloracetophenone in the presence of sodium O-benzylisovanillate gave 5:7-dihydroxy-3'-benzyloxy-4'-methoxyflavone (O-benzyl-diosmetin), m. p. 240° after previous sintering. The product of hydrolysis could not be satisfactorily purified, but gave with acetic anhydride O-triacetyldiosmetin, m. p. 195–196°, hydrolysed by alkali to diosmetin, m. p. 253–254°. These were identical with samples of diosmetin and triacetyldiosmetin of

natural origin; the formulation of diosmetin as luteolin 4'-methyl ether (I) is thus confirmed.



*Luteolin 3'-methyl ether* (anhydrous and  $H_2O$ ), m. p. 330–331° (triacetyl compound, m. p. 220–221°), was similarly synthesised by the use of benzylvanillic acid (anhydride, m. p. 135–136°) instead of the *iso*-acid; 5:7-dihydroxy-4'-benzyloxy-3-methoxyflavone ( $+1/2 H_2O$ ), m. p. 265–267°, and its diacetyl compound, m. p. 195°, were isolated as intermediate products.

**XII. Anisoylpyruvic acid**, m. p. 162.5° (ethyl ester, m. p. 54°), was obtained by the condensation of *p*-methoxyacetophenone with ethyl oxalate in presence of sodium ethoxide. Interaction with 2:6-dimethoxyquinol under the influence of hydrogen chloride gave 6-hydroxy-5:7:4'-trimethoxy-4-carboxyflavylium chloride, m. p. 170–180° (crude) (II) [picrate

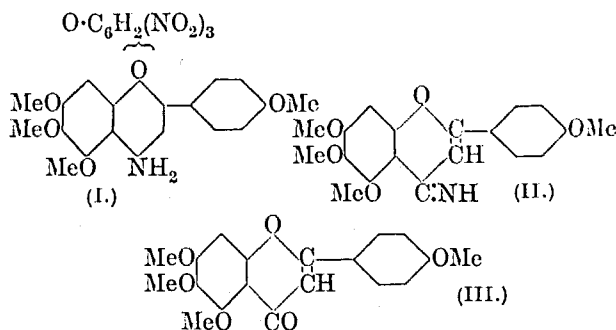


( $+1H_2O$ ), decomp. 224°, betaine ( $+1 1/2 H_2O$ ), decomp. 182°]. The corresponding 5:6:7:4'-tetramethoxy-4-carboxyflavylium derivatives [betaine ( $+1 1/2 H_2O$ ), m. p. 127–130°; picrate (anhydrous and  $+1H_2O$ ), decomp. 204–205°] were obtained when antiarol was used in the place of dimethoxyquinol in a similar condensation. Negative results were obtained on attempting to oxidise the chlorides or betaines to scutellarein derivatives (cf. Bülow and Wagner, A., 1903, i, 647). Interaction of phosphorus pentachloride with the betaine appeared to yield the acid chloride flavylium chloride, but this did not react normally with ammonia or hydrazine.

Sodio- $\omega$ -hydroxymethylene-*p*-methoxyacetophenone with hydroxylamine hydrochloride gave anisoylacetaldoxime, m. p. 120°, dehydrated by acetyl chloride to 5-anisylisooxazole, m. p. 63° (isomerised by alcoholic sodium hydroxide to the known  $\omega$ -cyano-*p*-methoxyacetophenone). 5-Anisylisooxazole methosulphate, m. p. 142.5°, was converted by potassium cyanide into  $\alpha$ -methylimino- $\beta$ -anisoylpropionitrile, m. p. 109°, hydrolysed by dilute acid in the cold to anisoylpyruvamide, decomp. 192°. (Attempts to prepare this amide from the acid chloride or ester, or by the interaction of ethyl oxamate with *p*-methoxyacetophenone failed.)

A crude sample only of 4-carbamyl-5:6:7:4'-tetramethoxyflavylium chloride, very readily hydrolysed to the 4-carboxy-compound, could be isolated from the product from the condensation of anisoylpyruvamide with antiarol: it was converted by the Hofmann reaction into 4-amino-5:6:7:4'-tetramethoxyflavylium picrate (I), decomp. 281° (chloride not analysed). The corresponding base appears to be the

flavone imine (II) for on hydrolysis it yields 5:6:7:4'-tetramethoxyflavone, m. p. 161° (III),



identical in all respects with scutellarein tetramethyl ether from natural scutellarein. Scutellarein has already been synthesised, but by an ambiguous method (Bargellini, A., 1915, i, 84); this is therefore the first unambiguous synthesis of the tetramethyl ether.

In repeating the work of Bülow and Wagner (*loc. cit.*) 7-hydroxy-4-carboxyflavylium chloride, orange-red, decomp. 250°, and its ethyl ester, decomp. 198°, were prepared. H. A. PIGGOTT.

**Cyclic nitrones.** E. P. KOHLER and C. R. ADDINALL (J. Amer. Chem. Soc., 1930, 52, 1590—1604).—The purple anhydride obtained by treatment of  $\alpha$ -oximino- $\gamma$ -diketo- $\alpha\beta$ -triphenylbutane with hydrogen chloride in chloroform solution (cf. A., 1926, 309) is now considered to be 3-keto-2:4:5-triphenylpyrrolenine oxide (I),  $\begin{matrix} \text{CO-CPh} \\ \text{CPh:CPh} \end{matrix} \text{NO}$ , m. p. 175—177°. 3-Keto-4:5-diphenyl-2-p-chlorophenyl- (II), m. p. 201°, and 3-keto-5-phenyl-4-p-chlorophenyl-2-p-bromophenylpyrrolenine oxide, sinters at 180°, are prepared similarly from the corresponding oximes.  $\alpha$ -Oximino- $\gamma$ -diketo- $\alpha\beta$ -diphenyl- $\delta$ -p-chlorophenylbutane (+Et<sub>2</sub>O), m. p. 112° (decomp.), is prepared by the method previously described (A., 1924, i, 998; *loc. cit.*) by way of p-chlorophenyl  $\gamma$ -nitro- $\beta\gamma$ -diphenylpropyl ketone, m. p. 176°, its  $\alpha$ -bromo-derivative, m. p. 178°, 5-hydroxy-5-p-chlorobenzoyl-3:4-diphenylisooxazoline, m. p. 165°, and 5-p-chlorobenzoyl-3:4-diphenylisooxazole, m. p. 164°.

Ozonisation of I affords benzoic acid and benzonitrile, whilst II yields benzoic acid and p-chlorobenzonitrile. Treatment of I with magnesium phenyl bromide under carefully regulated conditions gives 1-hydroxy-2:2:4:5-tetraphenyl-3-pyrrolidone (sodium salt; benzoate +C<sub>6</sub>H<sub>5</sub>, m. p. 225°); addition of the Grignard reagent across a double linking occurs. This ketone is stable only in the solid state and when heated, melts at 184° to a green liquid, which then evolves gas and resolidifies to a high-melting yellow solid. 1-Methoxy-2:2:4:5-tetraphenyl-3-pyrrolidone, m. p. about 185° (decomp.), prepared from the above sodium salt and methyl sulphate, is stable. Oxidation of the hydroxy-compound with chromic acid in acetic acid solution gives  $\gamma$ -hydroxy- $\alpha\gamma\gamma$ -triphenylbutane- $\alpha\beta$ -dione (*loc. cit.*). Ozonisation of the methoxy-compound affords benzoic acid and O-methylbenzophenoneoxime, whilst chromic acid oxidation furnishes  $\alpha$ -N-methoxybenzamido- $\beta\gamma$ -diketo- $\alpha\gamma$ -tri-

phenylpropane, COBz·CPh<sub>2</sub>·NBz·OMe, m. p. 160°. Treatment of this with methyl-alcoholic sodium methoxide yields a mixture of benzoylformic acid and a substance, m. p. 165°, together with diphenylmethylenbenzamide, NBz·CPh<sub>2</sub>, m. p. 115° (acid hydrolysis products benzophenone and benzamide), and N-methoxybenzodiphenylmethanimide, OMe·NBz·CHPh<sub>2</sub>, m. p. 155—160° (decomp.). Thermal decomposition of the last-named compound affords methyl alcohol and diphenylmethylenbenzamide. Oxidation of 1-methoxy-2:5-diphenyl-4-p-chlorophenyl-2-p-bromophenyl-3-pyrrolidone, m. p. about 158° (decomp.), with chromic acid yields  $\alpha$ -N-methoxybenzamido- $\beta\gamma$ -diketo- $\alpha$ -phenyl- $\gamma$ -p-chlorophenyl- $\alpha$ -p-bromophenylpropane, m. p. about 170° (decomp.), degraded by methyl-alcoholic sodium methoxide to p-chlorobenzoylformic acid (phenylhydrazone, m. p. 188°) and N-methoxybenz-p-bromodiphenylmethanimide, decomp. about 140°. The last-named compound undergoes thermal decomposition to methyl alcohol and p-bromodiphenylmethylenbenzamide, NBz·CPh·C<sub>6</sub>H<sub>4</sub>Br, which is hydrolysed by hydrochloric acid to benzamide and p-bromobenzophenone.

Successive treatment of I with dilute methyl-alcoholic sodium methoxide and sulphur dioxide yields 1-hydroxy-2-methoxy-2:4:5-triphenyl-3-pyrrolidone, m. p. 163—165° (decomp.) [methyl ether, m. p. 175—180° (decomp.)]. H. BURTON.

**Piperidine derivatives. VIII. Substituted piperidinoalkyl benzoates.** C. F. BAILEY and S. M. McELVAIN (J. Amer. Chem. Soc., 1930, 52, 1633—1640).—Details are given for the isolation of 4-methylpiperidine from coal-tar bases and its reduction by sodium and alcohol to 4-methylpiperidine. Reduction of 2-benzyl-, and 2- and 4-styryl-pyridines in presence of alcohol and a nickel catalyst at 150—165°/150—200 atm. gives 2-benzyl-, b. p. 266·6—269°,  $d_4^{20}$  0·9749,  $n_D^{20}$  1·5237, 2- $\beta$ -phenylethyl-, b. p. 137·5—138·5°/3 mm.,  $d_4^{20}$  0·9483,  $n_D^{20}$  1·5207 [hydrochloride, m. p. 156—158° (lit. 155°); benzenesulphonyl derivative, m. p. 129—130°], and 4- $\beta$ -phenylethylpiperidines, b. p. 126—130°/3 mm.,  $d_4^{20}$  0·9713,  $n_D^{20}$  1·5293 (hydrochloride, m. p. 171—173°; benzenesulphonyl derivative, m. p. 130—131°), respectively. The following benzoate hydrochlorides are prepared from the requisite piperidine derivative and  $\beta$ -chloroethyl or  $\gamma$ -chloropropyl benzoate:  $\beta$ -4-methylpiperidinoethyl-, m. p. 181—184°;  $\gamma$ -4-methylpiperidinopropyl-, m. p. 165—168°;  $\gamma$ -2-benzylpiperidinopropyl-, m. p. 169—171°;  $\beta$ -(2- $\beta$ -phenylethylpiperidino)ethyl-, an oil (free ester, b. p. 202—207°/1 mm.);  $\gamma$ -(2- $\beta$ -phenylethylpiperidino)propyl-, m. p. 123—125° and 149—151°;  $\beta$ -(4- $\beta$ -phenylethylpiperidino)ethyl-, m. p. 163—165°. Several of these hydrochlorides have powerful anæsthetic properties. H. BURTON.

**Catalytic reduction of 1-phenyl- and 1-benzyl-4-piperidones.** N. W. BOLYARD (J. Amer. Chem. Soc., 1930, 52, 1030—1032).—Whilst the benzene nucleus is reduced when either 1-phenyl- or 1-benzyl-3-carbethoxy-4-piperidone is hydrogenated in presence of platinum oxide-platinum-black (Thayer and McElvain, A., 1928, 72) and 1-alkyl-4-piperidones are more readily reduced to 1-alkyl-4-hydroxypiperidines (A., 1929, 577), 1-phenyl-4-piperidone



hydrochloride, m. p. 145—147° (prepared by boiling the 3-carbethoxy-derivative with 20% hydrochloric acid), yields on reduction and benzooylation of the product 1-cyclohexyl-4-piperidyl benzoate hydrochloride (I), m. p. 250—252°, and 1-benzyl-4-piperidone hydrochloride, m. p. 159—161° (from the 3-carbethoxy-derivative), yields 1-benzyl-4-piperidyl benzoate hydrochloride (II), m. p. 198—200°. In local anaesthetic power I exceeds II, whilst I has a lower subcutaneous and a higher intravenous toxicity than II.

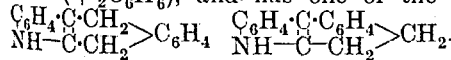
R. K. CALLOW.

**Action of chloral hydrate and hydroxylamine hydrochloride on the isomeric phenylenediamines.** K. MORSCH (Monatsh., 1930, 55, 144—150).—Treatment of *o*-phenylenediamine hydrochloride with chloral hydrate and hydroxylamine hydrochloride in sodium sulphate solution gives a 40—50% yield of 2-hydroxyquinoxaline, m. p. 269.5—271° (lit. 265°).

[With W. SCHULZE.]—Similar treatment of *m*- and *p*-phenylenediamines affords 80 and 67%, respectively, of the corresponding *di*(oximinoacetamido)-derivatives. When treated with sulphuric acid at 50°, these furnish 6(or 4)-oximinoacetamidoisatin and 5-oximinoacetamidoisatin, respectively (cf. Borsche and others, A., 1924, i, 986).

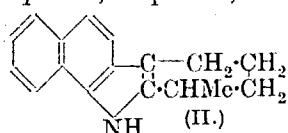
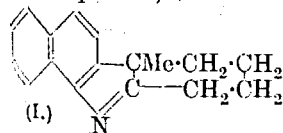
H. BURTON.

**Nuclear homologues of hydrogenated carbazole and pyrazolone derivatives of  $\alpha$ -tetralone.** E. GHIGI (Gazzetta, 1930, 60, 194—199).—Indole condensation of  $\alpha$ -tetralone phenylhydrazine yields 1:2-benzo-3:4-dihydrocarbazole, white needles, m. p. 160°, identical with Titley's 1:2-indolo-(2:3)-3:4-dihydronaphthalene, dark reddish plates, m. p. 161° (A., 1928, 1241). The *N*-methyl ether of this compound, m. p. 130°, is similarly obtained from the  $\alpha$ -phenylmethylhydrazine of  $\alpha$ -tetralone. The action of phenylhydrazine on ethyl  $\alpha$ -tetralone- $\beta$ -carboxylate gives 1-phenyl-3:4-tetralin-5-pyrazolone, which yields 1-phenyl-2-methyl-3:4-tetralin-5-pyrazolone when treated with methyl iodide. The action to methyl iodide on 1:2-benzo-3:4-dihydrocarbazole in a sealed tube at 120—125° gives a base of unknown constitution, forming a crystalline picrate. When distilled in a vacuum or condensed by means of 10% sulphuric acid,  $\beta$ -tetralonephenylhydrazine gives a compound, m. p. 97—98°, which forms a picrate, m. p. 128° (+ $\frac{1}{2}$ C<sub>6</sub>H<sub>6</sub>), and has one of the two formulæ



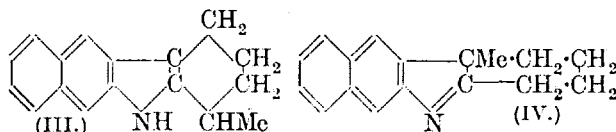
T. H. POPE.

**Investigations and syntheses in the series of hydrogenated derivatives of carbazole.** B. CECCHETTI and E. GHIGI (Gazzetta, 1930, 60, 185—189).—In presence of dilute sulphuric acid, 1-methylcyclohexan-2-one- $\alpha$ -naphthylhydrazine undergoes condensation giving 11-methyl- $\Delta^7$ :7:8-benzocarbazolenine (I), m. p. 135°, which forms a picrate, m. p. 175°, and



1-methyl-7:8-benzotetrahydrocarbazole (II), m. p. 126°, which also forms a picrate. Similarly, the corre-

sponding  $\beta$ -naphthylhydrazine gives 11-methyl- $\Delta^7$ :6:7-benzocarbazolenine (IV), which forms a picrate,



m. p. 162—163°, and 1-methyl-6:7-benzotetrahydrocarbazole (III), b. p. 250° (in a vacuum), which forms a picrate, m. p. 190°. Under similar conditions 1-methylcyclohexan-3-one- $\alpha$ -naphthylhydrazine gives a homologue of benzotetrahydrocarbazole, m. p. 148°, b. p. 273—274°/20 mm., no second isomeride being obtainable in this case.

T. H. POPE.

**Aldehyde syntheses: comparison of the three simplest five-ring heterocyclic compounds.** T. REICHSTEIN (Helv. Chim. Acta, 1930, 13, 349—356).—The ease with which simple heterocyclic compounds undergo the Gattermann aldehyde condensation is in the order pyrrole, furan, thiophen. Under the conditions used for the furan derivatives (this vol., 783), 1-methyl-, 1-butyl-, and 1-isoamyl-pyrroles (A., 1927, 573) afford 1-methyl-, 1-butyl-, b. p. about 75°/2 mm. [semicarbazone, m. p. 146—147.5° (corr.)], and 1-isoamyl-pyrrole-2-aldehydes, b. p. about 90°/2 mm. [semicarbazone, m. p. 155—157° (corr.)], respectively. Dry distillation of a mixture of saccharic acid and furfurylamine gives 1-furfurylpyrrole, b. p. 76—78°/1 mm. [p-methoxybenzeneazo-derivative, m. p. 94—95° (corr.); p-tolueneazo-derivative, an oil (trinitrobenzene compound, m. p. 97—98°); 2-naphthaleneazo-derivative, m. p. 87—88° (trinitrobenzene compound, m. p. 110—111°)], together with 1-furfurylpyrrole-2-carboxylic acid, m. p. 120—122°, and 1-furfurylpyrrole-2-carboxylfurfurylamine, m. p. 79—80°. 1-Furfurylpyrrole-2-aldehyde, b. p. about 100°/2 mm. [semicarbazone, m. p. 174—175° (corr.)], and ethyl 5-aldehydopyrrole-2-carboxylate, m. p. 72.5—73.5° [free acid, m. p. about 212—215° (corr.; decomp.) after darkening about 185°], are prepared from 1-furfurylpyrrole and ethyl pyrrole-2-carboxylate, m. p. about 30° (cf. Oddo, A., 1909, i, 672), respectively. Aldehydes were not obtained from pyrrole, 2-acetylpyrrole, and pyrrole-2-carboxylic acid.

Thiophen condenses with hydrogen cyanide in presence of benzene, aluminium chloride, and hydrogen chloride forming a small amount of thiophen-2-aldehyde, b. p. 77—78°/12 mm. [semicarbazone, m. p. 227—228° (corr.; decomp.)]; no reaction occurs with hydrogen chloride alone as the condensing agent.

H. BURTON.

**Isolation of an arsenic compound of pyridine and observations concerning the phase system arsenic trichloride-pyridine.** W. B. SHIREY (J. Amer. Chem. Soc., 1930, 52, 1720).—Arsenic trichloride and an excess of pyridine give the additive compound, AsCl<sub>3</sub>·2C<sub>5</sub>H<sub>5</sub>N. Phase rule applications to the system arsenic trichloride-pyridine are difficult owing to the tendency for obtaining abnormal time-temperature curves and supercooling.

H. BURTON.

[Preparation of] l-tryptophan. G. J. COX and (Miss) H. KING (Organic Syntheses, 1930, 10, 100—105).

**Bases in the kerosene distillate of California petroleum.** E. J. POTH, W. A. SCHULZE, W. A. KING, W. C. THOMPSON, W. M. SLAGLE, W. W. FLOYD, and J. R. BAILEY (J. Amer. Chem. Soc., 1930, 52, 1239—1250).—Kerosene distillates from California petroleum (nitrogen content 0.055%) refined by the Edcleanu process yield a residue containing hydrocarbons and nitrogenous bases. The latter can be extracted by dilute sulphuric acid, and the investigation has been carried out with 50 litres of the product thus obtained. A partial separation is attained by fractional distillation under reduced pressure, and the isolation of bases from the fraction of b. p. 274—280°/748 mm. by further treatment is now described.

2:3:8-Trimethylquinoline, m. p. 55—56°, b. p. 280°/747 mm. with slight decomposition,  $n_D^{20}$  1.5828 [hydrogen sulphate, decomp. 275°; hydrochloride, darkens 230°, decomp. 260°; nitrate, m. p. 160.5° (decomp.); picrate, decomp. 242—245°; insoluble chloroaurate, chloroplatinate, chromate, ferrocyanide, and complex salts with zinc chloride and mercuric chloride], is separated as the picrate from acetic acid, or as the hydrogen sulphate with 50% sulphuric acid. Its constitution is deduced from the reactions given below and is confirmed by its synthesis by the Doebner-von Miller reaction by the action of hydrochloric acid on a mixture of *o*-toluidine and tiglic aldehyde. It does not form a methiodide, indicating substitution in positions 3 and 8. It condenses with 2 mols. of formaldehyde to give 3:8-dimethyl-2-dimethylolmethylquinoline, m. p. 111.5°, b. p. 170—172°/3 mm. (picrate, m. p. 180°), which is oxidised by permanganate in acetone in presence of acetic acid, or by 50% nitric acid, to 3:8-dimethylquinoline-2-carboxylic acid, m. p. 157.5° (decomp.), which, when distilled with soda-lime, gives 3:8-dimethylquinoline, b. p. 269°/751 mm.,  $d_4^{20}$  1.051,  $n_D^{20}$  1.6063 [picrate, m. p. 207° (decomp.); picrolonate, m. p. 199° (decomp.); methiodide, m. p. 197°; oxalate, m. p. 128°]. The last-named compound is also obtained by the Doebner-von Miller synthesis from *o*-toluidine, propaldehyde, and methylal. 3:8-Dimethyl-2-hydroxyethylquinoline, m. p. 99° [picrate, m. p. 162° (decomp.)], is a product of the above permanganate oxidation in the absence of acetic acid. 2:3:8-Trimethylquinoline condenses with benzaldehyde in presence of zinc chloride to give the dibenzylidene compound, sinters 198°, decomp. 205°, which is converted by hot acetic acid into 2-styryl-3:8-dimethylquinoline, m. p. 120°. Oxidation of 2:3:8-trimethylquinoline with chromic acid yields 2:3-dimethylquinoline-8-carboxylic acid, m. p. 202°, converted by distillation with soda-lime into the known 2:3-dimethylquinoline.

Two other bases have been separated from the fraction examined. The base  $C_{16}H_{25}N$ , b. p. 278°/746 mm.,  $n_D^{20}$  1.4958, separates as the picrate, soluble in benzene or alcohol, with the picrate of 2:3:8-trimethylquinoline, and forms a soluble sulphate. The base  $C_{12}H_{13}N$ , m. p. 43°, b. p. 278.9°/748 mm.,  $n_D^{20}$  1.5828, also occurs in the soluble sulphate fraction.

R. K. CALLOW.

**Manufacture of [therapeutically active] basic nitro-derivatives of 9-aminoacridine.** I. G. FARBENIND.—See B., 1930, 486.

**5:5-Substituted barbituric acids.** E. H. VOLWILER and D. L. TABERN (J. Amer. Chem. Soc., 1930, 52, 1676—1679).—The following disubstituted barbituric acids are prepared from the requisite malonic ester and carbamide in presence of sodium ethoxide at 80—85°: 5-ethyl-5- $\beta$ -methylbutyl-, m. p. 135—136°; 5-ethyl-5- $\alpha$ -methylbutyl-, m. p. 129—130°; 5-n-amy-5-allyl-, m. p. 97—100°; 5-n-butyl-5- $\beta$ -methylbutyl-, m. p. 146—148°; 5-n-butyl-5-n-amy-, m. p. 118—120°; 5-n-amy-5-isopropyl-, m. p. 100—102°; 5-n-amy-5-isobutyl-, m. p. 105—107°; 5-isobutyl-5-isoamyl-, m. p. 146—147°; 5- $\beta$ -methylbutyl-5-allyl-, m. p. 97—99°; 5-n-butyl-5- $\alpha$ -ethylpropyl-, m. p. 108—109°; 5-n-butyl-5- $\alpha$ -methylbutyl-, m. p. 111—112°; 5-n-butyl-5- $\alpha$ -methylheptyl-, and 5- $\alpha$ -methylheptyl-5-allyl-, m. p. 148—150°. The first two of these acids are the most efficient hypnotics. Physical data for 26 substituted malonic esters are given.

H. BURTON.

**Action of benzyl azide on barbituric acid.** T. CURTIUS and W. KLAVEN (J. pr. Chem., 1930, [ii], 125, 464—465).—A quantitative yield of 5-benzylaminobarbituric acid (benzyluramil) is obtained from benzyl azide and anhydrous barbituric acid at 165°. The azide decomposes into the radical  $CH_2Ph\cdot N$ , which then combines with the acid.

H. BURTON.

**Microscopical identification of barbituric acid drugs.** G. DENIGÈS (Bull. Soc. Pharm. Bordeaux, 1929, 67, 165—173; Chem. Zentr., 1929, ii, 3044).—The barbituric acid derivatives are precipitated from ammoniacal solution with acid and the form of the crystals is observed microscopically.

A. A. ELDRIDGE.

**Action of iodine and of hydrogen iodide on piperazine.** S. OTOLSKI (Rocz. Chem., 1930, 10, 259—271).—Piperazine, when heated in aqueous solution with iodine, yields a hydriodide, m. p. 245°, the same product being obtained by treating with hydriodic acid, in the presence of excess of which a dihydriodide, decomp. 250°, is obtained. *NN*-Diiodopiperazine is produced by the action of iodine in alkaline solution; this derivative when added to aqueous piperazine is converted into the above hydriodide and an iodate:  $6C_4H_{10}N_2 + 3I_2 + 3H_2O = 5C_4H_{10}N_2\cdot HI + C_4H_{10}N_2\cdot HIO_3$ . R. TRUSZKOWSKI.

**Structure and rate of hydrolysis of diketopiperazines. II. Hydrolysis by alkali.** P. A. LEVENE, A. ROTHEN, R. E. STEIGER, and M. OSAKI (J. Biol. Chem., 1930, 86, 723—732).—The anhydrides of glycyl-*D*-alanine, glycyl-*L*-asparagine, glycyl-*L*-phenylglycine, glycyl-*L*-leucine, glycyl-*L*-tyrosine, glycyl-*DL*-valine, and glycyl-*D*-isovaline were hydrolysed by alkali (5 mols. of 0.5*N*-sodium hydroxide at 25°) at decreasing rates in the order mentioned.

C. R. HARINGTON.

**Racemisation. IX. Action of alkali on diketopiperazines. Action of hydrochloric acid on amino-acids, peptides, and diketopiperazines.** P. A. LEVENE and R. E. STEIGER (J. Biol. Chem., 1930, 86, 703—722).—The anhydrides of glycyl-*L*-asparagine, glycyl-*L*-phenylglycine, glycyl-*D*-phenylalanine, and glycyl-*L*-tyrosine were treated with sodium hydroxide (1 mol. at 0.1*N* concentration in 57%

aqueous pyridine) for 48 hrs. at 25°; racemisation to the extent of 89, 100, 92, and 10%, respectively, was produced; the low figure in the last case is ascribed to the disturbing effect of the phenolic group of tyrosine. *l*-Phenylglycine was partly racemised by prolonged heating with 20.3% hydrochloric acid at 100°, whilst similar treatment had no effect on *d*-phenylalanine. Hydrolysis of various peptides and diketopiperazines with hydrochloric acid produced partial racemisation of the aromatic but not of the aliphatic amino-acids. *Glycyl-l-asparagine anhydride* had  $[\alpha]_D^{25} +46.7^\circ$  in aqueous pyridine; *glycyl-l-phenylglycine anhydride*,  $[\alpha]_D^{25} -76.9^\circ$  in acetic acid; *glycyl-d-phenylalanine anhydride*,  $[\alpha]_D^{25} -100.76^\circ$  in acetic acid.

C. R. HARRINGTON.

**Action of diazomethane on the pyrimidine constituents of nucleic acids.** F. H. CASE and A. J. HILL (J. Amer. Chem. Soc., 1930, 52, 1536—1542).—Uracil, 4-methyluracil, and thymine are all converted into the corresponding 1:3-dimethyl derivatives by treatment with an ethereal solution of diazomethane. Cytosine affords only a small amount of 6-methylamino-2-hydroxypyrimidine. When the recovered (ether-insoluble) cytosine is crystallised from aqueous acetone a new form of cytosine is obtained. Dehydration of this and recrystallisation gives the normal variety. No pyrimidine derivative could be isolated by hydrolysis of the product formed from diazomethane and yeast-nucleic acid.

H. BURTON.

**Pyrimidines. CXIII. Improved method for the synthesis of cytosine [6-amino-2-hydroxypyrimidine].** G. B. HILBERT and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 1152—1157).—The increased availability of uracil (Davidson and Baudisch, A., 1926, 1154) has led to the following synthesis of cytosine, more convenient than that previously described (Wheeler and Johnson, A., 1903, 1, 526).

2:6-Dichloropyrimidine is prepared by a modification of the method of Gabriel (A., 1905, i, 481) by heating uracil with phosphoryl chloride at 110—120°. This reacts with cold alcoholic ammonia to give a mixture of 40% of 2-chloro-6-aminopyrimidine (I), m. p. 219—220°, and 60% of 6-chloro-2-aminopyrimidine (II), decomp. 168° after darkening. The latter compound is separated by distillation in steam from ammoniacal solution. The residue contains I and the cytosine derived from it. Cytosine and isocytosine, respectively, may be obtained from I by heating with water at 140° for 2 hrs., and from II by refluxing with water for 20 hrs., but better yields are obtained by way of the methoxy-derivatives. 6-Amino-2-methoxypyrimidine (III), m. p. 174° (sinters at 169°), is obtained by boiling the mixture of chloro-aminopyrimidines with methyl-alcoholic sodium methoxide, whilst 2-amino-6-methoxypyrimidine, m. p. 125—126°, is obtained from the mother-liquors, but is best prepared from II. Cytosine is obtained in quantitative yield by evaporating III with hydrochloric acid.

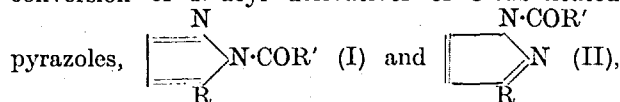
R. K. CALLOW.

**Pyrimidines. CXIV. Rearrangement of ethyl 2-ethylthiol-6-thiocyanopyrimidine-5-carboxylate into its thiocarbimide modification.**

F. B. JOHNSON and J. F. CHU (J. Amer. Chem. Soc., 1930, 52, 1580—1584).—*Ethyl 2-ethylthiol-6-thiocyanopyrimidine-5-carboxylate* (I), b. p. 204—205°/4 mm., m. p. 104—105°, obtained from the corresponding 6-chloro-derivative and potassium thiocyanate in alcohol, is converted into *ethyl 2-ethylthiol-6-thiocarbimidopyrimidine-5-carboxylate*, m. p. 32—33°, when a solution in benzene is heated at 190°. When heated with alcohol at 150°, I is also converted into the thiocarbimide, which subsequently reacts with the alcohol, forming a mixture of *ethyl 2-ethylthiol-6-thiourethanopyrimidine-5-carboxylate*, m. p. 119° (free acid, m. p. 180—181°), and *ethyl 6-amino-2-ethylthiolpyrimidine-5-carboxylate*, m. p. 101—102°. The yield of this amino-derivative is increased by prolonged heating at 150°. Treatment of I with thioacetic acid affords *ethyl 2-ethylthiol-6-acetylthiourethanopyrimidine-5-carboxylate*, m. p. 142—143°. *Ethyl 2-ethylthiol-6-thiocarbamido- and -6-phenylthiocarbamido-pyrimidine-5-carboxylates* have m. p. 165—168° and 134—135°, respectively.

H. BURTON.

**Acylpyrazoles.** I. K. VON AUWERS and E. CAUER (J. pr. Chem., 1930, [ii], 126, 146—176).—In order to study the possibility of isomeric inter-conversion of *N*-acyl derivatives of 5-substituted



various methods of determining the constitution of such derivatives have been investigated. Application of the von Meyer esterification rule to the 4-bromo-derivatives of such pyrazole-3-carboxylic acids, type II being difficult to esterify owing to steric hindrance, fails, since the *N*-acyl group is eliminated under esterification conditions when a negative group is present in the 4-position. Thus 5-methylpyrazole-3-carboxylic acid (*methyl ester*, m. p. 75—78°) is converted by bromine in hot acetic acid into the same 4-bromo-derivative (Rojahn and Kühling, A., 1926, 846) [*1-acetyl derivative*, m. p. 179—180° (decomp.)] as is obtained by similar bromination of its 1-acetyl derivative. Similarly, the ethyl ester [or its 1-acetyl derivative (below)] is converted into its 4-bromo-derivative, m. p. 105—108° (*hydrobromide*, m. p. 188°), the corresponding 4-chloro-derivative, m. p. 103—104° (free acid, m. p. 257—258°), being obtained by the action of sulphuryl chloride on the ester in ether. Acetylpyruvic acid reacts with ethyl hydrazino-carboxylate, acetyl-, benzoyl-, and *o*-nitrobenzoyl-hydrazine in aqueous-alcoholic solution at 30—40° to give, respectively, 1-carbethoxy-, m. p. 174—175°, 1-acetyl-, m. p. 173—174° (also obtained by heating 5-methylpyrazole-3-carboxylic acid with acetyl chloride or acetic anhydride; *ethyl ester*, b. p. 141—143°, m. p. 68.5—69.5°), 1-benzoyl-, m. p. 180°, and 1-*o*-nitrobenzoyl-, m. p. 222—224° (also by heating the acetyl derivative with *o*-nitrobenzoyl chloride; could not be converted into its bromo-derivative; heated above its m. p. gives, in poor yield, *N*-*o*-nitrobenzoyl-3(5)-methylpyrazole; *methyl ester*, m. p. 163—165°) 5-methylpyrazole-3-carboxylic acid. All these *N*-acyl derivatives lose the acyl group fairly readily when treated with dry hydrogen chloride

in ether-chloroform solution. Methyl 5-methylpyrazole-3-carboxylate is converted by heating with acetyl chloride or ethyl chloroformate into its 1-acetyl-, m. p. 67—68°, and 1-carbethoxy-, m. p. 91—92°, derivatives, respectively. Structural evidence based on the formation of derivatives of the type under consideration from the corresponding open-chain hydrazones is also untrustworthy. Whilst free acetylpyruvic acid condenses with acylhydrazines to yield acylpyrazoles directly, its ester readily yields the open-chain hydrazones, but these cannot be cyclised to pyrazole derivatives. Thus are obtained the carbethoxy-, m. p. 94.5—95.5°, acetyl-, m. p. 93°, benzoyl-, m. p. 163—164°, and *o*-nitrobenzoyl-, m. p. 198.5—199.5°, hydrazones of ethyl acetylpyruvate, the condensation following the course  $\text{COMe}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{R} + \text{NH}_2\cdot\text{NHAc} \rightarrow \text{COMe}\cdot\text{CH}_2\cdot\text{C}(\text{OH})(\text{CO}_2\text{R})\cdot\text{NH}\cdot\text{NHAc} \rightarrow \text{COMe}\cdot\text{CH}_2\cdot\text{C}(\text{N}\cdot\text{NHAc})\cdot\text{CO}_2\text{R} + \text{H}_2\text{O}$  and not  $\rightarrow \text{CMe}(\text{N}\cdot\text{NHAc})\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{R} + \text{H}_2\text{O}$ , since the same products are obtained when ethyl acetylpyruvate is replaced by its *O*-methyl ether,  $\text{COMe}\cdot\text{CH}\cdot\text{C}(\text{OMe})\cdot\text{CO}_2\text{Et}$ . Whilst acetylpyruvic acid reacts with semicarbazide even at low temperatures to give only 5-methylpyrazole-3-carboxylic acid, its ethyl ester affords ethyl 1-carbamido-5-methylpyrazole-3-carboxylate, m. p. 131° (decomp.). 4-Methylpyrazole 3-carboxylic acid (converted on heating into 4-methylpyrazole, b. p. 95°/13 mm.,  $d_4^{25}$  1.0183,  $n_D$  1.48951) is similarly converted by the action of the appropriate acid chloride into its 1-acetyl-, m. p. 198—199° (methyl ester, b. p. 134°/12 mm., m. p. 98—99°, by similar acetylation of the methyl ester), 1-carbethoxy-, m. p. 156—157° (methyl ester, b. p. 177°/13 mm., m. p. 86—87°), and 1-*o*-nitrobenzoyl-, m. p. 225—226° (methyl ester, m. p. 150.5—151.5°), derivatives, the last-named being converted into 1-*o*-nitrobenzoyl-4-methylpyrazole, b. p. 195—215°/15 mm., m. p. 107°, when heated above its m. p. Methylation of methyl 4-methylpyrazole-3-carboxylate with methyl iodide and methyl-alcoholic sodium methoxide gives a mixture of methyl 1:4-dimethylpyrazole-5-carboxylate, b. p. 95°/12 mm., m. p. 25—26°,  $d_4^{25}$  1.1288,  $n_D$  1.49094, and -3-carboxylate, b. p. 139°/12 mm., m. p. 37—38°,  $d_4^{25}$  1.1052,  $n_D$  1.48291. Methyl 4:5-dimethylpyrazole-3-carboxylate, m. p. 140—142° [prepared by the action of bromine on an ethereal solution of the corresponding pyrazoline ester (Auwers and Cauer, A., 1929, 1080)], is hydrolysed to the free acid, m. p. 276—277°, converted on heating into 4:5-dimethylpyrazole (*N*-*o*-nitrobenzoyl derivative, m. p. 149—150°), and by methods similar to those described above into its 1-acetyl-, m. p. 197—199° (methyl ester, b. p. 155—156°/14 mm., m. p. 82.5—83.5°), and 1-carbethoxy-, m. p. 148.5—149.5° (together with a substance, m. p. 121.5—123°; methyl ester, b. p. 185°/10 mm., m. p. 84.5—86°; converted mainly into a diketopiperazine on heating), derivatives. With *o*-nitrobenzoyl chloride the free acid gives only a diketopiperazine, but its methyl ester yields its 1-*o*-nitrobenzoyl derivative, m. p. 140.5—141.5°. Attempted oxidation of methyl 1-benzoyl-4-methylpyrazoline-3-carboxylate (*loc. cit.*) and 1-benzoyl-5-phenyl-3-methylpyrazoline, m. p. 138—138.5°, with iodine, nitric acid, nitrous gases, or nitrous acid was unsuccessful as a method for pre-

paring pyrazole derivatives of known structure, whilst bromine only causes fission of the first-named into benzoic acid and methyl 4-methylpyrazole-3-carboxylate.

[With E. WOLTER.]—*o*-Nitrobenzoylhydrazine condenses with methylacetylacetone in alcohol at 30—40° to give 1-*o*-nitrobenzoyl-3:4:5-trimethylpyrazole, m. p. 128—129°, but with benzoylacetone it yields the *o*-nitrobenzoylhydrazone,  $\text{CH}_2\text{Bz}\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , m. p. 162°, converted by heating with acetic acid, or, better, by the action of phosphoryl chloride, into 1-*o*-nitrobenzoyl-5-phenyl-3-methylpyrazole, m. p. 157—157.5°, the structure of which is therefore definitely of type I. This is isomerised by heating under reduced pressure and subsequent distillation (b. p. 220—240°) into 2-*o*-nitrobenzoyl-5-phenyl-3-methylpyrazole, m. p. 107° (type II), identical with a specimen obtained by the action of *o*-nitrobenzoyl chloride and pyridine on the parent pyrazole at 0°. J. W. BAKER.

Colour of complex diazoles. III. Reduced pyrrole-iminazole compounds. M. V. BETRABET and G. C. CHAKRAVARTI (J. Indian Chem. Soc., 1930, 7, 191—197).—A description of the preparation of reduced pyrrole-iminazole derivatives similar to those studied in Part II (Chakravarti and Sen-Gupta, A., 1925, i, 980). Succinic acid, condensed with *o*-phenylenediamine yielded *N*-*o*-aminophenylsuccinamic acid, m. p. 148—150°, the formation of the additive compound of Anderlini (A., 1894, i, 375) not being confirmed. This, when boiled in absolute alcoholic solution, gave benziminazole-2-propionic acid, m. p. 225—226° (Philips, A., 1928, 1381), which, when heated to 230° or boiled with acetic anhydride, gave 1:2-ketotrimethylenebenziminazole,

$\text{CH}_2\begin{matrix} \diagup \text{CO}\cdot\text{N}\cdot\text{C}_6\text{H}_4 \\ \diagdown \text{CH}_2\cdot\text{C}\cdot\text{N} \end{matrix}$ , m. p. 172—175°. Hexahydrophthalic acid, obtained in almost theoretical yield by the hydrogenation of phthalic acid in presence of platinum oxide, condensed with *o*-phenylenediamine to give a mixture of benziminazole-2-hexahydro-*o*-benzoic acid, m. p. 245—247° (softens at about 200°), and *o*-aminohexahydrophthalanil, m. p. 195—196° (acetyl compound, m. p. 261—263°). The former when boiled with acetic anhydride gave (1':2')-hexahydrobenzoylenebenziminazole, m. p. 175—176°,  $\text{CO}\text{---}\text{N}\cdot\text{C}_6\text{H}_4\text{---}\text{C}_6\text{H}_4\text{---}\text{C}\cdot\text{N}$  (alcohol and a little sodium ethoxide decompose this to ethyl benziminazole-2-hexahydro-*o*-benzoate, m. p. 163—164°). 3:4-Diaminotoluene and hexahydrophthalic anhydride yielded but little *N*-*o*-aminotolylhexahydrophthalamic acid, m. p. 264—266°, and much *o*-aminotolylhexahydrophthalamide, m. p. 274—276° (acetyl compound, m. p. 289—291°); the latter when heated to 280° for some time gave (1':2')-hexahydrobenzoylenemethylbenziminazole, m. p. 186—187°. Similarly, 1:2-naphthylenediamine gave naphthiminazole-2-hexahydro-*o*-benzoic acid, m. p. 263—265°, and aminonaphthylhexahydrophthalimide, m. p. 241—243° (acetyl derivative, m. p. 217—218°), and, by ring closure of the former, (1':2')-hexahydrobenzoylenenaphthiminazole, m. p. 223—224°. H. A. PIGGOTT.

[Two isomeric *ms*-tetrahydro-9:9'-diacridyls.] E. BERGMANN and O. BLUM-BERGMANN

(Ber., 1930, 63, [B], 757—762).—Repetition of the work of Schlenk and Bergmann (A., 1928, 1031) gives a tetrahydro-9 : 9'-diacridyl, m. p. 260—265° according to mode of heating (lit. m. p. 279°); as by-product, an *ethyl-* or a *dimethyl-dihydroacridine*, m. p. 112—113°, is described. The preparation of 9 : 9'-diacridyl from *N*-methylacridone is described in detail (cf. Decker and Dunant, A., 1909, i, 433). When reduced with zinc and glacial acetic acid it gives a mixture of Schlenk and Bergmann's tetrahydro-9 : 9'-diacridyl and unchanged material; the tetrahydro-9 : 9'-diacridyl, m. p. 214°, of Lehmstedt (A., 1929, 1079) could not be prepared by this method or through 9-cyanoacridane.

Addition of sodium to acridine in ether yields primarily the colourless disodium derivative of tetrahydro-9 : 9'-diacridyl; subsequently the 9 : 9' C—C linking becomes ruptured with production of coloured compounds containing the metal attached to carbon.

H. WREN.

**Action of benzyl azide on succinic, fumaric, and acetylenedicarboxylic esters.** T. CURTIUS and K. RASCHIG (J. pr. Chem., 1930, [ii], 125, 466—497).—When benzyl azide is heated with ethyl succinate at 180°, the products formed are diphenylbenzylpyrrodiazole (A., 1922, i, 775), triphenylglyoxaline, and benzylidenebenzylamine. These arise through the intermediate radicals  $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$ ,  $\text{Ph}\cdot\text{CH}\cdot$ , and  $\text{CPh}\cdot\text{N}\cdot$  (cf. *loc. cit.*). With ethyl fumarate at 70° a mixture of benzylamine, dibenzylloxamide, and benzylamine benzylloxamate, m. p. 168° (lit. 158°) (sodium, ammonium, and silver salts), is produced. When the reaction is carried out at 85° for a short time and the resulting product is treated with alcoholic hydrazine hydrate, 1-benzyl-4 : 5-dihydro-1 : 2 : 3-triazole-4 : 5-dicarboxyhydrazide, m. p. 142° (decomp.) [dibenzylidene derivative, m. p. 158° (decomp.)], is obtained. This decomposes on attempted crystallisation from hot water or alcohol, liberates nitrogen when treated with acids, and affords an impure azide. It is formed from the intermediate ethyl ester, which results from addition of the reactants. Benzyl azide and methyl fumarate at 85° give methyl 1-benzyl-4 : 5-dihydro-1 : 2 : 3-triazole-4 : 5-dicarboxylate, m. p. 75° (30% yield), which on treatment with concentrated aqueous ammonia furnishes a poor yield of 1-benzyl-1 : 2 : 3-triazole-4 : 5-dicarboxylamide, m. p. 199°, and a substance, darkens at 270°.

Ethyl benzylloxamate (methyl ester, m. p. 119°) reacts with aqueous-alcoholic hydrazine forming benzylloxamylhydrazide, m. p. 192° (hydrochloride, m. p. 265°; benzylidene derivative, m. p. 228°; isopropylidene derivative, m. p. 138°), converted by nitrous acid into benzylloxamazide, decomp. 80—90°. The azide reacts with aniline and *p*-toluidine in acetone, yielding benzylloxam-anilide, m. p. 173°, and *p*-toluidide, m. p. 168°, respectively. When the azide is added gradually to boiling *p*-toluidine a mixture of the above *p*-toluidide and a small amount of *p*-tolylbenzylbiuret, m. p. 264°, is formed. Methyl, m. p. 132°, ethyl, m. p. 102°, and benzyl benzylallophanates, m. p. 131°, are prepared from benzylloxamazide and the appropriate alcohol, whilst decomposition with water gives benzylcarbamide.

Benzyl azide reacts readily with methyl or ethyl

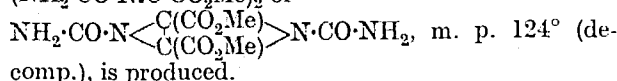
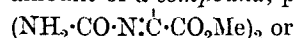
acetylenedicarboxylate, furnishing methyl, m. p. 48—49°, or ethyl 1-benzyl-1 : 2 : 3-triazole-4 : 5-dicarboxylate, an oil. The corresponding acid, m. p. 183° with elimination of carbon dioxide, decomposes to 1-benzyl-1 : 2 : 3-triazole, b. p. 180—183°/15—16 mm., m. p. 61°, also formed from benzyl azide and acetylene. 1-Benzyl-1 : 2 : 3-triazole-4 : 5-dicarboxyhydrazide (dibenzylidene derivative, m. p. 230°) has m. p. 175—176°.

4 : 5-Diphenyl-1-benzyl-1 : 2 : 3-triazole, m. p. 111°, is obtained from benzyl azide and tolane at 140—150°; triazoles could not be prepared from tetramethyl- or tetraphenyl-ethylene.

H. BURTON.

**Action of azido-fatty acid esters and carbamazide on acetylenedicarboxylic esters.** T. CURTIUS and W. KLAVERHN (J. pr. Chem., 1930, [ii], 125, 498—523).—Methyl azidoacetate reacts with methyl acetylenedicarboxylate at 55—60° (the temperature must be controlled or explosions occur) giving a quantitative yield of the trimethyl ester, m. p. 108°, of 4 : 5-dicarboxy-1 : 2 : 3-triazole-1-acetic acid, m. p. 136° (decomp.) (the m. p. rises on keeping) [triethyl ester, an oil; 4 : 5-dimethyl 1-ethyl ester, m. p. 124°; triamide, decomp. 252°; trihydrazide, decomp. 203° (tribenzylidene derivative, decomp. 265°)]. Thermal decomposition of the tricarboxylic acid at 150° affords 1 : 2 : 3-triazole-1-acetic acid, m. p. 209° (decomp.). Methyl  $\alpha$ - and  $\beta$ -azidopropionates react similarly, forming the trimethyl esters, m. p. 63—64° and 44°, respectively, of 4 : 5-dicarboxy-1 : 2 : 3-triazole-1- $\alpha$ -propionic acid [trihydrazide, m. p. 193° (decomp.)] and 4 : 5-dicarboxy-1 : 2 : 3-triazole-1- $\beta$ -propionic acid, m. p. 173° with elimination of carbon dioxide {trihydrazide, m. p. 184° [tribenzylidene derivative, m. p. 243°; triisopropylidene derivative, m. p. 234° (decomp.)]; 1-methyl ester-4 : 5-diamide, m. p. 191°, prepared by the action of aqueous ammonia on the trimethyl ester}. Methyl azidoformate (obtained conveniently from methyl chloroformate and sodium azide) and methyl acetylenedicarboxylate react only with difficulty giving a 20% yield of the trimethyl ester, m. p. 117.5°, of 1 : 2 : 3-triazole-1 : 4 : 5-tricarboxylic acid [triamide, darkens at 286°; 1 : 4 (or 5)-dimethyl ester-5 (or 4)-amide, m. p. 173° (decomp.)], obtained from the trimethyl ester and alcoholic ammonia; trihydrazide, decomp. above 280° with sublimation (tribenzylidene derivative, decomp. 258°)].

Carbamazide and methyl acetylenedicarboxylate react at 100° (bath)/14 mm., forming a small amount of methyl 1 : 2 : 3-triazole-4 : 5-dicarboxylate-1-carboxylamide, m. p. 181° (decomp.). When a mixture of carbamazide and an excess of the ester is heated rapidly to not higher than 115—120° under atmospheric pressure, nitrogen is evolved and a small amount of a compound, probably



Treatment of the reaction product formed when ethyl azidoacetate is heated with ethyl fumarate at 135°, with an excess of alcoholic hydrazine hydrate furnishes the hydrazine salt, decomp. above 280° with sublimation, of the trihydrazide, decomp. 232° with

darkening (*tribenzylidene* derivative, decomp.  $211^{\circ}$ ), of 4:5-dicarboxy-4:5-dihydrotriazole-1-acetic acid. The trihydrazide is liberated from an aqueous solution of its salt by carbon dioxide; acetic and mineral acids cause decomposition. H. BURTON.

**Isomeric 1-nitro- and 1-amino-phenyl-3:5-dimethyl-1:2:4-triazoles and their salts.** F. HERNLER (Monatsh., 1930, 55, 3—13).—A mixture of *o*-nitrophenylhydrazine hydrochloride (1 mol.) and diacetamide (2 mols.) was boiled, the product boiled with hydrochloric acid and with alkali, Fehling's solution was added, and the whole then heated at  $100^{\circ}$ . There resulted 1-*o*-nitrophenyl-3:5-dimethyl-1:2:4-triazole (I), m. p.  $186$ — $189^{\circ}$ , in 4% yield, together with a substance,  $C_{22}H_{31}O_2N_{13}$ , m. p.  $232$ — $234^{\circ}$  (18% yield); I was reduced to 1-*o*-aminophenyl-3:5-dimethyl-1:2:4-triazole, m. p.  $170^{\circ}$  (hydrochloride). *m*-Nitrophenylhydrazine hydrochloride similarly afforded 1-*m*-nitrophenyl-3:5-dimethyl-1:2:4-triazole, m. p.  $136$ — $137^{\circ}$ , in 60% yield [picrate, m. p.  $184$ — $186^{\circ}$  (decomp.); hydrochloride, m. p.  $129$ — $129.5^{\circ}$ , loses hydrochloric acid in a vacuum; chloroplatinate, m. p.  $287^{\circ}$  (decomp.)], reduced to 1-*m*-aminophenyl-3:5-dimethyl-1:2:4-triazole, m. p.  $47$ — $48^{\circ}$  [hydrochloride, m. p.  $202$ — $204^{\circ}$ ; picrate, m. p.  $180$ — $182^{\circ}$  (decomp.); chloroplatinate, unmelted at  $360^{\circ}$ ]. 1-*p*-Nitrophenyl-3:5-dimethyl-1:2:4-triazole, m. p.  $154$ — $154.5^{\circ}$  (hydrochloride, m. p.  $176^{\circ}$ ; picrate, m. p.  $141$ — $141.5^{\circ}$ ; chloroplatinate,  $+2H_2O$ , decomp.  $267^{\circ}$ ), reduced to 1-*p*-aminophenyl-3:5-dimethyl-1:2:4-triazole, m. p.  $186$ — $186.5^{\circ}$  [hydrochloride, m. p.  $242$ — $245^{\circ}$ ; mono-, m. p.  $177$ — $177.5^{\circ}$ , and di-picrate, m. p.  $162$ — $164^{\circ}$ ; chloroplatinates:  $(C_{10}H_{12}N_4)_2 \cdot H_2PtCl_6$ , decomp.  $250^{\circ}$ ;  $C_{10}H_{12}N_4 \cdot H_2PtCl_6 \cdot 2H_2O$ , unmelted at  $360^{\circ}$ ;  $C_{10}H_{12}N_4 \cdot H_2PtCl_6$ , were similarly prepared from *p*-nitrophenylhydrazine hydrochloride and were identical with the corresponding products from the nitration of 1-phenyl-3:5-dimethyl-1:2:4-triazole (Hernler and Matthes, A., 1927, 468). A. I. VOGEL.

**Rearrangement of quinazolones into triazole derivatives.** G. HELLER [with R. MECKE] (J. pr. Chem., 1930, [ii], 126, 76—80; cf. A., 1928, 1381).—3-Benzamido-2-*p*-chlorophenyl-4-quinazalone, m. p.  $297^{\circ}$ , and 3-*p*-chlorobenzamido-2-phenyl-4-quinazalone, m. p.  $212^{\circ}$ , yield, on warming with dilute alkali, the same 2-phenyl-5-*p*-chlorophenyl-1-*o*-carboxyphenyl-1:3:4-triazole, m. p.  $205^{\circ}$ , and in the case of the latter quinazolone only, an unidentified substance of m. p.  $297^{\circ}$ . The hydrazides from which, by heating to their m. p., these quinazolones are prepared (cf. loc. cit.: an improved method of preparation of the hydrazides is now given) yield the same triazole, but in poor yield and accompanied by other products.

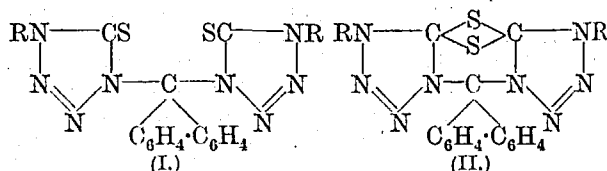
H. A. PRIGGOTT.

**Manufacture of organic nitrogen compounds.** KNOLL & Co.—See B., 1930, 409.

**Derivatives of dihydrotetrazole.** R. STOLLÉ, F. POLLECOFF, and F. HENKE-STARK (Ber., 1930, 63, [B], 965—972; cf. A., 1929, 828; this vol., 620).—5-Thio-1-phenyl-4-methyl-4:5-dihydrotetrazole is converted by cautious treatment with bromine water into 5-keto-1-phenyl-4-methyl-4:5-dihydrotetrazole, m. p.  $72^{\circ}$ , and by excess of the reagent into (?)5-keto-1-bromophenyl-4-methyl-4:5-dihydrotetrazole, m. p.  $103^{\circ}$ .

The 5-keto-1-phenyl compound is also obtained from the thio-derivative by oxidation with aqueous permanganate or hydrogen peroxide in alcohol; when added to hot hydrogen peroxide it gives *N'*-phenyl-*N*-methylcarbamide in small yield. 5-Keto-1-phenyl-4-methyl-4:5-dihydrotetrazole does not react with magnesium phenyl bromide, hydrazine hydrate, phenylcarbimide, benzoyl chloride, or phosphoryl chloride; with nitric acid it gives (?)5-keto-1-nitrophenyl-4-methyl-4:5-dihydrotetrazole, m. p.  $168^{\circ}$  (5-hydroxy-1-phenyltetrazole and nitric and sulphuric acids afford 5-hydroxy-1-nitrophenyltetrazole, decomp.  $213^{\circ}$ ). 5-Keto-1-phenyl-4-methyl-4:5-dihydrotetrazole is decomposed by boiling 40% sodium hydroxide with production of methylamine and phenyl azide.

Di-1-phenyl-5-tetrazolyl disulphide is transformed by diphenylenediazomethane into di-[5-thio-1-phenyl-4:5-dihydro]-4:4'-diphenylenemethyleneditetrazole (I or II, R=Ph), m. p.  $162^{\circ}$  (decomp.), reduced by zinc dust and acetic acid to 5-thio-1-phenyl-4-*ms*-fluorenyl-



4:5-dihydrotetrazole, m. p.  $186^{\circ}$ , which is transformed by hydrogen peroxide in alcohol into 5-keto-1-phenyl-4-*ms*-fluorenyl-4:5-dihydrotetrazole, m. p.  $192^{\circ}$ , and *N*-phenyl-*N'*-*ms*-fluorenylcarbamide, m. p. about  $300^{\circ}$ .

The silver compound of 5-thiol-1-phenyltetrazole and fluorenone dichloride yield fluorenyldi-5-thiol-1-phenyltetrazole, m. p.  $159^{\circ}$  (decomp.).

Di-1-methyl-5-tetrazolyl disulphide and diphenylenediazomethane yield di-[5-thio-1-methyl-4:5-dihydro]-4:4'-diphenylmethyleneditetrazole (cf. I and II, R=Me), m. p.  $181^{\circ}$  (decomp.). Fluorenyldi-5-thiol-1-methyltetrazole, m. p.  $172^{\circ}$ , is derived from fluorenone dichloride and the silver salt of 5-thiol-1-methyltetrazole. 5-Hydroxymethoxy-1-phenyltetrazole, m. p.  $72^{\circ}$ , is derived from 5-hydroxy-1-phenyltetrazole and formaldehyde. H. WREN.

**Action of hydrazine on *m*-cyanobenzoic acid.** T. CURTIUS and A. HESS (J. pr. Chem., 1930, [ii], 125, 40—53).—*m*-Cyanobenzoic acid reacts with anhydrous hydrazine forming the dihydrazine salt (I), m. p.  $203^{\circ}$  (decomp.) after shrinking at  $200^{\circ}$ , of 3:6-diphenyldihydro-1:2:4:5-tetrazine-3':3''-dicarboxylic acid, amorphous, not melted at  $285^{\circ}$  (cf. Müller and Herrdegen, A., 1921, i, 741); the acid is isolated by decomposing the salt with benzaldehyde whereby dibenzaldazine is also produced. Prolonged oxidation of an aqueous solution of I with air gives the hydrazine hydrogen salt, not melted at  $277^{\circ}$ , of 3:6-diphenyl-1:2:4:5-tetrazine-3':3''-dicarboxylic acid (II), not melted at  $285^{\circ}$ ; the free acid is isolated when a solution of the salt in sulphuric acid is mixed with ice. Oxidation of I with nitrous acid also gives II. When II is heated at  $270$ — $280^{\circ}$  it decomposes into *m*-cyanobenzoic acid and nitrogen; the pyridine salt of II decomposes at  $300$ — $310^{\circ}$  into pyridine and the same products. Reduction of II with ammonium



sulphide in aqueous suspension furnishes the above dihydro-acid, whilst hydrolysis with 75% sulphuric acid gives isophthalic acid, nitrogen, ammonia, and hydrazine.

H. BURTON.

**Chlorophyll series. II. Reduction and catalytic hydrogenation.** J. B. CONANT and F. B. HYDE (J. Amer. Chem. Soc., 1930, 52, 1233—1239; cf. this vol., 225).—Sodium hyposulphite in alkaline aqueous solution at 80° reduces magnesium-free chlorophyll derivatives (phæophorbides, chlorin *e*, and rhodin *g*) with a change of colour. Porphyrins and isochlorophyllin are not affected. Similar results are obtained with hydrogen and palladised asbestos in aqueous alkaline solution at 23°. The amount of hydrogen absorbed is measured in a special micro-apparatus. The magnesium-free chlorophyll compounds take up approximately 2 mols. of hydrogen. Catalytic hydrogenation of porphyrins and chlorophyll derivatives in presence of platinum oxide-platinum-black in acetic acid leads to the formation of leuco-compounds with the absorption of 3—4 mols. of hydrogen. On reoxidation in air the porphyrins are regenerated, whilst the chlorophyll compounds yield a mixture of products containing some porphyrins. Two porphyrins from chlorin *e* have been isolated and their absorption spectra measured.

R. K. CALLOW.

**Phylloerythrin.** L. MARCHLEWSKI (Bull. Soc. Chim. biol., 1930, 12, 105—108).—The empirical formula of phylloerythrin obtained from the analysis of three purified specimens was  $C_{33}H_{34}O_3N_4$  and corresponds fairly closely with that of phylloporphyrin,  $C_{33}H_{36}O_2N_4$ . The spectral properties suggest (cf. A., 1929, 727) that phylloerythrin is closely related to the protochlorophyll of Monteverde and Lubimenko (A., 1912, ii, 800).

P. W. CLUTTERBUCK.

**New method of formation of pyrrole-blacks.** I and II. A. QUILICO and M. FRERI (Atti R. Accad. Lincei, 1930, [vi], 11, 296—301, 409—415).—One of the most striking facts indicating the analogy between phenol and pyrrole is the ease with which the latter and its homologues, in alkaline, neutral, or acid solution, couple with diazo-compounds to form stable, crystalline azo- and disazo-pyrroles. If, however, the pyrrole is added to an alcoholic or a glacial acetic acid solution of a diazonium salt, kept cold and in continuous agitation, a deep violet-red coloration appears at once and is soon followed by separation of a black infusible powder, which is insoluble in all solvents and has the appearance and properties of typical pyrrole-blacks, except that it is almost insoluble in alkalis. Such substances contain, not only pyrrole nuclei, but also aromatic nuclei in the form of diazo-compounds or their reduction products, probably as phenylhydrazones. If prepared from halogenated (sulphonated) anilines, the blacks contain considerable proportions of halogen (sulphur). The compound obtained from sulphanilic acid appears to be formed according to the equation  $5C_6H_5N + 3SO_3H \cdot C_6H_4 \cdot NO : NH + 5O \rightarrow C_{32}H_{23}O_9N_9S_3 + 4H_2O$ , and that formed from *p*-bromoaniline has the formula  $C_{48}H_{47}O_{13}N_{13}Br_2$  and results from the interaction of 9 mols. of pyrrole and 2 mols. of the diazo-compound.

3c

It is suggested that these pyrrole blacks have the structure



The compounds obtained from the diazo-compounds of aniline and its 2:4-dinitro-, 2-nitro-, 3-nitro-, 4-nitro-, 4-bromo-, and 2:4-dichloro-derivatives and sulphanilic acid are described.

T. H. POPE.

**Synthesis of thiazoles containing phenol and pyrocatechol groups. II.** C. M. SUTER and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 1585—1587).—The following thiazoles have been prepared from the requisite thioamide and bromoacetal, chloroacetone, or 4-chloroacetylpyrocatechol by the usual method (A., 1929, 943): 2-*p*-methoxyphenyl-, m. p. 156—158°/6 mm., m. p. 12—15° (hydrochloride, m. p. 167—169°); 2-*p*-hydroxyphenyl-, m. p. 163—165° (hydrochloride + 0.5EtOH, m. p. 178—180°), prepared by demethylation of the preceding compound; 2-*p*-methoxyphenyl-4-methyl-, m. p. 57° (hydrochloride + 0.5EtOH, m. p. 130—132°); 2-*p*-hydroxyphenyl-4-methyl-, m. p. 220—221° (hydrochloride, m. p. 250—253°); 2-*p*-methoxyphenyl-4-3':4'-dihydroxyphenyl- (+2H<sub>2</sub>O), m. p. 154—155° (hydrochloride, m. p. 206—208°); 2-*p*-hydroxyphenyl-4-3':4'-dihydroxyphenyl- (+2H<sub>2</sub>O), m. p. 212—213°; 2:4-di-(3':4'-dihydroxyphenyl)- (+H<sub>2</sub>O), m. p. 207°; 2-3':4'-dihydroxyphenyl-, m. p. 181° (hydrochloride, m. p. 215—218°); 2-3':4'-dihydroxyphenyl-4-methyl- (hydrochloride, m. p. 250°); 2-3':4'-methylenedioxyphenyl-, m. p. 84—85° (hydrochloride, m. p. 216°); 2-3':4'-methylenedioxyphenyl-4-methyl-, m. p. 94—95° (hydrochloride + EtOH); 4-3':4'-dihydroxyphenyl-2-3':4'-methylenedioxyphenyl- (+2H<sub>2</sub>O), m. p. (anhydrous) 185° (hydrochloride, m. p. 212—216°). Piperonylthioamide and 3:4-dihydroxybenzthioamide have m. p. 180° and 153—154°, respectively. The thiazoles described possess definite analgesic and anaesthetic properties.

H. BURTON.

**Preparation and study of some assimilation products of *Pleurococcus vulgaris*.** J. G. VAN DER SANDE (Rec. trav. chim., 1930, 49, 471—478).—The so-called "phytic acid" isolated by Lamy (Ann. chim. phys., 1852, 35, 129) from *P. vulgaris* is best extracted from the algae by boiling 70% alcohol, filtering hot, decolorisation of the filtrate with norit, concentration in a vacuum at 60—70°, and crystallisation of the solution at 0° (yield 9.45 g., together with 73.2 g. of erythritol which remains in the alcoholic mother-liquor, from 27 kg. of the algae which contain 27% of moisture and 10—15% of foreign material). The substance, m. p. 136°, probably has the composition  $C_{27}H_{51}N(OH)_4$ , is saturated and optically inactive, and a study of its chemical reactions shows that it is not an acid, a free base, aldehyde, ketone, amino-acid, anhydride, lactone, nitro-, nitroso-, or isonitroso-derivative, or an ether, nor is it a phytosterol, a carbamide, or an anthracene derivative, and it does not afford decomposition products either of a sugar or glycerol. By heating with acetic anhydride and sodium acetate it is con-

verted into an *acetyl* derivative,  $C_{27}H_{51}N(OAc)_4$ , m. p.  $63.5^\circ$ , which, on hydrolysis, yields, not the original material, but a nitrogen-free substance, m. p.  $56-57^\circ$ . A trace of acetic acid is the only recognisable product when the original substance is oxidised with nitric acid ( $d\ 1.2$ ), and long boiling with alcoholic potassium hydroxide and subsequent acidification gives a small quantity of a nitrogen-free substance, m. p.  $154^\circ$ . It is considered probable that the so-called "phytic acid" is a cyclic nitrogen derivative of the coniine type.

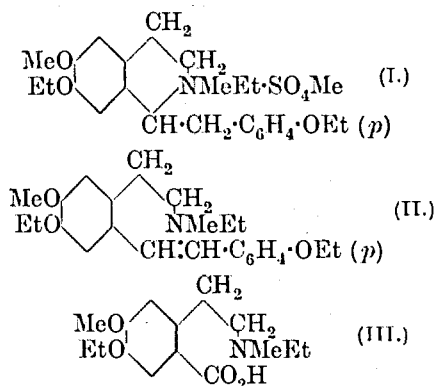
J. W. BAKER.

**Isomeride of yohimbine.** R. LILLIG.—See B., 1930, 485.

**Compound of quinine with phenyl carbonate.** S. ICHIKAWA and S. FUDA (Bull. Hyg. Res. Inst. Japan, 1929, 35, 139—141).

## CHEMICAL ABSTRACTS.

**The alkaloid coclaurine from *Cocculus laurifolius*, DC.** H. KONDO and T. KONDO (J. pr. Chem., 1930, [ii], 126, 24—52; cf. A., 1926, 82).—A reprint, in part, of results previously published in J. Pharm. Soc. Japan. This alkaloid has now been proved to be 7-hydroxy-6-methoxy-1-(4'-hydroxybenzyl)-1:2:3:4-tetrahydroisoquinoline, the ultimate proof resting on the Hofmann degradation of triethylcoclaurine methomethylsulphate (I) to a methine base (II) which on oxidation yields *p*-ethoxybenzoic acid and an acid (probably III); this, when subjected to the Hofmann degradation, gives 4-methoxy-3-ethoxy-6-vinylbenzoic acid, identified by reduction to the corresponding ethylbenzoic acid.



Distillation of coclaurine with zinc dust gives *p*-cresol, ammonia, methylamine, an unidentified primary amine [*chloroaurate*, m. p.  $202^\circ$  (decomp.), *chloroplatinate*, m. p.  $205-206^\circ$  (decomp.)], and a hydrocarbon of m. p.  $188-189^\circ$ . *Trimethylcoclaurine* is obtained by methylating coclaurine with diazomethane, m. p.  $202-203^\circ$  (*chloroplatinate*, m. p.  $202^\circ$ ; *picrate*, m. p.  $168^\circ$ ), whilst methyl sulphate and alkali give *tetramethylcoclaurine methomethylsulphate*, m. p.  $175^\circ$ , which with hot alkali gives *tetramethylcoclaurimethine*, m. p.  $86^\circ$  (*hydrochloride*, m. p.  $228.5-229^\circ$ ; *chloroplatinate*, m. p.  $202^\circ$ ). Further methyl sulphate-alkali treatment yields 4:3':4'-trimethoxy-6'-vinyl-*s*-diphenylethylene, m. p.  $79^\circ$ , and trimethylamine: the former is oxidised to anisic, oxalic, and an unidentified acid. *Tetramethylcoclaurimethine* is oxidised to anisic acid and an amino-acid which on

methylation and treatment with alkali gives trimethylamine and 3:4-dimethoxy-6-vinylbenzoic acid, m. p.  $184^\circ$ , and this with hydrogen and palladium yields 3:4-dimethoxy-6-ethylbenzoic acid, m. p.  $142-143^\circ$  (Shinoda, J. Pharm. Soc. Japan, 1927, No. 548, 860). The constitution of tetramethylcoclaurimethine was confirmed by synthesis from *homoveratrylamine*, which was converted into *p*-methoxyphenylacetohomoveratrylamide, m. p.  $123.5^\circ$ ; this with phosphorus oxychloride yields 1-(4'-methoxybenzyl)-6:7-dimethoxy-3:4-dihydroisoquinoline, obtained as an oil (*hydrochloride*, m. p.  $190-191^\circ$ ; *picrate*, m. p.  $177^\circ$ ; *methiodide*, m. p.  $224^\circ$ ). Hydrogen, in presence of palladium, reduces this to 6:7-dimethoxy-1-(4'-methoxybenzyl)-1:2:3:4-tetrahydroisoquinoline (*hydrochloride*, m. p.  $182^\circ$ ), the methomethylsulphate of which, m. p.  $175^\circ$  [*methochloroaurate*, m. p.  $174^\circ$  (decomp.)], on treatment with alkali gives tetramethylcoclaurimethine.

With ethyl bromide and alkali coclaurine yields *triethylcoclaurine*, an oil [*hydrochloride*, m. p.  $162^\circ$ ; *chloroplatinate*, m. p.  $130-131^\circ$ ; *methochloroplatinate*, m. p.  $175^\circ$ ]: the *methomethylsulphate*, m. p.  $122^\circ$ , yields with alkali *methyltriethylcoclaurimethine*, an oil which on oxidation yields *p*-ethoxybenzoic acid, a little *p*-ethoxybenzaldehyde, and the acid (III); this with methyl sulphate and alkali yields 4-methoxy-3-ethoxy-6-vinylbenzoic acid, m. p.  $165^\circ$ , reduced by palladium and hydrogen to 4-methoxy-3-ethoxy-6-ethylbenzoic acid, m. p.  $137.5-138.5^\circ$ , identical with the synthetic product. The relative positions of the hydroxyl and methoxyl groups in the alkaloid molecule are thus established. The 4-methoxy-3-ethoxy-6-ethylbenzoic acid was synthesised as follows: *guaiacol ethyl ether*, condensed with acetyl chloride by the Friedel-Crafts reaction, yields a product, b. p.  $138-144^\circ/4\text{ mm.}$ , m. p.  $79^\circ$ , which is oxidised to 5-methoxy-4-ethoxybenzoic acid and is therefore 5-methoxy-4-ethoxyacetophenone. This, reduced by Clemmensen's method, gives 5-methoxy-4-ethoxy-1-ethylbenzene, b. p.  $95^\circ/5\text{ mm.}$ , and further condensation with acetyl chloride yields 4-methoxy-3-ethoxy-6-ethylacetophenone, m. p.  $50^\circ$ , oxidised by hypiodite to 4-methoxy-3-ethoxy-6-ethylbenzoic acid.

H. A. PIACOTT.

**Action of nitrous acid on morphine and its derivatives.** E. SPEYER and L. WALTHER (Ber., 1930, 63, [B], 852—855).—Cyclic amines with a tertiary nitrogen atom can be converted into secondary amines by nitrous acid; the yields are approximately the same as those obtained by the cyanogen bromide method.

*Diacylmorphine* dissolved in an excess of aqueous sodium nitrite is converted by sulphuric acid at  $70-85^\circ$  into *nitrosonordiacetylmorphine*, m. p.  $202-203^\circ$ , converted by 2*N*-sodium hydroxide into *nitrosonormorphine*, decomp.  $267^\circ$ , from which *normorphine*, m. p.  $263-264^\circ$  (cf. von Braun, A., 1914, i, 1138), is obtained by means of alcoholic hydrochloric acid. Similarly, *codeine* affords successively *nitrosonorcodeine*, m. p.  $246^\circ$ , and *norcodeine*, m. p.  $186^\circ$ , whilst *nitrosonordihydrocodeine* and *nitrosohydroxy-nordihydrocodeinone*, m. p.  $259^\circ$  (cf. Speyer and Sarre, A., 1924, i, 1230), are derived from *dihydrocodeine* and *hydroxydihydrocodeinone*, respectively.

In presence of acetic instead of sulphuric acid, codeinone yields *nitrosonorcodeinone*, m. p. 241—242°.

H. WREN.

**Further degradative experiments in the morphine group.** R. S. CAHN (J.C.S., 1930, 702—705; cf. A., 1926, 1264).—The quaternary base from dihydrothebainemethine methiodide gave, when boiled in isoamyl alcohol, dihydrothebainemethine (50%) and 6-methoxy-13-vinyltetrahydromorphenol methyl ether (30% of theory), m. p. 120—121°; the latter, on hydrolysis with aqueous-alcoholic hydrochloric acid, gave 6-keto-13-vinylhexamorphenol methyl ether, m. p. 149°, reduced by hydrogen and palladised charcoal to the octahydro-ether, m. p. 113° (*semi-carbazone*, m. p. 191° with previous sintering), which was further reduced by aluminium amalgam to the known 6-keto-13-ethyloctahydromorphol 3-methyl ether and uncrySTALLISABLE products.

H. A. PIGGOTT.

**Decomposition of alkaloids in aqueous solution.**

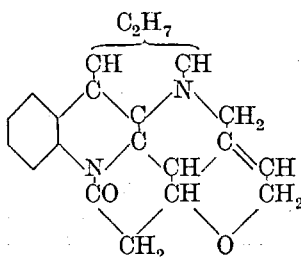
**III. Berberine.** R. DIETZEL and K. SOLLNER (Arch. Pharm., 1930, 268, 223—242).—Berberine chloride in 0.1% aqueous solution is not decomposed by prolonged heating at 100°, alone or in presence of dilute acid or alkali, or in a stream or air. It is converted to the extent of 5% by 8 hrs.' heating of the solution at 150° into berberubin. Alcoholic solutions of berberinal (cf. Tinkler, J.C.S., 1911, 99, 1340) do not obey Beer's law. The absorption curves indicate that they contain the amino-aldehyde modification in equilibrium with a little of the carbinol. When a solution of berberine hydroxide obtained from the sulphate and barium hydroxide is evaporated at the ordinary temperature, the blackish-brown *ammonium base* is obtained. It is readily soluble in water and its absorption spectrum in methyl alcohol is nearly identical with that of berberine chloride in water.

H. E. F. NOTTON.

**Strychnine and brucine. X. Degradation of dinitrostrycholcarboxylic acid: its recognition as a derivative of quinoline and consequent modifications of the constitutional formulæ for the *Strychnos* bases proposed in VII.** K. N. MENON, (the late) W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1930, 830—843; cf. this vol., 625).—During the preparation of dinitrostrycholcarboxylic acid by oxidation of strychnine with nitric acid a small quantity of 3:5-dinitrobenzoic acid was isolated. Dinitrostrycholcarboxylic acid with alcohol and sulphuric acid gave *ethyl dinitro-O-ethylstrycholcarboxylate*, m. p. 111—112°, converted by hydrazine hydrate into *dinitro-O-ethylstrycholcarbohydrazide*, m. p. 218—219° (decomp.). Further application of the Curtius reaction gave the azide (not analysed), m. p. 110° (decomp.), and finally *dinitrostrychylurethane*, m. p. 199—200°. Unlike dinitrostrycholcarboxylic acid, this was degraded by nitric acid to picric acid; further, when heated with sulphuric acid and then oxidised with aqueous permanganate, 5:7-dinitroisatin, m. p. 209—210°, was formed. Addition of ammonia to the hydrolysed solution of the urethane before oxidation precipitated an orange base, soluble in acid to a yellow solution; it was capable of diazotisation, and would also couple with diazo-salts,

and self-coupling was readily observed; mild oxidation in acid solution gave a reddish-brown, sparingly soluble substance, apparently of indigoid or indirubinoid nature. 5:7-Dinitroisatin was also obtained in almost quantitative yield by direct nitration of isatin, and was oxidised by boiling nitric acid to picric acid.

As strychnol is not 2:4-dihydroxypyridine (cf. *loc. cit.*) dinitrostrycholcarboxylic acid must be either 6:8-dinitro-2:3-dihydroxyquinoline-4-carboxylic acid or 6:8-dinitro-3:4-dihydroxyquinoline-2-carboxylic acid, but most probably the former. The



3-hydroxyl group in the acid is now regarded as marking the position of the b-N of strychnine, for which the annexed formula is suggested.

Attempts to prepare dinitrodimethylstrychol were fruitless, but *dinitro-O-methylstrychol*, m. p. 195—196°, was obtained quantitatively. It gave with hydrazine hydrate, *dinitrohydrazinodeoxystrychol*, m. p. 253° (decomp.), [acetyl derivative, m. p. 311—313° (decomp.); isopropylidene derivative, m. p. 279—281° (decomp.)], and a basic substance, m. p. 202—204°. Dinitrostrychol was regenerated by oxidation of the hydrazine with ferric chloride or permanganate in very dilute acid solution.

6:8-Dinitrohydrocarbostyryl, m. p. 175° (cf. van Dorp, A., 1905, i, 81) was obtained by nitration of hydrocarbostyryl. It was unchanged by boiling nitric acid or by bromine in hot acetic acid. An alkaline aqueous solution lost ammonia on boiling, presumably with formation of the dinitrohydroxyphenylpropionic acid.

H. A. PIGGOTT.

**Sinomenine and disinomenine. XV. Reduction of bromosinomenine with nascent hydrogen.** K. GOTO and R. INABA (Bull. Chem. Soc. Japan, 1930, 5, 93—98).—Reduction of bromosinomenine with sodium amalgam in 2% sodium hydroxide solution gives 1:1'-*dibromobis-8:8'-dimethoxydihydrosinomenine*, m. p. 227°,  $[\alpha]_D^{25} +19.02^\circ$  in alcohol [oxime, m. p. 237° (decomp.); methiodide, m. p. 253—255°]. Similar reduction of bromodihydrosinomenine affords 1-bromodemethoxydihydrosinomenine, m. p. 119°,  $[\alpha]_D^{25} +57.57^\circ$  in alcohol [oxime, m. p. 263° (decomp.); methiodide, decomp. 127° (sinters 119°)]. Reduction of bromosinomenine hydrobromide by Clemmensen's method converts it into 1-bromodemethoxydeoxydihydrosinomenine, m. p. 127°,  $[\alpha]_D^{25} +40.44^\circ$  in alcohol (methiodide, m. p. 253—255°), whilst reduction of bromosinomenine with zinc and 4% hydrochloric acid gives bromodihydrosinomenine, m. p. 236°. In each case reduction proceeds in the same manner as that previously observed in the case of the corresponding unbrominated derivatives (Goto and Sudzuki, this vol., 230) and the products here described are all identical with those obtained by direct bromination of the corresponding unbrominated reduction products. *Bromo-β-tetrahydrodeoxycodeine*, m. p. 127°,  $[\alpha]_D^{25} -39.52^\circ$  in alcohol

(obtained by the action of bromine in acetic acid on  $\beta$ -tetrahydrodeoxycodeine), is completely racemised by 1-bromodemethoxydeoxydihydrosinomenine (above), giving a *dl*-product, sinters 119°, decomp. 122°. This observation further supports the view (*loc. cit.*) that demethoxydeoxydihydrosinomenine is the optical antipode of  $\beta$ -tetrahydrodeoxycodeine.

J. W. BAKER.

**Microchemical reactions of veratrine.** M. WAGENAR (Pharm. Weekblad, 1930, 67, 393—394).—A résumé of the literature. Picric acid and potassium dichromate both give precipitates with 5 mg. at a dilution of 1:200.

S. I. LEVY.

**Fritzsche's reagent [for alkaloids].** H. M. DE LISSNER (Rev. Cent. Est. Farm. Biochim., 1929, 18, 348—352; Chem. Zentr., 1929, ii, 3241).—Dinitroanthraquinone is unsuitable and untrustworthy as a general precipitant for alkaloids.

A. A. ELDRIDGE.

**Trypanocidal action and chemical constitution.**  
**IX. Aromatic acids containing an amide group.** G. A. C. GOUGH and H. KING (J.C.S., 1930, 669—694).—Benzamide-*p*-arsinic acid is found to be more active against *T. equiperdum* than *p*-aminophenylarsinic acid (atoxyl), and, in general, trypanocidically inactive carboxylic and sulphonic acids become active when converted to amides. Benzamide-*p*-arsinous acid, although much more toxic, is not proportionally effective. Its condensation product with  $\alpha$ -thiolacetic acid [ $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{As}(\text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H})_2$ ] is readily hydrolysed, and even in neutral solution free  $\alpha$ -thiolacetic acid can be detected. It is more readily tolerated and correspondingly more effective than the arsinous acid. The suggestion is made, therefore, that the "active" arsinic acids are reduced, probably by thiol compounds present in living tissues, to arsinous acids followed by combination to thioarsinates which are sufficiently non-toxic to be tolerated by the organism, yet slowly hydrolyse and maintain a minute concentration of highly toxic arsinous acids (*cf. A.*, 1928, 1231).

1-Amino-3:6-disulpho-8-naphthol-7-azobenzene-4'-arsinic acid (+2.5H<sub>2</sub>O) was prepared by coupling diazotised *p*-aminophenylarsinic acid with H-acid. Monosodium salts (apparently sodium sulphonates) of the following acids are described. 1-Benzamido-3:6-disulphonaphthalene-4'-arsinous acid (+H<sub>2</sub>O) was obtained by the action of benzoyl chloride-*p*-dichloroarsine on Freund's acid in presence of alkali. On oxidation it gave 1-benzamido-3:6-disulphonaphthalene-4'-arsinic acid (+3H<sub>2</sub>O). H-acid in the place of Freund's acid gave 1-benzamido-3:6-disulpho-8-naphthol-4'-arsinous (+8H<sub>2</sub>O) and -arsinic (+10H<sub>2</sub>O) acids, whilst with 1-*m*-aminobenzamido-H-acid, 1-benzamido-*m*-benzamido-3:6-disulpho-8-naphthol-4'-arsinous (+8H<sub>2</sub>O) and -arsinic (+14H<sub>2</sub>O) acids resulted. The first was active, although less so than the corresponding stibinic acid (*cf. Dunning and Macht, A.*, 1928, 444); the remainder were inactive.

Benzamide-*p*-arsenious oxide, prepared from ammonia and benzoyl chloride-*p*-dichloroarsine, when boiled with aqueous  $\alpha$ -thiolacetic acid gave di(carboxymethyl) benzamide-*p*-thioarsinite, m. p. 168—169°, readily hydrolysed by sodium hydrogen carbonate

and partly also by water. The arsenious oxide was readily oxidised to benzamide-*p*-arsinic acid. With aqueous dimethylamine, benzoyl chloride-*p*-dichloroarsine reacted to give benzdimethylamide-*p*-dichloroarsine, m. p. 192°, oxidised in alkaline solution to benzdimethylamide-*p*-arsinic acid, m. p. 216—218°. Benzethylamide-*p*-arsinous acid was obtained by hydrolysis of the product from benzoyl chloride-*p*-dichloroarsine and ethylamine, and on oxidation yielded the *p*-arsinic acid. The following were prepared by appropriate applications of the above methods: Benzmethylamide-*p*-arsinous and -arsinic acids; benzdiethylamide-*p*-dichloroarsine, m. p. 185—186°, -*p*-arsinic acid, m. p. 193—195°; benz-*n*-propylamide-*p*-arsenious oxide and the -*p*-arsinic acid; benzisoamylamide-*p*-arsenious oxide and -arsinic acid; benzpiperidine-*p*-dichloroarsine, m. p. 166—167°, and -*p*-arsinic acid, m. p. 230°; benz- $\beta$ -hydroxyethylamide-*p*-arsenious oxide, and -*p*-arsinic acid, m. p. 180° (decomp.). By the use of hippuryl chloride-*p*-dichloroarsine, obtained in an impure condition by the action of phosphorus pentachloride on benzoylglycine-*p*-arsenious oxide suspended in acetyl chloride, the following were obtained: benzoylglycine-ethylamide-*p*-arsinic acid, m. p. 270° (decomp.); benzoylglycine-*n*-propylamide-*p*-arsenious oxide.  $\beta$ -Diethylaminoethanol and benzoyl chloride-*p*-dichloroarsine condensed to a product which, after hydrolysis, could not be crystallised; it was therefore oxidised to  $\beta$ -diethylaminoethyl benzoate-*p*-arsinic acid, m. p. 186° (decomp.).

*m*-Aminobenzoic acid was submitted to the Bart reaction, and the product reduced without isolation to *m*-benzarsinous acid (purified through benzoyl chloride-*m*-dichloroarsine, m. p. 54—55°). This reacted readily with aqueous hydrochloric acid to form benzoic acid-*m*-dichloroarsine. From benzoyl chloride-*m*-dichloroarsine were prepared: benzamide-*m*-arsenious oxide, benzamide-*m*-dichloroarsine, m. p. 76—80°, and benzamide-*m*-arsinic acid, m. p. above 300°; "benzmethylamide-*m*-arsenious acid," and -arsinic acid, m. p. 238° (decomp.); and benzisoamylamide-*m*-arsinic acid.

Salicylic acid-5-arsinous acid was prepared by reduction of the corresponding arsinic acid (preparation from 5-nitrosalicylic acid, and an improved method for the latter described). Salicylic acid-5-dichloroarsine resulted when the arsinic acid was reduced in the presence of concentrated hydrochloric acid. Methyl salicylate-5-arsinic acid, m. p. 208° (decomp.), readily reacted with hydrogen chloride to give methyl salicylate-5-dichloroarsine, m. p. 168°; the latter could also be obtained from salicylic acid-5-arsinous acid or salicylic acid-5-dichloroarsine and methyl-alcoholic hydrochloric acid, and by hydrolytic oxidation was readily reconverted into methyl salicylate-5-arsinic acid. Salicylamide-5-arsinic acid was prepared from the methyl ester and ammonia.

isoPhthalic acid-4-arsinic acid (improved preparation from *m*-xylyl-4-arsinic acid, and preparation of the latter from *m*-4-xyldine described), when treated in succession with thionyl chloride, ammonia, and hydrogen peroxide gave isophthalamide-6-arsinic acid (anhydrous and +1H<sub>2</sub>O). Phosphorus pentachloride (5.5 mols.) followed by ammonia gave 3:4-di-

chlorobenzamide, 4-chloroisophthalimide, m. p. 223—226°, and, on oxidising the mother-liquors, isophthalamic acid-6-arsinic acid. With 6.5 mols. of the pentachloride the last-named product could not be traced. Methyl-alcoholic hydrogen chloride reduced the acid, and methyl isophthalate-4-arsinous acid resulted, readily reoxidised to the -4-arsinic acid (plates), m. p. 185° (needles), m. p. 197° (decomp. with formation of a solid anhydride in each case). When this esterification was carried out at -5° instead of at the b. p., and with synthetic methyl alcohol in the place of purified wood spirit, methyl isophthalate-4-arsine tetrachloride, m. p. 110—115° (decomp.), was formed, free from tervalent arsenic compounds. It gave with sodium hydrogen carbonate at 0° methyl isophthalate-4-arsinic acid. This acid yielded with ammonia on long keeping isophthalamic acid-6-arsinic acid (acid ammonium salt).

Benzenesulphonyl chloride-p-dichloroarsine (from p-sulphophenylarsinic acid and phosphorus pentachloride) was hydrolysed by water to benzenesulphonyl chloride-p-arsenious oxide and p-sulphophenylarsinous acid. With ammonia it gave benzenesulphonamide-p-arsenious oxide, readily converted by hydrochloric acid into the p-dichloroarsine, m. p. 176—178°, and by hydrogen peroxide into benzenesulphonamide-p-arsinic acid. H. A. PIGGOTT.

**Aromatic stibinic acids containing phenyl and quinolyl radicals.** G. T. MORGAN and J. W. COOK (J.C.S., 1930, 737—745).—*m*-Aminophenylstibinic acid hydrochloride gave with potassium cyanate in aqueous sodium acetate and acetic acid *m*-carbamidophenylstibinic acid (+H<sub>2</sub>O) [purified through the stibinic chloride; sodium salt], with chloroacetamide it yielded *N*-phenylglycineamide-*m*-stibinic acid (+ $\frac{1}{2}$ H<sub>2</sub>O) [sodium salt], and with chloroacetomethylamide the corresponding methylamide (sodium salt). *p*-Acetamidophenylstibinous chloride hydrochloride, boiled with much 0.005*N*-sodium hydroxide, gave antimony oxide and *pp'*-diacetamidodiphenylstibinous hydroxide, a simpler method than that of Schmidt (A., 1922, i, 1203); the diaminodiphenylstibinic acid prepared from this gave only aniline and resinous products with chloroacetamide.

4-Chloro-3-nitrophenylstibinic acid reacted with piperidine to give 3-nitro-4-piperidinostibinic acid (+ $\frac{1}{2}$ H<sub>2</sub>O) [isolated as the stibinic chloride hydrochloride, decomp. 185—187°, which gave the stibinic acid hydrochloride (+H<sub>2</sub>O) with water], converted by reduction with ferrous hydroxide into 3-amino-4-piperidinostibinic acid (+ $\frac{1}{2}$ H<sub>2</sub>O) (sodium salt). 3-Nitro-4-ethylaminostibinic acid (+ $\frac{1}{2}$ H<sub>2</sub>O) (stibinic chloride) and 3-nitro-4-methylaminophenylstibinic chloride were similarly prepared by the use of ethylamine and methylamine, respectively. These acids generally were insoluble or sparingly soluble in water.

3-Amino-4-hydroxyphenylstibinic acid gave with acetic anhydride a very soluble stibinic acid, which is either the anhydrous *N*-acetyl derivative, or, more probably, the monohydrated benzoxazolestibinic acid.

The following quinolinestibinic acids were obtained by the Bart-Schmidt reaction from the appropriate aminoquinoline, and purified through the stibinic chloride: quinoline-5-stibinic acid (+H<sub>2</sub>O) (sodium

salt; stibinic chloride hydrochloride, m. p. 222°); quinoline-6-stibinic acid (+H<sub>2</sub>O) (sodium salt; stibinic chloride hydrochloride, m. p. 237°); quinoline-8-stibinic acid (stibinic chloride hydrochloride, decomp. 200—210°) exists in a form insoluble in water [+ $\frac{3}{2}$ H<sub>2</sub>O]; converted by evaporation of its solution in dilute acetic acid into a soluble form (+H<sub>2</sub>O), reconverted immediately by alkali into the insoluble form. The stibinic acids were found to possess only slight trypanocidal activity against *T. equiperdum*. (Where no m. p. is recorded, the compound generally decomposes, without melting, on being heated.)

H. A. PIGGOTT.

**Antimonial analogues of the carbazole series.** G. T. MORGAN and G. R. DAVIES (Proc. Roy. Soc., 1930, A, 127, 1—8; cf. A., 1926, 507; Aeschlimann and others, A., 1925, i, 319).—Antimony is introduced into the diphenyl nucleus by converting *o*-aminodiphenyl, prepared by pyrolysis of diazoaminobenzene in presence of benzene (yield 18%) or, better, by reduction of *o*-nitrodiphenyl, through the diazo-reaction into diphenyl-*o*-diazonium antimony tetrachloride. On digesting with cold aqueous sodium hydroxide and acidifying the alkaline solution xenyl-*o*-stibinic acid is obtained as an amorphous white precipitate. Xenyl-*o*-stibine tetrachloride and xenyl-*o*-stibine ammonium pentachloride are described. Reduction of the stibinic acid with sulphur dioxide in the presence of methyl-alcoholic hydrochloric acid containing a trace of potassium iodide leads to xenyl-*o*-stibine dichloride, m. p. 76°, and the corresponding di-iodide, m. p. 95—96°, is obtained from this by the addition of sodium iodide in acetone solution.

Xenylene-2 : 2'-stibine chloride, m. p. 209°, may be prepared by removal of hydrogen chloride from the dichloride by heating to 100° at 25 mm. or by dehydration of xenyl-*o*-stibinic acid. By double decomposition with sodium iodide the corresponding iodide, m. p. 222°, is formed, and this gives rise, by Grignard's method, to the antimonial analogues of the *N*-alkylcarbazoles. Thus magnesium methyl-iodide yields 2 : 2'-xenylene-methylstibine, m. p. 57°; this does not combine additively with methyl iodide, although it furnishes a dibromide, m. p. 207°. Bis-2 : 2'-xenylene-stibine oxide, m. p. 177—179°, is obtained by treating xenylene-stibine chloride or iodide with ammonia or aqueous alkalis. Tetrakis-*o*-xenylstibine oxide, (Ph·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>Sb·O·Sb(C<sub>6</sub>H<sub>4</sub>·Ph)<sub>2</sub>, m. p. 157°, is produced together with antimonious oxide when xenyl-*o*-stibine dichloride is digested with warm dilute alkali; this dissolves in alcoholic hydrochloric acid to give di-*o*-xenylstibine chloride, (Ph·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SbCl, m. p. 125.5°, which can be utilised as the starting point for another series of antimonial analogues of carbazole. By direct addition of chlorine to this monochloride in chloroform solution di-*o*-xenylstibine trichloride, (Ph·C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SbCl<sub>3</sub>, m. p. 177°, is obtained; on gently warming under reduced pressure this loses hydrogen chloride and passes with ring closure into 2 : 2'-xenylene-*o*-xenylstibine dichloride, m. p. 212°, whilst this cyclic antimonial loses its chlorine on prolonged treatment with zinc dust and gives rise to 2 : 2'-xenylene-*o*-xenylstibine, m. p. 106—107°, a tertiary aromatic stibine which is an analogue of the *N*-arylcabazoles. L. I. BIRCUMSHAW.

**Valency problem of boron. IV. Valency phenomena of boron in boron tribenzyl, tri-*p*-xylyl, and tri- $\alpha$ -naphthyl.** E. KRAUSE and P. NOBBE (Ber., 1930, 63, [B], 934—944; cf. A., 1928, 435).—Among the new boron triaryls, only the tri-*p*-xylyl compound is closely related to boron triphenyl. The tri- $\alpha$ -naphthyl derivative is distinguished by almost complete stability to air when dry, probably in consequence of the almost complete covering of the boron atom by the bulky naphthyl groups. Boron tribenzyl resembles the alkyl compounds in its low m. p. and great sensitiveness to air, but is related to the triaryls by its ability to combine with alkali metals giving compounds which regenerate boron tribenzyl when treated with mercury.

The following compounds are described: *boron tribenzyl*, m. p. 47° (corr.) (detailed method of preparation), oxidised by air to dibenzyl and boric acid, and its additive compounds,  $B(CH_2Ph)_3 \cdot NH_3$ , m. p. 194—196° (in closed capillary);  $B(CH_2Ph)_3 \cdot NH_2Me$ , m. p. 105—112° after softening at 81°, according to the rate of heating;  $B(CH_2Ph)_3 \cdot NMe_3$ , m. p. above 128° after softening at 108°;  $B(CH_2Ph)_3 \cdot C_5H_5N$ , m. p. 129—131°;  $B(CH_2Ph)_3 \cdot C_5H_{11}N$ , m. p. 104—106°; *boron tri-*p*-xylyl*, b. p. 221°/12 mm., m. p. 146—147° (corr.), and the compounds,  $B(C_6H_9)_3 \cdot NH_3$ , m. p. 181—182° (decomp.);  $B(C_6H_9)_3 \cdot NH_2Me$ , m. p. 155—156° (decomp.);  $B(C_6H_9)_3 \cdot C_5H_5N$ , m. p. 146—148° after softening;  $B(C_6H_9)_3 \cdot C_5H_{11}N$ , m. p. 109—110°; *boron tri- $\alpha$ -naphthyl*, m. p. 203° (corr.), or +2C<sub>6</sub>H<sub>6</sub>, m. p. 170° (corr., vac.), slowly oxidised by hydrogen peroxide to  $\beta$ -naphthol, and its additive compounds,  $B(C_{10}H_7)_3 \cdot NH_3$ , m. p. 193—194° (decomp.);  $B(C_{10}H_7)_3 \cdot NH_2Me$ , m. p. 192—193° (decomp.) after softening at 155°;  $B(C_{10}H_7)_3 \cdot NMe_3$ , m. p. 180° after softening at 178°;  $B(C_{10}H_7)_3 \cdot 3C_5H_5N$ , m. p. (indef.) 202—206°;  $B(C_{10}H_7)_3 \cdot 2C_5H_{11}N$ , m. p. 160°.

H. WREN.

**Organic compounds of selenium. I. Action of selenium oxychloride on ketones.** R. E. NELSON and R. N. JONES (J. Amer. Chem. Soc., 1930, 52, 1588—1590).—Selenium oxychloride generally reacts with ketones in ethereal solution at the ordinary temperature thus:  $2R \cdot CO \cdot Me + SeOCl_2 \rightarrow (R \cdot CO \cdot CH_2)_2SeCl_2 + H_2O$ . The following are described: *diacetonyl*-, m. p. 81°; *diphenacyl*-, m. p. 121.5°; *di-*p*-chlorophenacyl*-, m. p. 126°; *di-( $\beta$ -benzoyl-ethyl)*-, m. p. 118°; *di-*p*-methylphenacyl*-, m. p. 129°, and *di-2-methyl-5-isopropylphenacyl-selenium dichlorides*, m. p. 133°. These compounds are more or less unstable. Diethyl, methyl ethyl, and methyl *n*-hexyl ketones evolve hydrogen chloride when treated with selenium oxychloride; solid products could not be isolated. Benzophenone and the oxychloride react in presence of carbon disulphide and aluminium chloride forming a crystalline compound (from chloroform), which decomposes when freed from solvent.

H. BURTON.

**Reaction between magnesium diphenyl and bromine. Historical note on the first preparation of magnesium phenyl bromide.** H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, 52, 1181—1185).—Reinvestigation of the action of bromine on magnesium diphenyl in ether (Fleck, A., 1893,

i, 622) confirms Fleck's assumption of the reaction:  $MgPh_2 + 2Br_2 = 2PhBr + MgBr_2$ , but also indicates that with 1 mol. of bromine the reaction is that which Fleck sought, viz.,  $MgPh_2 + Br_2 = MgPhBr + PhBr$ . First, the resulting solution reacts with *n*-valeronitrile at the same rate as magnesium phenyl bromide does, and, secondly, the reaction  $MgPh_2 + MgBr_2 = 2MgPhBr$  has been shown to take place, for when a mixture of magnesium diphenyl and magnesium bromide or iodide is treated with magnesium and benzophenone no benzpinacol is formed, although this reduction takes place in presence of magnesium bromide or iodide (cf. Gomberg and Bachmann, A., 1927, 245).

R. K. CALLOW.

**Mercuri-organic compounds of carbazole and tetrahydrocarbazole. I.** B. CECCHETTI and U. SARTI (Gazzetta, 1930, 60, 189—194).—The interaction of carbazole (2 mols.) and mercuric acetate (1 mol.) in alcoholic solution containing acetic acid yields the compound,  $Hg(C_6H_3 < \begin{smallmatrix} CH \\ NH \end{smallmatrix} > C_6H_4)_2$ , which decomposes without melting at above 200°, and becomes coloured, but does not lose its mercury when treated with a solution of bromine in potassium bromide. With 3 mols. of mercuric acetate and 2 mols. of carbazole, the reaction gives the compound  $C_{24}H_{12}(NH)_2(Hg \cdot OAc)_2 \cdot Hg$ , which loses part of its mercury when treated with bromine in potassium bromide solution. Similarly, tetrahydrocarbazole forms the compounds,  $C_{24}H_{22}N_2Hg \cdot H_2O$  and  $C_{28}H_{28}O_4N_2Hg \cdot H_2O$ , which decompose without melting.

T. H. PORE.

**Phase-rule studies on the proteins. II. Quinquevalent nitrogen in organic compounds. I.** W. D. BANCROFT and C. E. BARNETT (J. Physical Chem., 1930, 34, 753—798).—A theoretical paper in which the addition of hydrogen chloride to tervalent nitrogen compounds is discussed. L. S. THEOBALD.

**Action of nitrous acid on caseinogen.** F. H. WILEY and H. B. LEWIS (J. Biol. Chem., 1930, 86, 511—528).—Caseinogen was deaminised by treatment with nitrous acid at various temperatures and the products were analysed. By isolation methods it was found that the arginine content was not affected by deamination, whilst the lysine was entirely destroyed and the histidine destroyed to the extent of 50%; results obtained by the Van Slyke method of analysis were not in good agreement with those of the isolation methods. The tryptophan content of caseinogen was not affected by deamination, whilst the tyrosine content was apparently reduced, probably owing to the formation of a nitrogenous derivative of this amino-acid which failed to react normally in the colorimetric determination. C. R. HARRINGTON.

**Action of proteins on ferric hydroxide sol.** G. LINDAU (Biochem. Z., 1930, 219, 385—408; cf. A., 1929, 879).—Results of experiments with egg-albumin, haemoglobin, and paraglobulin show that the sensitising action of the proteins is due to fixation of ions by them, for there is a parallelism between the magnitude of the sensitising action of a protein and its power to fix ferric ions. The extent of the protective action of higher concentrations of proteins increases in proportion as their power to peptise coarse particles of



ferric oxide increases, and this behaviour agrees with the view that protective action results from envelopment of the micellæ of the sol by protein. The alterations with time of the coagulation values also support this view. Denaturation of the proteins, which occurs as their concentrations are increased, causes their power to peptise ferric oxide to decrease after a maximum has been reached.

W. MCCARTNEY.

**Precipitation of proteins with ferric hydroxide.** G. LUNDE and K. WÜLFERT (Biochem. Z., 1930, 219, 171—185).—Colloidal ferric hydroxide shows specific behaviour with ampholytoid colloids and may be used for characterising and fractionating proteins when other methods fail.

P. W. CLUTTERBUCK.

**[Preparation of] caseinogen.** E. J. COHN and J. L. HENDRY (Organic Syntheses, 1930, 10, 16—19).

**Biuret reaction for the characterisation of proteins.** H. KÜHL (Pharm.-Ztg., 1930, 75, 546—548).—The colour reactions in (a) faintly alkaline solution at 50° and in strongly alkaline solution (b) at the ordinary temperature, and (c) at 50° of copper sulphate with 11 amino-acids and 8 proteins are tabulated. Series (a) shows the most characteristic differences. The examination of protein fractions from wheat gluten by this method is described.

H. E. F. NOTTON.

**Sources of error in organic elementary analysis.** J. LINDNER [with F. HERNLER].—See this vol., 726.

**General method for determination of halogens in organic compounds.** J. J. THOMPSON and U. O. OAKDALE (J. Amer. Chem. Soc., 1930, 52, 1195—1200).—The method depends on the liberation of halogen when the compound is heated with fuming sulphuric acid alone or with chromic acid or a persulphate. The halogen is absorbed by alkaline sodium arsenite and determined in the usual way. In the case of iodine compounds, liberation of iodine is completed by addition of concentrated hydrogen peroxide and of hydrazine sulphate. In the case of chlorine and bromine compounds copper sulphate is added, and potassium persulphate, or, in the case of compounds decomposed with difficulty, chromic acid. Complete liberation of halogen from mercury compounds is attained by treatment with zinc. Arsenic, antimony,

and bismuth may be determined in the same sample by appropriate treatment of the acid solutions.

R. K. CALLOW.

**Rapid determination of sulphur in organic compounds.** E. WERTHEIM (J. Amer. Chem. Soc., 1930, 52, 1075—1078).—The substance is decomposed by Parr's method (A., 1908, ii, 628) and, after removal of carbon dioxide and peroxide from the solution, sulphate is determined by a modification of Wildenstein's volumetric method, in which chromate solution is added to a concentration which gives a "standard end-point" with an external ferrous thiocyanate indicator, barium chloride is then added in slight excess, and chromate solution again added to give the standard end-point.

R. K. CALLOW.

**Determination of sulphur in liquid organic compounds.** E. WERTHEIM (J. Amer. Chem. Soc., 1930, 52, 1086—1088).—The method of oxidation described by Leonard (A., 1923, ii, 177) has been modified by replacing the platinum catalyst by chips of pyrex glass. Air is used in place of oxygen and the possibility of flashing thus decreased. The method is recommended for liquids and solids for which Parr's method is unsuitable (cf. preceding abstract).

R. K. CALLOW.

**Micro-determination of sulphur by fusion.** H. EMERSON (J. Amer. Chem. Soc., 1930, 52, 1291—1292).—The substance is fused with sodium carbonate and potassium nitrate and barium sulphate is precipitated and weighed in a micro-Neubauer crucible.

R. K. CALLOW.

**Micro-determination of arsenic in organic substances.** T. VON FELLEBERG (Biochem. Z., 1930, 218, 283—299).—The material to be analysed is decomposed with sulphuric acid and hydrogen peroxide, fuming nitric acid being added if necessary to complete the decomposition. The arsenic present is then converted, by the addition of hydrochloric acid, into trichloride and this is distilled from a special flask into water, hydrogen sulphide is passed into the distillate, and the precipitated trisulphide determined either by Mörner's method (A., 1902, ii, 694) or, for very small amounts of arsenic, by a modification of the method of Sanger and Black (A., 1908, ii, 64). Excluding the time required for decomposition the determination occupies 15—35 min. Tables and factors for calculation are given, the equivalent assumed by Mörner having been found inapplicable.

W. MCCARTNEY.

## Biochemistry.

**Determination of ethyl iodide in alveolar, expired, and inspired air.** H. R. OLIVIER, J. BRETEY, and M. HERBAIN (Compt. rend. Soc. Biol., 1929, 100, 533—534; Chem. Zentr., 1929, ii, 3043).—The ethyl iodide is decomposed at a platinum spiral, the products are absorbed in potassium hydroxide, and the contraction in volume is observed.

A. A. ELDRIDGE.

**Rate of dissolution of carbon dioxide in liquids.** M. N. J. DIRKEN and H. W. MOOK (Biochem. Z., 1930, 219, 452—462).—Determinations of the rate

at which carbon dioxide dissolves in water, Ringer solution, sodium and potassium hydroxide solutions, hæmoglobin solution, and serum show that the gas dissolves practically instantaneously in the surface layer of the liquid and hence that the rate of uptake of gas depends exclusively on diffusion and mixing, although knowledge of this rate does not permit the deduction of the rate of any reaction which may take place within the liquid. In serum there probably occurs a slow fixation of carbon dioxide. Carbon dioxide combines more slowly with hæmoglobin than

with alkali and the combination of hæmoglobin with the gas is slower than that with oxygen.

W. MCCARTNEY.

**Examination of blood.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 415—437).—A critical examination is made of the methods described in the literature. The formation of hæmin or hæmatin chloride crystals in Teichmann's test is improved by the presence of sodium salicylate; an improved method of carrying out the test is described. Hæmochromogen crystals are more easily and certainly obtained than Teichmann's crystals; lactose or sodium thio-sulphate in alkaline solution containing glycerol as well as pyridine is recommended as a suitable reducing agent. This test is found to be very trustworthy, and gives good results even with old, exposed, and partly decomposed stains; bloodstains ten years old on linen which had been heated for 10 hrs. at 125° before the test were at once recognised, and dirt, grease, and common metals do not inhibit. The occurrence and relationships of hæmatoporphyrin are discussed. A simple form of microspectroscope, by means of which the absorption bands can be observed with a dilution of 1 : 16,000, is described.

Determinations based on the nitrogen content of the extract obtained with salt solution may be made trustworthy by simultaneous determination of the iron. Experience has shown that the ratio protein : iron is almost constant at 360 for blood, and that 360 mg. of protein and 1 mg. of iron correspond with 2 g. of blood. Colorimetric determination may be made by macerating the material to be examined for 15 min. at 90° with a reducing solution covered with a layer of paraffin, the intensity of the colour resulting from formation of hæmochromogen being compared with that of solutions from fresh blood and from unstained material. The hæmochromogen test may be employed after the material has been heated at 105° for several weeks, or at 125° for some hours, or at 230° for 5 min., whilst the absorption bands can still be detected after heating at 250° for 15 min.

S. I. LEVY.

**Identification of *d*- $\alpha$ -aminovaleric acid (norvaline) in addition to *d*- $\alpha$ -aminoisovaleric acid (valine) among the products of fission of globin by means of the differing rates of amination of the corresponding  $\alpha$ -bromo-compounds.** E. ABDERHALDEN and A. BAHN (Ber., 1930, 63, [B], 914—921).—The velocity of conversion of *dl*- $\alpha$ -bromoisohexioic acid into the corresponding amino-acid by 25% ammonia at 37° or 18° is somewhat less than that of  $\alpha$ -bromo-*n*-valeric acid, but much greater than that of  $\alpha$ -bromoisovaleric acid, thus giving a method for the identification of norvaline in presence of valine. Hydrolysis of globin followed by esterification of the product yields a fraction consisting mainly of leucine and valine, but yielding also norvaline, m. p. 300—303° (corr.),  $[\alpha]_D^{25} +22.8$  in 20% hydrochloric acid. The final identification of the last-named compound depends on its conversion into the corresponding bromo-acid and comparison of its rate of amination with that of the bromo-acid from valine. The applicability of the process to the determination of mixtures of  $\alpha$ -bromo-*n*- and -*iso*-valeric acid is established. With optically active halogeno-acids the

course of amination can be followed polarimetrically. Interruption of amination after suitable intervals and removal of unchanged halogenated acids by ether after acidification permits the identification of the two bromo-acids in their mixtures and thus of valine and norvaline in their mixtures even when the amount of one component greatly predominates. The method cannot necessarily be extended to other cases. Thus the rates of amination of  $\alpha$ -bromohexioic and  $\alpha$ -bromo- $\gamma$ -methylvaleric acids do not differ sufficiently from one another to permit the certain identification of either.

H. WREN.

**Enzyme content of blood. I. Normal.** F. DELHOUGNE (Deut. Arch. klin. Med., 1929, 165, 213—222; Chem. Zentr., 1929, ii, 3156).—The protease content of the blood normally varies considerably; catalase, peroxidase, and esterase values are more regular. Bodily work increases the catalase and peroxidase, and to a smaller degree the esterase.

A. A. ELDRIDGE.

**Oxidase reaction of blood.** R. GUYOT (Bull. Soc. Pharm. Bordeaux, 1929, 67, 131—140; Chem. Zentr., 1929, ii, 3168).—Tyrosine from *Russula nigricans* was not oxidised to melanin by blood, but the juice of *Boletus cyanescens* became blue on treatment with blood, hæmoglobin, iron lactate, manganese lactate, etc.

A. A. ELDRIDGE.

**Enzymic decomposition of acetylcholine in blood and its inhibition by physostigmine.** E. ENGELHART and O. LOEWI (Arch. exp. Path. Pharm., 1930, 150, 1—13).—The loss of activity of acetylcholine brought about by serum, plasma, corpuscles, or stromata or by human blood dried at 38° is inhibited by physostigmine in concentrations as low as 1 : 40,000,000, but not by strychnine or morphine. After being heated to 58°, ox-blood but not human blood fails to destroy acetylcholine, but human blood does not inactivate acetylcholine after being dried at 58°. Blood irradiated by fluorescent light inactivates acetylcholine. The inactivation is brought about by an esterase which is inhibited by physostigmine.

W. O. KERMACK.

**Effect of non-electrolytes on the stability of animal fluids.** M. PIETRE (Compt. rend., 1930, 190, 1012—1014).—Horse and ox sera were dialysed against water at 1—3°, through cellophan, until the water showed no trace of chloride or alkali. Even so, all electrolytes were not removed. On centrifuging the fluid a mixture of serum-globulin, myxoprotein, serum-albumin, and part of the lipins was precipitated, leaving a stable liquid, the solid contents of which remained soluble after freezing or evaporation, although containing 75% of the globulin. This solution was evaporated to dryness and the solid residue repeatedly extracted with ether, whereby the remaining lipins were removed. The residue on treatment with water flocculates, separating most of the globulin, but the last traces can be removed only by treatment with 0.01*N*-hydrochloric acid.

C. A. SILBERRAD.

**Mineral content and acid-base equilibrium of infants' serum.** A. NITSCHKE and G. M. ZU HÖRSTE (Jahrb. Kinderheilk., 1928, 121, 111—122; Chem. Zentr., 1929, ii, 2575).—In infants' serum the organic acid content is smaller than for adults. Increase in

serum-organic acids can be regulated by increasing the total base, or decreasing the hydrogen carbonate or chloride. The effect of rickets is considered.

A. A. ELDRIDGE.

**Determination of total calcium in blood-serum.** J. PATTERSON (Biochem. J., 1930, 24, 355—356).—Improvements in the technique of the Trevan and Bainbridge method, dealing mainly with the heating conditions which bring the oxalate-carbonate conversion under complete control, are described.

S. S. ZILVA.

**Composition of bone. IX. Equilibrium of blood-serum with calcium hydrogen phosphate.** M. J. SHEAR and B. KRAMER (J. Biol. Chem., 1930, 86, 677—694).—Normal blood-sera of the calf, the lamb, and of man, were equilibrated with calcium hydrogen phosphate by shaking with the crystalline salt. In all cases an increase in phosphate concentration and in most cases an increase of calcium concentration were observed, so that the product  $[Ca^{++}] \times [HPO_4^{--}]$  was invariably raised. A very slight decrease in the  $p_H$  of the serum occurred. Normal serum is therefore under-saturated with respect to calcium hydrogen phosphate, the least degree of under-saturation being observed in growing animals.

C. R. HARRINGTON.

**Ether-soluble acids of blood. Determination of lactic acid in blood.** S. L. ØRSKOV (Biochem. Z., 1930, 219, 409—421).—The ether-soluble acids of blood are most satisfactorily determined in the filtrate from blood treated with sulphuric acid and sodium sulphate, a modified form of Widmark's rocking extraction tube being used (A., 1929, 109). The lactic acid in 1.5 c.c. of blood can be extracted in this way and then accurately determined by conversion into acetaldehyde by the method of Lehnartz (*ibid.*, 48).

W. MCCARTNEY.

**Blood-lactic acid. I. Resting value and distribution. II. Permeability of blood-cells to *dl*-, *d*-, and *l*-lactic acid.** K. NOSHI (J. Biochem. Japan, 1929, 11, 307—320, 321—331).—Great individual variations were observed with dog, rabbit, pigeon, and frog blood. Resting values are: frog 10.3, pigeon 14.7, rabbit 8.4 mg. per 100 c.c. The red cells always contain lactic acid, the content (%) being: man 9, rabbit 6, pigeon 5, frog 5; they are permeable *in vivo* to the serum-lactic acid. The cells are more readily permeable to *d*-lactic than to *l*-lactic acid in a phosphate mixture of  $p_H$  7.7.

CHEMICAL ABSTRACTS.

**Blood filtrates for sugar determination.** M. SOMOGYI (J. Biol. Chem., 1930, 86, 655—663).—Laked blood is treated with zinc sulphate and sodium hydroxide and filtered. Filtrates obtained in this manner contain no reducing substances other than sugar.

C. R. HARRINGTON.

**Validity of blood-sugar determinations. VI, VIII. Variation in results obtained by deproteinisation with tungstic acid and mercuric filtrate. VII. Sugar in the plasma. IX. Phenomenon of "mercurial dilution."** G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1930, 12, 264—298).—VI, VIII. Blood filtrates obtained by means of tungstic acid always give higher

values for reducing sugars than those prepared by mercury precipitation. Mercuric nitrate gives the same results on the tungstic acid filtrate as on the original blood filtrates, and these, after brief hydrolysis with dilute acid, become almost equal to the original values of the tungstic acid filtrate. The presence of a glucoside possibly accounts for these phenomena. Subcutaneous injection of adrenaline in dogs (1 mg. per kg. body-weight) produces a rise in the glucoside content of the blood as well as the dextrose, whilst compression of the portal vein or injection of morphine does not affect it. Insulin decreases the amount of reducing carbohydrate until, at the crisis, it is non-existent. This sugar is entirely metabolised by yeast and living animal cells.

VII. Rapid production of insulin hypoglycæmia affects the plasma-sugar only, although the sugar of the corpuscles is also affected after prolonged hypoglycæmia. The sugar of the corpuscles acts as a reserve for that of the plasma.

IX. If more than two volumes of water are added to whole blood or plasma before the mercury precipitation, minimal results for blood-sugar are not obtained (mercurial dilution). This phenomenon persists after injection of insulin and in the filtrate from the tungstic acid precipitation, and it appears to be due to some substance other than the reducing carbohydrate which appears in the tungstic acid filtrate.

P. G. MARSHALL.

**The Hagedorn-Jensen method applied to various sugars. Relation of reducing power to configuration.** H. SOBOTKA and M. REINER (Biochem. J., 1930, 24, 394—399).—The differences in the reducing power of the several sugars investigated are correlated with *trans*- and *cis*-configuration; in aldo- and keto-hexoses the configuration between the third and the fourth carbon atoms is the determining factor, in aldopentoses the configurations of  $C_2$ — $C_3$  and  $C_3$ — $C_4$  share the influence on the reducing power.

S. S. ZILVA.

**Effect of glutathione on the determination of blood-sugars.** F. K. HERBERT, M. C. BOURNE, and J. GROEN (Biochem. J., 1930, 24, 291—298).—Of the reagents examined, reduced glutathione has the greatest effect on the reduction of ferricyanide; next in order are the Shaffer-Hartmann (Somogyi) copper reduction and the Folin-Wu copper reduction. The copper reagent of Benedict is unaffected by it. In the tungstic acid precipitation applied to mixtures of plasma and glutathione all the added glutathione passes into the filtrate. In Somogyi's zinc hydroxide precipitation no glutathione passes into the filtrates. The zinc hydroxide precipitation of Hagedorn and Jensen allows a portion of the added glutathione to pass into the filtrates.

S. S. ZILVA.

**Non-sugar reducing substances of human blood with special reference to glutathione.** F. K. HERBERT and M. C. BOURNE (Biochem. J., 1930, 24, 299—309; see preceding abstract).—In normal human blood the Hagedorn-Jensen, the Shaffer-Hartmann, the Folin-Wu, and the Benedict methods agree when applied to the zinc hydroxide filtrates and the "sulphate-tungstic" filtrates which contain no glutathione. The Benedict method which

is unaffected by glutathione gives the same figure for these and for the Folin-Wu filtrate. Definite non-sugar reducing effects are observed when the Hagedorn-Jensen, Shaffer-Hartmann, and Folin-Wu methods are applied to Folin-Wu tungstic acid filtrates. The average values of these effects, expressed as dextrose, are for the ferricyanide method 28, for the Shaffer-Hartmann method 18, and for the Folin-Wu method 13 mg. per 100 c.c. These non-sugar reductions may be explained by the presence of non-diffusible reduced glutathione in the corpuscles. Hagedorn-Jensen filtrates give higher figures with the ferricyanide method than the Somogyi filtrates. By using isotonic sulphate solution instead of distilled water in the Folin-Wu tungstic acid precipitation the non-diffusible glutathione remains in the corpuscles while the dextrose diffuses freely throughout the mixture. S. S. ZILVA.

**Rate of disappearance of foreign sugar from the blood.** E. H. FISHBERG (J. Biol. Chem., 1930, 86, 665—670).—The disappearance of xylose and galactose from the blood of rabbits, after intravenous injection of these sugars, follows the course of a unimolecular reaction. C. R. HARRINGTON.

**Movement of sugar from the blood-corpuscle into the blood-plasma.** K. T. EKI (Chosen J. Med., 1929, 19, 405—497).—The sugar content of rabbit's blood is (%): whole blood 0.11, plasma 0.152, corpuscles 0.022, serum 0.149. No change is observed on addition of insulin or adrenaline *in vitro*, neither do these substances affect the saccharising action of the isolated liver. CHEMICAL ABSTRACTS.

**Effect of lecithin on blood-sugar.** C. SAKURAI (Osaka J. Med., 1928, 27, 2811—2820).—Slight hyperglycæmia is produced. CHEMICAL ABSTRACTS.

**Blood coagulation as a colloid-chemical problem.** B. STUBER (Kolloid-Z., 1930, 51, 144—152).—The enzyme theory of the coagulation of blood is critically reviewed and the possibilities of an interpretation in terms of colloid-chemical processes are discussed. E. S. HEDGES.

**Calcium in the coagulation of blood.** M. M. LOUCKS and F. H. SCOTT (Amer. J. Physiol., 1929, 91, 27—46).—It is doubtful if prothrombin exists. Thrombin is probably a calcium "tissue juice" compound. Some blood-calcium is combined with ether-extractable lipins. E. BOYLAND.

**Activity of lecithin in blood coagulation.** A. WADSWORTH, F. MALTANER, and E. MALTANER (Amer. J. Physiol., 1930, 91, 423—428).—The fraction of hydrolysed lecithin precipitated by alkaline calcium salts has a coagulative action, which pure lecithin has not. E. BOYLAND.

**Saponin hæmolysis.** H. D. KESTEN (Amer. J. Physiol., 1929, 91, 1—7).—Experiments on individual cells show no individual resistances to hæmolysis. E. BOYLAND.

**Hæmolysis.** K. C. SEN, A. C. RAY, and N. N. MITRA (Indian J. Med. Res., 1929, 17, 55—76).—Traces of acids accelerate the hæmolytic action of saponin and sodium taurocholate, but retard that of

oleate (unless present in low concentration). Sucrose inhibits the action. CHEMICAL ABSTRACTS.

**Serum hæmolysins.** L. GÓZONY and F. HOFFEN-REICH (Zentr. Bakt. Par., 1929, I, 113, 277—284; Chem. Zentr., 1930, i, 90).—The hæmolytic amboceptor behaves towards enzyme poisons (e.g., cyanide) like a lipase. The preparation and purification of hæmolytic substance is described; the hæmolysin is regarded as lipase. A. A. ELDRIDGE.

**Action of certain dyes on the bactericidal activity of normal serum and on the hæmolytic complement.** J. GORDON (J. Path. Bact., 1930, 33, 47—55). CHEMICAL ABSTRACTS.

**Precipitin for blood-corpuscles in red blood-corpuscles.** T. MITSUI (Hokkaido J. Med., 1929, 7, 229—235). CHEMICAL ABSTRACTS.

**Yeast in the Death Watch beetle.** L. N. STANLAND (Nature, 1930, 125, 635).—A yeast is invariably present in the larvæ and adults of this beetle. L. S. THEOBALD.

**Chemical constitution of *Pectinatella*.** W. MORSE (Science, 1930, 71, 265).—The protein and other solids make up 0.5% of the normal body of *Pectinatella*, the remainder being water. The protein reactions are typical of ovalbumin, serum-albumin, etc., whilst the biuret reaction is similar to that of egg-white and not like that of peptone or gelatin. Tyrosine, tryptophan, and cystine can be identified even in the cold, whilst sodium chloride and calcium are among the inorganic constituents. L. S. THEOBALD.

**Swelling of the cornea and skin of animals' and human eyes.** F. P. FISCHER (Kolloid-Z., 1930, 51, 160—162).—Measurements have been made of the following properties: degree of swelling, swelling velocity, density alterations during swelling, loss of water on exposure, change in refractive index during absorption and desorption of water. The results are compared, but no general conclusions are reached. E. S. HEDGES.

**Regulating power of the principal constituents of muscle-juice.** L. DE CARO (Atti R. Accad. Lincei, 1930, [vi], 11, 98—102).—Experiments on the pressed juice of striped muscle of the dog confirm previous results (A., 1929, 590). The buffering power (1) of the ash of the juice shows two minimum zones at  $p_H$  4.7 and 9.7 and a somewhat high value at about  $p_H$  6.5, which is explainable from the course of the neutralisation curve of phosphoric acid by an alkali; (2) of the colloidal fraction of the juice has a minimum at  $p_H$  5.7 (attributed to the isoelectric point of the myosin) and a zone of constancy between  $p_H$  8.2 and 6.2; (3) of the myoprotein represents only a small proportion of that of the colloidal fraction and becomes zero at the isoelectric point ( $p_H$  6.2); (4) of the colloidal fraction, in passing from  $p_H$  7.7 to 6.7, varies from 76 to 55% of the total buffering power of the juice and increases considerably on either the acid or the alkaline side of this zone. T. H. POPE.

**Hydrolysis products of fish-muscle.** I. Diamino-nitrogen of cod-muscle. J. C. KERNOT, J. KNAGGS, and N. E. SPEER (Biochem. J., 1930,

24, 379—382).—The percentages of basic nitrogen precipitated by phosphotungstic acid vary for a given period of hydrolysis with the conditions of precipitation. Even after prolonged hydrolysis cyclic compounds or ketopiperazines are found in the hydrolysate, and their percentage increases if the hydrolysis is prolonged. S. S. ZILVA.

**Distribution of glycogen in the ox heart.** T. MATSUMORI (J. Biochem. Japan, 1929, 11, 219—223). CHEMICAL ABSTRACTS.

**Thyroid gland and distribution of iodine in the human and animal organism.** STURM (Verh. Deut. Kong. inn. Med., 1928, 295; Chem. Zentr., 1929, ii, 3232).—A discussion. A. A. ELDRIDGE.

**Islets of Langerhans in the monkfish (*Lophius piscatorius*, L.).** E. JORPES (J. Biol. Chem., 1930, 86, 469—476).—The islets of Langerhans in the monkfish contain less nucleic acids and more phospholipins than does the pancreas of selachian fishes or that of mammals. It is suggested that the abundant nucleic acids of the pancreas may serve as buffer substances. C. R. HARRINGTON.

**Separation of ribopolynucleotides from thymonucleic acid, and of purine bases from ribopolynucleotides.** P. A. LEVENE and E. JORPES (J. Biol. Chem., 1930, 86, 389—401).—The mixed nucleic acids of the pancreas (cf. Jorpes, A., 1929, 463) can be purified by treatment of a 10% aqueous solution with a large excess of glacial acetic acid, which causes precipitation of the ribonucleic acid, the thymonucleic acid remaining in solution. The ribonucleic acid so obtained was hydrolysed with sulphuric acid and with methyl-alcoholic hydrogen chloride; in both cases yeast nucleic acid was submitted to similar treatment for comparison. The ribonucleic acid contained more guanine, less adenine, and more acid-labile phosphoric acid than the yeast nucleic acid. On partial hydrolysis of the ribonucleic acid with ammonia, guanosine and adenosine were obtained. C. R. HARRINGTON.

**Glutathione. II. Determination of reduced glutathione in tissues.** H. L. MASON (J. Biol. Chem., 1930, 86, 623—634).—In the determination of glutathione by iodine titration (cf. Tunnicliffe, A., 1925, i, 752) it is necessary to work in presence of excess of iodide, and starch is the most suitable indicator. Glutathione is better determined in tissue extracts, however, by adjustment of the latter to  $p_H$  5.9 followed by treatment with excess of potassium ferricyanide, adding ferric sulphate, and comparing the colour with that produced by a standard solution of cysteine similarly treated; a blank determination is made on the tissue extract after addition of formaldehyde, which specifically inhibits the reduction of ferricyanide by reduced glutathione. The new method gives results similar to those of iodine titration with blood and muscle, but much lower results with yeast, liver, and kidney, for which tissues the iodine titration method is unsuited. C. R. HARRINGTON.

**Properties of pure glutathione.** N. U. MELDRUM and M. DIXON (Biochem. J., 1930, 24, 472—496; cf. Hopkins and Dixon, A., 1923, i, 167; Harrison, A., 1925, i, 13; Hopkins, *ibid.*, 1499; Allott, A., 1926, 1172).—The autoxidation of glutathione

depends on the co-operation of two factors present as impurities, namely iron or copper and some substance able to form catalytic complexes with metals. Crystalline glutathione (cf. Hopkins, A., 1929, 1322; Kendall, McKenzie, and Mason, this vol., 113) absorbs oxygen at the rate of about 30 mm.<sup>3</sup> per 5 mg. of glutathione at  $p_H$  7.6 and 20°. This oxidation is due to the presence of traces of catalytic metals and to the second substance which is the limiting factor. The former can be removed from it with consequent inactivation by adsorption on kaolin. The addition of a trace of iron brings back the autoxidation to the original rate. On the other hand, the addition of iron to crystalline glutathione does not accelerate the rate of oxidation as it does in the case of cysteine. Cysteine is not inactivated by kaolin. Crystalline glutathione, unlike the earlier preparations, produces no oxygen uptake when added to "thermostable tissue preparations." When the disulphide form is added it becomes reduced by the tissue, but no oxygen is taken up. When the thiol form is added not only does it fail to oxidise the protein, but also its own autoxidation is completely inhibited. On removing the tissue the solutions of reduced glutathione are unable to react with oxygen or methylene-blue even after the addition of iron or copper, but become activated on addition of a small amount of impure glutathione. Pure glutathione or other peptides of cysteine are not able to form catalytic complexes with iron or copper. Certain other proteins behave like the "thermostable preparations" in inactivating glutathione. Its oxidation is also inhibited by fresh washed muscle. A mixture of crystalline glutathione and free cysteine behaves in the same way as impure glutathione; the catalytic impurity is, however, not identical with cysteine. In the oxidation of unsaturated fatty acids crystalline glutathione shows the same catalytic power as the early preparations.

S. S. ZILVA.

**Differential staining method for connective tissue combined with the hæmatoxylin-eosin stain.** E. E. LARSON (Stain Tech., 1930, 5, 73—74).—The sections were stained in hæmatein for 2—3 min., washed with water, and then stained with eosin-B for 1 min. After passing through alcohol baths of increasing concentration (up to 95%) they were treated with orange-G in 95% alcohol for about 15 sec., dehydrated with absolute alcohol, and mounted. The connective tissue fibres are stained by the orange-G and stand in strong contrast to the blue epithelium and pink cytoplasm in sections of skin. H. W. DUDLEY.

**Preparation of lecithin.** F. MALTNER (J. Amer. Chem. Soc., 1930, 52, 1718—1719).—In the isolation of lecithin from liver and heart by Levene and Rolf's method (A., 1927, 586) the precipitation as the cadmium salt is best carried out with a solution of cadmium chloride in 95% methyl alcohol. The final treatment with acetic acid can be omitted. Lecithin can also be extracted from the fraction containing the fats (cf. *loc. cit.*). H. BURTON.

**Composition of the mixed fatty acids present in the glycerides of cod-liver and certain other fish-liver oils.** K. D. GUHA, T. P. HILDITCH, and

J. A. LOVERN (Biochem. J., 1930, 24, 266—290).—The acids were divided into two or three groups, mainly saturated and mainly unsaturated by crystallisation of the less soluble lead salts from alcohol. This was followed by conversion of each group into methyl esters and systematic fractional distillation and refractionation of the latter. The following oils were examined: Newfoundland, Scottish, and Norwegian cod-liver oils, coal fish- (saith), hake-, ling-, skate-, and dogfish-liver oils. There is no correlation between the vitamin-A potency of the oils as determined by the colorimetric method and the composition of their fatty acids.

S. S. ZILVA.

**Insect oils and fats.** J. TIMON-DAVID (Bull. Soc. Chim. biol., 1930, 12, 395—403).—The larvæ of more than two dozen insects studied contain quantities of oil varying from 0.94 to 28.0%. The iodine values of the oils vary from about 1.2 in the case of some Aphidians (these oils have a high saponification value) to 164.5 for *Saturnia pyri*, Sch. The non-drying oils are most largely represented. The isolation of hexabromostearic acid by bromination of the acids from *Colaspidema atra*, Ol. (m. p. 178.5°), confirms the presence of linolenic acid in the oil of this insect. Oleic acid is widely distributed in insect oils. The amount of unsaponifiable matter varies from 0.75% in the oil of *Ergates faber*, L., to 12.5% in that of *Heliotaurus menticornis*, Reitt. The oils of tropical insects have a lower iodine value than those of insects inhabiting cold countries. Females generally are richer in fat than males. Related species yield oils of a similar type.

P. G. MARSHALL.

**Bull-frog oil.** Y. IWAMOTO and M. KISEGAWA (J. Soc. Chem. Ind. Japan, 1930, 33, 66—67B).—The oil in the oil-reservoirs of the bull frog (*Rana catesbiana*, Shaw) had  $d_4^{20}$  0.9216,  $n_D^{20}$  1.4733, and contained mixed fatty acids from which an ether-insoluble bromide,  $C_{18}H_{30}O_2Br_6$ , m. p. 180.5°, corresponding with linolenic acid, and an ether-soluble bromide,  $C_{18}H_{32}O_2Br_4$ , m. p. 112°, corresponding with linoleic acid, were isolated. After separation of solid and liquid fatty acids by the lead salt-ether method, the latter were oxidised by dilute alkaline permanganate giving dihydroxystearic, sativic, and linusic acids. The solid fatty acids, m. p. 58.5°, neutralisation value 215.35, appear to be palmitic acid (12%) and stearic acid (88%).

C. W. SHOPPEE.

**Composition of the saturated fatty acids of Japanese great herring oil (o-nishin oil).** S. UENO and H. IKUTA (J. Soc. Chem. Ind. Japan, 1930, 33, 62—64B; cf. B., 1926, 758).—Examination of the fractions obtained by distillation under reduced pressure of the methyl esters of the solid fatty acids (m. p. 46—47°) isolated from the oil shows palmitic acid to be the main constituent, accompanied by stearic and myristic acids, and traces of arachidic and behenic acids. The oil also appears to contain traces of water-soluble saturated fatty acids (butyric or valeric acid?).

C. W. SHOPPEE.

**Composition of oils and fats of Japanese birds.** S. UENO and H. IKUTA (J. Soc. Chem. Ind. Japan, 1930, 33, 76—78B).—The orange-yellow fragrant fats from the fresh internal organs of the "Hirenjaku"

(*Bombycilla japonica*, Siebold) and the "Mahiwa" (*Spinus spinus*, Linne) had, respectively,  $d_4^{20}$  0.89651, 0.89690; m. p. 29—30.5°, 27—28.5°;  $n_D^{20}$  1.4590, 1.4593; acid value 24.6, 96.6; saponification value 195.8, 185.3; iodine value (Wijs) 61.7, 75.2; unsaponifiable matter 0.85%, 1.12%. The mixed fatty acids had m. p. 38.5—39°, 36—36.5°; neutralisation value 204.9, 194.4; iodine value 62.5, 80.5. The fatty acids from "Hirenjaku" examined by the lead salt-ether method gave 32.3% of solid acids (m. p. 49.5—50°), and 68.7% of liquid acids, whilst those from "Mahiwa" gave 34.8% of solid acids (orange crystals, m. p. 44—44.5°) and 65.2% of liquid acids; the respective neutralisation values were 206.7, 194.6, 194.8, and 168 and iodine values 26.6, 86.0, 39.5, and 98.8. By distillation of the methyl esters of the solid acids palmitic and stearic acids were identified in both oils; further, the presence of water-soluble acids was confirmed. The ether-insoluble bromides of the liquid fatty acids (about 2.1 and 3.2%, respectively) blackened with decomposition between 220° and 230°.

E. LEWKOWITSCH.

**Relation between the amounts of urea in blood and in saliva.** S. MIYAZAKI (Bull. Kyoto Pref. Med. Coll., 1928, 2, 119—142).

CHEMICAL ABSTRACTS.

**Urea and ammonia in normal gastric juice.** D. SIMICI, R. VLADESCO, and M. POPESCO (Compt. rend. Soc. Biol., 1929, 101, 199—202, 202—204; Chem. Zentr., 1929, ii, 3030).—The gastric juice of fasting persons contains 0.014—0.042% of urea and 0.0048—0.0098% of ammonia, the values being scarcely affected by a test meal. Injection of urea (5—10 g. in 20 c.c. of water) raised the values to 0.06 and at least 0.03%, respectively. In pathological conditions not affecting the kidneys these values are not markedly changed; in those affecting the kidneys they are increased to 0.3 and 0.11%, respectively.

A. A. ELDRIDGE.

**Composition of pancreatic juice and blood-serum. Influence of acid and base. Influence of inorganic salts.** E. G. BALL (J. Biol. Chem., 1930, 86, 433—448, 449—462).—The  $p_H$  of pancreatic juice is chiefly determined by the rate of flow, being high during rapid secretion and low when secretion is slow; it is little affected by intravenous injections of hydrochloric acid or of sodium carbonate which produce marked alterations in the  $p_H$  of the blood-serum. The sum of the concentrations of hydrogen carbonate and chloride is maintained at an almost constant level irrespective of the rate of secretion. Intravenous injections of hydrochloric acid and of sodium carbonate cause decrease and increase, respectively, of the hydrogen carbonate of the pancreatic juice.

The osmotic pressures of blood-serum and pancreatic juice are, in normal circumstances, identical; the concentrations of sodium and potassium in the two fluids are the same and are raised to the same extent by injections of salts of these metals. The concentrations of calcium, magnesium, and phosphorus in pancreatic juice are considerably lower than those in blood and are little increased by intravenous injections of these substances. The total



organic matter of the pancreatic juice is larger in amount after a period of rest than after one of active secretion.

C. R. HARRINGTON.

**Variations in inorganic constituents of pancreatic juice during constant drainage of the pancreatic ducts.** C. G. JOHNSTON and E. G. BALL (J. Biol. Chem., 1930, 86, 643—653).—As drainage of the pancreas progressed in dogs with a permanent fistula the chloride of the juice diminished, whilst the hydrogen carbonate increased; a smaller decrease was observed in the calcium, but the total cation and anion concentrations remained almost constant. The  $p_H$  tended to increase from about 7.2 to 8.0.

C. R. HARRINGTON.

**Urea-excreting function of the liver.** I. Normal. II. Effect of plant poisons. M. SAKAI (J. Exp. Digest. Dis., Japan, 1929, 3, 1107—1118).—Rabbits' bile contained 24.58 mg. of residual- and 9.07 mg. of urea-nitrogen per 100 c.c. Injection of urea into the blood is followed by an increase in the bile-urea. Injection of adrenaline or pilocarpine increases the bile-urea, pilocarpine increases the blood-urea, but adrenaline and atropine cause no change.

CHEMICAL ABSTRACTS.

**Halogen excretion in the liver.** Y. MARUNO (J. Exp. Digest. Dis., Japan, 1929, 3, 939—954).—Organic halogen compounds injected into a rabbit are excreted in the bile more readily than inorganic compounds. The excretion of inorganic compounds is markedly dependent on the cation. Excretion of the halogens decreases in the order chlorine, bromine, iodine. Oral administration is followed by only slight excretion in the bile. CHEMICAL ABSTRACTS.

**Changes in the alkali reserve and the sugar content of the bile by the action of various physiological excitants.** I. W. KARATYGIN and A. HEFTER (Z. ges. exp. Med., 1929, 65, 183—197; Chem. Zentr., 1929, ii, 3160).—The alkali reserve of the bile varies in fasting dogs between 0 and 70—80%  $CO_2$ ; dextrose, casein, peptone, and meat extract shift the reaction towards the acid side, and soaps towards the alkali side. Excretion of sugar in the bile is increased by ingestion of carbohydrates, protein, and extractive materials, diminished by that of fat, and scarcely affected by water. A. A. ELDRIDGE.

**Excretion of sterol and sterol balance in total closure of the biliary duct.** M. BÜRGER and W. WINTERSEEL (Z. ges. exp. Med., 1929, 66, 459—474; Chem. Zentr., 1929, ii, 3160).—In pathological conditions of the liver disturbance of the fat- and cholesterol-resorption was observed.

A. A. ELDRIDGE.

**Composition of human milk in the later periods of lactation and a comparison with that of early milk.** S. T. WIDDOWS, M. F. LOWENFELD, M. BOND, and E. I. TAYLOR (Biochem. J., 1930, 24, 327—342).—The percentages of calcium and phosphorus in human milk follow parallel curves throughout the course of lactation, the variation in the latter being less than that of the former. The percentage of both is less in the early weeks, rising to a maximum at the end of the second month, and then slowly declining to the end of the tenth month. The per-

centage of ash is highest during the first two weeks and then falls continually throughout lactation, the steepest fall being during the last month. The percentages of calcium oxide and of phosphorus pentoxide gradually rise in the ash to reach a maximum during the last months. That of the former rises from 15.5 in the early weeks to 26.1 in the later months, whilst that of the latter rises from 13.56 to 21.13. The ratio of the percentage of calcium oxide to that of phosphorus pentoxide rises and falls during the different periods in accordance with the rise and fall of the calcium and phosphorus. The average rises from 1.35 to 1.42 and falls to 1.25 during the last months. The protein content decreases rapidly from a very high value immediately after parturition to the end of the first month and then falls gradually but continuously until it reaches an average of about 0.9337% by the end of the tenth month. The authors' figures for the average percentage of protein from the end of the first month until the tenth differ from those obtained by other workers. The percentage of sugar is at its lowest value in early milk. After the first month it varies little throughout lactation. The percentage of sugar in milk is affected and the value lowered when the breast is in a pathological condition.

S. S. ZILVA.

**Determination of iron in milk and other biological materials.** C. A. ELVEHJEM (J. Biol. Chem., 1930, 86, 463—467).—The material is incinerated and the ash taken up in dilute hydrochloric acid; excess of sodium hydroxide is added and the solution is boiled for 1 hr. After reacidification the iron is determined colorimetrically by the method of Kennedy (A., 1927, 987). The treatment with alkali eliminates the difficulty due to the presence of pyrophosphate in the ash. C. R. HARRINGTON.

**Fractional dialysis of urine.** A. BOIVIN (Compt. rend. Soc. Biol., 1929, 101, 722—724; Chem. Zentr., 1929, ii, 2905).—A vegetable diet increases the quantity of easily dialysable substances in urine, whilst a meat, and particularly a milk, diet has the reverse effect.

A. A. ELDRIDGE.

**Non-dialysable fraction of urine.** A. BOIVIN (Compt. rend. Soc. Biol., 1929, 101, 724—726; Chem. Zentr., 1929, ii, 2905).—The weight, C:N ratio, sulphur content, and phosphorus content of the non-dialysable fraction of human urine depend on the technique of the dialysis.

A. A. ELDRIDGE.

**Acetone and acetoacetic acid in urine.** C. OTTO (Pharm.-Ztg., 1930, 75, 479—481).—The methods available for the detection and determination of acetone and acetoacetic acid in urine are discussed.

W. O. KERMACK.

**Detection of acetone and acetoacetic acid in urine.** H. OTTO and H. IMHOFF (Süddeut. Apoth.-Ztg., 1929, 69, 553—554; Chem. Zentr., 1929, ii, 2918).—Acetone, and not acetoacetic acid, is detectable in urine with sodium nitroprusside; Lange's ring test is most convenient. For the detection of acetoacetic acid Gerhard's test with ferric chloride and Ondrejowich's test with methylene-blue and iodine are preferred.

A. A. ELDRIDGE.

**Detection of acetone and acetoacetic acid in urine.** P. HORKHEIMER (Süddeut. Apoth.-Ztg., 1929,

69, 596; Chem. Zentr., 1929, ii, 2918).—Polemical (cf. preceding abstract). A. A. ELDRIDGE.

**Acetone and acetoacetic acid in urine.** P. HORKHEIMER (Pharm.-Ztg., 1930, 75, 510).—Acetone is rarely present in fresh diabetic urine to the extent of more than 0.1%. A positive nitroprusside reaction is, therefore, not to be ascribed to acetone, but to acetoacetic acid, which gives the test at a much greater dilution than the former.

H. E. F. NOTTON.

**Dextrose in normal urine.** H. ROTH (Compt. rend. Soc. Biol., 1929, 101, 218—220; Chem. Zentr., 1929, ii, 3030).—The amount of dextrose in normal urine varies between 0.02 and 0.30%, varying with the time of day. After fermentation with yeast there remained in the urine 0.01—0.02% of reducing non-sugar substances.

A. A. ELDRIDGE.

**Reducing power of urine.** H. K. BARRENSCHEEN and G. DELL'ACQUA (Biochem. Z., 1930, 219, 297—319).—The dyes which confer reducing power on human urine can be obtained in the form of barium salts and contain thiol groups. In healthy persons the reducing power of the urine, determined by Folin's method (A., 1928, 786), remains constant for months. Consumption of food rich in protein increases the reducing power, whilst that of vegetable food decreases it. The variations in the reducing power which occur in certain physiological conditions and the decrease in the reducing power of the barium salts produced by formaldehyde indicate that the reducing power of the urine is due, in part, to urochrome.

W. MCCARTNEY.

**Effect of various indole derivatives on the urochrome content of urine.** S. KIMINAMI (Osaka J. Med., 1928, 27, 2791—2800).—In rabbits, indole, skatole, or *dl*-indole lactate causes no marked change; indole-2- or -3-carboxylic acid, given orally, causes a slight increase, whilst with *dl*- and *l*-tryptophan and pyruvic acid there is an appreciable increase.

CHEMICAL ABSTRACTS.

**Determination of uric acid [in urine].** L. TIXIER (Bull. Sci. pharmacol., 1929, 36, 77—79; Chem. Zentr., 1929, ii, 3043).—Urine (50 c.c.) is digested for 1 hr. with 20 c.c. of a solution prepared from copper sulphate (4 g.), ammonia solution (500 c.c.), and water (500 c.c.); after filtering and washing with 5 c.c. of 10% ammonia solution there are added to the filtrate 5 c.c. of a solution containing potassium cyanide (20 g.), ammonia (10 c.c.), and potassium iodide (60 g. per litre). Titration is carried out to permanent opalescence with 0.1N-silver nitrate; 0.1 c.c. is equivalent to 1 mg. of uric acid.

A. A. ELDRIDGE.

**Micro-determination of urea by Nicloux and Welter's method.** R. GUILLEMET and P. GOLAZ (Compt. rend. Soc. Biol., 1929, 101, 726—728; Chem. Zentr., 1929, ii, 2918).—The rapidity and precision of the method are increased by precipitating the serum with Tanret's reagent, treating the filtrate with 0.2 c.c. of a 5% solution of xanthhydrol in methyl alcohol (or 1% in acetic acid), and collecting the precipitate on a Jena filter. After washing, finally with saturated alcoholic dioxanthylcarbamide,

the precipitate is dried in a current of air at 125° for 5 min.

A. A. ELDRIDGE.

**Spontaneous and provoked variations in the distribution of chlorine between serum and blood-corpuscles in diseases.** C. ACHARD and M. ENACHESCO (Compt. rend., 1930, 190, 1037—1040).—The spontaneous variations of the chlorine content of the serum and corpuscles during acute and cyclic diseases, and the variations caused by chloridisation or alkalinisation of the organism during acyclic diseases have been studied. At the end of the subsidence of fever and before the onset of the chloridisation crisis of convalescence in cases of pneumonia, the alkaline reserve of the blood increases, the chlorine content of the serum diminishes or remains stationary, whilst that of the corpuscles rises. At the moment of the crisis the chlorine content of the serum increases, but that of the corpuscles varies.

Chloridisation of the organism in chronic and acyclic diseases generally causes an increase in the chlorine content of both serum and corpuscles, whilst alkalinisation produces variable effects on the distribution of the chlorine and also on its retention or non-retention.

H. BURTON.

**Affinity of hæmoglobin for oxygen in anæmia.** G. LITARCZEK, H. AUBERT, and I. COSMULESCO (Compt. rend. Soc. Biol., 1929, 101, 220—221, 222—223; Chem. Zentr., 1929, ii, 3233).—The affinity of hæmoglobin for oxygen is reduced in anæmia. The ratio of  $1/k$  to  $C_H \times 10^8$ , where  $k$  is the dissociation constant of the oxyhæmoglobin, is abnormally high in anæmia.

A. A. ELDRIDGE.

**Endogenous uric acid metabolism in pernicious anæmia.** M. C. RIDDLE (J. Clin. Invest., 1929, 8, 69—88).—During early remission of pernicious anæmia the excretion of uric acid is increased by uric acid probably resulting from the destruction of large numbers of newly matured erythrocytes.

CHEMICAL ABSTRACTS.

**Spasm-producing substance in sputum of patients with bronchial asthma.** J. HARKAVY (Arch. Int. Med., 1930, 45, 641—646).—The sputum extract was tested for spasm-producing properties on isolated intestine (cat and rabbit). The sputum of sensitive, asthmatic patients contained an alcohol-soluble substance which is capable of stimulating the contraction of smooth muscle. This was absent from the sputum of non-sensitive asthmatic patients or those without asthma.

T. R. SESHADRI.

**Predisposition, due to age, towards cancer. Changes, due to age, in the surface tension of blood-serum.** A. SAITSCHENKO (Biochem. Z., 1930, 219, 447—451).—Examination of serum from 315 healthy persons (ages 0—105 years) showed that the surface tension of the serum decreases as the age of the individuals from which it is taken increases. The results support the theory that predisposition towards cancer, which also increases with increasing age, is favoured by the decrease in the surface tension of the body-fluids.

W. MCCARTNEY.

**Effect of saccharic acid on the Pasteur reaction.** E. KRAH (Biochem. Z., 1930, 219, 444—446).—Saccharic acid inhibits the toxic action of ferrous iron

and strengthens the Pasteur reaction in carcinoma cells of the mouse, but it inhibits anaërobic fermentation in the Jensen sarcoma. W. McCARTNEY.

**Cancer-producing substances.** E. L. KENNAWAY (Biochem J., 1930, 24, 497—504).—Carcinogenic products have been obtained by the action of aluminium chloride on acetylene, xylene, naphthalene, naphthalene and bromobenzene, and tetrahydronaphthalene. Two cancers have been obtained in a series of 10 mice painted with a solution of a fairly pure specimen of 1:2:7:8-dibenzanthracene.

S. S. ZILVA.

**Spectra of cancer-producing tars and oils and of related substances.** I. HIEGER (Biochem. J., 1930, 24, 505—511).—The fluorescence spectra of many cancer-producing substances show the same bands at wave-lengths 4000, 4180, 4400 Å. These bands are remarkably like those of the fluorescence spectrum of 1:2-benzanthracene apart from their absolute wave-length. A study of the fluorescence spectra of a large number of condensed-ring aromatic hydrocarbons shows that the spectrum is characteristic for closely related derivatives of a hydrocarbon. Absorption spectra in the ultra-violet region also indicate some connexion between at least one powerfully cancer-producing material, i.e., the fraction boiling at 260—320°/14 mm. from the mixture obtained by the action of aluminium chloride on commercial tetrahydronaphthalene (cf. preceding abstract) and 1:2-benzanthracene.

S. S. ZILVA.

**Total and residual nitrogen contents of cerebrospinal fluid.** S. KURITA (Keio J. Med., 1928, 8, 1843—1858).—Normal values (mg. per 100 c.c.) for total, residual, and protein-nitrogen, respectively, are 17.2, 13.5, 23.0. Values for various pathological conditions are recorded. CHEMICAL ABSTRACTS.

**Dextrose content of the cerebrospinal fluid.** S. KURITA (Keio J. Med., 1928, 8, 1859—1868).—Values for the percentage total and residual reducing substance and dextrose in the fluid (deaminised, then treated with yeast) were normally 0.077, 0.025, and 0.052, respectively. Values for various pathological conditions are recorded. CHEMICAL ABSTRACTS.

**Iodine content of the cerebrospinal fluid.** K. ISHIKAWA (Med. News, Japan, 1928, No. 1241, 1331—1342).—The normal value is  $1.2 \times 10^{-6}$  g. per 100 c.c.; normal values were observed in diabetes, syphilis, and exophthalmic goitre. Considerable increases on ingestion or injection of potassium iodide are recorded. CHEMICAL ABSTRACTS.

**Human diabetes mellitus. I. Phosphate-carbohydrate metabolism.** H. HORSTERS (Z. ges. exp. Med., 1929, 66, 89—128; Chem. Zentr., 1929, ii, 3159—3160).—In dogs, insulin caused a diminution in the blood-sugar and -phosphate by about 50%, and dilution of the blood by about 20%. The reduction in normal man is not so great, and in diabetes it is small (max. 12%). In normal man the organically combined phosphorus often increased markedly. In diabetes the diminution in acid-soluble blood-phosphorus was often parallel with or followed a diminution in organically combined phosphorus.

A. A. ELDRIDGE.

**Residual carbon of human blood. I. Micro-determination. Values in diabetes.** W. STEPP and J. SAUER (Deut. Arch. klin. Med., 1929, 165, 223—231; Chem. Zentr., 1929, ii, 3168).—A slight modification of Pregl's method of combustion after deproteinisation was employed. Considerable variations are normally observed. Determinations in diabetes and after administration of dextrose are recorded.

A. A. ELDRIDGE.

**Carotenæmia and diabetes. II. Relationship between sugar, cholesterol, and carotene content of blood-plasma.** I. M. RABINOVITSCH (Arch. Int. Med., 1930, 45, 586—592).—For the determination of carotene in blood the protein is first precipitated with 95% alcohol, the carotene shaken out with light petroleum, and the solution compared spectroscopically with a standard.

Certain diabetic patients retain ingested vegetable pigments to a greater extent than others; these usually have a high blood-cholesterol content. In spite of their chemical relationship the presence of a large amount of carotene does not seem to be the only cause of the high cholesterol value. In analogy to the effect of cholesterol it is suggested that marked carotenæmia also indicates unfavourable prognosis.

T. R. SESHADRI.

**Acetoacetic acid in the diabetic organism.** J. KLEEBERG (Biochem. Z., 1930, 219, 381—384).—When concentrated sodium hydroxide solution is added to urine a part of any acetoacetic acid present is converted into the enol form and an improved result is obtained when the ferric chloride test is applied.

W. McCARTNEY.

**Occurrence of glycogen in a rabbit with experimental diabetes.** K. YOSHIDA (J. Study Micro-org., Japan, 1928, 22, 277—281).—Adrenaline or sodium chloride hyperglycæmia is accompanied by the appearance of glycogen in the superficial layers of the cæcum or colon.

CHEMICAL ABSTRACTS.

**Tissue metabolism. I. Phloridzin diabetes.** E. SHORR, R. O. LOEBEL, and H. B. RICHARDSON.

**II. Respiratory quotient of normal and diabetic tissue.** H. B. RICHARDSON, E. SHORR, and R. O. LOEBEL (J. Biol. Chem., 1930, 86, 529—549, 551—569).—I. The respiratory quotients of excised renal tissue of normal rats were determined with an error of  $\pm 0.014$  and fell between the limits 0.705—0.949, i.e., within the range characteristic for the intact animal; the value of the respiratory quotient was raised by addition of dextrose to the medium in the case of tissue obtained both from normal and phloridzinised animals, and the actual presence of phloridzin in the medium did not influence this result, although phloridzin exercised a narcotic effect in depressing the total respiratory exchange of the tissue. The action of phloridzin does not therefore involve direct interference with the carbohydrate metabolism of the tissues.

II. The respiratory quotients of excised renal or muscular tissue of normal dogs lay between 0.7 and 1.0, which indicates that the oxidative processes involved utilisation of fat; the quotients of tissues from depancreatized dogs were so low (0.7—0.75) as practically to exclude oxidation of sugar; these

tissues showed no increase in respiratory quotient when dextrose was added to the medium. The facts are against the theories that sugar is the essential fuel for muscle-tissue oxidation, and that the waste sugar in diabetes is formed from fat. C. R. HARRINGTON.

**Value of blood-amylase in diagnosis of pancreatic disease.** R. ELMAN, N. ARNESON, and E. A. GRAHAM (*Arch. Surg.*, 1929, 19, 943—967).—Blood-amylase, as measured by the decrease in viscosity of a standard starch solution, is high (7.8—150 units; normal, 4.3—6.8 units) in individuals with pancreatic lesions. CHEMICAL ABSTRACTS.

**Excretion of creatine and creatinine in the urine.** K. ISHIKAWA (*Med. News, Japan*, 1929, No. 1244, 137—153).—In exophthalmic goitre the urine contains creatine. Administration of thyroid extract increases, and of insulin decreases, the excretion of creatine and creatinine.

CHEMICAL ABSTRACTS.

**Magnesium and calcium in the liver of hyperthyroidised animals.** M. CAHANE (*Compt. rend. Soc. Biol.*, 1929, 100, 577—578; *Chem. Zentr.*, 1929, ii, 3025).—With guinea-pigs the increase was 0.0021 and 0.0015%, respectively. A. A. ELDRIDGE.

**Chloride determinations in cases of intestinal obstruction.** M. PAGET (*Bull. Soc. Chim. biol.*, 1930, 12, 409—410).—Chloride determinations in cases of high or low obstruction of the intestine should be made on whole blood when the alkaline reserve is increased and on the serum when it is normal.

P. G. MARSHALL.

**Urobilin and bilirubin in blood and urine in leprosy.** E. A. MOLINELLI and M. ROYER (*Semana Méd.*, 1929, 36, 1799—1801).—The blood and urine of leprosy do not contain urobilin; blood-bilirubin is normal, but the urine does not contain bilirubin or bile salts.

CHEMICAL ABSTRACTS.

**Metabolism of lymphocytes.** H. SCHLOSSMANN (*Biochem. Z.*, 1930, 219, 463—467).—Lymphocytes from the blood of a child suffering from lymphatic leucæmia were found to consume 10—14 c.c. of oxygen per mg. dry weight per hour.

W. MCCARTNEY.

**Cholæmia, urobilinæmia, and urobilinuria in various diseases of the liver.** R. DASSEN (*Semana Méd.*, 1930, 37, 30—36).—Blood-urobilin values (mg. per 100 c.c.) were: typhoid fever 3.6—4, cholelithiasis and cirrhosis 8—12, toxic hepatitis 8—60. The bile acids are normally 1.8—3 mg. per 100 c.c., but in liver diseases up to 5 mg. Normal blood contains no urobilin.

CHEMICAL ABSTRACTS.

**Phosphorus in the blood and urine.** I. SCHULZ (*Ann. Int. Med.*, 1930, 3, 667—689).—Normally the (fasting) level of plasma-inorganic phosphorus is not greater than the whole blood level; in nephritis the reverse holds. The excretion of injected phosphate was studied.

CHEMICAL ABSTRACTS.

**Lactic acid content of the blood in pleuritis.** F. YANO and T. YADA (*Juzenkaishi*, 1928, 33, 2015—2036).—The normal value, 9—16 parts per 1000, is increased to 8.5—33.8.

CHEMICAL ABSTRACTS.

**Pleuritis.** K. YOSHIMOTO and M. TAKAHASHI (*Juzenkaishi*, 1929, 34, 391—408).—The amount of

lipins in the exudate increases with progress of the disease; the cholesterol and lecithin contents increase at the curative period and again decrease.

CHEMICAL ABSTRACTS.

**Acid-base equilibrium of the blood in acute rheumatism.** L. G. PARSONS and S. H. EDGAR (*Arch. Dis. Childhood*, 1929, 4, 291—298).—The symptoms of rheumatism in children are not associated with an excess of acid in the tissues.

CHEMICAL ABSTRACTS.

**Nature of mineral particles enclosed in the lungs of miners.** A. POLICARD and J. DEVUNS (*Compt. rend.*, 1930, 190, 979—980).—The black or brown opaque particles (1—10  $\mu$ ) with angular edges consisted of coal. The smaller, translucent, irregular-shaped particles, rarely as large as 6—8  $\mu$ , consisted of silica.

C. C. N. VASS.

**Hypercholesterolaemia and excretion of cholesterol after splenectomy.** L. BUGNARD (*Compt. rend. Soc. Biol.*, 1929, 101, 765—766; *Chem. Zentr.*, 1929, ii, 2574).—After splenectomy the bile-cholesterol diminishes.

A. A. ELDRIDGE.

**Calcium and phosphorus metabolism of rats during pregnancy and lactation; influence of reaction of diet.** H. GOSS and C. L. A. SCHMIDT (*J. Biol. Chem.*, 1930, 86, 417—432).—The calcium and phosphorus balances of rats were almost invariably positive during pregnancy and markedly negative during lactation. Increased acidity or alkalinity of the diet had no pronounced effect on mother or young, except that lactation tended to fall off in the animals receiving excess of alkali. The positive calcium and phosphorus balance associated with normal pregnancy was observed also during resorption of the foetus in pregnant rats on a diet deficient in vitamin-B.

C. R. HARRINGTON.

**Reproductive disturbances caused by feeding protein-deficient and calcium-deficient rations to breeding pigs.** H. R. DAVIDSON (*J. Agric. Sci.*, 1930, 20, 233—264).—Neither protein- nor calcium-deficiency in the rations of breeding pigs appears to be the chief cause of partial foetal atrophy. Calcium deficiency results in an increase in the number of pigs born dead, and leads to the serious reduction and final failure of the sow's milk supply, both of which effects are intensified after two or three generations.

E. HOLMES.

**Application of microchemical reactions in the problem of calcification in osteogenesis.** W. SCHULZE (*Roux' Arch. Entw. Org.*, *Z. wiss. Biol.*, 1925, D, 106, 62—74; *Chem. Zentr.*, 1930, i, 98).

**Saline drinking water.** V. G. HELLER and C. H. LARWOOD (*Science*, 1930, 71, 223—224).—When present in the drinking water of animals (mainly rats), 1.5% of magnesium sulphate retards growth and increases mortality among the young; calcium chloride has an even greater effect, whilst 2% of sodium chloride causes stunted growth and 2.5% a rapid loss of weight. Sodium carbonate and, to a smaller extent, sodium hydrogen carbonate are also deleterious at similar concentrations. A mixture of 2% of sodium chloride and 0.5% of magnesium or calcium chloride inhibits growth. No antagonistic

action of ions has been detected. The chloride ion is more toxic than the sulphate or carbonate ion and the calcium and magnesium ions are more toxic than the sodium ion. L. S. THEOBALD.

**Intestinal elimination of iron in the dog.** V. HENRIQUÈS and A. ROCHE (Bull. Soc. Chim. biol., 1930, 12, 404—408).—A daily oral administration of iron (360—1675 mg.) as lactate does not affect elimination by the colon. The intestinal absorption of iron (determined by the titanous chloride method) varies with the salt used, and the results do not support the theory of absorption in the small intestine and elimination by the large intestine.

P. G. MARSHALL.

**Oxygen consumption of nerve in the presence of dextrose and galactose.** M. SHERIF and E. G. HOLMES (Biochem. J., 1930, 24, 400—401).—Both sugars prolong the period for which isolated mammalian nerves take up oxygen at a steady rate.

S. S. ZILVA.

**Effect of alterations in the concentration of the cations of Ringer solution on peripheral nerves.** B. MISSKE (Biochem. Z., 1930, 219, 320—329).—The effect of all possible isotonic mixtures of the cations of Ringer solution (sodium, potassium, calcium) on the excitation of the peripheral nerves of the frog has been deduced from results plotted on a triaxial system of co-ordinates. Antagonism exists between each pair of ions, although these may also act synergistically. Very small changes in the concentrations of the ions are sufficient to affect the action on the nerves and characteristic alterations occur as the concentration of the sodium ion increases while that of the potassium or calcium ion is zero. Paralysis is produced more rapidly by increased concentrations of potassium than by corresponding concentrations of calcium. In some cases the effects of increased concentrations of the ions are irreversible.

W. MCCARTNEY.

**Effect of alterations in the concentration of the cations of Ringer solution on striped muscle.** B. MISSKE (Biochem. Z., 1930, 219, 330—334; cf. preceding abstract).—From results plotted on a triaxial diagram it is seen that potassium and calcium are not merely antagonistic in their action on striped muscle, but also that there is often synergism between them and that this holds also for sodium with respect both to potassium and to calcium. W. MCCARTNEY.

**Movement of ions in gelatin gels and in the nerve substance.** I. Rate of movement, under the influence of direct electric current, of hydroxyl and hydrogen ions in gelatin gels of varying concentration. II. Absolute velocity of hydroxyl ions in nerve substance. III. Temperature coefficient of the rate of movement of hydroxyl ions in gelatin gels compared with the temperature coefficients of various phases of the process of stimulation in nerve and muscle. V. V. EFIMOV (Biochem. Z., 1930, 219, 349—353, 354—360, 361—363).—I. The absolute velocity of the hydroxyl and hydrogen ions moving in gelatin gels under the influence of direct electric current decreases rapidly and greatly as the concentration of gelatin increases.

3 II

II. In the frog nerve the absolute velocity of the hydroxyl ion varies from 0.000043 to 0.000240 cm./sec.

III. The temperature coefficient of the absolute velocity of the hydroxyl and hydrogen ions in gelatin gels is 1.4—1.65 and is very close to that of the propagation of the impulse in nerve and muscle. The coefficient is independent of the concentration of the gels. W. MCCARTNEY.

**Variations in the phosphorus content of Lepidoptera during nymphosis.** A. COURTOIS (Compt. rend., 1930, 190, 1078—1080).—The total phosphorus of the chrysalides of *Sphinx ligustri*, *Attacus pernyi*, *Saturnia pyri*, and *S. pavonia* is 0.2—0.266% of the fresh tissue. The inorganic phosphorus increases during histolysis and then diminishes during the reconstruction of the imago. The adults contain rather more total phosphorus than the chrysalides; the major part is in the genital products. The female contains considerably more inorganic phosphorus than the male adult.

H. BURTON.

**Metamorphosis of insects. VII. Composition of the blood of larvæ of *Deilephila euphorbiæ*. Changes in the composition during metamorphosis.** J. HELLER and A. MOKTOVSKA (Biochem. Z., 1930, 219, 473—489; cf. A., 1926, 197).—The blood of the ripe larvæ of *D. euphorbiæ* contains, on the average, per 100 c.c.: total nitrogen 1180 mg., protein-nitrogen 825 mg., amino-nitrogen 170 mg., peptide-nitrogen 120 mg., uric acid 20 mg., reducing substances (as dextrose) 127 mg., inorganic phosphorus 12 mg., calcium 41 mg., magnesium 43.5 mg., chlorine 48.6 mg., and iron 5.8 mg. During metamorphosis the content of residual and amino-nitrogen remains unchanged. In fasting larvæ and, more slowly, in pupæ (but not during pupation), the content of protein-nitrogen falls to 50—60% of the normal value. The content of reducing substances is smallest and decreases most rapidly during pupation and changes in this content are related to changes in the readiness of the blood to blacken when exposed to air. Pupation is possibly regulated by an oxidation-reduction process. During the pupal period the content of inorganic phosphorus first increases fivefold and then falls again. The argininephosphoric acid content of the blood, the depression of its f. p., and also its specific gravity, surface tension, reaction, and buffering power have been measured.

W. MCCARTNEY.

**Metabolism of phospholipins. I. Influence of diet on phospholipin fatty acids in tissues of the cat.** R. G. SINCLAIR (J. Biol. Chem., 1930, 86, 579—586).—The amount and composition of the phospholipins in various tissues of the cat were determined when the animals were fed on ox-kidney and when they were fed on ox-muscle, the former diet being the richer in unsaturated fatty acids. The total amount of phospholipin was not affected except that the livers of the animals on the kidney diet contained a larger quantity. The degree of unsaturation of the phospholipins was greater, however, in all tissues of the latter animals, and more particularly in the brain. C. R. HARRINGTON.

**Fatty acids essential in nutrition.** G. O. BURR and M. M. BURR (*J. Biol. Chem.*, 1930, **86**, 587—621).—The complete removal of fat from the diet of the rat (cf. A., 1929, 853) causes development of renal lesions which are particularly severe if the protein content of the diet be high. The consumption of water in these animals is much increased, the excess being excreted by the lungs and skin. Reproductive functions are profoundly deranged by deprivation of fat, ovulation being absent or irregular, and the males being impotent. The symptoms are relieved by administration of pure linoleic acid, or, more efficiently, by unsaturated fats, but not by saturated fatty acids or by butter. The condition is therefore thought to be due to the inability of the organism to synthesise the essential linoleic acid.

C. R. HARRINGTON.

**Histochemical study of aldehyde substances produced by fat metabolism.** J. VERNE (*Ann. Physiol. Physicochim. biol.*, 1929, **5**, 245—267; *Chem. Zentr.*, 1929, ii, 2576).—Feulgen's reaction, given by many animal tissues, is considered to be due to aldehydic substances, formed principally from unsaturated fatty acids. The reaction is not given if oxidation is carried on too far. The aldehydic substances must pre-exist in living tissue or occur as labile compounds from which they are easily liberated by weak acids or platinum chloride.

A. A. ELDRIDGE.

**Milking at three eight-hour intervals as a means of investigating variations in the fat and solids-not-fat.** K. W. D. CAMPBELL (*J. Agric. Sci.*, 1930, **20**, 213—232).—The average increase in milk yield of 9 cows due to milking three times a day was 19.3%, whilst the average increase with 3 heifers was only 5.6%. The high fat content of the bulk milk from this herd was due to the high fat level maintained by each individual cow at one specific milking, not, however, the same milking for all cows. It is suggested that there is some factor operative during the night which lowers the fat content of the morning milk independently of a long or short night milking interval.

E. HOLMES.

**Glycogen and the activity of the snail's heart.** M. LOEPER, A. LEMAIRE, and A. MOUGEOT (*Compt. rend.*, 1930, **190**, 950—951).—Glycogen is lost during work, and disappears when the heart is exhausted. Activity is maintained the longer, the richer the heart is in glycogen; the regularity, if not the intensity, of the beat is in general greater in hearts exhibiting normal glycogenesis. The heart retains glycogen for a longer period when immersed in Locke's medium, which contains sugar, than in Ringer's medium. Whilst the addition of starch rapidly stops the heart, and addition of glycogen does not activate it, association with amylolytic enzymes, especially pancreatic extract, furnishes reactivation analogous to that produced by dextrose. When administered without accompanying carbohydrate amylolytic enzymes rapidly stop the heart.

C. W. SHOPPEE.

**Glycogen of the heart and cardiac medications.** M. LOEPER, A. MOUGEOT, R. DEGOS, and S. DE SEZE (*Compt. rend.*, 1930, **190**, 971—972).—

The glycogen content of the heart-muscle (snail, rabbit, and guinea-pig) is unaffected during a sudden arrest caused by acetylcholine or by the retardation due to quinidine. Administration of adrenaline causes an immediate disappearance of glycogen.

C. C. N. VASS.

**Utilisation of sugars in muscle.** W. GRIESBACH (*Z. ges. exp. Med.*, 1929, **65**, 172—178; *Chem. Zentr.*, 1929, ii, 3161).—Lævulose and dextrose, but not galactose, and mannose only when dog's blood was used, disappeared in perfusion experiments with surviving extremities. Formation of glycogen could not be observed, and that of lactic acid could not be followed, since the lactic acid content of the perfusing blood depends in considerable degree on the supply of oxygen.

A. A. ELDRIDGE.

**Degradation of fatty acids in surviving dog's muscle.** W. GRIESBACH (*Z. ges. exp. Med.*, 1929, **65**, 179—182; *Chem. Zentr.*, 1929, ii, 3161).—Addition of lower fatty acids to the perfusing blood (cf. preceding abstract) did not lead, even with muscular activity, to the formation of a detectable quantity of acetone. Added acetoacetic acid was not more rapidly decomposed by active than by resting muscle.

A. A. ELDRIDGE.

**Relation between carbohydrate and fat metabolism.** I. S. GENESS and Z. DIENERSTEIN. II. Z. DIENERSTEIN and S. GENESS (*Z. ges. exp. Med.*, 1929, **65**, 362—370, 371—381; *Chem. Zentr.*, 1929, ii, 3235—3236).—On administration of neutral fat to the dog the blood-fat and -ketonic substances increase, whilst blood-lactic acid diminishes; administration of dextrose is followed by a rise of blood-sugar and -lactic acid and a fall of blood-ketonic substances. The results with splenectomised dogs are substantially similar.

A. A. ELDRIDGE.

**Induced variations in carbohydrate metabolism.** I. Methods and controls. II. Effects of insulin, pancreatectomy, and nervous manipulation of the pancreas. A. R. COLWELL (*Amer. J. Physiol.*, 1930, **91**, 664—678, 679—689).—I. The continuous intravenous injection of dextrose into cats produces glycosuria if the dextrose supplied is more than 0.35 g. per kg. per hr. The blood-sugar does not remain constant and shivering fits may produce an increased utilisation of the sugar.

II. Insulin diminishes and adrenaline increases the amount of sugar excretion. Removal of the pancreas causes all the injected sugar to be excreted, but nervous stimulation or denervation of the pancreas seems to be without effect.

E. BOYLAND.

**Rise in urinary acidity during work and its relation to fatigue.** M. S. REZNITSCHENKO (*Zhur. exp. Biol. Med.*, 1929, **11**, 86—94).—The curve of urinary  $p_H$  during work reflects the intensity of physical exertion.

CHEMICAL ABSTRACTS.

**Reaction changes of active muscle in connexion with the change of creatinephosphoric acid (phosphagen).** O. MEYERHOF and F. LIPMANN (*Naturwiss.*, 1930, **18**, 330—332).—Between  $p_H$  8 and 9 the hydrolysis of creatinephosphoric acid proceeds without change in the reaction, but for smaller  $p_H$  values free base is formed, with a maximum effect



at  $p_H$  6, when 0.75 equivalent of base is formed for each mol. decomposed. Using these facts in conjunction with Warburg's manometric method it is possible to find the amounts of phosphagen formed or destroyed. By means of the manometric method in which the gas space of the manometric vessel is filled with a mixture of nitrogen and carbon dioxide in different proportions, the  $p_H$  of the muscle can be varied between 8.2 and 6. Taking account of the lactic acid formed and the buffer effect of the muscle, the reaction displacement found in resting and active muscle agreed with that expected. A. J. MEE.

**Hydrolysis of phosphocreatine and lactic acid formation in frog's muscle.** H. MACKLER, J. M. D. OLIMSTED, and W. W. SIMPSON (Amer. J. Physiol., 1929, 91, 362—364).—Lactic acid formation at rest is accompanied by little or no decrease in phosphocreatine. On stimulation some phosphocreatine is decomposed, but it has no quantitative relation to the lactic acid formation. E. BOYLAND.

**Glandular metabolism. I. Source of lactic acid in the testicle and submaxillary gland.** H. E. HIMWICH and M. A. ADDAS (Amer. J. Physiol., 1929, 91, 172—177).—Glycogen is converted into lactic acid on incubation of glandular tissue. E. BOYLAND.

**Age and effect of unusual diets.** E. M. MACKAY and L. L. MACKAY (J. Biol. Chem., 1930, 86, 765—771).—The real effect on rats of diets containing given amounts of extra cystine, or large amounts of protein, is independent of the age of the animals. The apparently greater effects obtained in young animals are due to the proportionately greater food intake of the latter. C. R. HARRINGTON.

**Purine metabolism. III. Effect of diet and caging on allantoin excretion of the rabbit.** A. A. CHRISTMAN (J. Biol. Chem., 1930, 86, 477—489).—When rabbits are kept in metabolism cages on a constant diet the excretion of allantoin decreases very markedly. The excretion varies also in response to alterations in the non-protein constituents of the diet; it is increased by oral administration of calcium chloride and decreased by feeding with milk. C. R. HARRINGTON.

**Hyperallantoinuria and the existence of an organo-vegetative centre for purine metabolism.** C. KAYSER and A. E. Y COSTA (Ann. Physiol. Physicochim. biol., 1929, 5, 370—391; Chem. Zentr., 1929, ii, 2576—2577).—All kinds of polyuria are accompanied by an increase of allantoin in the urine; injection of pituitary extract causes the disappearance of both the hyperallantoinuria and the polyuria. A. A. ELDRIDGE.

**Basal metabolism of young college women in Florida.** J. TILT (J. Biol. Chem., 1930, 86, 635—641).—The average basal metabolic rate of 52 women of ages 17—25 was about 10% lower than the standard at present accepted. No effect of change of season or of increased physical activity was observed. C. R. HARRINGTON.

**Colloid chemistry of protoplasm. V. Surface precipitation reaction of living cells.** L. V. HEILBRUNN (Arch. exp. Zellforsch., 1927, 4, 246—263; Chem. Zentr., 1929, ii, 2899—2900).—A study

of the formation of a film at the surface of expressed protoplasm. In certain cases the presence of calcium or strontium is essential. Sea-urchin's eggs contain a substance, ovothrombin or cytothrombin, which causes the reaction in the absence of calcium or in presence of minimal quantities. Ovothrombin is not an enzyme and is not colloidal. A. A. ELDRIDGE.

**Ions, automatins, and sensitizers.** H. ZWAARDEMAKER (Arch. Néerland. Physiol., 1930, 15, 1—22).—A review and discussion of the rôle of radioactive elements in biology. Their action is apparently not dependent on the ordinary balance and antagonism of ions, but is catalytic in nature, choline, adrenaline, and histamine probably acting as sensitizers. W. O. KERMACK.

**Oxidation of some constituents of the body by activated charcoal.** O. FÜRTH and H. KAUNITZ (Bull. Soc. Chim. biol., 1930, 12, 411—412).—Amino-acids of high mol. wt. are deaminised more readily than those of low mol. wt. Amides, some dipeptides, proline, and histidine are not affected by charcoal. Phenolic substances are rapidly destroyed. Ordinary sugar charcoal is almost as active as animal charcoal. Deamination is in no case complete. P. G. MARSHALL.

**Pharmacological action of fresh defibrinated blood. I. II. Preparation and action of active principle.** K. ZIEFF and E. WAGENFELD (Arch. exp. Path. Pharm., 1930, 150, 70—90, 91—105).—The active principle of defibrinated blood may be freed from protein by precipitation of the latter with colloidal ferric hydroxide, Congo-red, and hydrochloric acid, or by ultrafiltration, and is soluble in water, insoluble in absolute alcohol or ether, is stable to brief boiling at neutral or slightly acid or alkaline reaction, but is destroyed by prolonged heating above 70°. It is not histamine, choline, or a choline ester. W. O. KERMACK.

**Pharmacological action of fresh defibrinated blood. III. Action of the toxic substance on surviving organs.** E. HAAKE (Arch. exp. Path. Pharm., 1930, 150, 119—132).—The pharmacological action has been investigated of ultrafiltrates of rabbits' whole blood and of filtrates prepared after precipitation by Congo-red and hydrochloric acid (cf. preceding abstract). W. O. KERMACK.

**Effect of cereal extracts on blood-calcium.** L. MIRVISH (Biochem. J., 1930, 24, 233—238).—The extraction of oatmeal with 5% hydrochloric acid yields a residue, free from starch, thermostable, dialysable, and soluble in alcohol, which when injected into rabbits produces a fall of blood-calcium. This drop is about 30% of the normal and occurs 24—48 hrs. after injection, returning to normal within 48—72 hrs., a type of calcium depression similar to that which follows the injection of bovine ovarian extract. The rachitogenic effect of Mellanby's and Holst's extracts from oatmeal is attributed to the calcium-reducing property of their extracts. Rickets and osteomalacia may be due to functional disturbances of the parathyroid secretion. S. S. ZILVA.

**Testing materials as repellents against the Japanese beetle.** F. W. METZGER (J. Agric. Res., 1930, 40, 659—671).—The materials most likely to

be good repellents are coal-tar cresotes and empyreumatic oils, followed by the phenols and cyclic nitrogen compounds. E. HOLMES.

**Liver function and blood-catalase. I—III.** T. TOMIOKA (J. Exp. Digest. Dis., Japan, 1928, 3, 1093—1106).—When the (rabbit's) liver function is hindered by injection of chloroform or carbon tetrachloride, or by ingestion of phosphorus, or by the action of X-rays, the blood-amylase is slightly increased and then decreased. Removal of part of the liver causes a decrease. X-Irradiation or phosphorus poisoning causes a decrease in blood-catalase of about 10—20%. Poisoning by chloroform or carbon tetrachloride increases the blood-catalase.

CHEMICAL ABSTRACTS.

**Behaviour of blood-bilirubin following the injection of bilirubin solution.** T. AKIYAMA (Chiba J. Med., 1929, 7, 423—443).—After phosphorus or carbon tetrachloride poisoning (rabbit) injection of a solution of bilirubin into a vein markedly increased the blood-bilirubin and the time during which it was present.

CHEMICAL ABSTRACTS.

**Effect of bile acids on urinary salt excretion.** T. SEKITOO (J. Biochem. Japan, 1929, 11, 251—264).—Administration of cholic acid does not affect the urinary salt excretion, but reduces that of nitrogen, sulphur, and phosphoric acid. The urinary and blood-calcium increases; the excretion of potassium is slightly decreased.

CHEMICAL ABSTRACTS.

**Relation of bile acids to carbohydrate metabolism. VII. Gaseous metabolism.** T. HATAKEYAMA (J. Biochem. Japan, 1929, 11, 273—283).—Administration of cholic or deoxycholic acid to rabbits reduces the respiratory quotient, apparently by polymerisation or inhibition of oxidation of dextrose.

CHEMICAL ABSTRACTS.

**Poisoning by oxalic acid.** A. SARTORI (Chem.-Ztg., 1930, 54, 310).—Details of the *post-mortem* findings in one case are given.

H. E. F. NOTTON.

**Lethal dose of hydrocyanic acid for ruminants.** W. L. HINDMARSH (J. Council Sci. Ind. Res. Australia, 1930, 3, 12—13).—The lethal dose of hydrocyanic acid for sheep is 1 mg. per lb. body-weight, and for the cow (one experiment) is roughly of the same order.

B. W. TOWN.

**Fatal dose for sheep of cyanogenetic plants containing sambunigrin or prunasin.** H. R. SEDDON and R. O. C. KING (J. Council Sci. Ind. Res. Australia, 1930, 3, 14—24).—Experiments carried out by feeding to sheep *Acacia glaucescens* and *Eremophila maculata* indicate that the administration of a cyanogenetic glucoside (in air-dried plant) at such a rate that the hydrogen cyanide content is equal to the minimum fatal dose of hydrogen cyanide itself is attended with fatal results, provided that sufficient enzyme is present. Since the plants themselves are relatively deficient in enzyme, this was supplied by the addition of sweet almonds. Whereas free hydrogen cyanide and the glucoside in the plants are fatal in doses equivalent to 1 mg. of hydrogen cyanide per lb. body-weight, the isolated glucosides were fatal only in doses corresponding with 2 mg. per lb. Plants

are considered dangerous if the percentage of hydrogen cyanide is greater than 0.02 in the fresh plant and 0.05 in the air-dried material. B. W. TOWN.

**Elimination of quinine in the bile.** F. CAUJOLLE (Bull. Soc. Chim. biol., 1930, 12, 299—306).—The presence of quinine in the bile of dogs, after intravenous injection of an isotonic solution of the neutral sulphate, is demonstrated by observing the fluorescence in sulphuric acid when exposed to light from a mercury-vapour lamp after passage through a suitable filter. Elimination is more rapid in the urine than in the bile.

P. G. MARSHALL.

**Mutual action of thyroid gland hormone and quinine hydrochloride.** S. OMURA (Japan. J. Int. Secretion, 1929, 4, 2130—2137).—Quinine hydrochloride produces in the white rat an increase in the muscle-, liver-, and kidney-fat; the increase is repressed by injection of thyroid gland.

CHEMICAL ABSTRACTS.

**Comparative effects of natural and synthetic *d*-, *l*-, and *r*-ephedrine on the blood-pressure.** L. LAUNOY and P. NICOLLE (Compt. rend. Soc. Biol., 1929, 100, 334—337; Chem. Zentr., 1930, i, 89).—*l*-Ephedrine is twice as active as *r*-ephedrine; *d*-ephedrine reduces the blood-pressure.

A. A. ELDRIDGE.

**Eriocomine, a constituent of *Eriocoma floribunda*.** M. L. TANTER and M. A. SEIDENFELD (J. Amer. Pharm. Assoc., 1930, 19, 229—231).—Eriocomine, injected intravenously in sub-toxic doses, has no action on the circulation. The claim that it is a uterine stimulant of the type of ergot is not confirmed. The extract is non-irritant to the tongue, neutral in reaction, and free from haemolytic agents.

H. E. F. NOTTON.

**Effect of santonin on blood-sugar.** S. ISHIKAWA (Japan. J. Pract. Med., 1929, 16, 518—535).—In the rabbit 0.05—0.1 g. of santonin per kg. does not affect the blood-sugar, whilst 0.5 g. per kg. causes temporary hyperglycaemia. Santonin does not affect adrenaline or dextrose hyperglycaemia, and its continued administration to man does not affect the "physiological" blood-sugar.

CHEMICAL ABSTRACTS.

**Effect of vagosplanchnicotomy on the threshold of sugar excretion.** S. KAWASHIMA and Y. IWANAGA (J. Biochem., Japan, 1929, 11, 293—305).—Vagotomy inhibits the effect of adrenaline without altering the normal threshold value. Acetylcholine causes a marked rise in the threshold in vagotomised dogs. A temporary rise in the sugar excretion threshold, accompanied by diminution of the assimilation of sugar, follows double splanchnicotomy.

CHEMICAL ABSTRACTS.

**Horsetail poisoning and its prevention.** GERLACH (Forts. Landw., 1929, 4, 377; Bied. Zentr., 1930, 59, 127—129).—The injurious effects of the marsh horsetail (*Equisetum palustre*) in meadow grasses when fed to cows are examined. During the experimental period the live weight of cows and their milk yields decreased, but the fat content of the milk increased slightly. The injurious effects persisted after ensilage of the fresh material by hot-pressure methods.

A. G. POLLARD.

Alveolar carbon dioxide tension in natural sleep and in that induced by soporifics. V. RABINOVITSCH (Z. ges. exp. Med., 1929, 66, 284—290; Chem. Zentr., 1929, ii, 3161).—The carbon dioxide tension increased during natural sleep; the curve affords a measure of depth of sleep. In chloral hydrate sleep, however, the carbon dioxide tension falls.

A. A. ELDRIDGE.

Blood-urea-nitrogen in scopalamine-morphine-nitrous oxide anaesthesia. B. VAN HOESSEN (Anæsth. and Analges., 1930, 9, 41—44).—Of 30 cases, 10 showed marked and 9 slight reduction, 10 a slight increase, whilst 1 was unchanged.

CHEMICAL ABSTRACTS.

Potassium and calcium content of the brain under magnesium sulphate anaesthesia. W. E. CALLISON, J. LANDER, and F. P. UNDERHILL (J. Pharm. Exp. Ther., 1930, 38, 385—388).—The water, potassium, and calcium contents of the brain of normal rabbits and animals anaesthetised with magnesium sulphate are almost identical with the values obtained for rabbits anaesthetised and allowed to recover by intravenous injection of 0.2N-calcium chloride.

P. G. MARSHALL.

Effect of various anaesthetics on the blood- and urinary sugar of the rabbit. K. KIKUCHI (Osaka J. Med., 1928, 27, 2747—2780).—The blood-sugar, but not the urinary sugar, is increased.

CHEMICAL ABSTRACTS.

Effect of ethylene on growth and enzyme action in animals. A. D. HIRSCHFELDER and E. T. CEDER (Amer. J. Physiol., 1930, 91, 624—636).—The presence of ethylene in the drinking water and in the inhaled air of rats had no effect on their growth. Amylase is activated, but pepsin, trypsin, and lipase are not.

E. BOYLAND.

Mechanism of effect of alcohol on sugar metabolism. H. MASAMUNE (Fukuoka J. Med., 1929, 22, 83—99).—Subcutaneous injection of absolute ethyl alcohol into a rabbit causes a decrease, and then often an increase, in the blood-sugar; adrenaline or pilocarpine hyperglycaemia is repressed by 3 c.c. Alcohol hyperglycaemia is repressed by atropine and ergotoxin. The blood-inorganic acids are increased.

CHEMICAL ABSTRACTS.

Excretion of alcohol and ether by the kidneys. A. BORNSTEIN and G. BUDELMANN (Arch. exp. Path. Pharm., 1930, 150, 47—69).—Administration to normal fasting adults or alcoholics of 0.5 g. of ethyl alcohol per kg. of body-weight dissolved in 100 c.c. of water causes a rapid rise of alcohol in the blood during the first 30 min. followed by a return to normal within the next 3—4 hrs. The alcohol content of the urine exhibits somewhat parallel variations and is rather higher than that of the blood. Similar concentration of ethyl alcohol by the kidney as well as of methyl alcohol, ethyl ether, and acetone is effected by the Starling heart-lung-kidney preparation. The artificially perfused frog kidney secretes urine containing a lower concentration of alcohol than that present in the perfusing fluid. W. O. KERMAK.

Pharmacology of lead. V. Resorption of the metal from the gastro-intestinal tract and the

possibility of influencing it. S. MIYASAKI (Arch. exp. Path. Pharm., 1930, 150, 39—46).—The absorption of lead from the gastro-intestinal tract appears to be a simple diffusion process. Administration of colloidal ferric hydroxide or of milk retards absorption of lead.

W. O. KERMAK.

Stability of ptyalin at various dilutions. R. EGE and E. OKLITZ (Biochem. Z., 1930, 219, 422—431).—At constant reaction and in presence of constant concentration of chlorine ions the stability of ptyalin decreases in proportion as the dilution of the saliva containing it increases, and it is supposed that this behaviour is due to the presence in the saliva of a colloidal stabilising substance. W. MCCARTNEY.

Biochemical studies on rice starch. III, IV. Action of enzymes on rice starch. I, II. W. S. TAO (Bull. Chem. Soc. Japan, 1930, 5, 87—90, 91—92).—I. The action of the diastase obtained by extraction of malted barley and germinated rice, respectively, with distilled water on 1% solutions of powdered rice starch (previously extracted with light petroleum and 0.3% sodium hydroxide solution), soluble starch, amylose, and amylopectin for 15 min. at 20°, 30°, 40°, and 50°, has been investigated by examination of the reducing power of the solution and the colour reaction with iodine. Both enzyme extracts, especially that from rice, act on soluble starch more readily than on the other samples, but whilst the hydrolytic action of barley diastase, in all cases, increases only slightly with rise in temperature, a marked increase is observed in the case of rice diastase. In agreement with the literature the optimum temperature for the activity of the extracts *in vitro* is about 50°. Purified rice and barley amylase, however, are very similar in their hydrolytic activity at 24° on both rice starch and soluble rice starch solutions.

II. The reaction products obtained by the action of rice diastase on a 3% solution of rice starch for 3 hrs. at 20° and 35° have been investigated and compared with those formed at the same temperatures in the germinating seeds (this vol., 648). In the former case, at the above temperatures, 50 and 33%, respectively, of the starch was converted into simple sugars (mainly maltose and dextrose; Pinoff's test indicated the absence of sucrose which was present in the germinating seeds), whilst in the germinating seeds the corresponding values were 20 and 17%. The subsequent decomposition of the sugars into carbon dioxide and water, observed in the germinating seeds, is not observed *in vitro*. J. W. BAKER.

Influence of acetate and phosphate on the activity of malt amylase. H. C. SHERMAN, M. L. CALDWELL, and H. H. BOYNTON (J. Amer. Chem. Soc., 1930, 52, 1669—1672).—The optimum activity of malt amylase in presence of 0.00005 and 0.1M-concentrations of acetate is at  $p_H$  4.5—4.8 and 5.0—5.4, respectively; for the same concentrations of phosphate the  $p_H$  values are 4.5 and 4.9, respectively. The activity of the enzyme is increased by either acetate or phosphate. Since the acetate is as effective as the phosphate, its use is preferred because it is a more efficient buffer. H. BURTON.

**Enzymes of barley malt. VI. Enzymic hydrolysis of viscose silk.** H. PRINGSHEIM and E. THILO (Cellulosechem., 1930, 11, 100—102; cf. Otto, B., 1929, 734).—The barley cellulase is isolated by cold aqueous extraction of the malt, dialysis, and concentration in a high vacuum at the ordinary temperature. This product contains reducing dextrins and proteins which may be removed by treatment with commercial pancreatin and subsequent dialysis. The relative rates found for the attack of the celluloses, regenerated from the xanthate in various ways, confirm the earlier results of Otto (*loc. cit.*). The cellulase prepared in this way causes a rapid hydrolysis of lichenin. T. H. MORTON.

**Active group of catalase.** H. VON EULER, K. ZEILE, and H. HELLSTRÖM (Svensk Kem. Tidskr., 1930, 42, 74—76).—Spectrophotometric observations have been made on a highly purified catalase preparation and compared with similar observations on solutions of hæmin. Comparisons have been made in solutions containing pyridine and sodium thio-sulphate and also in very dilute sodium hydroxide solutions. The similarity which exists suggests the possibility that the iron in catalase may exist in combination with a porphyrin. W. O. KERMACK.

**Xanthine oxidase in the avian embryo.** E. J. MORGAN (Biochem. J., 1930, 24, 410—414).—The oxidase is present in the kidney on the 15th day and in the pancreas on the 19th day, the earliest days on which the individual organs were tested. It is not present in the liver until the 21st day, when its appearance is strikingly sudden. S. S. ZILVA.

**Tyrosinase-tyrosine reaction. VII. Action of tyrosinase on certain substances related to tyrosine.** W. L. DULIÈRE and H. S. RAPER (Biochem. J., 1930, 24, 239—249).—5 : 6-Dihydroxyindole is produced when tyrosinase acts on tyramine or on 3 : 4-dihydroxyphenylethylamine. When 3 : 4-dihydroxyphenylethylamine is the substrate 5 : 6-dihydroxy-*N*-methylindole results, whilst *N*-methyltyrosine yields an indole derivative not yet identified, as well as a small amount of a pressor substance. 3 : 4-Dihydroxyphenylalanine and 3 : 4-dihydroxyphenylethylmethylamine yield 5 : 6-dihydroxyindole-2-carboxylic acid and 5 : 6-dihydroxy-*N*-methylindole, respectively, whether oxidised with silver oxide or by tyrosinase. In the production of melanin from tyrosine and tyramine approximately 5 atoms of oxygen are utilised per molecule of substrate, whereas 4 atoms are required by 3 : 4-dihydroxyphenylalanine and 3 : 4-dihydroxyphenylethylmethylamine. It is probable that 2 atoms of oxygen are needed to convert 5 : 6-dihydroxyindole into melanin. S. S. ZILVA.

**Methylene-blue method for studying biological dehydrogenation. II. Preparation of succinodehydrogenase solutions and determination of their activity.** J. LEHMANN (Skand. Arch. Physiol., 1929, 58, 45—64; Chem. Zentr., 1929, ii, 2900).—The activity of succinodehydrogenase solutions is determined by mixing 0.5 c.c. of the enzyme solution and 2 c.c. of *M*/15-phosphate buffer of  $p_H$  7.30 at 37° with 0.2 c.c. of 0.2*M* neutral potassium succinate solution and 0.3 c.c. of methylene-blue solution (1 in 2000). The decolorisation time in the absence of succinate is

also observed. The enzyme solution is prepared by extracting pressed minced ox or horse muscle, after extraction with water or 0.25% sodium chloride solution, with 2 vols. of *M*/15-disodium hydrogen phosphate solution. A. A. ELDRIDGE.

**Antiglyoxalase. I. Action of pancreatic extract on phenylglyoxal.** J. O. GIRŠAVIČIUS (Biochem. J., 1930, 24, 446—452).—A production of acid similar to that obtained with phenylglyoxal and liver extract is obtained when phenylglyoxal is added to a pancreatic extract. This is not due to a formation of mandelic acid, but to a reaction with amino-compounds, partly diamino-acids, with formation of a sparingly soluble orange substance (cf. Foster, A., 1925, i, 1495). The diamino-acid present in pancreatic extract cannot account for the whole of the reaction obtained, but it is found that polypeptides, including those of monoamino-acids, also react, whilst the monoamino-acids themselves do not. The production of the acid was followed by a modification of Warburg's method in which Barcroft's manometer was used for the measurement of the carbon dioxide evolved from sodium hydrogen carbonate. S. S. ZILVA.

**Catalysis by heavy metals of cell fermentation.** E. KRAH (Biochem. Z., 1930, 219, 432—443).—Glyceraldehyde and 8-hydroxyquinolinesulphonic acid inhibit glycolysis *in vivo*, and since these substances combine with copper and inhibit its toxic effect the hypothesis of Hecht and Eichholtz (A., 1929, 594) is confirmed. 2-Aminophenol-4-sulphonic acid and 1-amino- $\beta$ -naphthol-6-sulphonic acid which inhibit the toxic effect of ferrous iron (but not that of copper) also specifically inhibit the Pasteur reaction in tumour cells. Both glycolysis and this reaction are inhibited by 8-amino- $\alpha$ -naphthol-5-sulphonic acid and by 4-chloro-5-nitro-2-aminophenol, substances which inhibit the toxic effects of copper and of ferrous iron. It is concluded that the Pasteur reaction is catalysed by ferrous iron. W. MCCARTNEY.

**Action of salts on fumarase. I.** P. J. G. MANN and B. WOOLF (Biochem. J., 1930, 24, 427—434).—“Resting” *B. coli communis* washed free of all salts and suspended in distilled water in presence of 2 or 4% of propyl alcohol will convert fumaric acid into its equilibrium mixture with *l*-malic acid at a linear rate for the greater part of the reaction. In the absence of added salts the range of activity is between  $p_H$  5 and 7.7, the  $p_H$ -activity curve being symmetrical with an optimum at about 6.4. Phosphates accelerate between  $p_H$  6 and 8.8 in a way which suggests that they combine with the enzyme non-competitively with the substrate. The “affinity” of the enzyme for phosphate at any given  $p_H$  is proportional to the  $HPO_4$  concentration. In presence of 0.2*M*-phosphate which gives the maximum effect at every  $p_H$  a symmetrical  $p_H$ -activity curve is obtained with an optimum at 6.9. Citrates behave similarly, giving a greater activation at every  $p_H$  and an optimum at 7.1. Sulphates depress the activity, giving an optimum at  $p_H$  6.2. The enzyme appears to be active only when in the isoelectric state, the salt effect being due to an alteration in the proportion of the enzyme molecules in this active state at any given  $p_H$ . S. S. ZILVA.

**Production of hydrogen sulphide by animal tissues.** G. SLUITER (Biochem. J., 1930, 24, 549—563).—Animal tissues, thiol-containing solutions (glutathione or organ extracts) and a dehydrogenase solution from horse-flesh yielded hydrogen sulphide after addition of sulphur. In reduced glutathione as well as in tissue, hydrogen sulphide production is, during a certain time, directly proportional to the thiol group present. The hydrogen sulphide production by tissues is much more marked than that by a corresponding pure thiol compound. Dehydrogenase solutions produce very little hydrogen sulphide, but increase the production when added to normal tissue. Organs of small animals can produce more hydrogen sulphide than those of large animals with the same amount of thiol compound. Rise of temperature even up to the b. p. promotes hydrogen sulphide formation and decreases the thiol content of the tissue. In the heated tissue the hydrogen sulphide production decreases more quickly than the thiol content. The optimum hydrogen sulphide production takes place at about the neutral point. In strongly acid or alkaline solution little or no hydrogen sulphide is evolved. The addition of donors or of citrate increases the liberation of hydrogen sulphide. The former has little effect on tissues capable of producing a large amount of hydrogen sulphide. S. S. ZILVA.

**Use of urine in place of serum in the Abderhalden reaction.** E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1930, 11, 305—344).—The Willstätter technique employed for obtaining the enzymes from urine may be simplified by direct extraction of the urine with 87% glycerol followed by adsorption on aluminium hydroxide. Elution gives a product yielding trustworthy results. A simple dialysis of the urine may also be employed, but is not trustworthy. The recommended technique consists in precipitation of the enzymes with acetone at  $p_H$  6.98—7.15 (20 c.c. of acetone to 20 c.c. of urine). After centrifuging, the clear liquid is drained off and the precipitate is mixed with 1.5 c.c. of 0.9% sodium chloride solution and dialysed. Incubation with the substrate for 4 hrs. is in some cases sufficient to give the ninhydrin reaction; the maximum is 16 hrs. The method is also useful for the detection of carcinoma. The pregnancy reaction becomes negative at the ninth day after parturition. J. H. BIRKINSHAW.

**Comparison of the enzymes present in urine producing the Abderhalden reaction with pepsin and trypsin.** E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1930, 11, 361—381).—Acetone precipitates of urine of pregnancy gave a negative Abderhalden reaction at  $p_H$  8.30 and at 6.50, almost negative at  $p_H$  7.80. Of various organ substrates none was hydrolysed when buffered to  $p_H$  1.80 and only placenta in presence of 0.9% sodium chloride in place of the buffer mixture. Trypsin-kinase hydrolysed all the substrates in presence of sodium chloride, but more strongly at  $p_H$  8.30. Gastric juice attacked the substrates at  $p_H$  1.80. The urine precipitates with added kinase reacted negatively to all the substrates except placenta. Many other proteins were tested with the urine precipitates with and without addition of kinase. Only caseinogen, fibrin, edestin, and

pumpkin-seed protein gave a positive reaction. At  $p_H$  8.30, all the reactions were negative except for a weak positive reaction with placenta. Glycyl- and chloroacetyl-L-tyrosine were not hydrolysed by the enzymes of urine. Cooling below 0° or heating at 60° seems to produce slow destruction of the active enzyme. Some evidence of the fixation of the enzyme by placental substrate was obtained. There can be no question of the identity of the active enzyme with trypsin. J. H. BIRKINSHAW.

**Peptidase.** F. STURM (Z. ges. exp. Med., 1929, 66, 506—516; Chem. Zentr., 1929, ii, 3156).—Damage of liver tissue markedly increases the peptolytic index. A. A. ELDRIDGE.

**Degradation of oxy- and carbon monoxide-hæmoglobin by pepsin hydrochloride, trypsin-kinase, and erepsin.** E. ABDERHALDEN and M. DAMODARAN (Fermentforsch., 1930, 11, 345—349).—Oxyhæmoglobin and carbon monoxide-hæmoglobin are hydrolysed by pepsin hydrochloride (gastric juice) and by trypsin-kinase + erepsin to approximately the same extent. J. H. BIRKINSHAW.

**Action of N-alkali, erepsin, and trypsin-kinase on isomeric polypeptides derived from D-alanine, D-valine, and L-leucine.** E. ABDERHALDEN and J. KATO (Fermentforsch., 1930, 11, 271—286).—Of the dipeptides employed, L-leucyl-D-valine was most easily hydrolysed by N-alkali hydroxide. D-Valyl-D-alanine was not hydrolysed, D-valyl-L-leucine and L-leucyl-D-alanine only slightly, D-valyl-D-alanine not at all. Of the tripeptides L-leucyl-D-alanyl-D-valine was most readily hydrolysed, D-alanyl-L-leucyl-D-valine very slowly. The arrangement of the components in isomeric polypeptides is of great importance. Erepsin hydrolysed D-alanyl-D-valine, D-alanyl-L-leucine, D-valyl-D-alanine, and L-leucyl-D-valine readily, D-valyl-L-leucine and L-leucyl-D-alanine less readily. The tripeptides were easily hydrolysed. Trypsin-kinase did not attack the dipeptides, but all the tripeptides examined were hydrolysed. All the halogenoacyldipeptides tested were hydrolysed but not the four halogenoacylamino-acids. The polypeptides used included D- $\alpha$ -bromoisovaleryl-D-alanine, m. p. 123° (uncorr.),  $[\alpha]_D^{20} +16.0^\circ$ ; D-valyl-D-alanine, m. p. 246° (uncorr.),  $[\alpha]_D^{20} +12.4^\circ$ ; D- $\alpha$ -bromoisovaleryl-L-leucine, m. p. about 139°,  $[\alpha]_D^{20} -7.35^\circ$ ; D-valyl-L-leucine, m. p. about 270°,  $[\alpha]_D^{20} -36.5^\circ$ ; D- $\alpha$ -bromopropionyl-L-leucyl-D-valine, m. p. about 156°,  $[\alpha]_D^{20} -25.8^\circ$ ; D-alanyl-L-leucyl-D-valine, m. p. 245° (decomp.),  $[\alpha]_D^{20} -49.3^\circ$ ; D- $\alpha$ -bromoisovaleryl-D-alanyl-L-leucine, m. p. 184°,  $[\alpha]_D^{20} -13.3^\circ$ ; D-valyl-D-alanyl-L-leucine, m. p. 221° (becomes brown); D- $\alpha$ -bromoisovaleryl-L-leucyl-D-alanine, m. p. about 181°,  $[\alpha]_D^{20} -32.6^\circ$ ; D-valyl-L-leucyl-D-alanine, m. p. 280°; D- $\alpha$ -bromoisohexoyl-D-alanyl-D-valine, m. p. 159°,  $[\alpha]_D^{20} -19.0^\circ$ ; L-leucyl-D-alanyl-D-valine, m. p. about 237°,  $[\alpha]_D^{20} -50.5^\circ$ ; D- $\alpha$ -bromoisohexoyl-D-valyl-D-alanine, m. p. 171°,  $[\alpha]_D^{20} -15.15^\circ$ ; L-leucyl-D-valyl-D-alanine, m. p. 256°,  $[\alpha]_D^{20} -9.93^\circ$ . J. H. BIRKINSHAW.

**Effect of N-alkali, erepsin, and trypsin-kinase on polypeptides containing DL-serine or DL-isoserine and on their corresponding halogenoacyl compounds.** E. ABDERHALDEN and F. REICH (Fermentforsch., 1930, 11, 287—304).—The following

substrates were prepared: *dl*-leucyl-*dl*-isoserine, *glycyl*-*dl*-isoserine, m. p. 250° (decomp.); *glycyl*-*dl*-leucyl-*dl*-isoserine, m. p. 238° (decomp.); *dl*- $\alpha$ -bromo-*isohexoyl*-*dl*-serine, m. p. 170—172° (uncorr.), giving *dl*-leucyl-*dl*-serine, m. p. about 220° (decomp.); *chloroacetyl*-*dl*-leucyl-*dl*-serine, m. p. about 135°, giving *glycyl*-*dl*-leucyl-*dl*-serine, m. p. 235° (decomp.); *dl*- $\alpha$ -bromopropionyl-*dl*-leucyl-*dl*-serine, m. p. 136°, giving *dl*-alanyl-*dl*-leucyl-*dl*-serine, m. p. 208—210° (decomp.). *N*-Sodium hydroxide hydrolysed all the polypeptides; erepsin did likewise, but did not attack the two bromo-compounds. Erepsin hydrolysed the compounds containing *dl*-serine more readily than those containing *dl*-isoserine. The latter, in contrast to serine, strongly inhibited the hydrolysis of *dl*-leucylglycine by erepsin. Trypsin-kinase did not hydrolyse the dipeptides containing *dl*-isoserine or *dl*-leucyl-*dl*-serine. Of the tripeptides *dl*-alanyl-*dl*-leucyl-*dl*-serine was most readily attacked; the most easily hydrolysed substrate was *dl*- $\alpha$ -bromopropionyl-*dl*-leucyl-*dl*-serine. Methylation of the methyl ester of *dl*- $\alpha$ -bromoisohexoyl-*dl*-leucyl-*dl*-serine, decomp. 183°, gave *N*-methyl-*dl*-leucyl-*dl*-leucyl-*dl*-seryldecarboxyglycine, m. p. 132°, in which the amino- and carboxyl groups are protected. This was not hydrolysed by erepsin, trypsin-kinase, pepsin hydrochloride, or yeast maceration juice.

J. H. BIRKINSHAW.

**Behaviour of polypeptides containing *dl*- $\alpha$ -aminomyristic acid towards *N*-alkali, erepsin, and trypsin-kinase.** E. ABDERHALDEN and M. DAMODARAN (Fermentforsch., 1930, 11, 350—360).—*dl*- $\alpha$ -Aminomyristic acid, m. p. 252.5°, was prepared from *dl*- $\alpha$ -bromomyristic acid, m. p. 42—43° (the m. p. previously given is incorrect). The amino-acid (ethyl ester, m. p. about 25°; ethyl ester hydrochloride, m. p. 85°) was used to prepare the following polypeptides: *glycyl*-*dl*- $\alpha$ -aminomyristic acid by way of ethyl *chloroacetyl*-*dl*- $\alpha$ -aminomyristate, m. p. 58°; *dl*-leucyl-*dl*- $\alpha$ -aminomyristic acid, by way of methyl *dl*- $\alpha$ -bromoisohexoyl-*dl*- $\alpha$ -aminomyristate, m. p. 78° (corresponding ethyl ester, m. p. 48°); *glycylglycyl*-*dl*- $\alpha$ -aminomyristic acid, m. p. 231° (decomp.); *dl*- $\alpha$ -alanylglycyl-*dl*- $\alpha$ -aminomyristic acid, m. p. 215—216° (decomp.); *benzoylglycyl*-*dl*- $\alpha$ -aminomyristic acid, m. p. 187—188°; *methyl*-*dl*-alanyl-*dl*- $\alpha$ -aminomyristic acid, m. p. 199—200°, by way of methyl *dl*- $\alpha$ -bromopropionyl-*dl*- $\alpha$ -aminomyristate, m. p. 51°. *N*-Alkali hydroxide at 37° hydrolysed all the compounds. Erepsin hydrolysed the first three but not the second three compounds. Only the tripeptide *dl*-alanylglycyl-*dl*- $\alpha$ -aminomyristic acid was hydrolysed by trypsin.

J. H. BIRKINSHAW.

**Influence of buffer solutions at weak alkaline reaction, alone and in presence of enzymes, on the removal of halogen from halogenoacyl-amino-acid compounds.** E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1930, 11, 382—398).—With bromoacetic acid addition of active or inactivated trypsin-kinase produced an acceleration in the rate of removal of halogen. With *dl*- $\alpha$ -bromopropionic acid and  $\beta$ -iodopropionic acid no effect was observed, but the halogen was much more quickly removed from the latter at  $p_H$  8.4. In other cases, trypsin-kinase had no effect. A number of halogeno-

acyl derivatives of *dl*-phenylalanine buffered to  $p_H$  8.4 were studied at 37°. With increasing length of the unbranched bromoacyl chain the ionisation of the bromine is delayed; the effect is greater with a branched chain. The effect is less marked with the chloroacyl compounds. From the racemic *dl*- $\alpha$ -bromopropionyl-*dl*-norvaline *A*, bromine was more readily removed than from the *B* compound. Compound *A* is "hydrolysed" by trypsin-kinase, whilst *B* is not attacked. A part of this apparent hydrolysis value is due to the removal of halogen. This error is avoided by using the Van Slyke method for determining the degree of hydrolysis. Polypeptide derivatives containing the same halogenoacyl radical differ greatly in the rate of removal of halogen. The ionisation of the halogen of bromoacetyl-*dl*-phenylalanine was slow at  $p_H$  7.1, but more rapid at 8.4 and 9.3. Addition of trypsin-kinase produced in some cases marked acceleration, but inactivated trypsin-kinase or active erepsin had no effect.

J. H. BIRKINSHAW.

**Comparison of the influence of the constitution of homologous dipeptides of *l*-tyrosine and of the corresponding halogenoacyl compounds on their capacity for fission by alkali, erepsin, and trypsin-kinase.** E. ABDERHALDEN and A. BAHN (Fermentforsch., 1930, 11, 399—432).—The following dipeptides and precursors were prepared: *glycyl*-*l*-tyrosine, froths at 118—130°, solidifies at 150—170°, m. p. 270—271° (decomp.),  $[\alpha]_D^{25} + 43.7^\circ$ ; second form froths at 160°, solidifies at 180°, m. p. 263—268° (blackens),  $[\alpha]_D^{25} + 42.7^\circ$  (ethyl ester, m. p. 88—89°); *chloroacetyl*-*l*-tyrosine, m. p. 152—153°,  $[\alpha]_D^{25} + 63.3^\circ$ ; *bromoacetyl*-*l*-tyrosine, m. p. 150—152°,  $[\alpha]_D^{25} + 58^\circ$  (ethyl ester, m. p. 101°); *d*-alanyl-*l*-tyrosine, froths at 160—162°, m. p. 253—256° (decomp.),  $[\alpha]_D^{25} + 42.3^\circ$ ; the *l*-compound froths at 155—163°, m. p. 238—240° (decomp.),  $[\alpha]_D^{25} + 32.6^\circ$ ; *dl*- $\alpha$ -bromopropionyl-*l*-tyrosine, m. p. 151°,  $[\alpha]_D^{25} + 53.3^\circ$  (ethyl ester, m. p. 140°); *l*- $\alpha$ -bromopropionyl-*l*-tyrosine, m. p. 153—154°. *dl*- $\alpha$ -Amino-(*n*)-butyryl-*l*-tyrosine, froths at 160—165°, m. p. 223—227°,  $[\alpha]_D^{25} + 26.7^\circ$ ; *dl*- $\alpha$ -bromobutyryl-*l*-tyrosine, m. p. 134—136°,  $[\alpha]_D^{25} + 39.3^\circ$  (ethyl ester, m. p. 102—103°);  $\alpha$ -aminoisobutyryl-*l*-tyrosine, froths at 160—168°, m. p. 221—223°,  $[\alpha]_D^{25} + 37.7^\circ$ ;  $\alpha$ -bromoisobutyryl-*l*-tyrosine, m. p. 137—138°,  $[\alpha]_D^{25} + 38.8^\circ$  (ethyl ester, m. p. 88—89°); *d*-norvalyl-*l*-tyrosine, m. p. 265°,  $[\alpha]_D^{25} + 35.3^\circ$ ; *l*-compound,  $[\alpha]_D^{25} + 6.0^\circ$ ; *dl*- $\alpha$ -bromovaleryl-*l*-tyrosine, m. p. 128°,  $[\alpha]_D^{25} + 37^\circ$  (ethyl ester, m. p. 72—74°); *dl*-valyl-*l*-tyrosine, froths at 175—185°, m. p. about 245° (blackens),  $[\alpha]_D^{25} + 11^\circ$ ; *dl*- $\alpha$ -bromoisovaleryl-*l*-tyrosine, m. p. 141—142°,  $[\alpha]_D^{25} + 30.7^\circ$  (ethyl ester, m. p. 90—95°); *d*-norleucyl-*l*-tyrosine, m. p. 286—287°,  $[\alpha]_D^{25} + 31.7^\circ$ , *l*-compound, froths at 120—150°, m. p. 270—273°,  $[\alpha]_D^{25} + 9^\circ$  ( $[\alpha]_D^{25} + 4.7^\circ$  for another sample); *dl*- $\alpha$ -bromohexoyl-*l*-tyrosine, m. p. 120—121°,  $[\alpha]_D^{25} + 38^\circ$  (ethyl ester, m. p. 77—81°); *l*- $\alpha$ -bromohexoyl-*l*-tyrosine, m. p. 141°; *d*- $\alpha$ -bromohexoyl-*l*-tyrosine, m. p. 142°,  $[\alpha]_D^{25} + 42^\circ$  (ethyl ester, m. p. 107—109°); *d*-leucyl-*l*-tyrosine, froths at 180°, m. p. 250—260°,  $[\alpha]_D^{25} - 16^\circ$  (*l*-isomeride); *dl*- $\alpha$ -bromoisohexoyl-*l*-tyrosine, m. p. 140—141°,  $[\alpha]_D^{25} + 32.7^\circ$  (ethyl ester, m. p. 74—77°).

The rates of amination of and removal of hydroxyl from the halogenoacyl compounds were similar to



those observed for the corresponding derivatives of *dl*-phenylalanine. The amination of  $\alpha$ -bromoisobutyryl- and of  $\alpha$ -bromoisovaleryl-*l*-tyrosine was extremely slow. In the removal of halogen by alkali hydroxide chloroacetyl-*l*-tyrosine was much more sensitive than bromoacetyl-*l*-tyrosine. The most resistant were  $\alpha$ -bromoisobutyryl- and  $\alpha$ -bromoisovaleryl-*l*-tyrosine. The two last-named were not hydrolysed by trypsin-kinase. *dl*- $\alpha$ -Bromohexoyl-*l*-tyrosine was much more readily hydrolysed than the *l*- $\alpha$ -compound. Chloroacetyl-*l*-tyrosine was most readily, the bromoacetyl compound less readily, hydrolysed. (Cf. this vol., 356.)

As regards the dipeptides  $\alpha$ -aminoisobutyryl- and *dl*-valyl-*l*-tyrosine were resistant to 5*N*-sodium hydroxide; glycyl-*l*-tyrosine was most readily attacked. Erepsin did not hydrolyse *dl*- $\alpha$ -aminoisobutyryl-*l*-tyrosine or those dipeptides of *l*-tyrosine in which the amino-group component is the optical antipode of the corresponding amino-acid in protein. Trypsin-kinase attacked glycyl-*l*-tyrosine (contrary to the observation of Waldschmidt-Leitz) and other derivatives of *l*-tyrosine, the more readily the longer is the aminoacyl carbon chain. The optimum  $p_H$  for erepsin is 7.8–8.4, for trypsin-kinase 8.4 (higher for some substrates). The optimum is to some extent influenced by the special properties of the enzyme-substrate complex. J. H. BIRKINSHAW.

**Time factor in action of pancreatic enzymes.** L. MARTIN (Arch. Int. Med., 1930, 45, 535–537).—It is shown that when pancreatic diastase is diluted sufficiently, a definite relationship exists between the length of incubation and the amount of starch hydrolysed. T. R. SESHADRI.

**Effect of X-rays on proteolytic processes.** P. GASSUL and A. POLJAKOV (Zhur. exp. Biol. Med., 1929, 11, 15–20).—Small doses of X-rays temporarily increase, whilst large doses diminish or inhibit, proteolysis in the freshly extirpated spleen of the cat. X-Irradiation did not affect the blood-cholesterol.

#### CHEMICAL ABSTRACTS.

**Effect of various colouring matters on enzyme action.** I–III. Y. MARUNO (J. Exp. Digest. Dis., Japan, 1928, 3, 911–928, 1065–1073, 1074–1092).—The action of pepsin was repressed, but the proteolytic action of trypsin and pancreatin was scarcely affected. Quantitative experiments indicate that adsorption plays a part in the repression. *In vivo*, the proteolytic action of duodenal juice is repressed, and the starch-decomposing action variously affected, by addition of colouring matter. CHEMICAL ABSTRACTS.

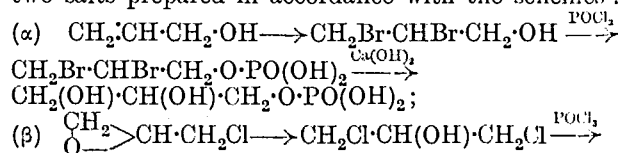
**Synthesis of fats in the presence of pancreatic extract.** A. GIBERTON (Compt. rend., 1930, 190, 951–953).—The biochemical synthesis of glycerides reported by Hamsik (A., 1910, ii, 427) has been re-examined, and the velocity of reaction and the yield have been improved. The preparation of active glycerol pancreatic extract is described; the extract retains its activity for several weeks, and with oleic acid readily forms an emulsion which is stable when slowly agitated. At 37° with slow agitation, the optimum mixture consists of 6 mols. of glycerol to 1 mol. of oleic acid, and attains an equilibrium point, at which 66% of oleic acid has combined, in

less than 48 hrs. The velocity of reaction under the above conditions may be increased four times by the addition of 2 mg. of bile salts per g. of mixture (cf. Hamsik, *loc. cit.*); the same equilibrium point is obtained (cf. Morel and Velluz, A., 1928, 328).

C. W. SHOPPEE.

**Reversibility of enzyme action. II. Synthesis of urea by urease.** B. SUZUKI and T. MARUYAMA (Proc. Imp. Acad. Tokyo, 1930, 6, 63–66).—The amount of carbamide formed by the action of urease on ammonium carbonate and carbamate has been determined and it is found that, whilst it is proportional to the concentration of carbonate, it shows no regular relationship to the carbamate concentration. Hence it is considered improbable that ammonium carbamate is an intermediate product in this reaction (cf. Mack and Villars, A., 1923, i, 405). Fearon's view (A., 1923, i, 497) that the reverse reaction involves the sequence, carbamide  $\rightarrow$  ammonium cyanate  $\rightarrow$  ammonium carbonate, urease affecting only the first of these changes, is considered untenable, since the quantity of ammonia liberated from a carbamide-urease solution is greater than that obtained from a more concentrated solution of ammonium cyanate. If ammonium cyanate were the intermediate the reverse should be the case, since the concentration of cyanate formed from the carbamide could never exceed that in the more concentrated ammonium cyanate solution. J. W. BAKER.

**Reversibility of enzyme action. III. Glycerophosphoric acid synthesised by glycerophosphatase.** B. SUZUKI and T. MARUYAMA (Proc. Imp. Acad. Tokyo, 1930, 6, 67–70).—Karrer's method (A., 1926, 384) for separating barium  $\alpha$ - and  $\beta$ -glycerophosphates has been tested on pure specimens of these two salts prepared in accordance with the schemes:



$[(\text{CH}_2\text{Cl})_2\cdot\text{CH}\cdot\text{O}]_2\text{PO}\cdot\text{OH} \xrightarrow{\text{Ca(OH)}_2} [(\text{CH}_2\text{OH})_2\cdot\text{CH}\cdot\text{O}]_2\text{PO}\cdot\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} [\text{CH}_2(\text{OH})]_2\cdot\text{CH}\cdot\text{O}\cdot\text{PO(OH)}_2$ . Barium  $\beta$ -glycerophosphate is almost quantitatively (98.9%) precipitated as the double salt  $2(\text{C}_3\text{H}_7\text{O}_6\text{P}\cdot\text{Ba}), \text{Ba}(\text{NO}_3)_2$ , whilst no precipitate is obtained with the salt of the  $\alpha$ -acid. Boiling with a 10% solution of barium hydroxide causes no wandering of the acyl group in either the  $\alpha$ - or the  $\beta$ -acid. Glycerophosphatase ("takadiastase" from *Aspergillus oryzae*) in glycerol solution acts on disodium hydrogen phosphate at  $p_H$  8.4 and 36°, to give a mixture of the  $\alpha$ - (52%) and  $\beta$ - (48%) glycerophosphates, which were separated by Karrer's methods and identified by preparation of derivatives. The enzyme is more effective in alkaline media, no synthesis being observed at  $p_H$  5.4. J. W. BAKER.

**Phosphoric esters in alcoholic fermentation. II. Pyrophosphate in yeast preparations.** E. BOYLAND (Biochem. J., 1930, 24, 350–354).—Pyrophosphate occurs in living yeast and forms about a quarter of the total phosphorus of yeast. When

pyrophosphate is added to fermenting zymine it is rapidly hydrolysed to orthophosphate, which reacts in the usual way by forming hexosephosphates and carbon dioxide. The acetone precipitate of yeast juice did not ferment sugar (having no hexosephosphatase), but in the presence of acetaldehyde reacted with both ortho- and pyro-phosphates to liberate the theoretical amount of carbon dioxide and form 90% of hexosemonophosphate; pyrophosphatase is therefore not identical with hexosephosphatase. A method for the separation of hexosediphosphate and pyrophosphate is based on the differential solubility of their barium salts in water. S. S. ZILVA.

**Production of pyruvic acid during fermentation with yeast.** C. NEUBERG and M. KOBEL (Biochem. Z., 1930, 219, 490—494).—When yeast acts on magnesium hexosediphosphate leading to production of pyruvic acid (cf. this vol., 374) equimolecular amounts of the acid and of glycerol are formed. A yield of 81% of acid plus glycerol may be obtained.

W. MCCARTNEY.

**Fermentation by yeast preparations.** A. HARDEN and M. G. MACFARLANE (Biochem. J., 1930, 24, 343—349).—Eighty % of the diminution in the rate of fermentation which occurs in the preparation of yeast-juice may be ascribed to grinding, during which process the yeast acquires the power of responding to phosphate. A further loss is incurred during pressing by the use of kieselguhr, which adsorbs active material. Experiments on the effect of various reagents on the fermenting power of yeast revealed that one group of reagents, which included phenol, pyridine, and formaldehyde, reduced and with increasing concentration finally stopped the fermentation. No response to added phosphate occurred and most of the cells did not stain with methylene-blue. Another group of reagents, which included toluene, benzene, and xylene, reduced the fermentation and reacted to phosphate, but all the cells stained with methylene-blue. This treatment affects mostly the hexosephosphatase action. An account is given of the preparation, by autolysis of dried baker's yeast, of an extract containing hexosephosphatase, but not zymase, which accelerates the fermentation rate of zymine. S. S. ZILVA.

**Soluble enzymes secreted by *Hymenomyces*. Hydrolysis of hemicelluloses.** L. LUTZ (Compt. rend., 1930, 190, 892—895).—The action of a number of fungi of the *Hymenomyces* species on various hemicelluloses has been investigated and it is concluded that the reaction presents the characteristics of total hydrolysis. Fermentation of gum tragacanth with *Stereum purpureum* gave after 3 months a syrup containing arabinose and galactose. *S. hirsutum*, *Coriolus versicolor*, and *Fomes ignarius* gave similar results but less rapidly. Liquefaction of carob-protein was similarly effected by the following, enumerated in decreasing order of activity: *Coriolus adustus*, *Corticium quercinum*, *F. ignarius*, *Polyporus pinicola*, *S. hirsutum*, *S. purpureum*, *C. versicolor*, *Ungulina betulina*, *Pleurotus ostreatus*, *Trametes medullaripanis*, and *P. Eryngii*. A. I. VOGEL.

**Physiological - morphological studies of *Funaria hygrometrica*, L., in pure culture.** G.

SCHWEIZER (Ber. deut. bot. Ges., 1930, 48, 75—84).—The spores of *F. hygrometrica* develop without injury in nutrient media of very high acidity,  $p_H$  1.55. The protonemata grow quickly and luxuriantly in media of higher or lower acidity and exhibit great resistance to chemical and osmotic forces. At the lower  $p_H$  values a slight inhibition of bud development occurs, but this check has no influence on later growth. The young plants develop thickly in culture flasks at high and low acidities, and with or without humic acids. In the presence of humic acids more sexual organs and more sporogonia are produced and the nutrient solutions become coloured; acidity has little effect on the development of sexual organs. E. HOLMES.

**Energy utilisation and carbon assimilation of autotrophic bacteria.** S. A. WAKSMAN (Proc. Int. Cong. Plant Sci., 1929, 1, 203—210).—The organisms are classified according to the elements or compounds which they can oxidise. CHEMICAL ABSTRACTS.

**Enzyme formation by bacteria. II.** H. KARSTRÖM (Suomen Kem., 1930, 3, 42—44).—The fermentation of sugar by bacteria is influenced by the sugar present in the media on which they have been growing. A lactic acid bacterium was capable of fermenting dextrose and sucrose independently of previous culture conditions, but other sugars were in general fermented only by strains which had become accustomed to them. Similar observations were made in the case of other bacteria, and it is possible to distinguish between the fermenting reactions characteristic of the organism and never lost and those which appear in a strain which has become adapted to a particular sugar. Analogous observations have been made with dry bacteria. With a suitable organism (*B. coli*) the invertase activity is much increased as the result of growing on sucrose. W. O. KERMACK.

**Aërobic fermentation of cellulose.** P. E. SIMOLA (Suomen Kem., 1930, 3, 45—48).—An obligate aërobic sporulating cellulose fermenter, capable of utilising inorganic nitrogen, has been isolated. It yields carbon dioxide, some formic acid and alcohol, as well as an organic acid of unknown constitution. A considerable quantity of protein is also formed. W. O. KERMACK.

**Gas production by bacteria. I. Apparatus for measuring rate of gas production.** J. A. CRANSTON (Biochem. J., 1930, 24, 525—528).—Three methods are described. In one the culture tube is attached to a pycnometer filled with mercury and the mercury which is displaced by the evolved gas is weighed. In the second method the culture tube is connected with a calibrated capillary and the production of gas is followed by the displacement of a thread of mercury in the capillary. In the third method, the gas evolved is collected in a gas burette by displacement of mercury. Samples of broth can be withdrawn periodically and the gas analysed in a Haldane apparatus. S. S. ZILVA.

**Gas production by bacteria. II. Denitrification and bacterial growth phases.** B. LLOYD and J. A. CRANSTON (Biochem. J., 1930, 24, 529—548).—The rate of denitrification curve shows a general

similarity to a bacterial growth curve. In nitrite-broth cultures the normal lag of 13 hrs. between the time of inoculation and the appearance of gas is made up of a bacterial lag of  $8\frac{1}{2}$  hrs. and a "chemical lag" of  $4\frac{1}{2}$  hrs. The time elapsing before evolution of nitrogen increases with increase in concentration of the nitrate. In nitrite-broth cultures there is a considerably shorter lag in gas production than in cultures containing an equivalent amount of nitrate and the nitrite-broth cultures show the same duration of lag in gas production as a culture of broth containing half the equivalent amount of nitrate. The nitrate and nitrite are evidently reduced to hypoxynitrite before the nitrogen is liberated. A formula is advanced for the calculation of the amount of oxygen consumed from the volume of nitrogen liberated allowing for the fact that the reaction occurs in stages. Increased acidity causes an increase in the lag in nitrogen production, a diminution of the rate of evolution of nitrogen when once started, and a progressive decrease in the maximum rate of gas production. In absence of nitrites or nitrates growth of the culture is accompanied by a fall of  $p_H$  of the broth from 8.5 to 8.2, rising again to  $p_H$  8.6 in the senescence stage of the culture. In presence of potassium nitrite there is at first a slight increase in acidity owing to the formation of carbon dioxide, but when nitrogen is evolved the  $p_H$  rises rapidly to about 9.3 if the concentration of nitrite is sufficiently high. In presence of potassium nitrate the  $p_H$  falls to 8.0 and then attains a value of 8.2–8.8 according to the initial concentration of nitrate. S. S. ZILVA.

**Action of *B. coli* on non-dextrose reducing substances of human blood.** R. S. HUBBARD and J. K. DEEGAN (J. Biol. Chem., 1930, 86, 575–577).—Incubation of protein- and dextrose-free blood filtrates after inoculation with *B. coli* caused diminution in the residual reducing substances; these substances (possibly lactose or galactose) are equally distributed between red blood-corpuscles and plasma. C. R. HARRINGTON.

**Oxidation-reduction potentials of cultures of hæmolytic streptococci.** I. L. F. HEWITT (Biochem. J., 1930, 24, 512–524).—The potentials varied widely with different cultural conditions. The presence of serum in broth inhibits the fall in potential during growth in aerobic cultures, which is due to an oxygen-carrying effect of the serum-proteins—possibly to the sulphur-containing units of the protein molecules. The fall in potential during growth is less in tryptic-digest medium than in peptone-infusion broth. In freshly-boiled broth the potential falls more rapidly and to a lower level than in unboiled broth and rises particularly in tryptic-digest medium more rapidly after the cessation of active proliferation. When cultures are aerated the potential falls less during growth and rises more rapidly after the logarithmic phase of multiplication. When peroxide is formed in the aëration, it has a marked effect on the potentials. Dextrose, lactic acid, etc. retard peroxide formation. The addition of a small quantity of hydrogen peroxide to broth before inoculation produces a long lag period, but after this the normal potential-time curve is obtained. The potential falls

rapidly in aerobic 1% dextrose-broth cultures, but less rapidly in sealed cultures. A short phase of rapid increase of potential is observed in aerobic dextrose cultures after a few hrs. growth. In aerated dextrose-broth cultures the potential falls very little, despite the very luxuriant growth obtained. Low oxidation-reduction potentials do not favour the growth of hæmolytic streptococci. S. S. ZILVA.

**Active iron.** II. H. PETOW, H. KOSTERLITZ, and H. FISCHGOLD (Z. ges. exp. Med., 1929, 66, 491–499; Chem. Zentr., 1929, ii, 3157).—A discussion of the X-activity of iron compounds for hæmophilic bacteria. A. A. ELDRIDGE.

**Vital conditions of ferruginous bacteria.** I. TUROWSKA (Bull. Acad. Polonaise, 1930, B, 255–282).—Iron bacteria are found in certain wells and other waters of Poland in which the iron content is usually greater than 2 mg. per litre and the reaction is between  $p_H$  5.88 and 7.60. Large concentrations of salts appear to be unfavourable. The bacteria are able to withstand temperatures down to 0°.

W. O. KERMACK.

**Lipins of tubercle bacilli.** XIII. Occurrence of mannose in the phosphatide from human tubercle bacilli. R. J. ANDERSON and A. G. RENFREW (J. Amer. Chem. Soc., 1930, 52, 1252–1254).—The supposed sugar-acid obtained by hydrolysis of the phosphatide (A., 1927, 1114) has now been identified as mannose. R. K. CALLOW.

**Lipins of tubercle bacilli.** XIV. Occurrence of inositol in the phosphatide from human tubercle bacilli. R. J. ANDERSON (J. Amer. Chem. Soc., 1930, 52, 1607–1608).—*i*-Inositol has been isolated from the water-soluble products obtained by the hydrolysis of the phosphatide from human tubercle bacilli (A., 1927, 1114) with dilute sulphuric acid. H. BURTON.

**Purification of toxins and antitoxins.** K. LINDERSTROM-LANG and S. SCHMIDT (Kolloid-Z., 1930, 51, 152–160).—The precipitate obtained by coagulating diphtheria serum with alcohol in the cold consists mainly of undenatured serum-proteins and contains practically all the antibody. The solution of this precipitate does not give the Raman precipitation reaction with toxin. The effective part of diphtheria serum is adsorbed preferentially by aluminium hydroxide and this property provides a means of purification. Through repeated adsorption combined with dialysis a solution can be obtained from which 99.5% of the inactive constituents of the crude toxin has been removed. E. S. HEDGES.

**Purification of diphtheria and tetanus antitoxins after concentration by fractionation with ammonium sulphate.** P. P. MURDICK (J. Immunol., 1929, 17, 269–272; Chem. Zentr., 1930, i, 90–91).

**Cholera toxin.** M. HAHN and J. HIRSCH (Z. Hyg., 1929, 110, 355–381; Chem. Zentr., 1929, ii, 2571).—The formation of toxin by cholera vibrios depends on the medium; it begins in 6–10 hrs., further alkalisation being then unnecessary. The toxin is non-dialysable with a parchment membrane. A. A. ELDRIDGE.

**Bacterial growth inhibitor (lactenin) of milk.** I. F. S. JONES and H. S. SIMMS (J. Exp. Med., 1930, 51, 327—339).—Lactenin can be separated by dialysis from salts and carbohydrates; it is removed by agents which precipitate the proteins of whey. After partial tryptic digestion of these proteins, followed by dialysis, there is no appreciable loss of lactic activity. The material, when desiccated, is stable.

CHEMICAL ABSTRACTS.

**Bacteriophage derivative of pancreatin.** T. INOUE (Okayama J. Med., 1929, 41, 93—109).—The substance resists being heated at 70—80°, is adsorbed by kaolin and bone charcoal, and is precipitated by ammonium sulphate.

CHEMICAL ABSTRACTS.

**Subvisible virus and colloid research.** H. BECHHOLD (Kolloid-Z., 1930, 51, 134—144).—Certain types of virus are of colloidal dimensions, and the author seeks to show how the methods of colloid-chemical research are applicable to the study of these types. The matters discussed from this point of view are the isolation and purification of the virus, filtration, ultrafiltration, adsorption and electric charge, determination of size, diffusion coefficient, sedimentation velocity, behaviour on centrifuging, and cataphoresis.

E. S. HEDGES.

**Colloid chemistry of antiseptics and chemotherapy. I. Mode of combination of antiseptic dyes with proteins.** A. D. HIRSCHFELDER and H. N. WRIGHT (J. Pharm. Exp. Ther., 1930, 38, 411—431).—The affinity of coagulated egg-albumin for various dyes is determined by adding varying amounts of dyes to a solution containing a constant amount of protein at  $pH$  7.3, heating to produce coagulation, and determining colorimetrically the amount of dye left in the supernatant liquid after centrifuging. The affinity for three dyes used is in the order crystal-violet > gentian-violet > rose-bengal. Addition of protein to solutions of mercurochrome greatly decreases the rate of dialysis of the antiseptic. With the crystalloid dyes of the triphenylmethane series the amount bound by egg-albumin in solution decreases with increasing protein concentration, although the mass of protein remains constant. Malachite-green has only a slight tendency to precipitate egg-albumin and is adsorbed only to a small extent. Crystal-violet more readily precipitates protein, brilliant-green being intermediate between it and malachite-green. Basic fuchsin does not precipitate protein in any concentration, the tendency to such precipitation being increased with the introduction of alkyl groups into the dyes, with consequent increase in the basicity of the dye cation.

P. G. MARSHALL.

**Colloid chemistry of antiseptics and chemotherapy. II. Does an antiseptic adsorbed on protein still exert antiseptic action?** H. N. WRIGHT and A. D. HIRSCHFELDER (J. Pharm. Exp. Ther., 1930, 38, 433—449).—The effect of differing concentrations of some triphenylmethane dyes on the carbon dioxide production of yeast from 4% sucrose is determined, both in presence and in absence of egg-albumin. The reduction of antiseptic power in presence of protein is not parallel to the degree of adsorption occurring, and the adsorbed dye must

exert some antiseptic power. The ratio of the antiseptic power of the adsorbed dye to that of the free dye increases rapidly with dilution.

P. G. MARSHALL.

**Action of irradiated sea-water on lactic fermentation.** C. RICHEL and M. FAGUET (Compt. rend., 1930, 190, 843—844).—The effect of previous irradiation of sea-water with X-rays for varying periods on the fermentation of lactose has been investigated by measurements of the acidity produced (cf. A., 1929, 1109). An acceleration is apparent after irradiation for 10 min.; this reaches a maximum after 30 min. and then decreases. There is no effect with distilled water after 20 min.

A. I. VOGEL.

**Effect of adrenaline and cholic acid on excretion of creatinine.** K. KAZIRO and A. TAKU (J. Biochem. Japan, 1929, 11, 203—217).—Administration of adrenaline increases, and of cholic acid decreases, the amount of creatinine excreted by the rabbit; the normal value is 0.1—0.3 mg. per 2 hrs.

CHEMICAL ABSTRACTS.

**Physiology of glycogen and the rôle of insulin and adrenaline in carbohydrate metabolism.** J. J. R. MACLEOD (Lancet, 1929, 217, 1—7, 55—60, 107—112).—Two lectures.

L. S. THEOBALD.

**Effect of insulin on the biological oxidation of carbohydrates and on the energy exchanges in animals receiving carbohydrates.** B. RITLOP (Biochem. Z., 1930, 219, 277—296).—The combustion of intravenously administered dextrose in curarised dogs of which the respiration is artificially controlled is increased by subcutaneous injection of insulin, which also accelerates the onset of the increased combustion. The dextrose also stimulates the energy exchanges in the animals, but administration of insulin has no detectable effect on these.

W. MCCARTNEY.

**Insulin inactivation by human blood-cells and plasma *in vitro*: effect of normal and of diabetic blood on insulin action.** S. KARELITZ, P. COHEN, and S. D. LEADER (Arch. Int. Med., 1930, 45, 546—558).—The blood of a diabetic child who did not respond normally to insulin inhibited insulin action in rabbits. The same phenomenon is shown to occur with blood from normal persons, although the effect is greater with blood from diabetic patients. A greater inhibition was caused by blood-cells than by plasma and a further marked increase was observed when the cells were laked. The inactivation is not due to dilution, viscosity of the fluid, rate of absorption, adsorption by the cells, or  $pH$  of the blood.

T. R. SESHADRI.

**Isolation of *l*-thyroxine from the thyroid gland by the action of proteolytic enzymes.** C. R. HARRINGTON and W. T. SALTER (Biochem. J., 1930, 24, 456—471).—The successive action of pepsin and trypsin on iodothyroglobulin and on desiccated thyroid gland has yielded digestion products readily soluble in alkali and much less soluble in acid, possessing maximum flocculation at  $pH$  5.0, and containing 12—17% I and 5—8% N. *l*-Thyroxine was isolated as follows. An alkaline sodium chloride extract of the thyroid gland was digested by successive additions of trypsin at  $pH$  8.5, precipitated at  $pH$  5, extracted with acid acetone, and reprecipitated with ether. This

precipitate was subjected to further tryptic digestion, after which it was precipitated at  $p_H$  5 and redissolved in water with the aid of the least possible amount of ammonia. Pigmented impurities were then removed by boiling with barium hydroxide. After precipitation at  $p_H$  5 and dissolving in alkaline 80% alcohol, further impurities were precipitated with acid acetone. Animal crepsin or yeast peptidase produced no further hydrolysis of the digestion product. Acid hydrolysis at  $110^\circ$  with 90% acetic acid saturated with gaseous hydrogen chloride at  $0^\circ$ , on the other hand, yielded at this stage partly racemised thyroxine, converting at the same time the whole of the nitrogen into the amino-condition. The losses involved by the liberation of iodine were, however, great. *L*-Thyroxine was finally isolated from this mixture of free thyroxine and thyroxine-peptides by a less drastic procedure. The product was dissolved in pyridine, precipitated by dilution with water, dissolved in potassium carbonate, decomposed with acetic acid, and reprecipitated as the monosodium salt of thyroxine on cooling after boiling with sodium carbonate. The sodium salt on decomposition with acetic acid yielded *L*-thyroxine. Comparative physiological tests on the digestion product and on pure *L*-thyroxine have shown that there is no reason to presume the existence in the thyroid gland of an active principle other than thyroxine or of its existence there in "activated" form.

S. S. ZILVA.

Rate of thermal decomposition of the oxytocic principle of the posterior lobe of the pituitary gland. II. Effect of temperature. T. D. GEROUGH and R. W. BATES (J. Amer. Chem. Soc., 1930, 52, 1098—1101; cf. this vol., 503).—Determinations were made over a range of temperatures from  $35.7^\circ$  to  $121^\circ$  with pituitary extract and with purified oxytocic principle at  $p_H$  3.35 and 3.55. The relation between  $1/T$  and  $\log 1/k$  is linear, and extrapolation indicates an exceedingly slow rate of destruction at  $0$ – $20^\circ$ . Purification does not alter thermal stability.

R. K. CALLOW.

Influence of the hypophysis on metabolism, growth, and sexual organs of male rats and rabbits. II. Influence of extracts of hypophysis on the body-weight, weight of fat, of sexual organs, and of endocrine organs of rats. V. KORENCHESKY (Biochem. J., 1930, 24, 383—393).—A glycerol extract from the anterior lobe of the pituitary of oxen kept at  $-5^\circ$  and brought to  $p_H$  7.4 was injected intraperitoneally into normal, cryptorchid, and castrated young and adult male rats in amounts of 1–2 c.c. No decided influence was noticed on the growth, but the body-fat was decreased. The weight of sexual organs was decreased to the greatest extent in cryptorchid animals; this effect was less in normal and absent in castrated rats, showing that a correlation exists between the extracted hypophyseal substances and a special testicular tissue. The weight of the thyroids was decreased by about 17% in normal and cryptorchid animals, but not significantly in castrated rats. The anterior lobe therefore contains substances which diminish the weight of the above organs and glands, and possibly act antagonistically to the growth and male gonad-stimulating hormones,

as evidenced by implantation experiments, and to the growth-promoting hormone prepared by Evans and his co-workers.

S. S. ZILVA.

Oestrin. III. Improved method of preparation and isolation of active crystalline material. G. F. MARRIAN (Biochem. J., 1930, 24, 435—445).—Acidification and extraction with ether of urine from pregnant women yields a preparation of oestrin varying from 8000 to 40,000 mouse units per litre. The decomposition of the saponified product of this preparation with carbon dioxide and further fractionation with ether, acetone, 50% alcohol, and alkali greatly purified it with a loss of only 40% of the activity. This loss occurs entirely in the initial stage of saponification. The mouse unit of these purified fractions is of the order of 0.0006 mg. By dissolving this concentrate in alcohol, precipitating it with ether and decolorising it, crystals,  $C_{18}H_{24}O_3$ , were obtained from 57% methyl alcohol, m. p.  $256$ – $260^\circ$  (decomp.), with an activity m.u. = 0.00011 mg. There is no proof that this substance is actually the pure hormone. The possible identity of this substance with those obtained by other workers is discussed.

S. S. ZILVA.

Crystalline ovarian hormone (oestrin) from urine of pregnant women. E. A. DORSY, C. D. VILER, and S. THAYER (J. Biol. Chem., 1930, 86, 499—509).—Urine is acidified to  $p_H$  4.0 with hydrochloric acid, and the uric acid allowed to separate: the oestrin may then conveniently be extracted with olive oil. The olive oil solution is extracted with hot 95% alcohol, and the resulting solution concentrated, and freed from oil by addition of a little water, acidified to Congo-red, and extracted with light petroleum. The residue obtained by evaporation of the alcoholic solution is dissolved in butyl alcohol, and the solution, after washing with dilute sodium hydroxide and with hydrochloric acid, is again evaporated to dryness. The active substance is leached out of the residue with ether, and, after clearing and evaporation of the latter, is dissolved in a mixture of butyl alcohol and light petroleum. The hormone can be extracted from this solution by shaking with dilute hydrochloric acid, or, more efficiently, with sodium hydroxide; further purification was effected by extracting the substance from the aqueous solution with ether, and again treating with butyl alcohol–light petroleum followed by aqueous extraction. Finally the aqueous solution was extracted with ether, the latter was evaporated, and the residue leached out with dry ether; the latter on evaporation yielded a crystalline compound possessing an activity of about 3000 rat units per mg. Neither this activity nor the physical properties of the substance were altered by repeated recrystallisation.

C. R. HARRINGTON.

Physiology of secretin. I. Preparation and isolation. E. U. STILL (Amer. J. Physiol., 1930, 91, 405—408).—The acidic extract of dog's duodenum is treated with sodium chloride, when secretin is precipitated. This precipitate is extracted with acid alcohol and impurities are precipitated with alcoholic brucine and pyridine; the secretin is then precipitated with acetone and other. Finally the

secretin is extracted from this precipitate with boiling methyl alcohol.

E. BOYLAND.

**Pancreas. VII. Mellanby procedure for isolation and purification of secretin.** B. MORTIMER and A. C. IVY (Amer. J. Physiol., 1929, **91**, 220—224).—The "bile salt" precipitation method was unsatisfactory and variable yields were obtained.

E. BOYLAND.

**Vitamin-A.** O. H. CADY and J. M. LUCK (J. Biol. Chem., 1930, **86**, 743—754).—Treatment of cod-liver oil with sulphur dioxide, phosphorus pentachloride, chlorine, acetyl chloride, nitrous fumes, Benedict's reagent, and sodium hydrogen sulphite (in the last case for a prolonged period) destroyed the vitamin-A; this was not affected by treatment of the oil with hydrogen sulphide, ethylene, ammonia, and Benedict's reagent after neutralisation, and but slightly affected by formaldehyde and hydrogen peroxide. No destruction of vitamin-A was observed in lucerne or spinach, and only partial destruction in butter on treatment of these materials with sulphur dioxide. The destruction by sulphur dioxide was irreversible. It is concluded that vitamin-A activity is the property of a specific grouping rather than of a specific molecule, and that, in cod-liver oil, it is associated with an aldehydic group.

C. R. HARINGTON.

**Alleged contamination of carotene by vitamin-A.** N. S. CAPPER (Biochem. J., 1930, **24**, 453—455).—A sample of carotene of m. p. 178° (uncorr.) which was found weight for weight to be more active than a cod-liver oil concentrate showed considerably less absorption at 328  $\mu$  (which is considered to be characteristic of vitamin-A) than did the concentrate.

S. S. ZILVA.

**Urinary syndrome of metabolic disturbances caused by lack of vitamin-B in the rat.** J. ROCHE (Bull. Soc. Chim. biol., 1930, **12**, 342—356).—In rats receiving *ad libitum* the diet of Randoin and Simonnet, the C/N ratio of the urine and faeces is practically constant for a normal animal on a given diet, although the actual value varies according to the age of the rat. On a diet deficient in vitamin-B the ratio increases (more rapidly as the point of death is approached). Ingestion of yeast temporarily reduces the ratio. The consequences of lack of vitamin-B are manifested sooner on a diet rich in carbohydrate. Death is not due to inanition, which would cause a fall in the C/N ratio.

P. G. MARSHALL.

**Vitamin-C. I. Occurrence of vitamin-C in celery. II. Germination of seeds and vitamin-C. I. II. Germination of seeds and vitamin-C. II.** T. MATSUOKA (Mem. Coll. Agric. Kyōtō, 1930, **9**, 1—13, 15—21, 23—27).—I. 1—2 G. of celery per day per 100 g. body-weight fed to guinea-pigs on a ration otherwise deficient in vitamin-C is sufficient to prevent scurvy. Celery therefore has a high vitamin-C content.

II. Dry rice seeds contain a very small amount of vitamin-C. This is not appreciably increased when the seeds after soaking for 24 hrs. in water are germinated for 2 days in the dark.

III. Considerable quantities of vitamin-C are

contained in rice or barley seeds germinated in sunlight, but less in oat seeds similarly germinated.

W. O. KERMACK.

**Absorption spectrum of vitamin-D.** R. B. BOURDILLON, R. G. C. JENKINS, and T. A. WEBSTER (Nature, 1930, **125**, 635).—Preparations showing high antirachitic power but relatively low absorption at 280  $\mu$  have now been obtained. The substance showing the intense maximum at this wave-length and produced in the early stages of irradiation of ergosterol by a mercury-vapour lamp without light filters is not vitamin-D (cf. A., 1929, 727).

L. S. THEOBALD.

**Toxicity of large doses of irradiated ergosterol in animals.** H. SIMONNET and G. TANRET (Bull. Soc. Chim. biol., 1930, **12**, 371—394).—Pure ergosterol,  $[\alpha]_D -126^\circ$ , was used in all cases. Daily feeding of 4 c.c. of butter containing 40 mg. of the non-irradiated sterol produced normal growth in rabbits and caused no lesions. Small quantities of irradiated ether (containing some peroxides) are almost innocuous. The toxicity of irradiated ergosterol varies with the time of irradiation. A daily dose of 40 mg. of ergosterol irradiated for 45 min. does not kill rabbits for several months, but the animals show lesions of advanced calcification. A similar dose of ergosterol irradiated for 6 hrs. causes death in rabbits in 2—3 weeks. Heating the irradiated sterol for short periods at temperatures between 120° and 150° does not diminish either the toxicity or the calcifying power, these two properties being indissolubly connected. The resinous substances obtained from ergosterol by irradiation are toxic to rabbits irrespective of the time of irradiation. Cholesterol is innocuous to rabbits, however long it is irradiated. An animal which is given an overdose of irradiated ergosterol may lose 40% of its weight and suffer from acute diarrhoea and many other disabilities. Crystalline ergosterol peroxide,  $[\alpha]_D -35^\circ$ , is non-toxic to rabbits and shows no antirachitic power. An overdose of irradiated ergosterol to rabbits in gestation does not produce lesions in the young at birth. The effect of such an overdose varies with different species.

P. G. MARSHALL.

**Chemical reaction for vitamins and hormones.** E. CHRISTENSEN (Münch. med. Woch., 1928, **75**, 1883; Chem. Zentr., 1929, ii, 3241).—Stöltzner's colour reaction of the antirachitic vitamin with phosphorus pentoxide is not specific for that vitamin.

A. A. ELDRIDGE.

**Carbon dioxide assimilation of arctic plants and the dependence of the assimilation on the temperature.** D. MÜLLER (Planta, Arch. wiss. Bot., 1928, **6**, 22—39; Chem. Zentr., 1929, ii, 2570).—Experiments on *Salix glauca*, L., and *Chamaenerium latifolium* were performed in West Greenland.

A. A. ELDRIDGE.

**Mineral content of pastures.** A. E. V. RICHARDSON (Council Sci. Ind. Res. Australia, Pamphlet 17, 1930, 29 pp.).—A progress report.

E. HOLMES.

**Distribution and storage of the most important alkali salts in the potato stalk.** W. VON BREHMNER and J. BÄRNER (Ernähr. Pflanze, 1929, **25**, 300—306; Chem. Zentr., 1929, ii, 2570).—The storage of potassium in the important tissues of the plant is directly proportional to the quantity of potash present



until the optimal growth of the plant is attained; if the plant is over-fertilised, plant development is reciprocally related to the storage of potash.

A. A. ELDRIDGE.

**Content of potassium and sodium in plants found in salt lagoons or on the sea-shore.** G. BERTRAND and M. ROSENBLATT (Compt. rend., 1930, 190, 985—988).—The K/Na ratios in the ashes of the following plants, collected in flower from salt lagoons, were: *Salsola kali*, L., 10.56; *S. soda*, L., (in flower) 5.45, (in fruit) 1.40; *Obione portulacoides*, Moq., 1.45; *Sueda fruticosa*, L., 0.83; *Salicornia fruticosa*, L., 0.77; *S. radicans*, Sm., 1.76; *Aster tripolium*, L., 0.63; *Inula crithmoides*, L., 0.45. Samples collected from dunes showed: *Pancratium maritimum*, L., 7.63; *Crucianella maritima*, L., 6.59; and *Medicago marina*, L., 5.49. In the case of the tidal zone the ratios were: *O. portulacoides*, Moq., 2.2; *Euphorbia Paralias*, L., 2.02; and *Cakile maritima*, Scap., 1.58 and 1.17. There is therefore no sharp transition between purely terrestrial and purely marine plants.

T. H. MORTON.

**Distribution of nickel and cobalt in plants.** G. BERTRAND and M. MOKRAGNATZ (Bull. Soc. chim., 1930, [iv], 47, 326—331).—Nickel and cobalt have been found in all plants examined, but in very small proportions. The relative proportions of nickel and cobalt present are roughly parallel, organs relatively rich in cobalt being correspondingly rich in nickel. The proportions are highest in the leaves, dried leaves of the following plants named containing the weight indicated (mg. per kg.) of nickel and cobalt (parenthetical figures): lettuce, 1.51 (0.054); carrot, 1.83 (0.314); spinach, 2.37 (0.74); lime, 2.50 (0.20); apricot, 3.0 (0.40); beech, 3.0 (0.35); cabbage, 3.3 (0.07). Seeds or berries, after the leaves, are richest in nickel and cobalt, containing (per kg. of dried matter) from 0.14 to 2.25 mg. of nickel in maize and peas, respectively, and up to 0.36 mg. of cobalt in buckwheat and 0.35 mg. in lentils, the amount in oats being too small to be determined. The teguments of the berries are richer in nickel and cobalt than the kernels, oat bran containing 0.44 mg. of nickel and 0.011 mg. of cobalt and wheat bran 0.39 mg. of nickel and 0.011 mg. of cobalt. The kernel of decorticated and polished rice is extremely poor in nickel and cobalt, containing only 0.02 and 0.006 mg., respectively, this being parallel with the poverty in manganese, zinc, and titanium already noted. Nickel and cobalt are more abundant in the bark than in the wood, beech wood containing 0.12 mg. of nickel and 0.01 mg. of cobalt and the bark 0.40 and 0.10 mg., respectively. The lignified shells protecting certain seeds are poor in both metals. Edible organs or parenchymatous tissues of fruits, roots, bulbs, or tubercles when dry contain moderate amounts of nickel and cobalt, the highest amount found being 3.5 mg. of nickel and 2.13 mg. of cobalt per kg. of dried *Cantharellus cibarius*, Fr. Nickel and cobalt may act as catalysts in vegetable cells.

R. BRIGHTMAN.

**Distribution of titanium in cryptogams.** G. BERTRAND and VORONCA-SPIRT (Ann. Inst. Pasteur, 1930, 44, 270—272).—For recognition of titanium the material is ashed, the residue dissolved in sulphuric acid, and the solution treated with hydrogen peroxide

to give the yellow pertitanic acid. Fungi (three varieties) contain about 0.5 mg. per kg. fresh weight and bakers' yeast less than 0.1 mg. *Aspergillus niger* does not contain titanium. Cryptogams normally contain titanium, as do all flowering plants.

P. G. MARSHALL.

**Compounds of inositolphosphoric acids with molybdic acid.** N. SELIGSON (Arch. Pharm., 1930, 268, 147—151).—A solution containing phytin, nitric acid, and ammonium nitrate gives with ammonium molybdate a white precipitate ( $\alpha$ ), which redissolves in excess of the reagent. The resulting solution soon deposits ammonium phosphomolybdate, formed from phosphates present as impurities, and then contains compounds of phytin with molybdic acid, from which phosphoric acid is more readily eliminated than from phytin itself. Thus, hydrolysis proceeds with constant velocity for several months at the ordinary temperature, and is rapidly completed at 100°. Phytin is not hydrolysed by the nitric acid solution alone below 60° and is only slowly attacked at 100°. The precipitate,  $\alpha$ , contains compounds of inositolphosphoric acids with molybdic acid and is free from inorganic phosphates, although these are present in the original material. The phytin recovered from it has a slightly higher P/C ratio than the original. Brucine inositolhexaphosphate and molybdic acid give a compound,

$C_6H_6(NH_4HPO_4)_6.6MoO_3.15H_2O$ , losing  $10H_2O$  in a vacuum.

H. E. F. NOTTON.

**Mode of combination of iodine in *Laminaria digitata*.** G. LUNDE and K. CLOSS (Biochem. Z., 1930, 219, 198—217).—A table summarises the iodine contents of the stems, leaves, and roots of *L. digitata*, the total iodine being divided into the following fractions: water-soluble, water- and alcohol-soluble, iodide, united with calcium (possibly as iodate), present in the alginic acid complex and liberated only on boiling with acids, and an insoluble residue existing chiefly in the roots. P. W. CLUTTERBUCK.

**Iodine content of fresh, air-dried, and fermented tobacco leaves.** J. SCHWAIBOLD (Biochem. Z., 1930, 218, 318—320).—Iodine was present in very varying amounts in all the tobaccos. The variations appeared to depend both on the place of growth and on the species of plant. In the tobaccos examined it was frequently found that the iodine content varied inversely with the calcium content.

W. MCCARTNEY.

**Rôle of chlorine in nutrition and growth of the tobacco plant and its effect on the quality of the cured leaf.** W. W. GARNER, J. E. McMURTRY, jun., J. D. BOWLING, and E. G. MOSS (J. Agric. Res., 1930, 40, 627—648).—In field experiments 20—30 lb. of chlorine per acre were added in the form of potassium chloride to tobacco on light sandy and sandy loam soils and gave an average increased yield of about 10%. The effect of the chlorine was reduced by the addition of dolomitic limestone, but the chlorine increased the availability to the plants of the small amounts of magnesium in these soils. The chlorine ion increases the water content of the tobacco leaves. Excess of chlorine in the tobacco leaf, however, disturbs carbohydrate metabolism with a resulting accumulation of

starch; such effects are observable with additions of only 40—60 lb. of chlorine per acre, but are intensified in sandy soils of limited buffering properties.

E. HOLMES.

**Nitrogenous compounds of tobacco smoke.** A. W. KOPERINA (Biochem. Z., 1930, 219, 258—276).—The composition of smoke from tobacco varies greatly according to the conditions under which it is burned. Of the total nitrogen in the smoke 30—40% may be present in the form of two or more unidentified compounds which are non-volatile in steam and from which the nitrogen can be partly separated as ammonia by acid hydrolysis; they consist chiefly of purine bases or related substances, although compounds of the pyrrole type are also present. W. MCCARTNEY.

**Sulphur in organic and inorganic combination in pasture grasses.** H. A. A. AITKEN (Biochem. J., 1930, 24, 250—256).—Five grasses, cocksfoot (*Dactylis glomerata*), perennial rye (*Lolium perenne*), prairie grass (*Bromus unioloides*), Yorkshire fog (*Holcus lanatus*), and hair grass (*Festuca bromoides*), were examined. There was no relation between the nutritive value and the organic sulphur content of the grasses. The water-soluble protein obtained from grass did not contain sulphur. The quantity of cystine did not correspond with the organic sulphur content of the grasses. A method for the determination of sulphate-sulphur is described in which the colloids are removed from the extracts by charcoal before determining the sulphate gravimetrically.

S. S. ZILVA.

**Determination of sulphur in plants.** D. E. FREAR (J. Biol. Chem., 1930, 86, 285—289).—The method of Benedict (A., 1909, ii, 827) as modified by Denis (A., 1911, ii, 66) has been adapted to the determination of sulphur in plant material with an error of  $\pm 2.7\%$ .

C. R. HARINGTON.

**Sulphur content of leaves.** E. TIEGS (Ber. deut. bot. Ges., 1930, 48, 58—63).—The weight of solid matter and the absolute sulphur content per 100 sq. cm. surface of leaves of *Prunus domestica*, *Aesculus hippocastanum*, and *Fraxinus excelsior* have been determined and from these the percentage of sulphur in the solid matter has been calculated. These values vary considerably during the course of the day as well as during the vegetation period.

T. R. SESHADRI.

**Determination of nitrate in green tomato and lettuce tissues.** E. M. ENMERT (Plant Physiol., 1929, 4, 519—528).—A modification of the phenol-disulphonic acid method abandons the use of charcoal.

CHEMICAL ABSTRACTS.

**Colloid-chemical structure of wood.** H. WISLICENUS (Naturwiss., 1930, 18, 387—392).—The formation of wood in trees is discussed on the basis of colloid chemistry. The nature of cellulose and lignin is mentioned. Wood is chiefly the result of a synthesis brought about by colloidal adsorption, lignin being the total of everything adsorbed from the sap hydrosol on the cellular and fibre membranes. The colloidal nature of sap is discussed, and curves showing the colloid content of sap during different times of the year for various trees are given.

A. J. MEE.

**Chlorophyll from the leaves of various plants.** M. JANISEK (Mezög. Kutat., 1929, 2, 402—409; Chem. Zentr., 1929, ii, 3022—3023).—The width and intensity of the adsorption bands (1% alcoholic solution) are not proportional to the concentration of chlorophyll; this result is attributed to the presence of other colouring materials. Yields afforded by various plants are recorded. A. A. ELDRIDGE.

**Decarboxylation of pectin.** F. V. LINGGOOD (Biochem. J., 1930, 24, 262—265).—Pectin can be decarboxylated by means of hot water under pressure if the evolved carbon dioxide is removed. An insoluble substance, probably a hemicellulose, and one or more soluble products, probably sugars, are obtained by the decarboxylation. The hemicellulose-like substance has a uronic anhydride content of 6.2%.

S. S. ZILVA.

**Pectin. IV. Oxidation of pectin by Fenton's reagent and its bearing on the genesis of the hemicelluloses.** A. G. NORMAN and F. W. NORRIS (Biochem. J., 1930, 24, 402—409).—Pectin may be readily oxidised by means of Fenton's reagent. The reaction temperature must be 30—35°. The products of this reaction yield on hydrolysis galactose and galacturonic acid and resemble in appearance and general properties the structural hemicelluloses such as those obtained from wheat bran, beech wood, and cereal straws. They are possibly polymerides containing mainly galactose-monogalacturonic acid and galactose-digalacturonic acid, although the presence of other conjugated acids containing galactose and galacturonic acid is not excluded. Hemicellulose may be formed in nature by the protracted mild oxidation of pectin.

S. S. ZILVA.

**Transformation of carbohydrates in the banana.** H. BELVAL (Compt. rend., 1930, 190, 886—888).—The edges of the leaves contain throughout development an almost constant composition of sucrose and inactive reducing sugars, in which sucrose predominates. During passage down the central vein and leaf stalk the sucrose undergoes inversion which is almost complete when it reaches the peduncle. No appreciable difference in the concentrations of the sugars is observed in the peduncle and the base of the leaf stalk, but a sudden change occurs as soon as the fruit is reached. Even in ripe fruits, there is a high percentage of starch, the concentration of the reducing sugars is negligible, whilst sucrose forms almost the whole of the soluble carbohydrate reserve. The starch reserve of the green fruit is elaborated almost entirely at the expense of the reducing sugars.

C. C. N. VASS.

**Rôle of phosphorus in the intermediate carbohydrate metabolism of plants. II.** H. K. BARRENSCHEEN and J. PANY (Biochem. Z., 1930, 219, 364—380; cf. A., 1928, 1162).—From assimilating *Elodea canadensis* there was obtained a reducing hexosemonophosphoric acid of the laevulose series which differs from the products of Neuberg, Robison, and Embden. The amount of the acid in the plant increased regularly as assimilation proceeded. The octa-amylose previously isolated from wheat has been shown to be a normal product of intermediate carbohydrate metabolism and from it a reducing

hexosephosphoric acid, also of the lævulose series, was obtained by the action of takadiastase which produced the same acid by the partial decomposition of an artificially phosphorylated starch (cf. Kerb, A., 1920, i, 714). W. McCARTNEY.

**Temperature and catalase activity in germinating maize.** C. W. LANTZ (Proc. Iowa Acad. Sci., 1928, 35, 147—149).—The catalase activity decreases as the temperature is raised from 30° to 40°; low-protein maize is more markedly injured by the higher temperature than is high-protein maize. The injury may be due to accumulation of injurious peroxides. CHEMICAL ABSTRACTS.

**Seasonal changes in the tracheal sap of pear and apricot trees.** F. G. ANDERSSON (Plant Physiol., 1929, 4, 459—476).—Changes in reaction and in the proportions of the constituents of the tracheal sap were observed.

CHEMICAL ABSTRACTS.

**Sugar of the *Floridæ*.** H. COLIN and E. GUÉGUEN (Compt. rend., 1930, 190, 653—655).—The sugar obtained by Kylin (A., 1915, i, 931) from the alcoholic extract of *Rhodymenia palmata*, and considered by him to be trehalose, is shown to be a compound of  $\alpha$ -galactose. The sugar,  $[\alpha]_D +149$ — $150^\circ$  (crystallographic data), softens at 90° and loses 6.9% of water at 150° (or in a vacuum above 50°) to give an anhydrous product,  $[\alpha]_D +160$ — $161^\circ$ . It is unaffected by invertase and emulsin, but readily converted by the autolysate of bottom-fermentation yeast into galactose, identified by m. p. 166—168°, optical properties, oxidation with nitric acid to mucic acid, and formation of the osazone.

C. W. SHOPPEE.

**Seasonal variations of sugar content in *Floridæ*.** H. COLIN and E. GUÉGUEN (Compt. rend., 1930, 190, 884—886).—The sugar content of the juice of *Rhodymenia palmata* was determined at approximately monthly intervals during 1927 and 1928, and was found to be greatest in the summer months. The mean sugar contents in 1927 and 1928 were 3.32% and 5.87%, respectively, the greater yield in 1928 being related to the larger amount of sunshine in that year. A. I. VOGEL.

**Occurrence of *d*-mannose in seaweed; separation of *l*-fucose and *d*-mannose.** R. H. F. MANSKE (J. Biol. Chem., 1930, 86, 571—573).—The crystalline sugar obtained by concentration of the first mother-liquor during the isolation of fucose from seaweed by the method of Clark (A., 1923, i, 16) yielded, when treated with hydrogen cyanide and ammonia and hydrolysed, a small amount of *d*-mannoheptolactone, indicating the presence of *d*-mannose. Further, extraction with pyridine of the mixed phenylhydrazones prepared from the final mother-liquor removed the fucosephenylhydrazone, and left 10% of residue consisting of *d*-mannosephenylhydrazone. C. R. HARRINGTON.

**Starch envelopes of pyrenoids.** F. O. HOWITT (Nature, 1930, 125, 412—413).—Irradiation of ovalbumin by ultra-violet light increases the hydrogen-ion concentration of the solution, and at or near the isoelectric point the protein is partly or

completely denatured. Formaldehyde, or a substance resembling it, is produced by irradiation of ovalbumin. Since formaldehyde functions as a precursor of carbohydrates it may be that the protein of the pyrenoids can give rise to the carbohydrate of their envelopes. L. S. THEOBALD.

**Piceoside of black willow bark.** M. BRIDEL and J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 332—341).—The extraction of the glucoside (see this vol., 258) is described. P. G. MARSHALL.

**Constitution of amelarioside: identity with piceoside (picein of Tanret).** J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 146—155).—See this vol., 258.

**Determination of æsculin by fluorescence measurements.** G. KLEIN and H. LINSE (Biochem. Z., 1930, 219, 51—71).—A method is described for the determination of fluorescing substances in terms of their fluorescence in which the relative intensity is estimated nephelometrically. The method, which is worked out for æsculin, is especially suitable for glucosides and alkaloids and is applied to the determination of the distribution of æsculin in *Asculus hippocastanum*. P. W. CLUTTERBUCK.

**Preparation and properties of laminarin (laminaroloside) from *Laminaria flexicaulis*.** H. COLIN and P. RICARD (Bull. Soc. Chim. biol., 1930, 12, 88—96).—The preparation and purification of laminarin and its physical and chemical properties are described. It has  $[\alpha]_D -11.3^\circ$  and on hydrolysis yields only dextrose. P. W. CLUTTERBUCK.

**Microchemical detection of arbutin and ursone [ursolic acid] in plants.** R. FISCHER and E. LINSE (Arch. Pharm., 1930, 268, 185—190).—Microchemical methods for the hydrolysis of arbutin in 0.5—1.0 g. of dried vegetable matter and the isolation and identification of the resulting quinol are described. The presence of arbutin in *Arctostaphylos alpina*, *A. uva ursi*, *Vaccinium vitis idæa*, *Pirola secunda*, *P. rotundifolia*, *P. uniflora*, and *P. umbellata* (but not in *Ledum palustre*) is confirmed, and it has been observed for the first time in *P. minor* and *P. media*. Ursone (ursolic acid), isolated by ether extraction and sublimation, is identified microchemically by the formation of its sparingly soluble potassium salt. It has been detected in *Ilex aquifolium*, *P. umbellata*, *P. rotundifolia*, *V. vitis idæa*, *V. myrtillus*, and *Erica arborea*, also, for the first time, in *P. minor*, *E. mediterranea*, and *E. carnea*. The substances in *Ledum palustre* and *Rhododendron ferrugineum* which Nooyen (A., 1921, i, 117) regarded as ursone are probably resins resembling ericolin. The detection of arbutin and of ursone may be carried out on the same sample. In addition, chimaphillin has been sublimed from the ether extracts of *P. umbellata* and *P. rotundifolia* and a yellow substance, subliming at 110°, from that of *P. uniflora*.

H. E. F. NOTTON.

**Micro-sublimation and the micro-gas-chamber method as aids to the evaluation of plant products.** A. NIETHAMMER (Mikrochem., 1930, 8, 53—62).—Klein's micro-gas-chamber process for the detection of flavones has been utilised in the examination of a number of woods, fruits, and plants with a

view to provide a means for their detection and identification. The presence of amygdalin in fruits can be readily detected by the above method if the section is treated with chloroform, when the hydrocyanic acid evolved from the hydrolysis of the glucoside may be identified by the silver nitrate test. The results of the examination of a number of drugs, fruits, and coffee substitutes by the micro-sublimation method are also given. H. F. HARWOOD.

**Glutathione in plant tissues.** V. B. WHITE (Science, 1930, 71, 74—76).—Using the method of Fink (A., 1927, 691), glutathione has been detected in different parts of certain members of the thallophytes, bryophytes, pteridophytes, and spermatophytes, and in herbaceous and woody stems, in bulbs and in tubers. Exposure to X-rays of the embryos of maize grains resulted in an increase in intensity of the colour reaction. L. S. THEOBALD.

**Proline and hydroxyproline in plant proteins.** H. SPÖRER and J. KAPFHAMMER (Z. physiol. Chem., 1930, 187, 84—88).—The following amounts of proline were isolated from plant proteins: wheat gliadin 9.86%, wheat glutenin 5.98%, soya-bean meal 3.11%. In no case was hydroxyproline detected. It is suggested that the animal body can convert proline into hydroxyproline. J. H. BIRKINSHAW.

**Isolation and purification of the alcohol-soluble protein (prolamin) in English ryegrass (*Lolium perenne*).** S. L. JODIDI (J. Agric. Res., 1930, 40, 361—370).—Extraction of dry English ryegrass with 70% alcohol at 57° removes up to 4.9% of a prolamin for which the name *lolin* is proposed. Repeated treatment with alcohol during purification renders a portion of this compound insoluble but does not appear to alter its ultimate composition. E. HOLMES.

**Protein content of reed canary grass on peat soils.** F. J. ALWAY and G. H. NESOM (J. Agric. Res., 1930, 40, 297—320).—The percentage of protein in the entire grass (*Phalaris arundinacea*, L.) grown in Minnesota from Russian, German, and American seed, varied from 25.2 to 6.6% (moisture-free basis), in the culms from 11.9 to 2.8%, in the leaves from 23.5 to 8.5%, and in the panicles from 30.5 to 9.4%. With maturing of the first growth of grass up to the time of blooming, there was a rapid decline in the proportion of dry matter in the leaves without a corresponding decline in their protein content. A high protein content was favoured by early cutting, thin stands, and an increased supply of available nitrogen, the plant being particularly sensitive to the last-named condition. E. HOLMES.

**Colour reaction of proteins of wheat grain.** E. RABATÉ and J. FLECKINGER (Compt. rend., 1930, 190, 748—750).—Treatment of sections of the cells of the embryo and protein stratum with Denigès' potassium bromide-sulphuric acid reagent causes a red coloration similar to that found for copper salts. The calcined grain does not give a reaction with the same reagent; it does, however, give a positive test for copper with Bach's reagent (formaloxime). It is considered that the coloration with the above reagent is due to protein. H. BURTON.

**Variation in the percentage of protein in the grain of a single wheat plant.** W. F. GERICKE (Science, 1930, 71, 73—74).—Variations in the percentages of protein in the grain of the different heads of the same wheat plant are recorded for different varieties of wheat. An ample supply of nitrogen during the early growth period of stalks results in a low-protein grain, whilst during later growth it favours high-protein grain. The longer is the interval between the ripening of the grain of two stalks the greater is the difference in protein content, a difference of 1 day being detectable in the composition of the grain. L. S. THEOBALD.

**Purification of soya-bean protein. III. Influence of acid or alkali on purification by dilute lower alcohols.** M. MASHINO (J. Soc. Chem. Ind. Japan, 1930, 33, 55—56B; cf. this vol., 384).—Addition of 1 part of 0.1N-hydrochloric acid to 4 parts of 60% methyl alcohol reduces the amount of crude protein dissolved by the latter medium to 0.41%. With 60% ethyl alcohol (4 parts) and 0.25N-hydrochloric acid (1 part), the figure is 2.24%. C. W. SHOPPEE.

**Properties of arachin and conarachin and the proportionate occurrence of these proteins in the peanut.** D. B. JONES and M. J. HORN (J. Agric. Res., 1930, 40, 673—682).—Oil-free meal from ground, shelled groundnuts contained 7.36% N (=40.48% of crude protein). The meal contained approximately 25% and 8% of arachin and conarachin, respectively. Arachin has  $[\alpha]_D^{25}$  —39.5°, does not coagulate in boiling 10% sodium chloride solution, but is precipitated completely from 10% salt solution containing 40% of ammonium sulphate. Conarachin has  $[\alpha]_D^{25}$  —42.7°, coagulates in 10% salt solution at 80°, and is precipitated at 85% concentration of ammonium sulphate. No appreciable quantities of albumin, prolamin, or glutelin were found. E. HOLMES.

**Marrubiin content of *Marrubium vulgare*.** A. MCCREA (J. Amer. Pharm. Assoc., 1930, 19, 231).—Flowering plants of *Marrubium vulgare*, L., grown under comparable conditions from seeds of French, German, and American origin, and dried at 40°, contain 0.34, 1.00, and 0.47%, respectively, of marrubiin. H. E. F. NOTTON.

**Variations in the composition of fresh branches of *Amelanchier vulgaris*, Moench, during vegetation.** M. BRIDEL and J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 139—145).—See this vol., 121.

**Composition of *Castalia odorata*, *Najas flexilis*, and stonewort.** H. A. SCHUETTE and H. ALDER (Trans. Wisconsin Acad. Sci. Arts Letters, 1929, 24, 135—139, 141—145).—Analytical values are recorded and compared.

#### CHEMICAL ABSTRACTS.

**Presence of bios in lotus fruit believed to be several hundred years old.** T. YOSHITOSHI (Manchurian J. Med., 1929, 9, 821—824).—The presence of bios was indicated by stimulation of the growth of yeast.

#### CHEMICAL ABSTRACTS.

**Jute seeds—*Corchorus capsularis*. III. Chemical composition.** N. K. SEN (J. Indian Chem. Soc., 1930, 7, 83—94).—Analysis of jute seeds

gives moisture 7.1; ash 6.0; protein 26.62; crude fibre 20.76; free invert-sugar 3.079; and sugar by inversion 5.95%. The main constituents of the ash are  $P_2O_5$  33.16,  $CaO$  20.73,  $K_2O$  25.45,  $MgO$  8.21,  $Na_2O$  3.23,  $SO_4$  4.24,  $SiO_2$  1.30%. Water extracts 3.4% of a crude nitrogenous substance which contains catalase. The seeds were extracted with various organic solvents (cf. A., 1929, 477, for the light petroleum extract). From the ethereal extract (1.36%) was isolated a fatty acid, m. p. 30–32°, neutralisation value 181.5, iodine value 54.6 (Hübl), sterols, m. p. 126.5–128°, and a microcrystalline substance of phenolic character; hydrolysis gave a mixture of oleic, linoleic, palmitic, and stearic acids. Extraction with chloroform gives only a resin (1.9%), from which no crystalline substance could be isolated. Subsequent extraction with alcohol (15.72%) yields raffinose (3%), thus confirming Annett's observation (A., 1917, i, 506), whilst from the mother-liquor is isolated a crystalline, extremely bitter glucoside, *corchorin*,  $C_{22}H_{36}O_8$  (yield 0.4% of dried seeds), m. p. 174–175°,  $[\alpha]_D^{20} +33.4^\circ$  in alcohol, which is probably a cyclic alcohol (hydrolysing to dextrose and a substance, m. p. 114–115°), together with a small quantity of a crystalline substance,  $C_{10}H_{22}O_2$ , m. p. 95–98°, and a resin from which chloroform extracts a further quantity of *corchorin*, and ethyl acetate extracts a substance, m. p. 165–168°. *Corchorin* has saponin-like properties, but it has no hæmolytic action on red blood-corpuscles. It has no bactericidal effect on *B. coli*. J. W. BAKER.

**Composition of the odoriferous compounds of roasted chicory.** T. REICHSTEIN and H. BEITTE (Ber., 1930, 63, [B], 816–826).—Freshly roasted (unfermented) chicory is heated at about 110° with continuous stirring in a high vacuum and the volatile matter is condensed. The following substances have been identified: acetaldehyde, acetone, diacetyl,  $\beta$ -diketopentane, furfuraldehyde, 5-hydroxymethylfurfuraldehyde, maltol, furan, methyl and furfuryl alcohols, carbon dioxide, acetic, pyruvic, lactic, pyromucic, and palmitic acids. Other acids, small quantities of phenols, and a neutral oil await further investigation. Compounds containing nitrogen or sulphur (characteristic of coffee) are absent. The identified substances, regarded mainly as products of the pyrogenic decomposition of carbohydrates, have been identified in coffee with the exception of pyruvic and lactic acids, although wide variation is shown in the relative quantities. Characteristic of chicory is the high content of furfuraldehyde and, particularly, hydroxymethylfurfuraldehyde derived from inulin. H. WREN.

**Lycopene from *Solanum dulcamara*.** L. ZECHMEISTER and L. VON CHOLNOKY (Ber., 1930, 63, [B], 787–790).—The fresh berries are crushed and preserved under alcohol for two days. The undissolved matter is dried and either percolated with carbon disulphide or extracted with ether and then treated with methyl-alcoholic potassium hydroxide. Nearly 60% of the total lycopene is thus obtained crystalline and, since the mother-liquors give a very strong although somewhat blurred lycopene spectrum, it is improbable that subsidiary colouring matters are

present in marked amount. The identity of the lycopene with that derived from *Tamus communis* (this vol., 506) and tomato (Willstätter and Escher, A., 1910, i, 330) is confirmed. H. WREN.

**Orizatoxin.** T. TERUUCHI, C. WADA, and T. OYAMA (Japan. J. Pract. Med., 1928, 16, 825–832).—Evidence is adduced in support of the view that rice which has been hulled and cleaned contains a toxin, “*orizatoxin*,” another poison also insoluble in ethyl alcohol, and a third substance which opposes the action of this poison. *Orizatoxin* is destroyed at 200° in 1 hr., or by alkalis, but is resistant to the action of acids. CHEMICAL ABSTRACTS.

**Toxic constituent of rayless golden-rod.** J. F. COUCH (J. Agric. Res., 1930, 40, 649–658).—The toxic constituent of *Aplopappus heterophyllus* which causes “trembles” of sheep etc. in alkali areas is tremetol,  $C_{16}H_{22}O_3$ , previously isolated from *Eupatorium urticifolium*. The plant loses its toxicity slowly and animals poisoned by it develop a ketosis and excrete acetone. E. HOLMES.

**Chemical composition and enzymes of sugar-cane pollen.** N. L. DUTT and K. V. G. AYYAR (Agric. J. India, 1930, 25, 31–33; cf. Amer. J. Bot., 1921, 8, 471–501).—Diastase and invertase, but not lipase, cytase, or erepsin, have been observed in sugar-cane pollen. Pepsin and trypsin may be present. The pollen examined contained 48.7% to 51.1% of water, 16.25% of starch, 19.49% of sugar, 16.66% of protein, and 6.26% of amino-compounds, calculated on the dry material. E. HOLMES.

**Extinction of light by [solutions of] chromoproteins of algæ.** R. LEMBERG (Biochem. Z., 1930, 219, 255–257).—The results of Svedberg and Katsurai (this vol., 233) concerning the extinction of visible light by solutions of the pigments from algæ are unsatisfactory and do not prove the identity of the pigment from *Porphyræ tenera* with that from *Aphanizomenon Flos aquæ*. There may be some doubt about the identity of the organisms used, and the pigments from these may vary with variations in the environment in which the algæ grow. W. MCCARTNEY.

**Nitrogen fixation by blue-green algæ.** F. E. ALLISON and H. J. MORRIS (Science, 1930, 71, 221–223).—Repeated tests on cultures of the green algæ *Chlamydomonas*, *Chlorella*, and *Scenedesmus* for nitrogen fixation were negative. Pure cultures of blue-green algæ, however, fix gaseous nitrogen when grown on a nitrogen-free medium in sunlight.

L. S. THEOBALD.

**Migration of alkaloids during the germination of seeds and formation of seedlings: *Lupinus mutabilis*.** A. GUILLAUME (Compt. rend., 1930, 190, 1068–1070).—When the seeds of *L. mutabilis* are germinated on wet cotton in the light, there is an initial diminution in the amount of alkaloid in the seedlings. The alkaloid content of the seedlings increases, however, with the development. There is a decrease in the protein content and a small amount of ammonia is formed. The ammonia probably arises by the photo-decomposition of a small amount of the alkaloid which has passed (by osmosis) from the grain to the wet

cotton at the beginning of the germination. When the seeds are germinated in the dark, the seedlings contain more alkaloid and less protein than the original seeds; ammonia is not evolved. H. BURTON.

**Effects of defoliation and root pruning on the chemical composition of sweet-corn kernels.** C. W. CULPEPPER and C. A. MAGOON (*J. Agric. Res.*, 1930, **40**, 575—583).—Defoliation of the plants at the time of "silking" considerably decreased crop yields without markedly affecting the chemical composition of the grain, there being a slight decrease in the contents of acid-hydrolysable matter and total solids varying with the extent of the defoliation. Defoliation 10—15 days after silking, *i.e.*, when grain formation was well in evidence, produced some grain of similar nature to that obtained when defoliation occurred at silking and a proportion of shrivelled grain with low contents of sugar, total solids, and acid-hydrolysable substances. The effect of root pruning was more severe than that of defoliation and the grain produced had high proportions of total solids and acid-hydrolysable matter. A. G. POLLARD.

**Method of investigating gas exchanges of living tissues.** T. A. B. CLARK (*Nature*, 1930, **125**, 492—493).—A method and apparatus for determining simultaneously the carbon dioxide evolved and the oxygen taken up by living tissues while the composition of the surrounding gaseous mixture is kept constant are described. Rapid changes in the rates of gas exchange can be followed. L. S. THEOBALD.

**Apparatus for the study of respiratory quotient and basal metabolism of mice.** A. H. EBELING and R. B. COREY (*J. Exp. Med.*, 1930, **51**, 41—50).—The carbon dioxide produced by the animal is absorbed in 0.05*N*-barium hydroxide which is run into the apparatus to replace oxygen absorbed. E. BOYLAND.

**Sources of error in weights of small muscles frozen in liquid air.** G. GIRAGOSINTZ and J. M. D. OLMSTED (*Amer. J. Physiol.*, 1930, **92**, 414—419).—Frozen muscles lose weight due to evaporation of water when exposed to air. E. BOYLAND.

**Determination of traces of iodine. IV. Iodine in small quantities of thyroid and other tissues.** R. E. REMINGTON, J. F. McCLENDON, H. VON KOLNITZ, and F. B. CULP (*J. Amer. Chem. Soc.*, 1930, **52**, 980—985).—The method previously described (A., 1928, 607) is modified for the rapid micro-determination of iodine in glands. The powdered fat-free material (0.01—0.2 g.) diluted with excess of calcium oxide in a nickel boat is ashed in oxygen by direct contact with an oxygen-gas flame. The vapours are aspirated through dilute sodium sulphite solution. The solution and the washings of the ash are evaporated and fused with sodium hydroxide in a boat. Results for 37 human thyroids and other material are recorded. J. G. A. GRIFFITHS.

**Determination of nitrates and nitrites in biological fluids.** M. WHELAN (*J. Biol. Chem.*, 1930, **86**, 189—197).—The material is treated with

excess of mercuric chloride solution and filtered; the filtrate is mixed with a solution of diphenylbenzidine in sulphuric acid containing sodium chloride and with sulphuric acid, care being taken to avoid rise of temperature; after 1½ hrs. the colour is compared with that developed by a standard solution of potassium nitrate similarly treated. The presence of nitrites is indicated by immediate development of colour on mixing with the reagent. C. R. HARINGTON.

**Determination of reducing sugars by alkaline mercuric solutions.** P. FLEURY and J. MARQUE (*Bull. Soc. Chim. biol.*, 1930, **12**, 58—66).—The method of Baudouin and Lewin (A., 1927, 476) is improved by addition before reduction of a little barium sulphate which assists dissolution of the mercury in the iodine. The method is adapted for macro-determination of dextrose in urine and lactose in milk. Although alkaline mercuric solutions can oxidise not only sugars but also polyalcohols in hot solution, the method gives accurate results for dextrose (provided the exact technique of Baudouin and Lewin is followed) in presence of two to three times its amount of mannitol and up to ten times of sucrose. The determination of dextrose and mannitol in mixtures was attempted. P. W. CLUTTERBUCK.

**Determination of uric acid based on the carbamide produced by fermentation and hydrolysis.** R. FOSSE, A. BRUNEL, and P. DE GRAEVE (*Compt. rend.*, 1930, **190**, 693—695).—The method is based on the degradation of uric acid by the uricase and allantoinase, present in extracts of beef kidney and soya bean, to allantoinic acid, and on the hydrolysis of allantoinic acid by hydrochloric acid to carbamide, 2 mols. of which are produced per mol. of uric acid (*cf.* Fosse and others, A., 1929, 196, 353, 847, 1107; this vol, 250). The carbamide thus produced is determined as xanthylcarbamide. In examining solutions containing less than 0.2 g. of uric acid, this is concentrated by precipitation with mercuric sulphate and regeneration from the precipitate (*cf.* Boivin, A., 1927, 488). In solutions containing carbamide this is first destroyed by treatment with urease. H. A. PIGGOTT.

**Colorimetric determination of the cystine content of proteins.** A. BLANKENSTEIN (*Biochem. Z.*, 1930, **218**, 321—330).—The protein (0.5—1.0 g.) is boiled for 12 hrs. with sulphuric acid (20%; 15—20 c.c.) and the hydrolysate is decolorised with kaolin, which is then filtered off, the filtrate being made up to 50 c.c. To 10 c.c. of the filtrate and to 10 c.c. of a standard cystine solution in 25-c.c. flasks are added successively 5 c.c. of 0.02*N*-potassium cyanide solution and 6 c.c. of ammonia, the flasks are heated at 100° for 15 min. and then cooled rapidly. The solutions are now made up to 25 c.c. with ammonia, 6—8 drops of freshly-prepared 5% sodium nitroprusside solution are added to each, and the colours produced are at once compared in a colorimeter. The standard solution is made by mixing 20 c.c. of a 0.1% solution of cystine in *N*-sulphuric acid, 30 c.c. of 20% (by volume) sulphuric acid, and 50 c.c. of *N*-sulphuric acid. W. MCCARTNEY.



# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

JULY, 1930.

### General, Physical, and Inorganic Chemistry.

**Existence limits of excitation levels of hydrogen atoms in intense electric fields.** H. R. VON TRAUBENBERG, R. GEBAUER, and G. LEWIN (*Naturwiss.*, 1930, 18, 417—418).—An extension of earlier experiments (cf. A., 1929, 963) on the disappearance of  $H_\alpha$  components in intense Stark electric fields to the  $H_\gamma$ ,  $H_\delta$ , and  $H_\epsilon$  components. The field intensities at which the lines first vanish are now determined, and agree with theoretical calculations (cf. Lanczos, this vol., 652). A. B. D. CASSIE.

**Gas discharge in hydrogen. II.** E. LAU and O. REICHENHEIM (*Ann. Physik*, 1930, [v], 5, 296—304; cf. this vol., 123).—The dependence of the production of the blue striæ in the hydrogen discharge on the concentration of admixed gas, pressure, current strength, and form of tube was investigated. The observations lead to a satisfactory method for determining the excitation potentials of other gases. The excitation potential for the continuous spectrum, and the effect of the mixture of foreign gases on the spectral intensity distribution were also discussed. All the experiments were in agreement with the theory that the continuous spectrum occurs for the dissociation  $H_2 \rightarrow 2H$  by electronic collision, and the excitation potential required for this is below that required for the excitation of the multiple line spectrum of hydrogen. A. J. MEE.

**Structure of the lithium line 6708.** A. BOGROS (*Compt. rend.*, 1930, 190, 1185—1187).—The author's atomic jet method (A., 1926, 874) has been used to confirm the existence of a third component of less intensity and greater wave-length than the two principal components corresponding with the sodium doublet  $D_1D_2$  (cf. Schüller, A., 1927, 489). The interval between the two principal components ( $2S-2P_{1/2}$ ) and ( $2S-2P_{3/2}$ ) of  $Li^7$  is 0.150 Å., and that between the satellite ( $2S-2P_{1/2}$  of  $Li^6$ ) and the former component is 0.156 Å. J. GRANT.

**Spectra of trebly-ionised oxygen (O IV) and trebly-ionised nitrogen (N IV).** L. J. FREEMAN (*Proc. Roy. Soc.*, 1930, A, 127, 330—338).—The spectrum of trebly-ionised oxygen has been photographed in the region 7000—1250 Å. by using strongly-condensed discharges in vacuum tubes containing oxygen, and about 50 lines have been newly classified. The  $3s^2S$ ,  $3p^2P$ ,  $3d^2D$  terms of the doublet system and the  $3s^1$ ,  $3p^1$ , and  $3d^1$  terms of the quadruplet system are identified from their combinations occurring in the visible and near ultra-violet regions. In the spectrum of trebly-ionised nitrogen, only the  $3s^3S$ ,  $3p^3P$ , and  $3d^3D$  terms have been identified with

certainty, the  $S$  and  $P$  terms combining to give a triplet at 3484 Å., and the  $P$  and  $D$  terms a group at 7123 Å. Provisional classifications of four other lines are given. L. L. BIRCUMSHAW.

**Resonance spectrum of sulphur vapour.** P. SWINGS (*Z. Physik*, 1930, 61, 681—699, and *Compt. rend.*, 1930, 190, 1010—1011).—By means of a new method, allowing very intense illumination, the resonance spectrum excited in sulphur vapour by the mercury arc has been investigated. The series excited by the lines 3132, 3126, 3022, 2298, and 2894 Å. have been measured, and four series of rotation doublets, excited by the lines 3655, 3132, 3126, and 2698 Å., have been discovered. The rotational quantum numbers for these series can be calculated, and it is shown that the apparently complicated structure of the  $S_2$  resonance spectrum is due to the superposition of several doublet series. The relative intensities of the components of the doublets have been investigated at various temperatures and pressures, and it is shown that the ratio of probability of the emission of the components of the doublets is a function of density and temperature. E. B. ROBERTSON.

**Zeeman effect in the spark spectrum of argon (A II).** II. C. J. BAKKER and T. L. DE BRUIN (*Z. Physik*, 1930, 62, 32—42).—Previous work (cf. A., 1929, 3, 364) has been completed. With the aid of the Zeeman effect the  $g$  values (magnetic splitting factor) of the  $4s$ ,  $4p$  ( $^3P$ ,  $^1D$ ,  $^1S$ ) groups have been estimated and tabulated. The values and differences for  $4s$  and  $4p$  electrons are given; very good agreement is obtained between observed  $g$  values and those deduced from Landé's formula. The law of summation of the  $g$  terms has been established for these groups. The dissymmetry of the Zeeman effect of the lines of certain multiplets is explained by the partial Paschen-Back effect. W. R. ANGUS.

**Effect of gas pressure on the colour of halogen vapours.** A. SHEARER and R. WRIGHT (*J.C.S.*, 1930, 1201—1202; cf. Wright and McGregor, A., 1929, 977).—Absorption spectrum photographs were taken of iodine vapour at pressures from 0 to 2 atm.; a deepening of colour was produced with increase of pressure. The presence of air with bromine vapour produced a slight increase of absorption. The ultra-violet absorption spectrum of chlorine, alone, at 0.5 atm., and in presence of air, was photographed. No change in absorption was found. N. M. BIGH.

**Arc spectrum of bromine and its structure.** C. C. KIESS and T. L. DE BRUIN (*Bur. Stand. J. Res.*,

1930, 4, 667—692).—A Geissler tube containing bromine at pressures ranging from 10 to 20 mm. emits the arc spectrum characteristic of the neutral atom when excited by the uncondensed discharge from a high-voltage transformer. This spectrum was photographed from the ultra-violet to beyond 9300 Å. in the infra-red. Of the 300 lines of Br I which were recorded 60% have been classified as combinations between terms of the doublet and quadruplet systems. The terms arise from adding *s*, *p*, and *d* electrons to the basic and metastable terms  $^3P$ ,  $^1D$ , and  $^1S$  of Br II. Eleven sets of series forming terms have been found. From these the distance between  $^2P_2$ , the basic term of Br I, and  $^3P_2$ , the basic term of Br II, has been calculated as 95,550  $\text{cm}^{-1}$ , which gives an ionisation potential of 11.80 volts for the neutral bromine atom.

W. E. DOWNEY.

**Absorption spectrum of selenium vapour.** (FRL.) M. MORACZEVSKA (Z. Physik, 1930, 62, 270—278).—The investigation of the absorption spectrum of selenium vapour has been extended at each end of Rosen's limits (A., 1927, 608) from 4179 to 4638 Å. and from 3238 to 2099 Å. The results are given for an examination at high temperatures and pressures. The values for the visible region fit Rosen's scheme. In the ultra-violet two new regions of absorption were discovered. The first group of bands extends from 3150 to 2758 Å. with a frequency separation of approximately 230  $\text{cm}^{-1}$ . These bands are similar to the series already recorded, but cannot be represented as a continuation; instead they are arranged as a series due to another electronic state of selenium. The second group of bands extends from 2295 to 2099 Å. with a frequency separation of 360  $\text{cm}^{-1}$ ; the arrangement of the bands in this group is discussed.

W. R. ANGUS.

**Measurement of the spark spectrum of iodine.** L. BLOCH and E. BLOCH (Z. Physik, 1930, 61, 873).—The authors direct attention to a paper which they published almost simultaneously with that of Kerris (this vol., 389) and indicate the good agreement between the two sets of results.

W. R. ANGUS.

**Measurement of spark spectrum of iodine.** W. KERRIS (Z. Physik, 1930, 61, 874).—A reply to Bloch and Bloch (see preceding abstract).

W. R. ANGUS.

**Iodine spectra of feeble excitation.** G. BALASSE and G. GALET (Bull. Acad. roy. Belg., 1929, [v], 15, 913—927).—A study has been made of the spectra of iodine vapour, excited by an electrodeless high-frequency discharge (approx. 70 m.) at temperatures up to 800°. Maxima, degraded regularly towards the violet, at 3430 and 4770 Å., attributed respectively to the iodine atom and molecule, were observed at ordinary temperatures. As the temperature was raised the maximum due to the molecule of iodine disappeared in the neighbourhood of 600°. By cooling one portion of the tube to 0° and raising the temperature of the rest to 700° it was found that both maxima were absent at temperatures above 410°.

F. G. TRYHORN.

**New line in the absorption spectrum of samarium.** P. W. SELWOOD (J. Amer. Chem. Soc., 1930, 52, 1937—1938; cf. A., 1929, 119).—A faint line at

5960 Å. has been observed in the absorption spectrum of samarium nitrate solution. J. G. A. GRIFFITHS.

**Absorption spectra of vapours of bismuth and antimony.** New terms in the arc spectra of both elements. F. CHAROLA (Physikal. Z., 1930, 31, 457—463).—The absorption spectra of bismuth and antimony vapours have been examined at temperatures varying between 800° and 1500° for bismuth and between 1000° and 2300° for antimony. The results agree with those of previous workers. New terms in the arc spectra of both elements have been established, and by their help a number of hitherto unplaced lines have been classified.

F. L. USHER.

**Voltage-intensity relations in the mercury arc spectrum.** P. B. TAYLOR (J. Franklin Inst., 1929, 207, 95—106).—The photographic intensities of 29 lines of the mercury arc spectrum have been measured as a function of the potential gradient in the arc. The mercury arc was maintained in a quartz tube 1 cm. diam. with an electrode spacing of 16 cm.; a constant direct current of 4 amp. was used, and the electrode *P.D.* was varied from 23 to 118 volts. The measurement of the potential gradient in the arc is not described. For values of this gradient less than 1.5 volts per cm. very considerable variations in the relative intensities are recorded; when the gradient exceeds this value the intensities when plotted against a logarithmic scale of gradient lie on approximately parallel straight lines.

R. W. LUNT.

**Excitation function of mercury lines.** W. SCHAFFERNICHT (Z. Physik, 1930, 62, 106—142; cf. this vol., 392).—The method of opposed fields was used to give electrons of known velocity between 7 and 500 volts. The variation with electron velocity of the intensity of some seventy lines emitted by excited mercury atoms was studied photographically. Triplet lines all show one sharp maximum just beyond the excitation potential of the upper level. Singlet lines show one broad maximum much above the optical excitation potential. The  $^1S_0$  and  $^3D_2$  levels are exceptions, both showing two maxima; one maximum is characteristic of a triplet term, the other of a singlet term. Generally, lines with the same upper term have similar intensity-electron velocity curves. This accords with the hypothesis that transition probabilities are independent of the mode of excitation of the upper level. The absence of second maxima shows excitation, chiefly one of electron collision, and not due to electron return from still higher levels. Variation in pressure between 1 and  $4 \times 10^{-7}$  mm., and variation of current density between  $10^{-4}$  and  $10^{-2}$  amp., do not influence these curves. Curves are also given for Hg II, III, and IV lines. The relative intensity of neighbouring lines in relation to electron velocity was investigated. The energy distributions in the mercury lamp and electron tube spectra are compared.

A. B. D. CASSIDY.

**Stark effect.** J. S. FOSTER (J. Franklin Inst., 1930, 209, 585—624).—Theoretical. A general survey of the Stark effect is given. Experimental methods for the generation and investigation of the effect and its theoretical interpretation are described and reviewed for hydrogen, ortho- and par-helium,

and other complex spectra. The Stark and Zeeman effects are compared; the Paschen-Back analogue, and the effect of parallel and crossed magnetic and electric fields on the helium spectrum, are discussed.

N. M. BLIGH.

**Theory of the quadratic Stark effect of doublets and triplets.** A. WOLF (Z. Physik, 1930, 61, 619—625).—The fine structure of regular doublets and triplets in intense electric fields is investigated by means of the Pauli-Darwin equation. When the field is strong enough, the Stark effect has essentially two parts. One is a displacement proportional to the square of the field. The other arises from electron spin, and consists of a fine structure that overlays the displacement, and is, in the limit, independent of the field intensity.

A. B. D. CASSIE.

**Coupling broadening of spectral lines.** L. SCHUTZ-MENSING (Z. Physik, 1930, 61, 655—659).—A more exact calculation of broadening due to the reciprocal action of atoms, based on wave mechanics, gives the line width directly proportional to the pressure, and not proportional to its square root, as Frenkel (this vol., 126) has shown.

A. B. D. CASSIE.

**Behaviour of strongly excited atoms in an electric field.** H. KUHN (Z. Physik, 1930, 61, 805—815).—Changes in the absorption lines and limits of potassium subjected to an electric field of 1–300 volts per centimetre were investigated. Components due to absorption of light the electric vector of which is parallel to the field suddenly disappear with increasing quantum number, whilst the perpendicular components split up to give new lines at the centre of the interval between the original lines. The original principal series disappears with increasing frequency, but the new series remains. This new series is attributed to the forbidden transition  $1S \rightarrow nD$ . The change from discrete to continuous absorption is greater than theory predicts because of ionic fields (cf. A., 1928, 807).

A. B. D. CASSIE.

**Intensities in band spectra.** E. HUTCHISSON (Nature, 1930, 125, 746).—The intensities of the lines associated with vibrational electronic transitions can be calculated and expressed in terms of the change in separation of the nuclei during the transition; in the case of the alkali metal molecule these calculated values are in good agreement with the experimental.

L. S. THEOBALD.

**Double rotation terms from singlet  $\Sigma$  terms.** W. WEIZEL (Z. Physik, 1930, 61, 602—603).— $\Sigma$  and  $\Sigma'$  terms may have the same electron energies, but rotation separates the two and gives two rotation series, analogous to the  $A$  and  $B$  sub-levels of  $\pi$  and  $\Delta$  terms. A possible application is to the satellites of the OH bands.

A. B. D. CASSIE.

**Significance of some predissociation phenomena in band spectra.** G. STENVINKEL (Z. Physik, 1930, 62, 201—207).—The intensity of rotation emission lines is usually proportional to the weight of each rotation state multiplied by the Boltzmann temperature distribution factor. If, however, discontinuous rotation states of the upper electronic level overlay continuous states of a lower

level, this intensity distribution may no longer hold (cf. Herzberg, following abstract). Predissociation then appears in emission. Increasing pressure tends to restore the temperature distribution, and so increases the observed number of rotation lines (cf. this vol., 264).

A. B. D. CASSIE.

**The significance of diffuse molecular spectra. (Predissociation.)** G. HERZBERG (Z. Physik, 1930, 61, 604—614).—Diffuse molecular spectra are not due to dissociation when the energy of rotational degrees of freedom exceeds some definite value, but may be explained by the presence of a third electronic energy level (cf. A., 1928, 569), which cannot combine in transitions with the ground level. A molecule, excited to this third level, may dissociate before its total energy (electronic and vibrational) equals that of possible vibrational levels in the upper state to which transitions from the ground state take it; i.e., a continuous and a discontinuous series of spectral terms exist in the same range of energy, and quantum mechanics predicts possible radiationless transitions between such series. Diffuse spectra may therefore be explained on the supposition of a double transition that appears as an absorption from the ground state to a dissociated state, but the apparent energy of dissociation is not the energy of dissociation in the upper electronic state. Radiationless transitions occur only when the average life in the upper excited state is less than the period of rotation of the molecule. When the average life exceeds this, discrete absorption reappears (cf. Rosen, A., 1929, 119).

A. B. D. CASSIE.

**Electronic Raman effect.** A. CARRELLI (Z. Physik, 1930, 61, 632—639).—An expression is derived for the intensity of a Raman line due to an electronic transition during scattering of X-radiation. The expression shows that success in obtaining these lines is most likely when: (i) the scattering substance has absorption lines in the X-ray region; (ii) it has small atomic number; (iii) the primary beam expels Compton electrons with little recoil energy compared with the electron's binding energy; (iv) the direction of observed scattered radiation is such that the recoil energy is not too great.

A. B. D. CASSIE.

**Fermi intensity formula for the principal series doublets of the alkalis.** S. SAMBURSKY (Z. Physik, 1930, 61, 660—662).—The Fermi formula (cf. this vol., 388) is compared with experimental results.

A. B. D. CASSIE.

**Predissociation of diatomic molecules from high rotational states.** D. S. VILLARS and E. U. CONDON (Physical Rev., 1930, [ii], 35, 1028—1032).—Theoretical. Explanations are discussed of the instability of molecules in high rotational states as observed in mercury and aluminium hydrides, and shown by the sudden termination of certain sets of rotational levels and the broadening of the last few levels. From a comparison of the rotational vibrational curves (cf. Morse, A., 1929, 975) and the quantum mechanical curves for radioactive disintegration it is shown that the quantum mechanical explanation is closely analogous to that of the radioactive disintegration of atomic nuclei (cf. Gurney and Condon, A., 1929, 374). The heat of dissociation

of aluminium hydride from its normal state is estimated to be 3.07 volts. N. M. BLIGH.

**Cathode of an arc drawn in vacuum.** R. TANBERG (Physical Rev., 1930, [ii], 35, 1080—1089; cf. A., 1929, 1121).—The velocity of the vapour, contributed only by the cathode for the maintenance of an electric arc under very low gas pressure, was determined by measuring the force of reaction of the vapour on the cathode and the rate of vaporisation of the cathode material, and by determining the force exerted by the vapour on a vane suspended in front of the cathode spot and the rate of vapour condensation on the vane. The velocity by both methods was of the order  $16 \times 10^5$  cm./sec., leading to a calculated temperature of 500,000° Abs. at the cathode spot. N. M. BLIGH.

**Highly attenuated sodium flames. Sodium-bromine and sodium-mercuric bromide [flame].** H. OOTUKA (Z. physikal. Chem., 1930, B, 7, 407—421; cf. A., 1928, 1339).—An extension and confirmation of earlier work on similar flames of sodium with chlorine, iodine, and mercuric chloride. The two reactions are shown by the three tests previously described to have different mechanisms: the sodium-bromine flame belongs to type I and is similar to the sodium-chlorine flame, whilst the sodium-mercuric bromide flame (like sodium-mercuric chloride) shows the characteristics of type II. The decrease in intensity of the light caused by superheating the reaction zone in the first reaction gives a measure of the heat of dissociation of the sodium molecule. The result so obtained is  $19 \pm 1$  kg.-cal. compared with  $18 \pm 2$  kg.-cal. for the sodium-chlorine flame, in agreement with the value deduced from spectroscopic measurements. The "true light emission" is 0.5—1. F. L. USHER.

**Highly attenuated flames of potassium vapour with halogens.** H. OOTUKA (Z. physikal. Chem., 1930, B, 7, 422—438; cf. preceding abstract).—By the usual experimental tests the flame is shown to have the characteristics of type I, and the luminosity of the reaction is due to decomposition of the molecule of alkali vapour. In order to make the flame visible a known amount (about 7%) of sodium vapour was mixed with the potassium vapour. Experiments on the superheating of the reaction zone lead to a value of the heat of dissociation of the effective alkali vapour molecule (either  $K_2$  or, more probably,  $NaK$ ) of 12.5 kg.-cal. A mechanism in agreement with these results is: (1) primary reaction,  $K + Cl_2 \rightarrow KCl + Cl$ ; (2) secondary reactions,  $K_2 + Cl \rightarrow KCl^* + K$ ,  $KCl^* + Na \rightarrow KCl + Na^*$ . F. L. USHER.

**Effect of a nuclear spin on the optical spectra.** III. J. HARGREAVES (Proc. Roy. Soc., 1930, A, 127, 407—416).—In order to describe the multiple energy levels correctly, the interaction energy of the nuclear and electron spins must be determined, in addition to the energy increments previously calculated (A., 1929, 972; this vol., 652). This has been carried out for the cases  $i_n = 1/2, 1, 3/2$ , and  $9/2$ . For the  $p_{1/2}$  levels the interaction energy of the two spins is found to be equal to that of the nuclear spin and orbital momentum, whilst for the  $p_{3/2}$  levels the ratio is  $-1/5$ . By making certain

simple assumptions the results are brought into line with those obtained by Jackson in the case of caesium (A., 1929, 1). A simple description is given of the hyperfine structure of the Zeeman effect in strong fields, and the energy levels of the multiplets are calculated. The results agree well with Back and Goudsmidt's observations for bismuth (A., 1929, 1353), and confirm the validity of the empirical equations given in previous papers (*loc. cit.*).

L. L. BIRCUMSHAW.

**Nature of activation heats. Calculation of heat of activation from band spectra data.** D. S. VILLARS (J. Amer. Chem. Soc., 1930, 52, 1733—1741; cf. Langer, A., 1929, 983).—Theoretical. The concept of degeneracy is extended to systems of atoms. Two atoms, in different molecules, may be expected to interchange their allegiance only if the energy of the second state is equal to that of the first, and therefore in a chemical reaction the sum of the potential energies of the colliding molecules plus the heat of reaction must equal the sum of the potential energies which the resulting molecules would have if their respective nuclei remained stationary during the change of allegiance. Reaction is most probable when the total kinetic energy of translation and rotation is unchanged by the collision. The energy of activation is the sum of the vibrational energies of the colliding molecules plus the energy of repulsion at the collision distance.

Calculations based on these principles are applied to the decomposition of hydrogen iodide.

J. G. A. GRIFFITHS.

**Photographic study of the solar spectrum in the region  $\lambda$  10,000—11,000 Å.** H. D. BABCOCK (Phot. J., 1930, 70, 126—131).—Neocyanine-sensitised plates show a maximum sensitivity at  $\lambda$  8300 Å., but retain a diminishing sensitivity far beyond this region. A special filter consisting of a modified form of neocyanine dissolved in chloroform (water and alcohol are unsuitable since they are partly opaque in the region of  $\lambda$  11,000 Å.) was used to absorb the wave-lengths between  $\lambda$  8000 and  $\lambda$  9000, but certain precautions must be taken, as the absorption of this filter is affected on exposure to sunlight. The position and approximate intensities of more than 350 lines have been determined between  $\lambda$  9867 and  $\lambda$  11,634, but those of solar and atmospheric origin have not yet been distinguished. J. W. GLASSETT.

**Spectroscopic notes.** K. BURNS (Pub. Allegheny Obs. Univ. Pittsburgh, 1930, 8, 1—14).—Corrections for reducing Bonn's iron wave-lengths to the international Ångström scale are given. Wave-lengths for the following are recorded: iron as impurity in copper and carbon arcs in air, titanium in air and vacuum arcs, calcium in vacuum arcs, manganese and chromium present as impurities in iron vacuum arcs.

CHEMICAL ABSTRACTS.

**Arrangement for the inspection of photographic plates of line spectra.** W. LINNIK (Z. Physik, 1930, 61, 700—702).—An attachment to a microscope for the examination of the photographs of line spectra taken on highly sensitive plates where, owing to the large grain size, the lines are not clearly defined consists of two acute prisms fixed to the

tube holding the eye-piece, from which the objective is suspended by hooks. The objective is set vibrating relative to the eye-piece and the table holding the photographic plate is rotated until the lines of the spectrum are parallel to the direction of swing, when the image becomes very much better defined.

H. A. JAHN.

**Fine structure of  $K$ -absorption limit of silicon oxide.** G. B. DEODHAR (Nature, 1930, 125, 777—778).—The fine structure of the  $K$ -absorption limit for quartz has been obtained by using the analysing quartz crystal itself as the absorber with an anticathode of tungsten operated at a high current density. A photographic record is reproduced.

L. S. THEOBALD.

**Scattering of X-rays by bound electrons.** B. B. RAY (Nature, 1930, 125, 746).—A part of monochromatic X-rays undergoes a change in frequency and appears on the longer wave-length side of the primary radiation in passing through carbon. The  $K\alpha$  radiation of copper in passing through carbon gave rise to a new diffuse band of wave-length 1592X ( $\nu/R=572$ ). The origin of the line may be explained by the fact that the  $K\alpha$  radiation loses a part of its energy equal to that of removing the electron from the  $K$ -shell either to the optical level or to infinity. Nickel  $K\alpha$  radiation produces a similar effect on passing through carbon.

L. S. THEOBALD.

**Polarised and directed X-radiation from a crystal.** J. STARK (Nature, 1930, 125, 745).—Theoretical.

L. S. THEOBALD.

**New phenomena in X-ray scattering.** J. A. GRAY and W. H. ZINN (Canad. J. Res., 1930, 2, 291—293).—The intensity ( $I_\phi$ ) of the radiation produced by the scattering of X-rays of average wave-lengths 0.7 and 1.9 Å. by various samples of charcoal at various angles ( $\phi$ ) has been measured, and  $I_\phi/\phi$  curves have been plotted. With blood charcoal the intensity increases abnormally for angles less than  $5^\circ$  (e.g., for  $\lambda=1.9$  Å.  $I_{0.36}=56,000 \times I_{99}$ ), and is similar to the scattering of  $\alpha$ -particles. The results point to an approximate relation  $I_\phi=\lambda^3/\phi^4$ . Other varieties of charcoal show somewhat similar but less marked peculiarities.

C. A. SILBERRAD.

**Scattering of radiation by bound and free electrons according to Dirac's relativity mechanics.** I. WALLER (Z. Physik, 1930, 61, 837—851).—Mathematical. The significance of negative energy in relation to scattering is, in particular, discussed. Both negative and positive energy levels are required for deduction of the intensity of scattered radiation.

A. B. D. CASSIE.

**Scattering power of the carbon atom in diamond for X-rays.** G. W. BRINDLEY (Phil. Mag., 1930, [vii], 9, 204—208).—It is shown that the curve of the scattering power of the carbon atom for X-rays calculated by the method previously described (A., 1929, 973) is in close agreement with the experimental results of Armstrong (*ibid.*, 1354) for the carbon atom in diamond. This offers confirmation of the previous conclusion that beyond  $\sin \theta=0.3$  the scattering depends almost entirely on the  $K$  electrons. At large values of  $\sin \theta$  the experimental values of the

scattering factor tend to be less than the theoretical. It is suggested that this divergence arises from the small amplitude of vibration of the carbon atoms in diamond, which whilst having little effect on the spectra of lower order will affect the higher order spectra. A further explanation is based on the evidence for the distortion of the  $L$  electron shell, with the result that between the atomic planes there is sufficient density of charge to scatter radiation appreciably out of phase with that scattered by the charge near the planes.

A. E. MITCHELL.

**Ionisation in nitrogen.** J. H. BRUCE (Nature, 1930, 125, 780).—Experiments on corona discharges in purified nitrogen at low pressures show that the mobility of the negative carriers is much lower than that found for electrons by Townsend and Bailey (A., 1922, ii, 43); the carriers cannot all be electronic.

L. S. THEOBALD.

**Sparking potential of pure gases at low pressures.** K. ZUBER (Z. Physik, 1930, 61, 750—766).—Theoretical. The sparking potential of a pure gas can be expressed in terms of the gas pressure, and the minimum sparking potential and corresponding pressure, for pressures between this critical pressure and one seven times its value. Formulae are given for the mean lag of discharge behind potential. The dependence on the gas, of the minimum sparking potential, and of the corresponding product of pressure times the electrode separation is discussed. Positive ions are probably formed only near the cathode.

A. B. D. CASSIE.

**Measurements of the excitation potential for spectral lines and their application to the many line spectrum of hydrogen.** W. FINKELNBURG, E. LAU, and O. REICHENHEIM (Z. Physik, 1930, 61, 782—791; cf. this vol., 267).—The potential gradient at the Faraday dark space limit of the anode column gives electrons of increasing velocity. The possible excited level of an atom or ion is therefore higher as it approaches the anode. The spectrometer slit is placed parallel to the discharge, and this edge of the anode column is focussed on the slit. The length of any spectral line then gives a measure of the emitter's initial excited state. The Faraday dark space must be fully developed to give electrons of small initial velocity, and to give a gradual increase in velocity. Mercury vapour increases the last effect in a discharge through hydrogen. A graph of the excitation potential against spectral line length was plotted from known hydrogen lines. The possible error is 0.1 volt. This graph was then used to give the excitation levels emitting some 40 hitherto unarranged lines in the  $H_2$  spectrum. The initial levels have excitation potentials of 13.85 and 14.55 volts, belonging to levels of total quantum number three and four, respectively. The final level is 11.8 volts above the normal level, and has probably a total quantum number two.

A. B. D. CASSIE.

**Ionisation formula and the new statistics.** S. CHANDRASEKHAR (Phil. Mag., 1930, [vii], 9, 292—299).—A modification of the Saha ionisation formula has been obtained by the application of Fermi-Dirac statistics to the degeneracy of the electrons. The modified formula indicates that under conditions

existing in the interior of dwarf stars the degree of ionisation is zero. The bearing of this result on the theory of dwarf stars is discussed.

A. E. MITCHELL.

**Determination of electron distributions from measurements of scattered X-rays.** A. H. COMPTON (Physical Rev., 1930, [ii], 35, 925–938).—Theoretical. An expression is derived for the radial distribution of the electrons in an atom, assuming that they have random orientation, and can be evaluated from observed intensities of the scattered X-rays for different wave-lengths and angles. Barrett's experimental data for the scattering of X-rays by helium (cf. A., 1928, 939) are analysed by the new method, and give results in good agreement with those calculated by Pauling for the distribution of the electrons in the atom (cf. A., 1927, 394) on the basis of wave mechanics.

N. M. BLIGH.

**Secondary electrons from contaminated surfaces.** P. L. COPELAND (Physical Rev., 1930, [ii], 35, 982–988).—The fields in the neighbourhood of cold metallic surfaces, clean and contaminated, were investigated, using currents obtained by reflexion and secondary emission of electrons at the surface. It was found that strong fields are set up near the contaminated surface and retard the escape of reflected electrons; in extreme cases of oil contamination the impurities form an insulating film which breaks down (cf. Watson and Menon, B., 1929, 361) at a critical value of the applied field varying with the energy of the incident electrons. The bearing of the results on suggested interpretations of the effect is discussed.

N. M. BLIGH.

**Electron diffraction at non-metallic uni-crystals.** M. VON LAUE and E. RUPF (Ann. Physik, 1930, [v], 4, 1097–1120; cf. this vol., 6).—Experiments previously described have been repeated and extended. The crystals used were sodium chloride (natural and synthetic), potassium chloride, potassium bromide, lead iodide, thallium chloride, lithium fluoride, iron pyrites, galena, fluorite, cuprous iodide, and zinc blende. The inner potentials for these crystals are given at temperatures from 20° to 370°. As far as these experiments go there is no difference as regards electron diffraction between different surfaces of the same crystal. It is pointed out that the inner potential of a single crystal is not necessarily the true value for the substance.

A. J. MEE.

**Dynamics of edge layers of a crystal of sodium chloride type.** M. VON LAUE (Ann. Physik, 1930, [v], 4, 1121–1126; cf. preceding abstract).—A theoretical discussion connected with that on the diffraction of electrons at crystals.

A. J. MEE.

**Diffraction of electrons. Electronic analysis.** M. PONTE (Ann. Physique, 1930, [x], 13, 395–452; cf. A., 1929, 367, 494).—A short survey is given of the de Broglie electron wave and the experimental investigation of electron diffraction by crystals. An apparatus is described employing an incandescent tungsten filament cathode as a source of electrons which are diffracted by crystalline powders in thin deposits on threads or metallic diaphragms. Results are given for the diffraction of 7–17,000-volt electrons by powdered oxides of magnesium, cadmium, and

zinc; de Broglie's law is verified and lattice structures are determined. The method is applied to the study of thin gold leaf, surface oxidation of brass, and a smoked plate.

N. M. BLIGH.

**Comparison of protons and electrons in the excitation of X-radiation by impact.** H. A. BARTON (J. Franklin Inst., 1930, 209, 1–19).—From measurements of the X-radiation emitted by a copper target due to the impact of beams of electrons and of protons of known number and energy it is shown that the relative efficiency of protons is small; a preliminary experiment gave for the ratio of electron/proton efficiency 740, and two later and more carefully controlled experiments gave 237,000 and 6400, respectively.

R. W. LUNT.

**Amplitude of vibration of ions in the crystals sodium chloride and fluoride, lithium fluoride, and potassium chloride.** G. W. BRINDLEY (Phil. Mag., 1930, [vii], 9, 193–203).—The dependence of the intensity of reflexion of X-rays on the thermal vibration and charge distribution of the scattering centres in a crystal is discussed. It is shown that the experimental work of James, Waller, and others on crystals of the above halides supports the assumption that the charge distribution in an ion at rest in a crystal is given approximately by Hartree's method (A., 1928, 216) of calculation of the charge distribution in a free ion. Experimental X-ray scattering curves for the ions Na<sup>+</sup>, Li<sup>+</sup>, Cl<sup>−</sup>, and F<sup>−</sup> at the ordinary temperature are compared with the corresponding theoretical curves for the ions at rest and the comparison is used to estimate the amplitudes of vibration of the ions at the ordinary temperature.

A. E. MITCHELL.

**Electron distribution of magnesium oxide.** E. O. WOLLAN (Physical Rev., 1930, [ii], 35, 1019–1027).—Using Havighurst's method (cf. A., 1927, 95, 191) the intensity of X-rays reflected from powdered crystals of magnesium oxide was measured up to angles of 45°. Structure factor (*F*) curves were plotted, and using the values of *F* as coefficients in Compton's Fourier series, the radial electron distribution for the atoms of magnesium and oxygen was determined. The results indicate a non-polar rather than a polar form for crystals of the magnesium oxide type. The electron distribution curves are similar to those for sodium chloride and fluoride.

N. M. BLIGH.

**Electron and radiation.** R. D. KLEEMAN (Science, 1930, 71, 340–341).—Theoretical. The external field of an electron decreases with an increase of its internal energy.

L. S. THEOBALD.

**Liberation of electrons from metal surfaces by positive ions.** I. Experimental. M. L. E. OLIPHANT. II. Theoretical. M. L. E. OLIPHANT and P. B. MOON (Proc. Roy. Soc., 1930, A, 127, 373–387, 388–406).—I. A description of experiments carried out to determine the precise nature of the reaction taking place between He<sup>+</sup> ions, of energy up to about 1000 volts, and a metal surface (molybdenum or nickel). A method is described, based on the Langmuir "probe" theory, for obtaining a homogeneous beam of He<sup>+</sup> ions of fair intensity. Two methods of examining the emitted electrons were



employed, the results obtained by a retarding potential method being confirmed by experiments, using magnetic analysis of the velocity distribution. Curves are reproduced showing the variation of the total electron emission with the energy of the positive ions, for a cold and a red-hot molybdenum target; the effect of variation of the angle of incidence of the bombarding ions; and the energy distribution of the secondary electrons under varying conditions of the target surface and for a large range of energy of the incident ions. With a cold target, the velocity distribution curve resembles that found for the electrons liberated by metastable atoms of helium, and the form of the curve is practically independent of the velocity of the bombarding ions over the range 120 to 1000 volts. With a gas-free target, the curve exhibits a number of maxima in the same position for nickel, molybdenum, and tungsten targets. The total number of electrons ejected is smaller than for a gas-covered surface, but the relative number possessing the higher energies increases considerably. Experimental curves are recorded which show the velocity distribution among the electrons ejected from various surfaces by singly-charged potassium ions from a thermionic source.

II. The process of electron capture by positive ions at a metal surface and the emission of electrons which occurs as a secondary phenomenon are considered. A critical *résumé* is given of existing theories regarding electrical conditions near a metal surface. A discussion of the origin and form of the surface potential barrier leads to the conclusion that the greater part of the barrier is due to "space-charge," the portion which occurs furthest from the surface being due to "image-force." Calculations are made of the auto-electronic emission from a metallic surface under the influence of the electric field of an approaching positive ion. Most slow ions will probably be neutralised in this manner while still several atom-diameters from the surface, but faster ions have an increasing chance of reaching the metal before capturing an electron. A more correct treatment is suggested in which the process is regarded as the transition through the potential barrier of an electron of given energy, from the metal to a state of equal energy associated with the ion. The results are applied to an explanation of the mechanism of secondary electron emission, and the theory is found to be in good agreement with the observed energy distribution of secondary electrons produced by ions of various kinds and at various velocities.

L. L. BIRCHUMSHAW.

Variation of the number of free electrons in metals with temperature. H. MARGENAU (Physical Z., 1930, 31, 540—546).—Mathematical. Sommerfeld's theory of electrical and thermal conductivity of metals depends on the artificial assumption that at every temperature each atom contributes one free electron. The quantum statistical equilibrium of electrons, ions, and atoms in a metal is determined by Fowler's method. This shows the number of free electrons to have zero temperature coefficient, and so avoids Sommerfeld's assumption. A. B. D. CASSIE.

Reflexion of positive ions by crystals. A. J. DEMPSTER (Nature, 1930, 125, 741).—Different

samples of calcite show large differences in reflecting power for hydrogen positive rays. Reflected rays have also been obtained with a diamond, but none was obtained with rock salt, galena, or magnetite. The strongest parts of the reflexion patterns are produced by rays having energies corresponding with more than 6000 volts. Hydrogen molecules, tri-atomic hydrogen molecules, heavier ions, probably of oxygen, as well as the hydrogen atoms previously reported (this vol., 129) are all present in the reflected pattern. Small changes in the angle of incidence produce a regular series of changes in the direction of the deflected rays.

L. S. THEOBALD.

#### Velocities of ions in the cathode dark space.

K. G. EMBLEUS (Proc. Roy. Irish Acad., 1930, 39, A, 49—57).—Theoretical. In a glow discharge of a cold cathode bombarded by positive ions electrons are liberated for the maintenance of the discharge, and some disintegration of the cathode takes place. Secondary electron emission and sputtering depend on the velocities of the positive ions. The general evidence of investigations and existing data on the distribution of velocities is discussed. The information from positive rays is considered with regard to the ray parabolas, the Doppler effect in the light emitted in the line of motion of the ions, and the current carried to an auxiliary electrode in a retarding field. The distribution of velocities at the cathode is calculated for certain conditions of discharge, and the effect of the primary dark space and cathode glow, and the phenomenon of sputtering are discussed.

N. M. BLIGH.

Mobility of ions in ion-rays. W. FROHBERG (Ann. Physik, 1930, [v], 5, 59—72).—Koether's experiments (cf. A., 1927, 397) were repeated with the upper plate as source. This avoids errors due to convection currents, which have given Koether too high values for the mobility. Mobility increases with the frequency of alternations in potential. This may be due to ions not forming complexes, or to polarisation of the salt acting as source. Moisture diminishes ionic mobility; rise in temperature of the source increases it. Silver ions in carbon dioxide show two distinct mobilities.

A. B. D. CASSIE.

#### Reflexion of lithium ions from metal surfaces.

R. B. SAWYER (Physical Rev., 1930, [ii], 35, 1090—1097; cf. Read, A., 1928, 568; Gurney, *ibid.*, 1169).—The reflexion of lithium ions from hot and cold reflectors of platinum foil and of nickel crystals deposited on tungsten foil was investigated, using spodumene as a source of ions, and with special precautions against contamination of the reflector. Superposed on a diffuse scattering of ions were two reflected beams, one reflected nearly specularly, the angle of maximum reflexion being independent of accelerating potential, the other beam appearing only above 200 volts and being found between the incident beam and the normal to the surface at angles independent of the accelerating potential up to 700 volts. The independence of angle on voltage eliminates diffraction interpretations; a provisional explanation is discussed.

N. M. BLIGH.

Mobility of ions in air. J. L. HAMSHIRE (Proc. Roy. Soc., 1930, A, 127, 298—314).—An improved

form of the apparatus previously described (A., 1929, 618) is used to study in greater detail the effect of water vapour, methyl alcohol, and ethyl ether on the mobility distribution for positive and negative ions in air. Results in dry air at atmospheric pressure confirm the finite distribution band obtained with the earlier apparatus. Attempts to detect the "young" ions of mobility 1.9, found by Erikson (A., 1929, 483) and Tyndall and Grindley (A., 1926, 219), were unsuccessful. The addition of water vapour causes a marked narrowing of the negative ion band, which is almost entirely due to the disappearance of the faster ions. There is also a shift of the band as a whole in the direction of lower mobility, which is more clearly shown at higher concentrations. The positive ion curves are only slightly affected. On addition of methyl alcohol vapour the whole curve for the negative ions undergoes the abnormal initial decrease in mobility found by Tyndall and Phillips (A., 1926, 877), without change of breadth. There is, however, a broadening of the peak. The positive band is abnormally narrowed by the disappearance of the slower ions. In ether vapour, the negative ion band is unchanged in breadth and there is no marked abnormality; the positive ions, however, show both effects. The "selective cluster" theory of Loeb may be modified to account, at any rate qualitatively, for the present results. L. L. BIRCUMSHAW.

**Effective cross-section and molecular structure of the isomerides of the formula  $C_4H_{10}$ .** E. BRÜCHE (Ann. Physik, 1930, [v], 5, 281—295).—The Ramsauer magnetic method was used without any alteration of apparatus. The effective cross-sections of *n*- and *iso*-butane were found for six velocities between 0.5 and 7  $\sqrt{\text{volts}}$ , and curves were drawn between the velocities and the cross-sections. Between 6.3 and 1.9  $\sqrt{\text{volts}}$  the effective cross-sections are the same for the two isomerides within the experimental error. The determinations from 1.5 to 0.5  $\sqrt{\text{volts}}$  indicate, however, that at about 1.15  $\sqrt{\text{volts}}$  the effective cross-sections of *n*- and *iso*-butane cease to be identical, that of *isobutane* being somewhat smaller. This is in agreement with physical data already available. The results are discussed. The quantitative comparison of other physical data, e.g., van der Waals constants, *m. p.*, *b. p.*, and critical data, for these two isomerides and other hydrocarbons indicates that at the higher velocities any difference in the effective cross-section should be within the experimental error. The structural formulæ of the two isomerides are discussed on the basis of this work. The identity of cross-sections at the higher velocities cannot be explained by the straight-chain formula if *n*- and *iso*-butane have to possess markedly different structures. In this case the difference in structural formulæ leads to false conclusions concerning the structure of both molecules. The structural formula can therefore be regarded as giving only a rough idea of molecular fields. If it is assumed that the carbon atoms in *n*-butane do not lie in a straight line, but that the lines joining adjacent atoms are inclined to each other, it is possible to have an ellipsoidal structure to which the *isobutane* molecule is similar as regards its external field. A. J. MEE.

**Protons and electrical conductivity in metals.** A. COEHN and W. SPECHT (Z. Physik, 1930, 62, 1—31).—The diffusion of electrolytic hydrogen in a palladium wire can be followed for several centimetres by potential measurements. The velocity of diffusion and its temperature coefficient are determined. The resistance of the wire is independent of the distribution of hydrogen within it, and gives a good measure of the hydrogen content. The hydrogen moves towards the negative pole. The velocity of this motion and its dependence on temperature are determined. A. B. D. CASSIE.

**Photo-effect of ions in solution.** K. BUTKOV (Z. Physik, 1930, 62, 71—76).—The action of visible and ultra-violet light on aqueous solutions of alkali halides has been investigated. A photo-effect due to the relation  $X^- + h\nu = X + e$  ( $X$ =halogen) has been observed. 0.5*N*-Solutions of sodium, potassium, and caesium iodide, potassium bromide and chloride were illuminated by condensed aluminium, zinc, and cadmium sparks. The conditions under which free halogen appears are discussed. The limits of the photo-effect are in good agreement with the heads of the absorption bands for halogen ions. When alcoholic solutions of the three iodides were irradiated by ultra-violet light free iodine was liberated.

W. R. ANGUS.

**At. wt. of actinium-lead, the final product of the actinium disintegration series.** A. VON GROSSE (Z. anorg. Chem., 1930, 190, 188—189).—A criticism (cf. Lotze, A., 1928, 684). R. CUTHILL.

**At. wt. of actinium-lead.** F. LOTZE (Z. anorg. Chem., 1930, 190, 190—192).—A reply to von Grosse (cf. preceding abstract). R. CUTHILL.

**Probability of radiative transitions.** J. R. OPPENHEIMER (Physical Rev., 1930, [ii], 35, 939—947).—On Dirac's theory (cf. this vol., 271) the empty states of negative energy are protons, and the filling of these states should correspond with the annihilation of an electron and a proton. The transition probability is calculated, and leads to a mean lifetime for matter of the order of  $10^{-10}$  sec. On Dirac's radiation theory the relative probability of radiative and radiationless transitions is calculated, and gives a result equivalent to that of Heisenberg and Pauli (Z. Physik, 1929, 56, 1) in their relativistic treatment of the interaction of radiation and matter.

N. M. BLIGH.

**Thermal ionisation in degenerate systems.** R. MAJUMDAR and D. S. KOTHEARI (Z. Physik, 1930, 61, 712—718).—The Saha and Sur theory of the influence of radiation on the thermal ionisation equilibrium is extended by means of the Sommerfeld theory of degenerate systems (A., 1928, i, 467) and also by the Einstein-Bose statistics to systems having degenerate components. The resulting equation is applied to the white dwarf stars and shows that they are in a state of complete ionisation, i.e., consist merely of free nuclei and electrons. H. A. JAHN.

**Measurement [of the thermal ionic dissociation of alkali iodides and calculation therefrom] of the electron affinity of iodine.** J. E. MAYER (Z. Physik, 1930, 61, 798—804).—The equilibrium in

the thermal ionic dissociation of the vapours of caesium and potassium iodides at high temperatures is determined by measurement of the current carried out by the ions through a hole in the evacuated vessel containing the molten salt. From this equilibrium the free energy of the dissociation of the iodides into ions at 0° Abs. is calculated. Using the value of Sommer-meyer (A., 1929, 1363) for the energy of the atomic dissociation of these iodides and the values of Born and Heisenberg (A., 1924, ii, 434) for the energy of ionisation of caesium and potassium, the electron affinity of the iodine atom at 0° Abs. is determined to be  $72.6 \pm 2$  kg.-cal. This is in fair agreement with the value 79 kg.-cal. derived by Born from consideration of the lattice energies of the iodides.

H. A. JAHN.

**Conductivity of a high-frequency discharge in hydrogen.** C. J. BRASEFIELD (Physical Rev., 1930, [ii], 35, 1073—1079; cf. this vol., 268).—To determine the most efficient pressure and oscillation frequency of the discharge, measurements were made of the voltage between electrodes necessary to produce a current of 100 milliamp. in the discharge, for gas pressures of 0.005—1 mm. and frequencies of  $1.25 \times 10^6$  cycles/sec., using high-frequency voltages applied to external electrodes. It was found that the discharge had a maximum conductivity at  $15 \times 10^6$  cycles and 0.015 mm. pressure. Theory indicates that an electron makes an inelastic collision with a gas molecule, every electronic mean free path having been under the influence of the electric force for one half cycle, and that for higher frequencies the electric force and gas pressure for maximum conductivity will increase directly with the frequency.

N. M. BLYTH.

**Operational wave equation and the energy levels of the hydrogen atom.** G. TEMPLE (Proc. Roy. Soc., 1930, A, 127, 349—360; cf. *ibid.*, 339).—The operational wave equation used is a generalisation of Dirac's linear wave equation, in which Dirac's matrices are replaced by four linear operators  $A_1, A_2, A_3, A_4$ , which satisfy the conditions  $1/2(A_m A_n + A_n A_m) = 0$  if  $m \neq n$ , and  $=1$  if  $m = n$ . The operational wave equation for a purely electrostatic field is used to obtain the energy levels of hydrogen-like atoms.

L. L. BIRCUMSHAW.

**Search for an inactive isotope of the element 84 (polonium).** G. VON HEVESY and A. GUENTHER (Nature, 1930, 125, 744).—An investigation of hessite, calaverite, nagyagite, tetradyomite, bismuth glance, and native bismuth failed to detect an inactive isotope of element 84.

L. S. THEOBALD.

**Systematisation of isotopes. III.** G. BECK (Z. Physik, 1930, 61, 615—618).—An attempt to describe the behaviour of nuclear electrons, in the structure of isotope systems, more exactly by use of the Pauli principle and the conception of electron-spin.

A. B. D. CASSIE.

**Heat of radiation of polonium.** A. DORABIALSKA (Rocz. Chem., 1930, 10, 304—313).—The heat of radiation,  $Q$ , of polonium is  $1.81 \times 10^{-5} (\pm 0.9\%)$  g.-cal./hr. per e.s.u. of polonium, or 24.2 g.-cal./hr. per curie of polonium. The value calculated on the basis of that of  $Q$  for the number of  $\alpha$ -particles emitted by

1 g. of radium per sec. is  $3.4 \times 10^{10}$ ; this is identical with the value given by Geiger and Werner (A., 1924, ii, 226).

R. TRUSZKOWSKI.

**Anomalous scattering of  $\alpha$ -particles by lighter elements.** C. MÖLLER (Z. Physik, 1930, 62, 54—70).—Theoretical. The potential barrier model for the nucleus is used; with wave mechanics it gives a qualitative account of anomalous scattering of  $\alpha$ -particles by aluminium and magnesium. A general method is given for determination of the form of the nuclear barrier from the empirical scattering curves.

A. B. D. CASSIE.

**Scattering of  $\alpha$ -particles by light atoms.** A. C. BANERJI (Phil. Mag., 1930, [vii], 9, 273—292).—The problem of the scattering of  $\alpha$ -particles by atoms has been attacked by means of wave mechanics, employing the Schrödinger wave equation for the motion of any charged particle round the nucleus and assuming the law of force to be that of the inverse cube. In the case of aluminium the calculated probabilities of scattering are in fair agreement with the observed results of Bieler (Proc. Camb. Phil. Soc., 1923, 21, 686), whilst calculated values for magnesium show wide differences from Bieler's results. It is suggested that the experimental values for magnesium should be redetermined. Attempts to express the scattering as a function of the energy of the  $\alpha$ -particles, whilst being in rough agreement over a portion of the energy range, show wide discrepancies in the region of minimum scattering. It is concluded that this discrepancy is attributable to the Schrödinger form of the wave equation of the electron, and attempts are being made to adopt the Dirac wave equation to the treatment of the bombarding  $\alpha$ -particle.

A. E. MITCHELL.

**Fine structure of the magnetic spectrum of  $\alpha$ -rays.** S. ROSENBLUM (Compt. rend., 1930, 190, 1124—1127).—The velocities of the  $\alpha$ -radiations of thorium-C', radium-A, and radium-C' relative to that of thorium-C have been determined using a magnetic field of  $23.2$  kilogauss. The values  $\alpha\text{Th-C'}/\alpha\text{Th-C } 1.209 \pm 0.0015$ ,  $\alpha\text{Th-C'}/\text{Ra-C' } 1.070(6) \pm 0.0015$ ,  $\alpha\text{Ra-C'}/\alpha\text{Ra-A } 1.135(8) \pm 1.0015$ , and  $\alpha\text{Ra-A'}/\alpha\text{Th-C } 0.996(2) \pm 0.001$  were found, and thence the following energy differences (in kilovolt-electrons) were calculated with an accuracy of 2%:  $\alpha_1 \rightarrow \alpha\text{Th-C } 40.6$ ,  $\alpha_2 \rightarrow \alpha\text{Th-C } 287$ ,  $\alpha_3 \rightarrow \alpha\text{Th-C' } 442$ , and ( $\alpha_4 \rightarrow \alpha\text{Th-C } 421$  ?). A nuclear  $\gamma$ -radiation corresponding with 40.8 kilovolt-electrons exists in the group (Th-C + Th-C').

J. GRANT.

**Measurement of the activity of radium emanation by a torsion balance.** J. ZAHRADNÍČEK (Z. Physik, 1930, 61, 719—724).—The activity of radium emanation is measured directly from the deflexion of a highly-damped torsion balance completely cased in metal. A platinum-iridium suspension is used, and the deflexion recorded automatically on a revolving drum. The "ion-wind" set up by the emanation acts as if the emanation attracts the arm of the balance, and the absolute value of the attractive force is obtained by comparison with the deflexion caused by 10-kg. lead spheres. It is found that the deflexion is directly proportional to the electrically measured activity of the emanation and is a function

of the distance separating the preparation from the arm of the balance. H. A. JAHN.

**Sensitive surface of the Geiger tube electron counter.** L. F. CURTISS (Bur. Stand. J. Res., 1930, 4, 601—608).—No preparation of the central wire electrode is necessary (cf. Geiger and Müller, A., 1929, 1123). Bare copper, bare steel, lacquered steel, oxidised tungsten, and oxidised nichrome work satisfactorily. All these wires ceased to work when gases such as hydrogen sulphide, sulphur dioxide, ethylene, or water vapour were present. W. E. DOWNEY.

**Active nitrogen.** VIII. (I) Influence of photogens and of surfaces on glow phenomena in nitrogen. (II) Effects of addition of other gases to luminous nitrogen. E. J. B. WILLEY (J.C.S., 1930, 1146—1157; cf. this vol., 524).—Observations were made on nitrogen subjected to a powerful discharge, alone and in presence of similarly treated hydrogen, and nitrogen-oxygen mixtures, and surfaces treated with various waxes and varnishes. It was found that the introduction of a photogen after nitrogen had been sparked induces the after-glow in pure nitrogen; a strong glow appeared in presence of a paraffined surface. The amount of chemical reaction between the wax and the active nitrogen is much less in photogenic than in non-photogenic nitrogen. Results indicate that photogens are wall-poisons and convert the non-luminous heterogeneous re-association of atoms into a homogeneous reaction accompanied by emission of light. Observations were made on the addition to the after-glow of other purified gases, hydrogen, carbon monoxide, nitrous oxide, carbon dioxide, and nitrogen, and results are shown to be in accordance with the three-body collision theory of the emission of the after-glow, provided that the condition of the walls is such that they do not interfere. N. M. BLIGH.

**Quantum mechanics of an electron or other particle.** E. H. KENNARD (J. Franklin Inst., 1929, 207, 47—78).—A general account of the electron in quantum and wave mechanics. R. W. LUNT.

**Band spectrum of silver chloride.** B. A. BRICE (Physical Rev., 1930, [ii], 35, 960—972; cf. Franck and Kuhn, A., 1927, 1007).—The electronic band system of silver chloride from  $\lambda$  3124 to  $\lambda$  3400 was obtained and photographed in emission, and in absorption under high dispersion. Wave-lengths and wave-numbers of observed heads are tabulated. A complete vibrational quantum analysis is given, and an expression is obtained for the band heads of the molecule  $\text{Ag}^{107}\text{Cl}^{35}$ . Vibrational quantum numbers are assigned for silver bromide and iodide. The vibrational isotope effect was observed for chlorine and silver atoms. The complete spectrum consists of four overlapping systems due to the four possible isotopic molecules  $\text{Ag}^{107}\text{Cl}^{35}$ ,  $\text{Ag}^{109}\text{Cl}^{35}$ ,  $\text{Ag}^{107}\text{Cl}^{37}$ , and  $\text{Ag}^{109}\text{Cl}^{37}$ . The order of magnitude of the isotope shift for the chlorine and silver isotope effect was 1—30 and 1—4  $\text{cm}^{-1}$ , respectively. The heats of dissociation of the  $\text{AgCl}$  molecule are  $D_0''=3.11$  in the normal state, and  $D_0'=0.31$  volt in the excited state. The energy of excitation of the atoms resulting by dissociation from the excited state is  $1.10 \pm 0.12$

volts in agreement with the assumption that  $^2D'$  states exist in silver as in copper and gold. It is concluded that the silver halides dissociate from the excited state into a silver atom in a  $^2D'$  state and a halogen atom in the metastable  $^2P_{1/2}$  state.

N. M. BLIGH.

**Relation between the intensity and position of the overtones of some organic liquids.** P. E. SHEARIN (Physical Rev., 1930, [ii], 35, 973—976).—Theoretical. Using the data of Spence and Easley (cf. A., 1929, 1215) for the absorption bands of several organic liquids the intensities of the first and second overtones were calculated by graphical integration under the experimental curve for the absorption coefficient, and are tabulated together with the ratio of these intensities; results are also given for three diatomic gases, carbon monoxide, hydrogen chloride, and hydrogen bromide. The products of the ratio and the correction factor are of the same order of magnitude and approximately constant for the liquids and gases investigated. N. M. BLIGH.

**Space configuration of molecules. Ultra-violet absorption of methyl and methylene groups.** (MME.) RAMART-LUCAS, (MLLE.) BIQUARD, and GRUNFELDT (Compt. rend., 1930, 190, 1196—1198).—The absorption curve of formic acid is displaced more towards the visible than those of acetic, butyric, hexoic, octoic, myristic, palmitic, and stearic acids. The absorption coefficient of all the acids is essentially the same, indicating that the methyl and methylene groups are not chromophores. All measurements were made in alcoholic solution in the region 2200—2500 Å. H. BURTON.

**Fourth positive bands of carbon monoxide.** L. B. HEADRICK and G. W. FOX (Physical Rev., 1930, [ii], 35, 1033—1037; cf. Birge, A., 1927, 184; Estey, this vol., 520).—Using low-voltage arc excitation, new measurements of the fourth positive band system of carbon monoxide between 2174 and 1280 Å. were made from plates photographed with a one-metre vacuum spectrograph; the densities of the band edges were determined from a microphotometric trace. A few new band edges lying below the fourth positive system were found. Results are in good agreement with existing data.

N. M. BLIGH.

**Heat of dissociation of carbon monoxide.** J. KAPLAN (Physical Rev., 1930, [ii], 35, 957—959; cf. A., 1929, 651).—Theoretical. The heat of dissociation of carbon monoxide is calculated by the method previously used for nitrogen, based on band spectra, the products of dissociation from the  $b$  level being a normal carbon and a normal oxygen atom (cf. Johnson, A., 1929, 1349). From the value obtained, 10.3 volts, the dissociation products of the molecule are discussed for several electronic levels, and McLennan's value of 1.3 volts for the energy of the metastable  $^1D_2$  state of oxygen is supported (cf. this vol., 2).

N. M. BLIGH.

**Band spectra of copper oxide.** P. C. MAHANTI (Nature, 1930, 125, 819).—Bands in the spectrum of copper oxide have been obtained by arcing between copper electrodes in an atmosphere of oxygen. They are degraded towards the red and occur in pairs of

which the component of shorter wave-length is relatively weak. The system is probably due to the transition  ${}^2\Sigma \rightarrow {}^2\Sigma$  and the frequencies of vibration for infinitesimal amplitude are approximately 620 and 345  $\text{cm}^{-1}$ , respectively, for the final and initial states.

L. S. THEOBALD.

**Absorption bands of gaseous ammonia in the visible.** R. M. BADGER (Physical Rev., 1930, [ii], 35, 1038—1046; cf. Badger and Mecke, A., 1929, 1363).—Measurements were made of the absorption spectrum of gaseous ammonia in the visible region, using a column of 280 cm. A very weak absorption region was found at 5490 Å. For a band at 6474 Å. measurements of 57 lines are tabulated and the structure is discussed. Comparison is made with existing data for the 7919 Å. band, the three constituting the sixth, fifth, and fourth harmonics of the 3  $\mu$  band (cf. Stinchcomb and Barker, A., 1929, 488). A representation of the five series of the two stronger harmonic bands by a scheme of transitions is given and discussed. Other portions of the spectrum are discussed in connexion with Barker's analysis (cf. A., 1929, 740) of the complex band at 10  $\mu$ .

N. M. BLIGH.

**Spectral excitation distribution of phosphorescence bands at different temperatures.** F. SCHMIDT (Ann. Physik, 1930, [v], 4, 1127—1136).—An experimental method is described which demonstrates the changes of spectral excitation distribution of phosphorescence bands for different temperatures in a spectrum with equal energy for all wave-lengths. In the momentary distribution of the BaS-Cu- $\alpha$  and CaS-Mn- $\alpha$  bands there were found previously unrecorded maxima.

A. J. MEE.

**Spectra of scintillations of zinc sulphide-copper phosphor.** W. KUTZNER (Physikal. Z., 1930, 31, 501—503; cf. A., 1927, 1121).—The scintillation spectra of the phosphor with the addition of small quantities of alkali and alkaline-earth halides were investigated. The composition of the phosphor was 1 g. of zinc sulphide, 0.0001 g. of copper, and 0.1 g. of the halide. The spectra were photographed. Keeping the general composition of the phosphor the same, the addition of chlorides of different alkali and alkaline-earth metals resulted in the production of very similar spectra as far as the position of the bands was concerned, provided that the method of preparation and duration of glowing were the same. There are, however, some marked differences in the intensity distribution of the spectra. The maximum intensity moves along the spectrum from the long- to the short-wave region as the at. wt. of the metal of the halide increased. Experiments with fluorides led to similar results. Changing the halogen appears to exert a much more profound effect on the character of the spectrum than changing the metal. Not only the position of the bands, but also the intensity distribution is different. An explanation of the phenomenon cannot be obtained from the photographic method, but it is proposed to continue the work by a photo-electric method.

A. J. MEE.

**Luminescence resulting from some aryl magnesium halides with nitro-compounds.** H. GILMAN, J. McGLUMPHY, and R. E. FOTHERGILL

(Rec. trav. chim., 1930, 49, 526—531).—Chemiluminescence has been observed in the interaction of magnesium *p*-chloro- and *p*-bromo-phenyl bromide with a large number of nitro-compounds which are tabulated. Although the phenomenon appears to be due to oxidation of the Grignard reagent, no generalisation can be made, since some nitro-compounds (e.g., *p*-nitro-diethylaniline, -aniline, -diphenylamine, and -phenylhydrazine, dinitroresorcinol, phenylnitromethane, and ethyl nitrate) afford no luminescence. No glow occurs in the reaction with nitroso-compounds.

J. W. BAKER.

**Raman effect in the proximity of the critical point.** S. L. ZIEMECKI and K. NARKIEWICZ-JODKO (Phil. Mag., 1930, [vii], 9, 299—305, also Naturwiss., 1929, 17, 876; cf. this vol., 14).—The failure of Bogros and Rocard (A., 1928, 571) and of Martin (*ibid.*, 1170) to observe Raman spectra at the critical point of phenol-water is attributed to the masking effect of the continuous background of the mercury spectrum on the weak Raman lines and to the effects of absorption accompanying the colour change in the liquid.

A. E. MITCHELL.

**Raman effect for water.** I. E. H. L. MEYER and I. PORT (Physikal. Z., 1930, 31, 509—510).—The intensity changes of the blue and violet Raman bands for water are discussed. Two photometer curves of intensity relationships at 2° and 98° are given, which show that the expected intensity changes are real. This is in opposition to the view of Pringsheim and Schlivitch (cf. this vol., 521), who have recently stated that the intensities of the Raman lines are unaffected by temperature. The conclusion has been reached that the two Raman bands 4696 and 4171 Å. are not independent, but originate in the same primary line. The band at 4696 Å. belongs to the ( $\text{H}_2\text{O}$ ) molecule, whilst that at 4171 Å. belongs to the aggregate ( $\text{H}_2\text{O}$ )<sub>2</sub>. As the amount of the latter decreases with rising temperature, the band should get less intense at higher temperatures. Pringsheim and Schlivitch have also shown that the violet Raman line has a separate existence, contrary to views formerly held. Experiments were also undertaken to see whether there are similar phenomena in the ultra-violet. The difficulties of using a quartz mercury-vapour lamp for the purpose are mentioned. Although the bands at 3375, 3306, and 2918 Å. are equal in intensity at 11.5°, at 55° this is no longer so. The two bands at 3375 and 2918 Å. are still equal in intensity, but the band at 3306 Å. is about 20% stronger.

A. J. MEE.

**Raman effect for water.** II. E. H. L. MEYER (Physikal. Z., 1930, 31, 510—511).—Experiments with the 4696 Å. band, using a glass spectrograph, appear to show that it is made up of two lines. As, however, the photometer method gives only one intensity maximum, and one bulge on the short-wave side, it seems that the optical observation must be an illusion. The Raman band at 3507 Å. was photographed at 11.5°, 55°, and 100°. There is a change in the shape of the photometric curves, the peaks getting flatter and wider as the temperature rises. The curves are not symmetrical. This change with

temperature may be connected with the presence of molecular aggregates in the water. A. J. MEE.

**Intensity of Raman radiation and the frequency of the incident beam.** L. S. ORNSTEIN and J. REKVELD (Z. Physik, 1930, 61, 593—597).—Measurements of light scattered by carbon tetrachloride show the intensity of Raman lines proportional to the fourth power of the frequency of the incident beam, as in Rayleigh scattering. A. B. D. CASSIE.

**Rotation-Raman spectra of nitrogen and oxygen.** F. RASETTI (Z. Physik, 1930, 61, 598—601).—The rotation-Raman spectra of nitrogen and oxygen were photographed with a dispersion of 3 Å. per mm. Earlier data (A., 1929, 627, 975) on the intensity of even and odd rotation lines were found correct. A. B. D. CASSIE.

**Raman spectra of crystalline nitrates.** W. GERLACH (Nature, 1930, 125, 819).—The frequency differences of the inactive Raman frequency of the nitrate ion in various uni- and bi-valent salts are recorded. In agreement with Krishnamurti (this vol., 522), a displacement of the inactive nitrate frequency depending on the cation has been observed (cf. this vol., 663). L. S. THEOBALD.

**Raman spectra of crystalline and dissolved nitrates.** W. GERLACH (Ann. Physik, 1930, [v], 5, 196—204).—A more detailed account of work already noted (cf. this vol., 663, and preceding abstract).

**Study of electrolytic dissociation by the Raman effect.** I. Nitric acid. I. R. RAO (Proc. Roy. Soc., 1930, A, 127, 279—289).—The Raman effect was studied in solutions of nitric acid at different concentrations (65—9.7%), and the progress in the electrolytic dissociation of the acid has been traced by measuring the changes in the intensities of the Raman lines due to the undissociated molecules and to the ions. Ten Raman lines are observed, four corresponding with undissociated nitric acid molecules, three (found also with nitrates) with the  $\text{NO}_3^-$  ion, and three with pure water. The fact that the lines corresponding with the acid molecule diminish rapidly in intensity with increasing dilution, whilst the  $\text{NO}_3^-$  lines increase in intensity, yields direct evidence of the electrolytic dissociation of nitric acid. The relative intensities of the Raman lines at 4566.8 Å. (due to the  $\text{NO}_3^-$  ion) with various concentrations of the acid are roughly estimated from the deflexions in microphotometric records, and from these the relative amounts of dissociation are calculated. The curves giving the relation between the concentration and the degree of dissociation as obtained (a) by the present method, (b) from Kohlrausch's conductivity formula, and (c) from the viscosity-conductivity formula are found to be widely divergent, although of roughly similar form. The causes of the discrepancies are discussed. It is considered that since the intensity of the Raman line is directly proportional to the number of free ions present, and is independent of either their mobility or their concentration, this is the only method by which the true degree of dissociation can be determined. L. L. BIRUMSHAW.

**Intensity and polarisation of coherent and incoherent radiation scattered by diatomic molecules.** C. MANNEBACK (Z. Physik, 1930, 62, 224—252).—Theoretical. Experimental data on the intensity and polarisation of unmodified and modified lines are summarised. The Kramers-Heisenberg dispersion formula is used to calculate the components of the electric moment induced in a molecule when polarised light falls on it. Expressions for the intensity and polarisation of scattered radiation are then deduced. Particular attention is given to rotational fine structure. A. B. D. CASSIE.

**Raman spectra of some organic halogen compounds.** S. BHAGAVANTAM and S. VENKATESWARAN (Proc. Roy. Soc., 1930, A, 127, 360—373).—Tables are given showing the analysis of the Raman spectra of 17 halogen derivatives of the aliphatic and aromatic hydrocarbons. It is considered that the presence of combinational frequencies or overtones, if they occur at all, is very rare, and that the frequency shifts usually observed are to be interpreted as primarily due to the fundamental oscillations in the molecules. This view is supported by the occurrence of several small frequency shifts in all the substances studied. A comparison of the frequency shifts in corresponding chlorine and bromine compounds shows that they are invariably further from the exciting line in the former, on account of the large difference in the masses of the chlorine and bromine atoms. The Raman lines corresponding with the frequencies 750 and 660  $\text{cm}^{-1}$  are ascribed to vibrations in the C-Cl and C-Br linkings, respectively. The diffuse nature of these lines is particularly conspicuous in chloroform, bromoform, and carbon tetrachloride, and may be due to an unresolved structure arising from the presence of isotopes in chlorine and bromine. The band at about 3.3  $\mu$  which has been assigned to the aliphatic C-H vibration, and usually consists of several components in the higher members, gives place to a single line in chloroform and bromoform. It is suggested that the fine structure of this band depends to some extent on the complexity of the molecule.

L. L. BIRUMSHAW.

**Light scattering in liquids.** R. M. LANGER and W. F. MEGGERS (Bur. Stand. J. Res., 1930, 4, 711—735).—The incoherent scattering observed by Raman and Krishnan has been studied, using a special mercury arc and the liquids benzene, toluene, chloroform, and carbon tetrachloride. Comparison of the results for frequency shifts with the available data on infra-red absorption spectra shows no simple, direct correspondence. The exact connexion of constants derived from the study of light scattered by complex molecules with other molecular data remains obscure at present. W. E. DOWNEY.

**Raman effect in binary mixtures.** A. DADIEU and K. W. F. KOHLRAUSCH (Physikal. Z., 1930, 31, 514—519).—Fifteen binary liquid mixtures have been examined, mostly at the ordinary temperature, but the mixtures ethyl alcohol-hexachloroethane, benzene-acetic acid, and benzene-benzoic acid were examined at 65°, 68°, and 75°, respectively. Within the limits of experimental error mixtures exhibit the spectra of



their components except in those cases where the two components react chemically. Where one of the components is associated a weak but definite change is observable in the Raman frequency characteristic of the substance due to the increased intermolecular forces. The possibility of employing Raman measurements to study the mechanism of association and complex formation is mentioned. W. R. ANGUS.

**Properties of dielectrics. I. Electric moment and molecular structure.** C. P. SMYTH (J. Franklin Inst., 1929, 207, 813—824).—A *résumé* of the theoretical relationships between electric moments, molecular polarisation, and molecular structure.

R. W. LUNT.

**Properties of dielectrics. II. Dielectric constant.** F. M. CLARK (J. Franklin Inst., 1929, 208, 17—44).—After a brief *résumé* of the theory of Debye and of recent work on the temperature variation of the dielectric constant of gases, the relation of the dielectric constant to other factors is discussed at length with particular consideration of their relevance in the design of high-tension apparatus and machinery. The following relationships are reviewed, and in each case a compilation of the available data has been made: temperature variation for gases, liquids, liquid-liquid mixtures, solutions of solids in liquids; change of state solid-liquid, liquid-gas; frequency variation for gases and liquids; pressure variation for gases and liquids; the influence of the number and nature of substituent groups on various hydrocarbon molecules; and the variation of the constant with the resistivity.

R. W. LUNT.

**Multiple association in liquid dielectrics.** M. WOLKE (Physikal. Z., 1930, 31, 498—501; cf. A., 1929, 13).—Mathematical. The statistical theory of association in liquid dielectrics previously developed is extended to multiple association. The results of the calculation agree satisfactorily with experimental observations on *n*- and *iso*-butyl and propyl alcohols.

A. J. MEE.

**Polar molecules, their contribution to energy loss in dielectrics.** F. HAMBURGER, jun. (Physical Rev., 1930, [ii], 35, 1119—1124; cf. Kitchin and Müller, A., 1929, 242).—Theoretical. Debye's theory of polar molecules and existing experimental data for glycerol (cf. Mizushima, A., 1929, 380) are applied to an examination of the suggestion that at low frequencies, as in commercial power circuits, the theory of molecular orientation may serve as some explanation of the dielectric energy loss. It is concluded that the contribution of the former to the latter for glycerol and insulating oils is negligible above 0° and below 10,000 cycles per sec.

N. M. BLIGH.

**Evidence for quantisation from the electric polarisation of acetic acid vapour.** C. T. ZAHN (Physical Rev., 1930, [ii], 35, 1047—1055; cf. this vol., 666).—The dielectric constant of acetic acid vapour was measured at various pressures and temperatures; the results indicate a departure from Debye's theory suggesting an internal transition, with respect to temperature variation, from one type of single molecule to another. The anomaly is discussed quantum-mechanically, and a suggestion that the effect is due to a transition from one state to a

higher state of vibration associated with the OH group is supported by Dadiou and Kohlrausch's investigation of the Raman spectrum (cf. A., 1929, 976). The data are interpreted in terms of the proposed extension of Van Vleck's theory (cf. A., 1927, 812, and following abstract). Anomalies of the vapour with respect to van der Waals' equation and to viscosity are discussed. N. M. BLIGH.

**Extension of Van Vleck's theory of dielectric polarisation.** C. T. ZAHN (Physical Rev., 1930, [ii], 35, 1056—1058).—Theoretical. Deviations found (cf. preceding abstract) from the equation derived by Debye on his theory of dielectric polarisation suggest an effect of vibrational quantisation where the electric moment depends on the vibrational quantum number. Van Vleck's theory, in which the electric moment is assumed fixed for all states of low energy, is extended to include the effect by admitting the possibility of different fixed electric moments for different vibrational states.

N. M. BLIGH.

**Dipole moments of the disubstituted benzenes.** H. M. SMALLWOOD and K. F. HERZFELD (J. Amer. Chem. Soc., 1930, 52, 1919—1927).—The electric moments of 29 disubstituted benzene derivatives are calculated from the individual moments of the substituent groups, assuming the group moments to be directed along the valency linkings, but taking into account the effects due to the mutual induction of the dipoles, which are assumed to be located on the circumferences of the carbon atoms. The correction leads to closer agreement between observed and calculated results.

J. G. A. GRIFFITHS.

**Dielectric polarisation of liquids. VIII. Acetic and butyric acids.** C. P. SMYTH and H. E. ROGERS (J. Amer. Chem. Soc., 1930, 52, 1824—1830).—Dielectric constants and densities of 0—100% concentration of acetic acid in benzene and 0—100% acetic acid in ether have been determined at temperatures within the ranges 0—70° and 0—30°, respectively. Analogous data are recorded for butyric acid-benzene mixtures between 10° and 70°. The dielectric constants of pure acetic and butyric acids rise with temperature, and since that of benzene falls, that of benzene containing a 0.6134 mol. fraction of acetic acid shows little variation with temperature. The abnormal temperature coefficients are attributed largely to changes in the equilibria between the single and double molecules of the acids. The electric moments of the former are about  $1.4 \times 10^{-18}$  e.s.u., whilst those of the latter are believed to be negligible, owing to the formation of complexes in which the carboxyl groups are in contact with one another.

J. G. A. GRIFFITHS.

**Dipole moment of homologous series.** P. C. MAHANTI (Physikal. Z., 1930, 31, 546—555).—A detailed description of the design and calibration of the apparatus is given. Methyl, ethyl, and *n*-propyl halides and allyl chloride were examined in the vapour state and their dipole moments calculated from the temperature relation of the dielectric constant according to Debye's theory. The dipole moment of the chlorides was found to be  $2.00 \times 10^{-18}$  e.s.u.; whilst the bromides and the iodides gave  $1.79 \times 10^{-18}$  and  $1.62 \times 10^{-18}$  e.s.u., respectively. Values for the

dielectric constant of these substances are given for temperatures between 300° and 420°. The close similarity between the value of the dielectric constant at normal temperature and pressure and the square of the refractive index is illustrated by a table. As in the case of alcohols and other substitution products of hydrocarbons, neither the number of the carbon atoms nor the linkings within the carbon chain affect the values of the dipole moment, which are governed solely by the substituent group. The length and strength of the alkyl-halogen linking are discussed from the experimental data and from the infra-red spectra of the compounds. W. R. ANGUS.

**Dispersion of mercury vapour in the ultra-violet and a quantitative relation between dispersion and absorption.** R. LADENBURG [with WOLFSOHN, H. KOPFERMANN, and W. TIETZE] (Nachr. Ges. Wiss. Göttingen, 1929, 1—5; Chem. Zentr., 1930, i, 174).

**Optical properties of potassium lithium sulphate.** H. BLITTERSDORF (Z. Krist., 1929, 71, 141—167; Chem. Zentr., 1930, i, 487).—Potassium lithium sulphate exhibits a transition point at 435°, and shows "subnormal" interference colours. The refractive index and double refraction were determined. A. A. ELDRIDGE.

**Quantitative theory of homopolar binding.** M. DELBRÜCK (Ann. Physik, 1930, [v], 5, 36—58).—Mathematical. The Heitler-London method was used to investigate the lithium molecule. The "eigenfunction" that represents approximately the lithium atom gives the nucleus and two *K* electrons a resultant charge of 1.5 electronic units. Two such "eigenfunctions" and their corresponding exchange energies determine the lithium molecule. Values are deduced for the required exchange integrals. In contrast to hydrogen, the exchange energy of the *L* electrons is positive for distances at which the exchange energy of the closed *K* rings is negligible. The weakness of the lithium-lithium linking is therefore not due to repulsion by *K* electrons, but to the small exchange energy of two 2s electrons. A. B. D. CASSIE.

**Electronic theory of valency. VII. Etch-figures of sylvine.** T. M. LOWRY and M. A. VERNON (Phil. Mag., 1930, [vii], 9, 233—240).—The etching of natural crystals of sylvine with a concentrated solution of potassium chloride disclosed no unsymmetrical pyramids except by the flotation of detached fragments. On artificial crystals there was complete absence of unsymmetrical etch figures even in the presence of optically active impurities. It is concluded therefore that there is no trustworthy crystallographic evidence of a lower order of symmetry in sylvine than that deduced from X-ray analysis. Similarly, there is no evidence of the existence of linkings between individual atoms of potassium and chlorine and the ionic structure is accepted. Objection is, however, taken to the view that crystals of ice and quartz and the anions of oxygenated acids in crystals such as calcite and barytes are merely aggregates of O<sup>2-</sup> ions with the corresponding cations. The formation of ice is suggested as a process of polymerisation in which additional linkings are

formed rather than a process of ionisation in which all the linkings between atoms are destroyed. Similarly, it is suggested that the oxygen atoms in the carbonate, nitrate, sulphate, and silicate ions are linked to the central atom by single linkings and therefore carry only single negative charges. A network of single linkings is postulated for quartz in which the atoms of quadrivalent silicon and bivalent oxygen would be electrically neutral.

A. E. MITCHELL.

**Types of linking in diatomic molecules.** H. LESSHEIM and R. SAMUEL (Z. Physik, 1930, 62, 208—223; cf. A., 1929, 1367).—Types of linking may be inferred from band spectra. There are two classes, atomic and ionic linking. In atomic linkings the potential energy may be electrostatic or exchange energy. Molecules with an even number of valency electrons have exchange energy linking only, and have a smaller energy of dissociation in the excited than in the unexcited state, i.e., their bands degrade towards the red. Molecules with an odd number of electrons may have exchange energy linking, when their potential energy-nuclear distance curves are like those for molecules with an even number of electrons, except that curves for different electronic levels may intersect. The Coulomb linkings have all greater energy of dissociation in the excited state; i.e., the bands degrade towards the violet. Normal chemical molecules, whether atomic or ionic, are those that have greatest energy of dissociation when two unexcited atoms or ions form them. All unexcited molecules with an odd number of electrons are formed from an excited and an unexcited atom or ion, and are chemically unstable. A. B. D. CASSIE.

**Parachor and molecular volume.** S. SUGDEN (Nature, 1930, 125, 778—779).—A reply to Ferguson (this vol., 669). L. S. THEOBALD.

**Properties of the chlorides of sulphur. IV. Density and surface tension. Parachors of mixtures.** T. M. LOWRY and G. JESSOP (J.C.S., 1930, 1005—1015).—With the object of finding a sensitive method of detecting sulphur tetrachloride based on the deficiency in the parachor exhibited by "pervalent" compounds, the densities of equilibrium mixtures of the chlorides of sulphur were measured from -4° to 30° and for the composition range 37 at-% of chlorine to pure liquid chlorine. Surface tensions were measured by the capillary rise method. Densities and surface tensions were also measured for mixtures of uncombined sulphur monochloride and chlorine, in which the red colour of the dichloride had not yet developed. Discontinuities occurred at the composition of the dichloride, but not of the tetrachloride. The densities and surface tensions of uncombined mixtures are lower than after combination has taken place; such mixtures show a parachor deficiency greatest at about 75 at-% of chlorine, and falling to a minimum at the composition of the dichloride when combination takes place. There was no analogous indication of the formation of the tetrachloride. N. M. BLIGH.

**X-Ray studies of particle size in silica.** R. H. ABORN and R. L. DAVIDSON (J. Franklin Inst., 1929, 208, 59—71).—The possibility of determining particle

size in the microscopic range by the Debye-Scherrer method has been investigated for silica particles. The geometric mean particle size ranged from 1.73 to 36  $\mu$ , and the deviation of particle size was varied over the range 1.28–2.17 arbitrary units. The results indicate that it may be possible to develop a quantitative determination of particle size from a comparison of spectrograms, but only in those cases in which the deviation of particle size is approximately constant.

R. W. LUNT.

**X-Ray interference bands and atomic size.** P. DEBYE (Physikal. Z., 1930, 31, 419–428; cf. Ann. Physik, 1915, 46, 809).—Formulae are developed showing the intensity of the X-radiation scattered by gases in relation to the angle of scattering when the sizes as well as the distances apart of the atoms are taken into account. If the ratio of atomic size to atomic distance is small, a diatomic molecule can give recognisable interference maxima and minima, but with increasing value of this ratio the maxima and minima become flattened and finally a smooth curve is obtained. In agreement with theory it is found that neither oxygen nor nitrogen gives a recognisable first maximum, but that two chlorine atoms attached to one carbon atom do so. The positions of the first three maxima and minima for carbon tetrachloride have been calculated: (1) neglecting the influence of the central carbon atom and considering the chlorine atoms as points; (2) taking the carbon atom into consideration and regarding all the atoms as points, and (3) taking into account the atomic sizes. Only the values calculated by the third method agree with those experimentally determined. The distance between the chlorine atoms calculated by the new formula is 2.99 Å. ( $\pm 1\%$ ), compared with 3.1 Å. given by the formula taking no account of the size of the atoms. The behaviour of carbon dioxide and of carbon disulphide is discussed. With *trans*-dichloroethylene the first maximum occurs at a smaller angular distance than with the *cis*-compound, corresponding with the greater distance apart of the chlorine atoms in the former.

F. L. USHER.

**Camera for structural investigations.** C. LEISS (Z. Physik, 1930, 61, 663–666).—A detailed and illustrated account of a form of camera suitable for the structural investigation of crystalline powders by X-rays and also of rubber and fibre-like substances in the form of thin stretched threads. The camera takes a complete cylindrical film which can be removed and replaced in daylight. The object investigated is placed along the axis of the film and can be rotated about its own axis.

H. A. JAHN.

**Scattering of X-radiation in liquids and other substances. Effect of eliminating stray radiation. Absorption coefficients of liquid fatty acids.** J. THIBAUD and J. J. TRILLAT (Z. Physik, 1930, 61, 816–836; cf. this vol., 4, 19).—The distribution of intensity of radiation with wave-length has a large maximum at the wave-length characteristic of the anode, and a smaller maximum at a shorter wave-length dependent on the electron velocity. Thin absorbing layers give a ring, A, due to systematic reflexion of the anode K-radiation. Thick absorbing layers absorb the K-radiation, but may not absorb

all the shorter wave-lengths. Thus, layers of liquid fatty acids greater than 2 mm. thick show a second ring, B, due to systematic reflexion of the maximum characteristic of the exciting potential. As the thickness increases so does ring B predominate, and this has given a wrong interpretation to some results. The absorption coefficients of the fatty acids were measured for the K $\alpha$ -radiation from copper ( $\mu_1$ ), and from molybdenum ( $\mu_2$ ). Their values are: acetic acid  $\mu_1=7.9$ ,  $\mu_2=0.73$ ; heptic acid,  $\mu_2=0.65$ ; nonic acid  $\mu_1=4.5$ ,  $\mu_2=0.5$ ; molten stearic acid,  $\mu_1=3.72$ ,  $\mu_2=0.5$ . This verifies the additive rule for atomic absorption coefficients.

A. B. D. CASSIE.

**Determination of intensity of X-rays by the ionisation method.** J. SCHECHTMANN (Ann. Physik, 1930, [v], 5, 153–195).—A number of factors influencing the determination of the intensity of X-rays by the ionisation method are investigated, concerning particularly the dimensions of different parts of the apparatus, and the potentials used.

A. J. MEE.

**Reflexion of X-rays at an artificially prepared laminated body.** W. DEUBNER (Ann. Physik, 1930, [v], 5, 261–280).—Laminated bodies of silver and gold consisting of superimposed very thin layers of the metals were prepared by an electrolytic method. The body was then investigated for crystalline structure by the usual method, with the exception that a specially constructed tube was used. It was found that all the interference lines obtained originated from the crystalline structure of the metal layers, and not from any phenomena occurring at the boundaries of the layers. Laminated bodies prepared by cathodic sputtering were also investigated in the same way, and with the same results.

A. J. MEE.

**Internal lattice potential of natural and of yellow sodium chloride.** E. RUPP (Z. Physik, 1930, 61, 587–592).—With the method previously described (this vol., 6) of electron reflexion with a constant angle of incidence and a varying velocity of the electrons, the maxima in the curves showing electron intensity against velocity in volts are determined, and the internal lattice potential  $E_0$  is thereby calculated, for natural colourless and blue sodium chloride, and also for sodium chloride crystals coloured yellow by exposure to 150,000-volt electrons. The value  $E_0=-2.8$  volts found for yellow sodium chloride is larger than the value  $E_0=-3.5$  volts found for colourless crystals, and this increase is connected with the greater freedom of the electrons in the yellow crystal as shown by its photo-electric conductivity. Reflexion experiments were carried out while the yellow crystal was being decolorised by exposure to light from a white-hot tungsten filament, and the corresponding change in  $E_0$  was observed. Blue sodium chloride crystals gave no maxima in the curves corresponding with  $E_0=0$ , which is explained by the colloidal sodium, to which the colour is due, hindering the freedom of the electrons of the crystal. Experiments were also made on a layer, 0.001 mm. thick, of sodium chloride sublimed in high vacuum, and an extremely large maximum was observed at 42 volts, corresponding with a 2.5 order interference spectrum, which could not be explained. Sodium

chloride crystals, made synthetically by the method of Kyropoulos, were examined, and shown to give maxima at the same voltages as the natural crystals, but of different intensities. The synthetic crystals were coloured much more strongly by cathode rays, but the colouring was much less permanent and the change in  $E_0$  during the decolorisation could not be followed quantitatively, although qualitatively it was the same as with the natural crystals. H. A. JAHN.

**Structure of tremolite,  $\text{Ca}_2\text{Mg}_5\text{H}_2(\text{SiO}_3)_8$ .** B. E. WARREN (Z. Krist., 1929, 72, 42—57; Chem. Zentr., 1930, i, 190—191).—Tremolite has  $a$  9.78,  $b$  17.8,  $c$  5.26 Å. ( $a:b:c=0.550:1:0.295$ ; crystallographically, 0.551:1:0.294). The space-group is  $2C_i-3$ ; there are 2 mols. in the unit cell.

A. A. ELDRIDGE.

**Structure of *d*-tyrosine hydrochloride, methyl methanetetra-carboxylate, and toluene-*o*-sulphonamide.** A. BURGEM, F. HALLA, and O. KRALKY (Z. Krist., 1929, 71, 263—268; Chem. Zentr., 1930, i, 6—7).—Crystallographic data are recorded. The densities are 1.426, 1.33, and 1.44, the space-groups probably  $C_2^2$ ,  $C_2^2$ , and  $C_2$ , and the number of molecules in a unit cell 4, 2, and 16, respectively.

A. A. ELDRIDGE.

**Crystal structure of the normal paraffins at temperatures ranging from that of liquid air to the m. p.** A. MÜLLER (Proc. Roy. Soc., 1930, A, 127, 417—430).—An X-ray investigation has been made of the structures of a number of normal paraffins ranging from pentane to triacontane, at liquid air temperature, atmospheric temperature, and in the neighbourhood of the m. p. Linear expansion measurements show that the lengths of both the  $a$  and  $b$  axes increase considerably with rise of temperature, the coefficient of expansion of the  $a$  axis being three or four times as large as that of the  $b$  axis. The expansion of the  $c$  axis is very much smaller, and does not exceed one tenth of that of the  $a$  axis. These facts indicate that the forces which hold the atoms together in the molecule are different in magnitude from those which keep the molecules apart from each other; the chemical conception of the entity of the molecule is thus confirmed for the solid state. The higher members of the paraffin series crystallise in the so-called "normal" form previously described (Müller and Saville, A., 1925, ii, 367), which is found to be stable between the m. p. and liquid air temperature. Differences in the behaviour of the odd and even members begin to appear as the number of carbon atoms decreases, docosane and lower members existing in two alternative forms. Within a small range of temperatures near the m. p. the normal form is stable, but at lower temperatures a second crystal structure appears and persists down to the temperature of liquid air. The change from one form to the other is reversible for docosane, eicosane, and octadecane. The change from the normal to the other form occurs between undecane and nonane in the series of the odd members. These abrupt changes in structure are discussed and a qualitative explanation is suggested. Observations taken in the immediate neighbourhood of the m. p. indicate that these substances tend to form layer

structures, and it is shown how the normal form could be transformed into such a structure in a simple manner.

L. L. BIRCUMSHAW.

**Thomson effect in zinc crystals.** L. A. WARE (Physical Rev., 1930, [ii], 35, 989—997).—The Thomson coefficient  $\sigma$  was determined directly for a group of zinc crystal rods over a range of orientations; results appeared to obey the Voigt-Thomson symmetry relation. The values obtained for  $\sigma$  at 49.5° and 125°, perpendicular and parallel, respectively, were  $\times 10^{-6}$ , 0.98, 0.38, 2.09 and, 1.08 g.-cal./coulomb deg., and for the lower temperature agree with calculations from Sommerfeld's theory of conduction. Values for the specific resistivity and temperature coefficient of resistivity were also determined.

N. M. BLIGH.

**Optical rotatory power of quartz on either side of an infra-red absorption band.** T. M. LOWRY and C. P. SNOW (Proc. Roy. Soc., 1930, A, 127, 271—278; cf. Lowry and Coode-Adams, A., 1927, 813).—The accuracy and range of previous observations on the optical rotatory power of quartz in the infra-red region have now been extended to the extreme limit of the improved experimental methods available. The column of quartz was the same as that used in the earlier experiments (*loc. cit.*), and the grating spectrometer recently described by Snow and Taylor (A., 1929, 865) was employed, the gas tubes being replaced by a simple polarimeter. The accuracy claimed for the observations is about  $\pm 5^\circ$ , but actually individual groups of readings are consistent within about  $1^\circ$ . The readings are in two series, the first covering the range 18,000—28,000 Å., the second the range 31,800—32,100 Å., and the results afford convincing proof of the optical inactivity of the infra-red absorption band at 30,000 Å., and indirect evidence that the activity of the others, if it exists at all, is too insignificant to be demonstrated experimentally.

L. L. BIRCUMSHAW.

**Hall effect for nickel, iron, and copper in weak magnetic fields.** E. BOSSA (Atti R. Accad. Lincei, 1930, [vi], 11, 482—489).—The gradual increase observed in the Hall effect of nickel and iron in strong magnetic fields as the strength of the latter falls becomes a rapid increase at about 30 (for nickel) or 6.2 (for iron) gauss; with these metals dissymmetry of the galvanometer deviations occurs if the magnetic field is inverted. With copper, however, there is no such dissymmetry and the slow increase of the Hall coefficient with diminution of the magnetic field never changes to a rapid one.

T. H. POPE.

**Theory of ferromagnetism.** E. TELLER (Z. Physik, 1930, 62, 102—105).—Mathematical. In an atomic lattice with one valency electron per atom in the state of highest multiplicity the lowest ferromagnetism occurs when all the exchange energy is positive, and the highest when the exchange energy is negative.

J. FARQUHARSON.

**Theory of the magnetisation curve.** R. BECKER (Z. Physik, 1930, 62, 253—269).—Mathematical. The energy between parallel dipoles in a cubic lattice is dependent solely on the direction of the dipole, when the lattice undergoes an elastic deformation.

The essential features of technical magnetisation curves are discussed. J. FARQUHARSON.

**Cohesion limits of rock-salt crystals.** F. BLANK (Z. Physik, 1930, 61, 727—749).—The cohesion properties of rock salt are studied systematically. Absolutely distinct values for the limiting tensions and rupturing strengths were obtained for twelve natural samples of different origin. Tempering near 600° lowered, whilst tempering above 600° increased these values. For purest mechanically undisturbed natural rock-salt crystals the value of the limiting tensions is at most 70 g./mm.<sup>2</sup> and the value of the rupturing strengths is certainly beyond 217 g./mm.<sup>2</sup> Crystals obtained from a fused mass gave inconsistent values. The influence of impurities is discussed (cf. this vol., 675). W. R. ANGUS.

**Dependence on temperature of crystal plasticity.** W. BOAS and E. SCHMID (Z. Physik, 1930, 61, 767—781; cf. A., 1929, 634, 1370).—The constant of the critical limiting tension in a wide temperature range below the m. p. of cadmium crystals has been observed and is probably a general characteristic. The dependence of the critical limiting tension on the tension velocity was studied between 85° and 473° Abs. The solidification coefficient is only slightly influenced by temperature at the lower and upper limits of the temperature range, but in the middle of the range there is considerable dependence. The influence of the tension velocity on the solidification coefficient is slight at very low and very high temperatures and reaches a maximum if the experimental velocity and velocity of recovery are of the same magnitude. The tension work of the primary basis translation for cadmium crystals is a constant equal to 8.7 joules/cm.<sup>3</sup>, independent of temperature and tension velocity. Similar investigations have been conducted with zinc crystals. At 100°, 150°, and 200° stretched zinc crystals exhibit a transverse striation due possibly to surface splitting. W. R. ANGUS.

**Elasticity constants of anisotropic materials.** P. BECHTEREV (Z. Krist., 1929, 71, 274—276; Chem. Zentr., 1930, i, 323).—A classification.

A. A. ELDRIDGE.

**Elastic moduli of alkali halides.** P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1929, 64, 19—38).—Values for sodium and potassium chlorides and bromides and for potassium iodide are recorded; they satisfy the Cauchy relation. CHEMICAL ABSTRACTS.

**Behaviour of a single crystal of antimony subjected to alternating torsional stresses.** H. J. GOUGH and H. L. COX (Proc. Roy. Soc., 1930, A, 127, 431—453).—From previous work on the failure by fatigue of single crystals of aluminium, iron, and zinc, there seems to be little doubt that the tendency to slip is a function of the atomic density on the slip plane and of the linear density in the slip direction; recent experiments have indicated that the latter is perhaps the more important factor (cf. Taylor and Elam, A., 1926, 997; Gough and Cox, A. 1929, 634). Since the structure of antimony is such that the planes of maximum density do not contain any of the lines of maximum density, it was considered that definite evidence as to the relative

importance of the two factors could be obtained from a determination of the type of the slip plane. The experimental results, however, are inconclusive. The specimen did not deform by slip, and no definite slip bands were found. A number of fine lines or cracks were, however, observed, corresponding with the traces of planes perpendicular to the axis of trigonal symmetry; these might be expected to act as slip planes. The twinning planes are identified as of the 011 type, and twins were observed on all three planes (011, 101, and 110) of this type. Observation of secondary twins and fine lines and cracks within the primary twin bands establishes the "mirror image" nature of the structure within the bands. In general, the cracks and fracture faces follow well-defined crystallographic planes. The first cracks were found to be parallel to the traces of the 111 plane of the original structure or of the twinned structures, although some of the larger cracks tended to follow the direction of the twins themselves. Final fracture occurred by complete cleavage parallel to one of the twinning planes. L. L. BIRCUMSHAW.

**Behaviour of single crystals of zinc subjected to alternating torsional stresses.** H. J. GOUGH and H. L. COX (Proc. Roy. Soc., 1930, A, 127, 453—479; cf. A., 1929, 634).—Previous work has shown that the slip plane of zinc operative under fatigue stresses is the basal plane; the position of maximum intensity of slip bands and its agreement with that of maximum resolved shear stress completely identifies the slip direction. Tests have now been made on a single crystal of zinc of suitable relative orientation of the crystallographic and straining axes, such that all three slip directions become operative, and the above results are completely confirmed. The twinning planes are the six planes of the general type 1012. For reference purposes, the circumference of the specimen is regarded as being divided into six consecutive portions, in each of which one slip direction is operative, and it is shown that: (a) twins on complementary twinning planes are always present in the same operative slip region, thus reducing the total of six possible twinning planes to three pairs; (b) three slip directions are involved; (c) one pair of twinning planes only appears in each operative slip direction; (d) a change in slip direction is accompanied by a change in the pair of twinning planes operative; (e) in any operative slip region, the twinning planes containing that slip direction do not appear; (f) normal stress alone does not determine the choice of operative twinning plane. The conclusion is reached that the occurrence of twins, as well as of slip bands, is controlled by the simple criterion of maximum resolved shear stress on the slip plane. The significance of long, widely-spaced black "marks" which appeared on the surface of the specimens is discussed. These may represent the effects of block shear movement on prismatic planes rendered necessary to preserve the continuity of the specimen. L. L. BIRCUMSHAW.

**Impedance of crystal growth by slight deformation.** A. E. VAN ARKEL and J. J. A. PLOOS VAN AMSTEL (Z. Physik, 1930, 62, 43—45).—Technically pure aluminium was rolled into a thin sheet and

indented so that, when it was stretched, the extension of the sheet was not uniform. The sheet was etched after various periods of heating and the recrystallisation followed. It has been found that slight deformation impedes greatly the growth of the crystal by recrystallisation. W. R. ANGUS.

**Recrystallisation of stretched tin crystals.** A. E. VAN ARKEL and J. J. PLOOS VAN AMSTEL (*Z. Physik*, 1930, 62, 46—48).—Polemical against Póányi (cf. A., 1928, 9). The majority of extensible crystals are not constricted in one point, but the stretching proceeds equally over the whole length of the crystal. The crystal was embedded in picene, the picene block clamped in the stretching apparatus, and the crystal heated to 218°. It was then etched and photographed. Nuclei of recrystallisation are formed principally in the stretched parts of the crystal and not at the transition point. W. R. ANGUS.

**Optically void crystalline liquids and the different kinds of crystalline liquids.** D. VORLÄNDER (*Physikal. Z.*, 1930, 31, 428—435).—The viscosity coefficient of the ethyl ester of *p*-ethoxybenzylidene-*p*-amino- $\alpha$ -methylcinnamic acid has been measured at small temperature intervals between 75° and 130°. The curve showing the variation of this coefficient with temperature has discontinuities at 75.5° and 122°, corresponding with the transition *cryst. liquid II*  $\rightarrow$  *cryst. liquid I* and *cryst. liquid I*  $\rightarrow$  *amorphous liquid*, respectively. The latent heats of transformation were detected by means of heating and cooling curves. Similar measurements have been made with the ethyl ester of anisylidene-*p*-aminocinnamic acid, which forms three crystalline liquid phases. The classification of crystalline liquids is discussed. F. L. USHER.

**Recrystallisation of lead.** B. GARRE and A. MÜLLER (*Z. anorg. Chem.*, 1930, 190, 120—122).—Recrystallisation diagrams have been constructed for pure lead and commercial lead. The effect of the addition of 0.5% of a foreign metal on the size of grain after casting and after rolling followed by recrystallisation has also been examined. R. CUTHILL.

**Effect of temperature at which molten aluminium is heated prior to crystallisation on number of crystallites.** G. TAMMANN and K. RÖTH (*Z. anorg. Chem.*, 1930, 189, 388—390; cf. Scheil, B., 1929, 721).—The higher is the temperature at which molten aluminium is heated, the smaller is the number of crystallites formed on cooling. R. CUTHILL.

**Structure of iron oxide prepared by autoclave treatment.** T. KATSURAI and T. WATANABE (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, 13, 89—92).—X-Ray analyses of the precipitates obtained by heating ferric chloride solution in an autoclave at 150° show that the structure is identical with that of hematite and of ferric hydroxide prepared by precipitation with ammonia, viz., rhombohedral,  $\alpha = 55^\circ 17'$ ,  $a = 5.42 \text{ \AA}$ . C. W. GIBBY.

**Distribution and velocity of the corrosion of metals.** U. R. EVANS (*J. Franklin Inst.*, 1929, 208, 45—58).—A lecture. R. W. LUNT.

**Spontaneous crystallisation of polymorphous substances from the supercooled state.** E. P.

VOLOTSCHNEVA (*J. Russ. Phys. Chem. Soc.*, 1930, 62, 77—93).—The first crystals to appear in spontaneously crystallising supercooled fused resorcinol, betol, triphenylamine, apiol, salol, or thiosinamine are those of the unstable polymorph of these substances. A new modification of apiole, m. p. 18—19°, and two new forms of 1-chloro-3:4-dinitrobenzene, m. p. 26° and 36.6—36.9°, are described. The same enantiomorph of *p*-dichlorobenzene crystallises out from supercooled masses at temperatures both above and below its transition point. R. TRUSZKOWSKI.

**Comparison of the ultracentrifuge method for mol. wt. determination with the classical methods.** J. B. NICHOLS (*Nature*, 1930, 125, 814—815).—Data for sodium eosinate and erythro-sinate obtained by the ultracentrifuge method are compared with those obtained by the b.p. method. When sufficient sodium chloride is added to eliminate the electrical potential arising from the partial separation of ions in the centrifuge the values found for mol. wt. (1343 for the eosinate) show that both dyes in solution consist of double molecules with two dissociated sodium ions. L. S. THEOBALD.

**Magnetic susceptibility of rubidium.** C. T. LANE (*Physical Rev.*, 1930, [ii], 35, 977—981; cf. Sucksmith, A., 1926, 782; McLennan, A., 1927, 1017).—The magnetic susceptibility of highly-purified rubidium was determined by the Gouy method at nine field strengths from 9 to 25 kilogauss, with an accuracy of 2—3%, and was found to be uniform to within 2%. The mean value of the mass susceptibility was  $+0.21 \times 10^{-6}$  at 20°. Results are discussed in relation to Pauli's theory, from which the theoretical value is  $+0.32 \times 10^{-6}$ . N. M. BLIGH.

***E.M.F.*, resistance, and capacitance phenomena in photovoltaic cells containing Grignard reagents.** H. E. HAMMOND (*Physical Rev.*, 1930, [ii], 35, 998—1007; cf. Dufford and others, A., 1927, 918; 1929, 378, 1364).—To determine whether the known voltage variations with illumination are due to ionisation changes or to electrode-film variations, the *E.M.F.*, resistance, and polarisation capacitance were measured in light-sensitive cells containing ethereal solutions of Grignard reagents. Voltage alterations with illumination or X-ray irradiation are described. Resistance variations with illumination were found for magnesium ethyl bromide, but not for magnesium phenyl bromide cells until a "forming" process had been carried out. The small reversible changes in conductivity were attributed to alterations in solvation of the ions rather than to changes in ionisation. Capacitance changes seemed unrelated to other phenomena. Film thicknesses are estimated to be of approximately molecular dimensions, greater for benzene ring compounds than for short-chain compounds. Evidence indicates that voltage variations are due to phenomena at or very near electrode surfaces. N. M. BLIGH.

**Superconductivity of carbides and nitrides.** W. MEISSNER and H. FRANZ (*Naturwiss.*, 1930, 18, 418—419).—The carbides of molybdenum, niobium, tantalum, and probably titanium, and the nitrides of vanadium and titanium are superconductive. A. B. D. CASSIE.



**Theory of conductivity.** R. PEIERTS (Ann. Physik, 1930, [v], 5, 244—246; cf. this vol., 281, 283).—Mathematical. The lattice oscillations of crystals and the limiting conditions of thermal equilibrium of the lattice oscillations are discussed.

A. J. MEE.

**Relativistic mechanics in the Fermi-Dirac statistics and the magnetic susceptibility of gases at high temperatures.** K. BASU (Z. Physik, 1930, 62, 279—288).—Mathematical. The formula derived has the same form as the classical Langevin formula.

J. FARQUHARSON.

**Electrical differential method for measuring the specific heat of gases at constant volume.** III. **Velocity of cooling and temperature conductivity of gases.** M. TRAUTZ and M. GÜRSCHING (Ann. Physik, 1930, [v], 4, 985—1016; cf. A., 1927, 817; 1928, 827).—A method for the manometric determination of the rate of cooling of heated gases is described and was tested experimentally. The heat loss of air, carbon dioxide, and methane was measured. The sources of error are discussed, and it is shown that the loss of heat can be determined quite definitely, and that the values are reproducible to  $\pm 0.5\%$ . By means of an approximate calculation it is possible to obtain the temperature conductivity of the gas, but with an error of about 5%.

A. J. MEE.

**Fusion diagrams of highly refractory oxides.** II. H. VON WARTENBERG and H. WERTH (Z. anorg. Chem., 1930, 190, 178—184; cf. A., 1929, 30).—The existence of the compound  $3\text{BeO} \cdot 2\text{ZrO}_2$ , m. p.  $2550^\circ$ , has been demonstrated by means of a fusion diagram. The m. p. of the metazirconates of magnesium and barium are  $2130^\circ$  and about  $2700^\circ$ , respectively, whilst that of the strontium salt lies above  $2700^\circ$ . The m. p. of chromic oxide in an oxidising atmosphere is above  $2200^\circ$ , and the vapour pressure exceeds 1 atm. even below the m. p. Alumina and chromic oxide form no compounds, and no evidence of the existence of the compound  $2\text{MgO} \cdot 3\text{ZrO}_2$  (Ruff and Ebert, B., 1929, 474) was obtained.

R. CUTHILL.

**Polymethylbenzenes.** III. **Vapour pressures of the tetramethylbenzenes and penta- and hexa-methylbenzene.** F. H. MACDOUGALL [with L. I. SMITH] (J. Amer. Chem. Soc., 1930, 52, 1998—2001).—The vapour-pressure curves for durene, *iso*-durene, prehnitene, and penta- and hexa-methylbenzene are given; those for durene and *isodurene* are almost identical. The latent heats of vaporisation are calculated to be 10,880, 10,470, 10,760, 11,650, and 12,870, respectively, for the above series.

H. BURTON.

**Temperature variation of the entropy of a crystal and its glass.** G. TAMMANN (Ann. Physik, 1930, [v], 5, 107—112).—It is deduced from the results of Gibson and Giauque (A., 1923, ii, 124) on the specific heats of crystalline and amorphous glycerol that at  $-35^\circ$  the difference of entropy between the crystal and its glass becomes zero, at  $-43^\circ$  the difference of energy between the two states is zero, and at  $-91^\circ$  the difference between the thermodynamic potential of the two states passes through zero. Below this temperature glycerol crystals would change into the glass. These results and those of other

investigators on the specific heats of ethyl alcohol, propyl alcohol, betol, and benzophenone lead to the conclusion that at  $0^\circ$  Abs. the difference of entropy between a crystal and its glass is not necessarily zero, even when there is no appreciable difference between the specific heat of the crystal and its glass at temperatures near  $0^\circ$  Abs.

H. A. JAHN.

**Inaccessibility of the absolute zero.** N. DE KOLOSOVSKI (Phil. Mag., 1930, [vii], 9, 208—210).—It is pointed out that the principle of the inaccessibility of the absolute zero generally attributed to Nernst (1912) was originally formulated by Clausius (Pogg. Ann., 1862, 116, 73).

A. E. MITCHELL.

**Vapour pressure and heats of fusion and vaporisation of formic acid.** A. S. COOLIDGE (J. Amer. Chem. Soc., 1930, 52, 1874—1887; cf. A., 1928, 1084).—The vapour pressure of pure solid and liquid formic acid has been determined at temperatures between  $-5^\circ$  and  $110^\circ$  within 0.1%. That of the solid is given by  $\log P(\text{mm.}) = 12.486 - 3160/T$ . Apparent mol. wts. are recorded.

Latent heats of fusion,  $L_f$ , and vaporisation,  $L_v$ , were determined chiefly by electrical heating, except for  $L_v$  at higher temperatures, where a condensation method was used to avoid errors due to decomposition.  $L_v$  is 430 and 483 joules per g., respectively, at  $0^\circ$  and  $100.5^\circ$ .  $L_v$  calculated from the vapour-density and vapour-pressure data by the Clapeyron equation has the values 432, 434, and 477, respectively, at  $0^\circ$ ,  $8.25^\circ$  (triple point), and  $100.5^\circ$ . These thermal properties are explained by a change of the dissociation equilibrium in the vapour.  $L_f$  has the values 268 and 276 (observed), and 277 and 282 (calculated), at  $0^\circ$  and  $8.25^\circ$ , respectively.

J. G. A. GRIFFITHS.

**Measurement of the pressure coefficients of helium to determine the absolute zero.** H. VAN DER HORST (Physica, 1929, 9, 331—336; Chem. Zentr., 1930, i, 181—182).—New measurements give  $\alpha_1 = 0.00366145$ ,  $0^\circ \text{ C.} = 273.12^\circ \text{ Abs.}$

A. A. ELDRIDGE.

**Equation of state for solids at high temperatures, and the quantity  $\gamma = (dp/dT)_v \times v/R$ .** J. J. VAN LAAR (Z. Physik, 1930, 62, 77—89).—Mention is made of the previous proof (A., 1926, 570) that at relatively high temperatures the equation of state for solids has the same general form as that for liquids, viz.,  $p + a/v^2 - \lambda/v(v-b) = RT/(v-b)$  and that this represents the compressibility and its dependence on temperature and pressure, for example, of copper, with great accuracy. It is emphasised that the common form of the equation (as given by Grüneisen, "Handbuch der Physik," Vol. X.) is incorrect and leads to absurd conclusions. It is shown that an equation of state cannot be derived from purely thermodynamic relations, and the basis of Grüneisen's error is pointed out. The above equation gives  $\gamma = v/(v-b)$ , whereas that of Grüneisen would give  $\gamma = (3n-1)/2$ , where  $n$  is the index of the repulsive force, and since  $\gamma$  varies from 2.5—3 (Sb, Bi, Te) to 8—9 (Os, Ir, Pt, Au, Pb), this would lead to a very improbable variation in the value of  $n$  from 2 to 6. The variation of  $\gamma$  is explained by variation in the freedom of motion of the atoms, as is also shown by

the difference in the compressibility. A table of the values of  $\gamma$  for about 50 metals is given and the results are arranged according to the periodic table. Maxima in the values of  $\gamma$  are shown to occur at the 8th group and at the *b* sub-group of the 4th group. The value of Magnus and Holzmänn (this vol., 24) for the coefficient of expansion of beryllium is shown to lead to the value 0.52 for  $\gamma$  instead of the value 4 to be expected from its position in the periodic table. This discrepancy may be due to the coefficient of expansion being measured only in one crystallographic direction, the mean value being quite different, as is the case with tellurium.

H. A. JAHN.

**New equation of state for fluids. V. Values of the constants for 14 gases in Amagat and Berlin units.** J. A. BEATTIE and O. C. BRIDGMAN (Z. Physik, 1930, 62, 95—101).—The values in three different sets of units of the constants in the Beattie-Bridgman equation of state (A., 1927, 819) are tabulated for the fourteen gases already considered (A., 1929, 252, 498) and the percentage deviation between the calculated and observed pressures is given. It is concluded that the equation represents the compressibility of these gases with approximately the same accuracy as the experimental data themselves. References are given to investigations on the use of the equation in the calculation of the thermodynamic properties of gases.

H. A. JAHN.

**Measurement of relative specific heats of gases at high temperatures.** P. M. S. BLACKETT and E. K. RIDEAL (Nature, 1930, 125, 816—817).—A method for measuring the relative specific heats of gases over a range of 20° at a temperature of 1300° by means of an electrically-heated platinum tube is described.

L. S. THEOBALD.

**Oscillation phenomena. IV. M. p. and solubility at 25° in water and in benzene of a series of *n*-monoalkylmalonic acids.** P. E. VERKADE and J. COOPS, jun. (Rec. trav. chim., 1930, 49, 568—577).—It is proposed to represent the position of a member of a homologous series of the general formula  $R_1[CH_2]_nR_2$  by the term number *n*, where  $R_1$  and  $R_2$  are the terminal groups (in compounds of the constitution  $CH_3 \dots R_1$  the hydrogen atom is considered as one of the terminal groups). A distinction is made between two kinds of oscillation of physical properties in a homologous series, viz., complete oscillation, where an increase and a decrease in the constant in question take place alternately with a regular increase in the term number, and incomplete oscillation, where only larger and smaller increases in the constant alternate with each other. Furthermore, if the decrease or increase of the constant occurs when passing from an even term to the next odd term, the oscillation is called even; if it occurs when passing from an odd term to the next even term the oscillation is odd. The m. p. of the monoalkylmalonic acids of the series  $C_nH_{2n+1}CH(CO_2H)_2$  up to the term  $n=14$  show a very clear minimum at the fifth term, amylmalonic acid, and the oscillation is complete and even. The m. p. found are as follows: the number in parentheses denoting the term number: (1) about 127°, (2) 114—115°, (3) 96—97.5°, (4) 103.5—105°, (5) 81.5—83°, (6) 106—107.5°, (7) 96.5—

98°, (8) 113.5—115°, (9) 104.5—105.5°, (10) 118.5—120°, (11) 109—110.5°, (12) 120—121.5°, (13) 111.5—112.5°, (14) 121.5—123.5°. These values do not agree with the view that in most homologous series the m. p. converges to a common limit of about 117° as the carbon chain increases (cf. Timmermans, Bull. Soc. chim. Belg., 1919, 28, 392). The solubility of the above acids in benzene shows a pronounced complete and odd oscillation. The solubility in water, measurements of which have also been made, is very great in the case of the acids with term numbers 2—5, and the oscillation is again complete and odd. With hexylmalonic acid there is a sudden decrease in the solubility, which gradually decreases still further with increase of the term number without any oscillation being perceptible.

O. J. WALKER.

**Accurate determination of  $c_p/c_v$  by a modification of the method of Rüchardt and Rinkel.** P. H. BRODERSEN (Z. Physik, 1930, 62, 180—187).—The oscillations of the steel ball in the apparatus of Rüchardt (A., 1929, 497; see also Rinkel, this vol., 143) are photographed using a rotating mirror and the time of oscillation is obtained with an accuracy of 0.1%. By considering the actual process to be composed of an adiabatic and an isothermal process occurring together, the corrected value of  $c_p/c_v$  for a completely adiabatic process is deduced and the values  $1.400 \pm 0.003$  for unpurified air and  $1.292 \pm 0.004$  for technical carbon dioxide are obtained.

H. A. JAHN.

**Compressibility and pressure coefficient of resistance of several elements and single crystals.** P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1929, 64, 51—73).—The pressure coefficient of electrical resistance was determined for indium, manganese, chromium, titanium, boron, and arsenic, and the compressibility for potassium, ammonium, and chrome alums, sodium chlorate, bromate, and nitrate, sodium potassium tartrate, tartaric acid, ammonium tartrate, diphenylamine, ethylammonium chlorostannate, and bakelite.

CHEMICAL ABSTRACTS.

**Compressibility of a gas and the correction for "supercompressibility."** H. S. BEAN (Bur. Stand. J. Res., 1930, 4, 645—661).—The deviation from Boyle's law for "natural" gas may be as much as 7 or 8% for a pressure range of 1—40 atm. To determine this deviation a sample of gas is collected at high pressure in a steel cylinder of known capacity. Successive small portions of this sample are withdrawn into a burette, where their volumes at atmospheric pressure are determined. This is continued until the whole sample has been reduced to atmospheric pressure. The sum of all these volumes at atmospheric pressure is then compared with the volume to which the initial sample of gas would have expanded if it had followed Boyle's law.

W. E. DOWNEY.

**Resistance to flow [of gas] in different parts of apparatus in the production of high vacua.** W. KLOSE (Physikal. Z., 1930, 31, 503—508).—The streaming of gases through tubes of different types was investigated. For tubes of large diameters bent into different shapes, T-tubes, and taps with wide bores, the same resistance to motion was found as

for a straight tube. For taps with small bores and cooling tubes, the resistance is increased by 15–30%. In general, for low pressures the shape of the tube is without appreciable effect on the velocity of streaming if the tube is sufficiently wide.

A. J. MEE.

**Viscosity formula for binary mixtures, the association degrees of constituents being taken into consideration. VI.** I. ISHIKAWA (Bull. Chem. Soc. Japan, 1930, 5, 117–121).—A discussion of Macleod's (cf. A., 1925, ii, 498) and other formulæ which have been put forward to express the connexion between mol. wt. and viscosity of pure liquids. These equations are not in complete agreement with published data.

J. O. CUTTER.

**Dielectric constants of binary mixtures. X. Electric moments of simple derivatives of cyclohexane and of dioxan. XI. Dioxan as a solvent for electric moment studies.** J. W. WILLIAMS (J. Amer. Chem. Soc., 1930, 52, 1831–1837, 1838–1841).—X. Density and dielectric constant data at 25° have been determined for binary mixtures (benzene as solvent) by an improved method. The following electric moments ( $\times 10^{-18}$  e.s.u.) are recorded: cyclohexane, 0; methylcyclohexane 0; chloro- and bromo-cyclohexane, 2.3; cyclohexanone, 2.8; cyclohexanol, 1.9; 1:4-dioxan, 0.4; 2-, 3-, and 4-methylcyclohexanol, 1.95, 1.9, and 1.9, respectively; cyclohexanecarboxylic acid, 0.9. Electric moment data for mono-substitution products of cyclohexane, methane, and benzene are compared.

XI. 1:4-Dioxan has a negligible electric moment, and may be used, in certain cases, for measurements by the method of binary mixtures. Values recorded are: chlorobenzene, 1.5; water, 1.9; chlorocyclohexane, 2.3; ethyl phthalate, 2.8 (or 2.7, with benzene as solvent).

J. G. A. GRIFFITHS.

**Application of the differential ebullioscope to the investigation of azeotropic mixtures of ethyl alcohol and water.** W. SWIENTOSŁAWSKI and I. ZŁOTOWSKI (Roczn. Chem., 1930, 10, 288–303).—The variation of the b. p. with the composition of alcohol–water mixtures has been studied for mixtures containing 0–7% of water, at pressures varying from 760 to 1900 mm., using an ordinary and a differential ebullioscope. A table is given containing differences between the b. p. of absolute alcohol and of aqueous alcohol at various pressures, from which the composition of a given mixture may be derived by a determination of its b. p.

R. TRUSZKOWSKI.

**Fractional condensation of binary mixtures.** E. KIRSCHBAUM (Chem. Fabr., 1930, 181–183, 189–191).—The action of a dephlegmator attached to a fractionating column in the separation of a mixture such as ethyl alcohol and water is considered. If  $A$  is the alcohol content of the vapour,  $a$  that of the condensate,  $v$  the ratio by weight of the alcohol in the vapour to that in the condensate, then  $\log(v+1) = \frac{A}{A-a}$ , the limiting values of the integral being the vapour concentrations entering and leaving the dephlegmator. The value  $(A-a)$  can be obtained from the evaporation and condensation curves. It is clear that for a given composition of the entering vapour the degree of enrichment depends only on the

amount of reflux  $v$ . A graphical method of integration is worked out which enables the degree of enrichment to be calculated, and curves are shown which give the relation between  $A_a$  and  $A_c$  for different values of  $v$ . With increase of reflux the number of trays in the column needed is reduced, but the heat consumption rises. Experiments both in the laboratory and on the large scale gave results in good agreement with these calculations, although some variation occurs according to the direction of vapour flow through the dephlegmator.

C. IRWIN.

**B. p. of constant-boiling hydrochloric acid.** W. D. BONNER and R. E. WALLACE (J. Amer. Chem. Soc., 1930, 52, 1747–1750).—The b. p. of aqueous hydrochloric acid solutions of constant b. p. used previously (this vol., 405) are determined at pressures between 50 and  $1220 \pm 0.1$  mm. with an accuracy increasing from  $\pm 0.02^\circ$  to  $0.004^\circ$  as the pressure is raised to 760 mm. Corresponding compositions and densities at 25° are recorded.

J. G. A. GRIFFITHS.

**Vapour pressures of molten mixtures of lead chloride and lead bromide at high temperatures.** K. JELLINEK and A. GOLUBOVSKI (Z. physikal. Chem., 1930, 147, 461–469).—The vapour pressures of lead chloride and lead bromide in molten mixtures of the two in the molecular proportions 3:1, 1:1, and 1:3 have been determined at 660°, 700°, 740°, and 780° and found to obey Raoult's law at all concentrations. The molecular heats of evaporation of both salts, either alone or mixed, are calculated to be 28,400 g.-cal. over the whole temperature range (cf. Wartenberg and Bosse, A., 1922, ii, 739).

R. CUTHILL.

**X-Ray investigation of the copper–antimony system of alloys.** E. V. HOWELLS and W. MORRIS-JONES (Phil. Mag., 1930, [vii], 9, 993–1014; cf. A., 1928, 6; Westgren, Hagg, and Eriksson, A., 1929, 1139).—The crystal structure of the copper–antimony alloys is discussed in relation to the equilibrium diagram. The  $\alpha$ -phase alloys are of face-centred cubic structure; the lattice constant varies from 3.61 to 3.67 Å. at the limit of 7% Sb. The  $\gamma$  phase, representing a series of solid solution from 70% Cu to  $\text{Cu}_3\text{Sb}$  (61% copper), has a close-packed hexagonal structure, the unit cell of which is characterised by  $a_0 = 2.728$ – $2.766$  Å. and a constant axial ratio of 1.572. The  $\text{Cu}_2\text{Sb}$  phase is of tetragonal crystal structure, the unit cell containing two  $\text{Cu}_2\text{Sb}$  molecules, with  $a_0 = 4.026$  Å. and axial ratio 1.524. No trace of a solid solution corresponding with the  $\epsilon$  phase has been found. For the unit cell of the rhombohedral lattice of antimony  $a_0 = 6.235$  Å.

N. M. BLIGH.

**X-Ray investigation of the systems  $\text{Fe}_2\text{O}_3$ – $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ – $\text{Mn}_2\text{O}_3$ .** P. E. WRETBLAD (Z. anorg. Chem., 1930, 189, 329–336).—By X-ray examination it has been shown that ferric oxide and chromic oxide form a continuous series of mixed crystals, whereas in the system ferric oxide–manganic oxide there is a miscibility gap.

R. CUTHILL.

**Solubility of gold in mercury. II.** A. A. SUNIER and C. M. WHITE (J. Amer. Chem. Soc., 1930, 52, 1842–1850).—The solubility of gold in mercury has been determined at temperatures between 7°

and 80° by a new shaking and sampling apparatus. Below 80°, the solubilities are higher than those calculated from the equation previously recorded (A., 1929, 874), but are lower than those of Britton and McBain (A., 1926, 474). At 20°, the saturated solution contains 0.1306 at.-% Au. The origin of the break in the curve is discussed.

J. G. A. GRIFFITHS.

**Solubility of calcium sulphate in aqueous solutions of alcohols.** T. YAMAMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 190—206).—The solubility of calcium sulphate dihydrate in aqueous solutions of methyl, ethyl, and *n*-propyl alcohols has been measured at 25°, at alcohol concentrations ranging from zero to 29, 24, and 46%, respectively. The logarithm of the solubility is an approximate linear function of the alcohol concentration, but in each case there is a break in the curve. Empirical formulæ applicable to the two portions of each curve have been derived. The discontinuity is ascribed to a change of hydration of the solvent alcohol, and not to a change in the solid phase.

H. F. GILLBE.

**Solubility curves of sulphur in polychlorides of benzene and their mixtures with benzene of b. p. 200—235°.** I. S. TELET'OV and N. D. PELICH (Ukraine Chem. J., 1929, 4, 457—461).—The solubility of sulphur in benzene (b. p. 200—235°) increases steadily with rise of temperature from 0.25% at 20° to 15% at 160°. The solubility of sulphur in benzene containing 25% of a technical mixture of *o*- and *p*-dichlorobenzene is increased by 60%, with 50% of dichlorobenzenes by 130—140%, and with 75% by 300%. The solubility of sulphur in dichlorobenzene alone rises from 15% at 80° to 50% at 105°, above which temperature complete miscibility in all proportions exists. In benzene-dichlorobenzene mixtures the solutions separate into two layers at 105°, the lower layer consisting of a saturated solution of sulphur in dichlorobenzene; above 105° the two layers are completely miscible.

R. TRUSZKOWSKI.

**Simultaneous solubility of two substances in one solution.** V. A. GOLTZSCHMIDT (J. Russ. Phys. Chem. Soc., 1930, 62, 171—175).—It is shown on theoretical grounds that the solubility of one solute should not, in ideal solutions, be affected by the presence of another. Where this is not the case, in the absence of chemical interaction between the two solutes, the solutions do not conform to the laws of ideal solutions.

R. TRUSZKOWSKI.

**Solubility, the transport coefficient, and velocity of dissolution.** E. N. GAPON (J. Russ. Phys. Chem. Soc., 1930, 62, 121—127).—A discussion of the work of various authors, from which it appears that the value of the transport coefficient of a solute is directly proportional to its concentration.

R. TRUSZKOWSKI.

**Oscillation phenomena.** V. Solubility of a number of dicarboxylic acids of the oxalic acid series in various solvents. P. E. VERKADE and J. COOPS (Rec. trav. chim., 1930, 49, 578—581; cf. this vol., 848).—The solubilities of the following odd members of the series have been determined; viz., malonic, glutaric, pimelic, azelaic, and nonane-

dicarboxylic acids. The solubilities of the even members are extremely small. The following rules are put forward: (1) the solubility in various media of a series of homologues always shows the same type of oscillation, i.e., either always even or always odd, and (2) the m. p. and the solubility exhibit opposite types of oscillation. O. J. WALKER.

**Relation between the surface energy of heteropolar substances and their solubility.** E. N. GAPON (J. Russ. Phys. Chem. Soc., 1930, 62, 129—131).—The following expressions are derived:  $\sigma(Mv)^{2/3} = k_1 T$ ,  $\alpha\beta = k_2$ ,  $LT = k_3(Mv)^{2/3}$ , and  $L = k_4\beta$ , where  $\sigma$  represents the specific surface energy of a heteropolar substance (alkali metal halides),  $M$  the mol. wt.,  $v$  the mol. volume,  $T$  the m. p.,  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  are constants, the value of which depends exclusively on the nature of the cation,  $\beta$  the coefficient of compressibility, and  $L$  the molar concentration of a saturated solution at 18°.

R. TRUSZKOWSKI.

**Adsorption of gas mixtures by glass.** C. DRUCKER and J. MARXEN (Z. physikal. Chem., 1930, 147, 371—389).—The velocity and extent of the adsorption of hydrogen and carbon dioxide by dry and moist glass surfaces have been determined at 25° by a method which is described. Both gases are taken up much more readily by a moist than by a dry glass surface, but equilibrium is attained much more slowly at a moist surface than at a dry one. The adsorption of carbon dioxide by moist glass does not follow the usual exponential law, but increases very markedly with increasing pressure. The greatest thickness of the adsorption layer of hydrogen observed on moist glass was approximately  $1 \times 10^{-8}$  cm., whilst that of carbon dioxide was more than  $26 \times 10^{-8}$  for a pressure of approximately 1 atm. In mixtures of hydrogen and carbon dioxide, therefore, the relative partial pressure of hydrogen has to be very large before an appreciable amount of the gas can be adsorbed. The curve showing the relation between adsorption and partial pressure for the mixture follows the course of the gas friction curve and affords a further confirmation of the relationship between gaseous friction and adsorption (cf. A., 1929, 1376).

M. S. BURR.

**Adsorption of iodine by barium sulphate.** L. DE BROUCKÈRE (Bull. Soc. chim. Belg., 1930, 39, 174—178).—The fact that reproducible results are obtained in the adsorption of iodides by barium sulphate only in the dark and in the absence of oxygen is attributed to the reactions  $4I' + O_2 + 4H^+ \rightleftharpoons 2I_2 + 2H_2O$ ,  $I_2 + I' \rightleftharpoons I_3'$  which occur in air and in diffuse light. The anomalies arise from the selective adsorption of the tri-iodide ions. To confirm this view a study has been made of the adsorption of iodine in potassium iodide solutions by barium sulphate. After equilibrium had been attained in the dark and in the absence of air, the adsorbed complex ions were reduced to iodine ions by Devarda's alloy in alkaline solution, and the free iodine was determined nephelometrically. In the presence of free iodine the ratio of adsorbed iodine to potassium is approximately 3:1. The fact that the adsorption isotherms for solutions containing iodine and iodide tend asymptotically to the same value suggests that the

$I_3'$  complex is of the chain type and that in adsorption it rests on the surface with its axis perpendicular to the surface.

F. G. TRYHORN.

**Influence of various chemical and physical factors on the activity of charcoal.** II. E. V. ALEXEEVSKI and A. P. MUSAKIN (J. Russ. Phys. Chem. Soc., 1930, 62, 205—219; cf. A., 1929, 658).—The effect on the adsorptive power of various wood charcoals of treating with water, carbonic, hydrochloric, hydrobromic, hydrofluoric, hydriodic, sulphuric, nitric, boric, acetic, phosphoric, chromic, sulphurous, arsenic, arsenious, and perchloric acids, also with chlorine, bromine, and iodine solutions and hydrogen sulphide has been studied. Enhanced adsorption of methylene-blue and Congo-red was obtained after treatment with perchloric acid, other substances having no noticeable effect. The degree of adsorption of *isoamyl* alcohol was not affected by any of the above substances. Enhanced adsorption of phenol from aqueous solutions was observed after treatment with perchloric, chromic, and nitric acids, and with bromine water. The most active charcoals for adsorption of acetylene from air were obtained by the use of nitric acid, perchloric acid, and bromine water, whilst the best adsorbents of benzene vapour were obtained by the action of nitric, perchloric, hydrofluoric, and chromic acids. In general, it appears that the adsorptive properties of wood charcoal are enhanced by the action of volatile oxidising substances.

R. TRUSZKOWSKI.

**Influence of the temperature of ignition of alumina on its adsorptive power with respect to the products of the reaction of dehydration of alcohols.** E. V. ALEXEEVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 221—226).—The optimum temperature of ignition of alumina gel for adsorption of ethyl and *isoamyl* alcohol vapour is 400—420°; for adsorption of ethylene, ethylenic hydrocarbons, and the Ipatiev mixture of amylenes, the optimum ignition temperature is 600—620°. It is probable that the catalytic action of alumina on the dehydration of alcohols is due to adsorptive factors.

R. TRUSZKOWSKI.

**Adsorption from solutions containing two solutes.** J. A. V. BUTLER and C. OCKRENT (Nature, 1930, 125, 853—854).—Determinations of the lowering of  $\eta$  at polarised mercury surfaces produced by solutions containing two surface-active substances have shown cases in which the lowering due to the mixture is the same as that produced by the more active substance when present alone; a mixture of 0.05M-sodium *o*-toluate and cinnamate is a case in point. With neutral substances the curves for the individual substances frequently intersect. This type of behaviour is shown by the systems caffeine-phenol, phenol-lactose, caffeine-lactose, and salicin-sucrose, all measured in 0.5M-sodium sulphate solution. A mathematical relationship is deduced.

L. S. THEOBALD.

**Condensation and adsorption.** N. SEMENOV (Z. physikal. Chem., 1930, B, 7, 471—479).—Theoretical. An equation similar to that deduced by Frenkel (A., 1925, ii, 194) on kinetic grounds and supported by the experimental work of Estermann

is put forward from static considerations. The critical condensation temperature is explained on the theory that the adsorbed unimolecular layer is analogous to a two-dimensional gas to which van der Waals' equation may be applied. At high pressures the layer may be regarded as a two-dimensional liquid and a saturated vapour phase. The theory shows the existence of an inversion temperature ( $T_i$ ) below which the critical condensation pressure exceeds and above which it is less than the pressure of the saturated vapour ( $p_g$ ). In the region  $T < T_i$  and at pressures below the critical the amount of adsorbed gas increases with pressure and forms a two-dimensional gas phase on the surface. When the critical pressure is reached, a liquid phase is formed which quickly covers the whole surface and is associated with a decrease of the outer gas pressure to  $p_g$ . In the region  $T > T_i$  and at pressures below the critical the same behaviour is found, but in this case the unimolecular liquid phase formed when the pressure reaches the critical value is stable, since it is less than  $p_g$ , and as  $p$  is increased the formation of a second layer begins. At a certain pressure there is a stable bimolecular adsorbed layer. Thus multimolecular adsorption occurs only when  $T > T_i$  and  $p_{crit.} < p < p_g$ . At  $p_{crit.}$  the adsorption isotherms should show a pronounced discontinuity. The reasons for the absence of this from the experimental curves are discussed.

F. L. USHER.

**Mechanical adsorption of molybdic anhydride in connexion with complex compound formation.** E. F. KRAUSE and A. V. NOVOSELOV (J. Russ. Phys. Chem. Soc., 1930, 62, 287—294).—When solutions of molybdenum trioxide are filtered through a collodion-covered Chamberland candle the molybdenum content of the solution on both sides of the membrane falls progressively. This effect is due to removal of larger aggregates of oxide by their mechanical adsorption in the pores of the membrane, thereby disturbing the equilibrium existing between small and large aggregates, and consequently leading to the formation of fresh aggregates, which are in turn again adsorbed. The process of adsorption is preceded by reaction between the aluminium silicate contained in the porcelain and hydrated molybdenum trioxide molecules. The velocity of adsorption over the range of concentrations of molybdic anhydride considered (0.033—0.15%) is not proportional to the concentration.

R. TRUSZKOWSKI.

**Collodion membranes, VII. Specific permeability of collodion membranes for a polydisperse chromic oxide sol.** E. MANEGOLD and R. HOFMANN (Kolloid-Z., 1930, 51, 308—315).—Sols of chromium hydroxide were prepared from chromic nitrate and sodium hydroxide and were passed through ultrafilters of known permeability. The rate of filtration and the concentration of the filtrate were determined. Both before and after filtration the membranes had the same specific permeability for water, but during filtration the permeability was less. This diminution of permeability is ascribed to stopping of the pores with sol particles of certain sizes in the polydisperse system.

E. S. HEDGES.

**Starch paste.** S. V. GORBATSCHEV (J. Russ. Phys. Chem. Soc., 1930, 62, 355—364).—Not only water, but also any solvent of similar dielectric constant is capable of forming a paste with starch. The effect of electrolytes on the temperature of paste formation depends on whether their presence enhances or diminishes the adsorption of water by starch. For sulphuric acid, magnesium chloride, and ammonium chloride, the curves connecting minimum temperature of paste formation,  $T$ , with concentration of electrolyte pass through a maximum; for iodine-potassium iodide solution the curve rises continually with iodine concentration, and for potassium iodide alone the curve falls uninterruptedly, whilst with glycerol and potassium carbonate it passes through a minimum. Those substances which neutralise the field of force of the hydrogen ions entering into the composition of the adsorbent surface of starch grains thereby enhance adsorption of water and diminish  $T$ . As the concentration of these substances rises, the osmotic pressure of the solvent falls, with consequent increase in  $T$ . R. TRUSZKOWSKI.

**Quantitative case of ionic adsorption determining potential.** E. LANGE and R. BERGER (Z. physikal. Chem., 1930, 147, 470—472).—The relationship  $\Delta x \sim \Delta \log_e a$  between the amount,  $x$ , of the ion determining the potential which is adsorbed by an electrode, and the activity,  $a$ , of this ion in the solution (this vol., 684) is in good agreement with the results of Bruns and Frumkin with platinised activated carbon (*ibid.*). R. CUTHILL.

**Surface films of batyl, chimyl, and selachyl alcohols.** B. C. J. G. KNIGHT (Biochem. J., 1930, 24, 257—261).—The values obtained between 10° and 40° for the cross-section of the heads of batyl and chimyl alcohols suggest that these alcohols have the unsymmetrical  $\alpha$ -glyceryl ether structure.

S. S. ZILVA.

**Dark-ground microscopy with very thin films on liquid surfaces.** H. ZOCHER and F. STIEBEL (Z. physikal. Chem., 1930, 147, 401—435).—The structure of unimolecular films on liquid surfaces has been examined with the aid of the ultra-microscope. The films formed by aliphatic compounds, such as the fatty acids, are homogeneous under low compressions, but in the case of palmitic, stearic, and oleic acid films the position of adhering dust particles revealed the presence of boundary lines in the film at the point at which the surface area begins to change only slowly with increase in pressure, the separation of a new phase being thus suggested. In all films, with increasing compression there appears, prior to actual collapse, a regular array of point-like colloid particles, usually of uniform size and colour, for which the name "point structure" is proposed. Collapse normally occurs through the film breaking up into granules, or into parallel strips at right angles to the direction of compression, or by the colloid particles aggregating into flakes, and may be reversible, *i.e.*, after a time the film may re-form. With palmitic and erucic acids, metastable films consisting of a network with circular or hexagonal meshes have been observed in addition to the normal films. Compression curves have been obtained for various oils; that

for linseed oil shows the existence of two condensed states. Substances capable of forming meso-phases do not give homogeneous films, and in such cases the compression curves apart from actual examination of the film are totally misleading. Ethyl *p*-azoxybenzoate, for instance, forms a film which at the ordinary temperature consists of a network, but at higher temperatures this breaks up into colloid particles with a pronounced Brownian motion. Casein and haemoglobin form homogeneous films, or films with embedded colloid particles, according to the conditions. The formation of a homogeneous film only 10 Å. in thickness from a protein of mol. wt. 64,000 has been observed, the molecules in such a film presumably being deformed into thin discs (*cf.* Gorter and Grendel, A., 1929, 88). The behaviour of cellulose derivatives depends on the method of preparation; in some cases perfectly homogeneous films are formed (*cf.* Katz and Samwel, *ibid.*, 1277). Rubber and resins do not give homogeneous films. Of the various homogeneous films examined, some seemed definitely liquid and others definitely solid, but many had the properties of soft plastic masses.

R. CUTHILL.

**Actual concentration of solutions and the investigation of their surface properties.** M. LEVAILLÉ-EZERSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 461—468).—The expression  $aC = \rho_n - 1$  is derived on theoretical grounds, where  $a$  is a constant,  $C$  is the actual concentration of a solute, and  $\rho_n$  is the difference between the relative densities of the surface layer of a solution and of the pure solvent. The above formula is verified for a number of solutions.

R. TRUSZKOWSKI.

**Frictional electricity.** P. E. SHAW (Phil. Mag., 1930, [vii], 9, 577—583).—A brief review of the present state of knowledge with regard to frictional electricity, the part played in its production by the presence of surface films, and the importance of the two factors, strain of surfaces and rise of temperature, as a result of rubbing. The difference between triboelectric charges and Volta's contact potential is indicated. M. S. BURR.

**Surface tension.** V. Jaeger's maximum pressure method. A. W. PORTER (Phil. Mag., 1930, [vii], 9, 1065—1073).—Jaeger's method for the determination of the surface tension of liquids has been examined. Curves are derived which connect the pressure due to that portion of the bubble which projects beyond the end of the tube with the (internal or external) radius of the tube for various angles of contact greater than 90°. Such curves enable a decision to be made as to whether the internal or external radius should be used in calculating the surface tension; they also indicate what is the most suitable radius in particular circumstances. When the internal radius is used, the calculation involves the angle of contact, otherwise not.

C. A. SILBERRAD.

**Determination of surface and interfacial tension from the maximum pull on a ring.** W. D. HARKINS and H. F. JORDAN (J. Amer. Chem. Soc., 1930, 52, 1751—1772; *cf.* A., 1927, 108).—The absolute surface tension,  $\gamma$ , of a liquid is determined, in



conjunction with the equation  $\gamma = Mg \cdot f(R^3/V, R/r)/4R$ , by the maximum pull ( $P = Mg$ ) required to detach from the surface a ring of radius  $R$  made from wire of radius  $r$ .  $V$  is the volume of liquid raised above the free surface of the liquid. Values of  $P$  have been determined for water, benzene, and bromobenzene, with rings of different dimensions, and by means of  $\gamma$  derived from measurements of capillary rise,  $f(R^3/V, R/r)$  has been evaluated and the results are tabulated. For benzene and bromobenzene at 25°,  $\gamma$  is 28.23 and 35.75 dynes per cm., respectively.

The technique and the chainomatic balance used in determining  $P$  are described, and sources of error are investigated. The angle of contact between the ring and the liquid must be zero, the ring must lie in one horizontal plane, and for a maximum radius of 0.8 cm. the diameter of the vessel which confines the liquid must not be less than 8 cm. Interfacial tensions may be determined by the ring method.

J. G. A. GRIFFITHS.

**Theory of the ring method for determination of surface tension.** B. B. FREUD and H. Z. FREUD (J. Amer. Chem. Soc., 1930, 52, 1772—1782).—Mathematical. Laplace's equation affords a basis for the absolute determination of the surface tension of liquids by the ring method. The mode of evaluation is demonstrated, and the results agree with those of Harkins and Jordan (preceding abstract).

J. G. A. GRIFFITHS.

**Affinity. II.** T. DE DONDER (Bull. Acad. roy. Belg., 1929, [v], 15, 900—912).—A generalised mathematical treatment of systems approaching equilibrium under the influence of osmotic, surface tension, and adsorptive forces.

F. G. TRYHORN.

**Thermodynamical study of surface tension, affinity, and rate of adsorption. II.** R. DEFAY (Bull. Acad. roy. Belg., 1929, [v], 15, 983—991).—Mathematical. Generalised forms of Kelvin's formulae are given, and equations are derived for the affinity corresponding with adsorption in surface layers, and with the passage of a constituent from one phase to another across a surface. The expressions are applied to the evaluation of the affinities of condensation and vaporisation of a drop of liquid in a vapour system of infinite volume.

F. G. TRYHORN.

**Thermodynamical study of surface tension, affinity, and rate of adsorption. III.** R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], 16, 143—156).—Mathematical. Certain catalytic factors are introduced into de Donder's expression (cf. this vol., 277) for the velocity of a reaction in terms of the affinity. The theory of catalysis at a distance is discussed.

O. J. WALKER.

**Thermodynamical study of surface tension, affinity, and rate of adsorption. IV.** R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], 16, 344—353).—A mathematical discussion of catalysis in surface reactions represented by a series of chain reactions following on adsorption. It is shown that when a process may be regarded as a series of chain reactions the total affinity changes in the latter are equal to the affinity of the isolated process. It is stated as a corollary that the final equilibrium of the process is

independent of the presence of the series of chain reactions brought about by such a catalyst.

F. G. TRYHORN.

**Thermodynamical study of surface tension, affinity, and rate of adsorption. V.** R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], 16, 468—487; cf. this vol., 420).—Mathematical.

J. R. I. HEPBURN.

**Ebullioscopic study of some aqueous equilibria at 100°.** E. ROUYER (Ann. Chim., 1930, [x], 13, 423—491).—The ebullioscopic method of Bourion and Rouyer (A., 1928, 1185) has been applied to the study of the molecular state of various phenols in aqueous solution at 100°. For pyrocatechol, resorcinol, quinol, pyrogallol, and 1:2:4-trihydroxybenzene, there is an equilibrium between simple and double molecules at  $c = 0.5$ — $1.75M$ , and between simple and triple molecules at  $c = 1.75$ — $2M$ . Phloroglucinol exhibits no association in water at 100°.

A study has been made of the neutralisation of acids by bases at 100° with results which show that temperature has no influence on the general course of the reaction.

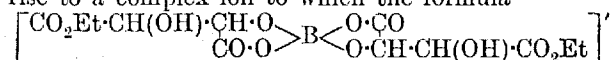
The b. p. of solutions containing mixtures of various salts have been determined, and by applying the mixture rule, the existence or otherwise of double salts has been inferred. In some cases, the equilibrium constants have been calculated. Thus by investigation of mixtures of magnesium chloride with lithium, sodium, potassium, or ammonium chlorides, and of magnesium bromide with potassium bromide, the double salts,  $MgX_2.MX$ , where  $X$  is a halogen element and  $M$  an alkali metal, are shown to exist. No double salts of magnesium chloride and calcium, strontium, or barium chloride are present in solution at 100°. The double salts  $(NH_4)_2SO_4.MSO_4$ , where  $M$  is  $Mg$ ,  $Zn$ ,  $Fe^{II}$ ,  $Ni$ ,  $Co$ ,  $Mn$ ,  $Cu$ , or  $Cd$ ;  $CuCl_2.MCl$ , where  $M$  is  $Li$ ,  $Na$ ,  $K$ , or  $NH_4$ ;  $2CuCl_2.3MCl_2$ , where  $M$  is  $Ca$ ,  $Sr$ , or  $Ba$ ;  $K_2[CdCl_4]$ ;  $Na_2[CdCl_4]$ ;  $KCdCl_3$ ;  $CdCl_2.MCl_2$ , where  $M$  is  $Ca$ ,  $Sr$ , or  $Ba$ ;  $CdBr_2.MgBr_2$ ;  $CdBr_2.2MBr$ , where  $M$  is  $Na$ ,  $K$ , or  $NH_4$ ;  $CdI_2.MI$ , where  $M$  is  $Na$  or  $NH_4$ ;  $CdI_2.SrI_2$ ;  $HgCl_2.MCl$  and  $HgCl_2.2MCl$ , where  $M$  is  $Na$ ,  $K$ , or  $NH_4$ ; and  $HgCl_2.MCl_2$ , where  $M$  is  $Ca$ ,  $Sr$ , or  $Ba$ , exist in solution at 100°.

A. I. VOGEL.

**Absorption of light by alkali halides in aqueous solution.** H. FROMHERZ and W. MENSCHICK (Z. physikal. Chem., 1930, B, 7, 439—467).—Previous work has been supplemented by the systematic investigation of the dependence on concentration of the whole absorption curve (both pronounced maxima and doubtful feeble bands) for the chlorides of all the alkali metals and for the bromides and iodides of lithium, sodium, and potassium, by the method already described (A., 1929, 119). The weak absorption bands in the ultra-violet found by previous workers are due, not to the pure alkali halides or their association products, but to chance impurities. With increasing concentration of the solutions there is observed (1) a widening of the absorption bands which is pronounced in iodides, feebler in bromides, and not detectable in chlorides, and (2) a displacement of the whole band toward the ultra-violet, very marked with chlorides, less prominent with bromides, and not seen with iodides even at saturation. In the presence of

an excess of chloride ions, bromides and iodides have their absorption bands displaced toward the ultra-violet to an extent which is proportional to the concentration of chloride ions. The cations have no detectable influence on the position or displacement of the bands. It is considered that a satisfactory comparison of the results of measurements of refraction and of absorption cannot be made until the absorption measurements have been extended to a wider region of the spectrum. F. L. USHER.

**Influence of boric acid on the rotatory power of malic and tartaric acids. III. Complex borotartrates.** E. DARMOIS (J. Chim. phys., 1930, 27, 179—190; cf. this vol., 399).—When added to ethyl tartrate solutions, sodium metaborate gives rise to a complex ion to which the formula



is assigned. The solutions undergo mutarotation owing to the hydrolysis of the tartrate by hydroxyl ions. The effect of additions of potassium and lithium chloride on the rate of mutarotation has been studied. It is considered that Lowry's salt,  $[(\text{C}_4\text{H}_4\text{O}_6)_2\text{B}]\text{K}$ , is an acid salt and that a neutral salt probably exists in solution. These salts undergo considerable hydrolysis and the rotatory power varies considerably with the concentration. The existence of levorotatory borotartrates containing one atom of boron to each molecule of ethyl tartrate is also confirmed. J. A. V. BUTLER.

**Colloidal synthesis of certain readily crystallisable organic compounds.** N. VON WEIMARN (Bull. Chem. Soc. Japan, 1930, 5, 122—123).—At low temperatures ( $-80^\circ$ ) naphthalene, papaverine, camphor, salol, and benzophenone give stable colloidal solutions in aqueous sucrose. Dispersions of anthracene, anthraquinone, and phenanthrene can be prepared by pouring dilute alcoholic solutions into water at the ordinary temperature. Organic substances of relatively low m. p. give emulsions which on ageing become suspensions.

J. O. CUTTER.

**Effect of multivalent hydroxy-compounds in the synthesis of hydrosols.** I. A. DUMANSKI and V. M. SIMONOVA (J. Russ. Phys. Chem. Soc., 1930, 62, 729—762).—See this vol., 691.

**Alteration of physico-chemical properties in the region between colloid and molecular disperse systems. III.** W. OSTWALD and A. QUAST (Kolloid-Z., 1930, 51, 361—370).—Recalculation of formerly determined diffusion constants of highly dispersed colloids by means of a new formula has led to alterations in the absolute values but not in the variation of the values with the composition of the dispersion medium. A maximum of dispersity occurs in 50% aqueous alcohol mixtures. Other respects in which the recalculated values differ from the previous values are discussed. E. S. HEDGES.

**Centrifuging hydrochloric acid solutions of polonium.** (ILLE.) C. CHAMIE and M. GUILLOT (Compt. rend., 1930, 190, 1187—1189).—No polonium is removed from solutions in *N*-hydrochloric acid by centrifuging (6000 revs. per min.) for 90 min.,

but increasingly large amounts are removed as the reaction approaches neutrality, and as the duration of centrifuging is increased; e.g., 98% is removed from a neutral solution containing the equivalent of 23 e.s.u./c.c. after 4 hrs. The rate of removal is increased by ammonium chloride but decreased by 50% of glycerol. The curves obtained indicate precipitation in a colloidal form of a water-insoluble hydrolysis product, in which no part is played by adsorption on colloidal silica. Photographs from a vaselined glass plate dipped in the *N*-solution showed that the atoms of polonium exist in groups in solution. J. GRANT.

**Dispersity of dyes.** A. NISTLER (Kolloidchem. Beih., 1930, 31, 1—58).—A micro-method for the determination of diffusion coefficients has been applied to the examination of the dispersity of dyes and the results agree with the values obtained by other methods where such data are available. The dispersity of a given dye was found always to lie between two fairly close limiting values. Many freshly-prepared solutions of dyes showed a rapid alteration in dispersity, reaching a stable state after some hours or days, which might persist or be followed by a further slow change in the direction of increased dispersity (aurantia, erythrosin, alkali-blue, methyl-green) or coarsening (eosin A, uranin). This peculiarity was shown especially with aurantia, the dispersity of which changed more during the first hour after preparation than during the following year. The effect is most noticeable in the more concentrated solutions. Safranine, acid fuchsin, Magdala-red, and other dyes showed no such ageing effect. No general statement can be made about the variation of dispersity with concentration, since this varies from dye to dye, but in many instances, and particularly with the more coarsely dispersed dyes, the dispersity remains constant. The diffusion coefficient and radius of particle for 27 dyes are tabulated for different concentrations and after ageing for different times. Over the concentration range 0.1—0.001% the particle size of the majority of the dyes lies between 0.6 and 3.0  $\mu$ .

E. S. HEDGES.

**Orientation of anisotropic particles in an electric field. I. General. II. Application to the determination of the double refraction of clays.** C. E. MARSHALL (Trans. Faraday Soc., 1930, 26, 173—189).—A comparatively simple apparatus which enables the double refraction of sols to be measured is described. The results obtained show that the orientation of anisotropic particles depends primarily on their fundamental electrical properties. Substances obeying Maxwell's rule show positive double refraction with respect to the lines of force, whilst those not obeying it show negative double refraction. Results obtained with clays indicate that the particles are crystalline, and that the value of the double refraction can be taken as a characteristic constant for a clay fraction saturated with a particular cation. The variation of the value with different cations indicates that they take up definite positions in the crystal lattice.

C. J. SMITHELLS.

**Optical rotation of colloidal silicic acid.** S. J. DIJATSCHEVSKI (Kolloid-Z., 1930, 51, 316—318).—

The change taking place in silicic acid sols when kept is marked by the appearance of optical activity in the sol and a tendency to crystallise. The direction of rotation was always to the left, but a method of preparation of the sol so as to give quantitatively reproducible results has not been found. Sols became optically active when prepared from sodium monosilicate, but not when prepared from sodium disilicate. Sols in the optically active state are unstable and soon become turbid. E. S. HEDGES.

**Viscosity of cellulose nitrate solutions in mixtures of various solvents.** S. N. USHAKOV and J. M. SHNEER (J. Appl. Chem. Russia, 1929, 2, 719—738).—Acetone or benzene diminishes, whilst amyl or ethyl acetate increases, the viscosity of solutions of cellulose nitrate in various solvents. Ethyl alcohol at first diminishes the viscosity, but further additions increase it. CHEMICAL ABSTRACTS.

**Lyophilic colloids. VIII. Thymus-nucleic acid sol.** H. G. B. DE JONG and O. S. GWAN (Kolloidchem. Beih., 1930, 31, 89—100).—Viscosity measurements with dilute sols of sodium nucleate at 42° show that Poiseuille's law is obeyed. The viscosity-concentration curve indicates that the value of  $(\eta - \eta_0)/c \cdot \eta_0$  increases with the dilution as in the case of agar and gum arabic. When, however, a sol already containing 5 mg.-equiv. of potassium chloride is diluted with a solution of 5 mg.-equiv. of potassium chloride, a small decrease in this value is observed instead of a rise. In the first case the electrical conductivity rises and in the second it falls. Small quantities of electrolytes lower the viscosity greatly, the effects due to the chlorides of lithium, sodium, and potassium, potassium sulphate and iodide being practically equal; a stronger effect is exerted by calcium, strontium, and barium chlorides and magnesium sulphate, but again these salts show only small differences. Multivalent cations lower the viscosity of the sol, and the viscosity-hydrogen-ion concentration curve has been constructed. Addition of alcohol causes a dehydration which becomes marked at concentrations higher than 50%. E. S. HEDGES.

**Stabilising effect of polar molecules.** B. JIRGENSONS (Kolloid-Z., 1930, 51, 290—299).—Aminoacetic acid, carbamide, acetamide, and formamide have a stabilising influence on sols of casein, lecithin, haemoglobin, and silver chloride towards precipitation by calcium chloride or barium bromide. Investigations of this effect were carried out for a constant concentration of sol by keeping either the amount of electrolyte or that of organic substance constant and varying the concentration of the other. Aminoacetic acid and carbamide exert the stabilising influence under all conditions, but acetamide and formamide are effective only when a certain amount is present and at higher concentrations of electrolyte. The substances can be arranged in the following order of effectiveness: aminoacetic acid > carbamide > acetamide > formamide, and this is also the order of decreasing polarity of the molecules. The cause of the stabilisation is considered to be the formation of a complex between the colloidal micelle and the organic compound linked together by means of the salt. E. S. HEDGES.

**Protective properties of sols prepared by the tartaric acid method.** A. V. DUMANSKI and B. S. PUTSCHKOVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 469—486).—The protective effect of stannic hydroxide, silicic acid, and titanate hydroxide sols, prepared by the tartaric acid method, on gold sols diminishes with increasing dilution and with ageing of the protective sol. Purple sols are obtained by the addition of titanium to gold sols; these sols are coagulated by the addition of sodium chloride, but the coagulum can readily be redissolved in water. Stannic hydroxide forms an adsorption compound with colloidal gold, which can be precipitated as a bluish-black coagulum by the addition of sodium chloride; this precipitate can be redissolved in water with the production of a red solution. R. TRUSZKOWSKI.

**Structure and stability of colloidal particles.** S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1930, 62, 31—38).—Von Weimarn's theory of homoatomic combination applied to colloidal reactions of the type  $n_1\text{Fe}(\text{OH})_3 + n_2\text{FeCl}_3 \rightarrow n_3\text{FeCl}_3 \cdot \text{Fe}(\text{OH})_3$  leads to  $x = KCS/(1 + KC)$ , where  $x$  is the number of molecules of double compound formed,  $S$  the number of molecules in the surface layer of the ferric hydroxide particles,  $C$  the number of ferric chloride molecules in solution at equilibrium, and  $K$  is a constant. The stability,  $b$ , of a colloidal solution of the above type is equal to  $x/S$ , and is greatest when  $x = S$ .

R. TRUSZKOWSKI.

**Electrical properties of oil-water emulsions with special reference to the structure of the plasmatic membrane.** H. A. DIXON and T. A. BENNET-CLARK (Sci. Proc. Roy. Dublin Soc., 1930, 19, 421—440).—The behaviour of certain oil-water emulsions simulates very closely that of the limiting plasmatic membrane and it is inferred that the essential structure of the latter is a lipid emulsion stabilised by fatty acids or their salts. The phase relations of olive oil-water emulsions stabilised by sodium oleate have been studied by measurements of the conductivity. With higher concentrations of oil the conductivity falls and there is a gradual reversal to the water-in-oil type. Near the inversion point the emulsion consists of large irregular drops of oil which enclose smaller droplets of the aqueous phase. The addition of calcium chloride favours the water-in-oil type, but this effect may be neutralised by the further addition of sodium chloride. An emulsion just reversed by calcium chloride is sensitive to an alternating electric field. The conductivity very quickly increases to a value twenty times the original and then gradually decreases. Microscopical investigation showed that the application of the field causes an instantaneous deformation and coalescence of the aqueous disperse phase. For any emulsion the response diminishes rapidly with the voltage. A unidirectional field causes a similar rapid rise in the conductivity. For a given response the product voltage  $\times \sqrt{\text{duration}}$  is constant and this is said to imply that the cause of the inversion (change in the interfacial tensions) lies in an electrolytic process opposed by diffusion. T. H. MORTON.

**Production of fog in the neutralisation of alkali with hydrogen halides. II. Significance**

of the presence of ammonia. R. W. ALDIS and J. C. PHILIP (J.C.S., 1930, 1103—1109; cf. A., 1927, 620).—The formation of these fogs is now shown to be conditional on the presence of small quantities of ammonia—of the order 0.001%—in the sodium hydroxide solution. The fog droplets are  $10^{-4}$  to  $10^{-5}$  cm. radius, and contain 2*N*-hydrochloric acid and 0.3*N*-ammonium chloride. In fog formation, a hygroscopic nucleus of ammonium chloride is probably first formed by the ammonia escaping into the gas bubble from the sodium hydroxide and the hydrogen chloride present in the bubble. Water vapour then condenses on the ammonium chloride particle, and hydrogen chloride dissolves in the solution so formed. The relatively low mobility of the droplets accounts for their escape as fog before they come into contact with the surface of the bubble. J. R. I. HEBURN.

**Systems soaps-cresol-water.** E. ANGELESCU and D. M. POPESCU (Kolloid-Z., 1930, 51, 336—348).—Measurements of solubility, viscosity, surface tension, and setting point have been made for the systems consisting of sodium, potassium, lithium, and ammonium stearate, oleate, and palmitate with *o*-cresol and water. Soap solutions increase the solubility of *o*-cresol in water to a greater extent than do sodium hydroxide solutions of equivalent concentration, sodium oleate and palmitate having the greatest effect. The phenomenon cannot be attributed to hydrolysis. The viscosity of dilute soap solutions varies almost linearly with the content of *o*-cresol, with some exceptions where the curve is more complicated. Sodium and potassium stearates at 40—50° give viscosity curves showing a maximum. This behaviour is characteristic of systems containing colloid particles and it is probable that the viscosity of sols is at a maximum for particles of intermediate size. When the colloid particles are dispersed to molecules by the added cresol a minimum viscosity is attained and this corresponds with that reached in cresol-sodium hydroxide solutions. The electrical conductivity of sodium oleate solutions rises when cresol is added and reaches a maximum which corresponds with the minimum of viscosity. The cooling curve for 0.2*N*-sodium stearate shows that the setting temperature and the thermal effect accompanying it are lowered by the presence of *o*-cresol. The curve connecting surface tension with concentration of *o*-cresol passes through a minimum for concentrated soap solutions, but the addition of cresol to dilute soap solutions gives a rise in the direction of the value for cresol. *o*-Cresol lowers the surface tension of sodium hydroxide solutions rapidly only when it is present in rather more than equivalent amount. All the experimental observations are in accordance with the view that the addition of *o*-cresol causes an increase in the degree of dispersion of the soap particles.

E. S. HEDGES.

**Identity of colloidal particles in soap sols and gels.** K. KRISHNAMURTI (Nature, 1930, 125, 746).—A reply to McBain and McBain (this vol., 292).

L. S. THEOBALD.

**Study of the kinetics of coagulation of colloids by the aid of a photoelement.** A. DUMANSKI and P. SCHERSCHNEV (J. Russ. Phys. Chem. Soc., 1930,

62, 187—196).—The curves connecting opacity with time for arsenic trisulphide sols after the addition of barium chloride, and for ferric hydroxide sols after the addition of potassium sulphate, at first rise, and then fall, with the commencement of flocculation. The expression  $\tau = ac^n$  is obtained, in which  $\tau$  is the time after addition of the coagulating electrolyte,  $c$  is the number of c.c. of the latter added, and  $a$  and  $n$  are constants for a given system.

R. TRUSZKOWSKI.

**Influence of temperature on the coagulation of sols, and the problem of acclimatisation of animals.** N. R. DHAR and S. PRAKASH (J. Physical Chem., 1930, 34, 954—962).—Sols of ferric, chromic, aluminium, stannic, and zirconium hydroxides, and of vanadium pentoxide and copper ferrocyanide require smaller amounts of an electrolyte at 60° for coagulation than at 30°. With sols of dammar resin, mastic, gamboge, Prussian-blue, and sheep's serum the reverse is the case at temperatures from 40° to 70°. A rise in temperature accentuates ageing. The greater longevity of cold-blooded over warm-blooded animals is explained in the light of these results.

L. S. THEOBALD.

**Effect of non-electrolytes on colloidal thorium hydroxide by progressive dialysis of the latter in presence and in absence of electrolytes.** A. M. PATEL and B. N. DESAI (Kolloid-Z., 1930, 51, 318—323).—The effect of methyl, ethyl, and isopropyl alcohols, carbamide, sucrose, and acetone on the coagulation of thorium hydroxide sol by sodium chloride has been studied by measuring the rate of coagulation of the sol by means of a photo-electric cell. Although the non-electrolytes have little or no influence on the coagulation of the ordinary sol by electrolytes, it is found that with progressive purification of the sol by dialysis the non-electrolyte exerts an increasing sensitising effect, and that when dialysis has been carried to a sufficient degree even the non-electrolytes cause coagulation in absence of electrolytes.

E. S. HEDGES.

**Problems of present-day colloid chemistry. VI. Hydration of hydrophilic colloids.** H. R. KRUYT (Chem. Weekblad, 1930, 27, 160—162).—The protective action of the water of hydration of a hydrophilic colloid is due to water molecules which are oriented around the colloid particle, the degree of orientation gradually diminishing as the distance from the particle increases. Two types of water envelope are recognised, viz., compact and diffuse; the latter, consisting of the outer layers of but slightly oriented molecules, may be removed from the colloid, e.g., by addition of alcohol at the isoelectric point. The inner, compact layer of fully oriented molecules remains intact and the surface energy gradient across the envelope is correspondingly increased owing to the abrupt transition from oriented hydration molecules to the molecules of the dispersion medium.

H. F. GILLBE.

**Production of oxygen in the flocculation of a negative colloid by an electrolyte.** O. M. URBAIN and J. N. MILLER (Kolloid-Z., 1930, 51, 324—328).—A sol of "algor" obtained from sea-weed evolves oxygen when coagulated by barium chloride. The

amount of oxygen evolved is directly proportional to the amount of colloid present and is also chemically equivalent to the amount of barium adsorbed. The solution also develops acidity on flocculation of the colloid, and the amount of acid is equivalent to the adsorbed barium.

E. S. HEDGES.

**Gel formation from silicic acid sols by means of acids.** K. WOLF and M. PRAETORIUS (Rec. trav. chim., 1930, 49, 582—587).—The conditions necessary for the gelatinisation of silica sols containing up to 25%  $\text{SiO}_2$  have been investigated. With inorganic acids, particularly sulphuric acid, gelatinisation occurs readily. Rise of temperature reduces the time of gelatinisation. Organic acids are less effective and their action decreases in the order citric, oxalic, tartaric, lactic, acetic acid, and phenol. Gel formation under the influence of sulphuric acid occurs just as readily with sols which have been sensitised with small quantities of alkali. Gelatinisation is quickest with sols containing 6—12%  $\text{SiO}_2$ . Sucrose, dextrose, tragacanth, gum arabic, and agar-agar do not form gels, but thick liquids. A sol containing 25%  $\text{SiO}_2$  mixes in all proportions with alcohol and forms very stable sols.

O. J. WALKER.

**State of combination of water in ferric and aluminium hydroxide gels.** D. BALAREV and S. KRASREV (Kolloid-Z., 1930, 51, 328—331).—From solutions of ferric chloride or aluminium chloride acidified with hydrochloric or sulphuric acid the hydroxide was precipitated and the precipitate was analysed for sulphate and chloride. With ferric hydroxide precipitated in the presence of increasing amounts of sulphate, only chloride was adsorbed at low concentrations of sulphate, both chloride and sulphate at medium concentrations, and only sulphate at higher concentrations. In the case of aluminium hydroxide, chloride alone was found in the precipitate below a certain concentration of sulphate, and above that concentration sulphate alone was found. The sulphate ion is adsorbed more strongly than the chloride ion. The experiments were extended to include other ions and the results suggest the following order of adsorption:  $\text{SO}_4 > \text{Cl} > \text{NO}_3 > \text{I} > \text{CNS}$ . The water content of the ferric and aluminium hydroxides after various drying processes was determined; although the substances were precipitated under the same conditions the amounts were very uneven. The salts are supposed to be held by the gel in a state of inner adsorption in the same way that potassium sulphate is held by microcrystalline barium sulphate, and the water serves to hydrate the adsorbed electrolyte.

E. S. HEDGES.

**Production of kaolin and kaolinite.** E. ENK (Kolloid-Z., 1930, 51, 356—359).—Carbon dioxide can decompose felspar under the catalytic influence of the sodium, potassium, and calcium salts contained, giving an alumina-silicic acid gel. On drying, this gives kaolin, and at a higher hydrogen-ion concentration produces kaolinite.

E. S. HEDGES.

**Capillarity. XIV. Migration of salts in gels in consequence of evaporation.** K. SCHULTZE (Kolloid-Z., 1930, 51, 299—308).—Experiments on the efflorescence of sodium chloride on a silicic acid

gel surface after addition of hydrochloric acid to sodium silicate are described. The form of the efflorescence depends on whether the gel is alkaline or contains excess of acid; in the latter case long, fibrous crystals are formed, a fact which is held to indicate a difference in structure of the gel.

E. S. HEDGES.

**Diffusion of sodium chloride and sulphate in concentrated gelatin gels.** A. E. ALEEV and A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1930, 62, 349—354).—The velocity of diffusion at 20° of sodium chloride from a saturated solution into gelatin gels of various concentrations is for a period of 7 days 4.0 cm. in 40% gels, 4.3 cm. in 40.4% gels, and 2.0 cm. in 74.2% gels; the corresponding values for sodium sulphate are 2.7 cm. in 40.0%, 2.4 cm. in 40.4%, 1.8 cm. in 51.2%, and 1.4 cm. in 72.3% gels.

R. TRUSZKOWSKI.

**Nature of isoelectric gelatin in solution. Evidence for the existence of the ampholyte ion.** I. Ionic displacement reactions. II. Conductivity titrations of gelatin with crystal-violet. A. E. STEARN (J. Physical Chem., 1930, 34, 973—980, 981—992).—I. The changes in  $p_H$  accompanying the mixing of solutions of gelatin and the dyes crystal-violet, malachite-green, acid fuchsin, and eosin as well as yeast-nucleic acid have been studied. Gelatin undergoes a replacement with acid and basic dyes; the former liberate hydroxyl ions or take up hydrogen ions, whilst the latter liberate hydrogen ions. The reaction is continuous throughout a  $p_H$  range extending to both sides of the isoelectric point. Although the mechanism appears to be one of ionic displacement, the data indicate that the dyes react, not only with free protein ions, but also with some other form of protein which may be an ampholyte ion, the form in which isoelectric protein may exist.

II. The effect of crystal-violet on the conductivity of gelatin solutions has been investigated. When the basic ion from crystal-violet reacts with gelatin a disappearance of ions, as indicated by a fall in conductivity, results, and with excess of the dye all the gelatin combines. This complete combination occurs for  $p_H$  values on both sides of the isoelectric point of gelatin. The mechanism appears to be a covalent linking of dye cation both to the gelatin anion and to an ampholyte ion representing the main isoelectric form of gelatin.

L. S. THEOBALD.

**Elasticity, double refraction, and swelling of isoelectric gelatin.** M. KUNITZ (J. Gen. Physiol., 1930, 13, 565—606; cf. A., 1926, 1005).—Gels cast on glass slides or in frames give rise to unidirectional stresses which can be determined accurately by measurement of the double refraction produced. The modulus of elasticity of gels during swelling is affected only slightly by salts at concentrations of less than  $M/8$  and is independent of  $p_H$  values between 2.0 and 10.0. Higher concentrations affect the modulus and salts behave in a manner parallel with that of the Hofmeister series. The swelling produced in isoelectric gelatin by salts is due primarily to the effect on the osmotic forces of the gel, but at high concentrations of certain salts the swelling is increased by the influence of the salt on the elasticity of the

gel, a result in agreement with the theory of Northrop and Kunitz (A., 1926, 352, 793, 1098).

F. O. HOWITT.

**Vapour tension of jellies.** P. BARY (Compt. rend., 1930, 190, 1227—1228).—The fact that a jelly formed by swelling a lyophile colloid (e.g., gelatin) in water contains much more water than one formed by swelling in an atmosphere saturated with water vapour—which excess it loses on exposure to such an atmosphere—is explained as due to the fact (cf. Wiedemann and Luedeking, A., 1885, 1031) that all such colloids absorb water at first with evolution and later with absorption of heat. The limit of absorption in saturated vapour is the point where heat is neither evolved nor absorbed. There is no conflict with the second law of thermodynamics (cf. Schroeder, A., 1903, ii, 721).

C. A. SILBERRAD.

**Structure of gelatin sols and gels. II. Anisotropy of gelatin gels.** S. E. SHEPPARD and J. G. McNALLY (Coll. Symp. Ann., 1930, 7, 17—39; cf. this vol., 541).—Above about 38° gelatin sols contain macromolecules of mol. wt.  $1-3 \times 10^4$ . Formation of gelatin from collagen is essentially a disorientation of the macromolecules of collagen crystallites. At and below 15°, ash-free gelatin shows limited, and at higher temperatures unlimited, swelling; lateral expansion of the sheet is preceded by an initial contraction indicating residual strain or anisotropy left in the sheet on drying. There is no evidence that the ultimate units in dilute solutions of gelatin have one dimension of "low molecular" thickness (7 Å.). Dry, unstretched, ash-free gelatin gives an X-ray powder diagram of broad "amorphous" rings, and a sharp interference ring of "crystalline" character; strongly-stretched gelatin gives a spectrum scarcely distinguishable from that of collagen.

CHEMICAL ABSTRACTS.

**"Adaptation" of colloids.** A. REYEYSKI (Zhur. exp. Biol. Med., 1929, 11, 1—7).—The coagulation of egg-albumin or globulin sol by gum mastic, colloidal ferric hydroxide, or Prussian-blue depends on the time elapsing between the successive additions of one substance to the other.

CHEMICAL ABSTRACTS.

**Pectins. VIII.** K. SMOLEŃSKI, W. WŁOSTOWSKA, and A. MŁYNARSKI (Rocz. Chem., 1930, 10, 329—341).—The colloidal properties of beet pectin galacturonide have been studied. The viscosity of galacturonide solutions rises at 35° from 1.11 for 0.038% solution to 13.3 for 2.5% solution. Maximum viscosity for a given solution is obtained at the isoelectric point ( $p_H$  7—7.5). The foaming of galacturonide solutions is due partly to their low surface tension, which is for 2.5% solutions 77% of that of water. Maximum values are found for surface tension at  $p_H$  7—7.5. The  $p_H$  of galacturonide solutions is practically constant (3—3.7) at concentrations of 2.5—0.08%; below 0.08% the  $p_H$  value rises abruptly. Galacturonide is a hydrophilic colloid, possessing many properties in common with polygalacturonic acid.

R. TRUSZKOWSKI.

**Syneresis.** S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1930, 62, 39—55).—The viscosity of viscose solutions falls slightly during the first 4—5 days after

preparation, and then rises sharply. The addition of sodium chloride accelerates this process. The decline in viscosity is ascribed to hydrolytic formation of cellulose, with the liberation of water of hydration, whilst the final abrupt increase in viscosity is caused by formation of cellulose aggregates. Since the former process takes place the more rapidly the higher is the temperature and the greater is the dilution of viscose, the velocity of gelation increases correspondingly with temperature and dilution, and the same applies to the velocity of syneresis. The addition of alkali or of carbon disulphide, which tend to reverse the hydrolytic process, retards gelation and syneresis.

R. TRUSZKOWSKI.

**Adsorption and swelling. III.** V. KUBELKA (Kolloid-Z., 1930, 51, 331—336).—When kept in water free from carbon dioxide at 20°, 1 g. of dried hide powder takes up 7 c.c. of water, but this amount is reduced in the presence of neutral salts of the alkali metals. This influence is due mainly to the anion and decreases in the order sulphate > citrate > acetate > chloride > nitrate > thiocyanate. At concentrations below 0.5 g.-mol. per litre this order does not hold. The order of influence of the cations varies with the concentration, and at higher concentrations is  $Na > K > Li$ .

E. S. HEDGES.

**Thermodynamics of caoutchouc. II. Temperature change of rubber under adiabatic stretching.** L. S. ORNSTEIN, J. WOUDE, and (Miss) J. G. EYMERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 273—279; cf. this vol., 420).—A specimen of rubber which shows no hysteresis effect on stretching has been examined. For elongations of 250—350% the length changes slightly with time, but this is attributed to a phase change. The change in specific heat with elongation leads to values for the heat developed on stretching which agree well with experiment up to 150% elongation. Above this the rises in temperature observed are greater than those calculated from the thermodynamical equation, this being attributed to the influence of the second phase.

J. W. SMITH.

**Heat of swelling of crude caoutchouc.** P. STAMBERGER and C. M. BLOW (Kolloid-Z., 1930, 51, 376).—Polemical (cf. Hock, this vol., 694).

E. S. HEDGES.

**Cataphoresis of small particles in water.** (Miss) D. A. NEWTON (Phil. Mag., 1930, [vii], 9, 769—787).—Helmholtz's theory of cataphoresis appears to hold for colloidal but not for microscopic particles, the effect of endosmosis having been neglected. It has been found that small traces of thorium nitrate in water reduce the charge on an oil drop and eventually reverse it. The cataphoretic velocity of an oil drop in water rises to a maximum of  $3.9 \times 10^{-4}$  cm./sec. for water of conductivity  $4 \times 10^{-6}$ , and is much less in purer water. Addition of 53% of alcohol to the water reduces the velocity to zero. For mixtures of alcohol and water the velocity  $v$  is found to be related to the specific inductive capacity  $K$  by the equation  $v = K(ax - b)$ , where  $a$  and  $b$  are constants and  $x$  is the percentage of water in the liquid. Spherical drops have a much higher cataphoretic velocity than irregularly shaped particles. All the



solid and liquid spherical drops examined have a velocity of  $3.9 \times 10^{-4}$  cm./sec. in water of conductivity  $4 \times 10^{-6}$ . X-Rays have no permanent effect on the charge of oil drops in water. N. M. BLIGH.

**Electric charge and velocity of infusoria *Paramœcium caudatum*.** E. V. ANDREJEVA (Kolloid-Z., 1930, 51, 348—355).—A negative electric charge of the nature of an adsorbed layer is present at the surface of the infusoria and the behaviour in an applied electric field is similar to that observed in the case of ordinary colloid particles. E. S. HEDGES.

**Electric behaviour of petroleum.** P. H. PRAUSNITZ (Kolloid-Z., 1930, 51, 359—360).—Using a sintered glass diaphragm, no electro-osmosis of dry petroleum could be observed when potentials up to 12,000 volts were applied. A fine suspension of glass particles in petroleum exhibited cataphoresis only under an applied potential of several thousand volts. E. S. HEDGES.

**Nature of electrolytic dissociation.** M. RABINOVITSCH (Z. physikal. Chem., 1930, 147, 345—370).—Theoretical. Experimental data relating to the electrical conductivity of salts in the solid and fused states and in solution have been considered with the view of studying the relationship between electrolytic dissociation and molecular structure. The influence of molecular polarisation, or ionisation within the molecule, is emphasised. Electrolytic conduction probably takes place by two different processes, viz., by ionic migration as in dilute solutions and by ionic exchange as in crystals. As a solution becomes more concentrated the second process gradually replaces the first, ionic interchange taking place within the complex molecular aggregates or solvates. The latter process often appears to be more rapid than the former; hence the anomalous form of the concentration-conductivity curves of some electrolytes and the existence of phenomena such as that observed by Rabinovitsch and Laskin (A., 1928, 835) that the dissociation constant of silicic acid in colloidal solution, as measured by electrical methods, is a thousand times as great as that of silicic acid in molecularly disperse solutions. The dielectric constant of the medium, since it influences the molecular polarisation of the electrolyte and, in dilute solutions, affects the electrostatic forces between isolated ions, plays an important part. M. S. BURR.

**Dissociation of strong electrolytes. I. Optical rotation and the theory of complete dissociation.** M. B. JACOBS and C. V. KING (J. Physical Chem., 1930, 34, 1013—1020).—Theoretical; the first of a series of papers critically discussing the evidence for complete dissociation of strong electrolytes in aqueous solution. Optical rotation data give little, if any, support to the theory. L. S. THEOBALD.

**Some recent contributions to the electrochemistry of strong electrolytes.** P. J. VAN RYSSELBERGE (Amer. Electrochem. Soc., May, 1930. Advance copy. 6 pp.).—An outline of observations which have some bearing on the modern views relating to strong electrolytes (cf. McBain and Ryszelberge, A., 1929, 143). The transport number of the potassium ion in potassium chloride dissolved

in a concentrated aqueous solution of sodium chloride or nitrate varies in a manner which agrees with that calculated on the basis of the law of mass action, using degrees of dissociation obtained from the data of Nernst and Orthmann for heats of dilution. A new method has been devised for calculating the concentrations of different ionic species in an electrolyte solution and has been applied to cadmium iodide and sulphate, which furnish several complex ions. The electrolytic dissociation theory has been treated mathematically, making use of the new Fermi statistics instead of the Maxwell-Boltzmann distribution law employed by Debye and Hückel. A new equation for the dependence of the activity coefficient of strong electrolytes on concentration has thus been deduced, and the activity coefficients of potassium chloride calculated from it agree better than those of Debye and Hückel with the experimental data. At higher concentrations the new calculated activity coefficients are higher than the experimental values, the ratio of the two being regarded as the degree of dissociation. A new definition of the ionic strength is developed. The general conclusions are that strong electrolytes cannot be regarded as completely dissociated, and that complex ions are formed more frequently than is usually supposed, especially in solutions containing bivalent ions.

H. J. T. ELLINGHAM.

**Behaviour of hydrogen chloride in different solvents.** W. F. K. WYNNE-JONES (J.C.S., 1930, 1064—1071).—In view of the hypothesis that the ionisation of an acid is determined by the basic character of the solvent rather than by its dielectric properties, measurements have been made of the distribution of hydrogen chloride between nitrobenzene and water and between benzene and water. In both non-aqueous solvents the concentration of hydrogen chloride is proportional to its partial pressure, indicating the absence of ionisation. The dielectric constants of nitrobenzene and benzene are 34 and 2.2, respectively. The ionisation of hydrochloric acid cannot be determined, therefore, by the dielectric constant of the solvent. On plotting vapour-pressure data for hydrochloric acid solutions the form of the curve suggests that, until the proportion of 3 mols. of water to 1 mol. of acid is reached, practically all the hydrogen chloride combines with water and exerts a negligible vapour pressure. Assuming that the partial pressure of hydrogen chloride for solutions above this concentration is always proportional to the mol. fraction of uncombined acid, and that all the combined acid is ionised, the value  $2.5 \times 10^7$  has been deduced for the ionisation constant of hydrochloric acid in water at 0°. This is of the same order as the value given by other investigators. M. S. BURR.

**Interpretation of colligative properties of weak electrolytes.** M. RANDALL and C. ALLEN (J. Amer. Chem. Soc., 1930, 52, 1814—1823).—Theoretical. The methods of Lewis and Randall are employed for the evaluation of the activity coefficients of weak electrolytes from cryoscopic and other data, on the assumptions that complete dissociation obtains at infinite dilution, that ions act like those of hydrochloric acid or sodium hydroxide at the same ion molality,

and that effects due to the ions are independent of those of the undissociated molecules, whilst the colligative properties are additive. The computation is facilitated by a knowledge of the true dissociation constant, and it is shown that this may be evaluated, for a moderately weak electrolyte, from the f.p. lowering of a 0.01M-solution.

The application of these methods to existing data shows that the postulates are valid for aqueous acetic acid solutions up to 0.4M.

J. G. A. GRIFFITHS.

**Redetermination of the titration dissociation constants of arginine and histidine with a demonstration of the "Zwitterion" constitution of these molecules.** T. W. BIRCH and L. J. HARRIS (Biochem. J., 1930, 24, 564—575; cf. Harris, A., 1923, i, 492; Hirsch, A., 1924, ii, 795; Simms, A., 1928, 837).—The three  $p_K$  constants for arginine are 13, 9.09, and 2.18 ( $t=23^\circ$ , 0.1N). The first of these values relates to the guanidine group, the second to an amino-group, and the third to the carboxyl group. The three  $p_K$  values for histidine are 8.95 for the amino-, 5.98 for the second iminazole, 1.78 (at  $23^\circ$  and 0.1N) for the third carboxyl group.

S. S. ZILVA.

**[Electrotitration curves of ortho- and pyrophosphoric acid.]** E. LEHNARTZ (Z. physiol. Chem., 1930, 188, 160).—Contrary to a previous statement by the author (cf. *ibid.*, 1929, 184, 46) and in agreement with Lohmann (cf. A., 1929, 208), orthophosphoric acid is more acid than pyrophosphoric acid only on the alkaline side of  $p_H$  6.81; on the acid side the reverse is the case.

J. H. BIRKINSHAW.

**Effect of isoelectric amino-acids on the  $p_H$  of a phosphate buffer solution.** H. BORSOOK and D. A. MACFADYEN (J. Gen. Physiol., 1930, 13, 509—527).—Isohydric phosphate buffers are treated with solutions of isoelectric amino-acids (alanine and glycine) of various ionic strengths and the change in  $p_H$  values is determined and compared with changes due to addition of aqueous solutions of potassium sulphate, potassium chloride, dextrose, ethyl alcohol, acetone, acetonitrile, carbamide, and phenol. The behaviour of phenol is exceptional, but the results generally are in agreement with the theory of amphoteric electrolytes advanced by Bjerrum (A., 1923, i, 444).

F. O. HOWITT.

**Equilibrium in the system ferric iron-quinol.** W. FRANKE (Annalen, 1930, 480, 1—38).—The following equilibrium has been investigated potentiometrically under varying conditions:  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{OH} + 2\text{Fe}^{+++} \rightleftharpoons \text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O} + 2\text{Fe}^{++} + 2\text{H}^+$ . In buffered solutions the equilibrium constant  $K$  shows a marked diminution with decrease of  $p_H$ ; the connexion is given by  $\log K = A + B \cdot p_H$ , where  $A$  and  $B$  are constants. The values obtained for  $K$  are in good agreement with those obtained by the distribution method previously employed (A., 1928, 965).  $K$  diminishes with rise of temperature, but the temperature coefficient depends on the  $p_H$  of the solution. At  $p_H$  5.33 the temperature coefficient,  $K_{30^\circ}/K_{20^\circ}$ , is 0.65 and at  $p_H$  4.13, 0.75.  $K$  is also dependent, to a very marked extent, on the nature of the buffer used, e.g., for  $p_H$  3.55  $K$  in a

tartrate buffer mixture is  $6.7 \times 10^5$ , and in a glycine-hydrochloric acid buffer  $3.98 \times 10^{-3}$ . In unbuffered solutions the  $p_H$  changes as the reaction proceeds to equilibrium.  $K$  diminishes as  $p_H$  increases; e.g., for  $p_H$  0,  $K=6.98$ , and for  $p_H$  4.13,  $K=5.77 \times 10^{-8}$ . Calculated values are in good agreement with experimental results. The presence of quinhidrone in the solid phase does not appreciably influence the equilibrium constant. At  $p_H$  3.05,  $K_{30^\circ}/K_{20^\circ}$  is 0.65 in unbuffered solutions and at  $p_H$  2.08 it is 0.57. The relationship between the position of equilibrium and the autoxidation phenomena previously observed (*loc. cit.*) is discussed.

M. S. BURR.

**Physicochemical studies of complex acids.**

**I. Tungstic acid.** H. T. S. BRITTON and W. L. GERMAN (J.C.S., 1930, 1249—1261).—The reaction between sodium tungstate and hydrochloric acid has been investigated by both potentiometric and conductometric titration methods. The results suggest that, at an early stage of the addition of hydrochloric acid to sodium tungstate, a sodium polytungstate is formed and behaves as a salt of a strong acid, resisting reaction with further hydrochloric acid. The latter thus remains in solution as such, imparting increased hydrogen-ion concentration and specific conductivity to the solution. The complex formed is probably  $\text{Na}_2\text{O}, 5\text{WO}_3$ . When a weak acid (phenylacetic or acetic acid) is employed, the polytungstate which appears to be formed in acid solution has the approximate composition  $\text{Na}_2\text{O}, 3\text{WO}_3$ . It is suggested that the sodium polytungstate is probably present in the form of a colloidal electrolyte, e.g.,  $2\text{Na}^+ + [\text{O}(\text{WO}_3)_2]^{--}$ , in which the anion contains tungstic oxide, either in a molecularly polymerised form, or, more probably, in a negatively-charged colloidal micelle. The results obtained explain the methods which have been adopted for the preparation of polytungstates. The ionisation constant of phenylacetic acid at  $18^\circ$  has been found by electrometric titration to be  $5.4 \times 10^{-5}$ .

M. S. BURR.

**Physicochemical studies of complex acids.**

**II. Vanadic acid.** H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1930, 1261—1274).—Conductometric titrations of sodium vanadates with hydrochloric acid, and of vanadic acid with sodium, ammonium, and barium hydroxides, have been performed. The potentiometric titration of sodium 3:1-vanadate ( $3\text{Na}_2\text{O}, \text{V}_2\text{O}_5$ ) by hydrochloric acid has also been attempted. The results are explained on the hypothesis that vanadium tends to form a heavy molecule on the border line between a true solute and a colloidal micelle, and of composition  $\text{Na}_2\text{O}, 2\text{V}_2\text{O}_5$  or  $\text{Na}_2\text{O}, 3\text{V}_2\text{O}_5$ .

M. S. BURR.

**Calculation of activity coefficients from solubility measurements: thallos chloride.** H. E. BLAYDEN and C. W. DAVIES (J.C.S., 1930, 949—956).—From the known solubility data relating to thallos chloride in the presence of other electrolytes, activity coefficients have been calculated taking into account the ionisation constants of thallos chloride (0.30) and of the other salts concerned. It has thus been shown that the value of the constant  $A$  in the Debye-Hückel equation  $-\log f = A\sqrt{\mu}$ , where  $f$  is the mean ion activity coefficient and  $\mu$  the ionic strength

of the solution, is not 0.505, the value accepted on the assumption of the complete dissociation of strong electrolytes, but 0.38, a value previously found for several univalent acids. The relationship thus obtained is valid up to values of the ionic strength considerably greater than 0.1, the limit usually accepted, and irregularities previously attributed to specific influences of the added ions disappear for concentrations of thallous chloride up to 0.1N. The disappearance of specific deviations on correcting for the incomplete dissociation of salts provides a strong support for the ionisation constants derived from conductivity measurements. The ionisation constant of thallous chlorate as determined from the equation  $-\log f = 0.38 \sqrt{\mu}$  is 0.34, and that of the  $\text{TlSO}_4'$  ion, in thallous sulphate solutions, is 0.036.

M. S. BURR.

**Ionic activity products and ionic activity constants.** I. M. KOLTHOFF (Chem. Weekblad, 1930, 27, 250—261).—A survey, based on the theory of complete ionisation of strong electrolytes.

H. F. GILLBE.

**Deviations from the law of Neumann, Joule, and Kopp.** I. N. DE KOLOSOVSKI. II. N. DE KOLOSOVSKI and I. M. SKULSKAJA (J. Russ. Phys. Chem. Soc., 1930, 62, 419—425, 427—460).—I. It is shown on theoretical grounds that the magnitude of the deviation for a compound is equal to the entropy change involved in its complete chemical transformation. The law in question should hold only for those compounds for which the heat of formation is independent of temperature.

II. See this vol., 544.

R. TRUSZKOWSKI.

**De Donder's chemical kinetics, and stable and metastable equilibria.** R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], 16, 157—167; cf. this vol., 420).—A further discussion of de Donder's theory of affinity, which, it is shown, leads to the conclusion that the affinity is zero for every state of true equilibrium. The conceptions of chemical friction ("frottement") and resistance and their relation to viscosity are discussed.

O. J. WALKER.

**Phase-rule studies on the proteins.** III. Quinquevalent nitrogen in organic compounds.

II. W. D. BANCROFT and C. E. BARNETT (J. Physical Chem., 1930, 34, 1217—1253).—The addition of hydrogen chloride by compounds containing two atoms of nitrogen in the molecule is discussed (cf. this vol., 798).

L. S. THEOBALD.

**Binary systems.** I. J. H. KOERS and F. E. C. SCHEFFER (Rec. trav. chim., 1930, 49, 588—621).—Mathematical. A derivation of the form of the van der Waals potential curves in three-phase binary systems, in which there is unmixing (cf. A., 1919, ii, 401).

O. J. WALKER.

**Ternary system lead-antimony-magnesium antimonide.** E. ABEL, O. REDLICH, and F. SPAUSTA (Z. anorg. Chem., 1930, 190, 79—89).—The above system has been investigated by the thermal and micrographic methods and the equilibrium diagram constructed. No mixed crystals are formed. The solid phase  $\text{PbMg}_2$  is unstable in contact with antimony, but magnesium antimonide is stable in contact with lead.

R. CUTHILL.

**Equilibrium in the system  $\text{Co}-\text{CO}_2-\text{CoO}-\text{CO}$ .** Indirect calculation of the water-gas equilibrium constant. P. H. EMMETT and J. F. SHULTZ (J. Amer. Chem. Soc., 1930, 52, 1782—1793).—The above equilibrium has been investigated by a flow method, the constants ( $P_{\text{CO}_2}/P_{\text{CO}}$ ) being 489.8, 245.9, and 148.4, respectively, at 450°, 515°, and 570°. No oxides other than cobaltous oxide were formed. Tests for carbon and metallic carbide in the cobalt after use were almost negative. In conjunction with previous data (this vol., 34), the constant  $[P_{\text{CO}}][P_{\text{H}_2}]/[P_{\text{CO}_2}][P_{\text{H}_2\text{O}}]$  has the values 7.31, 4.31, and 2.94, respectively, at 450°, 515°, and 570°, in agreement with the results of Neumann and Köhler (A., 1928, 707).

J. G. A. GRIFFITHS.

**Systematic doctrine of affinity. LI. Thermal decomposition of platinic, platinous, and cupric sulphides.** W. BILTZ and R. JUZA (Z. anorg. Chem., 1930, 190, 161—177; cf. A., 1929, 31).—Experiments on the progressive isothermal decomposition of platinic and platinous sulphides in which both the equilibrium pressure and the composition of the residue were recorded at each stage showed the two sulphides and also the lower sulphide and the metal to be slightly miscible, but gave no indication of the existence of other sulphides. From the results it is calculated that the heat of formation of solid platinous sulphide from platinum and rhombic sulphur is about +16 kg.-cal., and that of solid platinic sulphide from solid platinous sulphide and rhombic sulphur is about 5 kg.-cal. Similar experiments on the dissociation of cupric sulphide gave no evidence of the existence of sulphides other than cupric and cuprous sulphides.

R. CUTHILL.

**Double decomposition in the absence of a solvent. XI. The singular mutually irreversible system  $\text{TlNO}_3 + \text{KI} \rightarrow \text{KNO}_3 + \text{TII}$ .** A. P. PALKIN (J. Russ. Phys. Chem. Soc., 1930, 62, 57—76).—The m.-p. diagram of the system thallium iodide-potassium iodide shows a eutectic point at 90 mol.-% TII and 438°; above 65 mol.-% KI solid solution formation commences. The system potassium iodide-potassium nitrate shows a eutectic at 99.5 mol.-%  $\text{KNO}_3$  and 337°, and the existence of a compound,  $\text{KNO}_3\text{KI}$ , with a transition point at 358°, is indicated by the m.-p. curve. The formation of equimolecular compounds is indicated by the m.-p. diagrams of both the systems  $\text{TlNO}_3\text{-KI}$  and  $\text{KNO}_3\text{-TII}$ . The reaction  $\text{TlNO}_3 + \text{KI} \rightarrow \text{KNO}_3 + \text{TII}$  is practically irreversible owing to the insolubility of thallium iodide in the remaining constituents of the system, complete miscibility not being attained below 750°, as compared with 536° when potassium bromide is used in place of iodide.

R. TRUSZKOWSKI.

**System  $\text{K}_2\text{CO}_3\text{-Ca(OH)}_2\text{-KOH-CaCO}_3$ .** M. I. USSANOVITSCH and S. A. BOROVIK (Ukraine Chem. J., 1929, 4, 479—504).—The yield of potassium hydroxide obtained by the reaction between lime and potassium carbonate declines from 98% using 0.92M-potassium carbonate to 46% using 9.45M-solutions. The conditions of formation of the double compound  $\text{K}_2\text{CO}_3\text{CaCO}_3$  have been studied, and it is shown that the reaction  $\text{K}_2\text{CO}_3 + \text{CaCO}_3 \rightleftharpoons \text{K}_2\text{CO}_3\text{CaCO}_3$  is of the autocatalytic type, as the addition of the double

compound to its components greatly increases the velocity of its further production. The velocity of the above reaction in the presence of a number of insoluble catalysts is in the order  $K_2Mg(CO_3)_2 > MnO_2 > HgO > Fe > Cr_2O_3 > CuO > NiO > Ni_2O_3 > Cu_2O > Hg > SiO_2 > PbO > PbO_2 > Cu$ . The action of the first of these catalysts is similar to that of  $K_2CO_3 \cdot CaCO_3$ ; the remaining substances up to mercury inclusive do not affect the order of the reaction, but only its velocity; silica has no catalytic effect, and the remaining substances exert an increasingly inhibitive action. The reaction takes place exclusively in solution, its velocity agreeing with the Ostwald formula for autocatalysed reactions, taking as the active mass of potassium carbonate that part of it which is present in excess of that required for equilibrium (37.21%). R. TRUSZKOWSKI.

**Exchange of cations in the system aqueous soap solution-calcium permutite.** S. A. VOS-NESENSKI and L. P. ARTEMOVA (J. Russ. Phys. Chem. Soc., 1930, 62, 151—160).—The general character of the process of exchange of cations between calcium permutite and 0.05*N*-sodium oleate solution is the same as for ordinary salts, except in the case of very dilute oleate solutions, in which ionic exchange is to a certain extent inhibited, probably owing to the surface activity of soap. Ionic exchange is accelerated by raising the temperature and by the addition of alcohol. R. TRUSZKOWSKI.

**Homogeneity of thermochemical data.** W. SWIENTOSLAWSKI (Rec. trav. chim., 1930, 49, 564—567).—Polemical. A reply to Verkade and Coops (cf. this vol., 163). O. J. WALKER.

**Heat of formation of cementite.** T. WATASE (Z. physikal. Chem., 1929, 147, 390—395).—The heat of combustion of a sample of pure, gas-free cementite, mixed with sucrose or benzoic acid, has been determined. The molecular heat of formation of cementite from  $\alpha$ -iron and  $\beta$ -graphite, using Roth's data for the heat of oxidation of iron (A., 1929, 1389), is thus found to be  $-2500$  g.-cal. at  $20^\circ$  instead of  $-4800$  as previously obtained (A., 1929, 32). This is in fairly good agreement with Roth's value (*loc. cit.*)  $-3.9$ . M. S. BURR.

**Relation of the difference in heat content of a substance in the vitreous and crystalline states to the softening point of the glass and the m. p. of the crystals.** G. TAMMANN (Z. anorg. Chem., 1930, 190, 48—52).—It has been found for a number of organic substances that if  $T_1$  is the m. p. of a substance in the crystalline state and  $T_f$  is the softening point in the vitreous form, then  $\Delta E/\Delta W = T_f/(T_1 - T_f)$ , where  $\Delta E$  is the difference in energy content of the two forms at  $0^\circ$  Abs. and  $\Delta W$  is the difference in heat content at  $T_1$ , calculated from the specific heats. It appears probable, further, that  $\Delta r_{T=0} = \Delta r_{T_f}$  and  $\Delta r_{T_f}/\Delta r_{T_1} = T_f/T_1$ , where  $\Delta r$  is the difference in specific volume of the two forms at a particular temperature. R. CUTHILL.

**Application of moving boundaries to [the determination of transference numbers in] aqueous mixtures of hydrogen chloride and potassium chloride.** L. G. LONGSWORTH (J.

Amer. Chem. Soc., 1930, 52, 1897—1910; cf. A., 1929, 1014).—When the rising boundary method is applied to the above mixtures (chloride-ion concentration = 0.1*N*, at  $25^\circ$ ) two boundaries are produced: the lowest between the indicating electrolyte (initially, 0.1*N*-iodate ion) and pure potassium chloride, and the upper, indicated by methyl-violet, between the pure potassium chloride and a mixture of the latter with acid, produced in virtue of hydrogen ions having a greater mobility than potassium ions.

In conjunction with conductivity data it is shown that the mobility of the chloride ion varies linearly with the composition between the values for 0.1*N*-hydrogen chloride and 0.1*N*-potassium chloride; thus in these mixtures, the common ion does not cause the deviations of the conductivities from additivity. Qualitative agreement with the theory of Bennewitz and others (A., 1929, 1390) is obtained.

J. G. A. GRIFFITHS.

**Carbon line resistances.** J. B. SETH, C. ANAND, and G. L. PRII (Phil. Mag., 1930, [vii], 9, 415—422).—The influence of humidity on the resistances of pencil lines drawn on various insulators has been determined. For a humidity the resistance  $R$  is given by  $R^2 = kF^2t$ , where  $k$  is a constant dependent on the humidity,  $F$  is the rate of flow of the air current over the line, and  $t$  is the duration of the experiment. The application of the results to determination of the hygrometric condition of the atmosphere is discussed.

A. E. MITCHELL.

**Conductivity cell for eliminating electrode effects in measurements of electrolytic conductance.** T. SHEDLOVSKY (J. Amer. Chem. Soc., 1930, 52, 1806—1811).—The assumption of adsorption at the electrodes does not entirely explain the variations in cell constant which have been observed. The effect is eliminated by the use of a cell provided with three ring electrodes placed at intervals between the two end electrodes, each of the three being connected, in turn, with the detector and the bridge rebalanced. Data are recorded for potassium chloride and hydrochloric acid solutions.

J. G. A. GRIFFITHS.

**Screened bridge for the measurement of electrolytic conductance. I. Theory of capacity errors. II. Description of bridge.** T. SHEDLOVSKY (J. Amer. Chem. Soc., 1930, 52, 1793—1805).—I. A comprehensive discussion is given of the capacity effects to be considered in the design of a screened alternating-current Wheatstone bridge.

II. The above considerations are applied in the construction of a bridge, described in detail, for the accurate determination of conductivities.

J. G. A. GRIFFITHS.

**Comparison of simple and complex iron salts. I. Mobility of ions containing iron.** F. HOLL [with R. KÜGERL and K. ROETZANSKY] (Monatsh., 1930, 55, 132—143).—The conductivity of solutions of various simple and complex iron salts has been determined at  $25^\circ$ , and the mobility of the ions calculated from the deduced values of the limiting conductivity. The values, in reciprocal ohms, are found to be:  $\frac{1}{2}[\text{Fe}(\text{CN})_6]^{4-}$ , 100.8;  $\frac{1}{2}[\text{Fe}(\text{CN})_6]^{3-}$ , 97.3;  $\frac{1}{2}[\text{Fe}(\text{CN})_5\text{Me}]^{4-}$ , 92.4;  $\frac{1}{2}[\text{Fe}(\text{CN})_5\text{NO}]^{4-}$ , 71;  $\frac{1}{2}\text{Fe}^{++}$ , 68.4;  $\frac{1}{2}\text{Fe}^{3+}$ , 54. Assuming the validity of

Stokes' law, the ratio of the ionic radii for the above series is 100:103:109:142:147:187. The three symmetrical ions can be hydrated only to a relatively small extent.

H. BURTON.

**Systems dimethylpyrone-group V element halides.** V. S. FINKELSTEIN (J. Russ. Phys. Chem. Soc., 1930, 62, 161—169).—The molecular conductivity of mixtures of dimethylpyrone and arsenic trichloride falls from 6.00 in solutions containing 99.9% of the former substance to 0.12 at 23.44%. The molecular conductivity is reduced progressively by the addition of benzene to an extent which is proportional to the consequent dilution of dimethylpyrone, and conversely, is increased by the addition of dimethylpyrone to benzene-arsenic trichloride mixtures. The electrolyte in these systems probably consists of associated molecules of arsenic trichloride with dimethylpyrone; this view is further supported by cryoscopic measurements made on the system arsenic trichloride-benzene-dimethylpyrone.

R. TRUSZKOWSKI.

**Silver fluoride.** Conductivity of silver nitrate, silver fluoride, and hydrogen fluoride at 25°. E.M.F. of the chain  $\text{Ag}|\text{N}|\text{n}|\text{AgF}|\text{sat. KNO}_3|\text{N}|\text{m}|\text{AgNO}_3|\text{Ag}$  at 25°. E. V. CECHNOVITZER (J. Russ. Phys. Chem. Soc., 1930, 62, 133—149).—Hydrolytic dissociation takes place even in concentrated solutions of silver fluoride. Silver fluoride is reduced by the action of hydrogen to yield metallic silver and hydrogen fluoride. Semi-permeable membranes of silver hydroxide may be produced by the action of concentrated alkalis on silver nitrate solution. The molecular conductivity of silver fluoride is less than that of nitrate, as a result both of the smaller mobility of the fluoride ion, and of the smaller dissociation constant of the former salt in more concentrated solution. Conductivity measurements show that the value of this constant is the same for both salts at a concentration of N/60, whilst E.M.F. measurements indicate that equal dissociation takes place in 0.1N-solutions, and that  $\alpha$  is greater than 1.

R. TRUSZKOWSKI.

**Electrode potentials of silver in cyanide solutions.** C. G. FINK and G. B. HOGABOOM, jun. (Amer. Electrochem. Soc., May, 1930. Advance copy. 8 pp.).—During the electrolysis of a silver cyanide plating bath between silver electrodes at 0.54 amp.  $\text{dm}^2$  measurements were made of the anodic and cathodic polarisations at various regions of the electrode surfaces and at various times. The cathodic polarisation is always much greater than that at the anode and is slightly greater at the top of the electrode than at the bottom, whereas the reverse is true at the anode. These differences increase during the course of electrolysis and are attributed to the rise of a film of solution partly depleted in silver over the cathode surface and to the fall of a film of solution enriched in silver over that of the anode. This explanation is supported by a comparison of the polarisation values obtained when the electrodes are freely suspended in the solution and when they are set up in a Haring cell. The polarisation values thus depend on the thickness of the surface film and the

velocity with which it moves over the electrode surface.

H. J. T. ELLINGHAM.

**Potential of silver-zinc alloys.** G. PETRENKO, G. VINOBOV, A. DOBROWOLSKI, and B. PETRENKO (Ukraine Chem. J., 1929, 4, 429—437).—Measurements of the  $P.D.$  between electrodes of zinc and of zinc-silver alloys immersed in N-zinc sulphate solution indicate the existence of the alloys  $\text{AgZn}_2$ ,  $\text{AgZn}_3$ ,  $\text{Ag}_2\text{Zn}_3$ , and  $\text{AgZn}$ .

R. TRUSZKOWSKI.

**Hydrogen overvoltage.** M. G. RÆDER (Tidsskr. Kjemi Berg., 1930, 10, 37—40, 56—59).—A theoretical discussion.

H. F. HARWOOD.

**Cathodic polarisation of mercury.** E. SPITALSKI and N. I. NEKRASSOV (Z. physikal. Chem., 1930, 147, 321—344).—Mercury has been selected for the study of polarisation phenomena because of its high hydrogen overvoltage. Measurements of the polarisation voltage were made in an apparatus which allowed the direct and commutator methods to be employed in parallel. Two different types of hydrogen overvoltage have been observed, a higher and a lower. These differ in their dependence on the different factors involved. The state in which there is no overvoltage, described by Newbery (J.C.S., 1922, 121, 7), appears not to exist. The relation between "direct" cathodic polarisation voltage  $E$  and current density  $D$  is logarithmic,  $E = a - b \log D$ , the curve being the same in air and in hydrogen. For current densities 0.001—1.0 amp./sq. cm. the "commutator" polarisation voltage is independent of current density in hydrogen. For N-sulphuric acid it has a value of 0.8 volt referred to hydrogen. In air, however, the "commutator" polarisation decreases with increasing current density, but the values are not exactly reproducible. The rate of depolarisation at the cathode, after breaking the circuit, is greater in air than in hydrogen. After 0.01—0.05 sec. the rate of depolarisation in hydrogen is independent of the original current density, but in air the rate increases with increasing current density. Stirring of the solution does not affect the "direct" voltage, but causes a fall in the "commutator" voltage in air, although it has no influence in hydrogen. The rate of depolarisation is increased in air by stirring, but not in hydrogen. The effects obtained appear to be due to the bringing of oxygen to the cathode from other parts of the solution, and not to the removal of hydrogen. On stirring the mercury cathode during electrolysis no change is observed. On stirring during depolarisation a shift in the negative direction takes place after about 15 sec. This disappears at the end of a few minutes. Various phenomena observed at the surface of the mercury during polarisation are described. With decreasing hydrogen-ion concentration the "direct" potential increases. In air the "commutator" potential and rate of depolarisation increase with decreasing hydrogen-ion concentration, whilst the reverse is the case in hydrogen. The "commutator" potential under hydrogen is regarded as the true overvoltage, the presence of air causing disturbances due to secondary oxidation phenomena. The changes in the "direct" potential with current density are due to the ohmic resistance of the cathode boundary. The cause of the polarisation of mercury

lies in the accumulation of atomic hydrogen at the surface. This accumulation is due to the smallness of the catalytic influence of mercury on the reaction  $2\text{H} \rightarrow \text{H}_2$ . The behaviour of mercury is less complex than that of other metals because adsorption of hydrogen and chemical hydride formation are absent. A few observations have been made on the second or lower overvoltage. It can be obtained only by current densities which are lower than 0.025 amp./sq. cm. and it is very seldom obtained in an atmosphere of hydrogen. The presence of mercury salts or oxides is probably necessary.

M. S. BURR.

**Electrolytic polarisation. IX. Complex cyanides: (c) zinc, cadmium, and mercury.** S. GLASSSTONE (J.C.S., 1930, 1237—1247).—Measurements of cathode potential and current efficiency have been made during the electrolysis of solutions containing complex cyanides of zinc, cadmium, and mercury. The cathode potential observed depends on the ratio of cyanide to metal in the solution. The current efficiency for metal deposition is determined by the relative magnitudes of the potential of deposition of the metal in the presence of excess of cyanide to the potential of hydrogen evolution under the same conditions. For this reason the current efficiency for zinc can never reach 100%. For cadmium and mercury, however, the current efficiency for metal deposition is 100% as long as the rate of deposition does not exceed the rate of diffusion of the appropriate ions to the cathode. Beyond this limiting *C.D.*, the value of which may be calculated approximately, the cathode potential rises, hydrogen is evolved, and the current efficiency falls. As previously observed in similar cases, dilution reduces the limiting *C.D.* to an extent proportional to the reduction of concentration, whilst raising the temperature and stirring increase it. In order to explain the results there is no reason to suppose that complex cyanides dissociate slowly. Electrometric titration of zinc, cadmium, and mercury salt solutions with sodium cyanide, using electrodes of the corresponding metals, indicates that the following complex ions are formed:  $\text{Zn}(\text{CN})_4^{--}$ ,  $\text{Cd}(\text{CN})_3^{\cdot-}$ ,  $\text{Cd}(\text{CN})_4^{--}$ ,  $\text{Hg}(\text{CN})_3^{\cdot-}$ , and  $\text{Hg}(\text{CN})_4^{--}$ . There is a possibility that zinc forms a complex cation  $\text{Zn}_2(\text{CN})_2^{++}$  and that this, rather than the simple zinc ion, is discharged at the cathode during electrolysis.

M. S. BURR.

#### Activation of chemical reactions by salts.

**VI. Cathodic polarisation during electrolysis.** N. A. IZGARISCHEV and C. M. RAVIKOVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 255—259).—The cathode polarisation voltage obtained in the electrolytic deposition of nickel from nickel chloride solutions is affected by the addition of various chlorides in the order:  $\text{CdCl}_2 < \text{AlCl}_3 < \text{LiCl} < \text{CoCl}_2 < \text{MgCl}_2 < \text{NiCl}_2 < \text{NaCl} < \text{KCl} < \text{CaCl}_2 < \text{SrCl}_2 < \text{NH}_4\text{Cl} < \text{BaCl}_2 < \text{ZnCl}_2$ . The yields of nickel deposited per unit of current are as follows: in the presence of  $\text{NH}_4\text{Cl}$  68%,  $\text{NaCl}$  66%,  $\text{LiCl}$  64%,  $\text{KCl}$  60.1%,  $\text{MgCl}_2$  55.9%,  $\text{BaCl}_2$  52%,  $\text{SrCl}_2$  32.4%,  $\text{NiCl}_2$  35.4%, and  $\text{CaCl}_2$  30.8% of the theoretical. Of the above cations, only zinc and cadmium are deposited together with nickel on the cathode. The most lustrous deposits are obtained in the presence of lithium, sodium, ammonium, and

magnesium, whilst the toughest deposits are given by the addition of the first three of these metals and of cadmium. Evolution of gas at the cathode occurs to any considerable extent only in the presence of alkaline-earth metals.

R. TRUSZKOWSKI.

**Activation of chemical reactions by salts. VII. Oxidation-reduction systems.** N. A. IZGARISCHEV and A. V. TURKOVSKAJA (J. Russ. Phys. Chem. Soc., 1930, 62, 261—265).—The  $E_h$  of systems containing ferrous and ferric iron is increased by the addition of cadmium chloride, and is diminished by the addition of various other chlorides in the following order: action of  $\text{LiCl} < \text{MgCl}_2 < \text{CaCl}_2 < \text{BaCl}_2 < \text{NaCl} < \text{KCl} < \text{NH}_4\text{Cl}$ ; zinc chloride lowers  $E_h$  at concentrations below *N*, and raises  $E_h$  at higher concentrations, whilst the action of the remaining chlorides increases with their concentration. Nitrates raise the  $E_h$  value proportionately to their concentration in the order: action of  $\text{NH}_4\text{NO}_3 < \text{KNO}_3 < \text{NaNO}_3 < \text{Sr}(\text{NO}_3)_2 < \text{Ca}(\text{NO}_3)_2 < \text{LiNO}_3 < \text{Mg}(\text{NO}_3)_2 < \text{Cd}(\text{NO}_3)_2$ . The addition of sodium bromide raises  $E_h$  more than does sodium nitrate, and sodium sulphate depresses  $E_h$  to a greater extent than does sodium chloride. The above effects cannot be attributed to variations in  $p_H$  consequent on the addition of these salts, or to the formation of complex double salts with iron chlorides.

R. TRUSZKOWSKI.

**Adsorption phenomena occurring during the anodic oxidation of formic acid.** P. HERASYMENKO (Ukraine Chem. J., 1929, 4, 439—455).—The anodic oxidation of formic acid is investigated using revolving intermittently connected anodes, so that the products of oxidation are continually removed from each anode. The current-potential curves obtained differ from those found by Müller (A., 1923, i, 743; 1928, 377), using stationary anodes, in which the curves rise to a first maximum, fall, and then again rise; here the first maximum is absent. The addition of bromides or chlorides considerably reduces the current due to oxidation of formic acid, as a result of preferential adsorption on the anode, with consequent elution of formic acid. The saturation current corresponding with the deposition of bromine from a *M*-potassium bromide solution is fifty times as great as the first maximal oxidation current of *M*-formic acid, suggesting that only a part of the area of the anode activates oxidation. The first oxidation current is supposed to be due to oxidation of formic acid molecules activated by adsorption at certain active centres. This current becomes constant when equilibrium is attained between the molecules undergoing adsorption at the active centres and those undergoing oxidation. With stationary electrodes the active centres then become inactivated by exhaustion of the adsorptive forces; hence the diminution in oxidation current observed by Müller. At the second rise of the curves unadsorbed formic acid is oxidised over the whole anodal surface, the higher voltage (about 1.2 volts) supplying the necessary energy without the necessity of active centres.

R. TRUSZKOWSKI.

**Systems with particularly small asymmetric emission-work for electrons.** W. O. OSTWALD (Kol.



loid-Z., 1930, 51, 370—376).—Relations between certain types of electric rectifiers, contact catalysts, and photo-electric cells are discussed, especially in regard to their structure. A mixture of electrically conducting material with insulating material is particularly characteristic of these systems. The work of emission of the electrons for such systems is both small and asymmetrical or oriented.

E. S. HEDGES.

**Photogalvanic phenomena with irradiated cupric oxide electrodes (Becquerel effect).** M. KARSCHULIN (Biochem. Z., 1930, 220, 122—132).—The preparation of copper oxide electrodes is described and the *E.M.F.* of the photogalvanic cell prepared from them has been determined with water and solutions of the sodium halides as electrolytes. The cell filled with water showed only a slight increase of potential ascribed to the thermal absorption of the copper oxide. Large *P.D.* between sodium iodide and other halides are due to the occurrence of photo-chemical (formation of copper subiodide) and auto-catalytic (tri-iodide ion) processes.

P. W. CLUTTERBUCK.

**Rates of second-order gas reactions.** L. S. KASSEL (Proc. Nat. Acad. Sci., 1930, 16, 358—364).—Theoretical. The usual formula,  $-dN/dt = Ze^{-E/RT}$  is unsatisfactory. The reaction  $2\text{HI} = \text{I}_2 + \text{H}_2$  (Bodenstein, A., 1897, ii, 252) may be empirically represented by assuming a linear increase of the energy of activation with temperature; this requires the chance of reaction to increase continuously with the energy of collision. It is predicted from theoretical considerations that this linear increase will fail at temperatures only slightly higher than those yet reached in the hydrogen iodide decomposition (800°).

J. R. I. HEPBURN.

**Velocity of unimolecular reactions.** J. FRENKEL (Z. Physik, 1930, 62, 49—53).—Póányi and Wigner in their expression for the probability of dissociation or evaporation of a single molecule (A., 1929, 404) have made the implied assumption that the "inner" temperature of a molecule, due to the vibrational energy of its component atoms, coincides with its "external" temperature, defined by translational or rotational energy. Without this assumption and on the basis of the classical distribution law it is shown that Póányi and Wigner's expression  $ve^{-U/kT}$  is a limiting case which holds for complex molecules or generally as a first approximation. For the particular case of nitrogen pentoxide the following expression is obtained:  $A = \sqrt{2\pi(Nv/m!)} \cdot e^{-2\sqrt{Um/\gamma kT_0}} \times (Um/\gamma kT_0)^{m+3/4}$ . For such a simple molecule the theory gives only a qualitative result.

S. L. COWAN.

**Luminosity in gaseous combustion.** W. T. DAVID and W. DAVIES (Phil. Mag., 1930, [vii], 9, 390—401).—Photographic investigation of the explosions of carbon monoxide-oxygen mixtures shows that luminosity can be manifest in exploded gaseous mixtures long after chemical combination is complete. It is suggested that, since the more permanent gases present remain luminous at temperatures below which they are normally luminescent, the chemical combination leads to the formation of abnormal molecules which pass only slowly to normal

molecules. The heat evolved in the transition from abnormal to normal molecules is considered to represent an appreciable part of the heat of combustion.

A. E. MITCHELL.

**Temperature measurements in gaseous combustion.** W. T. DAVID and W. DAVIES (Phil. Mag., 1930, [vii], 9, 402—414).—The temperature as measured by a platinum wire in a gaseous explosion is always considerably higher than that indicated by pressure measurements during the explosion. The platinum wire maintains this higher temperature for about 1 sec. after the maximum pressure has been reached. The temperature of the wire is regarded as being equal to that of the gas plus a quantity corresponding with the reversion of abnormal to normal molecules (cf. preceding abstract).

A. E. MITCHELL.

**Rate of rearrangement of pinene to dipentene.** L. S. KASSEL (J. Amer. Chem. Soc., 1930, 52, 1935—1936).—In view of the results of Conant and Carlson (this vol., 92), the correct first-order velocity coefficients for the above rearrangement are twice those reported by Smith (A., 1927, 212).

J. G. A. GRIFFITHS.

**Kinetics of the reaction of reduction of arsenic anhydride in hydrochloric acid solution by phospho-nitrous [hypophosphorous ?] acid.** G. S. VOZDVIJENSKI and A. F. GERASIMOV (J. Russ. Phys. Chem. Soc., 1930, 62, 409—418).—The velocity of reduction by hypophosphorus acid of arsenic anhydride in hydrochloric acid solutions of various concentrations corresponds with that of a reaction of the second order, expressed by  $-dC_{\text{As}(\text{OH})_3}/dt = KC_{\text{As}(\text{OH})_3} \cdot C_{\text{H}_3\text{PO}_2} = KC_{\text{As}(\text{OH})_3} \{B - (C_0 - C)\}$ , where *B* and *C*<sub>0</sub> are respectively the initial concentrations of hypophosphorous and arsenic acids, and *C* is the concentration of the latter at time *t*. The velocity coefficients vary with the initial concentrations of the substrates and solvent. The reaction proceeds probably in three stages:  $\text{AsCl}_3 + \text{H}_3\text{PO}_2 = \text{As} + \cdot\text{PO}_2 + 3\text{HCl}$ ,  $\cdot\text{PO}_2 + \text{H}_2\text{O} = \cdot\text{PO}(\text{OH})_2$ ,  $2\{\cdot\text{PO}(\text{OH})_2\} = \text{H}_4\text{P}_2\text{O}_6$ .

R. TRUSZKOWSKI.

**Equation for the reaction between invertase and sucrose.** J. BERKSON and F. HOLLANDER (J. Washington Acad. Sci., 1930, 20, 157—171; cf. A., 1928, 797; 1929, 772).—The equation  $p' = 200/(1 + e^r)$ , where *p* is the percentage of unchanged sucrose and *r* is a rate parameter, quantitatively describes the reaction between sucrose and yeast invertase with variation of temperature, concentration of enzyme, and initial concentration of sucrose. The parameter *r* varies linearly with the concentration of invertase, non-linearly but regularly with concentration of sucrose and temperature.

J. R. I. HEPBURN.

**Law of periodicity. VI. Esterification of certain alcohols and activity of mesitylene.** A. RAVIKOVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 177—185).—The velocity of esterification of a number of homologous alcohols with acetic acid in the presence of hydrogen bromide varies periodically with the accumulation of similar radicals. Thus the velocity of formation of methyl acetate is greater than that of ethyl acetate, and that of both is smaller than that of

glycerol. The reverse is the case with the corresponding fully methylated derivatives; the order is here  $\text{CMe}_3\cdot\text{OH} < \text{CMe}\cdot\text{CMe}_2\cdot\text{OH}$ , and  $\text{CMe}_3\cdot\text{OH}$  and  $\text{CMe}_3\cdot\text{CMe}_2\cdot\text{OH} > \text{OH}\cdot\text{CMc}_2\cdot\text{CMe}_2\cdot\text{OH}$ . With accumulation of  $>\text{CH}\cdot\text{OH}$  groups the order of activity is  $\text{MeOH} < (\text{CH}_2\cdot\text{OH})_2 > [\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}]_2$ . Periodicity can also be observed in the reactivity of homologous aromatic compounds; thus benzene reacts more energetically with sulphuric acid than does toluene, whilst mesitylene is six times as active as in benzene. Mesitol is, on the contrary, less reactive with acetic acid in the presence of hydrogen bromide than is phenol.

R. TRUSZKOWSKI.

**Velocity of decomposition of diazo-compounds in water.** IV. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1930, 33, 177—178B; cf. this vol., 300, 337).—The rate of decomposition of benzenediazonium chloride at  $0^\circ$  is greatly increased in sunlight.

O. J. WALKER.

**Velocity measurements of intramolecular changes in *N*-chloroacet- $\alpha$ -naphthylamide.** A. P. J. HOOGEVEEN (Rec. trav. chim., 1930, 49, 503—525; cf. Fontein, A., 1928, 716).—The velocity of conversion of *N*-chloroacet- $\alpha$ -naphthylamide into 4-chloro-1-acetnaphthalide has been measured in mixtures of alcohol and water and of acetic acid and water, using varying quantities of hydrochloric acid as catalyst. In each case the reaction velocity has a minimum value in the mixtures containing 50 vol.-% of the non-aqueous solvent. Up to 20% of alcohol or acetic acid the effect of increasing the concentration of hydrochloric acid is very small. For equal percentages of alcohol and of acetic acid the reaction velocity in concentrated solutions is greater in the acetic acid mixtures, whilst in dilute solutions the velocity is greater in the alcohol mixtures. Above 50% of either acetic acid or alcohol the main product is 4-chloro-1-acetnaphthalide, with some of the 2-chloro-compound, but in dilute alcoholic solution chiefly resinous products are formed.

O. J. WALKER.

**Dissolution velocity of oxygen in water.** S. MIYAMOTO and T. KAYA (Bull. Chem. Soc. Japan, 1930, 5, 123—136).—The velocity of oxidation of aqueous sodium sulphite by a stream of purified air is independent of the concentration of solute, and is a linear function of the velocity of the air. The dissolution velocity of oxygen in water under conditions of zero concentration of oxygen in the dineric surface solution/air is deduced from the oxidation velocity coefficient.

J. O. CUTTER.

**Velocity of dissolution of metals in aqueous salt solutions.** III. **Velocity of dissolution of magnesium in ammonium chloride solution.** E. BEKIER and B. ZABŁOCKI (Rocz. Chem., 1930, 10, 314—327; cf. this vol., 549).—The process of dissolution of magnesium in aqueous ammonium chloride consists in the following reactions: (i)  $\text{Mg} + 2\text{H}_2\text{O} = \text{Mg}(\text{OH})_2 + 2\text{H}_2$ , (ii)  $2\text{H} \rightarrow \text{H}_2$ , (iii)  $\text{Mg}(\text{OH})_2 + 2\text{NH}_4\text{Cl} = \text{MgCl}_2 + 2\text{NH}_4\text{OH}$ . The velocity of dissolution is determined by the velocity of diffusion at the metal surface, i.e., it is proportional to the rate of stirring. The expression  $K = (v/st) \cdot \log_e V_0/(V_0 - v_0)$  is derived and experimentally verified, where  $K$  is

the velocity coefficient,  $v$  is the volume in c.c. of the solution,  $V_0$  is the number of c.c. at N.T.P. of hydrogen corresponding with the initial ammonium chloride content ( $2\text{NH}_4\text{Cl}$  equivalent to  $\text{H}_2$ ),  $v_0$  is the number of c.c. at N.T.P. of hydrogen evolved at time  $t$ , and  $s$  is the area in  $\text{cm}^2$  of the magnesium plate used. The temperature coefficient of the reaction is 1.72. The velocity of reaction at high concentrations of ammonium chloride is not proportional to the concentration, showing that factors other than diffusion, represented by equation iii above, enter into the reaction. In *N*-solutions of ammonium chloride the velocity of the third reaction rises, whilst that of reactions i and ii falls, thereby producing passivation of the metal surface. The value of  $K$  varies inversely with the concentration of ammonium chloride between 1.04 and 0.046*N*, below which the velocity again fails, owing to the covering of the metal surface by hydroxide. The addition of magnesium chloride or of ammonia solution retards the velocity of reaction, as a result of reversal of reaction iii; ammonia exerts, apart from this, a specific inhibitive action.

R. TRUSZKOWSKI.

**Velocity of crystallisation.** II. E. N. GAPON (Ukraine Chem. J., 1929, 4, 505—519; cf. A., 1929, 1232).—The absolute value of the velocity of crystallisation under identical conditions (temperature and number of nuclei) depends on the degree of supersaturation. The initial period of crystallisation is for many salts characterised by increase in the velocity coefficient and depends on the neutralisation of the charges on the surface of the nuclei. The expression  $(K_0 - K_n)/A = \text{const.}$  is derived, where  $K_0$  is the initial velocity coefficient,  $K_n$  is the mean coefficient of the succeeding period, and  $A$  represents the quantity of salt adsorbed. Electrolytes other than that crystallising either diminish the degree of adsorption of the substance or have no influence on adsorption; in the former case, their action is due to preferential adsorption with consequent weakening of the electrostatic field of force of the crystal surface. Such salts are those the degree of polarity of the ions of which is greater than that of the ions of the substance undergoing crystallisation, whilst for indifferent electrolytes their ions possess a smaller polarity. In the former case the velocity of crystallisation is enhanced, and in the latter case diminished. The ratio of the velocity coefficient of dissolution to that of crystallisation is for ammonium oxalate and oxalic acid equal to 1, for sodium oxalate to 2.46, and for sodium dinitrophenoxide to 12.2.

R. TRUSZKOWSKI.

**Kinetics of the heterogeneous thermal decomposition of methyl formate.** E. W. R. STEACIE (Proc. Roy. Soc., 1930, A, 127, 314—330).—Using an apparatus essentially the same as that employed by Hinshelwood (A., 1927, 630), the thermal decomposition of gaseous methyl formate has been investigated in silica vessels at  $368$ — $550^\circ$ . The results obtained for the rate of decomposition, together with the analysis of the products, indicate that the primary reaction is the decomposition of methyl formate into methyl alcohol and carbon monoxide, involving the doubling of the initial pressure; this is followed by a slow secondary reaction when the

alcohol decomposes in stages, with formation of formaldehyde, carbon monoxide, and hydrogen. The results of experiments in which the reaction vessel is packed with powdered silica indicate that the reaction takes place entirely at the surface of the silica. The complete heterogeneity of the reaction is further confirmed by the fact that the temperature coefficient is unaltered by the addition of powdered silica and is satisfactorily expressed by the Arrhenius equation. The heat of activation is calculated to be 48,700 g.-cal. per mol. Since the rate of the reaction is expressed by the equation  $-d/dt(\text{H}\cdot\text{CO}_2\text{Me}) = K(\text{H}\cdot\text{CO}_2\text{Me})/[1 + c(\text{MeOH})/a]$ , where  $c$  is a constant independent of the temperature and  $a$  is the initial concentration of methyl formate, one of the products must be adsorbed so strongly that the free space is inversely proportional to the pressure of the product (cf. Hinshelwood and Prichard, A., 1925, ii, 310). The effects of adding carbon dioxide, methane, carbon monoxide, hydrogen, water vapour, formaldehyde, and methyl alcohol were studied, but with the exception of methyl alcohol, for which the retarding effect, although considerable, is much less than the calculated amount, none of these addenda produced any alteration in the rate of reaction. It is considered probable that the retardation is actually caused by some product present in small amount which arises from the decomposition of the alcohol.

L. L. BIRCUMSHAW.

**Rapid determination of corrodibility.** K. KONOPICKY.—See B., 1930, 561.

**Discussion on catalytic reactions at high pressures** (Proc. Roy. Soc., 1930, A, 127, 240—267). G. T. MORGAN.—Pressure is employed in chemical reactions to diminish the volatility of reagents, thus retaining them in the liquid phase at higher temperatures, and to bring about a greater concentration of gaseous reagents. The use of pressure to facilitate chemical reaction is illustrated by the hydrolysis of fats and oils by water under pressure (in the presence of a catalyst), the alkylation of aromatic amines, and the interconversion of naphthols and naphthylamines. Work on the ammonia synthesis and on the synthesis of methyl alcohol from carbon monoxide and hydrogen is briefly and historically reviewed. The aldolisation hypothesis which accounts of the formation of higher aldehydes and alcohols in the latter synthesis is discussed.

W. A. BONE.—Work in the High Pressure Gas Research Laboratories at the Imperial College during the last three years is reviewed, with special reference to the formation of formaldehyde, methyl alcohol, and methane from carbon monoxide and hydrogen. By selecting a suitable catalyst and temperature any one of these three substances may be produced to the practical exclusion of the other two. The absence of satisfactory equilibrium data in regard to the methyl alcohol synthesis previous to the present series of investigations is pointed out, and the extreme importance of determining the equilibrium constant by approaching the equilibrium from both sides is emphasised. Errors due to the fact that at the high pressures used the equilibrium mixtures do not obey the simple gas laws are discussed.

M. P. APPLEBEY.—The need for accurate knowledge of the physical properties of gas mixtures at high pressures is reiterated. A theory is outlined to explain the fact that a very active catalyst for the ammonia synthesis is metallic iron reduced from magnetic iron oxide, with alumina present as promoter. The iron oxide is isomorphous with iron spinel,  $\text{Fe}(\text{AlO}_2)_2$ , and it is suggested that the alumina becomes uniformly disseminated through the iron catalyst, barriers of alumina being thus formed which prevent the growth and coalescence of the minute iron crystals on which the activity of the catalyst depends. The function of a catalyst is to lower the energy of activation of the reacting substance, and calculation shows that the total amount of energy necessary in industrial practice to fix a given amount of nitrogen by the use of a catalyst is about one quarter of the energy required to activate the same amount electrically. In the ammonia synthesis it is necessary to activate the nitrogen as well as the hydrogen. It is considered that recent experiments prove the intermediate formation of iron nitride, and iron has been prepared in a very active form which absorbs both hydrogen and nitrogen. Tungsten has also been prepared in an active form which decomposes ammonia at  $300^\circ$  according to the equation  $n\text{W} + \text{NH}_3 = \text{W}_n\text{NH} + \text{H}_2$ .

A. M. J. F. MICHELS.—Three ranges of pressure are arbitrarily defined: low, up to 2500 atm.; medium, 2500—10,000 atm.; high, above 10,000 atm. The effect of increased polarity in gases and gas mixtures at high pressures is pointed out, together with the fact that when molecules are compressed potential energy is stored, which may result in the reaction occurring with a lower kinetic energy, i.e., at a lower temperature. It is shown that the entropy is decreased by increasing pressure, and therefore  $c_p$  must also decrease. Work is proceeding in the Amsterdam High Pressure Laboratories on the effect of pressure on isotherms of gases, compressibilities of liquids and solids, viscosity of liquids and solids, solubility of gases in liquids, dielectric constants, refractive indices, specific heats, and electrical resistance of metals.

E. K. RIDEAL.—The question of the reproducibility of catalytic surfaces by building up a surface from volatilised metallic atoms or by disintegration of a macrocrystalline solid is discussed. The activation of catalysts is noted, and from experiments on the oxidation of copper the conclusion is reached that the surface of an active copper catalyst is broken up into a number of minute cracks, and that when the gas hits the surface the molecules of the former slide along the surface and down into the cracks. This confirms the use of alumina as a promoter in an iron catalyst. Recent work on the heats of adsorption of hydrogen on active catalysts shows that the quantity of gas passing into solution during the time interval necessary to measure the heat of adsorption is relatively great, and if correction is made for this quantity the heat of adsorption is independent of the quantity adsorbed. The heat of adsorption of hydrogen on an active catalyst is about 40,000 g.-cal., the value for inactive copper being about 12,000 g.-cal.

S. J. GREEN.—The necessity for a closer examination of the ultimate molecular structure of the surfaces

of catalysts is emphasised. Recent work is quoted, showing that in the decomposition of methyl alcohol by (a) copper, (b) zinc oxide, a parallelism exists between the change in the copper lattice and the percentage of methyl formate and formaldehyde produced, and the variation of the zinc oxide lattice and the percentage of carbon monoxide produced.

C. N. HINSHELWOOD.—Attention is directed to the important facts that energy must be supplied to the molecule before it can re-arrange itself, and that catalytic actions are very sensitive to the actual structure of the surface. Energy may be stored in molecules after their adsorption at a surface by distortion, and therefore less energy need be supplied in order to effect a breakdown or rearrangement of the molecule.

F. G. DONNAN.—Reference is made to the work of Donnan and Shaw and of Lush on the velocity of reduction of oleic acid by hydrogen under pressure in the presence of a nickel catalyst, which showed that the velocity is proportional to the square root of the gas pressure  $p$ . As the solubility of hydrogen in metals is proportional to  $\sqrt{p}$ , it is concluded that the active substance is atomic hydrogen.

A. C. EGERTON.—The action of lead compounds as anti-knocks supports the views advanced by Hinshelwood.

E. B. MAXTED.—The velocity of hydrogenation is sometimes proportional to  $\sqrt{p}$ , but may also be proportional to  $p$  or to some value between the two.

E. F. ARMSTRONG.—The increased activity due to the action of promoters may be due to chemical rather than to physical causes, and in some cases simply to the development of a greater surface. The development and maintenance of the greatest active surface is the essential fact connected with their activity. Increased activity of a catalyst, due to chemical causes, is illustrated by the effect of adding copper to a nickel catalyst.

L. L. BIRCUMSHAW.

**Oxidations in presence of ammonia and of cobalt salts. I. Potassium ferrocyanide. II. Potassium arsenite.** A. V. PAVLINOVA (Ukraine Chem. J., 1929, 4, 471–473, 475–477).—I. The amount of potassium ferrocyanide oxidised in solutions containing ammonia and cobaltous sulphate is proportional to the quantity of cobaltic salt produced, whence it follows that the reaction is an induced one, cobaltous salts activating atmospheric oxygen. The induction factor is 2.76.

II. Atmospheric oxygen oxidises arsenite in ammoniacal solution to arsenate only in the presence of cobaltous salts. The induction factor of this reaction is equal to 0.95, which corresponds with the oxidation by one atom of oxygen of 1 mol. of arsenious acid and of 2 mols. of cobaltous sulphate. The presence of either of the above substances catalyses the oxidation of the other.

R. TRUSZKOWSKI.

**Activation of chemical reactions by salts. IV. Electrochemical production of ammonium persulphate.** N. A. IZGARISCHEV and N. M. GRUZDEVA (J. Russ. Phys. Chem. Soc., 1930, 62, 241–247).—The addition of zinc, aluminium, manganous, and cadmium sulphates to the reaction solution retards the initial rate of electrolytic oxidation of ammonium

sulphate to persulphate, whilst potassium, sodium, lithium, magnesium, and cobaltous sulphates, and also the chlorides of all the above metals activate the reaction. The oxalates, citrates, tartrates, iodides, and hydrogen phosphates of potassium retard reaction, which is activated by other potassium salts in the order:  $\text{KNO}_3 < \text{KBr} < \text{K}_2\text{SO}_4 < \text{KCl} < \text{KF}$ . The most active ions are those of potassium and of fluorine, and their action increases with concentration to a maximum at 0.01N-solutions, after which it declines with further increase in concentration for potassium fluoride and chloride, but not acetate. The action of the above salts is not connected with the  $p_{\text{H}}$  of their solutions or with complex compound formation; it is supposed that the electrostatic field surrounding the ions is capable of influencing the velocity of electronic rearrangement of the substrate atoms, and hence of affecting the velocity of reaction.

R. TRUSZKOWSKI.

**Activation of chemical reactions by salts. V. Oxidation of potassium iodide by dichromate.** N. A. IZGARISCHEV and A. K. BELAIEV (J. Russ. Phys. Chem. Soc., 1930, 62, 249–253).—The velocity of oxidation of potassium iodide by potassium dichromate solution is retarded by chlorides in the order: action of  $\text{ZnCl}_2 < \text{LiCl} < \text{CoCl}_2 < \text{NiCl}_2 < \text{KCl} < \text{CdCl}_2$ ; sulphates have at equivalent concentrations a greater inhibitive effect, in the order  $\text{CoSO}_4 < \text{NiSO}_4 < \text{ZnSO}_4 < \text{MnSO}_4 < \text{MgSO}_4 < \text{Li}_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{K}_2\text{SO}_4 < \text{CdSO}_4$ . A maximum inhibitive concentration exists for each salt, above and below which reaction is more rapid, in some cases even exceeding that obtained in the absence of salts. The above results are in disagreement with the theories of Grube and Schmid (A., 1926, 474), and of Brönsted (A., 1922, ii, 699), being in no way related to the  $p_{\text{H}}$  of the solutions, to the dehydrative power of the ions added, or to changes in the activity coefficients.

R. TRUSZKOWSKI.

**Catalytic oxidation of mercurous nitrate solution by cupric ion.** F. G. GERMUTH (Amer. J. Pharm., 1930, 102, 263–273).—The rate of oxidation of mercurous nitrate in 0.1–10.0% solutions containing sufficient nitric acid to prevent precipitation is increased several times by the presence of 0.01% of copper as cupric nitrate. The catalytic effect is increased by heating, but not by the presence of larger amounts of copper.

H. E. F. NORTON.

**Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. I. Constitutional significance of hydrolytic stability maxima.** C. K. INGOLD (J.C.S., 1930, 1032–1039).—No relation appears to exist between hydrolytic velocity coefficients of esters and polar influence, probably owing to complications introduced by superimposed steric effects. The view is developed, and confirmed from existing experimental data, that the ratio  $k_{\text{OH}}/k_{\text{H}}$  (where  $k_{\text{H}}$  and  $k_{\text{OH}}$  are the catalytic coefficients for hydrogen and hydroxyl ions in hydrolysis) is probably, within wide limits, a function of polarity only, and is independent of steric effects. Values of the above ratio are calculated from the expression  $-2p_{\text{H}}^* - \log K_{\text{r}} = \log (k_{\text{OH}}/k_{\text{H}})$  (Dawson, A., 1927, 632), where  $k_{\text{r}}$  is the ionic product for water and  $p_{\text{H}}^*$  corresponds with the minimum velocity of an aqueous

reaction catalysed by hydrogen and hydroxyl ions, i.e., with the hydrolytic stability maximum.

J. R. I. HEPBURN.

**Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. II. Hydrolytic stability maxima of some glyceric esters.** C. M. GROOCECK, C. K. INGOLD, and A. JACKSON (J.C.S., 1930, 1039—1057).—The eight esters studied were methyl, ethyl, *n*- and *iso*-propyl, -butyl, and -amyl *dl*-glycerates in aqueous solution. In order to reduce to a minimum catalytic influences associated with the use of buffer solutions, a fixed amount of sodium hydroxide was added at the beginning of the reaction, the sodium glycerate formed constituting the constant salt constituent of the buffer, the glyceric acid liberated during the reaction forming the variable acid constituent. The method of calculation is fully described and values of  $p_H^*$  and  $k_{OH}/k_H$  for each ester are tabulated.

J. R. I. HEPBURN.

**Mechanism of the action of catalysts on the autoxidation of abietic acid.** G. DUPONT, J. LEVY, and J. ALLARD (Compt. rend., 1930, 190, 1302—1304).—The velocity-time curve of the catalytic oxidation of a 50% solution of abietic acid in the presence of 0.25% of cobalt oxide (as abietate) at constant pressure in an atmosphere of oxygen first increases to a maximum, indicative of an autocatalysed reaction, then commences to decrease near the point at which one atom of oxygen is absorbed, and decreases further, with an intermediate horizontal section, to beyond the absorption of two atoms of oxygen. If the proportion of cobalt abietate is decreased, the velocity of absorption decreases and remains positive above a concentration of 0.01%; at a concentration of 0.001% the catalytic effect is entirely negative, whilst at 0.005% it is first positive and then negative. A complex of cobalt abietate and the oxidised acid abietate is probably the active catalyst.

A. I. VOGEL.

**Catalysis of the oxidation of cysteine and thioglycollic acid by iron and copper.** K. A. C. ELLIOTT (Biochem. J., 1930, 24, 310—326).—The rate of oxidation of cysteine at  $p_H$  7.3 is proportional to the amount of iron present up to the highest concentration tried. On the other hand, it is proportional to the amount of copper present only up to a certain small concentration. Further increase of copper, provided it does not affect the  $p_H$ , causes no effect. The amount of copper required for the maximal effect is not significantly affected by change in temperature, oxygen tension,  $p_H$ , cysteine concentration, or by the presence of phosphate buffer or increased liquid-gas interface. The velocity of oxygen uptake is also proportional to the amount of cysteine originally present, and the curve is linear when the uptake is fairly rapid, falling when the reaction becomes slower. The addition of an extra amount of cysteine during the course of the oxidation of cysteine causes the velocity to increase to the rate that would be expected if both amounts of cysteine had been added at first in the case of both iron and copper catalysis. If, however, the extra cysteine is added when the oxidation of the first quantity is complete, the oxygen uptake recommences, when copper is the catalyst, at a rate to be

expected from the total cysteine, whilst in the case of iron the new velocity is only what would be expected from the fresh cysteine. The velocity of oxidation in presence of iron or copper is increased by increasing the oxygen tension. The velocity of oxygen uptake in presence of iron and copper is decreased by the presence of phosphate buffer. Thioglycollic acid in solution at  $p_H$  7.3 shows similar behaviour to cysteine, except that the velocity of oxygen uptake in the presence of iron is very low up to a certain concentration of iron and thereafter increases rapidly in proportion to the amount of extra iron added, and that higher concentration of thioglycollic acid decreases the rate of oxygen uptake in the presence of iron.

S. S. ZILVA.

**Factors affecting the catalytic action of copper in oxidation of cysteine.** C. A. ELVEHJEM (Biochem. J., 1930, 24, 415—426).—The oxygen uptake of a system of cysteine and heart-muscle preparation in orthophosphate buffer,  $p_H$  7.6, is increased two- or three-fold by the addition of pyrophosphate. The same acceleration is obtained when the muscle preparation is replaced by a minute amount of copper salts. The increased rate of oxidation in the presence of pyrophosphate is due to the formation of copper pyrophosphate, which is more soluble at  $p_H$  7.6 than copper phosphate and therefore more active catalytically. Curves are presented to show the rate of cysteine oxidation by copper in phosphate buffers of different concentrations and in a phosphate buffer plus pyrophosphate at varying hydrogen-ion concentrations. A study of the solubility of copper in different buffer solutions shows the decreased activity with increased  $p_H$  to be due to the formation of insoluble copper phosphates. The decrease in activity as the  $p_H$  becomes more acid can be explained only by the formation of a soluble inactive copper-cysteine complex. The optimum activity of copper in phosphate buffers containing pyrophosphate occurs at  $p_H$  8.0 at 20°. At this hydrogen-ion concentration the rate of oxidation is directly proportional to the copper present, provided that the copper is not in excess of  $4 \times 10^{-4}$  mg. Cu. Relatively large amounts of iron inhibit the activity of copper in the presence of pyrophosphate. This retarding effect can be eliminated by using large concentrations of pyrophosphate and by carrying out the reaction at 37°. At 37° the optimum activity is at  $p_H$  7.0, probably because the copper-cysteine complex is formed less at the higher temperature. The inhibiting action of cysteine at  $p_H$  7.0 disappears at 37°, but the copper is sufficiently insoluble in buffer or water solutions even at this  $p_H$  to prevent its complete activity in the absence of pyrophosphate. 0.001M-Hydrogen sulphide inhibits the activity of copper in phosphate buffer containing pyrophosphate to the extent of 60—70% at  $p_H$  7.0, but the degree of inhibition is much less at higher  $p_H$  values.

S. S. ZILVA.

**Reduction of carbon dioxide.** H. BAHR (Ges. Abh. Kennt. Kohle, 1928, 8, 219—224; Chem. Zentr., 1930, i, 185—186).—In the presence of copper the reaction  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$  can be detected at 200°. In experiments using various catalysts at temperatures between 200° and 450°, yields of carbon

monoxide up to 16% were obtained. On prolonged contact, especially with cobalt, further reduction to methane occurs.

A. A. ELDRIDGE.

**Solubility of zinc in sulphuric acid.** F. W. HARRIS (Amer. Electrochem. Soc., May, 1930. Advance copy, 12 pp.).—The influence of small amounts of various metallic impurities on the rate of dissolution of zinc (99.992%) in dilute sulphuric acid (18 g. per litre) has been investigated. Conical specimens of the metal were cast with various proportions of the impurities, and after preliminary treatment with sodium hydroxide solution these specimens were submerged in the acid and the rate of dissolution was followed by measuring the gas evolved. The conditions of casting were carefully controlled in order to obtain comparable results. Of the impurities tested, copper has the greatest effect in increasing the rate of dissolution, and is followed by iron and antimony. Even 0.004% of copper increases the rate more than five-fold. Lead and cadmium have a comparatively small effect, whilst aluminium lowered the rate in two cases. The appearance of the surface of the corroded metal is described in every case. Addition of small amounts of gelatin greatly diminishes the rate of dissolution. Sodium silicate has a very slight effect in this direction.

H. J. T. ELLINGHAM.

**Activation of chemical reactions by salts. III.**

**Dissolution of nickel.** N. A. ISGARISCHEV and S. A. SCHAPIRO (J. Russ. Phys. Chem. Soc., 1930, 62, 237—240).—The velocity of dissolution of nickel in sulphuric acid is enhanced by various chlorides in the following order:  $\text{NH}_4\text{Cl} < \text{NaCl} < \text{LiCl} < \text{KCl} < \text{MgCl}_2 < \text{FeCl}_2 < \text{ZnCl}_2 < \text{AlCl}_3 < \text{CuCl}_2 < \text{FeCl}_3$ , whilst the activating effect of various salts is in the order  $\text{K}_2\text{SO}_4 < \text{H}_2\text{SO}_4 < \text{KBr} < \text{KF} < \text{KCl} < \text{KI} < \text{KNO}_3 < \text{KClO}_3 < \text{KIO}_3 < \text{KBrO}_3$ . The latter series differs from that found for the dissolution of aluminium only in the order in which halogen ions are arranged.

R. TRUSZKOWSKI.

**Activation of chemical reactions by salts. II.**

**Dissolution of marble.** N. A. ISGARISCHEV and S. A. SCHAPIRO (J. Russ. Phys. Chem. Soc., 1930, 62, 233—236).—The velocity of dissolution of marble in hydrochloric acid is slightly depressed by the presence of zinc or manganous chlorides, is unaffected by the presence of the chlorides of ammonium, lithium, magnesium, and strontium, and is accelerated in the following order by other chlorides:  $\text{CoCl}_2 < \text{NiCl}_2 < \text{KCl} < \text{BaCl}_2 < \text{NaCl} < \text{AlCl}_3$ . The inhibitive or activating effects of the above chlorides do not appear to be in any definite way connected with the  $p_H$  of the solution or with the ionic volume of the cations. Ammonium, potassium, and sodium acetates retard the reaction of dissolution of marble in acetic acid to an equal extent, which is commensurate with the higher  $p_H$  values of solutions containing alkali acetates. The above results are in agreement with Debye and Hückel's theory of solutions (A., 1923, ii, 459, 724).

R. TRUSZKOWSKI.

**Surface reactions of atoms and radicals. I.**

**New approach to the problem of specific surface action.** H. S. TAYLOR and G. I. LAVIN (J. Amer. Chem. Soc., 1930, 52, 1910—1918).—A correlation

of available data shows that surfaces have specific effects on the combination of atoms and radicals, and in this connexion (a) the recombination of hydrogen atoms and (b) the formation of water from atomic hydrogen and hydroxyl have been studied. Reaction (a) is catalysed by metal surfaces, potassium hydroxide, potassium carbonate, and especially by a mixture of zinc and chromium oxides (dehydrogenation catalyst), but clean glass, potassium chloride, and alumina (dehydration catalyst) are inefficient. The last result is contrary to that of Bonhoeffer (A., 1925, ii, 52), and this discrepancy is explained. Reaction (b) is catalysed by clean glass, potassium chloride, and alumina (dehydrated at 300°), named in order of increasing effect. During the reactions, distinctive chemiluminescence is observed at some of the surfaces.

J. G. A. GRIFFITHS.

**Catalytic oxidation of paraffin and mineral oil.**

E. ZERNER.—See B., 1930, 543.

**Thermal decomposition of cresols.**

R. NAKAI (Bull. Chem. Soc. Japan, 1930, 5, 136—157).—It is concluded from indirect and direct evidence that the course of the thermal decomposition of *o*-, *m*-, and *p*-cresol at 600°, 650°, or 700° is, (a) the production of polymerides, (b) their decomposition into aromatic hydrocarbons, phenol, and ultimately into hydrogen, water, methane, carbon monoxide, and carbon. *m*-Cresol is the most and *p*-cresol the least stable towards heat treatment. Glass and porcelain tubes favour the formation of polymerides, a copper tube that of benzene, and an iron tube fundamental gaseous decomposition. An added catalyst, similar in composition to coal ash and alumina, favoured decomposition, especially gaseous decomposition. The reactions appeared to change during the decomposition; primarily gaseous decomposition was evident, but after deposition of carbon in the tube liquid products were formed.

J. O. CUTTER.

**Electrodeposition of metals from their liquid**

**ammonia solutions.** R. TAFT and H. BARHAM (J. Physical Chem., 1930, 34, 929—953).—The electrodeposition of lead, nickel, cadmium, copper, silver, zinc, chromium, and aluminium from solutions in liquid ammonia has been investigated and the optimum conditions have been determined. The effects of variations in current density, concentration of metal ion, nature of the anion, temperature, and hydrogen-ion concentration, together with the effect of stirring and the addition of colloids, are recorded. In most cases the best deposits result at lower current densities in ammonia solution than in aqueous solutions; with silver and zinc, however, these current densities are about the same. With lead, cadmium, and silver solutions the concentrations of metal are approximately equal, but with nickel, copper, and zinc the concentrations are lower in liquid ammonia solutions. The effect of lowering the temperature is small, but stirring eliminates growths and favours the formation of a smooth, adherent film. The electrodeposition of lead and cadmium from liquid ammonia solutions has industrial possibilities.

L. S. THEOBALD.

**Addition agents in electrodeposition. III.**  
**Application of the complex cation theory to base**



metals. G. FUSEYA, K. MURATA, and R. YUMOTO.—See B., 1930, 563.

**Photochemical hydrogen-oxygen reaction.** G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1930, 52, 1868—1874).—The photochemical reactions of mixtures of oxygen and hydrogen or nitrogen in light of wave-lengths 1854—1862 Å. and 1719—1725 Å. have been investigated by a dynamic method. Ozone only is formed by the 1854—1862 Å. radiation and the yield is slightly higher in oxygen-nitrogen than in oxygen-hydrogen mixtures. With 1719—1725 Å. radiation, and in the presence of hydrogen, the yield of ozone is only 25% of that in the presence of nitrogen, but an equal amount of hydrogen peroxide is formed in addition. The yields of ozone and hydrogen peroxide are approximately proportional to the relative concentrations of oxygen and hydrogen, respectively. Reaction mechanisms are discussed, and the following reactions of the oxygen atoms formed optically by the shorter wave-lengths are suggested: (a)  $O + O_2 + X = O_3 + X$ , (b)  $O + H_2 + X = H_2O + X$ , (c)  $O + H_2 = OH + H$ , where X denotes a molecule of oxygen or hydrogen. The probability of (c) is  $10^{-4}$  (approx.), which is much smaller than theory predicts. J. G. A. GRIFFITHS.

**Synthesis of carbonyl chloride by light and by  $\alpha$ -radiation.** H. N. ALYEA and S. C. LIND (J. Amer. Chem. Soc., 1930, 52, 1853—1868).—The effect of  $\alpha$ -radiation on mixtures of carbon monoxide and chlorine at total pressures of about 700 mm. has been compared with the action of light of wave-lengths 3130—4070 Å. The rate of reaction is directly proportional to the square root of (1) the concentration of radon (i.e., number of ion pairs) over an 83-fold range, (2) the concentration of carbon monoxide, and is directly proportional to that of chlorine over an approximately 10-fold range. These results are analogous with those obtained photochemically, and the number of molecules formed per quantum is approximately equal to the number produced per ion pair. Both reactions show induction periods, and oxygen has equal inhibiting effects on the reaction rates (cf. Bodenstein, A., 1929, 894). It is concluded that after the different primary processes of the two reactions, the chains are propagated in a similar manner by chlorine atoms. J. G. A. GRIFFITHS.

**Photosensitive preparations of selenium and tellurium.** T. PAVOLINI.—See B., 1930, 533.

**Photochemistry of silver nitrite.** M. BELENKY and W. P. JUSE (Z. anorg. Chem., 1930, 190, 277—284).—A saturated solution of silver nitrite is reduced to crystalline metallic silver when exposed to sunlight in a closed vessel, and to a grey cloud of silver under the action of intense ultra-violet radiation. The photochemical decomposition is unimolecular and expressed by the equation  $AgNO_2 + h\nu = Ag + NO_2$ . The most effective radiation has wave-lengths 313.5—380  $\mu$ . The possible use of the salt in photography is being investigated. F. L. USHER.

**Microscopic and ultra-microscopic studies with microtome sections of photographic layers.** K. SCHAUM and O. KLEIN (Z. wiss. Phot., 1930, 28, 43—71).—A parallel grating, consisting of a silver

mirror with a series of parallel opaque lines and clear spaces, was copied on a photographic plate by exposure, followed by microscopic and ultra-microscopic examination of transverse sections 2—10  $\mu$  in thickness, cut in a plane perpendicular to the surface and to the grating lines. The method of preparing and cutting the sections is described in detail. A large number of photographs with theoretical discussions illustrate the application of the method in studying the processes of development, intensification and reduction, determination of resolving power, reversal effects, and the colloid colouring of photographic layers. The results confirm earlier work.

J. R. I. HEPBURN.

**Point concentration theory and strain in crystal structure.** A. P. H. TRIVELLI (Z. wiss. Phot., 1930, 28, 41—42).—A question of priority (cf. A., 1929, 1152). The author's present view is that the pure silver halide is insensitive to light, and that a strain in, or deformation of, the crystal lattice, through the presence of a second halide, is necessary for photochemical decomposition. J. R. I. HEPBURN.

**Solutions for colorimetric standards. III. Colour of inorganic substances in organic and inorganic solvents.** M. G. MELLON and V. FOSTER (J. Physical Chem., 1930, 34, 963—972; cf. this vol., 155).—The colour and the effect of ordinary light, sunlight, and ultra-violet light on these colours are recorded for solutions of various inorganic substances, mainly salts, in different solvents.

L. S. THEOBALD.

**Photosensitisation by ammonia.** H. S. TAYLOR and H. J. EMELEUS (J. Amer. Chem. Soc., 1930, 52, 2150—2151; cf. Farkas and others, this vol., 554).—The rate of photosensitised polymerisation of ethylene by ammonia at the ordinary temperature, and at 100°, in the light of a mercury arc has been studied by the pressure decrease in the system. The rate of reaction is independent of the pressure of ethylene (5—15 cm.) and is unaffected by hydrogen, which, moreover, does not disappear from the system (cf. this vol., 46). The quantum efficiency is of the order of unity. The photodecomposition of ammonia is retarded by ethylene, and it is difficult to interpret this on the accepted views concerning predissociation.

J. G. A. GRIFFITHS.

**Photochemical reactions between fatty acids and chlorine in carbon tetrachloride solutions.** K. P. BASU and N. C. ROY (J. Indian Chem. Soc., 1930, 7, 229—237).—The photochlorination of acetic, propionic, and *n*-butyric acids at 30° is unimolecular with respect to chlorine (at a concentration less than that of the acids) in white and blue (436  $\mu$ ) light, the unimolecular velocity coefficient being proportional to the intensity of the incident light. The temperature coefficient at 25° in blue light is 1.4 in all cases. There is no induction period; that observed by Benrath and Hertel (A., 1924, i, 821) is attributed to the use of impure chlorine or of a chlorine concentration nearly double that of the acids. The quantum efficiencies are: acetic acid, 1; propionic acid, 5; butyric acid, 8. The chlorination, which does not take place in the dark, is not affected by the increased concentration of the hydrochloric acid which is con-

tinuously generated. A brief theoretical discussion is given (cf. A., 1929, 1022, 1023). S. K. TWEEDY.

**Photochemical oxidation of salts of some organic acids, lecithin, cholesterol, and some food materials by air.** C. C. PALIT and N. R. DHAR (J. Physical Chem., 1930, 34, 993—1005).—Aqueous solutions or suspensions of sodium formate or tartrate, lecithin, cholesterol, butter, milk, egg-white, and egg-yellow are oxidised by the passage of air in sunlight; zinc oxide is a photosensitiser in the first two cases. The photochemical oxidation of dextrose, starch, glycine,  $\alpha$ -alanine, hippuric acid, carbamide, sodium urate, formate, and tartrate, and potassium stearate and oleate is increased by the presence of ferric or uranium nitrate. Dilute solutions of lactic, oxalic, citric, and tartaric acids are also oxidised by air in sunlight. Dextrose, glycine, lecithin, butter, etc. are oxidised chiefly to carbon dioxide and not to an intermediate product, but compounds of the peroxide type are formed in the case of aqueous suspensions of cholesterol, olive oil, and butter. Einstein's law of photochemical equivalence holds approximately for photochemical oxidations by air of dextrose, lactose, and alanine. L. S. THEOBALD.

**Water of crystallisation of mineral and organic compounds.** A. SEYEWETZ and BRISAUD (Compt. rend., 1930, 190, 1131—1133).—Substances containing water of crystallisation are classified as follows: (1) Those which do not take up water of crystallisation on exposure after desiccation (e.g., calcium sulphate, borax, citric and gallic acids, sodium sulphite). (2) Those partly rehydrated (e.g., all alums except chrome alum, zinc sulphate, sodium carbonate). (3) Those which rehydrate completely (e.g., all the double sulphates of magnesium, sulphates of sodium, magnesium, nickel, copper, and cadmium, chlorides of cobalt, barium, and cadmium, sodium acetate, oxalic acid). (4) Those influenced by the degree of humidity of the air (e.g., chlorides of nickel, cobalt, and manganese). (5) Deliquescent substances (e.g., calcium chloride, nitrates of magnesium, nickel, cobalt, copper, and bismuth). Salts of class (3) are unaffected by the degree of humidity of the air.

J. GRANT.

**Production and utilisation of potassium phosphates.** P. ASKENASY and F. NESSLER (Z. anorg. Chem., 1930, 189, 305—328).—If potassium chloride is treated with an equimolecular amount of phosphoric acid a temperature of 350° is required for the complete displacement of the hydrochloric acid, the product being the metaphosphate. By using an excess of phosphoric acid or blowing steam on the reacting mass, however, complete reaction may be effected down to 200°, and with steam treatment below 250° the product is the orthophosphate. The equilibrium diagram of the system  $\text{KH}_2\text{PO}_4\text{--KCl--NH}_4\text{Cl--NH}_4\text{H}_2\text{PO}_4\text{--H}_2\text{O}$  at 0° has been obtained and used to determine the best conditions for the production of a mixed artificial fertiliser free from chloride by the reaction  $\text{KCl} + \text{NH}_4\text{H}_2\text{PO}_4 = \text{KH}_2\text{PO}_4 + \text{NH}_4\text{Cl}$ ; the two phosphates have been found to form a continuous series of mixed crystals. A hydrate of dipotassium hydrogen phosphate,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ , stable below 48.3°, has been prepared. The pro-

duction of potassium carbonate and hydrogen carbonate by reaction of dipotassium hydrogen phosphate with ammonium carbonate and hydrogen carbonate has been investigated. R. CUTHILL.

**Preparation of copper peroxide.** I. S. TELETOV and A. D. VELESCHINIEC (Ukraine Chem. J., 1929, 4, 463—470).—The first product of the reaction between 30% hydrogen peroxide and cuprammine is colloidal copper peroxide, which undergoes decomposition under the influence of water with the production of variously hydrated mixtures of the approximate compositions:  $\text{CuO} \cdot \text{CuO}_2$ ,  $\text{CuO} \cdot 2\text{CuO}_2$ ,  $2\text{CuO} \cdot 5\text{CuO}_2$ ,  $\text{CuO} \cdot 3\text{CuO}_2$ , and  $\text{CuO} \cdot 4\text{CuO}_2$ . All higher oxides of copper obtained up to the present by other workers represent such mixtures. R. TRUSZKOWSKI.

**Action of inorganic salts on magnesium.** N. A. SCHILOV and E. F. SCHATUNOVSKAJA (J. Russ. Phys. Chem. Soc., 1930, 62, 375—383).—The dissolution of magnesium in water is accelerated by the addition of various chlorides, in the order:  $\text{LiCl} < \text{KCl} < \text{CaCl}_2 < \text{BaCl}_2$ . The  $p_H$  of solutions in which magnesium is dissolving augments from an initial value of 6.22 to a final value of 9.76, that of a saturated solution of magnesium hydroxide. The velocity of reaction in the presence of the above chlorides is little affected by their concentration between 0.1N and N. The effect of the salts of this group is probably due to prevention of passivation of the metal surface by formation of a film of magnesium oxide. A second series of salts acts in the order:  $\text{MgCl}_2 < \text{MnCl}_2 < \text{CdCl}_2 < \text{NiCl}_2 < \text{CrCl}_3 < \text{AlCl}_3 < \text{ZnCl}_2 < \text{FeCl}_3$ ; the metals of this group can be precipitated from solution by metallic magnesium, and their chlorides react with magnesium hydroxide to yield magnesium chloride and metal hydroxide. Except in the case of magnesium chloride the catalytic action of the salts rises rapidly with their concentration. With cadmium chloride and iodide and silver and lead nitrates reaction practically ceases at the end of 10 min.; cadmium sulphate and nitrate possess a much smaller initial effect, but their catalytic action continues to be exerted as long as any magnesium remains. The former phenomenon is due to passivation of the magnesium surface by deposition of the metal in a continuous, impermeable layer, whilst in the latter case the layer is permeable. A third series of salts acts in the order  $\text{Zn}(\text{NO}_3)_2 < \text{Al}(\text{NO}_3)_3 < \text{ZnSO}_4 < \text{Al}_2(\text{SO}_4)_3 < \text{AlCl}_3 < \text{ZnCl}_2$ . Cupric and auric chlorides rapidly passivate magnesium, whilst mercuric and nickelous chlorides exert a catalytic effect increasing with their concentration. The initial catalytic effect of 0.2N-cupric sulphate is greater than for more dilute solutions, but after 1 hr. the quantity of magnesium dissolved is smaller than with 0.1 and 0.02N-solutions. A similar phenomenon is observed with auric chloride solutions. These effects are due probably to reduction to cuprous and aurous salts respectively, and these are then further reduced to copper and gold. R. TRUSZKOWSKI.

**Hydrated calcium aluminates.** A. TRAVERS and J. SEHNOUTKA (Ann. Chim., 1930, [x], 13, 255—335).—Potassium aluminate is prepared by the gradual addition of aluminium turnings to the calculated

quantity (plus 5% excess) of 5% potassium hydroxide solution in an atmosphere of carbon dioxide, concentrating in a vacuum at 35–40°, and allowing to crystallise in a vacuum. The product contains 0.2–0.6% of carbonate, which is removed by the addition of calcium hydroxide; subsequent precipitation with alcohol containing 15% of potassium hydroxide (pure alcohol yields a gel and also causes partial hydrolysis) yields pure  $K_2O, Al_2O_3, 3H_2O$ . Two mols. of water are removed at 120° and the third at about 500°. Crystalline alumina,  $Al_2O_3, 3H_2O$ , is produced by passing carbon dioxide into a boiling dilute solution of potassium aluminate (concentration 1–5%) or by boiling with aqueous alcohol (alcohol content not exceeding 75%) or with water. Interaction of lime water with aluminium nitrate afforded crystalline calcium aluminates, the composition of which varied between  $Al_2O_3, 3CaO, 12H_2O$  and  $Al_2O_3, 4CaO, 12H_2O$  according to the concentrations employed; the formation takes place in three stages involving the precipitation of aluminium hydroxide, followed by its dissolution in the lime water as monocalcium aluminate and its precipitation as polycalcium aluminate. A similar crystalline polycalcium aluminate is produced from potassium aluminate and lime water. Potassium aluminate reacts in solution with aqueous calcium nitrate containing lime water at  $p_H$  11.57–11.62 to give the pure crystalline  $Al_2O_3, 3CaO, 21H_2O$ ; products expressed by the formula  $Al_2O_3, 3–4CaO, 12H_2O$  are obtained from the mother-liquors.

Attempts to prepare hydrated calcium aluminates by the interaction of calcium ethoxide and potassium aluminate, of aluminium acetylacetonate and lime water, of calcium acetylacetonate and aluminium, of aluminium nitrate or acetylacetonate and solid lime, or of calcium ethoxide and aluminium in alcoholic solution, gave a very poor yield of a crystalline product. The solubilities of anhydrous and of hydrated polycalcium aluminates (the latter also at the boiling temperature) in water, saturated lime water, 10% potassium hydroxide, saturated calcium sulphate solution, saturated calcium, sodium, and magnesium chloride solutions have been determined and it is concluded that the first reaction in solution is the formation of monocalcium aluminate and the liberation of calcium hydroxide, the equilibrium  $Al_2O_3, nCaO, Aq \rightleftharpoons Al_2O_3, CaO + (n-1)CaO + Aq$  being present in the solution.

Attempts to prepare calcium chloroaluminates from aluminium chloride and excess of lime water gave complex calcium aluminium compounds. By treatment of hydrated calcium aluminate with excess of calcium, magnesium, or ammonium sulphate solution, or preferably by treatment of aluminium sulphate with lime water, crystalline calcium sulphoaluminate,  $Al_2O_3, 3CaO, 2.5CaSO_4, 30H_2O$ , is obtained. The solubility of this in water, by which it is decomposed into monocalcium aluminate and calcium sulphate, in saturated lime water, 10% potassium hydroxide solution, and in saturated solutions of calcium, magnesium, ammonium, and sodium sulphates has been determined and a probable explanation has thus been obtained of the resistance of cements to various mineral waters.

A. I. VOGEL.

**Calcium perchromate.** New type of red perchromate. J. A. RAYNOLDS and J. H. REEDY (J. Amer. Chem. Soc., 1930, 52, 1851–1853).—A solution of red perchromic acid is obtained by the action of 30% hydrogen peroxide on freshly-precipitated chromic hydroxide at 0°. A mechanism of the reaction is suggested. Calcium perchromate,  $Ca_3Cr_2O_{12}, 12H_2O$ , is precipitated at –5° to 0° either by adding 30% hydrogen peroxide to saturated calcium chromate solution or by mixing calcium acetate and red perchromic acid solutions. Dry calcium perchromate is a buff powder which explodes at 100°. When the aqueous solution is acidified, blue perchromic acid is formed. J. G. A. GRIFFITHS.

**Zinc ferrite.** Its formation, composition, and chemical and magnetic properties. Y. KATO and T. TAKEI (Amer. Electrochem. Soc., May, 1930. Advance copy, 16 pp.).—By heating mixtures of zinc and ferric oxides above 700° and extracting the product with ammonium chloride solution the insoluble portion was shown to have the composition  $ZnO, Fe_2O_3$ . This compound is formed with appreciable velocity at 600° and very rapidly above 700°. The magnetic properties of samples of zinc ferrite prepared under various conditions and cooled at various rates have been investigated in view of the importance of the magnetic separation of this substance in the electrolytic zinc extraction process. The most highly magnetic products were obtained by heating zinc and ferric oxides in the proportion 2 : 3. The product obtained by heating this mixture at 1130° and then quenching was black and almost non-magnetic, but if allowed to cool slowly in the air it was reddish-brown and either magnetic or non-magnetic, according to the rate of cooling. Black specimens turned reddish-brown and became more magnetic when heated at 450°. The magnetic character of the brown specimens is attributed mainly to mechanically mixed ferric oxide. Magnetite can form solid solutions with zinc ferrite and thereby greatly increases its magnetic character.

H. J. T. ELLINGHAM.

**Barium aluminates.** E. MARTIN.—See B., 1930, 555.

**Reactions in the solid state at high temperatures.** V. Effect of gases on reactions in the solid state. W. JANDER and W. STAMM (Z. anorg. Chem., 1930, 190, 65–78; cf. A., 1928, 971).—If the reaction of barium carbonate with silica or tungsten trioxide in the solid state at 500–1000° is carried out in a current of moist air the percentage reaction increases with increase in the partial pressure of water vapour. The water has the further effect both in these reactions and in the reaction of silica with calcium oxide or lanthanum oxide and of calcium carbonate with molybdenum trioxide of increasing the value of  $C$  in the equation for the temperature coefficient  $k = Ce^{-a/T}$ , the value of  $a$ , however, being unaffected. The action of the water appears to be purely physical, probably depending either on a loosening of the lattices as a result of water dissolving in the crystals, or on a reduction in size of the crystallites formed at the interface between the reactants with consequent increase in surface area in presence

of water. Experiments on the effect of ammonia and hydrogen on the rates of reaction indicate that here chemical reactions are involved. R. CUTHILL.

**Reduction with acetic anhydride.** II. J. B. MENKE (Rec. trav. chim., 1930, 49, 535—538).—The reduction of various metallic halides by acetic anhydride, acetic and other acids (cf. A., 1927, 131) has been investigated. Mercuric bromide and iodide, like the chloride, are reduced by heating with acetic anhydride or acetic acid and complex mercurous salts are formed. Reduction of cupric bromide, auric, platinum, and ferric chlorides also occurs under similar conditions. The reduction of ferric chloride by acetic anhydride is catalysed by sunlight, but no reduction occurs in acetic acid. When a mixture of hydrated ferric chloride ( $6\text{H}_2\text{O}$ ) is heated with toluene and acetic anhydride some *p*-toluic acid is formed. Since under these conditions the hexahydrate is dehydrated only to the trihydrate the catalyst cannot be anhydrous ferric chloride, but is more probably nascent chlorine. J. W. BAKER.

**Chlorination of oxides, alone and in presence of carbon.** V. SPITZIN (Z. anorg. Chem., 1930, 189, 337—366).—Hydrogen chloride starts to react with alumina at  $800^\circ$ , with silica at  $1000^\circ$ , and with ferric oxide at the ordinary temperature. With beryllium oxide there is a slight reaction at the ordinary temperature, but this ceases at  $140^\circ$ , owing to complete hydrolysis of the hydrated chloride, and reaction starts again at  $600^\circ$ , with formation of the anhydrous chloride. In all cases reaction is incomplete and an equilibrium between water vapour, anhydrous chloride, oxide, and hydrogen chloride is set up or approached, but with iron the equilibrium does not shift on cooling. Chlorine begins to react with ferric oxide at  $400^\circ$ , with beryllium oxide at  $600^\circ$ , with alumina at  $800^\circ$ , and with silica at  $1200^\circ$ . Equilibrium is approached in all cases, but, except with silica, cooling does not cause reversal of the reaction. The relative reactivities of the various oxides towards chlorine and hydrogen chloride correspond qualitatively with the heat effects of the several reactions. Carbon has no effect on the temperature at which reaction sets in; the probable reason of its accelerating effect is that it reacts with the oxygen or water produced by the main reaction, so preventing equilibrium being set up. R. CUTHILL.

**Gallium tribromide and tri-iodide.** W. C. JOHNSON and J. B. PARSONS (J. Physical Chem., 1930, 34, 1210—1214).—Gallium tribromide, m. p.  $122.5^\circ$ ,  $d^{120}_4$  3.123—3.138,  $d^{125}_4$  3.095—3.109, and gallium tri-iodide, m. p.  $213.5^\circ$  (slight decomp.), have been prepared directly from the elements. The white tribromide is hygroscopic and dissolves readily in water; the lemon-yellow tri-iodide liberates iodine on exposure to air and is hygroscopic. Both salts readily hydrolyse. L. S. THEOBALD.

**Rare-earth sulphides.** W. KLEMM, K. MEISEL, and H. U. VON VOGEL (Z. anorg. Chem., 1930, 190, 123—144).—The sesquisulphides of scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, dysprosium, erbium, and ytterbium and the disulphides of lanthanum and

cerium have been prepared by heating the chloride or sulphate in a current of hydrogen sulphide. The magnetic susceptibilities show the sesquisulphides to be salts and the disulphides to be polysulphides. The sesquisulphides form two groups, the  $\alpha$  group including the sulphides of lanthanum, cerium, praseodymium, neodymium, samarium, and gadolinium, and the  $\alpha$  form of dysprosium sulphide, whilst the  $\beta$  group consists of the sulphides of yttrium, erbium, ytterbium, and scandium, and the  $\beta$  form of dysprosium sulphide. In the  $\alpha$  group the lattices are very similar in structure, the mol. vol. diminishes continuously with increase in the atomic number of the metal, and the colour, except in the case of lanthanum sulphide, is dark brown to dark red. The  $\beta$ -sulphides, on the other hand, are ochre-yellow to lemon-yellow in colour, the lattices differ considerably one from another, although there are underlying similarities, and the mol. vol. varies in an irregular manner. R. CUTHILL.

**Rare earths.** J. ZERNIKE (Chem. Weekblad, 1930, 27, 154—158).—A survey is given of the atomic structure of the rare-earth elements together with a description of the methods of separation based on variations of basicity and of the solubilities of compounds. Goldschmidt's figures for the relative abundance of rare-earth minerals cannot be applied directly to the calculation of the relative abundance of the elements themselves, but by an exponential method of calculation the results obtained are in moderate agreement with those observed.

H. F. GILLBE.

**Solid additive compound of acetic acid and stannic chloride.** A. W. DAVIDSON (J. Physical Chem., 1930, 34, 1215—1216).—A compound, apparently  $\text{SnCl}_4 \cdot 4\text{AcOH}$ , has been isolated from solutions of stannic chloride in acetic acid.

L. S. THEOBALD.

**The octammines, with special reference to tin.** A. J. COOPER and W. WARDLAW (J.C.S., 1930, 1141—1145).—The existence of true octammines—coordination compounds of metals with a covalency of eight—is not yet definitely established. The work of Ephraim and Schmidt (A., 1909, ii, 1021) on the supposed octammine of tin ( $\text{Sn}_8\text{NH}_3\text{I}_4$ , prepared by passing gaseous ammonia through a solution of stannic iodide in carbon disulphide, has been repeated and extended. Although no compound could be isolated in the pure state, the substances obtained were of the type  $(\text{Sn}_x\text{NH}_3\text{I}_y\text{H}_2\text{O})\text{I}_4$ , where  $x+y=8$ , indicating that the ammonia molecules are rapidly replaced in air by water molecules. With pyridine or aniline, instead of ammonia, salts of the type  $\text{SnI}_4 \cdot 2.5\text{R}$  were isolated. J. R. I. HEPBURN.

**Accelerating action of stannous chloride in the silvering of glass.** H. VON WARTENBERG [with WOLLENBERG, A. MÜLLER, and BOBJAK] (Z. anorg. Chem., 1930, 190, 185—187).—The favourable effect in the silvering of glass of pre-treatment with stannous chloride solution depends on the adsorption of colloidal stannic oxide by the glass; other colloids have a similar action. Stannous chloride also promotes the deposition of gold on glass. R. CUTHILL.

**Formation and constitution of lead sodium thiosulphate.** B. ODDO and Q. MINGOIA (Boll. chim. farm., 1930, 69, 363—370).—The various methods reported in the literature for the preparation of a double thiosulphate of lead and sodium have been examined. A product of constant composition may be obtained under the following conditions. A cold saturated neutral solution of lead acetate (1 mol.) is added to a saturated solution of sodium thiosulphate (5 mols.), and the mixture poured into ten times its volume of 95% alcohol. A thick colourless oil separates; after about 12 hrs. it changes into a crystalline mass. This is separated, washed with alcohol, and dried in a vacuum desiccator, and purified by dissolving in water and reprecipitating with alcohol. The product so obtained is not a complex salt, but a double salt of the composition  $\text{Na}_3\text{Pb}(\text{S}_2\text{O}_3)_5 \cdot 6\text{H}_2\text{O}$ . The pharmacological use of this salt is described.

O. J. WALKER.

**Graphite and graphitic acid.** H. THIELE (Z. anorg. Chem., 1930, 190, 145—160).—Graphitic acid has been obtained in the pure state and shown to be a single substance with the empirical formula  $\text{C}_6\text{HO}$ . From its properties and mode of formation it appears probable that the molecular formula is  $\text{C}_6(\text{OH})_3$ , and that the carbon atoms in the crystal are arranged in rings of six, as in graphite, but are quadrivalent, not trivalent. The colour of the acid varies according to the method of preparation, but all the varieties have the same formula and are to some extent interconvertible. Under the influence of red light the blue and green forms are converted into the yellow and brown varieties, which fluoresce in ultra-violet light. Suspended in water the yellow and brown forms are negatively charged hydrophilic colloids with marked adsorbent power for cations, so that graphitic acid is comparable with silicic acid and forms salts with almost all metals. The acid is easily converted into humic acid, and may also be quantitatively reduced to graphitic carbon with stannous chloride or ferrous chloride, this reaction being catalysed by the platinum metals.

R. CUTHILL.

**Swelling of graphite and formation of graphitic acid.** U. HOFMANN and A. FRENZEL (Ber., 1930, 63, [B], 1248—1262).—The carbon atoms of graphite are arranged at the corners of vicinal regular hexagons in level planes. In these planes each carbon atom is united to the nearest three others by true, non-polar valency linkings. Metallic linkings above and below unite the hexagonal planes to crystals. If finely-divided graphite is suspended in anhydrous nitric acid or a mixture of concentrated nitric and sulphuric acids, the distance between the planes is increased from 3.39 to about 8 Å., whilst the planes remain unaffected. The graphite granules ultimately become brown and transparent and lose their metallic character. The change occurs without evolution of gas or sign of a violent reaction. Dilution with water followed by a thorough washing of the product leads to quantitative re-formation of the original graphite. The process consists therefore of a swelling perpendicular to the hexagon planes. The transformation of graphite into graphitic acid follows an analogous course. The chlorine dioxide from the

potassium chlorate penetrates between the planes and causes addition of oxygen. The arrangement of the carbon atoms in the planes remains undisturbed, since the two strongest interferences corresponding with this arrangement are found in all graphitic acid preparations in the same position as in graphite. The distance between the hexagon planes increases to 6.15 Å. Washing with water causes further swelling of the graphitic acid, which changes in colour from pale green to brown. After very protracted drying the water content of the product is diminished to about 8%; the substance is very hygroscopic and cannot be dehydrated by chemical treatment. It is a non-conductor of electricity. According to this conception, the form and size of the graphitic acid crystal must correspond closely with those of the original graphite and the rate of formation must depend on the manner in which the graphite crystals of the original carbon are arranged towards one another. In Ceylon graphite and carbon from carbon monoxide the change occurs rapidly; with Acheson or retort graphite, in which the very small crystallites are closely and irregularly packed, fine subdivision is necessary in order that the individual crystallites may be reached from the granule surface. The size of the graphitic acid crystallites corresponds in all cases with that of the original graphite crystallite and the stability towards further oxidation diminishes with diminishing size of crystallite from Ceylon to retort graphite. Every variety of carbon can be converted into graphitic acid if it has a pure carbon surface and is sufficiently finely-divided so that the reactant can reach all the carbon crystallites. H. WREN.

**Formation of carbonyl chloride by the action of carbon monoxide on the halides of the platinum metals.** W. MANCHOT and G. LEHMANN (Ber., 1930, 63, [B], 1221—1224).—The formation of carbonyl chloride is observed when carbon monoxide is passed over the heated chlorides of ruthenium, platinum, and gold, but not of rhodium, palladium, or osmium. With the last three metals the carbon monoxide is not inactive, since it greatly depresses the temperature of incipient evolution of chlorine. The absence of carbonyl chloride from the products of the reaction is due to its very ready catalytic decomposition by the metals and, particularly, by their chlorides. With ruthenium iodide, platinum and platinumous bromide, platinumic iodide, and auric bromide elimination of halogen occurs at a considerably lower temperature in carbon monoxide than in an indifferent gas. The production of carbonyl bromide or iodide could not be directly established. Attention is directed to the analogy between the action of carbon monoxide on the halides of the platinum metals and that of nitric oxide on the mercaptides of iron, cobalt, and nickel.

H. WREN.

**Metal carbonyls. VI. New types of compounds of carbon monoxide with iron halides and their chemical characterisation.** W. HIEBER and G. BADER. **VII. Volume of carbon monoxide in its compounds with metal salts and in metal carbonyls.** W. HIEBER, K. RIES, and G. BADER (Z. anorg. Chem., 1930, 190, 193—214, 215—226; cf. A., 1929, 41).—VI. A review of previous work.

Experimental details regarding the preparation and reactions of a number of compounds of metal carbonyls with iron halides are given and the main results of the work are summarised.

VII. The space occupied by carbon monoxide in various complex metal compounds has been calculated from measurements of their densities, using accepted values for the volumes of the other constituents. The following densities are given, all at  $25^{\circ}/4^{\circ}$  unless otherwise stated: potassium carbonyl ferrocyanide, 1.868; potassium carbonyl cobaltocyanide, 1.888; ferrous tetracarbonyl chloride, 1.941 at  $0^{\circ}/4^{\circ}$ ; bromide, 2.5042; iodide, 2.8390; platinum carbonyl chloride, 4.2346; platinum dicarbonyl chloride, 3.4882; platinum carbonyl bromide, 5.1154; iodide, 5.257;  $\text{Fe}_3(\text{CO})_5\text{en}_3$ , 1.768;  $\text{Fe}_3(\text{CO})_4(\text{C}_5\text{H}_5\text{N})_3$ , 1.569;  $\text{Fe}(\text{CO})_4\text{Hg}$ , 3.373;  $\text{Fe}(\text{CO})_4\text{Hg}_2\text{Cl}_2$ , 4.020;  $\text{Fe}(\text{CO})_3\text{Hg}_2\text{I}_2$ , 5.244;  $\text{Fe}(\text{CO})_4\text{Hg}_2\text{I}_2$ , 4.657. The zero volume of carbon monoxide derived by various methods of extrapolation is 25, approximately equal to that of the cyanide or iodide ion. The structurally similar hexacyano- and carbonyl pentacyano-salts of bi- and ter-valent iron or cobalt are isosteric. Normal values of the volume of carbon monoxide are obtained from the carbonyl halides of iron and of platinum only by taking into account the similarity in the character of carbon monoxide and the halogens. Among the volatile metal carbonyls stability and contraction of the volume of carbon monoxide run parallel and depend on the position of the metal in the periodic system. Iron carbonyls containing mercury form a special class in which an expansion of the carbon monoxide volume occurs, due to the presence of mercury.

F. L. USHER.

**Pseudo-halogens. VI. Cyanogen derivatives of volatile hydrides.** L. BIRCKENBACH and K. HUTTNER [with W. STEIN and F. ENSSLIN]. VII. **Volumes of cyanogen derivatives of volatile hydrides.** K. HUTTNER and S. KNAPPE. VIII. **Mobility of pseudo-halogen ions of cyanogen derivatives of volatile hydrides:**  $\text{OCN}^-$ ,  $\text{SCN}^-$ ,  $\text{SeCN}^-$ ,  $\text{N}(\text{CN})_2^-$ ,  $\text{C}(\text{CN})_3^-$ , and mobility of azide ion. L. BIRCKENBACH and K. HUTTNER (Z. anorg. Chem., 1930, 190, 1—26, 27—37, 38—47; cf. A., 1929, 1285).—VI. The chemical relationships between the cyanogen derivatives of the volatile hydrides are reviewed, and an investigation of the behaviour of certain of these compounds on hydrolysis is described. If sulphur dicyanide is treated with solid sodium ethoxide in alcoholic solution it is converted quantitatively into sodium thiocyanate,  $\text{S}(\text{CN})_2 + \text{H}_2\text{O} = \text{SCNH} + \text{HOCN}$ , and the product is essentially the same when the solid dicyanide is added to an alcoholic solution of sodium hydroxide or a very dilute alcoholic solution of alkali is added to the ethereal solution of the dicyanide. With an ethereal solution of dicyanide and concentrated alcoholic alkali, however, the following reaction occurs at the same time:  $3\text{S}(\text{CN})_2 + 8\text{NaOH} = 4\text{NaCN} + 2\text{NaSCN} + \text{Na}_2\text{SO}_4 + 4\text{H}_2\text{O}$ , and becomes more and more prominent as the alkali concentration increases. It is therefore suggested that sulphur dicyanide is electromeric:  $\text{SCN}^-\cdot\text{CN} \rightleftharpoons \text{SCN}^+\cdot\text{CN}^-$ . With selenium dicyanide the reaction

with sodium hydroxide is  $2\text{Se}(\text{CN})_2 + 6\text{NaOH} = 3\text{NaCN} + \text{Na}_2\text{SeO}_3 + \text{NaSeCN} + 3\text{H}_2\text{O}$ , but with sodium ethoxide this is accompanied by formation of thiocyanate, so that electromerism is postulated here as well. The only reaction with tellurium dicyanide is  $2\text{Te}(\text{CN})_2 + 2\text{H}_2\text{O} = \text{TeO}_2 + \text{Te} + 4\text{HCN}$ . On treatment of phosphorus tricyanide with water or aqueous solutions of acid or alkali, two concurrent reactions occur:  $\text{P}(\text{CN})_3 + 3\text{H}_2\text{O} = \text{PH}_3 + 3\text{HOCN}$  and  $\text{P}(\text{CN})_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCN}$ , the latter reaction predominating more and more as the concentration of acid or alkali is increased.

VII. The mol. volume relationships prevailing among the cyanogen derivatives of the volatile hydrides have been examined, existing data being supplemented with determinations of  $d_4^{25}$ .

VIII. The ionic mobilities of the pseudo-halogen ions of the cyanogen derivatives of the volatile hydrides have been determined from conductivity measurements with the potassium or sodium salts at  $18^{\circ}$  and  $25^{\circ}$ . The results show a marked resemblance to those obtained with the true halogen ions.

R. CUTHILL.

**Additive compounds of phosphine. I.** R. HÖLTJE (Z. anorg. Chem., 1930, 190, 241—250).—Additive compounds of phosphine and tetrahalides of the elements of group IV have been examined from the point of view of the valency theory and the doctrine of affinity. Only substances with a low m. p. react with phosphine; those with a high m. p. neither react nor dissolve, except plumbic chloride, which is reduced. Phosphine and hydrogen sulphide form analogous compounds, whilst ammonia shows marked differences. Germanium tetrachloride is shown to be related more closely to silicon tetrachloride than to stannic chloride. Despite the lower dipole moment of phosphine the decomposition pressures of its additive compounds are in general lower than those of the corresponding compounds with hydrogen sulphide, and the closer binding of the former thus indicated is considered to be due to the greater deformability of phosphine.

F. L. USHER.

**Oxidation of phosphorus by oxygen.** J. TAUSZ and H. GÖRLACHER (Z. anorg. Chem., 1930, 190, 95—119).—An investigation of the oxidation of phosphorus by oxygen and by air, both alone and in presence of moisture and of substances inhibiting phosphorescence, has led to the conclusion that the oxidation has its seat in the gas phase, and is autocatalysed by atomic oxygen. In moist oxygen, phosphorus vaporises (cf. Centnerszwer, A., 1913, ii, 1052) and hydrogen peroxide is formed, but no oxidation occurs, presumably because the atomic oxygen combines with water. In absence of water, however, the phosphorus is oxidised to trioxide, probably under the influence of ozone formed by the atomic oxygen, but unless the temperature is raised to  $67^{\circ}$  or air is admitted, phosphorescence and oxidation to pentoxide do not occur. In air the limiting pressure,  $p$ , necessary just to prevent phosphorescence is reduced by the presence of moisture, and by comparison with the values for pure oxygen it appears that nitrogen has a slight retarding influence on the oxidation, which seems, however, to be not directly



a chemical effect, for argon behaves similarly. In moist air under 1 atm. pressure the glow appears at  $7.8^\circ$ . The ionisation of air passing over phosphorus increases with rise in temperature and, up to a point, with increase in the surface of the solid exposed. Oxygen is ionised to a much greater extent than air, indicating that it is the oxidation to trioxide which gives rise to the ions. The inhibiting action of "poisons," such as sulphur dioxide, phosphine, iron pentacarbonyl, and hydrocarbons, on the oxidation in air and oxygen has been investigated by determinations of  $p$ . It is found empirically that if  $p_x$  is the limiting partial pressure of oxygen and if  $x$ , the vol.-% of poison, lies within certain limits, then  $p_x(x+a) = K$ , where  $K$  and  $a$  are constants depending on the poison and the composition of the gas phase. The value of  $1/K$  is a measure of the reactivity of the poison, which is the more effective the greater is its acceptor action towards atomic oxygen. It is in the gaseous phase, and not on the surface of the solid, that the poison exerts its retarding influence. Weiser and Garrison's theory of a surface poisoning action (A., 1921, ii, 695; cf. also Scharff, A., 1908, ii, 373) thus becomes untenable.

R. CUTHILL.

**Salts of hexafluorophosphoric acid,  $\text{HPF}_6$ .** W. LANGE and E. MÜLLER (Ber., 1930, 63, [B], 1058—1070; cf. A., 1928, 604).—The small amount of hexafluorophosphoric acid produced by the action of phosphoric oxide on aqueous hydrofluoric acid can be isolated if the mixture is preserved over-night, whereby the diacid is completely hydrolysed, after which the hexa-acid is precipitated as the nitron salt. From this salt the ammonium compound is isolated by treatment with aqueous ammonia and chloroform and then serves as a source for the other salts. Metals which yield sparingly soluble perchlorates give sparingly soluble, well-crystallised hexafluorophosphates. The salts are stable in aqueous solution unless the cation forms a sparingly soluble fluoride or phosphate, in which case they become extensively decomposed during evaporation. They are slowly hydrolysed by concentrated acids, but very stable towards alkali hydroxide. Crystallographically they differ from the perchlorates. The following hexafluorophosphates are described: ammonium,  $(\text{NH}_4)\text{PF}_6$ ,  $d_4^{25}$  2.180, which decomposes without melting when heated; hygroscopic lithium; sodium ( $+\text{H}_2\text{O}$ ); potassium,  $d_4^{25}$  2.591, also obtained by heating anhydrous potassium fluoride in phosphorus pentafluoride; rubidium,  $d_4^{25}$  3.057; cesium,  $d_4^{25}$  about 3.32° (oriented growths of the alkali salts on mica are described); barium; pentamminecopper, m. p. about  $226^\circ$  after softening at about  $218^\circ$  (also  $+\text{H}_2\text{O}$ ); the salts  $\text{Cu}(\text{PF}_6)_2 \cdot 2\text{en}$ ,  $\text{H}_2\text{O}$ ,  $d_4^{25}$  1.964, m. p. (indef.)  $112.5-115^\circ$ , and  $\text{Cu}(\text{PF}_6)_2 \cdot 5\text{C}_5\text{H}_5\text{N}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ; hexamminecobaltous, which loses ammonia at about  $130-196^\circ$ , leaving a residue, decomp.  $223^\circ$ ; hexamminenickel; tetramethylammonium,  $d_4^{25}$  1.617; tetraethylammonium, m. p. about  $331^\circ$  (decomp.); benzenediazonium,  $\text{PhN}_2\text{PF}_6$ , m. p.  $118.2^\circ$  with subsequent decomposition into fluorobenzene, stable to shock or blow; o-toluenediazonium, m. p.  $112^\circ$  (decomp.) when slowly heated, m. p. about  $123^\circ$  (decomp.) when rapidly

heated; diphenylene-4:4'-bisdiazonium,  $\text{C}_{12}\text{H}_8\text{N}_4(\text{PF}_6)_2$ , m. p.  $144.5^\circ$ , decomp.  $150^\circ$  with formation of 4:4'-difluorodiphenyl; pyridine, decomp.  $206^\circ$  after softening at  $170^\circ$ ; strychnine, decomp. above  $220^\circ$ ; brucine; morphine; cocaine, m. p.  $174.5^\circ$  after softening; nitron,  $d_4^{25}$  1.489. The ammonium salt affords very sparingly soluble precipitates with malachite-green and methylene-blue.

Evaporation of potassium dihydrogen arsenate with hydrofluoric acid followed by addition of ammonium and nitron acetates affords nitron hexafluoroarsenate,  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HAsF}_6\text{H}_2\text{O}$ , m. p. (anhydrous)  $210^\circ$ , slowly hydrolysed by cold water. Nitron hexafluoroantimonate,  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{HSbF}_6 \cdot 2\text{H}_2\text{O}$ ,  $d_4^{25}$  1.678 (anhydrous, m. p.  $193.5^\circ$ ,  $d_4^{25}$  1.700), obtained similarly from potassium pyroantimonate, is very difficultly hydrolysed.

H. WREN.

**Tantalum and its compounds.** V. SPITZIN and L. KASCHTANOV (J. Russ. Phys. Chem. Soc., 1930, 62, 295—312).—Tantalum containing not more than 5% of oxides can be obtained by the reduction by sodium in an atmosphere of hydrogen of potassium tantalofluoride. Reduction by magnesium of tantalum pentoxide yields a product the probable composition of which is expressed by  $\text{TaO}_2\text{Mg}$  or  $\text{Ta}_2\text{O}_4\text{Mg}$ . Metallic tantalum reacts with dry hydrogen chloride at  $700^\circ$  with the formation of tantalum pentachloride and hydrogen. Tantalum pentoxide reacts with hydrogen chloride according to the equation  $\text{Ta}_2\text{O}_5 + 10\text{HCl} \rightleftharpoons 2\text{TaCl}_5 + 5\text{H}_2\text{O}$ ; this reaction commences at  $500^\circ$ , and is completely reversible at lower temperatures. With small concentrations of water vapour tantalum pentachloride yields a black oxychloride,  $\text{TaO}_2\text{Cl}$ , and a white, unstable oxychloride, probably  $\text{TaOCl}_3$ . The velocity of the above reactions is greatly retarded by the presence in the hydrogen chloride of oxygen or moisture.

R. TRUSZKOWSKI.

**Action of ozone on ammonia.** W. MANCHOT (Ber., 1930, 63, [B], 1225—1226).—The intensity of the colour produced by the action of ozone on ammonia depends on the amount of water present and attains its maximum when the ratio  $\text{NH}_3 : \text{H}_2\text{O}$  2 : 1 is fulfilled. At  $-78^\circ$  the colour is red, becoming orange at  $-65^\circ$  and disappearing at  $-46^\circ$ . When cooled in liquid air the blue solution collects over the solid mass without imparting colour to it.

H. WREN.

**Oxygen fluoride,  $\text{OF}_2$ .** O. RUFF and W. MENZEL (Z. anorg. Chem., 1930, 190, 257—266; cf. A., 1929, 160).—Oxygen difluoride has been prepared in quantity by the action of fluorine on a dilute solution of sodium hydroxide and purified by fractional distillation. The pure substance is a colourless gas with a characteristic odour differing from that of fluorine and condenses to a yellow liquid,  $d_4^{-190}$  1.65, b. p.  $-146.5^\circ$ , m. p.  $-223.8^\circ$ . The heat of formation of the gas is  $-4.6 \pm 2$  kg.-cal.

F. L. USHER.

**Decomposition of hexabromoselenious acid and its salts.** J. MEYER and V. WURM (Z. anorg. Chem., 1930, 190, 90—94).—In contact with air solid hexabromoselenious acid loses bromine with formation of selenium monobromide. It is only this impure acid which gives colloidal selenium in contact

with water (Gutbier and Engeroff, A., 1915, i, 504; ii, 255); the pure acid dissolves without decomposition. The potassium and ammonium salts behave similarly, the loss of bromine from the solids in air becoming more and more rapid as the temperature is raised.

R. CUTHILL.

**Compounds of the trichromihexapropionato- (and -formiato)fluoro-complex [anions].** R. WEINLAND and J. LINDNER (Z. anorg. Chem., 1930, 190, 285—302; cf. A., 1929, 424).—New compounds have been prepared from the chloride or nitrate of the hexapropionatodihydroxytrichromic base. Treatment with aqueous guanidine fluoride yields green crystals of *guanidine hexapropionatodihydroxytrifluorochromiate*. In a similar manner the *aniline*, *o-toluidine*, and *pyridine* (+ 3H<sub>2</sub>O) salts have been prepared, all in the form of green crystals, having the general formula  $[\text{Cr}_3(\text{OH})_2(\text{EtCO}_2)_6\text{F}_3]_2(\text{Base})_2$ . The double compounds

$[\text{Cr}_3(\text{OH})_2(\text{EtCO}_2)_6\text{F}_3]\text{K}_2$ ,  $[\text{Cr}_3(\text{OH})_2(\text{EtCO}_2)_6\text{F}_2]\text{K}$  and  $[\text{Cr}_3(\text{OH})_2(\text{EtCO}_2)_6\text{F}_3](\text{NH}_4)_2$ ,  $[\text{Cr}_3(\text{OH})_2(\text{EtCO}_2)_6\text{F}_2]\text{NH}_4$  have also been obtained. By the interaction of the nitrate of the corresponding hexaformiato-base with neutral potassium fluoride there is formed *hexaformiatodihydroxymonofluorotrichromium*. If the chloride of the hexapropionato-base is treated with alkali thiocyanate in place of fluoride a complex cation is produced, and in this way *hexapropionatodihydroxytrichromium thiocyanate* (+4H<sub>2</sub>O) and (with pyridine) *hexapropionatodihydroxytripyridine-trichromium thiocyanate* have been prepared. A mixture of nitric and monochloroacetic acids gives with chromium hydroxide green crystals of *hexamonochloroacetatodihydroxytrichromium nitrate* (+5H<sub>2</sub>O). The constitution of the compounds is discussed.

F. L. USHER.

**New chlorine fluoride, ClF<sub>3</sub>.** O. RUFF and H. KRUG (Z. anorg. Chem., 1930, 190, 270—276; cf. A., 1929, 1226).—Chlorine trifluoride has been prepared by heating either chlorine or its monofluoride with excess of fluorine. Experimental details are given. The trifluoride is a colourless gas which condenses to a pale green liquid, b. p. 11°. The solid is colourless, m. p. -83°. Vapour pressures have been determined, and the substance is best characterised by the value at 0°, viz., 490 ± 5 mm. Chlorine trifluoride is extremely active chemically. Organic materials are instantly ignited, and the majority of the elements are attacked explosively.

F. L. USHER.

**Bromine chloride.** H. LUX (Ber., 1930, 63, [B], 1156—1158).—Slow distillation of a mixture of approximately equal quantities of chlorine and bromine with determinations of vapour tension and analyses of fractions establishes the formation of a volatile compound of bromine with a vapour tension greater than that of the halogen. A mixture of chlorine and bromine when submitted to distillation and fractional condensation in a high vacuum affords *bromine chloride*, BrCl, as an ochre-yellow solid, m. p. -54°, which rapidly decomposes in the vapour phase.

H. WREN.

**Existence of a volatile oxide of bromine.** E. ZINTL and G. RIENÄCKER (Ber., 1930, 63, [B], 1098—

1104).—The detection of small amounts of bromine oxide in presence of an excess of bromine vapour is effected by absorbing the mixture in halogen-free alkali hydroxide. The oxidising power and total bromine are determined by potentiometric titration in equal volumes of the resulting solution. The difference between the two results corresponds with the amount of bromine oxide present. An oxide of bromine does not appear to be produced by the decomposition of potassium bromate with concentrated sulphuric acid, the dehydration of hypobromous acid with phosphoric oxide, the extraction of aqueous hypobromous acid with carbon tetrachloride, or the action of bromine vapour on dry silver oxide. Mercuric oxide, precipitated at the ordinary temperature and dried in a high vacuum at 55°, does not react with bromine vapour at 0°; between 50° and 100° bromine oxide is formed in small amount, whereas at 200° oxygen is the sole product. A more highly reactive mercuric oxide is prepared by precipitating mercuric chloride with sodium hydroxide in very dilute solution at 50° and desiccation of the product at 150°. The oxide of bromine, probably Br<sub>2</sub>O, appears to be less volatile than bromine and to undergo decomposition relatively rapidly at 0°. Since the decomposition is probably catalytically accelerated by the active types of mercuric oxide, the successful preparation of a rich gas seems to demand unusual care in the quality of the oxide used.

H. WREN.

**Oxidation of ferrous hydroxide.** C. SANDON-NINI (Gazzetta, 1930, 60, 321—336).—The conditions under which the black ferrite can be formed by the oxidation of ferrous hydroxide have been studied. The observation of Deiss and Schikorr (A., 1928, 703) that at the ordinary temperature in excess of air ferrous hydroxide is oxidised directly to yellowish-red ferric hydroxide, even in presence of large quantities of dissolved salts, is confirmed. Black ferrite is formed when a dilute suspension of the ferrous hydroxide is boiled in presence of air, or at the ordinary temperature when the hydroxide is protected by a deep layer of water. In presence of chromic or aluminium hydroxides, however, no ferrite is formed even under these conditions. In an atmosphere of pure oxygen ferrous hydroxide is oxidised practically quantitatively to ferric hydroxide. A suspension of ferrous hydroxide in water which has been boiled for a long time in an atmosphere of hydrogen is oxidised directly to ferric hydroxide when subjected to the conditions which normally would give the black ferrite. No further evidence has been obtained for the formation of a green basic ferrite.

O. J. WALKER.

**System iron-nitrogen.** A. SIEVERTS and F. KRÜLL (Ber., 1930, 63, [B], 1071—1072).—The following values for *d*<sup>25</sup> of iron-nitrogen alloys have been observed, the figures in parentheses being the percentage of nitrogen: 6.501 (11.1), 6.742 (9.1), 6.946 (7.0), 7.073 (6.7), 7.110 (5.7), 7.507 (3.0), 7.855 (0.0). Molecular nitrogen is absorbed by  $\gamma$ -iron above 900° in amount proportional to the square root of the nitrogen pressure.

H. WREN.

**Quantitative analysis by X-rays.** G. VON HEVESY (Nature, 1930, 125, 776—777).—A reply to

Laby and Eddy (this vol., 560) in which the sensitivity of this method of analysis is discussed.

L. S. THEOBALD.

**Quantitative analysis by X-rays.** T. H. LABY (Nature, 1930, 125, 818).—In a reply to Hevesy (preceding abstract), it is reaffirmed that the  $K$  X-ray spectrum of an element present to less than 0.0001% in a metal can be photographed.

L. S. THEOBALD.

**Corrections for standard solutions of inconvenient concentrations.** S. GOTTLIEB (Ind. Eng. Chem. [Anal.], 1930, 2, 186).—Solutions which change their concentration rapidly are best not adjusted to concentration on each occasion. If  $r$  is the concentration factor,  $x$  the burette reading found in a titration, and  $c$  the necessary correction to the latter  $x = \pm c/(r - 1)$  and a table can be constructed giving the relation between  $x$  and  $c$ .

C. IRWIN.

**Indication of the sensitiveness of analytical reactions.** K. HELLER (Mikrochem., 1930, 8, 141—142).—A discussion of the suitability of various terms used in German to indicate the limiting dilution at which a reaction is detectable.

A. R. POWELL.

**Analytical separation by ether extraction.** O. VON GROSSMANN (Chem.-Ztg., 1930, 54, 402—403).—An apparatus for the separation of cobalt ammonium thiocyanate from the corresponding nickel salt by extraction with ether is described. The conditions necessary for the separation of nickel and cobalt from other metals by electrolysis, the formation of the thiocyanate, and the transformation of the isolated cobalt salt into the sulphate, which is electrolysed, are given. A method for the separation of ferric chloride from other metals in hydrochloric acid solution, in the same apparatus, and one for the separation of boric and lactic acids, are outlined.

E. H. SHARPLES.

**Methods of preparation and control of mutually concordant standard solutions for technical analysis.** H. D. STEENBERGEN (Chem. Weekblad, 1930, 27, 211—212).—As a primary standard, 0.1N-hydrochloric acid, standardised by precipitation of silver chloride, is recommended; 0.1N-sodium thiosulphate (standardised by iodate and iodide), 0.1N-hydrochloric acid, 0.1N-potassium permanganate, 0.1N-silver nitrate, and 0.1N-potassium thiocyanate form a convenient series of mutually concordant solutions.

H. F. GILLBE.

**Alkalimetric titration, indicators and titration errors.** I, II, III, and IV. C. J. VAN NIEUWEN-  
arzo (Chem. Weekblad, 1930, 27, 143—146, 158—160, 186—188, 206—209).—I. A general discussion of alkalimetric titration and the  $p_H$  of indicator changes.

II. The method of calculation of the  $p_H$  of an acid solution to which a known volume of alkali solution has been added is described for mono- and di-basic acids.

IV. The method of calculation of the  $p_H$  at which the indicator colour change should occur in order to obtain the most accurate result is described and examples are given for the titration of a weak mono-basic base such as pyridine with a strong acid. The

conditions under which phenolphthalein, methyl-red, and methyl-orange may be satisfactorily employed as indicators are described.

V. The titration of weak dibasic acids and bases is discussed, and a number of special cases are considered.

H. F. GILLBE.

**Determination of fluorine as calcium fluoride.** E. CARRIÈRE and JANSSENS (Compt. rend., 1930, 190, 1127—1128).—The fluoride is precipitated in a platinum vessel in a boiling ammoniacal medium by means of calcium chloride, washed free from chlorides with boiling ammonia solution, and weighed. The mean error is 0.6%, but rises to 6% if a porcelain vessel is used. In the presence of 0.2 g. of iron and/or aluminium, which may be removed when the solution is made ammoniacal, the accuracy is 1% for a 0.5% solution of sodium fluoride (cf. this vol., 180).

J. GRANT.

**Reliability of the Reich-Raschig method of determining sulphur dioxide.** H. E. WOISIN.—See B., 1930, 507.

**Determination of small concentrations of sulphur dioxide and hydrogen sulphide present together in air.** V. G. GUREVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 111—119).—Neutral 5% potassium chlorate solution quantitatively converts sulphur dioxide present in air into sulphuric acid; under the same conditions not more than 4% of hydrogen sulphide present in the same air undergoes oxidation. Hydrogen sulphide is oxidised to sulphuric acid by hydrogen peroxide solution contained in a second wash-bottle. By passing a known quantity of air through these two solutions sulphur dioxide and hydrogen sulphide at concentrations respectively of 0.017—0.60 mg. and 0.092—0.60 mg. per litre can be evaluated with satisfactory accuracy by determining the sulphuric acid formed.

R. TRUSZKOWSKI.

**Use of microchemical reactions in metallography.** I. Detection of sulphide segregations. M. NIESSNER (Mikrochem., 1930, 8, 121—130).—The sulphide prints obtained with mercuric chloride or silver bromide paper from a polished surface of iron or steel produce, when washed, dried, and treated with a drop of Feigl's sodium azide-iodine solution (A., 1928, 1106), bubbles of nitrogen in the drop, whereas phosphide prints similarly treated do not react. The test is extremely sensitive and will detect sulphide sulphur in the presence of a large excess of phosphide.

A. R. POWELL.

**Volumetric determination of sulphates.** M. DOMINKIEWICZ (Przemysł Chem., 1930, 14, 241—245).—The solution (about 100 c.c.) under examination is after acidification with hydrochloric acid brought to boiling, and excess of 0.1N-barium chloride solution is added. After boiling a further few minutes and neutralisation with ammonia, excess of barium is determined by titration with 0.1N-ammonium potassium chromate solution, titration being completed when a drop of solution gives a blue coloration with a spot of benzidine solution on filter-paper. The above method is particularly convenient for the determination of sulphates in urine, in which case phosphates should first be precipitated by the addition of magnesia mixture.

R. TRUSZKOWSKI.

**Reaction of nitrites with aminosulphonic acid and an identification and detection of nitrous acid in presence of nitric acid.** P. BAUMGARTEN and I. MARGGRAFF (Ber., 1930, **63**, [B], 1019—1024).—Nitrites react with aminosulphonic acid according to the equation  $\text{XNO}_2 + \text{NH}_2\cdot\text{SO}_3\text{H} = \text{XH}\text{SO}_4 + \text{N}_2 + \text{H}_2\text{O}$ , the change being almost instantaneous in dilute solutions. Nitric acid is therefore not produced during the destruction of nitrite by this method in dilute solution, but in the case of more concentrated solutions the prolongation of the change and its strongly exothermic nature lead to the formation of traces of nitric acid detected only by very sensitive reagents. Since nitrates do not disturb the reaction, minute amounts of nitrate in presence of much nitrite can be detected by use of diphenylamine after application of aminosulphonic acid. A very sensitive test for nitrite is based on the detection of the metal hydrogen sulphate produced by its decomposition (see above) by means of barium chloride; this can be extended to nitrate, which is reduced by zinc or magnesium. Determination of nitrite is based on measurement of the nitrogen evolved or weight of the barium sulphate produced. In the very dilute solutions used there is no danger of hydrolysis of aminosulphonic acid if ebullition of the solution is not prolonged.

H. WREN.

**Quantitative analysis of azides.** J. F. REITH and J. H. A. BOUWMAN (Pharm. Weekblad, 1930, **67**, 475—480).—Solutions of soluble azides can be titrated by means of sodium nitrite solution in presence of mineral acid, using as indicator a large excess of ferric chloride. The values obtained may be from 0.5 to 2.0% too low by removal of azoimide from the solution with the gases evolved.

S. I. LEVY.

**Direct determination of orthophosphoric acid in presence of the other acids of phosphorus.** A. DUNAIEV (Z. anal. Chem., 1930, **80**, 252—263).—The colorimetric method of Maljugin and Chrenova, based on the production of a blue colour when a sulphuric acid solution of the phosphate is treated with ammonium molybdate and stannous chloride, has been shown to be specific for orthophosphoric acid, and permits the determination of this acid in the presence of meta- and pyro-phosphoric, phosphorous, and hypophosphorous acids. The range of concentration in which the depth of colour produced is strictly proportional to the amount of phosphorus present is 1:5, and quantities of phosphorus between 0.002 and 2.5 mg. can be determined with an accuracy of 0.2—0.3%. Full working details are given. The method can also be used to follow the progressive hydration of meta- and pyro-phosphates, and a number of curves showing the rate of hydration of solutions of sodium pyrophosphate and metaphosphoric acid are appended.

H. F. HARWOOD

**Analysis of crude phosphates.** A. SUCHIER.—See B., 1930, 535.

**Titration of hydrofluosilicic and hydrofluoboric acids.** E. F. KERN and T. R. JONES (Amer. Electrochem. Soc., May, 1930. Advance copy, 6 pp.).—Using indicators which change colour below  $p_{\text{H}}$  4.5, the titration of solutions of these acids with *N*-sodium hydroxide gives end-points corresponding approxi-

mately with the reactions  $\text{H}_2\text{SiF}_6 + 2\text{NaOH} = \text{Na}_2\text{SiF}_6 + 2\text{H}_2\text{O}$  and  $\text{HBF}_4 + \text{NaOH} = \text{NaBF}_4 + \text{H}_2\text{O}$ , respectively. With indicators having a colour change above about  $p_{\text{H}}$  6.5 hydrofluosilicic acid gives an end-point corresponding with the reaction  $\text{H}_2\text{SiF}_6 + 6\text{NaOH} = 6\text{NaF} + \text{SiO}_2 + 4\text{H}_2\text{O}$  when the titration is completed at 60°, but hydrofluoboric acid gives a practically constant end-point, which does not correspond, however, with any definite simple reaction.

H. J. T. ELLINGHAM.

**Analysis of glass containing phosphate.** J. D. CAUWOOD, J. H. DAVIDSON, and V. DIMBLEBY.—See B., 1930, 557.

**Microchemical detection of carbonates.** F. FEIGL and P. KRUMHOLZ (Mikrochem., 1930, **8**, 131—135).—The substance is moistened with very dilute sulphuric acid in a small tube into which fits a glass stopper having a protuberance at its lower end on which is suspended one drop of a solution made by mixing 1 c.c. of 0.1*N*-sodium carbonate, 2 c.c. of 0.5% phenolphthalein solution, and 10 c.c. of water. In the presence of more than  $4 \times 10^{-6}$  g. of carbon dioxide the pink colour of the drop disappears in 10 min.; other volatile acids must be absent. Reducing acids may be oxidised with hydrogen peroxide and cyanides converted into ferrocyanides before making the test. The reaction may be used to detect oxalic acid, manganese sulphate and permanganate being added to the test solution prior to making the carbonate test.

A. R. POWELL.

**Separation of metals by "internal electrolysis."** H. J. S. SAND (Analyst, 1930, **55**, 309—312).—The method is similar in principle to that of Hollard (cf. A., 1903, ii, 335). The metal to be determined is deposited on a weighed platinum cathode in the absence of an externally generated current, an anode of the baser metal with which it is associated being placed in contact with a solution of one of its salts in a compartment separated from the solution to be examined by a parchment membrane. The two anodes, the cathode, and stirrer are fitted to a circular wooden lid resting on a ring held by a retort; the anodes are hollow and so shaped that the parchment diaphragms may be securely tied to them, and these consist of thimbles with lengthwise slots at their tops which allow of liquid from the anode chamber being forced into the cathode chamber by running fresh electrolyte from underneath. The stirrer is of the centrifugal type.

D. G. HEWER.

**Distillation of metals in a high vacuum, and detection of small amounts of foreign metals.** G. TAMMANN and K. L. DREYER (Z. anorg. Chem., 1930, **190**, 53—58).—Experiments have been made on the separation of mixtures of metals by sublimation under a pressure of 0.001 mm. in a tube along the wall of which there is a temperature gradient, the condensed metals forming separate rings on the wall. Small amounts of volatile metals in metals not readily volatilised and in rock can be detected in this way.

R. CUTHILL.

**Determination of sodium.** E. KAHANE (J. Pharm. Chim., 1930, [viii], **11**, 425—428).—A method is given for the quantitative precipitation of sodium as the triple sodium magnesium uranyl acetate,

$\text{NaMg}(\text{UO}_2)_3(\text{OAc})_9 \cdot 8\text{H}_2\text{O}$ , which may be dried at  $105^\circ$  and weighed, or ignited and weighed as  $\text{Na}_2\text{Mg}_2(\text{U}_2\text{O}_7)_3$ , the error in either case being 0.1–0.2%. Alternatively, a solution of the dried triple salt may either be reduced by copper and dilute sulphuric acid and titrated with permanganate (error, about 1%), or be analysed colorimetrically after addition of potassium ferrocyanide and acetic acid.

H. E. F. NOTTON.

**Gravimetric determination of potassium, rubidium, and caesium by the zirconium sulphate method.** N. A. YAJNIK and G. L. TANDON (J. Indian Chem. Soc., 1930, 7, 287–296).—Details are given for quantitatively precipitating the compounds  $\text{Zr}_2\text{O}_3 \cdot 2\text{MSO}_4 \cdot x\text{H}_2\text{O}$ , where  $\text{M}=\text{K}$  ( $x=8$ ),  $\text{Rb}$  ( $x=15$ ), or  $\text{Cs}$  ( $x=11$ ) from non-acid sulphate solutions (cf. Reed and Withrow, A., 1928, 858). Ammonium, lithium, and sodium ions are without influence, except that sodium ions prolong the precipitation time.

S. K. TWEEDY.

**Gravimetric determination of small amounts of rubidium.** E. BURKSER, W. L. MILGEVSKAJA, and R. W. FELDMANN (Z. anal. Chem., 1930, 80, 264–270).—The solubilities of rubidium chloride, potassium chloride, and rubidium chlorostannate in a mixture of 2 vols. of 96% alcohol and 1 vol. of fuming hydrochloric acid, and in this liquid diluted with varying amounts of water, have been determined. Rubidium chloride (0.005 g.) in presence of potassium chloride (0.005–0.05 g.) may be satisfactorily determined by treating the salts, dissolved in a little water, with sufficient of the above solvent to give a liquid finally containing 10% of water, and precipitating the rubidium by the addition of a solution of stannic chloride in boiling absolute alcohol. The precipitate of rubidium chlorostannate is filtered after keeping over-night, washed with absolute alcohol, and dried at  $110^\circ$ . Experiments with solutions of mixtures containing rubidium chloride (0.005–0.01%) together with the chlorides of sodium, potassium, and magnesium and the sulphates of calcium and magnesium showed that after removal of the sulphate by barium chloride, followed by precipitation of the calcium and excess of barium with sodium carbonate and removal of the bulk of the sodium and potassium chlorides by evaporation and crystallisation, the rubidium in the filtrate could be recovered to the extent of 56–80% of the original amount. In the case of a mixture of the chlorides of potassium, sodium, and rubidium, the last-named could still be detected by the above method, although initially present in the mixture to the extent of only 0.001%.

H. F. HARWOOD.

**Determination of small amounts of silver in pyrolusite.** A. KUNDERT.—See B., 1930, 507.

**Determination of calcium in the presence of iron and aluminium.** R. C. WILEY (Soil Sci., 1930, 29, 339–347).—Co-precipitation of calcium during the separation of iron and aluminium as hydroxides is avoided by eliminating all carbon dioxide from the solution before precipitation, and boiling off all excess of ammonia before filtering the iron–aluminium precipitate. The ammonia solution used for precipitation must be free from carbonate.

A. G. POLLARD.

**Determination of calcium by ignition of calcium oxalate to carbonate in air.** H. H. WILLARD and A. W. BOLDYREFF (J. Amer. Chem. Soc., 1930, 52, 1888–1892).—The ignition of precipitated calcium oxalate at temperatures between  $350^\circ$  and  $600^\circ$  has been investigated. Between  $450^\circ$  and  $500^\circ$ , calcium carbonate is produced quantitatively within 1–2 hrs., thus affording an accurate gravimetric determination of calcium. The product was white. Above about  $520^\circ$ , increasing quantities of calcium oxide were formed. J. G. A. GRIFFITHS.

**op-Dihydroxyazo-p-nitrobenzene as a test for the magnesium ion.** E. W. ENGEL (J. Amer. Chem. Soc., 1930, 52, 1812–1814; cf. Ruigh, A., 1929, 783).—A stain method for the detection of  $3 \times 10^{-6}$  g. of magnesium is described. The solution under test is evaporated to small volume; 5–10 c.c. of 6*N*-sodium hydroxide and 1 drop of the dye reagent are added. A light blue stain develops on the vessel. The colour is unchanged by concentrated ammonia solution, but becomes green on the addition of water. Cobalt and nickel behave differently, and other ions, whilst decreasing the sensitivity, generally do not invalidate the test. J. G. A. GRIFFITHS.

**Volumetric analysis of magnesium salts.** T. MAEDA and R. SYÖZI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 185–189).—The alkali precipitation method for the determination of magnesium has been investigated. The accuracy increases with increase of the time during which the precipitate is allowed to settle. The use of filter-paper always introduces a positive error, but by making use of centrifugal separation consistent results having an error of about –0.1% are obtained. H. F. GILLBE.

**Microchemical reactions. VI. Phytomicrochemical detection of magnesium.** L. ROSENTHALER (Mikrochem., 1930, 8, 151–153).—Magnesium compounds produce a characteristic crystalline precipitate with a saturated solution of caesium chloride and sodium selenite which closely resembles that produced by nickel salts (cf. Martini, this vol., 565). The reaction is given by magnesium carbonate and oxide, but not by the phosphate and is suitable for the phytochemical detection of magnesium, since calcium salts do not interfere. The nickel salt crystals are distinguished from those of magnesium by their reaction with dimethylglyoxime.

A. R. POWELL.

**Confirmatory test for zinc.** J. S. PIERCE and E. D. NAVE (Ind. Eng. Chem. [Anal.], 1930, 2, 190).—The ferrocyanide titration of zinc with uranyl acetate as inside indicator can be used as a confirmatory test for zinc if interfering ions are absent and will give an approximate idea of the amount present. It is usually sufficient to precipitate the zinc in a solution containing acetic acid and ammonium acetate with hydrogen sulphide, dissolve the precipitate in hydrochloric acid, evaporate, and redissolve in acetic acid. The number of drops of 0.5*N*-potassium ferrocyanide required to produce a distinct colour is noted.

C. IRWIN.

**Precipitation of small amounts of lead as chromate and their colorimetric determination.** B. JONES (Analyst, 1930, 55, 318–320).—The acid

lead solution is evaporated to dryness, 8 drops of hydrochloric acid (1 : 1) are added and then hot water; to the clear solution 10 c.c. of approximately 0.1N-potassium chromate solution are added, the liquid is made just alkaline with dilute ammonia solution, and just re-acidified with acetic acid (1 : 1). After boiling for 10 min. and cooling, the separated lead chromate is collected on asbestos pulp and washed with 2% potassium nitrate solution. After dissolution by addition of 10 c.c. of nitric acid (*d* 1.2) the liquid is filtered into a Nessler glass, the pulp washed, and the solution diluted to 100 c.c. The same amount of acid is put into another Nessler glass, diluted to 100 c.c., and to each are added 5 c.c. of a 0.1% solution of diphenylcarbazide in dilute acetic acid and the colour of the solution under examination is matched by titrating the liquid in the other glass with standard potassium dichromate. No indicator is necessary if more than 1 mg. of lead is present. The method will accurately determine amounts of lead of the order of a few mg. With small amounts of lead the amount of ammonium acetate present must be kept well under control, since the reagent has a distinct solvent effect on the lead chromate.

D. G. HEWER.

**Determination of metals by deposition in a galvanic cell.** P. S. TUTUNĐIĆ (Z. anorg. Chem., 1930, 190, 59—64).—The determination of copper by deposition on an electrode of copper gauze which forms one pole of a Daniell cell, and, together with the solution for analysis, is contained in the porous pot, is described. The solution contains about 1 c.c. of concentrated nitric acid per 100 c.c. as depolariser, and is stirred during deposition; the anode consists of a sheet of zinc which surrounds the outside of the pot and is immersed in a 5% solution of zinc sulphate. By this method copper may be separated from cadmium, cobalt, and nickel. The same apparatus may also be employed for the quantitative deposition of silver on a silver gauze electrode from a solution of a silver salt containing nitric acid and a little sulphuric acid, provided that a nickel electrode in a 2% solution of nickel sulphate is used for the anode and that the cell is not allowed to give a current exceeding 0.25—0.30 amp.

R. CUTHILL.

**Analysis of aluminium alloys.** F. L. HAHN.—See B., 1930, 512.

**Ferric chloride as indicator in the titration of potassium ferrocyanide with zinc sulphate.** P. F. FELKERS (Chem. Weekblad, 1930, 27, 209—210).—The method of employment of ferric chloride solution as an external indicator in the titration of ferrocyanide with zinc sulphate is fully described. The titration may be carried out at the ordinary temperature, and the results are concordant to within 0.3%. Variations of the acidity of the solutions markedly influence the results, and although potassium and ammonium chlorides are without influence, the presence of 0.2% of sodium chloride introduces errors of the order of 0.4%.

H. F. GILLBE.

**Gravimetric determination of nickel, cobalt, and cadmium.** P. B. SARKAR and B. K. DATTA-RAY (J. Indian Chem. Soc., 1930, 7, 251—258).—The insoluble hydrazine-thiocyanate compounds,

$M(SCN)_2 \cdot 2N_2H_4$ , of bivalent metals may be employed for the determination of cobalt, cadmium, and nickel when present alone (Ray and Sarkar, J.C.S., 1920, 117, 322). The following crystalline compounds are described:  $Fe(SCN)_2 \cdot 2N_2H_4$ , which reacts with water or dilute ammonia solution to form ferrous hydroxide, and  $Mg(CNS)_2 \cdot 2N_2H_4$ , which is very soluble in water.

S. K. TWEEDY.

**Volumetric determination of cobalt: application to special steels.** L. MALAPRADE.—See B., 1930, 561.

**Cobalt thiocyanate reaction for the detection of cobalt and thiocyanate.** I. M. KOLTHOFF (Mikrochem., 1930, 8, 176—181).—Addition of a saturated solution of potassium thiocyanate in acetone to an equal volume of a neutral solution of a cobalt salt produces a greenish-blue colour when the concentration of cobalt exceeds 25 mg. per litre. In the presence of iron sodium fluoride must be added; nickel does not interfere in concentrations up to 1000 times that of the cobalt, but copper gives a similar reaction to cobalt and must be removed before applying the test. Thiocyanate may be detected by mixing 1 drop of the solution with 1 drop of 1% cobalt sulphate solution, evaporating to dryness, and moistening the residue with a few drops of acetone; 0.001 mg. of thiocyanate produces the green colour.

A. R. POWELL.

**Microchemical mineral analysis. IV. [Reactions of chromium, phosphoric acid, and nickel and the use of acridine in microchemical analysis.]** A. MARTINI (Mikrochem., 1930, 8, 143—146).—Cæsium chromium alum may be distinguished from the corresponding aluminium alum by the fact that it darkens on treatment with ammonia. Chromic chloride yields with a saturated solution of oxalic acid containing quinoline colourless, triclinic prisms of quinoline chromioxalate. Phosphates yield characteristic crystals with a solution of cæsium chloride and quinoline, saturated with magnesium chloride; arsenates must be absent. Nickel chloride yields, with one drop of ammonia, one drop of a saturated solution of ammonium thiocyanate, and 1 drop of *o*-toluidine, colourless, highly-refracting, triclinic prisms of the compound

$[C_6H_4Me \cdot NH_2 \cdot HCNS]_4[Ni(NH_3)_4](CNS)_2$ . Cobalt chloride produces blue crystals of cobalt acridine thiocyanate when treated with acridine hydrochloride and ammonium thiocyanate; under similar conditions zinc salts produce a yellow precipitate, copper salts brown needles, and ferric salts red, triclinic prisms.

A. R. POWELL.

**Test for tin.** H. MEISSNER (Z. anal. Chem., 1930, 80, 247—252).—The substance or solution is treated in a porcelain dish with an excess of concentrated hydrochloric acid, and a piece of pure zinc rod is added. The mixture is well stirred by means of a test-tube filled with cold water, and the tube is then inserted into a non-luminous Bunsen flame. A blue mantle around the moistened part of the test-tube indicates the presence of tin; 0.035 mg. of tin in 1 c.c. of solution can thus be detected. Solutions of tin salts in which the chlorine ion is present afford a similar reaction. The cause of the coloration is



ascribed to the formation of an unstable hydride of tin, probably  $\text{SnH}_4$  (cf. Schröer and Balandin, this vol., 727).  
H. F. HARWOOD.

**Determination of titanium in alloy steels.** F. SPINDECK.—See B., 1930, 561.

**Analytical chemistry of element 91, ekatantalum, and its difference from tantalum.** A. V. GROSSE (J. Amer. Chem. Soc., 1930, 52, 1742—1747; cf. A., 1928, 259, 495).—Ekatantalum pentoxide is a heavy white powder of high m. p. and after ignition is almost insoluble in concentrated sulphuric, nitric, or hydrochloric acid. The oxide is not acidic, but definitely although feebly basic, and generally behaves towards reagents in a manner opposite to tantalum pentoxide. Both oxides are, however, soluble in 40% hydrofluoric acid, and are precipitated from acid solution by ammonia. Ekatantalum pentoxide is soluble in fused sodium hydrogen sulphate but not in fused potassium carbonate, and is completely precipitated from acid solution by hydrogen peroxide or phosphoric acid.

J. G. A. GRIFFITHS.

**Analysis of the platinum metals.** W. GRAULICH.—See B., 1930, 563.

**Geiger tube counter.** L. F. CURTISS (Bur. Stand. J. Res., 1930, 4, 593; cf. Geiger and Müller, A., 1929, 114).—An improved form of the now Geiger tube counter for detecting  $\gamma$ - or high-velocity  $\beta$ -radiation is described. It is portable, is independent of pumps, and contains a capsule of phosphorus pentoxide as a drying agent.

N. M. BLIGH.

[Laboratory devices.] F. HILDEBRANDT (Chem. Fabr., 1930, 175—176; cf. Weber, this vol., 567).—Criticisms and suggestions for simplification are offered.

S. I. LEVY.

**Simple thermostated room.** J. HEUBERGER (Svensk Kem. Tidskr., 1930, 42, 101—105).—A method is described by means of which a room may be maintained at constant temperature to  $\pm 0.1^\circ$  while still provided with ample ventilation. The linear expansion of an aluminium tube is used for temperature control in a new form of thermal relay, which is described in detail.

J. W. SMITH.

**Vacuum tube potentiometer for the determination of the true *E.M.F.* of a high-resistance cell.** R. J. FOSBINDER (J. Physical Chem., 1930, 34, 1294—1302).—The theory and construction of a vacuum tube potentiometer, using a vacuum tube amplifier as a null instrument, are described. An accuracy of  $\pm 0.0001$  volt is obtainable. The results of tests on various cells and on phosphate buffer solutions are recorded.

L. S. THEOBALD.

**Automatic thermoregulator.** J. A. BEATTIE and D. A. JACOBUS (J. Physical Chem., 1930, 34, 1254—1259).—An automatic thermoregulator involving the use of a platinum resistance thermometer, two photo-electric cells, and a three-electrode vacuum tube and capable of maintaining the temperature of a stirred liquid bath or of an air bath at any temperature from the ordinary up to  $450^\circ \pm 0.001^\circ$  is described.

L. S. THEOBALD.

**Use of the grid glow tube in a thermoregulator.** J. H. HIBBEN (Rev. Sci. Instr., 1930, 1, 285—288).—Modifications in the thermoregulator of White, Adams, and Roberts (cf. J. Opt. Soc. Amer., 1925, 11, 171) are described.

C. A. SILBERRAD.

**Relay for use in [thermo]regulating circuits.** L. G. WESSON (Ind. Eng. Chem. [Anal.], 1930, 2, 179—180).—The relay consists of two electromagnets each acting on one end of an approximately-balanced arm carrying a mercury switch. A wire carried on, but insulated from, each end of the arm dips into a mercury cup and makes or fails to make contact according to the position of the arm. The relay consumes current only while actually making or breaking contact and no sparking occurs even with currents up to 10 amp. It can be used, e.g., with a toluene thermoregulator fitted with maximum and minimum contacts.

C. IRWIN.

**Constant-temperature device.** A. C. EGERTON (J. Sci. Instr., 1930, 7, 172).—A small bath is surrounded by a cylindrical jacket of mercury, which by its expansion through a capillary tube actuates an electromagnetic relay. The heating coil is wound outside the mercury, and the temperature can be kept constant at  $25^\circ$  to  $\pm 0.01^\circ$ .

C. W. GIBBY.

**New form of Jamin's interference refractometer.** F. F. MARTENS (Z. Physik, 1930, 61, 363—367).—One of the blocks of the original arrangement of the refractometer is replaced by a right-angled prism, where the incident rays are doubly reflected and sent back in a direction parallel to their original paths. This arrangement makes the refractometer more sensitive, only about half as long as the Jamin instrument, and little affected by vibration. The mathematics of the new form of instrument is given. It can be used not only for the determination of refractive indices, but also for the investigation of sound fields.

A. J. MEE.

**Multiple standard colorimeter for *p<sub>H</sub>* determinations.** S. L. LEIBOFF (Ind. Eng. Chem. [Anal.], 1930, 2, 194).—The apparatus consists of a colorimeter with a rack and pinion which moves an improved block comparator through the field of vision, one half of which is occupied by light coming through both distilled water and the unknown solution containing indicator, and the other half by light coming through the unknown solution and the movable comparator.

E. H. SHARPLES.

**Integral microradiography.** A. DAUVILLIER (Compt. rend., 1930, 190, 1287—1289).—Highly-magnified images of microscopic sections a few microns thick have been obtained by the use of fine-grained colloidal silver emulsions (prepared by the method of Watteville and Leroy) placed in direct contact with the section. The apparatus is that used for crystal analysis, and penetrating electrons or soft X-rays are the usual sources of radiation. Oxygen has greater powers of absorption for the rays than carbon, and traces of sulphur produce opacity.

J. GRANT.

**Protection against acid vapours of ventilating fans in laboratories.** M. DREIFUSS and A. STAAB (Chem.-Ztg., 1930, 54, 391).—Prodorite lacquer, composed of finely powdered quartz and tar, efficiently

protects the sheet-metal parts of fans against acid vapours. It should be renewed every three months.

C. IRWIN.

**Calorimetric researches. III. Technique for adiabatic bomb calorimetry of high precision.** L. J. P. KEFFLER (*J. Physical Chem.*, 1930, **34**, 1006—1012).—An apparatus ensuring the adiabaticity of a calorimeter to within  $0.1^\circ$  during the first minute following ignition and to within  $0.01^\circ$  for the remainder of a combustion is described together with a device for the determination of an interval of temperature to within  $0.0001^\circ$ .

L. S. THEOBALD.

**Calorimetry of a fluid.** N. S. OSBORNE (*Bur. Stand. J. Res.*, 1930, **4**, 609—629).—A single calorimetric apparatus specially designed and with especial refinements provides a setting for a systematic group of experiments of four types, viz., constant mass, evaporation, throttling, and withdrawal of saturated liquid, in which four characteristic heat quantities are determined each as a function of temperature. These experimental data provide a basis for formulation of the thermodynamic behaviour of the fluid in terms of familiar and convenient properties within the limits of the observations.

W. E. DOWNEY.

**Laboratory siphons.** P. FUCHS (*Chem. Fabr.*, 1930, 173—175).—The construction and application of siphons suitable for various purposes are described.

S. I. LEVY.

**Simple water-jet air pump.** J. DE GRAAFF (*Chem. Weekblad*, 1930, **27**, 340—341).—A simple form of pressure receiver, into which a jet of water carrying entrained air is delivered, is described.

S. I. LEVY.

**Capillary mercury-vapour lamp.** L. J. HEIDT and F. DANIELS (*J. Amer. Chem. Soc.*, 1930, **52**, 2151—2152).—An inexpensive and easily-constructed mercury-vapour lamp yielding high light intensities is described.

J. G. A. GRIFFITHS.

**Standardisation of weights.** P. F. WEATHERILL (*J. Amer. Chem. Soc.*, 1930, **52**, 1938).—The accuracy of the Richards method can be doubled by weighing by transposition.

J. G. A. GRIFFITHS.

**Capillary gas valve.** H. N. ALYEA (*J. Amer. Chem. Soc.*, 1930, **52**, 1936—1937).—An all-glass capillary gas valve which may be used repeatedly is described. A thin-walled 1 mm. bore capillary tube has about 30 cm. of its length sealed inside a thin-walled tube of 12 mm. diameter. The enclosed end of the capillary is sealed by drawing off, in a flame, the end of the surrounding wide tube. The closed capillary is opened again by an iron-cored glass weight.

J. G. A. GRIFFITHS.

**Large glass distillation apparatus.** D. F. OTTMEYER.—See B., 1930, 535.

**Distillation apparatus for water.** F. FRIEDRICH (*Chem.-Ztg.*, 1930, **54**, 383).—The cooling water leaving the hard-glass condenser is fed to a simple constant-level feed device fitted into the side of a copper distillation flask.

E. LEWKOWITSCH.

**Reflex regulator for laboratory stills.** J. H. BRUUN (*Ind. Eng. Chem. [Anal.]*, 1930, **2**, 187—188).—A regulator intended to give a constant reflux ratio operates by condensing the vapour and dividing it

between two capillaries of the same bore but of different lengths, or of different bores, one of which returns liquid to the column and one to a receiver. The reflux ratio may be varied by surrounding one capillary with an electric heating coil which reduces the viscosity of the liquid. Another arrangement varies the reflux ratio by means of a stopcock and the returned condensate is measured by a capillary flow-meter.

C. IRWIN.

**Reversible microdistillation apparatus.** D. KLABISCHTSCHEV (*Mikrochem.*, 1930, **8**, 136—140).—The apparatus consists of two exactly similar graduated glass tubes with side-tube and closed with rubber stoppers carrying glass tubes, one reaching to the bottom and the other just below the cork. These tubes are joined together through a two-bulb distillation head, and the side-tube of the graduated tube which has the longer tube in the stopper is connected with a vacuum pump and that of the other graduated tube with a source of dry air. By immersing the latter tube in hot water and the former in cold water distillation of the more volatile constituent of the liquid mixture is effected. By reversal of the tubes after removing the undistilled liquid the distillate may be further fractionated. The apparatus is suitable for the recovery of methyl alcohol from 1—2 c.c. of ethyl alcohol.

A. R. POWELL.

**High-vacuum distillation with the aid of liquid air and active charcoal.** L. N. LEWIN (*J. pr. Chem.*, 1930, [ii], **126**, 217—219).—Distillation under high vacuum may be carried out in an ordinary vacuum-distillation apparatus using a water-pump if an absorption system containing active charcoal (previously dried by heating in a vacuum), cooled in liquid air, be inserted between the receiver and the pump. An exceedingly fine capillary must be used to prevent bumping. When the charcoal is saturated (marked by a rise in pressure) it may be partly freed from absorbed gases by removing the bath of liquid air, but eventually re-heating in a vacuum is necessary. The following b. p. were observed: glycerol,  $136^\circ/0.14$  mm.;  $120^\circ/0.07$  mm.; phenylhydrazine,  $77-78^\circ/0.052$  mm.; benzenesulphonyl chloride,  $76-77^\circ/0.03$  mm.; and *p*-nitrotoluene,  $64-65^\circ/0.052$  mm.

H. A. PIGGOTT.

**Stalagmometric measurement of liquid-liquid surface tension.** L. J. WEBER and J. TRAUBE (*Biochem. Z.*, 1930, **219**, 468—472).—By means of a slightly modified form of the stalagmometer of Traube and others (this vol., 496) surface tensions at liquid-liquid boundaries can be measured with satisfactory accuracy provided that, in the calculation of the results, the densities of the liquids are taken into consideration.

W. MCCARTNEY.

**Shaking machine for analytical work.** A. L. ROMANOFF (*Science*, 1930, **71**, 320).—Descriptive.

L. S. THEOBALD.

**New laboratory materials. II.** H. A. J. PIETERS (*Chem. Weekblad*, 1930, **27**, 289).—A short account of some laboratory apparatus and materials.

S. I. LEVY.

**Polarimetry of solutions of feeble rotation. I. Sensitivity of polarimetric determinations.** H. N. NAUMANN (*Biochem. Z.*, 1930, **220**, 217—226).—An

apparatus for carrying out micropolarimetric determinations with a high degree of accuracy is described.

P. W. CLUTTERBUCK.

**Baro-burette—a new accurate gas burette.** H. S. BOOTH (Ind. Eng. Chem. [Anal.], 1930, 2, 182–186).—The author's apparatus is an improvement on earlier gas burettes which balance the pressure of the gas by the pressure of a column of mercury only and not by that of the atmosphere. It is of all glass construction except for the connexion to the levelling bulb, rubber tubing having been found invariably to lead to leaks. The barometer tube has a level capillary connexion and is evacuated by the overflow method. Gas volumes may be measured at any pressure desired. Errors are discussed in detail and it is concluded that the accuracy should be always within 1%. The apparatus is well suited for determining the volume of the connexions of an apparatus and for determining vapour pressures.

C. IRWIN.

**Duplex weighing tube.** W. E. ESKEW and F. C. VILBRANDT (Ind. Eng. Chem. [Anal.], 1930, 2, 181).—A bent tube on a flat base with wide filling end and narrower delivery end each closed with ground glass stoppers is better than a watch glass or weighing bottle when the sample has to be washed or brushed out.

C. IRWIN.

**Electrolytic cell for use with the mercury cathode.** A. D. MELAVEN (Ind. Eng. Chem. [Anal.], 1930, 2, 180).—Difficulty occurs in the use of a mercury cathode cell for the separation of aluminium or magnesium in separating the amalgam from the electrolyte without resolution of the former. The use of a mercury levelling tube connected to the cell through a three-way cock enables the mercury containing the amalgam to be drawn off without difficulty and the electrolyte then drained out.

C. IRWIN.

**Device for rapid determination of the density of small amounts of solids.** E. R. CALEY (Ind. Eng. Chem. [Anal.], 1930, 2, 177–179).—A weighed portion of coarsely-ground material is introduced into an accurately graduated tube of 2.0–2.5 mm. diameter containing ether and the rise in the surface level is read by means of a microscope. With ether no difficulty arises from air bubbles, but a stopper must be used to prevent evaporation. The method is capable of considerable accuracy.

C. IRWIN.

**Visual method for the measurement of minute changes in length and application to the determination of coefficients of expansion of glasses and ceramic materials.** R. THILENIUS and H. HOLZMANN (Z. anorg. Chem., 1930, 189, 367–387).—An apparatus for the measurement of coefficients of expansion of solids is described. It consists of a vertical quartz tube closed at the lower end and carrying at its upper end a small vertical transparent mirror made by depositing a thin film of platinum on a plane strip of glass. Within the tube and coaxial with it is the test-piece of the material under examination in the form of a tube or rod which rests against the bottom of the tube and at its upper end is in contact with a quartz rod which is long enough to project from the upper end of the quartz tube. The

position of the axis of the rod is so adjusted that a mark on its upper end is in the same vertical plane as the virtual reflected image of a mark on the front face of the mirror, both being viewed simultaneously through a microscope. From the alteration in the distance apart of the two when that part of the quartz tube containing the test-piece is heated, the coefficient of expansion relative to quartz may be calculated. By means of this apparatus the coefficients of expansion of various glasses and ceramic materials have been determined up to about 1200°. The coefficients of expansion of magnesium oxide and zirconium dioxide are independent of the temperature of previous ignition (cf. Merritt, B., 1926, 947). R. CUTHILL.

**Pressure filtration in analysis.** R. V. STIGELL (Suomen Kem., 1930, 3, 63–65).—A pad of cotton wool forced slowly into a test tube by means of a glass rod will effect a filtration of a precipitate produced therein in a manner suitable for qualitative analysis. The same device if an open-ended thick-walled tube is used is applicable to quantitative analysis, one end or the other being closed with a rubber stopper. The filtration is quick and washing is simple. The method is specially recommended for the separation of the mechanical impurities of milk. With thick pads very high pressures can be used and bacterial cultures for instance filtered to sterilisation.

C. IRWIN.

**Sensitive silica manometers.** B. LOCKSPEISER (J. Sci. Instr., 1930, 7, 145–151).—Manipulative details for the construction of silica manometers of the Bourdon and diaphragm types are described. One of the latter kind can be made to withstand a total pressure of 1 atm. and measure to  $0.16 \times 10^{-3}$  mm.

C. W. GIBBY.

**Simple manometer and source for hot vapours.** C. T. ZAHN (Rev. Sci. Instr., 1930, 1, 299–301).—The apparatus is entirely of pyrex glass and consists of a U-tube, one side of which is constricted below to capillary dimensions, with an enlarged portion (A) above to act as a reservoir of the liquid under examination. It is connected with a manometer, an air-pump, and means whereby the liquid in desired quantity can be introduced. The top of the other side is connected with a hot gas container, the portion (B) of the tube immediately below being heated electrically by a nichrome wire wound round it. By adjustment of the pressure in A a suitable amount of liquid is driven into B, where the temperature is so regulated that it boils at a pressure determinable by the manometer and the difference in level on the two sides of the U-tube.

C. A. SILBERRAD.

**Sodium-argon glow-tube.** H. J. REICH (Rev. Sci. Instr., 1930, 1, 289–291).—A source of light essentially monochromatic but containing a number of lines of sufficient intensity to be employed to calibrate a spectrometer is obtained by electrolytically introducing sodium (or other alkali metal) into an argon glow-tube made of soda glass. The tube should be used on direct current (200–500 volts) with a 50-milliamp., 8000-ohm resistance in series.

C. A. SILBERRAD.

**Meters for velocities of gas streams.** E. A. J. H. NICOLAS (Chem. Weekblad, 1930, 27, 272–273).—

The ordinary flow meters dependent on viscosities are not trustworthy unless allowances are made for changes in viscosities caused by variations in temperature, humidity, etc. The fall in pressure of a gas escaping through a small aperture is independent of viscosity. A simple apparatus for measuring rates of flow is described; in conjunction with a density meter, it may be employed for different gases without repeated calibration. S. I. LEVY.

**Arrangements for micro-analysis.** A. CONSTANTINO (*Annali Chim. Appl.*, 1930, 20, 154—158).—Descriptions are given of: a Kjeldahl apparatus with

four micro-burners; an apparatus for removing the ammonia from ammonium salts at the ordinary temperature by means of a current of air; and a colorimeter with Eggertz tubes for the determination of 0.25—0.5 mg. of ammonia to within about 0.006 mg. T. H. PORE.

**Experiment illustrating voltaic polarisation.** H. P. CADY and R. TAFT (*J. Chem. Educ.*, 1929, 6, 952—957).—Polarisation may be due to concentration changes around the electrodes, a change in the nature of the electrodes, overvoltage, and the formation of a film of gas. An apparatus to show the effect of the variables is described. CHEMICAL ABSTRACTS.

## Geochemistry.

**Seasonal variations in the phosphate and silicate content of sea-water in relation to the phytoplankton crop.** V. November 1927 to April 1929, compared with earlier years from 1923. W. R. G. ATKINS (*J. Marine Biol. Assoc.*, 1930, 16, 821—852; cf. A., 1928, 389).—Falls in the phosphate and silicate content of water in the English Channel are correlated with outbursts of phytoplankton. C. W. GIBBY.

**Natural waters rich in radium.** V. VERNADSKY (*Compt. rend.*, 1930, 190, 1172—1175).—Recent investigations on springs in petroliferous areas of Russia indicate a radium content of up to  $1.46 \times 10^{-8}\%$ . The springs are derived from the deep vadose or phreatic sources associated with petroliferous areas. They contain organic acids and gaseous hydrocarbons, and it is suggested that the origin of these properties has a bearing on the genesis of petroleum. Free oxygen produced by decomposition of the water by the radium probably plays a part in the chemical reactions of the earth's crust. J. GRANT.

**Arsenic content of the Choussy well-water, La Bourboule, and fixation of this arsenic in the organism.** R. CLOGNE, (MLLE.) A. COURTOIS, and CAZALA (*Compt. rend.*, 1930, 190, 1133—1134).—Arsenic was determined by a modification of the Cribier-Léonardon method, the stain on the mercuric chloride paper being fixed by immersion in a 10% solution of potassium iodide and matched against standard stains prepared under the same conditions. A slight excess of potassium permanganate was added to the sample to avoid evolution of hydrogen sulphide or phosphine. Arsenic contents of 5.8—6.5 mg. per litre are recorded for the season 1928—9, and analyses of tadpoles kept in the water at the well for 8—10 days showed arsenic contents of  $3.25 \times 10^{-3}$  mg. of arsenic per g. ( $1.88 \times 10^{-3}$  mg. per g. in ordinary water). Tadpoles in bottled Choussy water, or in synthetic water of similar composition, contained only 2.73 and  $2.325 \times 10^{-3}$  mg. per g., respectively. J. GRANT.

**Radioactivity of Grozni bore-hole waters.** V. S. TVERTZUIN and V. B. MILIN (*Neft. Choz.*, 1929, 17, 656—661).—The water contains 0.0096—0.146 mg. of radium per metric ton; the oil contains only the emanation. CHEMICAL ABSTRACTS.

**Waters rich in sodium hydrogen carbonate and especially in iodine in East Prussia.** H. MATTHES and G. WALLRABE (*Pharm. Zentr.*, 1930, 71, 273—276).—Many waters commonly in use for domestic and drinking purposes in East Prussia contain much more hydrogen carbonate than corresponds with the calcium and magnesium present; in some cases sodium hydrogen carbonate is present to the extent of more than 1 g. per litre. These high values are usually accompanied by high sodium chloride and iodide contents. It is suggested that such waters point to the existence of seas in the area in earlier geological ages. S. I. LEVY.

**Alkaline waters of Lower Kostrivnica, Jugoslavia.** S. S. MIHOLIC (*Bull. Soc. Chim. Roy. Yougoslavie*, 1930, 7, Reprint, 16 pp.).—Analyses of these waters are given, and their origin is discussed. C. W. GIBBY.

**Nepheline syenites and pegmatites of Mount Royal, Montreal.** F. L. FINLEY (*Canad. J. Res.*, 1930, 2, 231—248).—The construction of a tunnel running from north to south under Mt. Royal has enabled the structure of this volcanic neck to be more accurately determined, and in particular shows that there were two distinct advances of a nepheline syenite magma, separated by an intrusion of camptonite. This with previous results indicates that the igneous sequence consists of alternate advances of acidic and basic magmas. The rocks and minerals found are described and new analyses of nepheline syenite (two varieties), nordmarkite-pegmatite, soda-rich monzonite, shonkinite porphyry, and syenite are given. The rare anorthic amphibole aenigmatite occurred as small prismatic grains at one place. One sample of pegmatite containing much crystalline limestone emitted a sulphurous odour when struck; this is attributed to brown patches of apparently organic origin in the limestone. C. A. SILBERRAD.

**Titanium content of bauxites.** J. DE LAPPARENT (*Compt. rend.*, 1930, 190, 1312—1314).—Titaniferous bauxites always contain rutile, anatase, or ilmenite in the form of a highly refractive dust (cf. A., 1927, 748) of detritic origin, or as crystals the geochemical history of which is closely associated with that of the bauxite. Basaltic bauxites from the Deccan may contain 8—12% of titanium oxide derived originally

from titaniferous iron compounds formed in the basalt. Ilmenite in thin layers is transparent, and brown to green in colour, indicating the presence of ferric and of ferrous oxide, respectively.

J. GRANT.

Some geochemical applications of measurements of hydrogen-ion concentration. W. R. G. ATKINS (Sci. Proc. Roy. Dublin Soc., 1930, 19, 455—460).—The rôle of hydrogen-ion concentration in the formation of iron beds in the neighbourhood of carboniferous deposits and of dolomite is reviewed. All samples of basalt examined were sufficiently soluble to impart a definite reaction to distilled water. With weathered rock acidity was usually developed, due possibly to a surface residue of iron carbonate or acid silicate. In some cases the acidity remained high after boiling with distilled water, but usually the acidity was diminished or an alkaline reaction developed.

T. H. MORTON.

Microstructure of New Zealand lignites. II. Lignites subjected to the influence of igneous intrusions. W. P. EVANS (New Zealand J. Sci. Tech., 1930, 11, 370—375).—Chemical analyses and photographs showing the microstructure of lignite from Acheron River, N.Z., are given. The seam was probably formed mainly *in situ*.

C. W. GIBBY.

Origin and nature of coals and chars. H. E. ARMSTRONG (Proc. Roy. Soc., 1930, A, 127, 268—271).—Various early views on the nature and mode of formation of coal are briefly reviewed, and the origin of graphite and shales is discussed. From a consideration of a deposit of lignite at Valdarno, in Tuscany, of which the original material was obviously

wood, the conclusion is reached that coal is "an organically re-wrought 'condensed' material, . . . a natural Bakelite."

L. L. BIRCUMSHAW.

Origin of coal. R. LIESKE; W. FUCHS.—See B., 1930, 540.

Causes of the differentiation of coals. A. DUPARQUE (Compt. rend., 1930, 190, 1200—1203).—The primordial deposits which determine the formation of cannel coals and of oils containing high and low percentages of volatile matter in the south and north Channel districts, respectively, belong to two distinct types characterised by cutinised vegetable debris (spores, cuticles, etc.) and by fragments of lignified tissue (wood, sclerenchyma). The chemical composition is approximately constant in each case, and secondary types of deposit have their origin in the subsequent changes undergone by these deposits. Evidence is advanced for the theory that these changes depend on the thickness of the layer of water covering the vegetable deposits, which increases from north to south, and produces a corresponding decrease in the amount of available oxygen. There is thus, in general, a transition from anthracite coals (volatile matter <18%) in the north, through coke coals, smith-coals, and cannel coals, to boghead coals (volatile matter 60%) in the south.

J. GRANT.

Helium and the genesis of petroleum. M. N. ROGERS (New Zealand J. Sci. Tech., 1930, 11, 389—393).—The author suggests that petroleum has been formed by the action on methane of  $\alpha$ -rays due to radioactive substances in the earth.

C. W. GIBBY.

## Organic Chemistry.

Action of ultra-violet light on aliphatic hydrocarbons. W. KEMULA (Rocz. Chem., 1930, 10, 273—287).—No dissociation of methane takes place under the influence of irradiation with a mercury-vapour lamp. Under analogous conditions ethane yields hydrogen, methane, butane, hexane, and a small amount of unidentified saturated and unsaturated liquid hydrocarbons. The products of photolysis and their relative amounts vary with the duration of irradiation of ethane. The reaction is best represented as  $n\text{C}_2\text{H}_6 \rightarrow (n-1)\text{H}_2 + \text{C}_{2n}\text{H}_{4n+2}$  (liquid), so that  $n$  volumes of ethane yield  $(n-1)$  volumes of hydrogen, i.e., the volume of gas diminishes.

R. TRUSZKOWSKI.

Pyrolysis of methane. F. DE RUDDER and H. BIEDERMANN (Compt. rend., 1930, 190, 1194—1196).—A study of the pyrolysis of methane at 900—1500°/20—760 mm. has been made. There is no appreciable decomposition below 1000°. Ethylene is formed in maximum amount (4% of the gaseous product) at 1200°/100 mm., whilst the production of acetylene increases rapidly with rise in the temperature; at 1500°/40 mm. the acetylene content of the gaseous product is 15%. Acetylene formation is always accompanied by decomposition of some of the methane to carbon and hydrogen. The amount of decomposition rises with increase in the volume of the

pyrolysis chamber. Hydrogen chloride, silica, thorium, and nickel do not catalyse the decomposition.

H. BURTON.

Production of higher hydrocarbons from methane. F. FISCHER and H. PICHLER.—See B., 1930, 500.

Derivatives of *n*-heptane. I. Preparation, identification, and physical constants. M. L. SHERRILL (J. Amer. Chem. Soc., 1930, 52, 1982—1992).—*n*-Heptyl alcohol and three *sec*-heptyl alcohols (prepared by the Grignard method) are converted into the corresponding chlorides by Norris and Taylor's method (A., 1924, i, 602), and into the bromides usually by repeated saturation with hydrogen bromide. The *sec*-alcohols are oxidised by potassium dichromate and dilute sulphuric acid. The following data (amongst others) are recorded: *n*-propyl alcohol, b. p. 175.9±0.1°/759.5 mm., 84.7°/20 mm. (all b. p. in vac. arc ±0.05°),  $d_4^{20}$  0.8227,  $n_D^{20}$  1.4245; methyl-*n*-amylcarbinol, b. p. 158.7±0.1°/740.5 mm., 66.7°/16.5 mm.,  $d_4^{20}$  0.8167,  $n_D^{20}$  1.4210; ethyl-*n*-butylcarbinol, b. p. 155.9±0.1°/740.5 mm., 65.8°/20 mm.,  $d_4^{20}$  0.8210,  $n_D^{20}$  1.4222; dipropylcarbinol, b. p. 155.4±0.1°/755.2 mm., 63.8°/16 mm., f. p. -41.5°,  $d_4^{20}$  0.8183,  $n_D^{20}$  1.4205; *n*-heptyl chloride, b. p. 61.4°/27 mm., f. p. -69.5°,  $d_4^{20}$  0.8725,  $n_D^{20}$  red 1.42261.

$\beta$ -chloroheptane, b. p.  $46^\circ/19.5$  mm.,  $d_4^{20}$  0.8672,  $n_D^{20}$  1.4221;  $\gamma$ -chloroheptane, b. p.  $48.3^\circ/21$  mm.,  $d_4^{20}$  0.8690,  $n_D^{20}$  1.4228;  $\delta$ -chloroheptane, b. p.  $48.9^\circ/21$  mm.,  $d_4^{20}$  0.8710,  $n_D^{20}$  1.4231;  $n$ -heptyl bromide, b. p.  $70.6^\circ/19$  mm., f. p.  $-58.25^\circ$ ,  $d_4^{20}$  1.1384,  $n_D^{20}$  1.44734;  $\beta$ -bromoheptane, b. p.  $66.2^\circ/24$  mm.,  $d_4^{20}$  1.1277,  $n_D^{20}$  1.4476;  $\gamma$ -bromoheptane, b. p.  $62^\circ/18$  mm.,  $d_4^{20}$  1.1362,  $n_D^{20}$  1.4503;  $\delta$ -bromoheptane, b. p.  $60^\circ/18$  mm.,  $d_4^{20}$  1.1351,  $n_D^{20}$  1.4495;  $n$ -heptyl iodide, b. p.  $97^\circ/26$  mm.,  $d_4^{20}$  1.3774,  $n_D^{20}$  1.48689;  $\gamma$ -iodoheptane, b. p.  $88.9^\circ/30$  mm.,  $d_4^{20}$  1.3676,  $n_D^{20}$  1.48812;  $n$ -heptaldehyde, b. p.  $59.6^\circ/30$  mm.,  $d_4^{20}$  0.8219,  $n_D^{20}$  1.40941; methyl amyl ketone, b. p.  $150.2 \pm 0.1^\circ/750$  mm.,  $d_4^{20}$  0.8018,  $n_D^{20}$  1.40660; ethyl butyl ketone, b. p.  $148.2 \pm 0.05^\circ/756$  mm.,  $d_4^{20}$  0.8183,  $n_D^{20}$  1.40649; dipropyl ketone, b. p.  $144.0 \pm 0.05^\circ/756$  mm.,  $d_4^{20}$  0.8175,  $n_D^{20}$  1.40459. H. BURTON.

**Derivatives of  $n$ -heptane. II. Dipole moments and molecular constitution.** J. ERRERA and M. L. SHERRILL (J. Amer. Chem. Soc., 1930, 52, 1993—1997).—The dipole moments of four heptyl alcohols, four heptyl chlorides, four heptyl bromides,  $\alpha$ - and  $\gamma$ -iodoheptanes,  $n$ -heptaldehyde, methyl amyl ketone, ethyl butyl ketone, and dipropyl ketone have been determined. In the case of the alcohols the dipole moment ( $1.70$ — $1.71 \times 10^{-18}$  e.s.u.) is independent of the position of the hydroxyl group. The moment is approximately the same ( $2.03$ — $2.06 \times 10^{-18}$ ) for the  $\beta$ -,  $\gamma$ -, and  $\delta$ -chloro- and -bromo-heptanes, but is smaller for the  $\alpha$ -derivative ( $1.85 \times 10^{-18}$ ).  $n$ -Heptaldehyde ( $2.56 \times 10^{-18}$ ) has approximately the same moment as methyl amyl ketone ( $2.59 \times 10^{-18}$ ), but has a smaller value than ethyl butyl ketone ( $2.78 \times 10^{-18}$ ) and dipropyl ketone ( $2.72 \times 10^{-18}$ ). The following dipole moments have also been determined:  $n$ -amyl alcohol,  $1.65 \times 10^{-18}$ ; methylpropylcarbinol,  $1.66 \times 10^{-18}$ , and diethylcarbinol,  $1.64 \times 10^{-18}$  e.s.u.

H. BURTON.

**Determination of the composition of butene mixtures by distillation methods.** H. J. LUCAS, R. T. DILLON, and W. G. YOUNG (J. Amer. Chem. Soc., 1930, 52, 1949—1953).—Dehydration of (a)  $n$ - and (b)  $sec$ -butyl alcohols by passing the vapours over aluminium oxide at  $300$ — $350^\circ$ , subsequent conversion of the mixtures of butenes obtained into the dibromides, and fractional distillation of these at 50 mm. gives the following approximate compositions:  $\Delta^a$ -butene, (a) 68, (b) 26%;  $\Delta^b$ -butene, b. p.  $0.3^\circ$ , (a) 12, (b) 26%;  $\Delta^c$ -butene, b. p.  $3^\circ$ , (a) 20, (b) 48%. When the mixture of butenes prepared from  $sec$ -butyl bromide and alcoholic potassium hydroxide is distilled under atmospheric pressure, 15—20% of  $\Delta^a$ -butene, b. p.  $-6.7^\circ$  to  $-6.5^\circ$ , is obtained. The remainder of the product consists of a mixture of the isomeric  $\Delta^b$ -butenes.  $\Delta^a$ -Butene reacts with hydrogen bromide in acetic acid solution at  $5^\circ$  forming almost pure  $sec$ -butyl bromide.

H. BURTON.

**Composition of butene mixtures resulting from the catalytic decomposition of  $n$ - and  $sec$ -butyl alcohols.** W. G. YOUNG and H. J. LUCAS (J. Amer. Chem. Soc., 1930, 52, 1964—1970).—The compositions of the mixtures of  $\Delta^a$ - and the two  $\Delta^b$ -butenes obtained by dehydration of  $n$ - and  $sec$ -butyl alcohols by various methods have been determined by

the method of Dillon, Young, and Lucas (see below). No  $\Delta^a$ -butene is formed when either the  $n$ - or  $sec$ -alcohol is decomposed with phosphoric oxide or 60% sulphuric acid below  $160^\circ$ ; an excess of  $trans$ - $\Delta^b$ -butene results. A similar result is found with  $sec$ -butyl alcohol and 85% phosphoric acid at  $95$ — $126^\circ$ ;  $n$ -butyl alcohol is unaffected by similar treatment.  $\Delta^a$ -Butene is formed in increasing amount from the  $n$ - (19.1, 56, 72.9%) or  $sec$ -alcohol (15.2, 18.8, 20.6%) with pumice impregnated with phosphoric acid at  $340$ — $400^\circ$ , aluminium phosphate at  $350$ — $450^\circ$ , and aluminium oxide at about  $350^\circ$ , respectively. The more acidic dehydrating agents favour the formation of  $trans$ - $\Delta^b$ -butene, whilst the less acidic favour  $\Delta^a$ - and  $cis$ - $\Delta^b$ -butene production.

Treatment of a mixture of  $\beta\gamma$ -dibromobutanes with zinc dust and alcohol gives a mixture of butenes convertible into the original dibromides. H. BURTON.

**Reaction between hydrogen chloride and the three butenes.** C. C. COFFIN, H. S. SUTHERLAND, and O. MAASS (Canad. J. Res., 1930, 2, 267—278).—Equimolecular quantities of  $\Delta^a$ -butene, b. p.  $-6.2^\circ/760$  mm., and hydrogen chloride react slowly at  $0^\circ$  (74% reaction after 20 days), forming  $sec$ -butyl chloride as the main product. Secondary products, which decompose when warmed in a vacuum, are also produced; these are probably  $\gamma$ -methyl- $\beta$ -ethyl- $\Delta^a$ -pentene and  $\gamma$ -methyl- $\delta$ -chloromethylhexane.  $sec$ -Butyl chloride is also the main product from  $\Delta^b$ -butene, b. p.  $1.1^\circ/760$  mm. (62% reaction after 35 days at  $0^\circ$ ); the by-products are probably  $\gamma\delta$ -dimethyl- $\Delta^a$ -hexene and  $\beta$ -chloro- $\gamma\delta$ -dimethylhexane. Hydrogen chloride and isobutene, b. p.  $-6.7^\circ/760$  mm., react instantaneously at  $-78.5^\circ$ , forming only  $tert$ -butyl chloride. H. BURTON.

**Formation of butadiene by cracking of hydrocarbons.** P. K. FROLICH, R. SIMARD, and A. WHITE.—See B., 1930, 547.

**Natural and synthetic rubber. IV. 8-Methyl- $\Delta^a$ -octene by isoprene ethylation. V. Tetramethyloctadiene.** T. MIDGLEY, jun., and A. L. HENNE (J. Amer. Chem. Soc., 1930, 52, 2075—2077, 2077—2078).—IV. Addition of an ethereal solution of 2 mols. of ethyl bromide or 1 mol. of ethyl sulphate to a mixture of potassium (2 mols.) and isoprene (1 mol.) gives about 4% of 8-methyl- $\Delta^a$ -octene, b. p.  $139^\circ$ ,  $d_4^{20}$  0.7495,  $n_D^{20}$  1.4228, oxidised by ozone to methyl butyl ketone and  $n$ -butyric acid. Ethylation occurs, therefore, in the  $\alpha\delta$ -positions of the isoprene molecule.

V.  $\beta\gamma$ -Dimethylbutadiene is reduced and polymerised by treatment with potassium and alcohol at  $70^\circ$  under the conditions previously described (A., 1929, 674) to a mixture of  $\beta\gamma\epsilon\zeta$ -tetramethyl- $\Delta^b$ -octadiene, b. p.  $87.5$ — $88.5^\circ/18$  mm.,  $d_4^{20}$  0.7971,  $n_D^{20}$  1.45963, and "methyl-rubber."  $\beta\gamma\epsilon\zeta$ -Tetramethyloctane has b. p.  $92^\circ/20$ — $22$  mm.,  $d_4^{20}$  0.7593,  $n_D^{20}$  1.42527. The structure of the "methyl-rubber" must be a long, open chain, and this is regarded as evidence in favour of the chain formula for natural rubber.

H. BURTON.

**Reaction rates of potassium iodide with  $\alpha\beta$ - and  $\beta\gamma$ -dibromobutanes.** Analysis of mixtures of  $\Delta^a$ - and  $\Delta^b$ -butenes. R. T. DILLON, W. G. YOUNG, and H. J. LUCAS (J. Amer. Chem. Soc., 1930,



52, 1953—1964).—The reactions between  $\alpha\beta$ -,  $r\beta\gamma$ -, and *meso*- $\beta\gamma$ -dibromobutanes and potassium iodide have been studied in 99% methyl alcohol at 60° and 75°, and found to be of the second order. The rate is considerably higher at 75° and it decreases in the order  $\alpha\beta$ , *meso*- $\beta\gamma$ ,  $r\beta\gamma$ . The compositions of binary mixtures can be calculated from the rate of the mixture, and of ternary mixtures from the rate and the density. The maximum deviation from the known composition is 4%. The composition of a mixture of  $\Delta^+$ - and  $\Delta^s$ -butenes can be determined by converting it into the mixture of dibromides and proceeding as above.

H. BURTON.

**Highly-polymerised compounds. XXXVIII.**  
**Poly-allyl chloride.** H. STAUDINGER and T. FLEITMANN (Annalen, 1930, 480, 92—108).—Allyl chloride is converted in the absence of air slowly on keeping, but more rapidly (30% in 8 days) under the influence of ultra-violet light, into polyallyl chloride,  $(C_3H_5Cl)_n$ , a pale yellow, viscous syrup,  $d_4^{20}$  1.258,  $n_D^{20}$  1.5292, which is not a single substance but a mixture of polymerides (mean value of  $n=10$ ), formed by normal valency unions and probably possessing the structure

$\cdots CH_2\cdot CH(CH_2Cl)\cdot CH_2\cdot [CH(CH_2Cl)]_n\cdot CH_2\cdot CH(CH_2Cl)\cdot \cdots$   
which is separated either by fractional precipitation of its ethereal solution with methyl alcohol or by fractional extraction with the latter solvent into a series of polymerides ( $n=9, 12, 5, 25, 11$ , and 7), the viscosities of which are determined, those of the highest mol. wt. being the least soluble. Reduction of polyallyl chloride with red phosphorus and 70% hydriodic acid at 150—160° gives a hydrocarbon,  $(C_3H_5)_{10}$ , b. p. 220—240°/0.05 mm., in which cyclisation has occurred, probably yielding the structure

$\cdots (CH_2\cdot CHMe\cdot CH_2\cdot CH\cdot CH_2\cdot CH\cdot CH_2\cdot CH\cdot CH_2\cdot CH\cdot) \cdots$   
 $\quad \quad \quad CH_2\quad\quad CH_2\quad\quad CH_2\quad\quad CH_2$

Attempts to oxidise the chloride directly to a polyacrylic acid with concentrated nitric acid only result in decomposition, whilst no chlorine-free product could be obtained by long hydrolysis with concentrated alcoholic potassium hydroxide. When polyallyl chloride is heated with triethylamine in benzene in a sealed tube at 100° elimination of hydrogen chloride occurs, and dialysis of the product affords a very hygroscopic, brown, resinous substance the analytical figures of which agree best with the structure  $[(C_3H_5Cl)_5(C_3H_5NEt_3Cl)]_n$ . Similar treatment with triethylphosphine gives a quaternary phosphonium salt,  $(C_3H_5Cl\cdot C_3H_5PEt_3Cl)_n$ , a similar salt being obtained with triphenylphosphine. Both these salts are solid yellow resins.

J. W. BAKER.

**Catalytic dehydration of saturated aliphatic alcohols in the presence of alkali hydrogen sulphates in the vapour phase.** J. B. SENDERENS (Compt. rend., 1930, 190, 1167—1170; cf. this vol., 431).—*n*-Propyl alcohol is dehydrated to propylene at 125—140° in the vapour phase by fused sodium hydrogen sulphate. When the crystalline salt or potassium hydrogen sulphate is used, evolution of propylene begins at about 210°. Dehydration of the following alcohols to the unsaturated hydrocarbon with fused sodium hydrogen sulphate occurs at the

temperatures given: isopropyl, 95—110°; isobutyl, 135°; ethyl, begins about 175°, increases up to 260°. Methyl alcohol is dehydrated at about 200° to dimethyl ether.

H. BURTON.

**Manufacture of absolute alcohol.** H. GUINOT.—See B., 1930, 527.

**Preparation of glycol by hydrolysis of ethylene dichloride.** H. BAHR and H. ZIEGLER.—See B., 1930, 499.

**Conversion of *n*-propyl alcohol into propyl ethers by means of sulphuric acid.** H. WUYTS and A. LACOURT (Bull. Soc. chim. Belg., 1930, 39, 157—173).—The method previously described for the conversion of primary alcohols into the corresponding ethers (Popelier, A., 1923, i, 532) has been worked out in detail for *n*-propyl alcohol and the effect of varying conditions investigated. An apparatus by means of which the process is rendered continuous is described, the alcohol being added to a mixture of alcohol and sulphuric acid. An azeotropic mixture of alcohol, ether, and water distils first, followed by a binary mixture of alcohol and ether. Repeated distillation of the non-aqueous portion of the combined distillates with a column eliminates the last traces of water and the residual mixture of alcohol and ether (richer in the ether than is the binary, azeotropic mixture which contains 67.8% of the ether) is treated with 50—55% sulphuric acid to dissolve out the alcohol, washed and dried, and the *n*-propyl ether, b. p. 90.00—90.08°,  $d_4^{24}$  0.7371, purified by careful fractionation. Some *n*-propyl isopropyl ether, b. p. 80.15—80.30°,  $d_4^{24}$  0.7370, is formed simultaneously even when low concentrations of sulphuric acid and moderate temperatures are used, and the proportion increases considerably (up to 19%) with increase in acid concentration and rise in temperature. This ether also forms binary and ternary azeotropic mixtures and can be separated from the *n*-propyl ether only by repeated fractionation, using an efficient column, although the *n*-ether is readily obtained pure. The mixed ether probably results from the propylene, which is also formed in the reaction. The best yield of *n*-propyl ether, with minimum formation of the mixed ether, results when the original alcohol-acid mixture contains about 35% of 95.6% sulphuric acid and the temperature is maintained at 115°. J. W. BAKER.

**Cyclic acetals.** H. HIBBERT (Rec. trav. chim., 1930, 49, 557—558).—Polemical against van Roon (A., 1929, 291).

J. W. BAKER.

**$\gamma\gamma$ -Diethoxy- $\Delta^s$ -propinene and bromomalondialdehyde.** J. GRARD (Ann. Chim., 1930, [x], 13, 336—383).— $\gamma\gamma$ -Diethoxy- $\Delta^s$ -propinene (I), b. p. 137—141° (copper, silver, and mercury derivatives), is prepared in 35% yield by conversion of acraldehyde below 5° into the dibromide, b. p. 73—75°/10 mm., followed by acetalisation with ethyl orthoformate and absolute alcohol, and treatment of the resultant acetal, b. p. 110°/10—15 mm., with 20% alcoholic potassium hydroxide. Oxidation of the copper derivative of I with potassium ferriocyanide yields  $\alpha\alpha\gamma\gamma$ -tetraethoxy- $\Delta^{2s}$ -hexadi-inene, b. p. 140—141°/3 mm.,  $d_4^{25}$  0.9730,  $n_D^{25}$  1.4638. Treatment of the silver derivative with 1 mol. of iodine in potassium iodide solution yields

$\alpha$ -iodo- $\gamma\gamma$ -diethoxy- $\Delta^a$ -propinene, m. p. 7–8°,  $d^{25}_4$  1.533,  $n^{25}_D$  1.502, b. p. 79–81°/3 mm.; with 2 mols. of iodine tri-iodoacetaldehyde, m. p. 129–130°, is produced. Urethane reacts with I in the presence of dilute hydrochloric acid to give a diurethane,  $\text{CH}_3\text{CH}(\text{C}(\text{NH}-\text{CO}_2\text{Et})_2)_2$ , m. p. 180–180.5° (dibromo-derivative, m. p. 170°), whilst carbamide affords a di-,  $\text{C}_5\text{H}_8\text{O}_2\text{N}_4$ , and a tri-ureide,  $\text{C}_9\text{H}_{12}\text{O}_3\text{N}_6$ . Gradual addition of magnesium ethyl bromide to I in dilute ethereal solution affords magnesium  $\gamma\gamma$ -diethoxy- $\alpha$ -propinene bromide (II), which reacts with acetaldehyde to give 8-hydroxy- $\alpha$ -diethoxy- $\Delta^b$ -pentinene, b. p. 106°/4.5 mm.,  $d^{25}_4$  0.995,  $n^{25}_D$  1.446, and is converted by warm aqueous oxalic acid into  $\alpha$ -aldehydo- $\gamma$ -hydroxy- $\Delta^a$ -butinene, b. p. 75–80°/2.7 mm. (diurethane, m. p. 168–168.5°). With acetaldehyde II affords the compound,  $\text{CH}_3\text{CH}(\text{CH}(\text{OH})\cdot\text{C}(\text{OEt})_2)_2$ ,  $d^{25}_4$  0.99,  $n^{25}_D$  1.461 (diurethane, m. p. 149.5–150°), whilst with iodine in ethereal solution  $\alpha$ -iodo- $\gamma\gamma$ -diethoxy- $\Delta^a$ -propinene is obtained. Addition of 1–2 mols. of magnesium methyl bromide gives magnesium  $\gamma$ -ethoxy- $\Delta^a$ -butinenyl- $\alpha$ -propinene bromide (III), decomposed by dilute hydrochloric acid to  $\gamma\gamma$ -ethoxy- $\Delta^a$ -butinene, b. p. 87–88°,  $d^{25}_4$  0.8075,  $n^{25}_D$  1.402 (silver derivative; tri-iodide, m. p. 47–48°; dibromo-derivative, b. p. 85–87°/15 mm.,  $d^{25}_4$  1.654,  $n^{25}_D$  1.501), converted by carbon dioxide into  $\gamma$ -ethoxy- $\Delta^a$ -pentinenoic acid, b. p. 107–108°/4 mm.,  $d^{25}_4$  1.0514,  $n^{25}_D$  1.458 (sodium, potassium, and silver salts; compound,  $\text{C}_6\text{H}_{10}\text{Cu}_2$ , on boiling potassium salt with excess of aqueous copper sulphate; ethyl ester, b. p. 68–70°/3 mm.,  $d$  0.9842,  $n$  1.444, also prepared from III and ethyl carbonate).  $\gamma$ -Ethoxy- $\Delta^a$ -pentinene, b. p. 108°,  $d^{25}_4$  0.8092,  $n^{25}_D$  1.4070 (mercury derivative), was similarly prepared with magnesium ethyl bromide. This yields methyl  $\alpha$ -ethoxypropyl ketone, b. p. 76°/67 mm.,  $d^{17}_4$  0.8849,  $n^{14}_D$  1.4075 (semicarbazone, m. p. 93–95°), on boiling with saturated aqueous mercuric chloride solution, and  $\beta$ -hydroxy- $\varepsilon$ -ethoxy- $\Delta\gamma$ -heptinene, b. p. 110°/12 mm.,  $d$  0.93,  $n$  1.449, with acetaldehyde. With magnesium phenyl bromide and I  $\gamma$ -ethoxy- $\gamma$ -phenyl- $\Delta^a$ -propinene, b. p. 100–105°/15 mm.,  $d^{17}_4$  1.023,  $n^{15}_D$  1.5365 (copper and mercury derivatives), is produced.

When  $\gamma\gamma$ -diethoxy- $\Delta^a$ -propinene is treated with bromine (1 mol.) in dry chloroform solution, and the residue, after removal of the chloroform, exposed to the atmosphere, bromomalondialdehyde (IV), m. p. 148°, best purified by sublimation in a vacuum below 110°, is formed. It gives an intense violet coloration with ferric chloride, and possesses marked acidic properties. Titration with bromine by the Meyer method indicates that the solid is the almost pure enolic form, that the equilibrium mixture in alcoholic solution attained after 48 hrs. contains 24% of the enolic modification, and that the keto-enolic equilibrium is considerably affected in favour of the ketonic form by rise of temperature. The sodium, copper, zinc, magnesium, nickel, cobalt, silver, and ferric salts were prepared. When bromomalondialdehyde is boiled with aqueous potassium hydroxide formic acid and potassium bromide are produced, whilst alcoholic sodium ethoxide affords  $\alpha$ -ethoxy- $\beta$ -hydroxyacetaldehyde, m. p. 135° (sodium derivative). Treatment of IV with magnesium methyl bromide, followed by addition of water and of sufficient ferric chloride to

remove the enolic form, yields  $\alpha$ -bromo- $\beta$ -hydroxybutaldehyde, b. p. 80°/10 mm.,  $d$  1.525,  $n$  1.5105.

A. I. VOGEL.

**Mechanism of oxidative processes. XXIV. Catalytic decomposition of ethyl peroxide by iron.** H. WIELAND and F. CHROMETZKA (Ber., 1930, 63, [B], 1028–1032).—Ethyl peroxide rapidly decomposes in presence of ferrous iron into ethyl alcohol and acetaldehyde. In contrast to hydrogen peroxide it is not affected by ferric iron, but this is not considered necessarily to invalidate the likeness of the changes, since with hydrogen peroxide a portion of the ferric iron is invariably converted into the ferrous state according to the scheme  $2\text{Fe}^{+++} + \text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{++} + \text{O}_2 + 2\text{H}$ . With ethyl peroxide the reaction  $\text{Et}_2\text{O}_2 + 2\text{Fe}^{++} + 2\text{H}^+ \rightarrow 2\text{EtOH} + 2\text{Fe}^{+++}$  occurs to a slight extent. Ethyl peroxide is activated by ferrous iron towards substances capable of dehydrogenation in the same manner as hydrogen peroxide, the compound acting as hydrogen acceptor:  $\text{Et}_2\text{O}_2 + \text{RH}_2 \rightarrow \text{R} + 2\text{EtOH}$ .

H. WREN.

**Course of the formation of boric esters from boron halides and ethers.** I. H. REMSER and E. WIBERG (Ber., 1930, 63, [B], 1136–1147).—The hydrolysis of boron trichloride by water is considered to take place by preliminary addition of water to the halide followed by loss of hydrogen halide and repetition of the process until all the halogen atoms are replaced. The mobility of the hydrogen atom is regarded as so great that the isolation of the intermediate compounds is impossible, but this drawback can be avoided by the use of an oxide with alkyl radicals. The behaviour of boron trichloride and diethyl ether has therefore been examined by Stock's high vacuum method. In the gaseous state the compounds unite in the molecular ratio 1 : 1, yielding the substance  $\text{BCl}_3\cdot\text{Et}_2\text{O}$ , m. p. 56° (slight decomp.), which, when heated for 10 hrs. at 50°, furnishes ethyl chloride and the ester  $\text{BCl}_2\cdot\text{OEt}$ . The last-named compound when heated for a long period at 50° is decomposed into ethyl chloride and boron oxychloride,  $\text{BOCl}$ , the existence of which is regarded as thus established, although it has not yet been isolated in the homogeneous condition. The ester combines with diethyl ether, giving the solid compound,  $(\text{BCl}_2\cdot\text{OEt})_2\cdot\text{Et}_2\text{O}$ , containing sexavalent oxygen, which decomposes at the atmospheric temperature into the (not isolated) ester  $\text{BCl}(\text{OEt})_2$  and the substance  $\text{BCl}_3\cdot\text{Et}_2\text{O}$ .

H. WREN.

**Physical constants of monoacetin, mono-propionin, and mono-*n*-butyrin.** H. A. SCHUETTE and J. T. HALE (J. Amer. Chem. Soc., 1930, 52, 1978–1981).—Glycerol monoacetate,  $d^{20}_4$  1.2060,  $n^{20}_D$  1.4517,  $\gamma_{20}$  47.1 dynes/cm.; monopropionate, b. p. 132–134°/3 mm.,  $d^{20}_4$  1.1537,  $n^{20}_D$  1.4503,  $\gamma_{20}$  40.3 dynes/cm., and monobutyrate, b. p. 139–140°/4 mm.,  $d^{20}_4$  1.1344,  $n^{20}_D$  1.4531,  $\gamma_{20}$  37.6 dynes/cm., are prepared by heating a mixture of glycerol (1 mol.), the requisite acid (1 mol.), 85% phosphoric acid (10 g.), and carbon tetrachloride (200 c.c.); water is removed from the reaction mixture as fast as it is produced. The phosphoric acid is then removed by the addition of the sodium salt of the fatty acid used and filtration of the sodium phosphate. The vapour pressures of the three

glycerides have been determined over the temperature range in which they are stable. The heats of vaporisation per 1 g. are calculated to be 132.4, 122.5, and 118.75 g.-cal. for monoacetin, monopropionin, and monobutylin, respectively. H. BURTON.

**Double salts of methionic acid.** H. J. BACKER and P. TERPSTRA (Rec. trav. chim., 1930, 49, 559—563).—By mixed crystallisation the following double salts of methanedisulphonic acid have been prepared. Full crystallographic data are recorded in each case: *sodium ammonium*,  $\text{MNaNH}_4 [\text{M}=\text{CH}_2(\text{SO}_3)_2]$ ; *ammonium silver*,  $\text{MgAgNH}_4$ ; *sodium copper*,  $\text{M}_2\text{Na}_2\text{Cu}+6\text{H}_2\text{O}$  (? also  $+4\text{H}_2\text{O}$ ), and *sodium silver*,  $\text{MgNa}+2\text{H}_2\text{O}$ . J. W. BAKER.

**Action of zinc dust and zinc oxide on the halogen derivatives of aliphatic sulphoxides and sulphones.** Divinylsulphone,  $\beta$ -chloroethylvinylsulphone, and their derivatives. A. E. KRETOV (J. Russ. Phys. Chem. Soc., 1930, 62, 1—29).—The action of zinc dust on halogen derivatives of sulphones and sulphoxides was investigated in alcoholic solution.

$\beta\beta'$ -Dichlorodiethylsulphone gave  $\beta$ -chloroethylvinylsulphone, b. p. 155—156°/22 mm.,  $d_{20}^{25}$  1.3680, and divinylsulphone, b. p. 118—121°/20 mm.,  $d_{20}^{25}$  1.1790, as main products; if pure zinc oxide is used, the rate of reaction is considerably increased. Both the above products add halogens, water, alcohols, and mercaptans at the double linking in the usual way. With the respective phenol divinylsulphone gives bis- $\beta$ -phenoxyethylsulphone, m. p. 108°, bis- $\beta$ -naphthoxyethylsulphone, m. p. 150°; bis- $\beta$ -toloxylethylsulphone, m. p. 120°, bis- $\beta$ -chlorophenoxyethylsulphone, m. p. 141°, and bis- $\beta$ -thymoxyethylsulphone (a viscous liquid). With  $\beta$ -chloroethylsulphone thymol gives  $\beta$ -thymolethylvinylsulphone (a viscous liquid). With hydrogen sulphates, sulphuric acid derivatives are formed. The sulphones are also obtained as intermediate products in the preparation of ethers from  $\beta\beta'$ -dichlorodiethylsulphone by the action of alkoxides and mercaptides. M. ZVEGINTZOV.

**Preparation of fatty acids.** R. LUKES (Chem. Listy, 1930, 24, 197—200).—A general method of synthesis of fatty acids from alcohols containing 4 carbon atoms less than the desired acid is as follows: the alcohol is converted into the alkyl bromide, and this is combined with magnesium to yield the corresponding Grignard reagent, which reacts with *N*-methylsuccinimide to yield a 1-methyl-5-alkylpyrrol-2-one. This on hydrolysis yields a  $\gamma$ -keto-acid possessing 4 carbon atoms more than the original alcohol, and this on electrolytic reduction yields the corresponding fatty acid. Hexoic, heptoic, octoic, nonoic, and decoic acids have been prepared in this way. The following hitherto unknown intermediate products are described: 1-methyl-5-*n*-amylpyrrol-2-one, b. p. 143—148°/10 mm., 1-methyl-5-*n*-hexylpyrrol-2-one, b. p. 148—150°/10 mm.;  $\gamma$ -ketononoic acid, m. p. 69°, and  $\gamma$ -ketodecoic acid, m. p. 70—71°.

R. TRUSZKOWSKI.

**Ruthenium acetates.** A. W. MOND (J.C.S., 1930, 1247—1249).—Freshly prepared ruthenium hydroxide yielded when boiled with acetic acid for 2 hrs. the substance  $\text{Ru}_2(\text{OAc})_4(\text{OH})_2(\text{H}_2\text{O})_2$ , which gave by brief

boiling (20 min.) with water the compounds  $\text{Ru}_2(\text{OAc})_3(\text{OH})_3(\text{H}_2\text{O})_2$  and  $\text{Ru}_2(\text{OAc})_4(\text{OH})_2$ , or by treatment with dilute acetic acid at 100° for 24 hrs. the compound  $\text{Ru}_2(\text{OAc})(\text{OH})_5(\text{H}_2\text{O})_2$ . Ruthenium hydroxide and 50% acetic acid yielded the compound  $\text{Ru}_2(\text{OAc})_5\text{OH}$ , whereas 50% formic acid gave a formate approximating in composition to  $\text{Ru}_2(\text{HCO}_2)_7(\text{OH})_2\cdot 5\text{H}_2\text{O}$ . Prolonged heating with water decomposed the last-named substance with production of a series of yellow, brown, and black products. R. J. W. LE FÈVRE.

***n*-Valerolactone. II. Vapour pressure.** H. A. SCHUETTE and R. W. THOMAS (J. Amer. Chem. Soc., 1930, 52, 2028—2030).—The vapour pressure of *n*-valerolactone has been determined by a dynamic and a static method at 69—203.4°. The expression  $\log P = -2540.44/T + 8.2059$  holds for temperatures up to 160°. Decomposition of the lactone occurs near the b. p. at ordinary pressure. H. BURTON.

**Development of rancidity in oleic acid.** K. TÄUFEL and J. MÜLLER (Biochem. Z., 1930, 219, 341—348).—In oleic acid or ethyl oleate which had been exposed to air and light until thoroughly rancid the fatty acids from formic to octoic and formaldehyde, heptaldehyde, and nonaldehyde have been found. W. MCCARTNEY.

**Linoleic acids and their oxidation by peracids.** W. C. SMIT (Rec. trav. chim., 1930, 49, 539—551).—A critical and comprehensive review of the literature indicates that it is still uncertain whether more than one linoleic acid is present in linseed and similar oils. Tetrabromostearic acid prepared from poppy and soya-bean oils has m. p. 116—117° (methyl ester, m. p. 63°, and ethyl ester, m. p. 63°). Debromination of the methyl ester with zinc and boiling methyl alcohol gives a methyl linoleate, b. p. 185—186°/5.6 mm., which on hydrolysis gives a linoleic acid, b. p. 210°/4.5 mm., solidif. point -12° to -11° (constant). Decomposition of the ozonide of this acid with water at the ordinary temperature yields azelaic and hexoic acids, an aldehydomalonic acid (oxidised with peracetic acid to a malonic acid), acetaldehyde, and carbon dioxide, indicating that the original acid is  $\Delta^{\alpha}$ -octadecadienoic acid,  $d_4^{25}$  0.8674,  $n_D^{25}$  1.4492. The solid acid, m. p. 54°, obtained by the thermal dehydration of ricinelaidic acid by Mangold's method (A., 1894, i, 492, who gives m. p. 52°), is similarly proved by ozonolysis to be  $\Delta^{\alpha}$ -octadecadienoic acid,  $d_4^{25}$  0.8659,  $n_D^{25}$  1.4624. Bromination of this acid in carbon tetrachloride solution at -8° gives a tetrabromostearic acid, m. p. 130°, whilst from the mother-liquor is isolated a second form, m. p. 64—65°. Debromination of the acid, m. p. 130°, does not give the original linoleic acid, m. p. 54°, exclusively, but a mixture of this with a liquid, stereoisomeric acid,  $d_4^{25}$  0.9976,  $n_D^{25}$  1.4813. Debromination of the acid, m. p. 64—65°, gives only a trace of the  $\Delta^{\alpha}$ -acid, m. p. 54°, the main product probably consisting of a liquid mixture of stereoisomeric  $\Delta^{\alpha}$ -acids,  $d_4^{25}$  0.9185,  $n_D^{25}$  1.4815. Contrary to Mangold's observation (*loc. cit.*) the acids obtained by distillation of ricinelaidic acid do not partly crystallise, the product being a colourless oil,  $d_4^{25}$  0.8667,  $n_D^{25}$  1.4574, iodine value (Wijs) 110 (calculated 181.1), which is a mixture of the conjugated

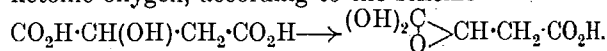
( $\Delta^{\alpha}$ -)linoleic acids mixed with some of the  $\Delta^{\alpha}$ -acid. Bromination of this acid mixture (addition of the second mol. of hydrogen bromide occurs very slowly) gives a mixture of solid tetrabromo-acids, separated into three fractions, m. p.  $124^{\circ}$ ,  $113^{\circ}$ , and below  $90^{\circ}$ , respectively. Debromination of the acid of m. p.  $124^{\circ}$  gives a linoleic acid, b. p.  $230^{\circ}/11$  mm., m. p.  $56^{\circ}$ ,  $d_4^{20}$  0.8630,  $n_D^{20}$  1.4028, which depresses the m. p. of the  $\Delta^{\alpha}$ -acid, m. p.  $54^{\circ}$  (above), and is almost certainly another stereoisomeride of this acid. Although the iodine value (Wijs) of conjugated acids is normally low (long keeping with a large excess of iodine chloride being required to reach the calculated value), the value obtained with a definite ratio of acid and Wijs solution is constant, and hence a curve was plotted of the iodine value obtained with varying weights of the  $\Delta^{\alpha}$ -acid, m. p.  $54^{\circ}$  (obtained by distillation of ricinelaic acid), and a constant quantity of Wijs solution. A determination of the iodine value of the acid obtained by debromination of tetrabromostearic acid, m. p.  $130^{\circ}$ , lies on this curve, whilst one of the acid, m. p.  $56^{\circ}$ , obtained similarly from the tetrabromostearic acid, m. p.  $124^{\circ}$ , does not, thus confirming the conclusion that the latter linoleic acid is a stereoisomeride of the former. J. W. BAKER.

**Propiolic acid.** F. STRAUS, W. HEYN, and E. SCHWEMER (Ber., 1930, **63**, [B], 1086—1092).—Anhydrous propiolic acid, readily obtained by distillation of the aqueous acid, has b. p.  $54$ – $55^{\circ}/10.5$  mm., m. p.  $18^{\circ}$ ,  $d_4^{20}$  1.1380,  $n_D^{20}$  1.44200; it is very hygroscopic. Examination of the f.-p. diagram of the aqueous acid discloses the existence of two hydrates,  $(\text{CH}_3\text{C}\cdot\text{CO}_2\text{H})_3\cdot\text{H}_2\text{O}$ , m. p.  $10^{\circ}$ , and  $\text{CH}_3\text{C}\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ , m. p.  $-0.3^{\circ}$ . The unstable copper salt,  $(\text{CH}_3\text{C}\cdot\text{CO}_2)_2\text{Cu}$  (also tetrahydrate), is prepared by treating an ethereal solution of the acid with the copper salt of ethyl acetate dissolved in benzene or with specially-prepared cupric hydroxide. It readily passes into black cupric acetylide. It gives a crystalline complex compound with pyridine which decomposes into carbon dioxide and acetylene; diacetylene is not produced. When treated with bivalent copper in strongly alkaline solution, propiolic acid immediately causes decolorisation, followed by separation of orange-red crystals which dissolve in water and then yield unstable greenish-yellow needles. Nickel propiolate is described. Copper tetrolate when treated with pyridine gives allene with a little dimethyldiacetylene. Under similar conditions, copper  $\Delta^{\alpha}$ -octinenoate affords heptinene with a considerable proportion of diheptinene. H. WREN.

**Formation of lactic acid by the oxidation of dextrose in the presence of animal charcoal.** V. BOLCATO (Boll. Soc. Ital. sperim., 1927, **2**, 884—887; Chem. Zentr., 1929, ii, 2771).—Treatment of a 2–3% dextrose solution with blood-charcoal at  $40^{\circ}$  for 75–100 hrs. results in a decrease of carbohydrate content and the appearance of lactic acid as shown by the guaiacol reaction. L. S. THEOBALD.

**Optical rotation of malic acid.** W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1930, **34**, 897—928).—The wide variation shown in the optical rotation of malic acid with a change in conditions has been investigated. The explanations advanced by

previous investigators and based on changes in ionisation, polymerisation, and the formation of *d*- from *l*-malic acid etc., are considered to be inadequate. The present work supports the alternative view that two forms of *l*-malic acid of opposite rotations exist. The ordinary form (I) of *l*-malic acid is laevorotatory, whilst the dextrorotatory form (II) arises by migration of the hydrogen of the alcoholic hydroxyl group to the ketonic oxygen, according to the scheme



Replacement of the mobile hydrogen by less labile groups to form methoxysuccinic, ethoxysuccinic, or propoxysuccinic acid yields rotations which are constant even on considerable dilution of the aqueous solutions. Replacement of the hydroxyl group by chlorine gives rotations which vary but little with changes in concentration or temperature, whilst replacement of the hydrogen directly attached to the asymmetric carbon atom by a methyl group gives rotations which vary with dilution but to a smaller extent than is the case with malic acid. Metallic derivatives, e.g., those of beryllium or uranyl, show constant rotations. Analogous cases of other organic compounds such as phenylazoacetic ester and dextrose are discussed. L. S. THEOBALD.

**Tautomeric form of malic acid.** W. D. BANCROFT and H. L. DAVIS (Proc. Nat. Acad. Sci., 1930, **16**, 293—296).—See preceding abstract.

**Isolation and identification of *d*-mannuronolactone from *Macrocystis pyrifera*.** W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1930, **52**, 2130—2132).—The cinchonine salt previously described (A., 1929, 910) is *cinchonine d-mannuronate*, since conversion into the barium salt and subsequent removal of barium with sulphuric acid affords *d-mannuronolactone*, m. p.  $140$ – $141^{\circ}$ , decomp.  $153$ – $155^{\circ}$ ,  $[\alpha]_D^{25} +89.8^{\circ}$  in water. Oxidation of this with bromine water in presence of barium benzoate gives *d*-mannosaccharic acid lactone. H. BURTON.

**Polygalacturonic acid.** W. WŁOSTOWSKA (Rocz. Chem., 1930, **10**, 342—348).—Only 94–95% of the theoretical quantity of sodium hydroxide solution is required in the electrometric titration of polygalacturonic acid; the remaining 5–7% is neutralised if sodium hydroxide is present in excess. This result points to the presence of certain of the carboxyl groups of this acid in the form of lactone. R. TRUSZKOWSKI.

**Legal's reaction.** J. J. L. ZWICKER (Pharm. Weekblad, 1930, **67**, 560—573).—The condensation products of the reaction between aldehydes and ketones and sodium nitroprusside are shown to be polychrome compounds containing an oximinoketone ring as part of a ferropentacyanogen complex. The blue (nitroso-enol) form of the sodium compound of ferropentacyano-oximinoacetone is obtained in formamide solution; the red form, obtained in aqueous solution, passes into a yellow form on keeping. The formula put forward by Cambi (A., 1913, i, 606; 1914, i, 967) is incorrect. S. I. LEVY.

**Action of salts of carbamic acid on form-aldehyde.** E. I. ORLOV (Ukraine Chem. J., 1929,

4, 521—524).—A glycine solution is saturated with carbon dioxide, excess of milk of lime is added, and excess of 40% formaldehyde is added to the filtrate. On keeping for some days a white powder, thought to be  $\text{Ca}(\text{CO}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{H})_2\cdot 2\text{H}\cdot\text{CHO}$ , separates.

R. TRUSZKOWSKI.

**Transformation of *l*-isopulegol into *d*-citronellal.** V. GRIGNARD and J. DÈUVRE (Compt. rend., 1930, 190, 1164—1167).—When *l*-isopulegol is passed over glass wool at  $500^\circ/25$  mm. at the rate of 10 g. per hr. (cf. A., 1926, 268), ring fission occurs; *d*-citronellal (mainly the  $\beta$ -form) is produced instead of the expected rhodinal, migration of a double linking taking place. It is unlikely that rhodinal is first produced and then converted into citronellal, since rhodinol is not transformed into citronellol by the same process. The observation (Bull. Schimmel, 1913, 91) that citronellol is formed when isopulegol is heated with alcoholic sodium ethoxide at  $210^\circ$  (better at  $230$ — $235^\circ$ ) is confirmed.

H. BURTON.

**Isomerism of the butylideneacetones.** E. N. ECCOTT and R. P. LINSTED (J.C.S., 1930, 905—919).—The condensation of *n*-butaldehyde and acetone, with aqueous sodium hydroxide as catalyst, gave under most conditions mixtures of unsaturated ketones and their corresponding ketols. Diminishing either the amount or concentration of alkali hydroxide lowered the yield. Methods are given for the preparation of the pure *cis*-*n*-butylideneacetone, b. p.  $67$ — $70^\circ/12$  mm.,  $d_4^{20}$  0.8507,  $n_D^{20}$  1.4470 (*semicarbazone*, m. p.  $152^\circ$ ), and heptan- $\delta$ -ol- $\beta$ -one, b. p.  $95^\circ/12$  mm.,  $d_4^{20}$  0.9296,  $n_D^{20}$  1.4357, directly. Dehydration of the last-named compound by iodine, acetic anhydride, or, best, oxalic acid, yielded a ketone, b. p.  $62$ — $64^\circ/12$  mm.,  $d_4^{20}$  0.8450,  $n_D^{20}$  1.4432, giving a *semicarbazone*, m. p.  $128^\circ$ , from which the ketone was regenerated with considerable loss. The two unsaturated ketones are therefore regarded as the *cis*- and *trans*-forms of *n*-butylideneacetone, respectively. Proof was afforded by the synthesis of the only possible alternative substance:  $\Delta^5$ -hepten- $\beta$ -one, b. p.  $61$ — $62^\circ/20$  mm.,  $d_4^{20}$  0.8618,  $n_D^{20}$  1.4290 (*semicarbazone*, m. p.  $109$ — $110^\circ$ ), from  $\Delta^5$ -*n*-hexenoyl chloride and zinc methyl iodide.

Treatment of the *cis*- and *trans*-ketones (but not the synthetic  $\Delta^5$ -hepten- $\beta$ -one) with alcoholic ethyl sodiummalonate afforded 5-*n*-propyldihydroresorcinol, m. p.  $107^\circ$ ; similarly, oxidation by potassium permanganate in the presence of aqueous sodium carbonate gave acetic and *n*-butyric acids. Unlike the synthetic  $\beta\gamma$ -ketone (which readily yielded an ozonide, decomposed by water with formation of propaldehyde), they were unattacked by ozone.

The isomeric *n*-butylideneacetones were resistant to configurational change, bromine in an inert solvent and boiling dilute sulphuric acid having no pronounced effect; hydrobromic acid, however, combined additively with both isomerides, giving *bromoketones* (from *trans*, b. p.  $70^\circ/15$  mm.,  $d_4^{20}$  0.8460; from *cis*, b. p.  $80^\circ/5$  mm.), which, when decomposed with aqueous potassium hydrogen carbonate, yielded the *trans*-ketone.

Tautomeric changes between the  $\beta\gamma$ - and the  $\alpha\beta$ -ketones under the conditions previously used for

such determinations could not be studied, because the ketones were readily converted into high-boiling products by the action of alkaline catalysts (e.g., sodium ethoxide, sodium isopropoxide, or piperidine). Boiling 20% sulphuric acid converted the  $\beta\gamma$ -ketone into the *trans*- $\alpha\beta$ -ketone.

The condensation of isobutaldehyde with acetone yielded  $\epsilon$ -methylhexan- $\delta$ -ol- $\beta$ -one, b. p.  $92^\circ/23$  mm.,  $d_4^{20}$  0.9432,  $n_D^{20}$  1.4357, and *trans*-isobutylideneacetone, b. p.  $63$ — $65^\circ/20$  mm.,  $d_4^{20}$  0.8407,  $n_D^{20}$  1.4395 (*semicarbazone*, m. p.  $126^\circ$ ). By dehydration of the ketol by oxalic acid or, better, iodine, *cis*-isobutylideneacetone, b. p.  $64^\circ/18$  mm.,  $d_4^{20}$  0.8558,  $n_D^{20}$  1.4374 (*semicarbazone*, m. p.  $160^\circ$ ), was obtained; it was synthesised also from  $\Delta^5$ -isohexenoyl chloride and zinc methyl iodide.

Pyroterebic acid, prepared by equilibration of  $\Delta^5$ -isohexenoic acid, was treated with phosphorus trichloride in dry benzene and the pyrotereboyl chloride (corresponding anilide, m. p.  $98^\circ$ ; lit.  $106^\circ$ ) treated with zinc methyl iodide,  $\epsilon$ -methyl- $\Delta^5$ -hexen- $\beta$ -one, b. p.  $72$ — $74^\circ/30$  mm.,  $d_4^{20}$  0.9012,  $n_D^{20}$  1.4317 (*semicarbazone*, m. p.  $159$ — $160^\circ$ ), being formed.

Treatment of the *trans*- $\alpha\beta$ -ketone with dilute sulphuric acid or hydrobromic acid, as with the corresponding *n*-compounds, caused conversion into the  $\beta\gamma$ -compound.

R. J. W. LE FÈVRE.

**Acyloins. II. Formation of acetoin from acetaldehyde and from pyruvic acid by irradiation with ultra-violet light.** W. DIRSCHERL (Z. physiol. Chem., 1930, 188, 225—246; cf. this vol., 454).—When aqueous solutions of acetaldehyde or pyruvic acid are irradiated with ultra-violet light acetoin is formed. When the incident light is filtered through acetaldehyde or acetone, acetaldehyde remains unchanged, but pyruvic acid is decarboxylated and produces acetoin quantitatively. The production of acetoin is therefore contingent on the breakdown of pyruvic acid (possibly yielding highly active acetaldehyde), and the assumption of a special "carbolygase" enzyme in yeast experiments is unnecessary. There is no explanation of the production of optically active acetoin by fresh yeast and of the racemic substance by maceration juice.

J. H. BIRKINSHAW.

**Action of selenoxanthhydrol on  $\beta$ -diketones and ethyl acetoacetate.** F. FRANÇOIS (Compt. rend., 1930, 190, 1306—1308).—Selenoxanthhydrol reacts in acetic acid solution with acetylacetone to give *selenoxanthylacetylacetone*,  $\text{Se} \left\langle \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} \right\rangle \text{CH}\cdot\text{CHAc}_2$ , m. p.  $145$ — $146^\circ$ ; *selenoxanthylbenzoylacetone*, m. p.  $136.5^\circ$ , was similarly prepared. *Ethyl selenoxanthylacetoacetate*, m. p.  $108$ — $110^\circ$ , is produced by heating together ethyl acetoacetate and selenoxanthhydrol at  $130$ — $135^\circ$ .

A. I. VOGEL.

**Dimorphism of gallium acetylacetonate.** F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 280—283).—*Gallium acetylacetonate*,  $\text{Ga}(\text{C}_5\text{H}_7\text{O}_2)_3$ , prepared from gallium hydroxide and boiling acetylacetone, crystallises from alcohol or carbon disulphide in orange-coloured, monoclinic plates,  $a:b:c=1.8514:1:1.0810$ ,  $d^{20}$  1.414, or from acetone or ethyl acetate in orthorhombic prisms,  $a:b:c=$

1-7124 : 1 : 2-0841,  $d^{20}$  1-408. Both modifications can co-exist for an undetermined time in contact with the mother-liquor.

J. W. SMITH.

**Elementary composition of the pentosan xylan.** K. P. LINK (J. Amer. Chem. Soc., 1930, 52, 2091—2094).—Micro-analyses of 15 specimens of purified xylan from various sources support the formula  $(C_5H_8O_4)_n$ .

H. BURTON.

**Rhamnose (mannomethylose) derivatives.** E. VOTOČEK, F. VALENTIN, and F. RÁC (Coll. Czech. Chem. Comm., 1930, 2, 402—413).—Concentration of a solution of equal weights of *l*- and *d*-rhamnose monohydrates (A., 1926, 940) in 96% alcohol at the ordinary temperature affords anhydrous crystals of *dl*-rhamnose, m. p. 151.3—153° (crystallographic data). Since the racemate is anhydrous it follows that the molecule of water in the active forms is water of crystallisation and not water of constitution as suggested by Raýman. Reduction of *d*-rhamnose with sodium amalgam affords *d*-rhamnitol, m. p. 123°,  $[\alpha]_D^{20}$  -12.4° in water, obtained crystalline by hydrolysis of its dibenzylidene derivative, m. p. 207°,  $[\alpha]_D^{20}$  +60.7° in chloroform (Lobry de Bruyn and van Ekenstein, A., 1899, i, 661, give m. p. 203°,  $[\alpha]_D^{20}$  -55°), the same physical constants being obtained when the derivative is prepared from *l*-rhamnose. Contrary to Bertrand's rule (A., 1904, ii, 760), it is found that neither *l*-rhamnose nor  $\alpha$ - or  $\beta$ -rhamnohexitol is oxidised by the sorbose bacteria, although mannitol is readily attacked, and hence it is concluded that attack by this culture does not depend on stereochemical configuration, but on the homologous series to which the alcohol belongs.  $\beta$ -Rhamnohexose (Fischer and Morrell, A., 1894, i, 218),  $[\alpha]_D^{20}$  approximately +16°, which could not be obtained crystalline, yields a crystalline *monobenzylidene* derivative, m. p. 233—234°,  $[\alpha]_D^{20}$  +50.8° in chloroform.

J. W. BAKER.

**Determination of monosaccharides in presence of lactose.** O. SVANBERG (Z. physiol. Chem., 1930, 189, 219—224).—The method involves the use of buffered Barfoed solution containing 10.4 g. of pure acetic acid, 66.5 g. of crystalline copper acetate, and 7 g. of crystalline sodium acetate per litre. The solution is kept at 37°. Two c.c. of sugar solution containing 1—5 mg. of monose are treated with 2 c.c. of the reagent in a test-tube, which is immersed for 6½ min. in boiling water. During the reduction a current of hydrogen is maintained through the liquid. The cuprous oxide is then collected, washed, and oxidised with ferric sulphate solution containing 50 g. of pure ferric sulphate and 200 g. of sulphuric acid per litre. The ferrous sulphate is titrated with standard permanganate. Lactose produces only very slight reduction, which may usually be neglected; galactose behaves like dextrose.

J. H. BIRKINSHAW.

**Crystalline monomethyldiethylmercaptoglucose.** P. E. PAPADAKIS (J. Amer. Chem. Soc., 1930, 52, 2147—2149).—*Monomethyldiethylmercaptoglucose*, m. p. 156—157°, has been isolated as a by-product from the preparation of pentamethyldiethylmercaptoglucose (Levene and Meyer, A., 1926, 1026); the new sugar separates from the aqueous residues.

H. BURTON.

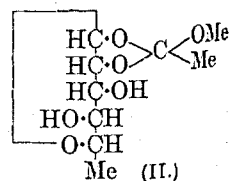
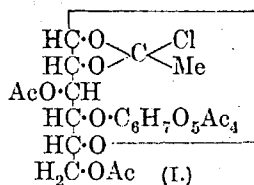
**Relations between rotatory power and structure in the sugar group. XXVIII. Conversion of *d*- $\alpha$ -glucoheptose into a new ketose, *d*-glucoheptulose.** W. C. AUSTIN (J. Amer. Chem. Soc., 1930, 52, 2106—2112).—A new ketose, *d*-glucoheptulose, m. p. 171—174° after softening at 167°,  $[\alpha]_D^{20}$  +67.66° in 10% aqueous solution, has been prepared from *d*- $\alpha$ -glucoheptose by the method described by Montgomery and Hudson (following abstract). The new sugar is not fermented by baker's yeast, it reduces hot Fehling's solution, gives Selivanov's test, and does not exhibit mutarotation. The rotation approximates to the value predicted. When treated with phenylhydrazine it furnishes *d*-glucoheptosazone. The ketose described by Bertrand and Nitzberg (A., 1928, 510, 620, 867) is *l*-glucoheptulose.

H. BURTON.

**Relations between rotatory power and structure in the sugar group. XXVII. Synthesis of a new disaccharide ketose (lactulose) from lactose.** E. M. MONTGOMERY and C. S. HUDSON (J. Amer. Chem. Soc., 1930, 52, 2101—2106).—A solution of  $\alpha$ -lactose monohydrate in 0.043*N*-calcium hydroxide shows a constant rotation after 36 hrs. at 35°. De-enolisation of the solution with sulphuric acid (cf. Wolfrom and Lewis, A., 1928, 509), subsequent neutralisation with calcium carbonate, evaporation of the solution in a vacuum, and removal of unchanged lactose from the residual syrup by crystallisation from alcohol affords an impure ketose, which is purified by oxidation of the remaining aldose with bromine water in presence of barium benzoate, separation of the aldobionic acid formed as a salt, and crystallisation of the residual sugar from methyl alcohol.  $\alpha$ -Lactulose,  $C_{12}H_{22}O_{11}$ , m. p. 158°,  $[\alpha]_D^{20}$  (in water) -23.8° after 2 min.  $\rightarrow$  -51.5° after 24 hrs., is thus obtained. The new sugar gives Selivanov's test, reduces heated Fehling's solution, and affords lactosazone. Hydrolysis with 1% sulphuric acid at 100° yields *d*-fructose and *d*-galactose. Lactulose is  $\alpha$ -4- $\beta$ -*d*-galactosido(1:4)- $\alpha$ -*d*-fructose.

H. BURTON.

**New form of isomerism in the sugar group.** K. FREUDENBERG (Naturwiss., 1930, 18, 393).—The third variety of hepta-acetylchloromaltose (Freudenberg and others, A., 1922, i, 523; 1925, i, 635; 1928, 1222) has the formula I, the chlorine being replaceable by methoxyl and acetoxyl. Fischer,



Bergmann, and Rabe's abnormal acetylmethylrhamnoside (A., 1921, i, 94) has the constitution II. The assumption of Haworth, Hirst, and Miller (this vol., 68) of a novel form of stereoisomerism for this compound is unnecessary.

Crystalline octamethylcellobiose has been synthesised (with Andersen and Go) from 1 : 2 : 3 : 6-tetramethylglucose and 1-chloro-2 : 3 : 4 : 6-tetramethylglucose.

A. I. VOGEL.



**New form of isomerism in the sugar group.** E. BRAUN (Naturwiss., 1930, 18, 393).—Freudenberg's cyclic structure (cf. preceding abstract) for acetyl-methylrhannoside receives support from absorption measurements, the absorption being about 1% of that of a carbonyl compound, e.g., methyl acetate.

A. I. VOGEL.

**Attempted glucosidation of  $\beta$ -hydroxy- $\beta$ -phenylethylamines.** K. H. SLOTTA and H. HELLER (Ber., 1930, 63, [B], 1024—1028).—Tetra-acetyl- $\beta$ -benzyl-*d*-glucoside can be prepared from acetobromoglucose, silver oxide, and a considerably smaller excess of benzyl alcohol than is recorded in the literature; it is smoothly hydrolysed by methyl-alcoholic ammonia to  $\beta$ -benzylglucoside, m. p. 123—125°. Deca-hydro- $\beta$ -naphthol, acetobromoglucose, and silver oxide in ether afford tetra-acetyl- $\beta$ -decahydro-2-naphthyl-*d*-glucoside, m. p. 149—151°, hydrolysed to  $\beta$ -decahydro-2-naphthyl-*d*-glucoside, m. p. 196°.  $\beta$ -Hydroxy- $\beta$ -phenylethylamine as base, salt, or carboxy-derivative, and *r*-adrenaline could not be caused to react with acetobromoglucose and silver carbonate in ether, acetone, or pyridine.

The preparation of  $\beta$ -hydroxy- $\beta$ -phenylethylamine is most conveniently effected by condensing  $\omega$ -bromoacetophenone with hexamethylenetetramine in chloroform and transformation of the product by alcoholic hydrogen chloride into  $\omega$ -aminoacetophenone hydrochloride. The salt is hydrogenated in aqueous solution in presence of palladised charcoal under 3 atm. and the product is isolated by addition of potassium carbonate to the concentrated solution, whereby  $\beta$ -hydroxy- $\beta$ -phenylethylamine carbonate is precipitated. The suspension of the salt in alcohol is treated with hydrogen chloride, thereby giving  $\beta$ -hydroxy- $\beta$ -phenylethylamine hydrochloride, m. p. 210°, from which the free base, m. p. 40°, is obtained by use of ammonia in presence of ether.

Ethyl chloroformate, sodium hydrogen carbonate, and  $\omega$ -aminoacetophenone salt in water afford *N*-carbethoxyaminoacetophenone, reduced by hydrogen in presence of palladised charcoal to *N*-carbethoxy- $\beta$ -hydroxy- $\beta$ -phenylethylamine, m. p. 85°.

The action of chloroacetyl chloride on pyrocatechol in presence of benzene yields chloroacetylpyrocatechol in 63% yield if the chloride is obtained by the action of phosphorus trichloride (not thionyl chloride) on chloroacetic acid and phosphoryl chloride in exactly controlled quantity is added.  $\omega$ -Methylaminoacetylpyrocatechol is very smoothly hydrogenated to *r*-adrenaline under 3 atm. in presence of palladised charcoal.

H. WREN.

**Hydrolytic products of oroboside, dextrose, and orobol.** M. BRIDEL and C. CHARAUX (J. Pharm. Chim., 1930, [viii], 11, 417—425).—Oroboside, the glucoside of *Orobos tuberosus*, L., is hydrolysed by emulsin or by 5% sulphuric acid to equal mols. of dextrose and orobol,  $C_{15}H_{10}O_6$ , m. p. 270.5°, and has, therefore, the formula  $C_{21}H_{20}O_{11}$ . Orobol gives colour reactions similar to those of oroboside, reduces Fehling's solution, contains no methoxyl groups, and is probably a tetrahydroxyflavone.

H. E. F. NOTTON.

**Synthesis of glucosides. IV. Alizarin glucoside.** A. ROBERTSON (J.C.S., 1930, 1136—

1141).—Addition of *O*-tetra-acetyl- $\alpha$ -glucosidyl bromide to a solution of 2-hydroxyanthraquinone and potassium hydroxide in aqueous acetone followed, after a few hours, by acidification with acetic acid, gave 2- $\beta$ -glucosidoxyanthraquinone tetra-acetate, m. p. 168° (lit. 164°); which underwent hydrolysis with methyl-alcoholic-aqueous sodium hydroxide to 2- $\beta$ -glucosidoxyanthraquinone monohydrate, m. p. 248—249°. Similar treatment of alizarin afforded 2-*O*-tetra-acetyl- $\beta$ -glucosidoxy-1-hydroxyanthraquinone, m. p. 206—207° (after sintering at 204°) [treatment with acetic anhydride and pyridine formed the penta-acetyl derivative, m. p. 196—197° (lit. 192—193°)], which (1) underwent deacetylation by warming with methyl-alcoholic-aqueous sodium hydroxide or with methyl-alcoholic ammonia with formation of 2- $\beta$ -glucosidoxy-1-hydroxyanthraquinone, m. p. 237°, and (2) by treatment with methyl iodide, silver oxide, and acetone yielded 2-*O*-tetra- $\beta$ -glucosidoxy-1-methoxyanthraquinone, m. p. 155—156°,  $[\alpha]_D^{25}$  -71.72° in acetone, hydrolysis of which by methyl-alcoholic sodium hydroxide afforded 2- $\beta$ -glucosidoxy-1-methoxyanthraquinone, m. p. 230—231°.

The preparation of *O*-hepta-acetylmaltosidyl bromide from acetic anhydride, octa-acetylmaltose, and hydrogen bromide is described; it reacted in ethereal solution with alizarin, potassium hydroxide, and aqueous acetone to give, after acetylation with acetic anhydride and sodium acetate, alizarin octa-acetylmaltoside, m. p. 185°,  $[\alpha]_D^{25}$  -20.05°, which was not identical with ruberythric acid octa-acetate.

R. J. W. LE FÈVRE.

**Amylose.** J. EFFRONT (Compt. rend., 1930, 190, 1170—1172).—Successive treatment of "retrograde starch" (deposited from an old specimen of starch paste) with malt extract and boiling water affords a product soluble in water at 150°. When such a solution is cooled, amylose is precipitated. During the various treatments, reducing sugars are produced. The amylose obtained is insoluble in boiling alcohol, is not fermented by yeast, does not give an osazone, and is not homogeneous, since extraction with water at 50—100° affords solutions showing approximately the same rotatory power but differing in their reducing power. Two specimens of amylose (showing differing reducing power) had the empirical composition  $(C_6H_{10}O_5)_{12} \cdot H_2O$ . Amylose is readily precipitated from its aqueous solution by cooling, but superheated solutions do not show this behaviour. The amount of reducing sugar increases with superheating, but the quantity of fermentable sugar does not; the original molecule is depolymerised by hydrolysis.

H. BURTON.

**Plant colloids. XXV. Potato starch from different varieties of *Solanum tuberosum*.** J. KAVČIČ.—See B., 1930, 526.

**Starch. XXIII. Glycogen.** J. REILLY, H. PRINGSHEIM, and P. P. DONOVAN (Ber., 1930, 63, [B], 1093—1095; cf. A., 1929, 798).—In freezing acetamide, the mol. wt. of glycogen in 0.7% solution corresponds with the formula  $C_6H_{10}O_5$ ; with increasing concentration association is marked and the value in 1.38—1.62% solution corresponds with  $(C_6H_{10}O_5)_2$ . Glycogesan, precipitated from acetamide by alcohol,

is similar in its behaviour to inulan, except that it exhibits a greater tendency toward re-association. The lowest value observed for the mol. wt. in water of the recovered material is 250. The re-association process appears governed by undetermined factors. Determinations of the mol. wt. of glycogen in formamide are less satisfactory. The recovered glycogen is simpler than that from acetamide, approaching closely in a (non-reproducible) case to the simple hexose anhydride. Both glycogen preparations give the brownish-red coloration of glycogen with iodine, showing that the effect does not depend on the state of aggregation.

H. WREN.

**Inulin. IX.** H. PRINGSHEIM and W. G. HENSEL (Ber., 1930, 63, [B], 1096—1097; cf. A., 1929, 1282).—The preparation of inulin acetate in crystalline form is most readily effected by dissolution of the crude material in a cold mixture of methyl alcohol and glacial acetic acid (3 : 1) followed by repeated crystallisation from hot methyl alcohol. The mol. wt. of the compound in freezing acetic acid at sufficient dilution corresponds with that of a difructose anhydride acetate. The mol. wt. of inulin in formamide is double that in acetamide,  $4 \times C_6$  instead of  $2 \times C_6$ . Addition of acetone to the formamide solution gives immediately a water-soluble inulin of unchanged specific rotation.

H. WREN.

**Polysaccharides. I. Inulin and inulan.** J. REILLY and P. P. DONOVAN (Sci. Proc. Roy. Dublin Soc., 1930, 19, 409—414).—The mol. wt. of inulin, found by cryoscopy in acetamide, agrees with that of a difructosan. This depolymerised product, inulan, may be isolated by heating inulin in molten acetamide for 2 hrs. at  $90^\circ$  and subsequent precipitation with alcohol. An immediate determination of the mol. wt. of inulan by cryoscopy in water agrees with the formula  $(C_6H_{10}O_5)_2$ . On keeping, however, aggregation occurs and after 4 months the mol. wt. had risen to 2500, a value twice as great as that found for the original inulin. All the products have an identical specific rotation. The hydrolysis of lævulosan, inulan, inulin, and sucrose by water at  $100^\circ$  has been followed by the determination of the reducing power. Inulin is regarded as a co-ordinate complex of di-fructosan units.

T. H. MORTON.

**Polysaccharides. II. Purification of the natural products.** J. REILLY and D. T. MCSWEENEY (Sci. Proc. Roy. Dublin Soc., 1930, 19, 451—453).—A simple apparatus, employing parchment membranes, suitable for the purification by electrodialysis of crude polysaccharides is described. By its use salep-mannan, inulin, and glycogen have been isolated free from ash.

T. H. MORTON.

**Structure of B-cellulose.** J. EGGERT and F. LUFT (Z. physikal. Chem., 1930, B, 7, 468—470).—X-Ray diagrams of two specimens of B-cellulose, one apparently homogeneous and the other with a laminar structure, have been shown to be qualitatively identical. The moist or swollen material is amorphous, but when dried again gives the same diagram as cellulose (cf. Mark and von Susich, A., 1929, 245, 1132). The horny B-cellulose, once swollen and dried, cannot be made to swell again, nor will any treatment with water or alcohol render it amorphous. If the

swollen material is stretched before drying a pronounced orientation of the diagram is produced and the photographs then obtained correspond with those of Mark and von Susich. In every case the (101) plane is turned in the direction of the deformation.

F. L. USHER.

**Alkali-cellulose from cellulose acetate.** V. I. SHARKOV (J. Appl. Chem., Russia, 1929, 2, 776—776).—The composition of alkali-cellulose prepared by Pringsheim and Aronovski's method corresponds with the formula  $2C_6H_{10}O_5 \cdot NaOH$ .

CHEMICAL ABSTRACTS.

**New type of quaternary ammonium compound in which hydrogen is completely or partly substituted by aldehydic residues.** T. G. LEVI (Gazzetta, 1930, 60, 309—321).—The new compounds are dialkylideneammonium arylalkyldithiocarbamates,  $NArAlk-CS-S-N(CHR)_2$  (I) and dialkylalkylideneammonium dialkyldithiocarbamates,  $NAlk_2-CS-S-N(Alk)_2:CHR$  (II); the corresponding ammonium hydroxides could not be isolated, but the substances appear to be true ammonium salts. Compounds of type I are decomposed by water or acids into the arylalkylamine, ammonia, carbon disulphide, and the aldehyde  $R \cdot CHO$ , whilst compounds of type II afford secondary amines, carbon disulphide, and the appropriate aldehyde. Mulder's formula (given above), as opposed to that proposed by Delépine, is supported.

Ammonium monophenyldithiocarbamate (Losanitsch, A., 1892, i, 55) reacts with formaldehyde and acetaldehyde in aqueous solution to give *dimethyleneammonium monophenyldithiocarbamate*, m. p.  $70^\circ$  (decomp.), and *diethylideneammonium monophenyldithiocarbamate*, m. p.  $83^\circ$  (decomp.), decomposed by hot water or acids to phenylthiocarbimide, ammonia, carbon disulphide, and formaldehyde or acetaldehyde. Ammonium mono-*p*-tolylidithiocarbamate (Losanitsch, loc. cit.) and acetaldehyde similarly afford *diethylideneammonium mono-p-tolylidithiocarbamate*, m. p.  $90^\circ$  (decomp.); the foregoing all tend to resinify on keeping. The following *dithiocarbamates*, obtained by condensation of the appropriate ammonium *N*-disubstituted dithiocarbamates with formaldehyde or acetaldehyde, are described: *dimethyleneammonium phenylmethyl-*, m. p.  $60^\circ$  (decomp.), decomposed by zinc acetate solution to give *zinc phenylmethyl-*; *dimethyleneammonium phenylethyl-*, m. p.  $60^\circ$ ; *dimethyleneammonium dibenzyl-*, m. p.  $55$ — $62^\circ$ , and *diethylideneammonium dibenzyl-*, obtained from *ammonium dibenzyl-*, m. p.  $130$ — $133^\circ$  (prepared by the method of Losanitsch, loc. cit.), both decomposed by zinc salts to yield *zinc dibenzyl-*; *dimethyleneammonium piperidyl-*, m. p.  $45^\circ$ , decomposed by zinc salts to give *zinc piperidyl-dithiocarbamate*.

The following *dithiocarbamates* are obtained by condensation of the appropriate amine dithiocarbamates with formaldehyde or acetaldehyde: *dimethyleneammonium dimethyl-*, m. p.  $39$ — $40^\circ$ , decomposed by heavy metal salts to give the corresponding metal dimethyl-, and oxidised by iodine in ethereal solution to tetramethylthiuram disulphide, m. p.  $146^\circ$ ; *dimethylethylideneammonium dimethyl-*; *diethylmethyleneammonium-*; *cyclopentylmethyleneammonium piperidyl-*, m. p.  $61^\circ$ , decomposed

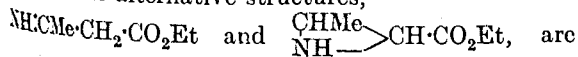
by zinc salts to yield zinc *cyclopentyl*-, and oxidised by iodine to piperidylthiuram disulphide, m. p. 130°.

Ammonium phenylmethyldithiocarbamate reacts abnormally with acetaldehyde to give *phenylmethyldithiolenecarbonium phenylmethyldithiocarbamate*, m. p. 72°, decomposed by cold water into methylaniline, carbon disulphide, and acetaldehyde. Ammonium *N*-disubstituted dithiocarbamates,  $\text{NRR}'\cdot\text{CS}\cdot\text{SNH}_4$ , react with glyoxal to yield solids which resinify more or less rapidly. C. W. SHOPPEE.

Local anaesthetics derived from dialkylaminopropanediols. I. Phenylurethanes. T. H. RIDER (J. Amer. Chem. Soc., 1930, 52, 2115—2118).— $\gamma$ -Di-*n*-butylaminopropane- $\alpha\beta$ -diol, b. p. 127°/3 mm., is prepared from equimolecular quantities of di-*n*-butylamine and glycidol (this vol., 738). Successive treatment of a  $\gamma$ -dialkylaminopropane- $\alpha\beta$ -diol with ethereal solutions of phenylcarbimide (1 mol.) and hydrogen chloride gives the  $\alpha$ -phenylurethane hydrochloride, of which the following are described: *dimethylamino*-, m. p. 138—140°; *diethylamino*-, m. p. 135°; *di-n-propylamino*-, m. p. 163—164°; *diisobutylamino*-, m. p. 125—127°; *di-n-butylamino*-, m. p. 128—129°; *di-n-amylamino*-, m. p. 101—103°, and *piperidino*-, m. p. 176—177°. The following  $\alpha\beta$ -diphenylurethane hydrochlorides are prepared similarly, using 2 mols. of phenylcarbimide: *diethylamino*-, m. p. 109°; *di-n-propylamino*-, m. p. 183—188°; *diisobutylamino*-, m. p. 116—118°, and *piperidino*-, m. p. 197—198°. The *diphenylurethane* of  $\gamma$ -diethylaminopropane- $\alpha\beta$ -diol has m. p. 106.5°, and is probably identical with the monophenylurethane previously described (G.P. 272,529). The monophenylurethanes are decomposed by alkali. The above hydrochlorides have anaesthetic properties. H. BURTON.

Test for small amounts of glycine. W. ZIMMERMANN (Z. physiol. Chem., 1930, 189, 4—6).—A specific reaction for glycine consists in adding to about a 1% solution 10 drops of 2*N*-sodium hydroxide and 8 drops of aqueous phthaldialdehyde solution, shaking, and adding after 10 sec. 10 drops of concentrated hydrochloric acid. An intense violet coloration or precipitate is produced. The reaction is not given by the other monoamino-acids of the protein molecule. Histidine, histamine, carnosine, and arginine give a positive reaction, but may be precipitated with phosphotungstic acid before testing. Cysteine, which responds, may be oxidised to cystine, which gives a negative reaction. J. H. BIRKINSHAW.

Ketimine-enamine tautomerism. K. VON AUWERS and W. SUSEMHL (Ber., 1930, 63, [B], 1072—1086).—Attempts are described to apply spectrochemical evidence to the discrimination between such constitutions as  $\text{NR}\cdot\text{CR}\cdot\text{CH}_2\cdot\text{CO}_2\text{R}'$  and  $\text{NHR}\cdot\text{CR}\cdot\text{CH}\cdot\text{CO}_2\text{R}'$ ,  $\text{NH}\cdot\text{CR}\cdot\text{CH}_2\cdot\text{CN}$  and  $\text{NH}_2\cdot\text{CR}\cdot\text{CH}\cdot\text{CN}$ . The behaviour of ketimines must be optically normal, whereas enamines with the system  $\text{N}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{O}$  should exhibit marked exaltation. Particularly in the case of ethyl  $\beta$ -aminocrotonate and its derivatives, the optical data are shown to be in harmony with the constitution  $\text{NR}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , whereas the alternative structures,



optically inexplicable. Marked differences are observed between the keto-enolic and ketimine-enamine types of tautomerism, since with the latter type an equilibrium mixture dependent on the nature of the compound and the external conditions does not appear to exist in the molten material in which the enamine form predominates. The highly-unsaturated trivalent nitrogen atom exerts a more powerful attraction on the hydrogen atoms of vicinal methyl or methylene groups than does the more saturated, bivalent oxygen atom. The conditions which determine the degree of enolisation are little if at all active with nitrogenous compounds. The following data, *inter alia*, are recorded. The nomenclature of the substances is based on spectrochemical evidence: ethyl  $\beta$ -diethylaminoacrylate,  $d_{418}^{25}$  0.9659,  $n_{\text{D}}^{25}$  1.50280; ethyl  $\beta$ -piperidinoacrylate,  $d_{418}^{25}$  1.0293,  $n_{\text{D}}^{25}$  1.53186; ethyl  $\beta$ -aminocrotonate,  $d_{418}^{25}$  1.0262,  $n_{\text{D}}^{25}$  1.50186; ethyl  $\beta$ -methylaminocrotonate,  $d_{418}^{25}$  1.0113,  $n_{\text{D}}^{25}$  1.50614; ethyl  $\beta$ -amino- $\alpha$ -ethylcrotonate,  $d_{418}^{25}$  0.9236,  $n_{\text{D}}^{25}$  1.46296; ethyl  $\beta$ -diethylaminocrotonate,  $d_{418}^{25}$  0.9796,  $n_{\text{D}}^{25}$  1.51348; methyl  $\beta$ -anilinoacrylate,  $d_{418}^{25}$  1.0580,  $n_{\text{D}}^{25}$  1.57736; ethyl  $\beta$ -anilinoacrylate,  $d_{418}^{25}$  1.0636,  $n_{\text{D}}^{25}$  1.56853; ethyl  $\beta$ -phenylhydrazinocrotonate,  $d_{418}^{25}$  1.0564,  $n_{\text{D}}^{25}$  1.54189; ethyl  $\beta$ -phenylhydrazino- $\alpha$ -methylcrotonate,  $d_{418}^{25}$  1.0773,  $n_{\text{D}}^{25}$  1.55708; ethyl dimethylacetoacetate phenylhydrazone,  $d_{418}^{25}$  1.0629,  $n_{\text{D}}^{25}$  1.53492;  $\beta$ -aminocrotononitrile (diacetonitrile),  $d_{418}^{25}$  0.9731,  $n_{\text{D}}^{25}$  1.49853; ethylaminomethylenepinacolin, b. p. 105°/11 mm.,  $d_{418}^{25}$  0.906,  $n_{\text{D}}^{25}$  1.5045; *diethylaminomethylenepinacolin*, b. p. 138°/11 mm.,  $d_{418}^{25}$  0.903,  $n_{\text{D}}^{25}$  1.5128; *anilinoethylenepinacolin*, b. p. 162°/11 mm., m. p. 95°,  $d_{418}^{25}$  1.0098,  $n_{\text{D}}^{25}$  1.60718;  $\alpha$ -aminoethylidenecetone,  $d_{418}^{25}$  0.9427,  $n_{\text{D}}^{25}$  1.51736;  $\alpha$ -ethylaminoethylidenecetone,  $d_{418}^{25}$  0.9443,  $n_{\text{D}}^{25}$  1.51775;  $\alpha$ -diethylaminoethylidenecetone,  $d_{418}^{25}$  0.9462,  $n_{\text{D}}^{25}$  1.54433;  $\alpha$ -anilinoethylidenecetone,  $d_{418}^{25}$  0.9853,  $n_{\text{D}}^{25}$  1.58090;  $\alpha$ -methylaminoethylidenecetophenone,  $d_{418}^{25}$  1.0194,  $n_{\text{D}}^{25}$  1.61032;  $\alpha$ -anilinoethylidenecetophenone,  $d_{418}^{25}$  1.0323,  $n_{\text{D}}^{25}$  1.62595; ethyl  $\alpha$ -aminomethylcneacetoacetate,  $d_{418}^{25}$  1.1062,  $n_{\text{D}}^{25}$  1.51368.

H. WREN.

Complex salts of  $\alpha$ -amino- $\alpha$ -oximinopropionic acid and  $\beta$ -amino- $\beta$ -oximinopropionic acid. I. DE PAOLINI and G. WALDE (Gazzetta, 1930, 60, 267—270).— $\alpha$ -Amino- $\alpha$ -oximinopropionic acid, m. p. 156° (decomp.), obtained by partial hydrolysis of diamidoglyoxime (Holleman, A., 1897, i, 23), by treatment with copper sulphate in cold aqueous solution gives a green copper salt,  $(\text{C}_2\text{H}_3\text{O}_3\text{N}_2)_2\text{Cu}\cdot 2\text{H}_2\text{O}$ , and with nickel acetate an azure-blue nickel salt,  $(\text{C}_2\text{H}_3\text{O}_3\text{N}_2)_2\text{Ni}\cdot 2\text{H}_2\text{O}$ ; both these complexes are soluble in ammonia solution.

$\beta$ -Amino- $\beta$ -oximinopropionic acid, m. p. 144° (decomp.), prepared by treatment of cyanoacetic acid with hydroxylamine at 40—50° (Modeen, Diss., Helsingfors, 1894) furnishes with copper sulphate solution a bluish-violet copper salt,  $(\text{C}_3\text{H}_5\text{O}_3\text{N}_2)_2\text{Cu}$ , which is not identical with the copper salt of the product obtained by Schiff (A., 1902, i, 429) by the action of hydroxylamine on the semiamide of ethyl malonate. With nickel acetate solution, the acid gives a bluish-violet nickel salt,  $(\text{C}_3\text{H}_5\text{O}_3\text{N}_2)_2\text{Ni}\cdot 3\text{H}_2\text{O}$ ; both salts are soluble in ammonia solution.

C. W. SHOPPEE.



**Oxalhydroxamic acid and malonhydroxamic acid.** I. DE PAOLINI and G. CARBONE (Gazzetta, 1930, 60, 261—266).—The disodium salt of oxalhydroxamic acid (cf. Dimroth and Dienstbach, A., 1909, i, 62, 63) is prepared by treatment of ethyl hydrogen oxalate with methyl-alcoholic hydroxylamine at 30—40° and addition of 20% sodium hydroxide solution. The same substance is obtained, together with ammonia, by hydrolysis at the ordinary temperature with 20% sodium hydroxide of a 15% solution of amido-oxalhydroxamic acid, the constitution of which,  $\text{NH}_2\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}\cdot\text{OH} \rightleftharpoons \text{NH}_2\cdot\text{CO}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$  (cf. Pickard and others, J.C.S., 1902, 81, 1563), is confirmed. With barium chloride, disodium oxalhydroxamate yields the insoluble barium salt; a solution of disodium oxalhydroxamate in dilute hydrochloric acid by treatment with the appropriate acetate gives the lithium hydrogen, sodium hydrogen, and potassium hydrogen salts,  $\text{CO}_2\text{X}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ . The sodium hydrogen salt with copper sulphate solution furnishes a bright bluish-green copper salt dihydrate,  $\text{C}_2\text{H}_3\text{O}_4\text{NCu}\cdot 2\text{H}_2\text{O}$ , converted by suspension in dilute copper acetate solution at 100° into the dihydrate of a basic copper salt,  $\text{C}_2\text{H}_3\text{O}_4\text{NCu}_2$ , and affording with ammonia solution an ammonium copper salt,  $\text{C}_2\text{H}_4\text{O}_4\text{N}_2\text{Cu}$ .

**Sodium hydrogen malonhydroxamate**,  $\text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ , decomp. about 200°, is obtained from ethyl hydrogen malonate and hydroxylamine and subsequent addition of sodium ethoxide solution; the copper salt, obtained as described above, contains at least two equivalents of copper for each acid residue. C. W. SHOPPEE.

**Dioximes.** LXIII. I. DE PAOLINI and G. LONGO (Gazzetta, 1930, 60, 257—260; cf. A., 1927, 134, 135).—Hydrolysis of the benzoyl derivative, m. p. 157°, of amido-oxalhydroxamic acid (Holleman, A., 1897, i, 23) with cold 20% sodium hydroxide affords both benzoic and benzhydroxamic acids, the production of the latter appearing to involve migration of the benzoyl group. It is suggested that the simultaneous formation of two products is to be traced to the dual enolic possibilities of acylhydroxamic acids,  $\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{O}\cdot\text{COR}_2 \rightarrow \text{R}\cdot\text{C}(\text{OH})\cdot\text{NO}\cdot\text{COR}_2$  (I) or  $\text{R}\cdot\text{CO}\cdot\text{N}=\text{C}(\text{OH})\cdot\text{OR}_2$  (II), the enolide I giving by hydrolysis  $\text{R}\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$  and  $\text{R}_2\cdot\text{CO}_2\text{H}$ , and the enolide II yielding by scission of the carbon-nitrogen linking  $\text{R}\cdot\text{CO}_2\text{H} + \text{R}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{OH}$ . The occurrence and relative extent of abnormal hydrolysis (of the enolide II) depend on the additive powers of the two carbonyl groups present in acylhydroxamic acids, and hence on the nature of the groups R and  $\text{R}_2$ . Other benzoylhydroxamic acids ( $\text{R}_2 = \text{Ph}$ ) are stated to behave in a manner similar to that described above; most of the acetylhydroxamic acids ( $\text{R}_2 = \text{Me}$ ) described in the literature yield by hydrolysis a single product only (acetic acid).

The changes undergone by diacyl derivatives of  $\alpha$ -aminophenols (cf. Auwers and Eisenlohr, A., 1909, i, 915) are discussed, and the apparent migration of benzoyl groups is explained by means of a scheme analogous to that given above. C. W. SHOPPEE.

**Proteins.** VI. Degradation of polypeptides by hypobromite. S. GOLDSCHMIDT and K.

STRAUSS (Ber., 1930, 63, [B], 1218—1221; cf. A., 1929, 937).—Ethyl isothiocyanacetate and ethyl  $\alpha$ -aminoisovalerate in ether yield a non-crystalline product converted by concentrated hydrochloric acid into 5-isopropyl-2-thiohydantoin-3-acetic acid, m. p. 168°, from which 5-isopropylthiohydantoin-3-acetic acid, m. p. 148°, is obtained by treatment with chloroacetic acid. It is transformed by 1 mol. of hypobromite into 5-isopropyl-1:5-dehydrohydantoin-3-acetic acid, m. p. 227° (cf. loc. cit.).

$\alpha$ -Bromoisohexoyl chloride and dileucylglycine afford bromoisohexoyldileucylglycine, m. p. 200°, converted by ammonia at 100° into trileucylglycine ( $+ \text{H}_2\text{O}$ ), m. p. 240—270° (decomp.). The tetrapeptide is degraded by potassium hypobromite and treatment of the product with boiling 5N-hydrochloric acid to 5-isobutyl-1:5-dehydrohydantoin-3-isohexioic acid, m. p. 175° (identified by conversion into ketoisohexioic acid and leucine), and glycine. H. WREN.

**Diglutamyl-L-cystine.** I. Peptides of glutamic acid. W. VOSS, R. GUTTMANN, and L. KLEMM (Biochem. Z., 1930, 220, 327—341).—The preparation of glutamyl monobromide by the method of Stewart and Tunnicliffe (A., 1925, i, 795) yields a product containing at most 12% of the substance, and since, in the supposed synthesis of glutathione, aqueous-alkaline hydrolysis of unchanged cystine dimethyl ester yields substances other than cystine which contaminate the condensation product this cannot thus be obtained pure. Dibenzoyl-L-cystine dimethyl ester, prepared by the action of benzoyl chloride on the chloroform solution of the ester and also by esterification of dibenzoyl-L-cystine made by the method of Curtius (A., 1918, i, 44), has m. p. 176—177°. Dibenzoyl-L-cystine, prepared from the dimethyl ester by acid hydrolysis and also from cystine and benzoyl chloride according to Curtius (loc. cit.), has m. p. 195.5—196.5°. Diacetyl-L-cystine dimethyl ester, from acetyl chloride and the ester, has m. p. 125.5—126.5°. W. MCCARTNEY.

**Dithiocarbamic acids.** K. BODENDORF (J. pr. Chem., 1930, [ii], 126, 233—240).—Methylamine N-methyldithiocarbamate, m. p. 110—113° (decomp.) [114—115° (decomp.) in a vacuum], prepared by the interaction of carbon disulphide and methylamine, yields with acetic anhydride S-acetyl-N-methyldithiocarbamic acid,  $\text{NHMe}\cdot\text{CS}\cdot\text{SAc}$ , m. p. 69°. This is deacetylated by amines: strongly basic ones give the corresponding methyldithiocarbamate [piperidine N-methyldithiocarbamate, m. p. 111—113° (decomp.)]; whilst bases such as aniline re-form methylamine N-methyldithiocarbamate, due apparently to part of the methyldithiocarbamic acid set free decomposing to form carbon disulphide and methylamine.

S-Benzoyl-N-methyldithiocarbamic acid, m. p. 91°, is prepared similarly and shows the same reactions with amines; when maintained at its m. p. for a short time it yields methylbenzamide and an odour of methylcarbamide.

Methylamine methyldithiocarbamate condenses with formaldehyde to 2:4-dimethyl-2-methylthiocarbaldine, m. p. 106—107°, decomposed by 10% aqueous sodium hydroxide with the liberation of formaldehyde; with benzaldehyde to 2:4-dimethyl-3-phenyl-2-



*benzylidene-carbothialdine*,  $\text{CS} \begin{smallmatrix} \text{S} - \text{NMe} \cdot \text{CHPh} \\ \text{NMe} \cdot \text{CHPh} \end{smallmatrix}$ , m. p. 159–160°; with benzoylacetone to benzoylacetone methylimide, m. p. 74–75° (Beyer, A., 1891, i, 1090); and with hydroxymethylbenzamide to *benzamidomethyl-N-methyldithiourethane*, m. p. 121–122°, unchanged by crystallisation from acetic anhydride. H. A. PIGGOTT.

**Azidodithiocarbonic acid.** V. Alkyl and acyl derivatives. L. F. AUDRIETH, J. R. JOHNSON, and A. W. BROWNE [with C. W. MASON] (J. Amer. Chem. Soc., 1930, 52, 1928–1935).—The reaction, in acetone, between sodium azidodithiocarbonate and methyl, benzyl, benzhydryl, triphenylmethyl, benzoyl, or *p*-bromobenzoyl chloride or bromide yields the corresponding organic azidodithiocarbonates of respective m. p. 32°, 64·5°, 67·5°, 132° (decomp.), 119–120° (decomp.), and 127° (decomp.) (Maquenne block). The compounds are white, crystalline, and stable at 0°, but undergo slow spontaneous decomposition at the ordinary temperature into the corresponding thiocyanate or thiocarbimide, sulphur, and nitrogen. The rates of decomposition at 40° have been investigated. The compounds are not explosive, and are not photosensitive, presumably because of the molecular character of their lattices (cf. A., 1927, 49, 1044). Crystallographic data are recorded. *p*-Bromobenzoylthiocarbimide, m. p. 55°, and its condensation products with alcohol, m. p. 99°, and with aniline, m. p. 151°, have been prepared.

J. G. A. GRIFFITHS.

**Potassium rutheninitrosopentacyanide**, an analogue of potassium nitroprusside. W. MANGROT and J. DÜSING (Ber., 1930, 63, [B], 1226–1228).—Ruthenium trichloride is converted by potassium cyanide into potassium ruthenocyanide, which, when warmed on the water-bath with nitric acid (*d* 1·4) mixed with an equal volume of water, is transformed into the compound  $\text{K}_2\text{Ru}(\text{CN})_5(\text{NO}) \cdot 2\text{H}_2\text{O}$  (also anhydrous). With ammonium sulphide it yields a red coloration, rapidly destroyed by an excess of ammonium or alkali sulphide. The sensitiveness towards an excess of the reagent is also shown by sodium nitroprusside. H. WREN.

**Anomalous fifth carbon atom in *n*-fatty nitriles.** R. A. FULTON and W. B. LEE (J.C.S., 1930, 1057–1059).—Each of five consecutive nitriles ( $\text{C}_2$  to  $\text{C}_6$  inclusive) of the *n*-fatty acids, together with potassium in equimolecular amount, was electrolysed in liquid ammonia solution and the anode products were analysed for methane and ethane; they showed distinct anomaly at  $\text{C}_5$ . The same nitriles were heated with potassium at 350°; the gaseous products were examined with the same result, although a certain regularity is observable as the "chain length" increases. R. J. W. LE FÈVRE.

**Spectrochemistry of aliphatic diazo-compounds.** K. VON AUWERS (Ber., 1930, 63, [B], 1242–1246).—Contrary to Lindemann (this vol., 345), the author considers that spectrochemical evidence, as far as it is available, points decidedly to the open-chain structure of aliphatic diazo-compounds without excluding the possible presence of cyclic structures in small proportion. The high excitations,

a sign of marked unsaturation, accord excellently with the open formula and would constitute an isolated anomaly if the cyclic structure is attributed to these compounds. The material available for spectroscopic purposes is too vast to justify such anomaly without very strong reasons and it appears more reasonable to assume that in peculiar structures such as aliphatic diazo-compounds the individual components of the molecule do not all possess their normal parachor equivalents. H. WREN.

**Constitution of aliphatic diazo-compounds.** H. LINDEMANN (Ber., 1930, 63, [B], 1246–1248; cf. this vol., 586).—Mainly a reply to von Auwers (preceding abstract). The evidence afforded by the parachor values is considered as conclusive as that based on spectroscopy. The b. p. of the diazo-compounds are not compatible with the open structure and the small specific rotations of all known optically active diazo-compounds can scarcely be explained by an exclusively open form. The possibility that the ease of racemisation of the active diazo-compounds may afford a clue to the problem is indicated. H. WREN.

**as-Dialkylarsine derivatives.** N. WIGREN (J. pr. Chem., 1930, [ii], 126, 223–232).—The following were prepared by methods previously described (A., 1924, i, 888; cf. Burrows and Turner, J.C.S., 1921, 119, 428): methylethyliodoarsine (Burrows and Turner, *loc. cit.*); methyl-, b. p. 73–74°/9 mm., and ethyl-*n*-propyliodoarsine, b. p. 83°/8 mm., 92–93°/12 mm. Reduction with the zinc-copper couple and hydrochloric acid gave methylethylarsine, b. p. 71°/770 mm., spontaneously inflammable in air, and methyl-*n*-propylarsine, b. p. 98°/749 mm., 101°/754 mm., immediately oxidised but not inflamed by air. The iodoarsines gave with concentrated aqueous sodium hydroxide *s*-methylethylarsine oxide, b. p. 67–68°/8 mm., 70–71°/10 mm., and 80–81°/15 mm.; *s*-methyl-, b. p. 96°/9 mm., and *s*-ethyl-*n*-propylarsine oxide, b. p. 117–118°/8 mm., 120°/11 mm.; and on oxidation methylethylarsinic acid, m. p. 120–121° (Guerbet, A., 1926, 507); methyl-*n*-propylarsinic acid, m. p. 118–119° (cf. Guerbet, *loc. cit.*); and ethyl-*n*-propylarsinic acid, m. p. 119–120° (nitrate: by oxidation of iodoarsine with nitric acid, m. p. 54°). The silver salts of these acids are described, as also is a method for the determination of iodine in the iodoarsines. H. A. PIGGOTT.

**Action of arsenic chloride on ethyl sodium-malonate.** E. V. ZAPPI (Anal. Assoc. Quím. Argentina, 1929, 17, 241–249).—When arsenic trichloride is added to an alcoholic solution of ethyl sodium-malonate, sodium chloride separates in colloidal form. Distillation of the liquid yields alcohol, a little ethyl arsenite, ethyl malonate, and a residue from which impure ethyl arsenotrimalonate may be extracted by acetone. The reaction is essentially between arsenic trichloride and sodium ethoxide. No intermediate additive compounds with ethyl sodium-malonate can be detected. R. K. CALLOW.

**Forced reaction between some hydrocarbons and a mixture of magnesium and magnesium halide.** H. GILMAN and J. A. LEEMAKERS (Rec. trav. chim., 1930, 49, 532–534; cf. this vol., 462).—In the forced reaction between tri- and di-phenyl-

methane with a mixture of magnesium and magnesium halide no detectable formation of an organomagnesium halide occurs, since when the reactants are heated at 60–65° in ethereal benzene in a current of carbon dioxide no carboxylic acid could be isolated and high recovery of the original hydrocarbon was effected. In the second case a trace of *s*-tetraphenylethane is formed.

J. W. BAKER.

**Preparation of lead diethyl dichloride and lead triethyl chloride.** H. GILMAN and J. D. ROBINSON (J. Amer. Chem. Soc., 1930, 52, 1975–1978).—Lead diethyl dichloride is prepared in 97.5% yield by passing dry hydrogen chloride into a solution of lead tetraethyl in toluene at 90° until precipitation is complete. Saturation of an ethereal solution of lead tetraethyl with hydrogen chloride at the ordinary temperature gives a 98.2% yield of lead triethyl chloride; moisture must be rigorously excluded.

H. BURTON.

**"Phenyltrimethylene."** M. LESPIEAU (Compt. rend., 1930, 190, 1129–1131).—Treatment of cinnamyl bromide with hydrogen bromide at the ordinary temperature and then at –20°, the saturated liquid being finally heated for 5 hrs. in a sealed tube, gave a product  $C_9H_{10}Br_2$ , b. p. 142–143°/10 mm.,  $d^{23}_4$  1.632,  $n_D$  1.5935, which after treatment with powdered zinc in 95% alcohol at 70° gave a mixture of allylbenzene, propenylbenzene, and "phenyltrimethylene," which when treated with 1% aqueous potassium permanganate at 20° gave benzoic and phenylacetic acids and "phenyltrimethylene," b. p. 60–61°/13 mm.,  $d^{20}_4$  0.9397,  $n_D$  1.5291.

C. C. N. VASS.

**Transformation of a cyclohexane into a benzene ring.** B. N. MENSCHUTKIN and M. B. WOLFF (Coll. Czech. Chem. Comm., 1930, 2, 396–401).—When cyclohexane is shaken with 25% oleum at 25°, 1 g. is absorbed by 27 g. of the acid and by repeated treatment the whole of the cyclohexane can be induced to react. Conversion of the diluted dark brown acid extract into barium salts and extraction of these with boiling water affords barium benzenesulphonate.

J. W. BAKER.

**2:3:4:6-Tetranitrotoluene.** A. F. HOLLEMAN (Rec. trav. chim., 1930, 49, 501–502).—2:4:6-Trinitro-*m*-toluidine, prepared by the action of boiling *N*-methyl-alcoholic ammonia on 2:4:6-trinitro-3-methoxytoluene (Blanksma, A., 1903, i, 164), is best converted (85.2% yield) into 2:3:4:6-tetranitrotoluene, m. p. 136.5°, by addition of a solution of potassium persulphate in sulphuric acid ( $d$  1.84) to its solution in the acid of same concentration, without cooling, the temperature rising to 100°. After keeping for 24 hrs., the product is filtered through glass wool, washed with 50% sulphuric acid and water, and crystallised from boiling nitric acid ( $d$  1.4) or from chloroform. The tetranitrotoluene is more stable than the corresponding 1:3:4:5-tetranitrobenzene, which is destroyed by boiling nitric acid, and is completely decomposed by water at 80° in a few minutes, the toluene derivative suffering only 57% decomposition in 1 day.

J. W. BAKER.

**Action of alkali metals and organic alkali compounds on aromatic sulfoxides.** K. FUCHS and P. GROSS (Ber., 1930, 63, [B], 1009–1019).—

Diphenyl sulfoxide and sodium in benzene slowly give a brown precipitate, whereas di-*pp*-tolyl sulfoxide with sodium or potassium affords a very dilute, intensely red solution and didiphenyl sulfoxide and potassium yield an almost black precipitate. Decomposition of the product from diphenyl sulfoxide by carbon dioxide gives diphenyl sulphide and a little sodium phenyl sulphide, unchanged sulfoxide, and sodium carbonate, whereas dimethyldibenzothiophen is derived from di-*pp*-tolyl sulfoxide. The formation of these products is readily explained by the hypothesis that the coloured compounds are analogous in structure to the metallic or dimetallic ketyls, but their insolubility renders their isolation as homogeneous substances difficult. Diphenyl sulfoxide does not appear to react with the potassium derivative of phenyl diphenyl ketone. Addition of a dilute solution of diphenyl sulfoxide to sodium triphenylmethyl in ether causes an immediate violet-red colour and, under definite conditions, a compound,  $Ph_2SO, NaCPh_3$ , can be isolated. It is decomposed by hydrogen chloride into sodium chloride, triphenylmethane, and diphenyl sulfoxide, with a small amount of a molecular compound of diphenyl sulfoxide and triphenylcarbinol which dissociates in acetone and benzene. By carbon dioxide it is decomposed mainly into sodium triphenylacetate and diphenyl sulfoxide. It is uncertain whether a substance possibly in equilibrium with its components is present or a molecular compound which must be appreciably undissociated in solution. Di-*pp*-anisyl and di-*pp*-tolyl sulfoxides react analogously with sodium triphenylmethyl. Diphenyl sulfoxide and the disodium compound of dihydroanthracene give a dark cinnabar-red solution which yields sodium carbonate, a little anthracene and diphenyl sulphide, and unchanged sulfoxide when treated with carbon dioxide; the presence of an anthracenecarboxylic acid could not be detected. Addition of solid diphenyl sulfoxide to a suspension of the sodium derivative of 9:10-dihydroanthracene in ether at –60° to –70°, followed by warming of the mixture to the atmospheric temperature, yields a red solution and a brownish-red precipitate. Decomposition of the solution with carbon dioxide leads to the production of anthracene, diphenyl sulphide, sodium carbonate, and diphenyl disulphide, whereas hydrogen chloride yields anthracene, diphenyl sulphide and disulphide, and sodium chloride; an anthracenecarboxylic acid is not observed. The precipitate, which differs from the compound present in the solution, is decomposed by carbon dioxide into sodium phenyl sulphide and much less anthracene than corresponds with the amount of thiophenol. It appears probable that the precipitate is not an anthracene compound. The solution contains an organo-sodium compound in which the metal is not united to carbon. Prolonged agitation of the solution with mercury causes partial disappearance of the colour and the mercury absorbs one tenth to one fifth of the dissolved sodium. Diphenyl sulfoxide does not appear to react with a little anthracene in presence of an excess of sodium.

H. WREN.

**Preparation and properties of sulfoxides and sulphones.** R. L. SHRINER, H. C. STRUCK, and



W. J. JORISON (J. Amer. Chem. Soc., 1930, 52, 2060—2069).—Modified methods of preparation of diphenyl, dibenzyl, and *phenyl benzyl sulphoxides*, m. p. 122—123°, are given. Thiophenol and methylene bromide react in presence of alcoholic sodium ethoxide, forming *di(phenylthiol)methane*, m. p. 35—36°, oxidised by 38% hydrogen peroxide in acetone solution to the corresponding *disulphoxide*, m. p. 188—189°. These sulphoxides do not react with sodium in benzene, do not form salts with alkali hydroxides, are not alkylated with alkyl iodide and sodium ethoxide, and do not give colorations with ferric chloride. There appears to be no tendency for the change  $\cdot\text{CH}_2\cdot\text{SO}\cdot\text{R} \rightleftharpoons \cdot\text{CH}\cdot\text{SR}\cdot\text{OH}$  to occur. Dibenzyl sulphone, *phenyl benzyl sulphone*, m. p. 146—146.5°, and *dibenzene-sulphonylmethane*, m. p. 118—119°, react slowly with sodium in benzene, but do not give colorations with ferric chloride. The last-named sulphone is readily soluble in alkali hydroxide and on methylation furnishes a *mono-*, m. p. 100—101°, and a *di-methyl* derivative, m. p. 181—182°. The other sulphones could not be methylated. The results show that the methylene hydrogen atom is activated more by the sulphone than by the sulphoxide group. It is pointed out that the sodium salt of dibenzenesulphonylmethane is formed, not owing to enolisation, but probably by combination of the sulphone with hydroxyl ion through a hydrogen atom, and subsequent elimination of water. An electronic representation of the reaction is given.

H. BURTON.

Orientation effects in the diphenyl series. VIII. Nitration of 4:4'-difluorodiphenyl. R. J. W. LE FÈVRE and E. E. TURNER (J.C.S., 1930, 1158—1162).—The product obtained by Schieman and Bolstad (A., 1928, 878) by mononitration of 4:4'-difluorodiphenyl is proved to be 4:4'-difluoro-2-nitrodiphenyl as follows: (1) it does not react with boiling piperidine; (2) it is identical with the product of thermal decomposition of the *bisdiazonium fluoroborate*, m. p. 129° (decomp.) after darkening at 125°, prepared from 2-nitrobenzidine; (3) further treatment with nitric acid (*d* 1.5) gave 4:4'-difluoro-2:3'-*dinitrodiphenyl*, m. p. 109—110° (identical with the direct dinitration product from 4:4'-difluorodiphenyl or with the mononitration product from synthetic 4:4'-difluoro-2-nitrodiphenyl), which interacted with piperidine even in the cold with formation of 4-fluoro-2:3'-*dinitro-4'-piperidinodiphenyl*, m. p. 126.5—127.5°.

R. J. W. LE FÈVRE.

Supposed existence of colourless triphenylmethyl salts. A. HANTZSCH and A. BURAWOY (Ber., 1930, 63, [B], 1181—1191).—Only colourless, ester-like pseudo-salts and coloured true salts exist in the triarylmethane series. By reaction with the solvent, the last-named substances can form equilibrium mixtures of the two isomerides or be converted by basic media such as pyridine into colourless, stable pyridinium salts. The erroneous assumption of the existence of colourless, true triarylcarbonium salts is due to the non-recognition by Lifschitz that the colourless triarylmethyl thiocyanates are relatively stable pseudo-salts (cf. A., 1928, 1001); they are intermediate between the cyanides stable towards alcohol and the halides and perchlorates which suffer almost complete

alcoholysis, and are therefore only partly alcoholysed in concentrated solution. The true triarylcarbonium salts can add solvent at the cations, of which the central carbon atom is co-ordinatively tervalent. The compounds thus become normal (tetrahedral) in configuration, but also more saturated and less absorbent. This is true, for example, for the yellow, solid perchlorate monohydrate,  $[\text{H}_2\text{O} \dots \text{CPh}_3]\text{ClO}_4$ . On the other hand, the colourless pseudo-halides can pass by similar addition into true salts by formation of analogously-constituted coloured cations. Such salts,  $[\text{R} \dots \text{CPh}_3](\text{Cl}, \text{Br})$ , must be considered present in the coloured solutions of the halides in phenol, hydrogen cyanide, and hot glacial acetic acid. The pseudo-salts can also be converted into the true, deeply-coloured salts by addition of acids to the halogen, which thereby becomes more negative and anionic. This must be assumed for the yellow trianisylmethyl thiocyanate, which, by addition of thiocyanic acid, becomes transformed into the intensely-red dithiocyanate,  $[\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_3][\text{SCN}, \text{HS}\cdot\text{CN}]$ , analogous to the sulphate,  $[\text{CPh}_3]\text{SO}_4\text{H}, \text{H}_2\text{SO}_4$ . The red, additive compound,  $\text{Cl}\cdot\text{CPh}_3\cdot 6\text{HCl}$ , formed by simultaneous addition of hydrogen chloride to triphenylmethyl and chlorine, is a true, coloured salt of the suggested structure,  $[(\text{HCl})_n \dots \text{CPh}_3][\text{Cl} \dots (\text{HCl})_n]$ .

The complete alcoholysis of triphenylmethyl chloride and bromide in methyl and ethyl alcohol is established by the identity of their absorption spectra with those of the triphenylmethyl alkyl ethers and by measurement of the acid concentration by the kinetic method of decomposition of ethyl diazoacetate. Initially the spectrum of triphenylmethyl thiocyanate in methyl or ethyl alcohol is identical with that of its ethereal solution, but after 24 hrs. has become identical with that of its ether. The liberated acid is also determined by the diazoacetic ester method. Triphenylmethyl perchlorate is analogously decomposed by methyl alcohol. *Trianisylmethyl thiocyanate*, m. p. 135—136° (decomp.), and the *hydrogen thiocyanate* are incidentally described. Triphenylmethylpyridinium perchlorate,  $[\text{CPh}_3\cdot\text{C}_5\text{H}_5\text{N}]\text{ClO}_4$ , m. p. 216—217° (decomp.), is prepared by evaporating a solution of triphenylcarbonium perchlorate in dry pyridine. *Triphenylmethylammonium perchlorate* is obtained from triphenylmethyl perchlorate and ammonia or from triphenylmethylamine and perchloric acid.

H. WREN.

Polymerisation. I. Two dimerides of *as*-diphenylethylene. E. BERGMANN and H. WEISS (Annalen, 1930, 480, 49—59).—The unsaturated dimeride of *as*-diphenylethylene (best prepared by the action of aluminium chloride in benzene solution; Wieland and Dorrer, this vol., 464) is identical with  $\alpha\alpha\gamma\gamma$ -tetraphenyl- $\Delta^2$ -butene obtained by Schlenk and Bergmann (A., 1928, 1031). It is reduced by sodium and boiling amyl alcohol or by red phosphorus and hydriodic acid (*d* 1.7) to  $\alpha\alpha\gamma\gamma$ -tetraphenyl-*n*-butane, m. p. 122°. Moreover, contrary to Staudinger's rule, it is readily depolymerised by heating with iodine in acetic acid. Reduction of  $\alpha\alpha\gamma\gamma$ -tetraphenylallyl ethyl ether (Schlenk and Bergmann, *loc. cit.*) with hydrogen and a palladium catalyst in boiling propyl alcohol gives  $\alpha\alpha\gamma\gamma$ -tetraphenylpropyl ethyl ether, b. p. 279—280°/21

mm., converted by long shaking with sodium and subsequent treatment with methyl iodide, not into  $\alpha\gamma\gamma$ -tetraphenylbutane, but into  $\alpha\gamma\gamma$ -tetraphenylpropene. The saturated dimeride of *as*-diphenylethylene, which is also prepared with equal ease by the action of sulphuric acid on the intermediate, unsaturated dimeride, is not a cyclobutane derivative, as previously supposed (Lebedev and others, A., 1923, i, 770; Wieland and Dorrer, *loc. cit.*), but is 1 : 3 : 3-triphenyl-1-methylhydrindene, m. p. 143°, the structure of which is proved by the following synthesis. 3 : 3-Diphenyl- $\alpha$ -hydrindone, prepared in the usual manner from  $\beta\beta$ -triphenylpropionic acid (Fosse, A., 1907, i, 764) through the corresponding acid chloride, reacts with magnesium phenyl bromide to give 1-hydroxy-1 : 3 : 3-triphenylhydrindene, m. p. 113—115° (converted by heating with acetyl chloride into 1 : 3 : 3-triphenylindene), which with finely-divided potassium and methyl iodide affords its methyl ether, m. p. 160—162°. This is converted by long shaking with powdered sodium into the 1-sodio-derivative of 1 : 3 : 3-triphenylhydrindene (giving the hydrocarbon by decomposition with alcohol), which by subsequent treatment with methyl iodide gives 1 : 3 : 3-triphenyl-1-methylhydrindene. On the basis of these results it is unlikely that the dimeride of stilbene has the cyclobutane structure assigned to it by Wieland and Dorrer (*loc. cit.*), although it is not identical with the expected 1 : 2-diphenyl-3-benzylhydrindene, m. p. 115°. Similarly, the "photodimeride," m. p. 163°, obtained by Ciamician and Silber (A., 1903, i, 171) is not identical either with 1 : 2 : 3-triphenyl-1- or 1 : 1 : 3-triphenyl-2-methylhydrindene (cf. following abstract).

J. W. BAKER.

**Action of lithium on the unsaturated dimeride of *as*-diphenylethylene.** E. BERGMANN and H. WEISS (Annalen, 1930, 480, 59—64).— $\alpha\gamma\gamma$ -Tetraphenyl- $\Delta^a$ -butene (cf. preceding abstract) does not react with sodium, but with lithium it forms a monolithium derivative, which on hydrolysis gives a mixture of 1 : 2 : 3-triphenyl-1-methylhydrindene,  $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^b$ -butene, and a small quantity of  $\alpha\alpha\delta\delta$ -tetraphenylbutadiene, separated by fractional crystallisation from propyl alcohol at low temperature after precipitation of the crude product with light petroleum, whilst titration of the residue from the petroleum mother-liquor with bromine indicates that this consists of a 50% mixture of *as*-diphenylethylene and *as*-diphenylethane. By treatment with carbon dioxide the lithium compound affords an insoluble lithium salt, which on acidification gives 1 : 2 : 3-triphenyl-1-methylhydrindene-1-(2 or 3)-carboxylic acid, m. p. 276° (methyl ester, m. p. 149°), and a soluble lithium salt, from which  $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^b$ -butene- $\alpha\delta$ -dicarboxylic acid (Schlenk and Bergmann, A., 1928, 1031) is obtained. The mechanism of the formation of these compounds is discussed in relation to similar condensation of  $\alpha\gamma\gamma$ -tetraphenylpropene (Schlenk and Bergmann, *loc. cit.*) and to an (incomplete) investigation with the dimeride of  $\alpha$ -methylstyrene.

J. W. BAKER.

**Derivatives of triphenylethylene, and  $\alpha$ -phenyl- $\beta\beta$ -didiphenylethylene.** E. A. SCHILOV (J. Russ. Phys. Chem. Soc., 1930, 62, 95—99).—Triphenyl-

ethylene, m. p. 68—70°, obtained from benzophenone and magnesium benzyl chloride, when treated with cold nitrogen oxides gave colourless crystals of  $\alpha\beta$ -dinitro- $\alpha\beta$ -triphenylethane, m. p. about 110°. On attempting to recrystallise the latter from aqueous alcohol or acetic acid, hydrolysis took place and nitro- $\alpha\beta$ -triphenylethanol, m. p. 122—122.5°, was obtained. Solutions of both of the dinitrotriphenylethane and nitrotriphenylethanol in glacial acetic acid on warming gave a 30% yield of lemon-yellow  $\beta$ -nitro- $\alpha\beta$ -triphenylethylene, m. p. 175—176°, together with benzophenone and *p*-nitrobenzoic acid. Nitrotriphenylethylene is not acted on by alkalis, but dissolves in concentrated sulphuric acid with an intense blue or green coloration. It does not react with halogens and darkens in sunlight. On reduction with zinc dust and glacial acetic acid,  $\alpha\beta$ -triphenylethanol, m. p. 136°, was obtained.

$\alpha$ -Phenyl- $\beta\beta$ -di-*p*-diphenylethylene, m. p. 195—196°, was synthesised from didiphenyl ketone, m. p. 236°, which was obtained from diphenyl and carbonyl chloride in the presence of aluminium chloride. Phenyl-didiphenylethylene resembled triphenylethylene in properties.

M. ZVEGINTZOV.

**"Superfluous" isomerides. I. Dehydration of  $\beta\beta\gamma$ -triphenylpropyl alcohol.** E. BERGMANN and H. WEISS (Ber., 1930, 63, [B], 1173—1175).—The preparation of  $\alpha\beta\gamma$ -triphenyl- $\Delta^a$ -propene, m. p. 63°, and a hydrocarbon, m. p. 89°, from  $\beta\beta\gamma$ -triphenylpropyl alcohol has been described by Ramart and Amagat (A., 1927, 241) and the identity of the second hydrocarbon with that obtained by Paternò and Chieffi (A., 1909, i, 393) by loss of water from the carbinol derived from benzophenone and ethylbenzene has been assumed. Its synthesis from methyldeoxybenzoin and magnesium phenyl bromide proves that the carbinol is  $\alpha\alpha\beta$ -triphenylpropyl alcohol and the hydrocarbon derived therefrom is  $\alpha\alpha\beta$ -triphenyl- $\Delta^a$ -propene. It is not identical with Ramart and Amagat's compound, m. p. 89°, which is shown to be 1 : 2-diphenylhydrindene. H. WREN.

***ms*-Alkylanthracenes and "transanellar tautomerism."** X. E. DE B. BARNETT and J. L. WILTSHIRE (Ber., 1930, 63, [B], 1114—1123; cf. this vol., 202).—The authors' hypothesis that a co-ordinated linking can exist between an  $\alpha$ -chloro-atom and a *meso*-hydrogen atom in the *peri*-position is experimentally examined. 10-Hydroxyanthrone is readily enolised; in accordance with expectation, it is found that this property is not greatly affected by the presence of a chlorine atom in position 1 or 8 or 1 and 8, whereas the hydrogen atom in position 10 is immobilised by a chlorine atom at 4 or 5 or 4 and 5. The increased effect caused by the presence of two chlorine atoms suggests that both are involved in the co-ordinated linking. 10-Phenylanthrone readily yields an acetate and the dihydroanthranols obtained from it with magnesium alkyl halides suffer transanellar loss of water. 1 : 8-Dichloro-10-phenylanthrone behaves similarly, differing thus from the isomeric 4 : 5-dichloro-10-phenylanthrone. The 1-chloro-compound resembles the 1 : 8-dichloro-substance, whereas the influence of the halogen atom of the 4-chloro-derivative is modified by the unsaturated

nature of the phenyl group. The possibility of coordinated linking with a halogen atom not attached to the anthracene nucleus is examined. The following compounds are described: 1:8-dichloro-10-bromoanthrone, not molten below 305°; 4:5-dichloro-10-bromoanthrone, m. p. 174° after softening; 1:8-dichloro-10-hydroxyanthrone, m. p. 227° (decomp.); 1-chloro-10-phenylanthrone, m. p. 169°, from 1-chloro-10-bromoanthrone, benzene, and aluminium chloride; 1-chloro-10-phenyl-9-benzyl-9:10-dihydroanthran-9-ol, m. p. 167°; 1-chloro-10-phenyl-9-benzylanthracene, m. p. 142°; 4-chloro-10-phenylanthrone, m. p. 192°; 4-chloro-10-phenyl-9-benzylanthracene, m. p. 151°; 1:8-dichloro-10-phenylanthrone, decomp. 235°; 1:8-dichloro-9-acetoxy-10-phenylanthracene, m. p. 165°; 4:5-dichloro-10-phenylanthrone, m. p. 237°; 1:8-dichloro-10-phenyl-9-benzyl-9:10-dihydroanthran-9-ol, m. p. 184°; 1:8-dichloro-10-phenyl-9-benzylanthracene, m. p. 189°; 4:5-dichloro-10-phenyl-9-benzyl-9:10-dihydroanthran-9-ol, m. p. 208° (decomp.); 4:5-dichloro-10-phenyl-9-benzylidene-9:10-dihydroanthracene, m. p. 205°; 10:10-di-o-chlorobenzylanthrone, m. p. 194° after softening, from anthrone, o-chlorobenzyl chloride, and potassium hydroxide; 1:8-dichloro-10:10-di-o-chlorobenzylanthrone, m. p. 233°; 4:5-dichloro-10-o-chlorobenzylanthrone, m. p. 155° after softening; 1:5-dichloro-10-o-chlorobenzylanthrone, m. p. 182°; 1:5-dichloro-9-o-anisyl-9:10-dihydroanthran-9-ol, m. p. 187°; 1:5-dichloro-9-o-anisylanthracene, m. p. 149°.

H. WREN.

**Transanellar isomerism.** E. BERGMANN (Ber., 1930, 63, [B], 1037—1044).—The isolation of two transanellar-isomeric hydrocarbons is described (cf. Barnett and co-workers, this vol., 465, and previous abstracts; the term "anellar" is introduced in place of "annular"). Benzhydrylideneanthrone (*hydrzone*, m. p. 178°) is converted by magnesium phenyl bromide into 10-hydroxy-10-phenyl-9-benzhydrylidene-9:10-dihydroanthracene, m. p. 221°, oxidised to hydroxyphenylanthrone. 9-Benzylidene- and 9-methylene-anthrone react vigorously with magnesium phenyl bromide, but yield anthraquinone as sole crystalline product. Reduction of the carbinol with sodium formate and anhydrous formic acid gives a mixture of 10-phenyl-9-benzhydrylidene-9:10-dihydroanthracene, m. p. 218°, and 10-phenyl-9-benzhydryl-anthracene, m. p. 154° (decomp.). The constitution of the hydrocarbons rests on the following evidence. The last-named compound is fluorescent and yields a dark orange-red mass when melted with trinitrotoluene, showing thus the behaviour typical of anthracene derivatives; these properties are not shown by the second compound, which, in contrast to the first, is thermochromic. The second compound readily adds two atoms of sodium, whereas the first substance slowly yields a monosodium derivative (decomposed with formation of the second hydrocarbon). Oxidation with chromic acid in glacial acetic acid affords less incisive evidence, since the reaction is accompanied by partial isomerisation; with each hydrocarbon hydroxyphenylanthrone and anthraquinone are produced, but the relative quantities of the products are in accordance with expectation.

10:10-Diphenyl-9-benzhydrylidene-9:10-dihydro-

anthracene readily yields a disodium compound, hydrolysed to 10:10-diphenyl-9-benzhydryl-9:10-dihydroanthracene, m. p. 276°. The synthesis of the compound by the successive action of sodium and benzhydryl bromide on 9-methoxy-10:10-diphenyl-9:10-dihydroanthracene is recorded. H. WREN.

**Polycyclic aromatic hydrocarbons. I. 1- and 2-Phenylanthracenes and derivatives of 1:2-benzanthracene.** J. W. COOK (J.C.S., 1930, 1087—1095).—Interaction of the Grignard reagent from o-iododiphenyl, b. p. 140°/3—4 mm., with o-toluoyle chloride led to 2-o-toluoyleldiphenyl, m. p. 66—67°, b. p. 190—192°/3—4 mm., converted by boiling into 1-phenylanthracene, m. p. 110—112° (which differed from 2-phenylanthracene, m. p. 207—207.5°, obtained by reduction of 2-phenyl-9-anthrone by zinc dust activated by copper and aqueous sodium hydroxide). Magnesium o-tolyl bromide with o-toluoyle chloride yielded di-o-tolyl ketone, m. p. 64—67°, which by pyrolysis gave mainly anthracene.

The interaction of aluminium chloride with p-phenylbenzoyl chloride and 2-methylnaphthalene in carbon disulphide solution afforded 1-p-phenylbenzoyl-2-methylnaphthalene, m. p. 109—110°, from which 6-phenyl-1:2-benzanthracene, m. p. 240—241°, was obtained by short boiling. Reduction of 3-methyl-1:2-benzanthraquinone by zinc dust and concentrated aqueous ammonia gave 3-methyl-1:2-benzanthracene, m. p. 153—154°.

Treatment of phenyl- $\alpha$ -naphthylmethane-2'-carboxylic acid with anhydrous zinc chloride at 180° afforded 1:2-benz-10-anthrone, converted by benzoic or acetic anhydride and pyridine at 100° into 1:2-benzanthranyl 10-benzoate, m. p. 171—172°, or the corresponding acetate, m. p. 156°, which with magnesium benzyl chloride gave 10-hydroxy-10-benzyl-9:10-dihydro-1:2-benzanthracene, m. p. 153—153.5°. A solution of the last compound in boiling ethyl alcohol with a little aqueous hydrogen chloride yielded 10-benzyl-1:2-benzanthracene, m. p. 195—196°, also obtained by heating together 1:2-benzanthracene, benzyl chloride, zinc dust, and carbon disulphide for 16 hrs.

Addition of aluminium powder to a solution of 1:2-benzanthraquinone in concentrated sulphuric acid, followed by treatment of the product with benzoic anhydride and pyridine, led to 1:2-benzanthranyl 9-benzoate, m. p. 201—202°. A boiling suspension of 1:2-benzanthraquinone in 10% potassium hydroxide solution when treated successively with an excess of aqueous sodium hyposulphite and benzyl chloride gave 10-benzyl-1:2-benzanthracene, m. p. 178—179°.

Dehydration of phenyl-3-acenaphthylmethane-2'-carboxylic acid by zinc chloride gave acenaphthantran-yl acetate, m. p. 229—230°, after treatment of the crude product with acetic anhydride and pyridine. This crude acenaphthanthrone was reduced by boiling with 2N-sodium hydroxide and zinc dust to acenaphthanthrone, m. p. 192°, whilst with magnesium benzyl chloride it yielded 10-benzylacenaphthanthrone, m. p. 199—200°.

R. J. W. LE FÈVRE.

[Use of] nascent iodine in the detection of some primary aromatic amines. W. RUCZKA (Z.

anal. Chem., 1930, **80**, 185—190).—The addition of 1 c.c. each of 10% potassium iodide solution and 3% potassium iodate solution to a hydrochloric acid solution of certain aromatic amines (the liberated iodine being removed by sodium thiosulphate either in the cold or after boiling the liquid for a short time) gives rise to coloured solutions or precipitates in the case of  $\alpha$ - and  $\beta$ -naphthylamines, *o*-, *m*-, and *p*-phenylenediamines, benzidine, and tolidine; with aniline, *o*-, *m*-, and *p*-toluidines, and *m*-4-xylylidine no characteristic reaction is produced.

H. F. HARWOOD.

**Preparation of sec.-alkylarylamines and their purification.** W. J. HICKINBOTTOM (J.C.S., 1930, 992—994).—The appropriate alkyl bromide is heated with  $2\frac{1}{2}$ —4 mols. of primary aromatic amine, tertiary amine formation being thus largely suppressed. A 50% solution of zinc chloride is then added to the product, and the sec.-amine separated from the precipitated zincchloride of the primary amine by extraction with light petroleum (cf. Morgan, A., 1917, i, 197). It is purified by crystallisation of the hydrobromide from alcohol (*isobutyl*) or benzene (*n*-butyl), or by distillation of the acetyl compound (*n*- and *iso*-propyl). The yields are generally more than 75% of the theoretical, except in the case of *isobutyl*-aniline (30—40%). *p*-Toluenesulphonisobutylanilide has m. p. 122—123°.

H. A. PIGGOTT.

**Nitration of substituted phenylbenzylamine derivatives.** J. REILLY, T. V. CREEDON, and P. J. DRUMM (Sci. Proc. Roy. Dublin Soc., 1930, **19**, 377—379; cf. A., 1928, 514; 1929, 691).—Benzyl-*m*-4-xylylidine, obtained by condensing the corresponding xylylidine with benzyl chloride, nitrated below 0° with a mixture of sulphuric and nitric acid (*d* 1.51, 2 mols.), yields *m*-nitrobenzyl-6-nitro-*m*-4-xylylidine, m. p. 152—153°, also obtained from 6-nitro-*m*-4-xylylidine and *m*-nitrobenzyl chloride. Using smaller quantities of nitric acid no mononitrated derivative could be isolated.

*o*-Nitro-, m. p. 83°, *m*-nitro-, m. p. 70°, and *p*-nitrobenzyl-*m*-4-xylylidine, m. p. 93°, are obtained by heating the corresponding nitrobenzyl chloride and *m*-4-xylylidine in alcoholic solution. With an excess of *m*-nitrobenzyl chloride, under the same conditions, *di*-*m*-nitrobenzyl-*m*-4-xylylidine, m. p. 116°, is obtained. Benzyl-6-nitro-*m*-4-xylylidine has m. p. 135°.

T. H. MORTON.

**Manufacture of N-substituted arylamine-sulphonyl chlorides.** I. G. FARBENIND. A.G.—See B., 1930, 501.

**Diphenyl series. IX. Further experiments with sulphonamides.** F. BELL (J.C.S., 1930, 1071—1077).—Unless otherwise stated, the sulphonamides and disulphonamides described below were prepared by interaction of the appropriate amine or sulphonamide and sulphonyl chloride in pyridine solution. 4-*m*-Nitrobenzenesulphonamidodiphenyl, m. p. 149°, on nitration in acetic acid yields 3-nitro-4-*m*-nitrobenzenesulphonamidodiphenyl, m. p. 170°, and on further nitration 3:5:4'-trinitro-4-*m*-nitrobenzenesulphonamidodiphenyl, m. p. 199°, hydrolysed in sulphuric acid solution to 3:5:4'-trinitro-4-aminodiphenyl, m. p. 282°. 3-Nitro-4-*di*-*m*-nitrobenzenesulphon-

amidodiphenyl has m. p. 187°, and 2-*m*-nitrobenzenesulphonamidodiphenyl, m. p. 128°; the latter on nitration gives the 5-nitro-derivative, m. p. 150°, with dilute aqueous nitric acid, and 3:5-dinitro-2-*m*-nitrobenzenesulphonamidodiphenyl, m. p. 148°, with nitric acid in acetic acid: on hydrolysis the last-named gave 3:5-dinitro-2-aminodiphenyl. Further nitration of the dinitro-compound gave the 3:5:4'-trinitro-derivative, m. p. 170—175°, again identified by hydrolysis to the trinitroaminodiphenyl. 5-Nitro-2-*di*-*m*-nitrobenzenesulphonamidodiphenyl, m. p. 222°, is converted by nitration into the 5:4' (?) -dinitro-compound, m. p. 240°, resistant to hydrolytic agents.

4-Methoxydiphenyl on bromination gives a mixture of about 60% of 3-bromo-, m. p. 79°, and 30% of 4'-bromo-4-methoxydiphenyl, m. p. 144° (identified by comparison with the methylated bromo-4-hydroxydiphenyls); both on further bromination give 3:4'-dibromo-4-methoxydiphenyl, m. p. 134°. 3:5-Dibromo-, m. p. 87°, and 3:5:4'-tribromo-4-methoxydiphenyl, m. p. 115°, are prepared by methylation of the corresponding phenols. 4-*p*-Toluenesulphonamidodiphenyl and its 4'-bromo-derivative both yield 3:5:4'-tribromo-4-aminodiphenyl and 3:4'-dibromo-4-*p*-toluenesulphonamidodiphenyl, m. p. 130°, on bromination in chloroform. 3:4'-Dibromo-4-*di*-*p*-toluenesulphonamidodiphenyl has m. p. 238° and the corresponding 3:5-dibromo-derivative m. p. 291°. 2-*p*-Toluenesulphonamidodiphenyl gives on bromination 5-bromo-2-*p*-toluenesulphonamidodiphenyl, m. p. 115°, also prepared from 5-bromo-2-aminodiphenyl; attempts at dibromination led to gummy masses containing 3:5-dibromo-2-aminodiphenyl.

2-Aminodiphenyl with methyl sulphate and alkali gives a mixture from which 2-nitrosomethylaminodiphenyl, m. p. 70°, is obtained by treatment with nitrous acid. *p*-Toluenesulphon-*m*-nitroanilide is converted by acetic anhydride and a few drops of concentrated sulphuric acid into *p*-toluenesulphon-*m*-nitroacetanilide, m. p. 165°; *m*-nitrobenzenesulphon-*p*-nitroacetanilide, m. p. 214°, is similarly prepared. *m*-Nitrobenzenesulphon-*m*-nitroanilide, m. p. 151°, is vigorously attacked by fuming nitric acid and gives a mixture of polynitro-compounds. *Di*-*m*-nitrobenzenesulphon-*m*-nitroanilide, m. p. 235°, is not attacked by fuming nitric acid. *m*-Nitrobenzenesulphon-*p*-toluenesulphon-*m*-nitroanilide, m. p. 207°; *di*-*p*-toluenesulphon-*m*-nitroanilide, m. p. 180°; *m*-nitrobenzenesulphon-*p*-nitro-*o*-toluidide, m. p. 189°, and the *di*-*m*-nitrobenzenesulphonyl derivative, m. p. 201°; *di*-*m*-nitrobenzenesulphon-*o*-nitro-*p*-toluidide, m. p. 215°; *di*-*m*-nitrobenzenesulphon-*o*-nitro-*o*-toluidide, m. p. 193°; and *di*-*p*-toluenesulphonanilide, m. p. 183°, are also described.

H. A. PIGGOTT.

**Effect of substituents on the shade of derivatives of stilbenesulphonic acids.** A. WAHL and JONICA (Compt. rend., 1930, **190**, 1198—1200).—Replacement of the amino-group in 4-nitro-4'-amino-stilbene-2:2'-disulphonic acid by hydroxyl or halogen changes the shade on wool from orange to yellow tints; the bromo- and iodo-derivatives are more orange than the chloro-compound. The 4'-acylamino-derivatives dye wool with a greenish-yellow shade which is fast to light; the shade of the acetyl or

benzoyl derivative is comparable with that of tartrazine. Coupling of 4-substituted 4'-aminostilbene-2:2'-disulphonic acids with  $\beta$ -naphthol and R-salt gives azo-compounds which dye wool (in an acid bath) red and violet-red, respectively. The shades of the two series are only slightly affected by the nature of the 4-substituent.

Oxidation of the leuco-compounds from dimethylaniline and 4-substituted benzaldehyde-2-sulphonic acids (prepared by oxidation of the corresponding stilbene derivatives with potassium permanganate) with lead peroxide gives triphenylmethane dyes with the following shades: 4-nitro-, dull bluish-green; 4-chloro- (bromo-, cyano-), purer bluish-green; 4-formamido- (acetamido-), blue.

H. BURTON.

**Molecular organic compounds. II. Molecular organic compounds of 2:4-dinitroaniline, 1-chloro- and 1-bromo-2:4-dinitrobenzene.** C. A. BUEHLER, A. HISEY, and J. H. WOOD (J. Amer. Chem. Soc., 1930, 52, 1939—1944; cf. A., 1927, 141).—The following molecular compounds have been prepared from 1-chloro-2:4-dinitrobenzene:  $\alpha$ -naphthylamine, blood-red, m. p. 72° (all m. p. are corr.; lit. 69—71.5°);  $\beta$ -naphthylamine, garnet-red, m. p. 65.3°; benzidine, black, m. p. 68.8°, obtained only in small amount; pyridine, colourless, m. p. about 189.6° (decomp.) (lit. 170—210°), which is violet when first prepared; naphthalene, colourless, m. p. 76.8° (lit. 78°); fluorene, pale yellow, m. p. about 39°; diphenyl, colourless, m. p. about 31°;  $\alpha$ -naphthol, deep yellow, m. p. 104.9°, and  $\beta$ -naphthol, deep yellow, m. p. 91.2°. The following are obtained from 1-bromo-2:4-dinitrobenzene:  $\alpha$ -naphthylamine, blood-red, m. p. 64.5°;  $\beta$ -naphthylamine, blood-red, m. p. 61.7°; pyridine, yellow, m. p. about 214° (decomp.) (lit. 225°); naphthalene, pale yellow, m. p. 72°;  $\alpha$ -naphthol, deep yellow, m. p. 97.9°, and  $\beta$ -naphthol, orange-yellow, m. p. 83°. All the above contain equimolecular proportions of the components. No compounds were obtained from 2:4-dinitroaniline. As a general rule, amines do not readily form molecular compounds with the 1-halogeno-2:4-dinitrobenzenes; elimination of hydrogen chloride usually occurs. When the above  $\alpha$ - and  $\beta$ -naphthylamine compounds are boiled with alcohol, elimination of hydrogen chloride occurs. From these and the results previously described (*loc. cit.*), it is found that the ease of molecular compound formation of a series of 1-substituted 2:4-dinitrobenzenes is  $\text{Cl} > \text{Br} > \text{OH} > \text{H} > \text{Me} > \text{NH}_2$ ; this is also the order of the electronegative character of the group.

An electronic formula is suggested for the molecular compounds from the above dinitro-derivatives and amines.

H. BURTON.

**Arylnitrosoferropentacyanides: formation from arylhydroxylamines and nitroprusside.** L. CAMBI and T. RICCI (Atti R. Accad. Lincei, 1930, [vi], 11, 443—447).—The interaction of sodium nitroprusside and phenylhydroxylamine in aqueous methyl alcohol solution in presence of sodium methoxide yields sodium aquoferropentacyanide (cf. Baudisch, A., 1921, ii, 290; Cambi, A., 1926, 277). The first stage of the reaction is probably  $[(\text{CN})_5\text{FeNO}]'' + \text{OH} \cdot \text{NHPH} + 2\text{OH}' \longrightarrow [(\text{CN})_5\text{Fe}''\text{N}'\text{O}]''' + \text{Ph} \cdot \text{NO} + 2\text{H}_2\text{O}$ . The hyponitrosoferrocyanide then gives alkali

hyponitrite, which decomposes readily to form nitrous oxide, giving the aquoferrocyanide,  $[(\text{CN})_5\text{FeNO}]''' + \text{H}_2\text{O} \longrightarrow [(\text{CN})_5\text{FeH}_2\text{O}]''' + (\text{NO}')$ . The action of the nitrosobenzene then yields the arylnitroso-complex,  $[(\text{CN})_5\text{FeNO}]''' + \text{Ph} \cdot \text{NO} \longrightarrow [(\text{CN})_5\text{Fe}(\text{NO})\text{Ph}]''' + (\text{NO}')$ . This last stage is analogous to the formation of the same arylnitrosoferrocyanide by the action of nitrosobenzene on ferrocyanide. Similar reactions take place with *o*-hydroxylaminobenzoic acid, which, in aqueous-alcoholic solution, reacts with nitroprusside to give a coloured complex analogous to that obtained from *o*-nitrosobenzoic acid and aquoferropentacyanide. The reaction between nitrosobenzene and phenylhydroxylamine is thus a general one. These results furnish a further proof of the marked reactivity and affinity existing between the iron of the group  $\text{Fe}''(\text{CN})_5$  and the nitrogen of arylnitroso-derivatives.

T. H. POPE.

**Oxidation of *p*-aminophenyltrimethylammonium methosulphate and some quaternary ammonium derivatives.** A. ZAKI (J.C.S., 1930, 1078—1084).—Attempts to synthesise *p*-nitrophenyltrimethylammonium salts by the methylation of *p*-nitrodimethylaniline or the oxidation with Caro's salt of *p*-aminophenyltrimethylammonium chloride failed. An oily substance, probably the  $\psi$ -methosulphate, was obtained by the action of methyl sulphate on nitrosodimethylaniline. *p*-Acetamidophenyltrimethylammonium methosulphate, m. p. 165°, is hydrolysed with concentrated hydrochloric acid and the product diazotised and coupled with  $\alpha$ -naphthol. The product is isolated as *p*- $\alpha$ -naphtholazophenyltrimethylammonium perchlorate, m. p. 247° (decomp.); the azo-compounds from  $\beta$ -naphthol (perchlorate), m. p. 267° (decomp.), and  $\alpha$ -naphthylamine (chloride), m. p. 196° (decomp.), were also prepared. *p*-Aminophenyltrimethylammonium chloride condenses with *p*-dimethylaminobenzaldehyde; *p*-dimethylaminobenzylidene-*p*-aminophenyltrimethylammonium perchlorate has m. p. 253° (decomp.): *p*-dimethylaminobenzeneazophenyltrimethylammonium perchlorate (decomp. above 280°) is similarly prepared using nitrosodimethylaniline. Oxidation of *p*-aminophenyltrimethylammonium chloride with Caro's salt gives a solution from which azoxybenzene-*pp'*-bistrimethylammonium perchlorate, m. p. 268° (explosive) (also isolated from the product of interaction of *pp'*-tetramethyldiaminoazoxybenzene and methyl sulphate), picrate, m. p. 244° (decomp.), and ferricyanide (amorphous, not analysed) were isolated. The chloride (impure) had m. p. 252° (decomp.) and the iodide m. p. 198° (decomp.). The perchlorate was analysed by the novel method (for the azoxy-group) of titration with standard titanous chloride until the yellow colour (apparently of the azoxy-compound) was destroyed. The nitrate, m. p. 220—222° (decomp.), of the azoxy-compound when dissolved in a mixture of sulphuric and fuming nitric acids gives a dinitro-compound [perchlorate, m. p. 265° (decomp.); chloride], which on reduction gives an *o*-diamine. Condensation products were obtained from diketohydrindene and nitrosodimethylaniline, m. p. 210° (decomp.), *p*-dimethylaminobenzaldehyde (known), and *p*-aldehydotrimethylammonium methosulphate (I), m. p. 243°

(decomp.). The *methosulphate* (1), m. p. 138—139° (*perchlorate*, m. p. 140—141°), is prepared from *p*-dimethylaminobenzaldehyde and methyl sulphate. The azoxy-quaternary salts (above) do not react with diketohydrindene. *Benzylideneaniline*-pp'-*bistri-methylammonium perchlorate*, charring at about 260°, is formed by interaction of the *p*-amino- and *p*-aldehyde-phenyltrimethylammonium salts. *m*-Nitro-phenyltrimethylammonium methosulphate, m. p. 220°, *picrate*, m. p. 150° (decomp.), *perchlorate*, m. p. 230—232° (decomp.), and *iodide*, m. p. 202°, and *phenyltri-methylammonium methosulphate* and *perchlorate* are also described. H. A. PIGGOTT.

**Azo-dyes of the fluorene series.** M. COURTOT (Rev. gén. Mat. Col., 1930, 34, 170—174).—Azo-dyes which appear to be new have been prepared by coupling diazotised 2-aminofluorene with  $\beta$ -naphthol,  $\beta$ -naphthol-3-carboxyanilide,  $\beta$ -naphthol-6-sulphonic acid,  $\beta$ -naphthol-7-sulphonic acid,  $\beta$ -naphthol-3:6-disulphonic acid, 1:8-dihydroxynaphthalene-3:6-disulphonic acid, and 8-amino- $\alpha$ -naphthol-3:6-disulphonic acid, and by coupling diazotised 2-aminofluorene, 2-aminofluorenol, 2-amino-7-chlorofluorene, -fluorenone, and -fluorenol, 2-amino-7-bromo-fluorene, -fluorenone, and -fluorenol, 2-amino-7-sulphofluorene, and 4-aminofluorenone with  $\beta$ -naphthol-3:6-disulphonic acid, 8-amino- $\alpha$ -naphthol-3:6- and -3:5-disulphonic acid. In some cases the dyes were produced by coupling on the fibre, but that from diazotised 2-aminofluorene and  $\beta$ -naphthol, presumably 1-(2-fluorenylazo)-2-naphthol, was obtained in reddish-brown crystals, m. p. 200—205°. *Disazo-dyes* were similarly prepared from tetrazotised 2:7-diaminofluorene (G.P. 39756/1886), 2:7-diaminofluorenone, 2:7-diaminofluorenol, 2:5-diaminofluorenone, and 2:5-diaminofluorenol and  $\beta$ -naphthol-3:6-disulphonic, 8-amino- $\alpha$ -naphthol-3:6- and -3:5-disulphonic acids. The products generally have affinity for cotton as well as for animal fibres. Taking the fluorene colours as a standard, the keto-group in the fluorenones has a hypsochromic, and the hydroxyl group in the fluorenols a bathochromic, influence.

H. A. PIGGOTT.

**Substantive dyes derived from 2:7-diaminofluorene.** A. NOVELLI (Anal. Fis. Quim., 1930, 28, 362—370).—Dyes have been prepared by coupling tetrazotised 2:7-diaminofluorene with 2 mols. of the following naphthalene derivatives:  $\beta$ -naphthylamine-3:6-disulphonic acid (*sodium* salt, deep violet, m. p. above 300°);  $\beta$ -naphthol-3:6-disulphonic acid (*hexa-sodium* salt, deep red);  $\alpha$ -naphthol-3:6- and -3:8-disulphonic acids (deep red); and two pairs of dyes by coupling 8-amino- $\alpha$ -naphthol-3:6- and -3:5-disulphonic acids in acid and alkaline media, respectively.

H. F. GILLBE.

**Colour and constitution from the point of view of recent electronic theory. III. Tautomerism of nitrophenols, nitrosation, influence of the methyl group on the colours of substituted benzene-azophenols, and diazotisation.** H. H. HODGSON (J. Soc. Dyers and Col., 1930, 46, 101—108).—In part a *résumé* of work already published (A., 1929, 1062; this vol., 209). The influence of the methyl group on the colour of benzeneazophenols as compared with the

influence of chlorine (B., 1929, 1008) is shown in the reddening of shade which increases in the following compounds in the order named: *p*-toluidine  $\rightarrow$  *o*-cresol (light yellow; 1.1 units of red), aniline  $\rightarrow$  *o*-cresol (1.1), *p*-toluidine  $\rightarrow$  phenol (1.1), *m*-toluidine  $\rightarrow$  phenol (1.1), aniline  $\rightarrow$  phenol (1.2), *m*-toluidine  $\rightarrow$  *o*-cresol (1.4), *o*-toluidine  $\rightarrow$  phenol (1.6), aniline  $\rightarrow$  *m*-cresol (1.9), *o*-toluidine  $\rightarrow$  *o*-cresol (2.0), *p*-toluidine  $\rightarrow$  *m*-cresol (2.1—2.2), *m*-toluidine  $\rightarrow$  *m*-cresol (2.2), and *o*-toluidine  $\rightarrow$  *m*-cresol (orange; 2.9), when dissolved in alcoholic solution. An electronic explanation is given of the removal of the *m*-nitro-group instead of the chloro-group when chloro-3:4-dinitrobenzene is treated with alkali. A. J. HALL.

**Oxidising power of diazohydrates and their analogies with nitrous acid.** A. ANGELI and A. POLVERINI (Atti R. Accad. Lincei, 1930, [vi], 11, 542—544).—The work of Quilico and Freri (this vol., 793) is discussed and evidence is advanced indicating the complete analogy in structure and behaviour between the three forms, O:O, OH:N:O, N<sub>2</sub>Ph:O.

T. H. POPE.

**Action of benzenediazonium chloride on  $\beta$ -nitroethyl alcohol and its derivatives.** E. C. S. JONES and J. KENNER (J.C.S., 1930, 919—928).—The sodium salt of  $\beta$ -nitropropyl alcohol, when treated with benzenediazonium chloride, yields, with elimination of formaldehyde,  $\omega$ -nitroacetaldehydephenylhydrazone, also obtained from sodium nitroethane and benzenediazonium chloride:  $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NO}_2 \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CMe}(\text{NO}_2)\cdot\text{N:NPh} \rightarrow \text{NO}_2\cdot\text{CMe}\cdot\text{N:NPh} + \text{CH}_2\text{O}$ . In the case of  $\beta$ -nitrotrimethylene glycol, this reaction leads to a *stereoisomeride* (probably *trans*-), m. p. 117—118°, of the  $\omega$ -nitroglycolaldehydephenylhydrazone, m. p. 108°, obtainable from  $\beta$ -nitroethyl alcohol (Demuth and Meyer, A., 1890, 857, give m. p. 104°), convertible into this lower-melting (*cis*-?) form by dissolving in alkali and reprecipitating with acid. Both forms are readily decomposed by heat with elimination of formaldehyde, but in the case of the lower-melting form other deep-seated changes make this difficult to detect. The hydrazone, m. p. 117—118°, is capable of further reaction with benzenediazonium chloride, the product at once decomposing into nitroformazyl and formaldehyde. This indicates coupling at the carbon atom carrying the nitro-group and is therefore presumptive evidence for the benzeneazo-formula for these hydrazones:  $\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{NO}_2)\cdot\text{N:NPh} \rightleftharpoons \text{OH}\cdot\text{CH}_2\cdot\text{CH}(\text{NO}_2)\cdot\text{N:NPh} \xrightarrow{\text{PhN:NCl}}$

$[\text{OH}\cdot\text{CH}_2\cdot\text{C}(\text{NO}_2)(\text{N:NPh})_2] \rightarrow \text{CH}_2\text{O} + \text{NPh}\cdot\text{N:C}(\text{NO}_2)\cdot\text{N:NPh}$ . This reaction is general for compounds of the type  $\text{OH}\cdot\text{CHR}\cdot\text{C}(\text{NO}_2)\cdot\text{N:NPh}$ , the aldehyde  $\text{R}\cdot\text{CHO}$  being eliminated. Elimination of formaldehyde on condensation with benzenediazonium chloride was also observed with  $\beta$ -nitrobutyl alcohol and  $\beta$ -nitroamyl alcohol ( $\omega$ -nitrobutaldehyde-phenylhydrazone, m. p. 63—66°).

Phenylhydrazones of the general formula  $\text{OH}\cdot\text{CHR}\cdot\text{C}(\text{NO}_2)\cdot\text{N:NPh}$  were also obtained from nitroisopropyl alcohol ( $\text{R}=\text{Me}$ ; m. p. 126—127°),  $\alpha$ -nitrobutan-3-ol ( $\text{R}=\text{Et}$ ; m. p. 100—102°),  $\alpha$ -nitropentan-3-ol ( $\text{R}=\text{Pr}$ ; m. p. 92—94°),  $\alpha$ -nitrohexan-



$\beta$ -ol ( $R=Bu^a$ ; m. p. 108—111°),  $\gamma\gamma$ -trichloro- $\alpha$ -nitropropan- $\beta$ -ol ( $R=CCl_3$ ; m. p. 129°), and  $\beta$ -nitro- $\alpha$ -phenylethyl alcohol ( $R=Ph$ ; m. p. 126°).  $\gamma$ -Nitrobutan- $\beta$ -ol gave  $\omega$ -nitroacetaldehydephenylhydrazones and acetaldehyde. These phenylhydrazones when coupled with benzenediazonium chloride yielded nitroformazyl and the aldehyde  $R\cdot CHO$ .

$\beta$ -Nitroamyl alcohol, b. p. 130—136°/28 mm. (sodium salt), is prepared by the condensation of nitrobutane and formaldehyde in the presence of a little potassium carbonate.  $\beta$ -Nitro- $\beta$ -hydroxymethylamyl alcohol, m. p. 80—83°, is formed as a by-product, and is reconverted by sodium ethoxide into  $\beta$ -nitroamyl alcohol.  $\alpha$ -Nitropentan- $\beta$ -ol, b. p. 117°/17 mm. (sodium salt), similarly prepared from nitromethane and *n*-butaldehyde, yields on chlorination  $\alpha$ -chloro- $\alpha$ -nitropentan- $\beta$ -ol, m. p. 38°. New sodium salts of  $\alpha$ -nitrobutan- $\beta$ -ol,  $\alpha$ -nitrohexan- $\beta$ -ol,  $\gamma$ -nitrobutan- $\beta$ -ol,  $\gamma$ -nitropentan- $\beta$ -ol, and  $\gamma$ -nitrohexan- $\beta$ -ol are described; during the preparation of the last two decomposition occurred with formation of acetaldehyde (an analogy with the aldols). H. A. PIGGOTT.

Use of aryl esters for the preparation of amides and derivatives of carbamide. U. HEUBAUM (J. Amer. Chem. Soc., 1930, 52, 2149—2150).—Phenyl carbonate and oxalate react much more readily with ammonia and amines than do the corresponding ethyl esters. H. BURTON.

Action of nitric acid on phenol in ethyl acetate solution. A. V. KARTASHEV and E. G. SAÏ-MOISEEVA (J. Russ. Phys. Chem. Soc., 1930, 62, 385—397).—The addition of a solution of nitric acid in ethyl acetate to phenol is followed by a period during which no apparent reaction takes place; after an interval of time, the length of which varies inversely with the concentration of acid taken, the mixture becomes yellow, and, after a further interval, quite abruptly becomes red; at this point the temperature rises sharply from 20° to 50—70°. The use of ethyl acetate as a solvent allows the reaction to commence at a lower temperature than when the solvent is water. The temperature at which reaction commences is, as for aqueous solutions, lower for impure, coloured phenol than for the freshly-distilled product. Nitrous acid has a more powerful catalytic effect in ethyl acetate than in aqueous solution; its action consists in shortening the first and second intervals before the temperature rises, and differs from that in aqueous solution in that tarry substances are not produced. R. TRUSZKOWSKI.

Scission of diaryl ethers and related compounds by piperidine. III. Nitration of 2:4-dibromo-2':4'-dinitrodiphenyl ether and of 2:4-dibromophenyl *p*-toluenesulphonate and benzoate. Chlorination and bromination of *m*-nitrophenol. (Miss) R. V. HENLEY and E. E. TURNER (J.C.S., 1930, 928—940).—2:4-Dibromophenyl *p*-toluenesulphonate, m. p. 120°, gives on dinitration 2:4-dibromo-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate, m. p. 122—123°, identified by conversion through the diamino-compound, m. p. 174—175°, into 2:4:5-tribromophenyl *o*-bromo-*p*-toluenesulphonate, m. p. 107—108°, which with piperidine gives 2:4:5-tribromophenol, m. p. 85—86° (Kohn and Pfeifer,

A., 1927, 966), also prepared from 2:4:5-tribromoaniline. The dinitro-compound, on scission with piperidine, gives 2:4-dibromo-5-nitrophenol, m. p. 77—78° [monohydrate, m. p. 92—94°, probably obtained by Garzino (A., 1890, 1108)], also prepared by nitration of 2:4-dibromophenyl benzoate and scission of the product with piperidine. A more convenient method of preparation of 2:4-dibromo-2':4'-dinitrodiphenyl ether (Le Fèvre, Saunders, and Turner, A., 1927, 660) is described. On nitration it gives 2:4-dibromo-5:2':4'-trinitrodiphenyl ether, m. p. 142°, which on scission with piperidine gives 2:4-dibromo-5-nitrophenol and 2:4-dinitrophenylpiperidine, and with aniline, 2:4-dinitrodiphenylamine. *m*-Nitrophenyl *p*-toluenesulphonate has m. p. 112—113°.

Attempts to dibrominate *m*-nitrophenol according to the directions of Lindner (A., 1885, 774) failed. When bromine vapour diluted with carbon dioxide is passed through the phenol at 120—140°, what appears to be Lindner's product is obtained, but actually it is a mixture, inseparable by crystallisation, of 4-bromo- and 2:4:6-tribromo-3-nitrophenol. 2:4:6-Tribromo-3-nitrophenyl *p*-toluenesulphonate, m. p. 146—147°, was reduced to the amino-compound, m. p. 146—147°, and this converted in the usual way into 2:3:4:6-tetrabromophenol, m. p. 113—114°. *N*-*p*-Bromophenylphthalimide, m. p. 204° (from *p*-bromoaniline and phthalic anhydride), gives on nitration and hydrolysis a mixture of much 4-bromo-2-nitroaniline with some 4-bromo-3-nitroaniline, but the latter could not be converted into 4-bromo-3-nitrophenol. *ON*-Diacetyl-3-nitro-4-aminophenol (method of preparation improved) was hydrolysed by concentrated hydrobromic acid and converted without isolation of the nitroaminophenol into 4-bromo-3-nitrophenol, m. p. 146.5—147.5° (Heller and Kammann, A., 1909, i, 567), identical with the product of monobromination of dry *m*-nitrophenol (considered by Schlieper, A., 1892, 704, to be 2-bromo-3-nitrophenol). 4-Chloro-3-nitrophenol was similarly prepared, but direct chlorination of *m*-nitrophenol gave nearly equal amounts of 4-chloro-3-nitrophenol and 2-chloro-3-nitrophenol (cf. Schlieper, *loc. cit.*; Meldola and Eyre, J.C.S., 1902, 81, 996). Monobromination of *m*-nitrophenol in glacial acetic acid gives 2-bromo-5-nitrophenol, m. p. 118.5—121° (Heller and Kammann, *loc. cit.*), oriented by successive conversion of its *p*-toluenesulphonate, m. p. 131.5—132.5°, into 2-bromo-5-aminophenyl *p*-toluenesulphonate, m. p. 135—136°, and 2:5-dibromophenol, m. p. 73—74° (*p*-toluenesulphonate, m. p. 109—110°), also obtained from 2:5-dibromoaniline. 3-Bromo-2-nitrophenyl *p*-toluenesulphonate, m. p. 136.5—137.5°, is similarly converted through 3-bromo-2-aminophenyl *p*-toluenesulphonate, m. p. 120—121°, into 2:3-dibromophenol, m. p. 68—69°. 4-Bromo-3-nitrophenol gives a mixture on attempted monobromination in acetic acid in the presence of sodium acetate. H. A. PIGGOTT.

Phenolic decomposition of mixed ethers. The velocity coefficient D. M. BIROSEL (J. Amer. Chem. Soc., 1930, 52, 1944—1948).—*p*-Bromoanisole is decomposed more readily than *o*-bromoanisole by treatment with hydrobromic acid in acetic acid solution at 100° (bath). Similarly, 2:4:6-tribromoanisole decomposes more readily than 2:4-dibromo-

anisole. The (first order) velocity coefficients for the decomposition of the dibromoanisole in presence of formic and acetic acids, and for the tribromoanisole in acetic acid, have been calculated. Decomposition is greater in acetic than in formic acid, and is proportional to the amount of hydrobromic acid used (with acetic acid as the solvent). H. BURTON.

**2 : 5-Dibromophenetidine.** G. BARGELLINI and A. GRIPPA (Atti R. Accad. Lincei, 1930, [vi], 11, 489—492; cf. A., 1929, 552).—Bromination of phenacetin (1 mol.) in acetic-hydrochloric acid solution with 4 atoms of bromine yields 2 : 5-dibromophenacetin, m. p. 169—171°, and this on hydrolysis gives 2 : 5-dibromophenetidine, m. p. 55—56°, which forms a *picrate*, m. p. 144—145°, a *benzoyl* derivative, m. p. 145—147°, and a *piperonylidene* derivative, m. p. 143—145°. 2 : 5-Dibromophenetidine condenses with 2 : 4-dinitrochlorobenzene, giving 2 : 5-dibromo-2' : 4'-dinitro-4-ethoxydiphenylamine, m. p. 145—165° (decomp.). Treatment of 2 : 5-dibromophenacetin with hydriodic acid gives 2 : 5-dibromo-4-aminophenol, m. p. 195—197°, which yields 2 : 5-dibromobenzoquinone on oxidation with chromic acid. T. H. POPE.

**2 : 6-Dibromo- and 3 : 5-dibromo-phenetidine.** G. BARGELLINI and L. MONTI (Atti R. Accad. Lincei, 1930, [vi], 11, 574—578; cf. preceding abstract).—2 : 6-Dibromophenetidine, obtained from 2 : 6-dibromo-4-nitrophenol by way of 2 : 6-dibromo-4-nitrophenetole, gives an acetyl derivative identical with the dibromophenacetin obtained by Fuchs by brominating *p*-acetamidophenol and ethylating the resulting 2 : 6-dibromo-4-acetamidophenol (A., 1915, i, 520). Like 3 : 5-dichlorophenetidine, the 3 : 5-dibromo-compound does not condense with chlorodinitrobenzene, benzaldehyde, or other compounds capable of reacting with the amino-group, the two bromine atoms exerting steric hindrance. 2 : 6-Dibromo-2' : 4'-dinitro-1-hydroxydiphenylamine, prepared from 2 : 6-dibromo-4-aminophenol and chlorodinitrobenzene in presence of sodium acetate, has m. p. 213—215°. *Piperonylidene*-2 : 6-dibromo-4-aminophenol has m. p. 150—152°; *benzylidene*-2 : 6-dibromo-4-aminophenol, m. p. 94—95°; and *benzoyl*-3 : 5-dibromophenetidine, m. p. 186—188°. T. H. POPE.

**Action of fuming nitric acid on the 4-halogeno-2 : 6-dibromo-phenols and -anisoles. Anomalous behaviour of fluorine derivatives.** H. H. HODGSON and J. NIXON (J.C.S., 1930, 1085—1087).—*p*-Fluorophenol is converted by a solution of bromine in aqueous potassium bromide into 2 : 6-dibromo-4-fluorophenol, m. p. 48°, methylated by Haworth and Lapworth's method (J.C.S., 1923, 123, 2986) to 2 : 6-dibromo-4-fluoroanisole, m. p. 55°. Both these substances are converted by nitric acid (*d* 1.5) at 0° into 2 : 6-dibromo-*p*-benzoquinone, which is also obtained similarly from 4-chloro-2 : 6-dibromo- and 2 : 4 : 6-tribromo-phenol, whilst the corresponding 4-iodo-compound suffers complete decomposition under these conditions. On the other hand, 4-chloro-2 : 6-dibromoanisole by similar treatment with nitric acid affords the 3-nitro-derivative (further nitrated to the 3 : 5-dinitro-derivative), 2 : 4 : 6-tribromoanisole yields 2 : 4 : 6-tribromo-3-nitroanisole, m. p. 82° [further nitrated to 2 : 4 : 6-tribromo-3 : 5-dinitro-

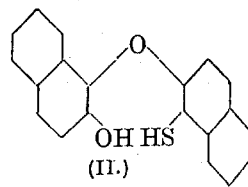
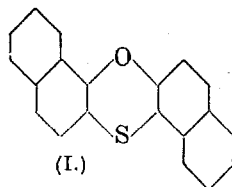
*anisole*, m. p. 148° (cf. Kohn and Rosenfeld, A., 1926, 282, whose results are confirmed], whilst 2 : 6-dibromo-4-iodoanisole gives 2 : 6-dibromo-4-nitroanisole. The mechanism of these replacements is discussed.

J. W. BAKER.

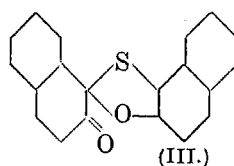
**Manufacture of *ar*-tetrahydronaphthols and their esters and ethers.** I. G. FARBININD. A. G.—See B., 1930, 549.

**Reaction of  $\alpha$ -naphthol.** O. CARLETTI (Giorn. Chim. Ind. Appl., 1930, 12, 178—179).—As little as 0.00001 g. of  $\alpha$ -naphthol may be detected by the intense reddish-violet coloration obtained when 2 c.c. of its aqueous solution are treated, with shaking, with 2 c.c. of saturated sodium hydrogen carbonate solution, 0.5 c.c. of 10% potassium cyanide solution, and 1 c.c. of 1% copper sulphate solution, in that order. With  $\beta$ -naphthol only a faint yellow coloration and green fluorescence are obtained in this way. Traces of  $\alpha$ - in  $\beta$ -naphthol may be detected by dissolving 0.1 g. in warm saturated sodium hydrogen carbonate solution, cooling the liquid, filtering, and testing the filtrate with potassium cyanide and copper sulphate as above. T. H. POPE.

***iso*- $\beta$ -Naphthol sulphide.** L. A. WARREN and S. SMILES (J.C.S., 1930, 956—963).—*iso*- $\beta$ -Naphthol sulphide readily forms an *S*-methyl ether, m. p. 134° (*benzoyl* derivative, m. p. 84—85°), when its zinc salt is heated with methyl iodide. This on oxidation gives the *S*-methylsulphone, m. p. 200° (*benzoyl* derivative, m. p. 149—150°). The product, m. p. 218°, described as the sulphone by Hinsberg (A., 1916, i, 723) is a mixture of sulfoxide and sulphone. The *mercuri-iodide* of the *dimethylsulphonium iodide* (+2COMe<sub>2</sub>), m. p. 101° (decomp.), is obtained from the *S*-methyl ether, methyl iodide, and mercuric iodide in acetone. The dimethyl ether of the *iso*-sulphide is an oil; it gives a *methosulphate*, m. p. 178° (decomp.). Reduction of the sulphone with sodium amalgam gives 2-hydroxy-1 : 2'-dinaphthyl ether, also obtained from the *S*-methyl ether with elimination of methyl mercaptan, or from the *isosulphide* or the dehydro-sulphide with elimination of hydrogen



sulphide, by reduction with hydrogen iodide. The constitution of this dinaphthyl ether (cf. Hinsberg, A., 1916, i, 207; Pummerer, A., 1919, i, 442) was confirmed by synthesis of its *methyl ether*, m. p. 161°, from potassium  $\beta$ -naphthoxide and 1-bromo-2-methoxynaphthalene. These reactions and others already known, particularly the conversion into



$\alpha\beta\beta'\alpha'$ -dinaphthathioxin (I) on dehydration, lead to the conclusion that *iso*- $\beta$ -naphthol sulphide is 2-hydroxy-1'-thiol-1 : 2'-dinaphthyl ether (II). The dehydro-sulphide is then best represented by (III), its formation from either  $\beta$ -naphthol 1-sulphide or the

isosulphide involving the oxidation of a ketonic form; its reduction to the isosulphide occurs by fission of the 5-membered ring. H. A. PRIGGOTT.

**Preparation of diphenyl ethers.** (Miss) R. V. HENLEY (J.C.S., 1930, 1222—1224).—The effects of varying proportions of the reactants, the presence of water, temperature, and time of heating on the yields of diphenyl ethers obtained by condensation of a phenol and a halogenonitro-compound in fused potassium hydroxide have been investigated. The best yields are obtained when 1 mol. of the halogenonitro-compound is added to 1.75 mols. of the phenol dissolved in 1.33 mols. of molten potassium hydroxide containing 0.1 mol. of water, and the reaction mixture is heated at 200—210° for 1 hr. No improvement results from the addition of copper-bronze. Extraction of the ether with carbon tetrachloride may be avoided by shaking the reaction mixture with dilute alkali until cold, the product separating as a crystalline meal. Under these conditions the yields of the diphenyl ether obtained from *o*-chloronitrobenzene and phenol, *o*- and *p*-chlorophenol, *o*-, *m*-, and *p*-cresol are, respectively, 95, 91, 86, 85, 87, and 94%, that obtained with phenol and with 2:5-dichloro- or 2:5-dibromo-nitrobenzene being 85%.

J. W. BAKER.

**Scission of diaryl ethers and related compounds by means of piperidine.** IV. Elimination of halogen atoms and scission reactions during substitution processes. D. L. FOX and E. E. TURNER (J.C.S., 1930, 1115—1124).—Under the conditions which convert 4:4'-dichloro- and 4:4'-dibromo-diphenyl ether into 2:2'-dinitro-compounds (A., 1927, 660), 4-chloro-4'-bromo-2- or -2'-nitrodiphenyl ether [converted by cold nitric acid (*d* 1.5) and acetic acid into the 2:2'-dinitro-derivative, m. p. 165°] undergoes partial replacement of the chlorine atom by a nitro-group, and at 100° conversion into 4-bromo-2:2':4'-trinitrodiphenyl ether, m. p. 154° (m. p. 148—149° after keeping; Raiford and Colbert, A., 1926, 1242, give m. p. 148.5°), is complete. Similarly, 4:4'-dichloro-2-(or 2'-)nitrodiphenyl ether is converted at 100° into 4-chloro-2:2':4'-trinitrodiphenyl ether, identical with a specimen prepared by nitration of the product obtained by condensing *p*-chlorophenol and 1-chloro-2:4-dinitrobenzene in fused moist potassium hydroxide. All the diphenyl ethers were prepared by this type of reaction, details of which are described, and thus from the appropriate halogenophenol and halogenonitro-compound the following are prepared: 2-chloro-2':4'-, m. p. 75—76°, and 4:2', m. p. 126—127°, -dinitro- (the latter being converted by nitric acid at 100° into the 4:2:4'-trinitro-compound, m. p. 135—136°), 4-bromo-2-nitro-, b. p. 228—230°/21 mm. (converted by bromine in acetic acid at 100° into 4:4'-dibromo-2-nitro-, and by prolonged nitration into 2:4:2':4'-tetranitrodiphenyl ether), 2-bromo-2':4'-dinitro-, m. p. 88—89° (converted by warm nitric and acetic acids into the 2-bromo-4:2':4'-trinitro-compound, m. p. 127—128°), 2-bromo-2'-nitro-, b. p. 251°/27 mm., m. p. 49—50° (similarly nitrated to the 2-bromo-4:2'-dinitro-compound, m. p. 128°), 4-chloro-2-nitro-4'-methyl-, m. p. 99° (converted by warm concentrated sulphuric acid into

2-nitro-4-sulpho-4'-methyl-diphenyl ether, m. p. 129—130°, and by a mixture of acetic and nitric acids at 100° into 4-chloro-2:2'-dinitro-4'-methyl-diphenyl ether, m. p. 115°, which loses hydrogen chloride on further treatment with nitric acid at 100°, giving a substance, m. p. 146—149°, which is probably a mixture of the 2:4:2'-trinitro-compound and unchanged material), and 4-chloro-2'-nitro-4'-methyl-, m. p. 52° [converted by nitric and acetic acids at 100° into the 2:2'-dinitro-compound identical with that obtained from the isomeric 2-nitro-derivative (above)], -diphenyl ether. Prolonged treatment of 2:4-dichloro- and 2:4-dibromo-5:2':4'-trinitrodiphenyl ether causes about 8—10% elimination of hydrogen halide. Bromine in acetic acid at 100° converts 2-nitrodiphenyl ether into 4-bromo-2'-nitrodiphenyl ether, m. p. 72° (Raiford and Colbert, *loc. cit.*, give m. p. 71°). Warm nitric acid (*d* 1.5) converts 4-bromo-2':4'-dinitrodiphenyl ether into the corresponding 2:2':4'-trinitro-compound. Although 4-chloro-2'-nitro-4'-methyl-diphenyl ether readily undergoes scission with piperidine at 100° (affording *o*-nitro-*p*-tolylpiperidine) the isomeric 2-nitro-compound is much more resistant to the attack of this reagent. Nitric acid (*d* 1.5) at 0° causes scission of 4-chloro-2- (or 2'-) nitro-4'-methyl-diphenyl ether, 4-chloro-2:6-dinitrophenol being the sole product isolated. The replacement of halogen by a nitro-group in an aromatic compound is considered to be determined by three main functions, of which the first is the most important: (1) that which determines the course of ordinary aromatic substitution, (2) the tendency of the halogen to separate as an anion, and (3) the tendency of the halogen to remain in co-valent attachment to the nuclear carbon atom. All m. p. given are corrected.

J. W. BAKER.

**Difference in the action of peracids on pyrogallol under the influence of peroxidase.** J. BÖESEKEN (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 134—136).—An attempt has been made to determine whether the action of peracetic acid on pyrogallol, under the influence of the peroxidase of horse-radish, is the same in character as, although less in extent than, that of hydrogen peroxide. The results suggest that the action is probably different. The extent to which the action of perbenzoic acid resembles that of peracetic acid or of hydrogen peroxide is also still in doubt. Benzoyl peroxide is entirely inactive. This is in agreement with Wieland and Sutter's conclusion (this vol., 372) with regard to disubstituted derivatives of hydrogen peroxide.

M. S. BURR.

**Esters of cyclohexylresorcinol and *p*-cyclohexylphenol.** V. G. LILLY and C. E. GARLAND (J. Amer. Chem. Soc., 1930, 52, 2112—2114).—*cyclohexylresorcinol* is esterified only with difficulty; the *dibenzoate*, m. p. 88°, is prepared by the Schotten-Baumann reaction. *p-cyclohexylphenyl β-phenylpropionate*, m. p. 74°, *m-nitrobenzoate*, m. p. 114°, and *p-nitrobenzoate*, m. p. 137°, are obtained from sodium *p-cyclohexylphenoxide* and the acid chlorides or from the phenol and acid in presence of thionyl chloride and phosphorus trichloride; the *salicylate*, m. p. 103.5°, is prepared from the phenol and salicylic acid in presence

of thionyl chloride, or from the sodium salts with phosphoryl chloride.  
H. BURTON.

**Nitrosation of phenols. VIII. Resorcinol monoethyl ether.** H. H. HODGSON and H. CLAY  
**IX. Nitrosation of *m*-bromophenol.** H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 963—967, 967—968; cf. this vol., 209).—VIII. Resorcinol monoethyl ether on nitrosation gives mainly 6-nitroso-3-ethoxyphenol (the  $\alpha$ -*o*-nitroso-3-ethoxyphenol of Kietaihl; A., 1899, i, 343), with a little 4-nitroso-3-ethoxyphenol. Nothing corresponding with Kietaihl's  $\beta$ -*o*-nitroso-3-ethoxyphenol was isolated, nor were any products other than 6-nitro- and 4-nitro-3-ethoxyphenol isolated from the product of oxidation of the nitrosation mixture. Nitration of resorcinol monoethyl ether gives similar proportions of 6- and 4-nitro-3-ethoxyphenol (cf. Weselsky and Benedikt, A., 1881, 726). Confirmation of the constitution of 6-nitro-3-ethoxyphenol is afforded by its ethylation to 4-nitro-resorcinol diethyl ether and by synthesis from 3-chloro-4-nitrophenetole, m. p. 39—40°, itself obtained by ethylation of 3-chloro-4-nitrophenol. Ethyl-alcoholic sodium ethoxide with 1:3-dichloro-4-nitrobenzene, gives, not 4-nitroresorcinol diethyl ether, but the known 3-chloro-6-nitrophenetole. 3-Chloro-2-nitrophenol similarly gives 3-chloro-2-nitrophenetole, m. p. 52°. An explanation of these results based on current electronic theories is given.

**IX. The alleged geometrical isomerides of 3-bromobenzoquinone-4-oxime** (Hodgson and Moore, A., 1925, i, 1408) prove to have been impure specimens of one individual, which is now described as separating from benzene in pale greenish-yellow crystals, m. p. 196°. Its methyl ether (also obtainable from 3-bromo-4-nitrosophenol) has m. p. 130°. 3-Bromo-4-nitrosophenyl benzoate has m. p. 181°, and 3-bromo-4-nitrosobenzonitrile, from the aminoanisole and Caro's acid, has m. p. 69°.  
H. A. PRIGGOTT.

**Constitution of sappanin.** E. SPÄTH and K. GIBIAN (Monatsh., 1930, 55, 342—351).—Sappanin,  $C_{12}H_{10}O_4$ , m. p. (vac.) 210—211° (Schreder, A., 1872, 818), is methylated with an excess of ethereal methyl-alcoholic diazomethane to a tetramethyl ether, m. p. 74—75°, and oxidised by nitric acid to styphnic acid. Methylation with diazomethane equivalent to about three hydroxyl groups and oxidation of the product formed with 1% potassium permanganate gives some veratric acid, indicating that sappanin is 2:4:3':4'-2:6:3':4'-, or 3:5:3':4'-tetrahydroxydiphenyl. The first of these constitutions is shown to be the correct one. Treatment of 4-iodoveratrole and 1-iodo-2:4-dimethoxybenzene with copper powder (Naturkupper C) at 260° in a current of carbon dioxide gives 3:4:3':4'-, m. p. 130—132°, and 2:4:2':4'-tetramethoxydiphenyl, m. p. 93°, respectively. Similar treatment of a mixture of the above iodo-compounds affords a mixture of the above tetramethoxy-derivatives and 2:4:3':4'-tetramethoxydiphenyl, m. p. 74—75°. Demethylation of these ethers with hydriodic acid (*d* 1.7) furnishes 3:4:3':4'-tetrahydroxydiphenyl, m. p. 229—230°, 2:4:2':4'-tetrahydroxydiphenyl, m. p. 226—227° (lit. 222°), and 2:4:3':4'-tetrahydroxydiphenyl (sappanin), m. p. 210—211°.  
H. BURTON.

**Aliphatic cholesteryl esters.** I. H. PAGE and H. RUDY (Biochem. Z., 1930, 220, 304—326).—The following cholesteryl esters have been prepared (m. p. and  $[\alpha]_D^{25}$  are given): lignocerate, 87°,  $-18.7^\circ$ ; undecenoate, 79°,  $-28.3^\circ$ ; elaidate, 56°,  $-23.7^\circ$ ; petroselate, —,  $-21.9^\circ$ ; erucate, 44°,  $-20.8^\circ$ ; linoleate, 41°,  $-23.9^\circ$ ; linolenate, 49°,  $-24.3^\circ$ ; hydrogen oxalate, —,  $-32.5^\circ$ ; oxalate, 220—230° (decomp.),  $-25.8^\circ$ ; hydrogen succinate; succinate, 220°,  $-38.6^\circ$ ; hydrogen adipate, —,  $-30.6^\circ$ ; adipate, 195°,  $-36.1^\circ$ ; hydrogen suberate, 127°,  $-29.2^\circ$ ; suberate, —,  $-34.9^\circ$ ; acetolactate, 120°, —; acetoricinoleate, about 30°, —. The solubilities of these and other aliphatic esters of cholesterol in various solvents, the iodine values of the esters, and their rates of hydrolysis by alkalis have been determined. For the determination of the iodine values the method of Rosenmund and Kuhnenn (A., 1923, ii, 886) gave satisfactory results for the esters of saturated acids and with slight modifications for those of unsaturated acids also. The chlorides of petroselic, linoleic, linolenic, and acetoricinoleic acids have the following b. p. respectively: 156°/3 mm., 167—168°/2.3 mm., 170—171°/2.5 mm., 220°/2 mm. Acetoricinoleic acid has m. p. about 30°.  
W. MCCARTNEY.

**Mechanism of Salkowski's colour test for cholesterol.** V. NIKOLAIIEV and S. KRASTELEVSKI (Biochem. Z., 1930, 220, 253—258).—From equivalent amounts of cholesterol and cold 95% sulphuric acid in chloroform cholesteryl hydrogen sulphate, red plates, m. p. 160°, can be obtained. The substance is very readily hydrolysed by water with loss of colour.

W. MCCARTNEY.

**Esters of ergosterol.** H. EMERSON and F. W. HEYL (J. Amer. Chem. Soc., 1930, 52, 2015—2016).—The following esters of ergosterol [phenylcarbimide derivative, m. p. 236.5—238° (corr.)] are described: hydrogen phthalate, m. p. 169°,  $[\alpha]_D^{25} -51^\circ$  [silver salt, m. p. 170—180° (decomp.); copper salt]; m-nitrobenzoate, m. p. 151°,  $[\alpha]_D^{25} -71^\circ$ , and p-nitrobenzoate, m. p. 182°,  $[\alpha]_D^{25} -49.5^\circ$  (both prepared by the pyridine method). isoErgosteryl chloroacetate, m. p. 190°,  $[\alpha]_D^{25} -45^\circ$ , and m- and p-nitrobenzoates, m. p. 172° and 189°, respectively, are obtained when ergosterol is heated with the appropriate acid chloride.  
H. BURTON.

**Isomerides of ergosterol and dihydroergosterol.** H. LETTRÉ (Z. physiol. Chem., 1930, 189, 1—3).—The  $\gamma$ -dihydroergosterol, m. p. 206°, of Heilbron, Johnstone, and Spring (A., 1929, 1442) is shown by precipitation with digitonin, also by fractional crystallisation of the acetate, to be a mixture of epidihydroergosterol and dihydroergosterol I. The new ergosteryl acetate, m. p. 133°, of Heilbron and Sexton (A., 1929, 809) appears to be a mixture or loose combination of ergosterol and ergosteryl acetate.

J. H. BIRKINSHAW.

**Sterols of ergot.** M. C. HART and F. W. HEYL (J. Amer. Chem. Soc., 1930, 52, 2013—2015; cf. Rosenheim and Webster, A., 1929, 105).—The unsaponifiable fraction of the residue from the benzene extract of Spanish ergot contains ergosterol, the fungisterol, m. p. 144—146°, of Tanret (A., 1908 i, 637), and a sterol, m. p. 120—125°,  $[\alpha]_D^{25} -2^\circ$  (acetate, m. p. 122—125°).  
H. BURTON.

**$\alpha$ -Ergosterol and its isomerisation to  $\beta$ -ergosterol.** M. C. HART, J. H. SPEER, and F. W. HEYL (J. Amer. Chem. Soc., 1930, 52, 2016—2019).—Catalytic reduction (Adams) of ergosteryl acetate, m. p. 170—172°, in acetic acid gives  $\alpha$ -ergostenyl acetate, m. p. 110—111°,  $[\alpha]_D^{20}$  0°, which could not be isomerised to the  $\beta$ -derivative by treatment with dry hydrogen chloride in chloroform (cf. Reindel, Walter, and Rauch, A., 1927, 241). Treatment of  $\alpha$ -ergosterol, m. p. 133°,  $[\alpha]_D^{20}$  +10.5°, with acetyl chloride affords the  $\alpha$ -acetate, whilst with chloroacetyl chloride the  $\beta$ -chloroacetate (*loc. cit.*) results. Acylation of  $\alpha$ -ergosterol with acyl chlorides sometimes affords the  $\alpha$ - and sometimes the  $\beta$ -derivative. The following are described:  $\alpha$ -ergostenyl dichloroacetate, m. p. 114°, benzoate, m. p. 117.5°, m-nitrobenzoate, m. p. 165°, and p-nitrobenzoate, m. p. 178°;  $\beta$ -ergostenyl trichloroacetate, m. p. 128°, propionate, m. p. 114—115°,  $\alpha$ -bromopropionate, m. p. 104.5°, and butyrate, m. p. 74—75°.  $\alpha$ -Ergostenyl trichloroacetate, m. p. 133.5°, propionate, m. p. 90°, and butyrate, m. p. 67—68°, are prepared by the pyridine method.

H. BURTON.

**Synthesis of 2-chloro-5-aminobenzoic acid.** N. A. NARISCHKIN (Ukraine Chem. J., 1929, 4, 525—530).—The yield of chloroaminobenzoic acid obtained by the reduction of 2-chloro-5-nitrobenzoic acid is the same (62—81%) whether stannous chloride and hydrochloric acid or tin and hydrochloric acid are used. Higher yields (90—94%) are obtained using Fierz-David's method of reduction by zinc dust in acetic acid.

R. TRUSZKOWSKI.

**Structure of the salts of aromatic nitriles.** F. W. UPSON, R. T. MAXWELL, and H. M. PARMELEE (J. Amer. Chem. Soc., 1930, 52, 1971—1975; cf. A., 1922, i, 343).—Phenylacetonitrile is added gradually to powdered sodium in gently boiling ether in absence of moisture, oxygen, and carbon dioxide, the mixture warmed until all the sodium dissolves, then cooled to 20°, and a small amount of sodium cyanide removed by filtration; the filtrate deposits slowly pure sodio-phenylacetonitrile (cf. Rising and others, A., 1928, 881; 1929, 312). Toluene is isolated from the mother-liquors. The changes occurring are:  $\text{CHPh}\cdot\text{C}\cdot\text{NH} + \text{Na} \rightarrow \text{CHPh}\cdot\text{C}\cdot\text{N}\cdot\text{Na} \xrightarrow{\text{H}_2} \text{Ph}\cdot\text{Me} + \text{NaNC}$ . When the sodio-derivative is heated rapidly, stilbene and sodium cyanide are produced. Atmospheric oxidation gives benzoic acid and sodium cyanide. The sodio-derivative condenses with phenyl styryl ketone in methyl-alcoholic solution, forming 97% of the theoretical amount of  $\gamma$ -cyano- $\alpha$ -dibenzoyl- $\beta$ - $\gamma$ -tri-phenylpentane, m. p. 264.5—265.5° (corr.) (lit. 257°). The sodio-derivative and alcoholic silver nitrate give an impure silver salt, which explodes when heated. Treatment of this with butyl iodide at the ordinary temperature and evaporation of the product formed with hydrochloric acid affords butylamino hydrochloride.

All the above reactions support the imide structure  $\text{CHPh}\cdot\text{C}\cdot\text{N}\cdot\text{Na}$ , for the sodio-derivative.

H. BURTON.

**Occurrence of free radicals in chemical reactions.** VI. Thermal fission of acyl peroxides. H. WIELAND and G. RAZUBAIEV (Annalen,

1930, 480, 157—172).—Thermal decomposition of acyl peroxides in solution is considered not to involve the formation of free radicals (cf. Gelissen and Hermans, A., 1925, i, 663; 1926, 63); reaction between the peroxide and the solvent probably occurs (cf. Meisenheimer and Link, this vol., 769). Successive treatment of p-phenylbenzoyl chloride in acetone with 10% hydrogen peroxide and N-potassium hydroxide affords p-phenylbenzoyl peroxide, m. p. 171° (decomp.). This is more stable than benzoyl peroxide; it decomposes in boiling xylene (not in benzene), yielding carbon dioxide (90.5%), diphenyl (65.7%), an acid, m. p. 217—222° (79.3%), and p-phenylbenzoic esters (=24.8% of acid). Cinnamoyl peroxide, decomp. 133°, and boiling benzene afford carbon dioxide (92%), cinnamic acid (11.8%), and an amorphous, polymerised styryl cinnamate, hydrolysed by 10% alcoholic potassium hydroxide to cinnamic and other acids. In this case, practically no reaction occurs between the peroxide and benzene. When benzoyl peroxide is decomposed in dioxan at 100°, only 42.7% of carbon dioxide is eliminated; a considerable amount of benzoic acid is formed, probably by the reducing action of the dioxan.

Decomposition of a series of as-peroxides,  $\text{RO}\cdot\text{OBz}$  (where R is a substituted benzoyl group), in benzene or toluene gives a much greater proportion of the acid  $\text{R}\cdot\text{OH}$  than of benzoic acid. Benzoyl p-phenylbenzoyl peroxide, m. p. 140° (slight decomp.), prepared from p-phenylbenzoyl chloride and sodium benzoyl peroxide in acetone, decomposes in toluene at 75—100°, yielding diphenyl, 4-methyldiphenyl, and p-phenylbenzoic and benzoic acids (free and combined); the molecular ratio of the acids is 2:3:1. Benzoyl p-chlorobenzoyl peroxide, m. p. 85°, benzoyl anisoyl peroxide, m. p. 73—74°, and benzoyl p-nitrobenzoyl peroxide, m. p. 113—115° (decomp.), decompose similarly in benzene, yielding diphenyl, the substituted diphenyl, benzoic acid, and the substituted benzoic acid (main product). Benzoyl acetyl peroxide decomposes in boiling benzene to carbon dioxide, methane, diphenyl, and about 50% of a mixture of benzoic and acetic acids (ratio, about 9). Benzoyl cinnamoyl peroxide has m. p. 92—93° (decomp.). Triphenylacetyl peroxide could not be isolated. H. BURTON.

**Stereochemistry of diphenyl compounds.** VI. Preparation and resolution of 2:4:6:2':4'-pentanitrodiphenyl-3-carboxylic acid. H. A. STEARNS and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 2070—2075).—Treatment of a mixture of 3-bromo-2:4:6-trinitrotoluene and 1-chloro-2:4-dinitrobenzene with copper bronze in nitrobenzene solution at 160—165° gives 2:4:6:2':4'-pentanitro-3-methyldiphenyl, m. p. 200—201°, oxidised by a mixture of sodium dichromate, 20% fuming sulphuric acid, and nitric acid (d 1.52) to 2:4:6:2':4'-pentanitrodiphenyl-3-carboxylic acid, m. p. 205—206°. This is resolved by means of strychnine into the d-acid, m. p. 229—231°,  $[\alpha]_D^{20}$  +98.8° in acetone (strychnine salt, m. p. 222—226° after turning red at 203—205°,  $[\alpha]_D^{20}$  +84.4° in pyridine), and l-acid, m. p. 233°,  $[\alpha]_D^{20}$  -105.3° in acetone (strychnine salt, m. p. between 270° and 280° (decomp.),  $[\alpha]_D^{20}$  -123.5° in pyridine). These acids are not racemised to any extent by

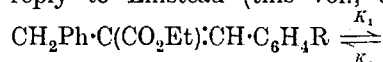
heating with acetic acid alone, or containing hydrochloric acid, or 5% ammonium carbonate solution. The factors affecting ease of racemisation of 2 : 6 : 2'-trisubstituted diphenyls are discussed. H. BURTON.

**Tervalent carbon. II.** H. ASPELUND (Ber., 1930, **63**, [B], 1191—1197; cf. Acta Acad. Aboensis, 1929, v, 1).—Benzoyldiphenylacetylhydrazide chloride is slowly converted by thionyl chloride into *benzoyldiphenylchloroacetylhydrazide chloride*,  $\text{C}_6\text{H}_5\text{Cl}\cdot\text{CCl}\cdot\text{N}\cdot\text{N}\cdot\text{CClPh}$ , m. p. 91.5°, which loses halogen when shaken with mercury in presence of benzene and oxygen, yielding the *peroxide*,  $[\cdot\text{O}\cdot\text{C}_6\text{H}_5\cdot\text{CCl}\cdot\text{N}\cdot\text{N}\cdot\text{CClPh}]_2$ , m. p. 167—168° (decomp.), tetraphenylsuccinonitrile, benzonitrile, and a halogen-free substance, m. p. 199°. The peroxide is converted by hydrazine hydrate into 3-phenyl-6-hydroxydiphenylmethyltetrazine, m. p. 134—135°, and by concentrated sulphuric acid into phenyl phenylfurodiazyl ketone, m. p. 139°. In the absence of air, elimination of chlorine from the chloroacetylhydrazide chloride leads to a complete alteration of the radical and production of diphenylsuccinonitrile and benzonitrile. In presence of hydrazobenzene and absence of air, elimination of chlorine leads more slowly to the same products, whereas in presence of *p*-benzoquinone the *compound*,  $\text{C}_6\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_5\cdot\text{CCl}\cdot\text{N}\cdot\text{N}\cdot\text{CClPh})_2$ , m. p. 175—176° (slight decomp.), and tetraphenylsuccinonitrile are formed.

*Phenylfurodiazyl diphenylmethyl chloride*,

$\text{C}_6\text{H}_5\text{Cl}\cdot\text{C}\begin{smallmatrix} \text{N}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{O} \end{smallmatrix}\cdot\text{O}\cdot\text{Ph}$ , m. p. 117°, prepared from benzoyldiphenylacetylhydrazide chloride and thionyl chloride and identified by conversion into the corresponding carbinol, is transformed by mercury into the corresponding peroxide. It is much more readily hydrolysed by water than is benzoyldiphenylchloroacetylhydrazide chloride. H. WREN.

**Symmetrical triad prototropic systems. VI.** Effect of substitution on tautomeric mobility and equilibrium in the  $\alpha\gamma$ -diphenylpropene system. C. W. SHOPPEE (J.C.S., 1930, 968—985).—In part a reply to Linstead (this vol., 64). In the system



$\text{CHPh}\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{R}$ , where R is a *p*-substituent and in which the tautomeric interchange is effected by the usual catalysts (cf. Ingold and Shoppee, A., 1929, 556, 927), the sum of the velocity coefficients ( $K_1 + K_2$ ) increases in the series  $p\text{-NMe}_2 < \text{OMe} < \text{I} < \text{Br} < \text{Cl}$ , being paralleled by the molecular electric moments of the compounds  $\text{C}_6\text{H}_5\text{R}$ . The position of equilibrium, however, is slightly anomalous in the series  $p\text{-NMe}_2\text{Et} > \text{OMe} > \text{Br} > \text{Cl} > \text{Me}$  (in order of decreasing proportion of the left-hand isomeride), in that the middle members of the series (R = OMe, Br, and Cl) are inverted among themselves. The cause of this anomaly has not yet been explained.

$\alpha$ -*p*-Methylbenzylcinnamic acid, m. p. 181° (ethyl ester, b. p. 178—180°/1 mm., 197—198°/6 mm.), is prepared by the Perkin condensation from benzaldehyde and sodium  $\beta$ -*p*-tolylpropionate.  $\alpha$ -Benzyl-*p*-methylcinnamic acid, m. p. 200° (ethyl ester, b. p. 205—207°/7 mm.,  $n_D^{20}$  1.58415), was similarly obtained from sodium  $\beta$ -phenylpropionate and *p*-tolualdehyde. Starting from the appropriate aldehyde and aryl-

propionic acid, the following were prepared:  $\alpha$ -*p*-chlorobenzylcinnamic acid, m. p. 194.5° (ethyl ester, b. p. 197°/3 mm., m. p. 55°); *p*-chloro- $\alpha$ -benzylcinnamic acid, m. p. 171.5° (ethyl ester, b. p. 208°/6 mm.);  $\alpha$ -*p*-bromobenzylcinnamic acid, m. p. 200° (ethyl ester, b. p. 200°/1 mm.); *p*-bromo- $\alpha$ -benzylcinnamic acid, m. p. 193° (ethyl ester, b. p. 200°/3 mm.);  $\alpha$ -*p*-iodobenzylcinnamic acid, m. p. 219.5° (ethyl ester, b. p. 212—214°/2 mm., m. p. 46.5°); *p*-iodo- $\alpha$ -benzylcinnamic acid, m. p. 232° (ethyl ester, m. p. 53.5°);  $\alpha$ -*p*-dimethylaminobenzylcinnamic acid, m. p. 146° (ethyl ester, m. p. 62.5°); *p*-dimethylamino- $\alpha$ -benzylcinnamic acid, m. p. 232° (decomp.). Silver  $\alpha$ -*p*-dimethylaminobenzylcinnamate with an excess of ethyl iodide gives a molecular compound of silver iodide and *p*- $\beta$ -carbethoxy- $\gamma$ -phenylallylphenyldimethylammonium iodide, m. p. 155—156°. The *picrate*, m. p. 130°, was obtained by decomposing this with silver hydroxide and adding picric acid. A substance with the properties and reactions of the betaine was isolated in an impure state. *p*-Acetamidobenzaldehyde, sodium  $\beta$ -phenylpropionate, and acetic anhydride at 180—200° gave an *acid*, m. p. 267°;  $\beta$ -*p*-acetamidophenylpropionic acid (*monohydrate*, m. p. 124° after softening at 87—88°), and benzaldehyde gave an *acid*, m. p. 233—234°.  $\beta$ -*p*-Iodophenylpropionic acid (Gabriel and Herzberg, A., 1883, 1123) is most conveniently prepared from  $\beta$ -phenylpropionic acid and iodine monochloride. H. A. PIGGOTT.

**"Superfluous" isomerides. II.** The two  $\beta\beta\beta$ -triphenylpropionitriles of Fosse. E. BERGMANN and H. A. WOLFF (Ber., 1930, **63**, [B], 1176—1180; cf. this vol., 902).—The two isomeric compounds obtained by Fosse (A., 1907, i, 764) are identified as  $\beta\beta\beta$ -triphenylpropionitrile, m. p. 140°, and *ketentriphenylmethylimine*,  $\text{CH}_2\cdot\text{C}\cdot\text{N}\cdot\text{CPh}_3$ , m. p. 211°. The reactions are formulated:  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CN} + \text{CPh}_3\cdot\text{OH} \rightarrow \text{CO}_2\text{H}\cdot\text{CH}(\text{CN})\cdot\text{CPh}_3 \rightarrow \text{CPh}_3\cdot\text{CH}_2\cdot\text{CN}$  and  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{C}\cdot\text{NH} + \text{CPh}_3\cdot\text{OH} \rightarrow \text{CO}_2\text{H}\cdot\text{CH}\cdot\text{C}\cdot\text{N}\cdot\text{CPh}_3 \rightarrow \text{CH}_2\cdot\text{C}\cdot\text{N}\cdot\text{CPh}_3$ .  $\beta\beta\beta$ -Triphenylpropionyl chloride is converted into the corresponding amide, m. p. 198°, which, when treated with phosphoryl chloride and phosphorus pentachloride, gives  $\beta\beta\beta$ -triphenylpropionitrile, m. p. 140°. The proof of the constitution of *ketentriphenylmethylimine* rests on its hydrolysis by boiling dilute sulphuric acid to triphenylcarbinol, ammonia, and acetic acid.

A concentrated ethereal solution of triphenylmethyl azide and triphenylphosphine deposits the additive *compound*  $\text{PPh}_3\cdot\text{Ph}_3\text{CN}_3$ , m. p. 104—105°, which is completely dissociated in benzene; elimination of nitrogen causes the production of a black resin.

Diphenyl- $\alpha$ -naphthylcarbinol and cyanoacetic acid at 140—160° afford 9-phenyl-1 : 2-benzofluorene.

H. WREN.

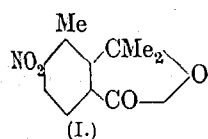
**Action of Grignard reagents on phthalide.** J. ALGAR and A. V. FLAEGEL (Proc. Roy. Irish Acad., 1930, **39**, 351—357).—Magnesium *o*-anisyl bromide reacts with phthalide in ethereal benzene solution to give  $\alpha$ -hydroxy- $\alpha$ -*o*-anisyl-3 : 4-benzo-2 : 5-dihydrofuran, m. p. 85—95° (decomp.), reduced in methyl-alcoholic solution by sodium amalgam to 2-methoxy-2'-methyl-diphenylcarbinol, m. p. 95—96°. By using twice the quantity of magnesium *o*-anisyl bromide 2' : 2"-di-



*methoxy-2-hydroxymethyltriphenylcarbinol*, m. p. 160—160.5°, is produced, dehydrated by treatment in glacial acetic acid solution with dry hydrochloric acid to 2:2-di-*o*-anisyl-3:4-benzo-2:5-dihydrofuran, m. p. 128—130°.

A. I. VOGEL.

**Cannabis Indica resin. I. Constitution of nitrocannabinolactone (oxycannabin).** R. S. CARR (J.C.S., 1930, 986—992).—The empirical formula  $C_{11}H_{11}O_4N$  of Wood, Spivey, and Easterfield (*ibid.*, 1899, 75, 20) has been confirmed, and an improved method for the preparation of aminocannabinol is described. This, on treatment with nitrous acid, gives *hydroxycannabinolactone*, m. p. 198—199° (*methyl ester*, m. p. 182°; *acetyl derivative*, m. p. 93°), obtained as a pale yellow substance that could, however, be recovered colourless from a low-temperature fusion with potassium hydroxide. When fused with potassium hydroxide at 290—300° it gives 6-hydroxy-*m*-toluic acid, a little cresol, and acetone.



Nitrocannabinolactone is therefore concluded to be 5-nitro-6-methyl- $\alpha$ -dimethylphthalide (I), which is more in agreement with the results of alkali fusion than the nitrotolyl- $\gamma$ -butyrolactone

formulae of Wood and collaborators (*loc. cit.*) and also explains the formation of a tribasic acid, most probably nitrobenzene-2:3:4-tricarboxylic acid (the alternative, nitrotrimellitic acid, is described by Schultz, A., 1909, i, 897), observed by these investigators.

As an example of a similar degradation of an  $\alpha$ -dimethylphthalide, the alkali fusion of 4-hydroxy- $\alpha$ -dimethylphthalide, m. p. 152° (*methyl ether*, m. p. 100°; *acetyl derivative*, m. p. 84°), prepared from the 4-amino-compound (Teppema, A., 1923, i, 256) gives *n*-hydroxybenzoic acid, acetone, and some phenol. When heated with aniline at 300° it gives 4-hydroxy-*N*-phenyl- $\alpha$ -dimethylphthalimidine (+1H<sub>2</sub>O; +1MeOH), m. p. (anhydrous) 214—215° (*acetyl compound*, m. p. 215°), also produced in a less pure state by the use of aniline and its hydrochloride at 210°. Bromination of the phthalide gives 3:5-dibromo-4-hydroxy- $\alpha$ -dimethylphthalide, m. p. (anhydrous) 125° (+1H<sub>2</sub>O) indefinite.

H. A. PIGGOTT.

**Addition of halogens to unsaturated acids and esters. III. Velocity of bromine addition.**

N. W. HANSON and D. M. WILLIAMS (J.C.S., 1930, 1059—1063).—The velocities of bromine addition to methyl *m*- and *p*-methoxycinnamates have been found to be of the same order as in the case of *o*-methoxycinnamic acid, i.e., several hundred times as great as to cinnamic acid (cf. Williams and James, A., 1928, 412). The nitro-groups in *o*-, *m*-, and *p*-nitrocinnamic acids, on the other hand, have an inhibiting effect, but this inhibition disappears when hydrogen bromide is added at the start. Hence it is concluded that the hydrogen bromide set free by nuclear bromination (considerable in the case of the methoxycinnamates) is responsible for the autocatalysis of the reaction. Substitution by halogens in the  $\alpha$ -position completely inhibits addition ( $\alpha$ -bromo-,  $\alpha$ -chloro-,  $\beta$ -dibromo-, and  $\beta$ -chloro- $\alpha$ -bromocinnamic acids: both forms in every case) even in the presence of hydrogen bromide, whereas a  $\beta$ -halogen atom does not

materially affect the rate ( $\beta$ -bromo- and  $\beta$ -chlorocinnamic acids, both *cis* and *trans* in each case). In every case addition of bromine occurs more readily to the *cis*- than to the *trans*-form; thus methyl fumarate in the presence of hydrogen bromide reacts only very slowly, whilst methyl maleate reacts very rapidly but is simultaneously partly converted into the fumarate.

H. A. PIGGOTT.

**Structural isomerides of bromo- $\beta$ -benzoylacrylic acid.** G. P. RICE (J. Amer. Chem. Soc., 1930, 52, 2094—2100).—Bromosuccinic anhydride and benzene react in presence of aluminium chloride, forming  $\alpha$ -bromo- $\beta$ -benzoylpropionic acid, m. p. 118°. Similarly, bromomaleic anhydride furnishes  $\alpha$ -bromo- $\beta$ -benzoylacrylic acid, m. p. 129° (*methyl ester*, b. p. 198—200°/25 mm.), and a small amount of the  $\beta$ -bromo-acid, m. p. 109°. The last-named acid is identical with the  $\alpha$ -bromo-acid of Bogert and Ritter (A., 1925, i, 816). Ozonisation of  $\alpha$ -bromo- $\beta$ -benzoylacrylic acid gives phenylglyoxal, treatment with ethereal diazomethane affords 5(or 4)-benzoylpyrazole-4(or 5)-carboxylic acid, m. p. 218° (decomp.), and saturation of a methyl-alcoholic solution with hydrogen chloride yields methyl  $\alpha$ -chloro- $\beta$ -benzoylacrylate. Treatment of  $\beta$ -benzoylacrylic acid with bromine in chloroform or acetic acid solution gives a mixture of  $\alpha\beta$ -dibromo- $\beta$ -benzoylpropionic acids, m. p. 148° and 150° (cf. Bogert and Ritter, *loc. cit.*) (corresponding methyl esters, m. p. 48° and 58°, respectively). Elimination of hydrogen bromide from the mixture of the dibromo-acids affords  $\beta$ -bromo- $\beta$ -benzoylacrylic acid of m. p. 109° (*methyl ester*, m. p. 86°). Bromination of methyl  $\beta$ -benzoylacrylate in carbon disulphide gives a liquid mixture of dibromides, which on treatment with potassium acetate in methyl alcohol furnishes a liquid mixture of methyl  $\beta$ -bromo- $\beta$ -benzoylacrylates. Exposure of this liquid to sunlight gives the above ester, m. p. 86°, as the sole product; the same ester is gradually deposited when the oil is kept.

The bromo-derivatives of 5-bromo-2:4-dimethoxybenzoylacrylic acid and its esters (Rice, A., 1928, 756) are all  $\beta$ -compounds.

H. BURTON.

**Conversion of coumarins into *o*-coumaric acids.** R. N. SEN and D. CHAKRAVARTI (J. Indian Chem. Soc., 1930, 7, 247—250).—When a dilute alkaline solution of a coumarin (containing a negative substituent in the 6-position) is boiled with a small amount of mercuric oxide, the coumarinate which is first formed undergoes inversion to the coumarate; the mercuric oxide is recovered unchanged. The following *o*-coumaric acids are prepared: 5-nitro-, decomp. 245—247°; 5-aldehydo-, decomp. 220° (*phenylhydrazone*, decomp. 237°; *semicarbazone*, decomp. 275°); 5-iodo-, decomp. 187°; 3:5-dichloro-, decomp. 242°, and 3:5-dibromo-, decomp. 230° (lit. 238°). The nitro- and dihalogeno-*o*-coumaric acids are also obtained when a solution of the requisite coumarin in sodium hydroxide is neutralised (or acidified) with acetic acid and then treated with aqueous mercuric acetate; the resulting precipitate is dissolved in alkali hydroxide and the solution acidified. Similar treatment of coumarin gives di-(acetoxymercuri)-*o*-coumaric acid, which when boiled

with dilute hydrochloric acid affords *o*-coumaric acid (cf. this vol., 487). Treatment of 4:6-dimethylcoumarin with mercuric oxide in alkaline solution and subsequent acidification with acetic acid furnishes 8-acetoxymercuri-4:6-dimethylcoumarin.

H. BURTON.

[Transformation of ethyl oxindonecarboxylate into a naphthalenecarboxylic ester.] F. ARNDT (Ber., 1930, 63, [B], 1180; cf. Hantzsch and Czapp, this vol., 599).—The transformation is effected by addition of diazomethane under the influence of methyl alcohol to the carbonyl group; this adds methylene to the intermediate step,  $>C<\overset{O}{\underset{CH_2}{\text{O}}}$ . The

vicinal ring carbon atom wanders to the methylene and the cyclic  $\cdot CO\cdot CH_2$  undergoes enolisation and subsequent methylation.

H. WREN.

**Spatial configuration of molecules.** (MME.) RAMART-LUCAS and J. HOCH (Ann. Chim., 1930, [x], 13, 385—422).—The configuration of both aryl-maleic and -fumaric acids can be determined by cyclisation, the former yielding anhydrides and the latter indones. Further, the absorption curve in the ultra-violet of the *cis* (maleic) form is nearer the visible part of the spectrum than the *trans* (fumaric) form.

When ethyl phenylbromoacetate is slowly added at the ordinary temperature to sodamide suspended in ether, the mixture heated at 30° for 2 hrs., and then poured on ice, the ethereal layer yields first ethyl diphenylsuccinate, m. p. 141°, and then ethyl diphenylmaleate (I), m. p. 53°, in 45% yield, whilst the aqueous solution gives diphenylsuccinic anhydride, m. p. 158° (anilic acid, m. p. 174°). Hydrolysis of I with alcoholic potassium hydroxide yields diphenylmaleic anhydride; reduction with zinc and hydrochloric acid in alcoholic solution affords the two ethyl diphenylsuccinates, m. p. 84° (10—30% yield) and 141° (50—65% yield), respectively, separated by crystallisation from alcohol. Similarly, methyl phenylbromoacetate, b. p. 154—155°/28 mm., gives methyl diphenylmaleate (II), m. p. 107°, and methyl diphenylsuccinate, m. p. 224° (lit. 219.5°). Attempts to prepare II from diphenylmaleic anhydride were unsuccessful. Addition of alcoholic potassium hydroxide to phenylbromoacetonitrile at -15° affords diphenylmaleonitrile, m. p. 160°, in 50% yield. *m*-Tolylbromoacetonitrile and excess of alcoholic potassium hydroxide react to give *di-m*-tolylmaleic anhydride, m. p. 97° (anilic acid, m. p. 144°), in 30% yield. This is converted by the theoretical quantity of aqueous potassium hydroxide into the potassium salt, which when heated with methyl iodide at 100° gives methyl *di-m*-tolylmaleate, m. p. 93°. The latter is reduced by zinc and hydrochloric acid to two isomeric methyl *di-m*-tolylsuccinates, m. p. 149—150° and 119—120°, respectively. *Di-p*-tolylmaleic anhydride, m. p. 168° (anilic acid, m. p. 174—175°), is similarly prepared in 10—20% yield from *p*-tolylbromoacetonitrile and is likewise converted into methyl *di-p*-tolylmaleate, m. p. 89°.

By the action of ultra-violet light in 95% alcoholic solution, the following substances were obtained. Ethyl diphenylmaleate gives ethyl diphenylfumarate, m. p. 76° (hydrolysed to the acid, m. p. 288—289°, and reduced by zinc and hydrochloric acid to the two

ethyl diphenylsuccinates, m. p. 141° and 84°, respectively), and an acid, probably 2-phenylindone-3-carboxylic acid (III), m. p. 315°. The methyl ester gives similar results. Sodium diphenylmaleate and also diphenylmaleic acid give the acid, m. p. 315°; further illumination of ethyl diphenylfumarate affords an ester, m. p. 89°, hydrolysed to III. Methyl *di-m*-tolylmaleate similarly yields first methyl *di-m*-tolylfumarate, m. p. 114—115°, and then a methyl *m*-tolylmethylindonecarboxylate (acid, m. p. 325°). Methyl *di-p*-tolylmaleate is likewise converted into methyl *di-p*-tolylfumarate, m. p. 150°.

The absorption curves in the ultra-violet of all the maleic and fumaric isomerides have been determined.

A. I. VOGEL.

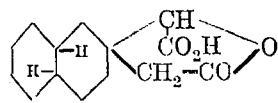
**Stereochemistry of diphenyl compounds.** V. Preparation and resolution of 2:4:6:2':4':6'-hexanitrodiphenyl-3:3'-dicarboxylic acid. L. H. BOCK, W. W. MOYER, and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 2054—2060).—Treatment of 3-bromo-2:4:6-trinitrotoluene with copper-bronze in nitrobenzene solution at 175—183° affords 2:4:6:2':4':6'-hexanitrodi-*m*-tolyl, m. p. 240—241°, oxidised by a mixture of sodium dichromate, 20% fuming sulphuric acid, and nitric acid (*d* 1.52) below 30° to 2:4:6:2':4':6'-hexanitrodiphenyl-3:3'-dicarboxylic acid, m. p. 292—293°. Resolution of this is effected by strychnine into the *d*-acid,  $[\alpha]_D^{25} +79.67$  in 5% sodium hydrogen carbonate (strychnine salt, decomp. above 250°,  $[\alpha]_D^{25} +60$  in pyridine), and *l*-acid, m. p. 230—240° (decomp.),  $[\alpha]_D^{25} -80.5$  in 5% sodium hydrogen carbonate (strychnine salt, decomp. above 250°,  $[\alpha]_D^{25} -74.7$  in pyridine). These acids are not racemised by heating with acetic acid or ammonium carbonate solution.

*Di-m*-tolyl can be nitrated only to a tetranitro-derivative, m. p. 234° (corr.). Hydrolysis of 4:4'-dicyanodi-*m*-tolyl with 60% sulphuric acid at 160° and nitration of the impure acid so obtained afford a tetranitrodi-*m*-tolyl-4:4'-dicarboxylic acid, m. p. 330—350° (decomp.) according to the rate of heating.

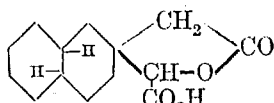
H. BURTON.

**"Strainless" rings.** II. Effect of the *trans*-decalin nucleus on the carbon tetrahedral angle. K. A. N. RAO (J.C.S., 1930, 1162—1184).—Ethyl hydrogen *trans*-decalin-2:2-diacetate (corresponding methyl ester and its silver salt described) is converted by phosphorus pentachloride into the chloride, which is treated with bromine and then with ethyl alcohol, when the monobromo-ester  $C_9H_{16}>C(CH_2\cdot CO_2Et)\cdot CHBr\cdot CO_2Et$  is formed [partly converted by distillation even under reduced pressure (b. p. 180—200°/2 mm.) into the lactonic ester] together with some of the acid monobromo-ester. The neutral monobromo-ester is hydrolysed by boiling sodium carbonate solution (saturated at 105°) to two stereoisomerides *A* (I), m. p. 156° (aniline salt, m. p. 126°; monoanilide, m. p. 154°), and *B* (type I), m. p. 163° (aniline salt, m. p. 147°; monoanilide, m. p. 172°), of the lactone of *trans*-decalin-2-acetic-2-glycolic acid (separated by fractional precipitation of a benzene solution with light petroleum), whilst the remaining two possible stereoisomerides *C* (II), m. p. 165—166° (monoanilide, m. p. 166°), and *D* (type II), m. p. 132° (aniline salt, m. p. 122°) (separated by fractionation of

their ethyl esters, b. p. 210—211°/6 mm. and b. p. 215°/6 mm., respectively, and subsequent hydrolysis and fractional precipitation as for the A and B forms), are obtained by similar hydrolysis of the acid monobromo-ester.

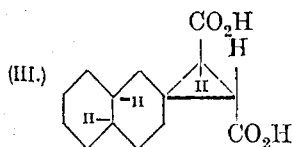


(I.)

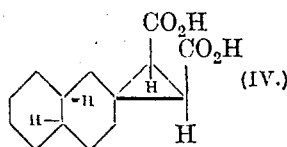


(II.)

Hydrolysis of either the neutral or acid monobromo-ester with 64% potassium hydroxide at 150° affords a mixture of three stereoisomerides of trans-decalin-β-spirocyclopropane-1:2-dicarboxylic acid. The trans-forms were roughly separated from the cis-forms by means of benzene, the latter being more soluble; the trans-A-form (III), m. p. 264° (least soluble) [dianilide, m. p. 307° (decomp.)], and the trans-B-form (type III), m. p. 250° (dianilide, m. p. 303°), were separated by fractional crystallisation from aqueous acetone. Esterification of the residue from benzene and hydrolysis of the fraction, b. p. 200°/7 mm., yields the cis-A-form (IV), m. p. 185—186° with the formation of the cis-anhydride, m. p. 107°, which is also obtained by distilling either of the trans-acids. The fourth possible isomeride (cis) was not obtained. Both the trans-spiro-acids are stable to 5% hydrochloric acid at 240°, but are completely decomposed by 10% hydrochloric acid at 240° or by 20% acid at 200°. Hydrolysis of the ester fractions, b. p. 214—215°/7 mm., and b. p. 224°/7 mm., affords the lactonic esters C and A (above), respectively.



(III.)



(IV.)

Dibromination of trans-decalin-2:2-diacetic acid with phosphorus pentachloride and bromine (2:2 mols.) at 50—60° affords trans-decalin-2:2-dibromoacetic acid, m. p. 199° (decomp.), the ethyl ester of which is converted by hydrolysis with boiling 64% potassium hydroxide solution into α-keto-trans-decalin-2:2-diacetic acid, m. p. 156° (49%) [quinoxaline derivative, m. p. 230°; semicarbazone of the monosodium salt +0.5H<sub>2</sub>O and anhydrous, m. p. 255° (decomp.)]; methyl ester, b. p. 228°/21 mm.; phenylhydrazone of methyl ester, m. p. 235° (decomp.)], together with a small quantity (4%) of Δ<sup>2</sup> (or Δ<sup>1</sup>)-trans-octahydronaphthalene-2-acetic acid, m. p. 100—101° (see below) (dibromide, m. p. 183°), the eliminated side-chain being isolated as oxalic acid. No hydroxy-spiro-acid is obtained. Oxidation of the keto-acid with hydrogen peroxide in sodium carbonate converts it into 2-carboxy-trans-decahydronaphthalene-2-acetic acid, m. p. 197° (A., 1929, 1297). Hydrolysis of the dibromo-ester with boiling methyl-alcoholic potassium hydroxide affords a mixture of trans-decalin-β-spiro-trans-1-methoxycyclopropane-1:2-dicarboxylic acid, B, m. p. 213° [converted into the keto-acid on boiling with hydrobromic acid (d 1.45)], and the corresponding cis-A-methoxy-acid, m. p. 204°, with formation of the cis-anhydride, m. p. 145°. These two acids probably

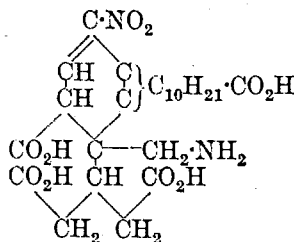
do not belong to the same series, since the trans-acid could not be converted into the cis-anhydride. trans-β-Decalone condenses with ethyl bromoacetate and zinc to give ethyl 2-hydroxy-trans-decalin-2-acetate, b. p. 179—180°/20 mm.,  $d_4^{25}$  1.045,  $n_D^{25}$  1.4832, which is dehydrated by heating with phosphorus oxychloride in dry benzene to the ethyl ester, b. p. 170/24° mm., of Δ<sup>1</sup> (or Δ<sup>2</sup>)-trans-octahydronaphthalene-2-acetic acid (above). Hydrolysis of the hydroxy-ester with 50% potassium hydroxide gives 2-hydroxy-trans-decalin-2-acetic acid, m. p. 102°, converted by boiling with acetic anhydride into trans-decahydronaphthylidene-2-acetic acid, m. p. 145° (dibromide, m. p. 170°). This αβ-acid is converted into the βγ-isomeride by boiling with 64% potassium hydroxide solution. The similar stability of these spiro-derivatives of (strainless) trans-decalin and of the analogous cyclopentane (Becker and Thorpe, J.C.S., 1920, 117, 1584) and cycloheptane (Baker and Ingold, *ibid.*, 1923, 123, 127; Baker, A., 1925, i, 1277) derivatives suggests that the average condition of cyclohexane is one possessing considerable strain.

J. W. BAKER.

**New hydroxydiaralkylsuccinic anhydride.** P. CORDIER (Compt. rend., 1930, 190, 1191—1193).—Short treatment of α-benzylidene-α'-benzylsuccinic acid with acetic anhydride at 100° (bath) gives the normal anhydride, m. p. 132°, whilst prolonged treatment with boiling acetic anhydride affords α-hydroxy-α'-dibenzylsuccinic anhydride, m. p. 55° (methyl ether, m. p. 56°). The hydroxy-anhydride is soluble in alkali without undergoing ring fission. Such fission does, however, occur with an excess of alkali, but acidification of the resulting solution regenerates the anhydride. For hydroxy-anhydride formation to occur, it appears necessary that succinic acid should be diaralkylated in the αα'-positions (A., 1929, 1273).

H. BURTON.

**Bile acids. XXVII.** M. SCHENCK and H. KIRCHHOFF (Z. physiol. Chem., 1930, 189, 85—96; cf. this vol., 474).—The action of concentrated sulphuric acid on the blue nitroso-compound obtained by the action of nitric acid on bilianic acid oximelactam regenerates the oximelactam. From the nitroso-compound obtained from bilianic acid dioxime sulphuric acid was expected to produce in like manner bilianic acid monoxime. Although this was not isolated, evidence of its formation was obtained. The prolonged action of nitric acid on bilianic acid oximelactam or its nitroso-derivative gives a compound, C<sub>24</sub>H<sub>38</sub>O<sub>10</sub>N<sub>2</sub>, which appears to contain an amino-



group. It titrates as tetrabasic. The probable constitution is shown in the annexed formula, but the formula may be C<sub>24</sub>H<sub>38</sub>O<sub>10</sub>N<sub>2</sub> (double linking eliminated). The action of sulphuric acid gives a product, m. p. 196° (not sharp).

J. H. BIRKINSHAW.

**Manufacture of compounds having hydrogenated ring-systems.** I. G. FARBERIND. A.-G., Ascees. of O. DIELS and K. ALDER.—See B., 1930, 549.

**Chloroimines. I. *o*-Chlorobenzylidenechloroimine and anisylidenechloroimine.** C. R. HAUSER and M. L. HAUSER (J. Amer. Chem. Soc., 1930, 52, 2050—2054).—Condensation of *o*-chlorobenzaldehyde and anisaldehyde with monochloroamine in cold aqueous solution gives the corresponding *chloroimines* (*N*-chloroaldimines), m. p. 28—29° and 43—44°, respectively. The former of these is the more stable, but both compounds liberate hydrogen chloride slowly at the ordinary temperature, furnishing the corresponding nitrile. When heated above the m. p. they decompose explosively. *o*-Chlorobenzylidenechloroimine decomposes slowly in alcoholic solution, forming mainly *o*-chlorobenzaldehyde. H. BURTON.

**Supposed mandeloisonitrile.** W. BAKER and R. G. A. NEW (J.C.S., 1930, 1274—1275).—The mandeloisonitrile, m. p. 196° (corr.), of Wood and Lilley (A., 1925, i, 400) has m. p. 198° and formula  $C_{23}H_{18}O_2N_2$ . It is completely hydrolysed by dilute acids, giving 1, 2, and 2 mols. of benzaldehyde, mandelic acid, and ammonia. It is therefore regarded as di-( $\alpha$ -cyanobenzoyloxy)phenylmethane,  $CHPh(O\cdot CHPh\cdot CN)_2$ . R. J. W. LE FÈVRE.

**Cannizzaro reaction.** G. LOCK (Monatsh., 1930, 55, 307—315).—Halogeno-3-hydroxybenzaldehydes containing chlorine or bromine in the 2- or 6-position undergo the Cannizzaro reaction (cf. A., 1929, 814), whereas 2:6-dihalogeno-3-hydroxybenzaldehydes do not. In the last case elimination of the aldehyde group occurs:  $R\cdot CHO + KOH \rightarrow H\cdot CO_2K + R\cdot H$ .

[With W. HÖSEUS, jun.].—Chlorination of *m*-hydroxybenzaldehyde in acetic acid solution with chlorine diluted with carbon dioxide gives 32.6% of the theoretical amount of 2-chloro-3-hydroxybenzaldehyde, m. p. 139° (all m. p. are corr.), together with a mixture of products, chlorinated further to 2:4:6-trichloro-3-hydroxybenzaldehyde (cf. Hodgson and Beard, A., 1926, 292). Treatment of 2-chloro- and 4:6-dibromo-3-hydroxybenzaldehydes with 50% potassium hydroxide solution at 60—70° affords 2-chloro-, m. p. 132° (methyl ether, m. p. 107—108°), and 4:6-dibromo-3-hydroxybenzyl alcohols, m. p. 161.5° (methyl ether, m. p. 138.5—139°), respectively, together with the corresponding benzoic acids. Similar treatment of 2:6-dichloro-, 2:4:6-trichloro-, and 2:4:6-tribromo-3-hydroxybenzaldehydes gives potassium formate and 2:4-dichloro-, 2:4:6-trichloro-, and 2:4:6-tribromo-phenol, respectively. Contrary to the statement of Hodgson and Beard (A., 1925, i, 674), 2:4:6-tribromo-3-hydroxybenzaldehyde cannot be prepared by brominating *m*-hydroxybenzaldehyde in chloroform solution.

H. BURTON.

**Optical resolution of racemic aldehydes. I.** M. BETTI [with P. PRATESI] (Atti R. Accad. Lincei, 1930, [vi], 11, 587—593).—Treatment of the racemic form of *p*-methoxyhydratropaldehyde with phenyl- $\beta$ -hydroxynaphthylmethylamine, yields a mixture of two dextrorotatory aldehyde-imines,  $[\alpha]_D +43.1^\circ$  and  $+40.4^\circ$ , respectively. Hydrolysis of these gives 1-*p*-methoxyhydratropaldehyde,  $[\alpha]_D -2.45^\circ$  (oxime,  $[\alpha]_D +7.9^\circ$ ), and d-*p*-methoxyhydratropaldehyde,  $[\alpha]_D -12.52^\circ$  (laevorotatory oxime). T. H. POPE.

**Reactions of 4-hydroxy-3-ethoxybenzaldehyde.** J. L. KLOTZ (Amer. J. Pharm., 1930, 102, 274—279).—Colour reactions do not distinguish between vanillin and ethylvanillin (4-hydroxy-3-ethoxybenzaldehyde), which is best characterised as the phenylhydrazone, m. p. 124—126°, and as dehydrodiethylvanillin, m. p. 232—235°. H. E. F. NOTTON.

**Derivatives of *m*-xylene.** E. G. BOYCE, W. P. RANKINE, and A. ROBERTSON (J.C.S., 1930, 1216—1217).—*m*-Xylorcinolcarboxylic acid, m. p. 199—200° (Kostanecki, A., 1887, 39, gives m. p. 196°), is conveniently prepared by heating together *m*-xylorcinol, potassium carbonate, and glycerol in an atmosphere of carbon dioxide at 130°, in a manner similar to that employed by Robertson and Robinson (A., 1927, 1084) for *p*-orsellinic acid. 4-Nitro-*m*-6-xyleneol methyl ether, m. p. 56—57° (prepared by the action of methyl sulphate on the parent phenol), is reduced by iron powder in boiling alcohol to 6-methoxy-*m*-4-xylydine, m. p. 83° (acetyl derivative, m. p. 160°), isolated as its hydrochloride which, by conversion of the amino-group through the diazo-compound affords 6-methoxy-*m*-4-xyleneol, m. p. 80°. Partial methylation of *m*-xylorcinolaldehyde (Robertson and Robinson, *loc. cit.*) with methyl iodide and an excess of potassium carbonate in boiling acetone affords 2-hydroxy-6-methoxy-3:5-dimethylbenzaldehyde, m. p. 52°, which condenses with  $\alpha$ -methoxyacetoveratrone in the presence of hydrogen chloride in ethyl acetate to give 3:5:3':4'-tetramethoxy-6:8-dimethylflavylium chloride (ferrichloride, m. p. 177—178°).

J. W. BAKER.

**Condensation products of aromatic aldehydes with  $\beta$ -angelicalactone.** W. F. VON OETTINGEN (J. Amer. Chem. Soc., 1930, 52, 2024—2025).— $\alpha$ -Salicylidene-, m. p. 96°,  $\alpha$ -resorcylicidene-, m. p. 167—168°,  $\alpha$ -anisylidene-, m. p. 99°,  $\alpha$ -vanillylidene-, m. p. 143°, and  $\alpha$ -piperonylidene- $\beta$ -angelicalactones, m. p. 125°, are obtained by condensation of the appropriate aldehyde in presence of a small amount of diethylamine. Pure products were not formed with benzaldehyde, cinnamaldehyde, and  $\beta$ -phenylpropaldehyde.

H. BURTON.

***o*- and *m*-Derivatives of simple phenyl alkyl ketones.** L. A. ELSON, C. S. GIBSON, and J. D. A. JOHNSON (J.C.S., 1930, 1128—1136).—Reduction of *m*-nitroacetophenone affords *m*-aminoacetophenone, m. p. 98—99° (Morgan and Moss, A., 1924, i, 57, give 92—93°) [semicarbazone, m. p. 196° (decomp.); *p*-toluenesulphonyl derivative, m. p. 130°], which is converted by the Sandmeyer reaction into *m*-bromoacetophenone, b. p. 127.5°/14 mm., m. p. 7—8° [semicarbazone, m. p. 232—233° (decomp.)]. This is converted by nitric acid (*d* 1.5) below 0° into 5-bromo-2-nitroacetophenone, b. p. 172—174°/14 mm., m. p. 51° [semicarbazone, m. p. 163—164° (decomp.)]. Similarly, *o*-aminoacetophenone, b. p. 130.5°/14 mm., m. p. 20° [semicarbazone, m. p. 290° (decomp.); *p*-toluenesulphonyl derivative, m. p. 148°], is converted into *o*-bromoacetophenone, b. p. 112°/10 mm. (semicarbazone, m. p. 177°). By similar processes propiophenone is converted into *m*-nitro-, m. p. 98—100°, *m*-amino-, b. p. 168—169°/15 mm., m. p. 42° (*p*-toluenesulphonyl derivative, m. p. 97°), *m*-bromo-

b. p. 143°/18 mm., m. p. 36° (semicarbazone, m. p. 180°), *o*-amino- [semicarbazone, m. p. 190° (decomp.)]; *p*-toluenesulphonyl derivative, softens at 125° and decomp. over a considerable range of temperature], *o*-bromo-, b. p. 125°/12 mm. (semicarbazone, m. p. 182°), and *o*: $\alpha$ -dibromo-, b. p. 154—155°/12 mm., m. p. 38—39°, -*propio*phenone. *n*-Butyrophenone is converted into *m*-nitro-, m. p. 62—63° (semicarbazone, m. p. 166—167°), *m*-amino-, b. p. 179—180°/16 mm., m. p. 27—28° (*p*-toluenesulphonyl derivative, m. p. 70°), *m*-bromo-, b. p. 152°/20 mm., m. p. 9—10° (semicarbazone, m. p. 158°), *o*-amino-, b. p. 153°/16 mm., m. p. 45° (*p*-toluenesulphonyl derivative, m. p. 110°), and *o*-bromo-*n*-butyrophenone, b. p. 143°/16 mm. (semicarbazone, m. p. 172°). The last is converted by bromine in acetic acid into (?) *o*: $\alpha$ -dibromo-, b. p. 172°/16 mm., and by bromine into (?) *o*: $\alpha$ -tri-bromo-, m. p. 27—28°, -*n*-butyrophenone. Condensation of  $\alpha$ -bromobutyryl chloride and chlorobenzene in carbon disulphide solution in the presence of aluminium chloride affords *p*-chloro- $\alpha$ -bromo-*n*-butyrophenone, b. p. 162°/14 mm., m. p. 43°, but attempts to prepare the *p*: $\alpha$ -dibromo-compound by a similar method gave only an impure product. When *o*-aminopropiophenone is heated with semicarbazide acetate it yields *o*-aminophenylethylketazine,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CET} \cdot \text{N})_2$ , m. p. 130° (which is also formed in small quantity with the semicarbazide in the cold), *o*-aminophenyl-*n*-propylketazine, m. p. 135°, being similarly prepared from *o*-amino-*n*-butyrophenone.

J. W. BAKER.

**Keto-oxidation product of  $\alpha$ -acetylnaphthalene.** K. DZIEWOŃSKI and J. REISS (Bull. Acad. Polonaise, 1930, A, 62—65).—Contrary to Graebe and Haas (A., 1903, i, 408) oxidation of 5-acetylnaphthalene (best prepared by the action of aluminium chloride on acetyl chloride and acenaphthene without solvent) with sodium dichromate and acetic acid at 50° gives only traces of 4-acetylnaphthalene-1:8-dicarboxylic acid, the main products being 5-acetyl-acenaphthenequinone, m. p. 192—193° [*diphenylhydrazone*, m. p. 240—242°; *dioxime*, m. p. 275—278° (decomp.)], and 2:2'-diketo-5:5'-diacetyldiacenaphthylidene, m. p. 295° (decomp.).

J. W. BAKER.

**Synthesis of acetyl derivatives of 1-benzyl-naphthalene. I. 4-Acetyl-1-benzyl-naphthalene.** K. DZIEWOŃSKI and J. MOSZEW (Bull. Acad. Polonaise, 1930, A, 66—71).—1-Benzyl-naphthalene reacts with acetyl chloride in the presence of aluminium chloride in carbon disulphide solution at the ordinary temperature to give 4-acetyl-1-benzyl-naphthalene, b. p. 240—245°/12 mm., m. p. 75° (*picrate*, m. p. 113°) (60%), together with a *diacetyl* derivative, b. p. 265—270°/12 mm., m. p. 135° (10%), as a by-product. The *oxime*, m. p. 240—241°, of 4-acetyl-1-benzyl-naphthalene undergoes a Beckmann rearrangement when its solution in acetic acid and acetic anhydride saturated with anhydrous hydrogen chloride is heated at 100°, to give 4-acetamido-1-benzyl-naphthalene, m. p. 208—209°, hydrolysed by boiling 6% hydrochloric acid to 4-benzyl- $\alpha$ -naphthylamine identical with a specimen obtained by the action of ammonia on 4-benzyl- $\alpha$ -naphthol (A., 1928, 405). Nitric acid (d 1.52) in acetic acid at 10—15° converts 4-acetyl-1-

benzyl-naphthalene into its 5-nitro-derivative, m. p. 153°, whilst boiling 10% nitric acid oxidises it to 4-benzoyl- $\alpha$ -naphthoic acid, m. p. 180—181°.

J. W. BAKER.

**Attempted syntheses of symmetrical aryl- and benzoyl-substituted ethanes.** S. GOLDSCHMIDT and F. NAGEL (Ber., 1930, 63, [B], 1212—1217).—The colourless variety of dibenzoylphenylmethane, m. p. 149°, is converted by bromine in boiling carbon tetrachloride into *dibenzoylphenylmethyl bromide*, m. p. 80°, which is slowly hydrolysed by boiling 60% alcohol and liberates iodine from acidified potassium iodide. It is transformed by silver powder in boiling benzene into a compound, m. p. 203°, with the composition of *s*-tetrabenzoyldiphenylethane, but doubts regarding its constitution arise, since it is little reactive and is transformed by bromine into a substance,  $\text{C}_{36}\text{H}_{25}\text{O}_4\text{Br}$ , m. p. 212°. 9-Bromo-9-benzoylfluorene and silver powder yield 9:9'-*dibenzoyldifluorenyl*, m. p. 199°, re-converted into the original compound by bromine. It gives coloured solutions which do not obey Beer's law in liquids of high b. p. The corresponding radical appears little sensitive to oxygen. 2:7-Dibromofluorene and ethyl benzoate yield 2:7-dibromo-9-benzoylfluorene, converted by bromine in chloroform in presence of a little red phosphorus into 2:7:9-tribromo-9-benzoylfluorene, m. p. 177°. The last-named substance and silver powder afford *di*-(2:7-dibromo-9-benzoyl-9-fluorenyl), m. p. 263°, obtained also from dibromobenzoylfluorene and a limited amount of bromine. It behaves like the bromine-free parent substance when heated. Treatment of benzoyldiphenylmethyl bromide with silver powder gives products in which the presence of an ethane is established by its power of dissociation; the compound cannot be caused to crystallise and does not appear to regenerate the bromide when treated with bromine.

Benzoyldiphenylcarbinol is converted by vanadous sulphate into benzoyldiphenylmethane, m. p. 133°; 9-bromo-9-benzoylfluorene similarly affords 9-benzoylfluorene.

The electronegative character of the central carbon atom of the benzoyl-substituted methane derivatives is shown by the liberation of iodine from a neutral solution of potassium iodide in acetone by dibenzoylphenylmethyl bromide and the removal of bromine by thiosulphate; in each case dibenzoylphenylmethane is produced. 9-Bromo-9-benzoylfluorene and potassium iodide slowly yield the corresponding ethane.

H. WREN.

**Supposed hexaphenylacetone.** W. SCHLENK and E. BERGMANN (Annalen, 1930, 480, 183—187).—The hexaphenylacetone, m. p. 80—81° (given in error for 180—181°), of Schlenk and Bergmann (A., 1928, 1040) is *p*-triphenylacetyltriphenylmethane (cf. Wieland and Kloss, A., 1929, 1053), since it is formed from sodium triphenylmethyl and *methyl p*-diphenylmethylbenzoate, m. p. 77°. The ketyl formed from the above ketone is best represented as  $\text{CPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{ONa}) \cdot \text{CPh}_3$  (cf. *loc. cit.*). When the ketyl is treated with iodine in benzene, *p*-triphenylacetyltriphenylmethyl peroxide ( $+\text{C}_3\text{H}_8\text{O}_2$ ), m. p. 200—201° (decomp.) (crystallised from dioxan), is obtained. Treatment of *p*-triphenylacetyltriphenylmethane with

sodium triphenylmethyl at 0° yields triphenylmethane, indicating that the ketyl (also formed during the reaction) arises from a substitution reaction.

H. BURTON.

### Isomerism among 9-substituted fluorenes (?).

III. A. KLEGL, F. WENG, and G. WIEST (Ber., 1930, **63**, [B], 1262—1270; cf. A., 1929, 812; Pfeiffer and Lübke, this vol., 779).—The sodium derivative of fluorene is converted by benzoyl chloride into a mixture of fluorene and a dibenzoylfluorene, m. p. 189.5—190°; the last-named product is also obtained by the action of benzoyl chloride in alkaline solution on Werner's benzoylfluorene, m. p. 138° (cf. A., 1906, i, 436) or by benzoylation in benzene solution in presence of pyridine. Treatment of the lithium derivative of fluorene with benzoyl chloride (cf. Schlenk and Bergmann, A., 1928, 1031 *seq.*) gives a product, m. p. 180°, having the composition of a dibenzoylfluorene. The existence of two isomeric 9-benzoylfluorenes is therefore not confirmed, whereas two isomeric benzoyl derivatives of 9-benzoylfluorene exist. The product of m. p. 180° is smoothly converted by hot acetic acid containing a little water into benzoic acid and 9-benzoylfluorene. Catalytic hydrogenation in presence of spongy platinum converts the isomeride, m. p. 189.5—190°, into the compound

$\text{C}_6\text{H}_4 > \text{CH} \cdot \text{CHPh} \cdot \text{OBz}$ , m. p. 181°, also prepared by benzoylation of *phenyl-9-fluorenylcarbinol*, m. p. 118.5—119°, obtained by reducing 9-benzoylfluorene with aluminium amalgam in moist ether. The compound of m. p. 180° remains unaffected by hydrogen. To the two isomerides the constitutions  $\text{C}_6\text{H}_4 > \text{C} : \text{CPh} \cdot \text{OBz}$  and  $\text{C}_6\text{H}_4 > \text{CBz}_2$  are therefore ascribed.

Analyses and determinations of mol. wt. of  $\beta$ -anisylidenefluorene, m. p. 141°, confirm the results of Schlenk and Bergmann (*loc. cit.*). Treatment of it and of the compound, m. p. 128—129°, with ozone affords fluorenone and anisaldehyde. A case of isomerism appears therefore to be presented and both compounds are regarded provisionally as 9-substituted fluorenes, but the intense colour of the  $\beta$ -form does not appear to receive explanation by the hypothesis of Schlenk and Bergmann. Treatment of  $\beta$ -anisylidenefluorene with aluminium amalgam in moist ether yields a mixture from which a substance, m. p. 272—273°, apparently derived from 2 mols. of the original material, is isolated. Catalytic hydrogenation in presence of spongy platinum transforms  $\alpha$ -benzylidene- and  $\alpha$ -anisylidene-fluorene into 9-benzyl- and 9-anisyl-fluorene, whereas the corresponding  $\beta$ -derivatives combine with four atoms of hydrogen yielding "*dihydrobenzylfluorene*," m. p. 71°, and "*dihydroanisylfluorene*," m. p. 61.5—62°. Demethylation of the last-named compound affords "*dihydro-p-hydroxybenzylfluorene*," m. p. 101.5—102°. This behaviour is not compatible with Schlenk and Bergmann's theories.

H. WREN.

**Benzoin condensation.** A. A. MORTON and J. R. STEVENS (J. Amer. Chem. Soc., 1930, **52**, 2031—2037).—When the benzoin condensation is carried out with potassium cyanide and a mixture (1 : 1) of

95% alcohol and light petroleum, the yield of product is higher than with the alcohol alone. The yield is diminished when a mixture of alcohol and carbon disulphide, ether, acetone, ethyl bromide, carbon tetrachloride, or chlorobenzene is used. Appreciable amounts of benzoin are formed when benzene, toluene, or xylene is used alone as the solvent. A small amount of benzoin is obtained by using potassium cyanide and a mixture (5 : 1) of light petroleum and 95% alcohol; replacement of the potassium with sodium cyanide increases the yield. The linear course of the reaction with sodium cyanide suggests that the solubility of the salt in the mixed solvent is the main factor (the sodium salt is 10.6 times as soluble as the potassium). Although sodium cyanide is 6 times as soluble in 95% alcohol as in the 5 : 1 mixture, reaction proceeds faster (per cyanide dissolved) in the latter solvent; the type of velocity curve is different with the two solvents. In all the reactions carried out in presence of light petroleum, an additive compound of equimolecular amounts of benzaldehyde and sodium cyanide is isolated. This is decomposed by water to the aldehyde and cyanide, but when kept in a desiccator it changes slowly to benzoin. Benzaldehyde and sodium cyanide also react in presence of dry light petroleum in an atmosphere of nitrogen, forming benzoin. Mechanisms involving ionisation are not applicable to the results obtained. A mechanism based on Pfeiffer's theory of additive compounds as catalysts (A., 1911, i, 788) and another involving the addition of sodium cyanide across the carbonyl double linking are suggested.

Additive compounds are formed from sodium cyanide and cinnamaldehyde, ethyl benzoate, or benzoyl cyanide. Mercuric, cuprous, thallous, triphenylmethyl, and *tert*-butyl cyanides do not catalyse the reaction in the 5 : 1 mixture of light petroleum and alcohol.

H. BURTON.

**Manufacture of compounds of the general formula  $\text{RCH} < \text{C} > \text{Ar}$ , especially derivatives of**

**1 : 3-diketohydrindene.** T. K. and L. M. WALKER, H. SHAW, and R. BLACK.—See B., 1930, 549.

**Azo-dyes derived from 4 : 6-diacetoresorcinol.** J. ALGAR and M. BOYLAN (Proc. Roy. Irish Acad., 1930, **39**, 343—350).—Poor yields of dyes are obtained by direct coupling of diazonium salts with dibenzylidenediacetoresorcinol (I). Better yields are obtained by first coupling the diazonium salts with diacetoresorcinol, followed by condensation with aldehydes in the presence of alcoholic hydrochloric acid or of piperidine. Thus diazotised *o*-toluidine and I in the presence of aqueous sodium hydroxide yield *o*-toluene-azodibenzylidenediacetoresorcinol, m. p. 231—232°. Benzeneazodibenzylidenediacetoresorcinol, m. p. 229—230°, is similarly obtained from aniline. Coupling of diazotised aniline with diacetoresorcinol in the presence of aqueous sodium hydroxide and carbonate yields benzeneazodiacetoresorcinol, m. p. 205—206°, which condenses with anisaldehyde, piperonaldehyde, and *p*-dimethylaminobenzaldehyde to give respectively benzeneazo-dianisylidene-, m. p. 232—233°, *di*-piperonylidene-, m. p. 261—262°, and *di*-*p*-dimethyl-



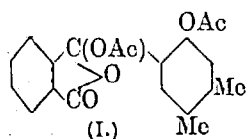
*aminobenzylidene-diacetoresorcinol*, m. p. 227—228°. *m*-4-*Xylene*-, m. p. 207—208°, and *p*-*toluene-azodi-acetoresorcinol* (II), m. p. 210—211°, were similarly prepared from *m*-xylidine and *p*-toluidine, respectively. II condenses with anisaldehyde and with piperonaldehyde to give *p*-*tolueneazo-di-anisylidene*-, m. p. 234—235°, and *-dipiperonylidene-diacetoresorcinol*-, m. p. 251—252°, respectively.

A. I. VOGEL.

**Preparation of tetrachloro-*p*-benzoquinone, trichloro-*p*-benzoquinone, and *s*-trichloroaniline from aniline by electrolysis.** J. ERDÉLYI (Ber., 1930, 63, [B], 1200—1203).—Electrolysis of aniline in hydrochloric acid solution between carbon electrodes causes chlorination to *s*-trichloroaniline or simultaneous oxidation and chlorination to chloroquinones. With increasing concentration of the acid, the degree of oxidation and chlorination decreases. In 10% solution tetrachloro-*p*-benzoquinone is obtained, in 20% solution trichloro-*p*-benzoquinone, and in concentrated hydrochloric acid exclusively *s*-trichloroaniline as final product. The best yields of the tetrachloroquinone are obtained when the temperature of the electrolyte is allowed to rise spontaneously to 35—40°. Trichloroquinone is obtained when the temperature is maintained at 5—15° and *s*-trichloroaniline when the cooling is moderate. In all cases the current density is 0.1 amp./sq. cm.

H. WREN.

**Synthesis of 1-methylantraquinones.** A. FAIRBOURNE and G. E. FOSTER (J.C.S., 1930, 1275—1276).—The method of Pickles and Weizmann (Proc. C.S., 1904, 20, 201) for the synthesis of anthraquinones by the action of the appropriate Grignard reagent on phthalic anhydride has been successfully applied to the preparation of 1-methylantraquinone. Interaction of magnesium *o*-tolyl bromide and phthalic anhydride under conditions maintaining a continuous excess of the anhydride, to minimise the formation of the diarylphthalide, affords 2-*o*-toluoylbenzoic acid, m. p. above 120°, readily converted into 1-methylantraquinone, identical with a specimen obtained by Fischer and Sapper's method (A., 1911, i, 279). 2-*o*-Hydroxyxyloylbenzoic acid (J.C.S., 1923,



(I.)

123, 1137) is converted by acetic anhydride and sodium acetate into a diacetate (I). The *hydroxyanthraquinone* is similarly acetylated to 4-acetoxy-1 : 2-dimethylantraquinone, m. p. 154°, which, however, could not be reduced, but by distillation with zinc dust affords a substance, m. p. 200°, which is not the unknown 1 : 2-dimethylantracene, since it is oxidised to a substance, m. p. 288°.

J. W. BAKER.

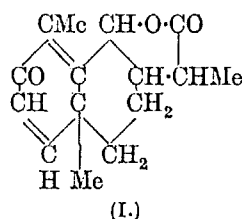
**Nitration of 2-hydroxy-3-methylantraquinone.** P. C. MITTER and S. C. PAL (J. Indian Chem. Soc., 1930, 7, 259—262).—2-Hydroxy-3-methylantraquinone is nitrated by potassium nitrate and sulphuric acid to 1-nitro-2-hydroxy-3-methylantraquinone, m. p. 267° (methyl ether, m. p. 206°, formed either by methylation or nitration of the 2-methoxy-derivative). Reduction of the nitro-derivatives with 5% sodium sulphide solution

gives 1-amino-2-hydroxy-, m. p. 215—216°, and 1-amino-2-methoxy-3-methylantraquinone, m. p. 195°. Treatment of the above nitromethoxy-derivative with methyl-alcoholic potassium methoxide affords 1 : 2-dimethoxy-3-methylantraquinone, m. p. 127°, demethylated by aluminium chloride at 200° to 3-methylalazarin [diacetyl derivative, m. p. 162° (given erroneously as 262° in A., 1929, 70)]. Reduction of 3-methylpurpurin (*loc. cit.*; triacetyl derivative, m. p. 213°) with stannous chloride and 10% sodium hydroxide solution furnishes rubiadin.

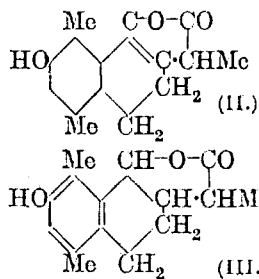
Nitration of 1 : 2-dimethoxy-3-methylantraquinone with potassium nitrate and sulphuric acid gives the 4(?)-nitro-derivative, m. p. 248°.

H. BURTON.

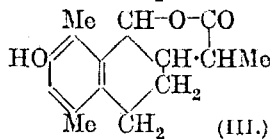
**Constitution of santonin. II. Synthesis of racemic desmotroposantonin.** G. R. CLEMO, R. D. HAWORTH, and E. WALTON (J.C.S., 1930, 1110—1115; cf. A., 1929, 1454).—The synthesis of a lactone possessing the structure III which is identical with racemic desmotroposantonin obtained from santonin (Andreocci, A., 1899, i, 301) necessitates a slight modification of the structure previously suggested for santonin (A., 1929, 1454), the formula (I) being now adopted.



(I.)



(II.)



(III.)

Ethyl- $\delta$ -4-methoxy-2 : 5-dimethylbenzoylbutane- $\beta\gamma$ -tricarboxylate is hydrolysed with aqueous alcoholic sodium hydroxide to the mixed racemates of  $\delta$ -4-methoxy-2 : 5-dimethylbenzoylbutane- $\beta\gamma$ -dicarboxylic acid (*loc. cit.*) (methyl ester, m. p. 73—74°), and the latter converted into the anhydride, m. p. 171°, by heating at 180° (a second form of this anhydride was not isolated); reduction of the anhydride by Clemmensen's method affords the low-melting form of  $\alpha$ -( $\beta$ -4-methoxy-2 : 5-dimethylphenylethyl)- $\alpha'$ -methylsuccinic acid, m. p. 131—132° (*loc. cit.*), which on demethylation with hydriodic acid, followed by treatment with warm sulphuric acid, is converted into the lactone (II) of the enolic form of  $\alpha$ -7-hydroxy-1-keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthyl-2-propionic acid, m. p. 250—253° (corresponding free acid, m. p. 191°). Reduction of II by means of sodium amalgam in alcohol yields the lactone (III) of  $\alpha$ -1 : 7-dihydroxy-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthyl-2-propionic acid, m. p. 200—201°, which is identical with desmotroposantonin from natural sources; acetyl-desmotroposantonin from either source has m. p. 146°.

Bromination of methyl and ethyl  $\beta$ -4-methoxy-2 : 5-dimethylbenzoylpropionates, m. p. 94—95° and 49—50°, respectively, leads to the corresponding  $\beta$ -bromo-esters, respective m. p. 96° and 98—100°; condensation of ethyl  $\beta$ -bromo- $\beta$ -4-methoxy-2 : 5-dimethylbenzoylpropionate with ethyl sodiummethyl-

malonate gives a tricarboxylate which is converted by hydrolysis and heating into the above-mentioned anhydride, m. p. 171°. The bearing of this observation on the structure of ethyl 8-4-methoxy-2:5-dimethylbenzoylbutane- $\beta\beta\gamma$ -tricarboxylate is discussed.

Supplementary details of the preparation of *desmotroposantonin* by the method of Andreocci (*loc. cit.*) are given. R. CHILD.

**Synthesis of methysticin.** V. LAMPE and Z. SANDROWSKI (Bull. Soc. chim., 1930, [iv], 47, 469—479).—See this vol., 611.

**Constitution of carthamin. I and II.** (MISS) C. KURODA (J.C.S., 1930, 752—765, 765—767).—A fuller account of work published elsewhere (see A., 1929, 430, 703). 2:3:4:6-Tetramethoxyacetophenoneoxime has m. p. 53—54°.

R. J. W. LE FÈVRE.

**Carotene. I. Oxygen equivalent.** J. H. C. SMITH and H. A. SPOEHR (J. Biol. Chem., 1930, 86, 87—92).—Carotene was kept at 40° with excess of a saturated pyridine solution of potassium permanganate, the excess of the latter being determined from time to time by titration with oxalic acid. In this way the oxygen equivalent of carotene was found to be 41.97.

C. R. HARRINGTON.

**Carotene. II. Volatile fatty acids obtained by oxidation of carotene and xanthophyll.** J. H. C. SMITH and H. A. SPOEHR (J. Biol. Chem., 1930, 86, 755—760).—When oxidised with potassium permanganate in pyridine solution, both carotene and xanthophyll yield 4 mols. of acetic acid.

C. R. HARRINGTON.

**Structure of betulin.** I. J. POSTOVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 101—109).—The products of oxidation of betulin by potassium permanganate in acetic acid solution, and of distillation, were investigated with a view of elucidating the structure of the compound. Betulin, m. p. 253—254°, was obtained by Schulze's method from birch bark and oxidised with potassium permanganate in 65% acetic acid solution at 60°. A compound, m. p. 207—208°, was obtained, containing either 3 or 6 carbon atoms less than the original betulin, giving a *monoacetyl* derivative, m. p. 210°, and a phenylhydrazone, thus indicating the presence of a hydroxyl and a carbonyl group. When betulin was distilled at 240—300°, a greenish oil was obtained, which deposited crystals, m. p. 242°, probably an isomeride of betulin. The liquid gave a blood-red coloration with concentrated sulphuric acid (due to diterpenes) and decolorised bromine and potassium permanganate, thus indicating the presence of a double linking.

M. ZVEGINTZOV.

**Nitration of abietic acid and the study of some of its nitrogen derivatives.** L. A. GOLDBLATT [with A. LOWY and W. B. BURNETT] (J. Amer. Chem. Soc., 1930, 52, 2132—2136).—When nitric acid (*d* 1.42) is added to a hot alcoholic solution of abietic acid, a violent reaction occurs and from the resulting solution a dinitro-acid,  $C_{19}H_{26}O_6N_2$ , m. p. 171.2—171.4° (all m. p. are corr.),  $[\alpha]_D^{25}$  -118° in 95% alcohol (cf. Dubourg, A., 1928, 764) (sodium salt; ethyl ester, m. p. 157.5—157.8°, prepared from

the sodium salt and ethyl sulphate or by the action of nitric acid on an alcoholic solution of ethyl abietate), and an amorphous, yellow nitrogenous product, decomp. above 100°,  $[\alpha]_D^{25}$  -36° in alcohol, are isolated. Reduction of the dinitro-acid in acid solution causes evolution of nitrogen oxides; in alkaline solution ammonia is evolved. Catalytic reduction (Adams) in ethyl acetate gives a substance, m. p. 171.5—172°, which evolves ammonia when treated with hot alcohol or cold aqueous alkali. The nitrogenous product, probably a nitrohydroxyabietic acid, affords a red alkaline solution which readily absorbs oxygen from the air; nitrogen oxides and ammonia are evolved during its reduction in acid and alkaline solution, respectively. H. BURTON.

**Action of zinc chloride on abietic acid.** G. ROUIN (Bull. Inst. Pin, 1929, 251—252; Chem. Zentr., 1930, ii, 2775).—Zinc chloride (5%), instead of forming the anhydride, decomposes abietic acid on heating at the ordinary pressure, yielding *octahydrotene*,  $C_{18}H_{26}$ , a colourless oil, b. p. 202—203°/15 mm.,  $d^{20}_4$  0.955,  $n^{20}_D$  1.5230, as the chief product.

L. S. THEOBALD.

**Cyclamyretin.** O. DAFERT and H. FETTINGER (Arch. Pharm., 1930, 268, 289—299).—The following reactions of cyclamyretin have been studied: semicarbazide gives the compound,  $C_{36}H_{59}O_5N_3$ , previously described (A., 1926, 1146); the Zeisel reaction is negative; bromine gives an amorphous *dibromide*; distillation with zinc dust gives no well-defined product; distillation in a vacuum gives a (?) sesquiterpene alcohol,  $n^{20}_D$  1.5073; oxidation with 5% potassium permanganate gives a monobasic acid,  $C_{35}H_{56}O_7$ , m. p. 235°, sintering from 230°, which gives with methyl alcohol and hydrogen chloride an anomalous product,  $C_{36}H_{62}$  or  $66O_4$ , m. p. 255°, sintering from 245°; oxidation with chromic acid gives indefinite products, but 30% hydrogen peroxide gives a mixture of the monobasic acids,  $C_{19}H_{28}O_7$ , and  $C_{16}H_{25}O_5$ ; ozonisation gives a monobasic acid, (?)  $C_{35}H_{56}O_8$ , m. p. about 207°, and oxidation with nitric acid a substance,  $C_{14}H_{19}O_6N$ , which, after purification through the calcium salt, resembles chrysolin (Michaud, A., 1888, 497) in composition, but not in properties, also a product,  $C_{11}H_{17}O_4N$ ; fusion with potassium hydroxide gives an acid,  $C_{22}H_{32}O_5$ , which contains two hydroxyl groups, and a monobasic acid,  $C_{33}H_{50}O_6$ ; dehydrogenation with selenium gives a substance  $C_{35}H_{52}O_4$ , decomp. 155°, charring at 265°. It is concluded that cyclamyretin contains four hydrogenated rings and one cyclic double linking. It is probably related in structure to cholesterol and to the resin acids. H. E. F. NOTTON.

**Pilzcerebrin.** I. F. REINDEL (Annalen, 1930, 480, 76—92).—Pilzcerebrin,  $C_{42}H_{85}O_5N$ , m. p. 143—144°,  $[\alpha]_D^{25}$  +12.1° in pyridine, isolated as a by-product in the hydrolysis of yeast or yeast-fat (A., 1928, 295) is identical with the substance isolated by Rosenthal (Monatsh., 1922, 43, 244) and by Hartmann and Zellner (A., 1929, 108) from *Polyporus pinicola* and is closely related to the cerebrosides. It is converted, best by heating with acetic anhydride and pyridine at 100°, into a triacetyl derivative, m. p. 68—69°,  $[\alpha]_D^{25}$  +19.6° (Rosenthal, *loc. cit.*, gives m. p. 62—63°),

and contains four hydroxyl and one  $\cdot\text{CO}\cdot\text{NH}\cdot$  group (Zerevitinov). When it is hydrolysed with boiling aqueous methyl-alcoholic hydrogen chloride, a portion is converted into *anhydrocerebrin*,  $\text{C}_{42}\text{H}_{83}\text{O}_4\text{N}$ , m. p. 118—119°,  $[\alpha]_D^{20} +15.5^\circ$  in pyridine, which remains insoluble, and  $\alpha$ -hydroxyhexacosic acid,  $\text{C}_{26}\text{H}_{52}\text{O}_3$ , m. p. 101—103.5° (sodium and potassium salts; chloralide, m. p. 67—68°; ethyl, m. p. 73—74.5°, and methyl, m. p. 70—72°, esters; acetyl derivative of ethyl ester, m. p. 53—55°), and the hydrochloride of a mixture of bases, which are separated by fractional crystallisation from the hydrolysate. The acid is not identical (mixed m. p. depression) either with cerebronic acid isolated from ox-brain, or with  $\alpha$ -hydroxy-*n*-pentacosic acid (Brigl, A., 1916, i, 463). It is reduced by red phosphorus and hydrogen iodide in acetic acid in a sealed tube at 125—130° to a hexacosic acid,  $\text{C}_{26}\text{H}_{52}\text{O}_2$ , m. p. 85.5—86.5° (lithium salt; ethyl ester, m. p. 60—61.5°), is oxidised by potassium permanganate in acetone or, better, by chromic oxide in acetic acid to a pentacosic acid,  $\text{C}_{25}\text{H}_{50}\text{O}_2$ , m. p. 79—81° (ethyl, m. p. 57—58°, and *p*-bromophenacyl, m. p. 93—95°, esters), and is converted by distillation under atmospheric pressure (220—250°) into a hydrocarbon  $\text{C}_{25}\text{H}_{52}$ , m. p. 49—51°. The mixture of bases liberated from the hydrochloride by aqueous sodium hydrogen carbonate at 60° is separated by extraction with ether into a soluble base,  $\text{C}_{17}\text{H}_{35}\text{O}_2\text{N}$ , m. p. 83—84°,  $[\alpha]_D^{20} +48.6^\circ$  in chloroform (sulphate, decomp. 283° after darkening at 220°; mono-, m. p. 83—85°, and di-, m. p. 69—71°, acetyl derivatives; dibenzoyl derivative, m. p. 114—115°,  $[\alpha]_D -57^\circ$  in chloroform, together with a second benzoyl derivative, m. p. 91—93°), and a small quantity of an ether-insoluble, acetone-soluble base, m. p. 106—108.5°,  $[\alpha]_D +15.5^\circ$ . If the hydrolysis of the cerebrin is represented by  $\text{C}_{42}\text{H}_{85}\text{O}_5\text{N} + \text{H}_2\text{O} = \text{C}_{26}\text{H}_{52}\text{O}_3 + \text{C}_{16}\text{H}_{33}\text{O}_3\text{N}$ , the base  $\text{C}_{17}\text{H}_{35}\text{O}_2\text{N}$  corresponds with a methyl derivative of the expected base which has lost 1 mol. of water. This base is not identical with sphingosine, but pilzocerebrin is probably a compound of similar type to cerebronylsphingosine (Klenk, A., 1926, 749), which must have the structure  $\text{C}_{22}\text{H}_{45}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_2\cdot\text{C}_{15}\text{H}_{29}$ , and is isomeric with anhydrocerebrin (above). The structure  $\text{C}_{21}\text{H}_{49}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{C}_{12}\text{H}_{25}$  is suggested for pilzocerebrin. J. W. BAKER.

**Menthol series. Hydrogenation of pulegone.** A. GONZALEZ (Anal. Fis. Quím., 1930, 28, 247—261).—During the catalytic hydrogenation of pulegone at the ordinary temperature and pressure the nature of the solvent employed is of greater importance than the acidity or alkalinity of the medium. Partial hydrogenation results in the production of *l*-menthone and *d*-isomenthone, whilst by total hydrogenation *l*-menthol and *d*-neomenthol are obtained. Observed differences of the rate of hydrolysis of the phthalates of *l*-menthol and *d*-neomenthol confirm Vavon's view that *cis*-esters are less readily hydrolysed than *trans*-esters. H. F. GILLBE.

**Optically active pinocarveol. II. Auto-oxidation of  $\beta$ -pinene.** H. SCHMIDT (Ber., 1930, 63, [B], 1129—1135; cf. this vol., 217).— $\beta$ -Pinene, b. p.

165—166°/760 mm.,  $d_{20}^{25} 0.873$ ,  $n_D^{20} 1.47837$ ,  $\alpha_D -17.40^\circ$ , readily undergoes auto-oxidation by moist oxygen in presence of cobalt resinate. The product is distilled with steam and treated successively with neutral sulphite solution and boric acid. The sulphite solution yields *l*-pinocarvone, b. p. 222—223°/760 mm.,  $d_{20}^{25} 0.9921$ ,  $n_D^{20} 1.50373$ ,  $\alpha_D -15^\circ$  [semicarbazone, m. p. 212—215° (decomp.) according to rate of heating; oxime, m. p. 68—69°,  $\alpha_D -2.60^\circ$  in methyl alcohol]. The ketone is also obtained by oxidising with chromium trioxide in acetone the product obtained by the oxidation of alcoholic  $\beta$ -pinene. Application of the same process to the *l*-pinocarveol from oil of *Eucalyptus globulus* (*loc. cit.*) leads to *d*-pinocarvone, b. p. 222—223°,  $d_{20}^{25} 0.991$ ,  $n_D^{20} 1.50390$ ,  $\alpha_D +13.50^\circ$ . Mixture of equal weights of the two isomerides gives *dl*-pinocarvone, b. p. 222—223°,  $d_{20}^{25} 0.992$ ,  $\alpha_D \pm 0^\circ$  (oxime, m. p. 98°; semicarbazone, m. p. 204°). The alcohols isolated from the boric acid treatment are purified by distillation and through the phenylurethanes, whereby *d*-pinocarveol, b. p. 208—209°/750 mm., m. p. 7°,  $d_{20}^{25} 0.9855$ ,  $n_D^{20} 1.49931$ ,  $\alpha_D +59^\circ$  (phenylurethane, m. p. 88—89°), is isolated. It is converted by 25% sulphuric acid into *d*-pinocarveol hydrate, m. p. 190—191°,  $[\alpha]_D^{20} +31^\circ$ . The alcoholic fraction contains also a levorotatory alcohol, possibly *l*-verbenol. H. WREN.

**Essential oil of *Backhousia angustifolia*. II. Isolation of naturally occurring  $\beta$ -diketones: angustione and dehydroangustione.** C. S. GIBSON, A. R. PENFOLD, and J. L. SIMONSEN (J.C.S., 1930, 1184—1201).—The "phenolic" constituent of the oil (Penfold, A., 1924, i, 1328) consists of two  $\beta$ -diketones, termed respectively *angustione* and *dehydroangustione*. The conditions governing which of the two occurs in a given sample have not been determined.



Angustione,  $\text{C}_{11}\text{H}_{16}\text{O}_3$  (not  $\text{C}_{10}\text{H}_{14}\text{O}_3$ , *loc. cit.*), b. p. 129°/15 mm.,  $d_{20}^{25} 1.089$ ,  $n_D^{20} 1.5137$ ,  $[\alpha]_{440}^{20} -5.56^\circ$ , purified through the amino-derivative,  $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$  (formerly described as an ammonium salt), m. p. 130—131°, or the copper derivative,  $\text{C}_{22}\text{H}_{30}\text{O}_6\text{Cu}$ , m. p. 192—193°, is shown to have the constitution (I), since hydrolysis with alcoholic potassium hydroxide affords 1 : 1 : 3-trimethylcyclohexane-4 : 6-dione, m. p. 131—132° (compound by condensation with piperonal,  $\text{C}_{26}\text{H}_{36}\text{O}_6$ , m. p. 192—193), and acetic acid. The constitution of the dione is established by its oxidation with potassium permanganate or hypobromite to  $\alpha\gamma$ -trimethylglutaric acid, m. p. 97° (anhydride, m. p. 95°; anilide, m. p. 165°); oxidation with ferric chloride yields 1 : 1 : 3-trimethyl- $\Delta^2$ -cyclohexene-4 : 6-dione, m. p. 159—160° (5-bromo-derivative, m. p. 126—127°; compound by condensation with piperonal,  $\text{C}_{26}\text{H}_{32}\text{O}_6$ , m. p. 208—210°), which is obtained also by similar oxidation of angustione; this trimethylcyclohexenedione on further oxidation with alkaline permanganate gives dimethylmalonic acid (whence follows the position of the double linking), is reconverted into the saturated dione by sodium amalgam, and is converted by phosphorus trichloride into 4 : 6-dichloro-1 : 2 : 3-trimethylbenzene, m. p.

77—78° (cf. Crossley and Hills, J.C.S., 1906, **89**, 881). A mixture of the saturated and unsaturated diones results from the oxidation of angustione with potassium ferricyanide; reduction with sodium and alcohol affords a mixture from which have been isolated an *alcohol*,  $C_{22}H_{42}O_8$ , m. p. 196—197°,  $[\alpha]_{D}^{25} -10.23^\circ$ , and the above *cyclohexanedione*. The following derivatives of angustione are described and their structures discussed: *anhydroangustione-4(or 6)-semicarbazone*, m. p. 145° (decomp.); *-4(or 6)-phenylhydrazone*, m. p. 119—120°; *-4(or 6)-p-bromophenylhydrazone*, m. p. 191° (reduced to a compound giving the Knorr pyrazoline reaction); *-4(or 6)-oxime*, m. p. 41—43° (not sharp), and a *piperonylidene* compound, m. p. 166—167°.

Dehydroangustione,  $C_{11}H_{14}O_3$ , b. p. 126—127°/11 mm.,  $d_{20}^{25} 1.103$ ,  $n_D^{20} 1.5255$ ,  $[\alpha]_{D}^{25} -2.03^\circ$ , purified through the *copper* derivative, m. p. 188—190°, gives the following series of derivatives similar to those formed by angustione: *aminodehydroangustione*, m. p. 151°; *piperonylidenedehydroangustione*, m. p. 169—170°; *anhydrodehydroangustione-4(or 6)- $\alpha$ -semicarbazone*, m. p. 138—139; *- $\beta$ -semicarbazone*, m. p. 173—175°; *-4(or 6)-p-bromophenylhydrazone*, m. p. 247—248°; *-4(or 6)-oxime*, m. p. 79—80°,  $[\alpha]_{D}^{25} +4.95^\circ$ . Oxidation with potassium hypobromite affords an unidentified *substance*,  $C_8H_{10}O_3$ , m. p. 88.5°, and *1- $\alpha$ -xy-trimethylglutaric acid*, m. p. 91—92°,  $[\alpha]_{D}^{25} -16.9^\circ$ , and with permanganate the latter acid and dimethylmalonic acid; alkaline hydrolysis is slow and yields 1:1:3-trimethyl- $\Delta^2$ -cyclohexene-4:6-dione, whilst hydrolysis with 50% sulphuric acid gives a good yield of the same product. Products identical with those obtained from angustione were obtained by reduction. The structure II is suggested and the possible course of the above reactions outlined. R. CHILD.

**Isomerism of borneol and isoborneol.** P. LIPP (Annalen, 1930, **480**, 298—307).—*isoBorneol* is dehydrated by treatment with dry zinc dust under the conditions described by Semmler (A., 1900, i, 351) to camphene; no *isocamphane* is produced. From the experiments now described and a survey of the literature it is concluded that there appears to be no reason to abandon the Bredt configurations for borneol and isoborneol.

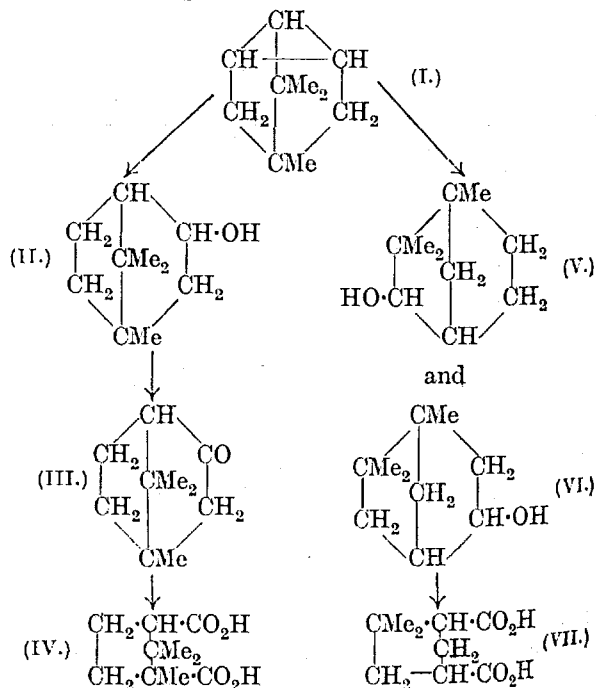
[With J. BUCHKREMER.]—Analytical and refractometric examinations of the product from *isoborneol* and dry zinc dust confirm the absence of *isocamphane*. *isoBorneol* is not affected by moist zinc dust, even at 250°. Dehydration of *isoborneol* to camphene occurs also with animal charcoal at 220° (quantitative yield), silica gel at 230°, and alumina at 210—215° (almost quantitative yield). Borneol,  $[\alpha]_D^{25} +25.87^\circ$  in 20% alcoholic solution, is dehydrated by alumina at 250° to camphene,  $[\alpha]_D +1.03^\circ$  in alcohol. The parachors of *dl*-bornyl and *dl*-isobornyl acetates are 463.3 and 462.6, respectively. H. BURTON.

**Homologues of the camphor group. VII. 4-Methylcamphor derivatives.** S. S. NAMETKIN and L. J. BRUSOVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 341—348).—An attempt to prepare methylisocyclenone by the elimination of hydrogen bromide from  $\alpha$ -bromomethylcamphor, m. p. 126—128°, was

not successful, as this compound is not acted on by aqueous alkali hydroxides, and alcoholic alkali converts it into methylcamphor, whilst with semicarbazide it yields the semicarbazone of methylcamphor. An *isomeride* of  $\alpha$ -bromomethylcamphor, m. p. 114—116°, is obtained by the action of ethylaniline on the original bromo-derivative. 4-Methylisocyclene was synthesised in the following way. Methylcamphor was converted by the action of sodamide and ethyl nitrite into *isonitrosomethylcamphor*, m. p. 174°, which with formalin and hydrochloric acid yielded *methylcamphorquinone*, m. p. 199—200°, the *hydrazone* of which, m. p. 108—109°, was converted by oxidation into *methylidiazocamphor*, m. p. 87—90°, and this, on heating, gave *methylisocyclenone*, m. p. 150° (*semicarbazone*, m. p. 251—253°; *hydrazone*, m. p. 89—92°). The hydrazone on heating with sodium ethoxide yields 4-methylisocyclene, which is in every respect identical with 4-methylcyclyene.

R. TRUSZKOWSKI.

**isoCyclene.** S. S. NAMETKIN and L. J. BRUSOVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 333—340).—*isoCyclene* (I) does not react with perbenzoic acid. With acetic acid it yields an *acetate*, b. p. 120.4—120.8°/27 mm., which on hydrolysis gives an *alcohol*, (II), m. p. 165—166°, and this, on oxidation with concentrated nitric acid, yields a *ketone* (III), m. p. 163—164° (*semicarbazone*, m. p. 210—211°). Both the ketone and the semicarbazone are mixtures, as is shown by the raising of the m. p. of the latter to 228—229° after four recrystallisations. The ketone on further oxidation with dilute nitric acid at 100° yields *methylapofenchocamphoric acid* (VII), together with *i*-camphoric acid (IV). The above reactions are represented as follows:



The alcohols II, V, and VI may be produced by the addition of water to *isocyclene*; II on oxidation yields IV, whilst VI yields 4-methylisocamphenyl-

one, which on further oxidation gives methylp-fenchocamphoric acid. R. TRUSZKOWSKI.

**Preparation and properties of furan derivatives.** F. N. PETERS, jun., and R. FISCHER (J. Amer. Chem. Soc., 1930, 52, 2079—2082).—The following 2-furylalkylcarbinols were prepared from furfuraldehyde and the requisite magnesium alkyl halide: *methyl*, b. p. 76—77°/23 mm.,  $d_{25}^{25}$  1.0771,  $n_D^{25}$  1.4785; *ethyl*, b. p. 89—90°/23 mm.,  $d_{25}^{25}$  1.0474,  $n_D^{25}$  1.4759 (*acetate*, b. p. 98°/37 mm.,  $d_{25}^{25}$  1.0427,  $n_D^{25}$  1.4589); *n-propyl*, b. p. 91—92°/12 mm.,  $d_{25}^{25}$  1.0179,  $n_D^{25}$  1.4768; *isopropyl*, b. p. 99—100°/38 mm.,  $d_{25}^{25}$  1.0111,  $n_D^{25}$  1.4715 (*acetate*, b. p. 99—100°/35 mm.,  $d_{25}^{25}$  1.0162,  $n_D^{25}$  1.4641); *n-butyl*, b. p. 94—96°/2 mm.,  $d_{25}^{25}$  0.9931,  $n_D^{25}$  1.4710; *isobutyl*, b. p. 102—103°/10 mm.,  $d_{25}^{25}$  0.9904,  $n_D^{25}$  1.4687 (*acetate*, b. p. 119—120°/30 mm.,  $d_{25}^{25}$  1.0004,  $n_D^{25}$  1.4600), and impure phenyl, b. p. 138—142°/10 mm.,  $d_{25}^{25}$  1.1423,  $n_D^{25}$  1.5522. The carbinols are usually resinified by treatment with acetyl or benzoyl chloride, hydrochloric acid, or phosphorus pentachloride. H. BURTON.

**Halogen derivatives of furan.** A. F. SHEPARD, N. R. WINSLOW, and J. R. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 2083—2090).—Halogenofurans are obtained by heating the corresponding furoic acids alone or in presence of copper powder, or, better, in presence of quinoline and copper powder. The following are described: 2-*chloro*-, b. p. 77.2—77.5° (all b. p. are corr.)/744 mm.,  $d_4^{20}$  1.1923,  $n_D^{20}$  1.45687; 3-*chloro*-, b. p. 79—79.4°/742 mm.,  $d_4^{20}$  1.2094,  $n_D^{20}$  1.46005; 3:4-*dichloro*-, b. p. 122.8—123.1°/744 mm., m. p. 3.8—4.0° (corr.),  $d_4^{20}$  1.4136,  $n_D^{20}$  1.48612; 2:3:4-*trichloro*-, b. p. 151.7—152.7°/734 mm.,  $d_4^{20}$  1.5471,  $n_D^{20}$  1.5057; 2-*bromo*-, b. p. 101.9—102.2°/744 mm.,  $d_4^{20}$  1.6500,  $n_D^{20}$  1.49805, and 3-*bromo*-furan, b. p. 102.5—102.6°/745 mm.,  $d_4^{20}$  1.6606,  $n_D^{20}$  1.49575. The halogen atoms in these derivatives are unreactive, and the compounds darken and resinify when kept. Oxidation of 3:4-dichlorofuran with nitric acid (*d* 1.42) gives the *lactone*,

$\text{OH}-\text{CH}-\text{O}-\text{CCl}-\text{CO}$  m. p. 124—125° (corr.); with nitric acid of *d* 1.49, dichloromaleic anhydride results. 2-Bromofuran reacts with an activated magnesium-copper alloy in ether, forming the Grignard reagent, which with carbon dioxide and phenylcarbimide gives furoic acid and its anilide, respectively.

When furoic acid is treated with aqueous mercuric acetate at 80°, carbon dioxide is evolved. Conversion of the mercuriacetate formed into the mercurichloride and treatment of this with iodine in potassium iodide led to a readily resinified oil, b. p. 120—140°.

Bromination of furoyl chloride gives rise to a mixture of 3:5- and 4:5-dibromofuroic acids. The halogenofuroic acids used were prepared by Hill's method (A., 1901, i, 555). The following are described: 3-*chloro*-, m. p. 148.5—149.5° (all corr.); 5-*chloro*-, m. p. 179—180°; 3:4-*dichloro*-, m. p. 169.5—170.5°; 3:4:5-*trichloro*-, m. p. 174.5—175.5°; 3-*bromo*-, m. p. 127—129°, and 5-*bromo*-furoic acids, m. p. 184—186° (*ethyl ester*, b. p. 134—136°/34 mm.). H. BURTON.

Attempted correlations of constitution with sweet taste in the furan series. Very high

sweetening power of 5-benzylfurfuraldoxime. H. GILMAN and J. B. DICKEY (J. Amer. Chem. Soc., 1930, 52, 2010—2013).—*syn*-5-Benzylfurfuraldoxime (Fenton and Robinson, J.C.S., 1909, 95, 1334) is 690 times as sweet as sucrose and about seven times as sweet as the *anti*-oxime. The 5-hydroxymethylfurfuraldoximes are devoid of sweet taste. There appears to be no correlation between geometrical isomerism and sweet taste in the furan series. H. BURTON.

[ $\alpha$ -Furylacetic (furan-2-acetic) acid and an interesting isomerisation in the furan series.] T. REICHSTEIN (Ber., 1930, 63, [B], 1283; cf. this vol., 611).—2-Furylacetaldehyde has been described previously by Rinkes (A., 1920, i, 322).

H. WREN.

**Preparation of furfurylidene diacetate.** H. GILMAN and G. F. WRIGHT (Iowa State Coll. J. Sci., 1929, 4, No. 1, 35—36).—Furfuraldehyde (4 g.-mol.) at 0° was added rapidly and with stirring to stannous chloride (1 g. of dihydrate) and acetic anhydride (4 g.-mol.) at -5°, the temperature being kept below -3°. After 24 hrs. the mixture was poured into water (2 litres), sodium carbonate and ice were added, the oil was dried in a vacuum over sulphuric acid, and distilled under 20 mm.; the substance has m. p. 52—53°. CHEMICAL ABSTRACTS.

**Magnesium  $\gamma$ -2-tetrahydrofuryl- $\alpha$ -methyl-propyl bromide.** H. GILMAN and J. B. DICKEY (J. Amer. Chem. Soc., 1930, 52, 2144—2147).—2- $\gamma$ -Hydroxybutylfuran (Kaufmann and Adams, A., 1924, i, 197) (*benzoate*, b. p. 164—166°/3 mm.) is converted by saturation of a benzene solution with hydrogen bromide into 2- $\gamma$ -bromobutylfuran, b. p. 79.5—80°/4 mm.,  $d_{25}^{25}$  1.2000,  $n_D^{25}$  1.4719. This readily forms a Grignard reagent from which are prepared by the usual methods  $\gamma$ -2-furyl- $\alpha$ -methylbutyric acid, b. p. 104—106°/0.2—0.3 mm.,  $d_{25}^{25}$  1.0401,  $n_D^{25}$  1.4528, and its  $\alpha$ -naphthylamide, m. p. 109.5—110°.

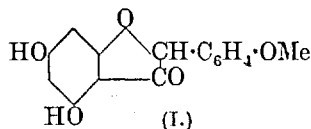
H. BURTON.

**Vesicant reaction of furfuryl chloroalkyl sulphides.** H. GILMAN and A. P. HEWLETT (J. Amer. Chem. Soc., 1930, 52, 2141—2144).—Difurfuryl disulphide is reduced with zinc dust and alcoholic acetic acid to  $\alpha$ -furfuryl mercaptan, b. p. 155°, which on successive treatment with magnesium ethyl bromide and  $\beta$ -chloroethyl *p*-toluenesulphonate affords furfuryl  $\beta$ -chloroethyl sulphide, b. p. 128°/5 mm.,  $d_{25}^{25}$  1.1914,  $n_D^{25}$  1.5200. This sulphide has vesicant properties. Furfuryl  $\gamma$ -chloropropyl sulphide, b. p. 135°/5 mm.,  $d_{25}^{25}$  1.1687,  $n_D^{25}$  1.4740, prepared similarly using  $\gamma$ -chloropropyl *p*-toluenesulphonate, has no vesicant action. H. BURTON.

**Structures capable of showing reversible oxidisability: the benzofuran group.** C. DU-FRAISSE and L. ENDERLIN (Compt. rend., 1930, 190, 1229—1230).—The photochemical oxidation of solutions of  $\alpha\delta$ -diphenyl- $\beta\gamma$ -benzofuran (cf. Guyot and Catel, A., 1907, i, 76) has been re-examined in the hope of finding evidence of reversible oxidisability, in analogy to rubrene, which is of analogous structure. No dissociable oxide appears to be formed.

R. K. CALLOW.

**2-Arylcoumaranones.** W. BAKER (J.C.S., 1930, 1015—1020).—Condensation of *O*-benzoylanisaldehydecyanohydrin and phloroglucinol in ether in the presence of hydrogen chloride, followed by boiling with concentrated hydrochloric acid, yielded 4:6-



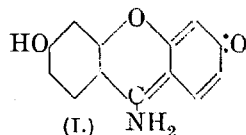
by boiling with water, and then with acetic anhydride and a little pyridine gave *anhydro-5-hydroxy-7-acetoxy-4- $\alpha$ -hydroxy-p-methoxybenzylcoumarin*, m. p. 181—182° (plates), and 3:4:6-triacetoxy-2-p-methoxyphenylcoumarone, m. p. 174—175° (thin needles), separated by physical means. Analogous condensation of *O*-benzoylanisaldehydecyanohydrin with resorcinol, followed by acetylation, yielded 6-acetoxy-2-p-methoxyphenylcoumaranone, m. p. 139°, and a substance,  $C_{30}H_{30}O_{11}$ , m. p. 217°, probably 3-keto-6:3':6'-triacetoxy-2:2'-di-p-methoxyphenyl-2:3'-dicoumaranyl, whilst interaction of *O*-benzoylbenzaldehydecyanohydrin and resorcinol under similar conditions, followed by acetylation, gave 2:4-diacetoxy-O-acetylbenzoin, m. p. 158°.

$\alpha$ -Bromo- $\beta$ -phenylpropionitrile and resorcinol react under the conditions of the Hoesch reaction to give, after acid hydrolysis, 6-hydroxy-2-benzylcoumaranone, m. p. 161°, converted by acetic anhydride and anhydrous sodium acetate into 3:6-diacetoxy-2-benzylcoumarone, m. p. 76°.

Contrary to Slater and Stephen (J.C.S., 1920, 117, 309) and in agreement with Karrer and Biedermann (A., 1927, 770) only  $\omega$ -hydroxyresacetophenone could be isolated from the condensation of glycollonitrile and resorcinol; this could not be converted into 6-hydroxycoumaranone by heating with hydrochloric acid or sulphuric acid, with or without zinc chloride.

A. I. VOGEL.

**Condensations of ethyl carbamate, phenylcarbamate, and diphenylcarbamate with resorcinol.** R. N. SEN and A. MUKHERJI (J. Indian Chem. Soc., 1930, 7, 275—278).—Resorcinol condenses with ethyl carbamate in presence of zinc chloride at 180°, forming the compound (I), softens at 210° (golden-yellow; the colours given in parentheses are the shades on wool and silk) [monopotassium and silver salts; *O*-chloroacetyl derivative, softens at 194°, prepared by the Schotten-Baumann method; di-

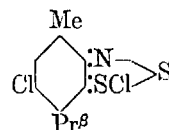


(chloroacetyl) derivative, m. p. 150°; tetrabromoderivative, decomp. 250° (red)]. Similarly, ethyl phenylcarbamate furnishes a compound (I,  $NH_2 = NHPh$ ), softens at 195° (reddish-yellow) [dibromoderivative, decomp. 295° (red)], and ethyl diphenylcarbamate gives the compound (I,  $NH_2 = NPh_2$ ), softens at 275° (reddish-brown) [dibromoderivative, decomp. 220° (bright red)]. Alcoholic and alkaline solutions of I and its *N*-phenyl and *NN*-diphenyl derivatives show bluish-green fluorescence. The amino-group in I is stable towards alcoholic potassium hydro-

oxide, hydrochloric acid, and fairly concentrated sulphuric acid.

H. BURTON.

**Methylisopropylthioindigoid dyes from p-cymene.** I. Dyes from 2-aminocymene. II. Dyes from sodium cymene-2-sulphonate. A. W. HIXSON and W. J. CAUWENBERG (J. Amer. Chem. Soc., 1930, 52, 2118—2125, 2125—2130).—I. Treatment of 2-aminocymene hydrochloride with sulphur chloride first at 20° and then at 50° gives the compound I, which chars at 120° without melting. Hydrolysis of this with water at 10°, treatment of the acid-free product with chloroacetic acid in alkaline solution, acidification of the reaction mixture with sulphuric acid, and warming to 70° gives the lactam, m. p. 159—



159-8°, of 5-chloro-2-aminocymene-3-thioglycollic acid. The same lactam is produced by a similar series of reactions from 5-chloro-2-aminocymene. Treatment of a mixture of the sodium salt of the above acid and sodium nitrite with hydrochloric acid at 10°, and coupling the diazo-solution with  $\beta$ -naphthol affords the corresponding *azo- $\beta$ -naphthol*. Treatment of the neutral diazo-solution with cuprous cyanide at  $p_H$  6.1 furnishes 5-chloro-2-cyanocymene-3-thioglycollic acid and tar. Successive treatment of the tar with alkali at 80° and boiling 25% sulphuric acid gives 6-chloro-3-hydroxy-4-methyl-7-isopropylthionaphthen, b. p. 191—193°/10 mm. (condensation products with isatin, red, isatin chloride, violet, and acenaphthenequinone), converted by treatment with sulphur in 5% sodium hydroxide solution into 6:6'-dichloro-4:4'-dimethyl-7:7'-diisopropylthioindigotin, red. The fastness of the above dyes to light and washing and spectrum analyses are recorded.

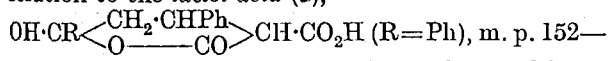
II. Reduction of cymene-2-sulphonyl chloride with zinc dust and dilute sulphuric acid first below 0° and then at the b. p. gives thiocarvacrol, b. p. 235—237°, the sodium salt of which reacts with chloroacetic acid, forming *cymene-2-thioglycollic acid*, m. p. 97°. Treatment of this with chlorosulphonic acid at 0° affords 3-hydroxy-7-methyl-4-isopropylthionaphthen, m. p. 86° (condensation products with isatin, isatin chloride, and acenaphthenequinone), converted as above into 7:7'-dimethyl-4:4'-diisopropylthioindigotin, dark red. Spectrum analyses and fastness of the dyes are tabulated.

H. BURTON.

**Piperidine derivatives.** IX. Methylpiperidinoalkyl cinnamates. C. F. BAILEY and S. M. McELVAIN (J. Amer. Chem. Soc., 1930, 52, 2007—2010).— $\beta$ -2-, -3-, and -4-methylpiperidinoethyl cinnamates, m. p. 178—180°, 161—163°, and 142—145°, respectively, and  $\gamma$ -2-, -3-, and -4-methylpiperidino-propyl cinnamates, m. p. 179—181°, 193—196°, and 178—181°, respectively, are prepared from the requisite methylpiperidine and  $\beta$ -chloroethyl, m. p. 35—37° (lit. 31°), and  $\gamma$ -chloropropyl cinnamates, b. p. 174—177°/3 mm.,  $d_4^{20}$  1.1512,  $n_D^{20}$  1.5677. The chloro-esters are obtained from cinnamoyl chloride and the requisite chlorohydrin. The methylpiperidinoalkyl cinnamates are generally more active and more toxic than the corresponding benzoates (this vol., 786), and the 4-methyl derivatives show greater physiological activity than the 2- or 3-compounds. H. BURTON.



**Reactivity of conjugated systems. I. Condensation of arylidene ketones with cyanoacetamide.** C. BARAT (J. Indian Chem. Soc., 1930, 7, 321—339).—The primary additive compound from phenyl styryl ketone and cyanoacetamide in presence of piperidine or diethylamine is considered to be 3-cyano-6-hydroxy-2-keto-4:6-diphenylpiperidine and not  $\alpha$ -cyano- $\gamma$ -benzoyl- $\beta$ -phenylbutyramide as stated by Kohler and Souther (A., 1923, i, 243), since the compound does not give ammonia when warmed with dilute alkali or alcoholic sodium ethoxide, and does not give a ketonic derivative. When the condensation is effected with an equivalent of sodium ethoxide, the tetrahydropyridine derivative of Kohler and Souther (*loc. cit.*) is formed; this is considered to be 3-cyano-2-keto-4:6-diphenyl-2:3:4:5-tetrahydropyridine rather than the 1:2:3:4-tetrahydro-derivative. The piperidine is converted into the pyridine by heating with acetic anhydride at 125—150°, or by Kohler and Souther's method. Hydrolysis of either of the above derivatives with cold sulphuric acid and addition of the resulting solution to cold methyl alcohol gives methyl  $\gamma$ -benzoyl- $\beta$ -phenylpropane- $\alpha\alpha$ -dicarboxylate, m. p. 108°, hydrolysed by 5% potassium hydroxide solution to the lactol acid (I),



154° (decomp.). Heating this affords the lactol form, m. p. 158°, of  $\gamma$ -benzoyl- $\beta$ -phenylbutyric acid [*semicarbazone*, m. p. 215° (decomp.)]. The above tetrahydropyridine is converted by nitrous acid into 3-cyano-2-keto-4:6-diphenyl-1:2-dihydropyridine, m. p. 320° (lit. 313—315°), hydrolysed by 75% sulphuric acid to 2-hydroxy-4:6-diphenylpyridine, m. p. 208° (lit. 210°). Phenyl styryl ketone and ethyl sodiomalonate afford ethyl  $\gamma$ -benzoyl- $\beta$ -phenylpropane- $\alpha\alpha$ -dicarboxylate, m. p. 150°, hydrolysed by potassium hydroxide solution to the above lactol acid. Elimination of carbon dioxide from this and treatment of the product with acetyl chloride or acetic anhydride gives the lactone of  $\delta$ -hydroxy- $\beta\beta$ -diphenyl- $\Delta\gamma$ -pentenoic acid. When this lactone is heated with dilute alkali, the lactol is regenerated.

*p*-Tolyl styryl ketone condenses with cyanoacetamide forming 3-cyano-6-hydroxy-2-keto-4-phenyl-6-*p*-tolylpiperidine, m. p. 230°, and 3-cyano-2-keto-4-phenyl-6-*p*-tolyl-2:3:4:5-tetrahydropyridine, m. p. 185°. These are hydrolysed as above to methyl  $\gamma$ -toluoyl- $\beta$ -phenylpropane- $\alpha\alpha$ -dicarboxylate, m. p. 95° (the ethyl ester, m. p. 123°, is formed from ethyl sodiomalonate and the original ketone), and thence to the lactol acid (I, R=C<sub>6</sub>H<sub>4</sub>·Me-*p*), m. p. 150° (decomp.). The lactol, m. p. 175° [*semicarbazone*, m. p. 222° (decomp.)], from this is dehydrated with acetic anhydride to the lactone, m. p. 98°, of  $\delta$ -hydroxy- $\beta$ -phenyl- $\delta$ -*p*-tolyl- $\Delta\gamma$ -pentenoic acid. 3-Cyano-2-keto-4-phenyl-6-*p*-tolyl-1:2-dihydropyridine, m. p. 268°, is hydrolysed by 75% sulphuric acid to 2-hydroxy-4-phenyl-6-*p*-tolylpyridine, m. p. 226—228°.

Styryl methyl ketone and cyanoacetamide give 3-cyano-6-hydroxy-2-keto-4-phenyl-6-methylpiperidine, m. p. 195—196° (decomp.), and 3-cyano-2-keto-4-phenyl-6-methyl-2:3:4:5-tetrahydropyridine, m. p. 267° after previous darkening. Hydrolysis of either of these compounds with 5% sulphuric acid at 125—

130° affords the lactol form, m. p. 85°, of  $\gamma$ -acetyl- $\beta$ -phenylbutyric acid. The same product is also formed when the dihydroresorcinol derivative formed from ethyl sodiomalonate and the original ketone is hydrolysed with barium hydroxide solution, and the resulting product heated. 3-Cyano-2-keto-4-phenyl-6-methyl-1:2-dihydropyridine, m. p. 275—276°, and 2-hydroxy-4-phenyl-6-methylpyridine, m. p. 206—207°, are described.

Styryl ethyl ketone furnishes 3-cyano-6-hydroxy-2-keto-4-phenyl-6-ethylpiperidine, m. p. 235—236° (decomp.), and 3-cyano-2-keto-4-phenyl-6-ethyl-2:3:4:5-tetrahydropyridine, m. p. 178—180°, both of which are hydrolysed by 10% sulphuric acid at 140—150° to the lactol form, m. p. 108°, of  $\gamma$ -propionyl- $\beta$ -phenylbutyric acid. This lactol is also obtained from ethyl 5-phenyl-2-methyldihydroresorcinol-4-carboxylate, m. p. 120°. 5-Phenyl-2-methyldihydroresorcinol has m. p. 214°. 3-Cyano-2-keto-4-phenyl-6-ethyl-1:2-dihydropyridine, m. p. 268°, and 2-hydroxy-4-phenyl-6-ethylpyridine, m. p. 165°, are prepared by the general method.

H. BURTON.

**Nitration of pyridine. Preparation of 2-nitropyridine.** H. J. DEN HERTOG, jun., and J. OVERHOFF (Rec. trav. chim., 1930, 49, 552—556).—When a solution of pyridine in twice its volume of 100% sulphuric acid is slowly dropped into molten potassium nitrate in a special apparatus (described), heated electrically at 300°, fractionation of the products affords a 4.5% yield of 3-nitropyridine (Friedl, A., 1912, i, 299) and 0.5% of 2-nitropyridine, m. p. 68°, whilst 50% of the pyridine is recovered. With rise in reaction temperature the proportion of the 2-nitro-compound increases (2% at 370°; 2.5% at 450°), whilst that of the 3-nitro-compound diminishes (4% at 370°; none at 450°), the recovery of pyridine being 40% in each case. 2-Nitropyridine will not form either a picrate or a nitrate, but its structure was proved by reduction to 2-aminopyridine with tin and 25% hydrochloric acid. Attempts to nitrate pyridine by passing the vapour with nitrogen peroxide over heated catalysts were unsuccessful. Thus with a vanadium oxide catalyst at 200—300°, 75% of the pyridine was recovered unchanged, the only other products being acetaldehyde and 3:3'-azopyridine, identical with a specimen prepared by reduction of the corresponding azoxy-compound (Friedl, *loc. cit.*).

J. W. BAKER.

**Reduction products of derivatives of aminopyridine.** A. E. TSCHITSCHIBABIN and M. P. GERTSCHUK (Ber., 1930, 63, [B], 1153—1156).—2:5-Diaminopyridine is reduced by sodium and ethyl alcohol at 90—145° to 3-aminopiperidine, b. p. 70—71°/10 mm.,  $d_{20}^{20}$  0.9608,  $n_D^{20}$  1.4846, which rapidly absorbs carbon dioxide and moisture from the atmosphere; the picrate, C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>·2C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>·OH, m. p. 226—226.5°, chloroplatinate, and very hygroscopic hydrochloride are described. Under similar conditions, 2-aminopyridine is converted into ammonia, piperidine, and 2-aminopiperidine, isolated as the dipicrate, m. p. 214°.

H. WREN.

**Quinoline derivatives. XII. 4-Bromo-2-phenylquinoline.** H. JOHN (J. pr. Chem., 1930, [ii], 126, 220—222).—The preparation of 4-bromo-2-

*phenylquinoline*, m. p. 91° (*picrate*, m. p. 169—170°), from 4-amino-2-phenylquinoline by Gattermann's reaction is described. Numerous salts are described but not characterised. H. A. PIGGOTT.

**Derivatives of 2-phenylquinolinecarboxylic acids.** F. BELLINO (*Annali Chim. Appl.*, 1930, 20, 222—224).—The action of bromine (1 mol.) on (1) 2-phenylquinoline-4-carboxylic acid in glacial acetic acid yields the *perbromide*,  $C_{16}H_{11}O_2N, HBr, Br, 2H_2O$ , m. p. 224° (not sharp), and (2) the hydrobromide of the acid under similar conditions gives the *compound*  $(C_{16}H_{11}O_2N)_2, HBr, Br_2$ , m. p. 248°. Immediate treatment of the mother-liquor from either (1) or (2) with sulphur dioxide precipitates the 2-phenylquinoline-4-carboxylic acid, which dissolves in excess of the sulphur dioxide. If the mother-liquor is left for some weeks (a month), especially if exposed to direct sunlight, sulphur dioxide precipitates the true *monobromo-derivative*,  $C_{16}H_{10}O_2NBr$ , m. p. 240°, which forms a white *sodium salt* ( $+H_2O$ ), turning pale yellow on drying. As little as 1 part of 2-phenylquinoline-4-carboxylic acid dissolved in 35,000 parts of 2*N*-hydrochloric acid is precipitated by a potassium iodide solution of iodine; the *precipitate* has the formula  $(C_{16}H_{11}O_2N, HI)_2I$ , and may be either bluish-black, m. p. 260°, or deep chestnut, m. p. 253—255°. T. H. POPE.

**Derivatives of 2-phenylquinolinecarboxylic acids.** G. OTTOLINO (*Annali Chim. Appl.*, 1930, 20, 224—228).—3-Phenyl- $\beta$ -anthraquinoline-1-carboxylic acid (cf. Ciusa and Musajo, A., 1929, 578) forms a *hydrochloride* ( $+HCl$ ), m. p. 245°, a *nitrate* ( $+HNO_3$ ), m. p. 267°, and a *sulphate* ( $+H_2SO_4$ ), m. p. 215°. 3-Phenyl- $\beta$ -naphthoquinoline-1-carboxylic acid forms a *hydrochloride*, m. p. 290—293°, a *nitrate*, m. p. 286°, and a *sulphate*, m. p. 240°. 2-Phenylquinoline-4-carboxylic acid forms a *mono-hydrochloride*, m. p. 225—230°, which is very sparingly soluble and serves to detect small quantities of the acid, a *dihydrochloride*, m. p. 220—225°; a *nitrate*, m. p. 230—234°, a *sulphate*, m. p. 262—266°, a *chromate*, and a *phosphate*, m. p. 220°. The acid may be detected in 0.05% concentration in 2*N*-hydrochloric acid by precipitation with bromine water (cf. Bellino, preceding abstract). T. H. POPE.

**Manufacture of reduction products of indoxyl, naphthindoxyl, their homologues and acyl derivatives.** I. G. FARBENIND.—See B., 1930, 549.

**Synthesis of 2-methylquinuclidine.** K. WINTERFELD (*Arch. Pharm.*, 1930, 268, 308—314).—2:4-Dimethylpyridine [*chloroplatinate*, m. p. 225° (decomp.); *mercurichloride*,  $C_7H_9N, HCl, 2HgCl_2, 0.5H_2O$ , m. p. 130°], refluxed for 48 hrs. with 20% aqueous-alcoholic formaldehyde yields about 10% of 2-methyl-4- $\beta$ -hydroxyethylpyridine [*mercurichloride*,  $C_8H_{11}ON, 5HgCl_2, 1\frac{1}{2}H_2O$ , m. p. 212°, softening from 175°; *chloroplatinate*, m. p. 164° (decomp.)], which is separated from more complex condensation products by dissolution in ether. It is reduced by activated platinum sponge to 2-methyl-4- $\beta$ -hydroxyethylpiperidine. This yields after refluxing for 10 hrs. with fuming hydriodic acid and red phosphorus 2-methyl-4- $\beta$ -iodoethylpiperidine hydriodide, the free

base from which passes in ethereal solution into the *hydriodide*, m. p. 229°, of 2-methylquinuclidine [*chloraurate*, m. p. 197—198° (decomp.); *mercurichloride*,  $C_8H_{15}N, 6HgCl_2$ , m. p. 230° (decomp.)]. This base is not oxidised by permanganate and dilute sulphuric acid. H. E. F. NOTTON.

**Acridine. V. Two isomeric *ms*-tetrahydro-9:9'-diacrydyls.** K. LEHMSTEDT and H. HUNDEDMARK (*Ber.*, 1930, 63, [B], 1229—1241; cf. A., 1929, 1079).—Re-examination of the tetrahydro-diacridyl, m. p. 279°, of Schlenk and Bergmann (A., 1928, 1039), for which m. p. 260—265° has been recorded subsequently (Bergmann and Blum-Bergmann, this vol., 790), shows that the last-mentioned m. p. can be observed only under very unusual conditions. Since the m. p. of the tetrahydrodiacridyls depend very greatly on experimental conditions, standard conditions have been selected. The temperature is raised 3° per min. and the isomerides of lower and higher m. p. are introduced at 200° and 230°, respectively. The m. p. thus observed are 214° and 249°, whereas Schlenk's compound has m. p. 247°.

9:9'-Diacridyl is conveniently prepared, mixed with acridine, by the action of copper powder on thioacridone in an atmosphere of carbon dioxide at 280°. Acridine hydrochloride is transformed by alcoholic potassium cyanide into tetrahydrodiacridyl, m. p. 214°, and 9-cyanoacridan, converted by moistening with 5% sodium hydroxide and subsequent exposure to air into 9-cyanoacridine (yield 85%). In place of potassium cyanide, alcoholic hydrogen cyanide may be used. The alcoholic mother-liquors, when treated with sodium amalgam, afford *ms*-tetrahydro-9:9'-diacridyl, m. p. 249°, and 9:10-*dihydro-acridine-9-carboxylic acid*, m. p. 208° (decomp.), decarboxylated to *ms*-dihydroacridine, m. p. 170°. In benzene, acridine and hydrogen cyanide react more slowly, giving *ms*-tetrahydro-9:9'-diacridyl, m. p. 214°, and 9-cyanoacridan. The diacridyl derivative, m. p. 249°, becomes disproportionated if crystallised from benzonitrile but not from pyridine; inhibition is due to the presence of a trace of alkali in the solvent. Treatment of the *ms*-tetrahydro-9:9'-diacridyls or of Schlenk and Bergmann's product with sulphuric acid affords sulphur dioxide and hydrogen sulphide, unchanged material, acridine, and the *base*  $[NHPh \cdot C_6H_4 \cdot CH(OH) \cdot]_2$  or its ethylene oxide form,  $NHPh \cdot C_6H_4 \cdot CH \cdot NHPh \cdot C_6H_4 \cdot CH > O$ , m. p. 165° (leaving a crystalline skeleton of *ms*-tetrahydro-9:9'-diacridyl, m. p. 214°). It is transformed by boiling glacial acetic acid into tetrahydrodiacridyl, m. p. 214°, and by sulphur into thioacridone. The *dihydrochloride* is described. A nitroso-compound or benzoyl derivative could not be prepared. Oxidation to a diketone could not be effected. Treatment of it with methyl iodide and magnesium oxide affords the di-*N*-methyl derivative,  $C_{28}H_{28}ON_2, 2HI, 2H_2O$ , m. p. 220°. It is converted by nitric acid (*d* 1.4) into *di*-3-nitro-6-2':4'-dinitro-anilinoethylene oxide.

Graebe's "insoluble hydroacridine" has m. p. 214° if brought into a bath pre-heated at 200°; when treated with sulphuric acid it affords the *base*, m. p. 165° (see above).

The nature of the isomerism of the *ms*-tetrahydro-9:9'-diacridyls is discussed at length. H. WREN.

**Piperazine.** Action of iodine and of hydrogen iodide on piperazine. S. OTOLSKI (Bull. Soc. chim., 1930, [iv], 47, 480—488).—See this vol., 788.

**Determination of constitution of acylated pyrazoles by physico-chemical methods.** K. VON AUWERS and E. CAUER (J. pr. Chem., 1930, [ii], 126, 177—197).—A comparison of the optical exaltations, b. p., viscosities, and heats of combustion of a number of *N*-alkyl- and *N*-aryl-pyrazoles did not indicate any regularity sufficient as a basis of a method of determining which nitrogen atom is substituted in *N*-acylpyrazoles. The following were prepared by heating the appropriate pyrazole with acetyl chloride or acetic anhydride in the case of the acetyl derivatives, and with ethyl chloroformate in the case of the carboxy-derivatives: 1-Acetyl-4-methylpyrazole, b. p. 177°,  $d_4^{17}$  1.0726,  $n_D^{18}$  1.48643; ethyl 4-methylpyrazole-1-carboxylate, b. p. 227°,  $d_4^{17}$  1.1059,  $n_D^{17}$  1.48148; 1-acetyl-3:5-dimethylpyrazole, b. p. 186—188°,  $d_4^{17}$  1.0517,  $n_D^{18}$  1.49254; 1-acetyl-4-phenylpyrazole, m. p. 81.5—82.5°, b. p. 159—161°/12 mm.,  $d_4^{19}$  1.0945,  $n_D^{19}$  1.56600; ethyl 4-phenylpyrazole-1-carboxylate, m. p. 78—78.5°, b. p. 192°/9 mm.,  $d_4^{19}$  1.1055,  $n_D^{19}$  1.54637; 1-acetyl-3:5-diphenylpyrazole, m. p. 86—86.5°, b. p. 226°/10 mm.,  $d_4^{19}$  1.1047,  $n_D^{19}$  1.60363; ethyl 3:5-diphenylpyrazole-1-carboxylate, m. p. 106—107°, b. p. 242°/10 mm.; 1-acetyl-3:4-dimethylpyrazole, b. p. 190°; ethyl 3:4-dimethylpyrazole-1-carboxylate, b. p. 238°,  $d_4^{19}$  1.0710,  $n_D^{19}$  1.48138; ethyl 3-phenylpyrazole-1-carboxylate, b. p. 195°/12 mm.,  $d_4^{19}$  1.1711,  $n_D^{18}$  1.57765; methyl 1-acetyl-4-phenylpyrazole-3-carboxylate, m. p. 129.5—130.5°. 4-Phenyl-1-methylpyrazole, m. p. 102—102.5°, was prepared by the action of methyl sulphate and alkali on 4-phenylpyrazole-3-carboxylic acid, and heating the mixture of acids produced. Methyl iodide reacted only incompletely with 4-phenylpyrazole and its carboxylic acid. 4-Phenyl-1-ethylpyrazole, m. p. 68.5—69°,  $d_4^{19}$  1.0057,  $n_D^{19}$  1.55250, was, however, obtained by ethylation of 4-phenylpyrazole. Methyl 1-methylpyrazole-3:5-dicarboxylate, m. p. 72—73.5°,  $d_4^{19}$  1.1817,  $n_D^{19}$  1.47903,  $d_4^{19}$  1.1809,  $n_D^{19}$  1.47753, and methyl 1-acetylpyrazole-3:5-dicarboxylate, m. p. 84.5—85°,  $d_4^{19}$  1.2132,  $n_D^{19}$  1.47559, were obtained by methylation and acetylation respectively of methyl pyrazole-3:5-dicarboxylate. Refractive indices for the  $\alpha$ ,  $\beta$ , and  $\gamma$  lines at the stated temperatures are also given. H. A. PIGGOTT.

**1:3:4- and 1:4:5-Trimethylpyrazoles.** K. VON AUWERS and E. CAUER (J. pr. Chem., 1930, [ii], 126, 198—203).—Methyl 3:4-dimethylpyrazole-5-carboxylate with methyl iodide and sodium methoxide gave mainly methyl 1:4:5-trimethylpyrazole-3-carboxylate, b. p. 161°/16 mm., m. p. 49—52.5°,  $d_4^{19}$  1.1218,  $n_D^{19}$  1.50567, mixed with a little methyl 1:3:4-trimethylpyrazole-5-carboxylate, b. p. 113°/16 mm.,  $d_4^{19}$  1.1011,  $n_D^{19}$  1.49472. 1:4:5-Trimethylpyrazole-3-carboxylic acid, m. p. 204.5—205.5°, was readily re-esterified, but 1:3:4-trimethylpyrazole-5-carboxylic acid, m. p. 178—179°, was completely unchanged under identical conditions, this behaviour confirming the constitutions assigned. When heated

above their m. p. these acids were decomposed into 1:4:5-trimethylpyrazole, b. p. 176—177°,  $d_4^{18}$  0.9685,  $n_D^{18}$  1.48485 (picrate, m. p. 175—176°), and 1:3:4-trimethylpyrazole, b. p. 160°,  $d_4^{17}$  0.9567,  $n_D^{17}$  1.4780 (picrate, m. p. 163.5—164.5°). The apparent isolation of a single trimethylpyrazole only by the methylation of 3:4-dimethylpyrazole (Auwers and Broche, A., 1923, i, 151), or by the condensation of phenylmethylhydrazine with  $\gamma$ -hydroxymethylene- $\beta$ -keto-*n*-butane or its benzoate (Auwers and Kohlhaas, A., 1924, i, 666), is explained by the fact that the apparently homogeneous "picrate, m. p. 147—148°," is actually a mixture of the above two picrates, m. p. 175—176° and 162°, and may be separated into its components by extraction with hot alcohol. Attempts to separate the mixture of trimethylpyrazoles by fractional distillation were unsuccessful. H. A. PIGGOTT.

**Acyl derivatives of tetrahydroindazole and of tetrahydroindazole-3-carboxylic acid.** K. VON AUWERS and E. WOLTER (J. pr. Chem., 1930, [ii], 126, 204—216; cf. A., 1927, 577).—The interaction of alkyl or arylhydrazines with ethyl 2-ketocyclohexylglyoxylate leads generally to a mixture of 1- and 2-alkyl-(or aryl-) tetrahydroindazole-3-carboxylic esters, the proportions depending on the reaction conditions. Thus methylhydrazine acetate gave approximately equal amounts of the two isomerides, whilst the sulphate gave mainly the 1-methyl derivative; phenylhydrazine behaved similarly, the ratios of 1- to 2-phenyl derivatives being, with the acetate 32:68, and with the hydrochloride 86:14. Ethyl hydrazinecarboxylate, however, when condensed with 2-ketocyclohexylglyoxylic acid, gave exclusively 1-carbethoxytetrahydroindazole-3-carboxylic acid, m. p. 158.5—159.5° (ethyl ester, m. p. 92—93.5°). This acid was also produced by the action of ethyl chloroformate on tetrahydroindazole-3-carboxylic acid, and the ethyl ester in a similar way; their formation in this manner, and the ready esterification of the acid, confirm the constitution assigned. An attempt at the synthesis of the ethyl ester from ethyl 2-ketocyclohexylglyoxylate failed.

Methyl and ethyl 1-acetyltetrahydroindazole-3-carboxylates, m. p. 77—78°, b. p. 182°/12 mm., and m. p. 94—95°, b. p. 182°/10 mm., respectively, were readily obtained by direct acetylation, but not by the use of acetylhydrazine in the above synthetic method. The interaction of 2-ketocyclohexylglyoxylic acid and acetylhydrazine occurred with simultaneous hydrolysis of the acetyl group, even when carried out in absolute methyl alcohol below 30°.

It seems most probable that in the case of 2-ketocyclohexylglyoxylic acid, hydrazone formation occurs at the carbonyl group in the side-chain, for whereas the acid is readily oxidised by hydrogen peroxide in alkaline solution, the *o*-nitrobenzoylhydrazone is quite unchanged. The behaviour of pyruvic acid and of its *p*-nitrophenylhydrazone is similar. The formation of 1-acyltetrahydroindazoles in the above synthesis is thus explained. 1-*o*-Nitrobenzoyltetrahydroindazole has m. p. 148—149°; the lower m. p., 129—130° (cf. A., 1924, i, 326), is due to the presence of impurities.

1-*p*-Toluyltetrahydroindazole, m. p. 82—83°, b. p. 214—216°,  $d_4^{19}$  1.0821,  $n_D^{19}$  1.56634, was obtained by

the action of *p*-toluoyl chloride on tetrahydroindazole; 2-*p*-toluoyltetrahydroindazole, m. p. 64–65°,  $d_4^{20}$  1.0862,  $n_D^{20}$  1.56251, resulted from the interaction of 1-hydroxymethylcyclohexanone and *p*-toluoylhydrazine [from the mother-liquors much 2:5-di-*p*-tolyl-1:3:4-oxadiazole, m. p. 175° (Stollé, A., 1904, i, 626), was obtained]; the latter was completely isomerised to the former by heating at 180° or by vacuum distillation. This is the first recorded case of the transformation of a solid 2-acyl- into a solid 1-acyltetrahydroindazole. H. A. PRIGOTT.

**Reaction between thiocarbanilide and chloroacetic acid in alcohol and acetic acid solution.** K. S. MARKLEY and E. E. REID (J. Amer. Chem. Soc., 1930, 52, 2137–2141).—Good yields of diphenylisothiohydantoin are obtained when the reaction between thiocarbanilide and chloroacetic acid is carried out in a relatively small amount of alcohol and acetic acid, provided the water and hydrogen chloride formed during the reaction are removed with anhydrous sodium acetate. When the sodium acetate is omitted, varying amounts of 2:4-diketo-3-phenyltetrahydrothiazole are formed in addition to the hydantoin. The thiazole arises from the action of the hydrogen chloride on the hydantoin. Phenylthiocarbimide, ethyl phenylthiocarbamate, and diphenylthiocarbamate are also formed as by-products when reaction is carried out in alcohol in absence of sodium acetate. H. BURTON.

**Action of guanidine carbonate and benzamidine hydrochloride on glyoxal sodium hydrogen sulphite.** J. B. EKELEY and J. M. FULMER (J. Amer. Chem. Soc., 1930, 52, 2026–2028).—Guanidine carbonate and glyoxal sodium hydrogen sulphite react in boiling aqueous solution forming the sodium aminoglyoxalinesulphonate,

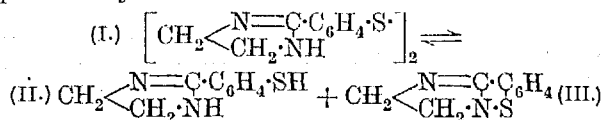
$\text{N} \begin{smallmatrix} \text{C}(\text{NH}_2)_2 \\ \text{CH} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{CH} \\ \text{CH} \end{smallmatrix} \text{SO}_3\text{Na}$ , converted by treatment with nitrous acid into the corresponding hydroxyglyoxalinesulphonic acid, m. p. 225°. Acidification of the sodium salt gives the neutral, internal ammonium salt, m. p. 172–174°, reconverted into the sodium salt by boiling with sodium hydroxide solution.

Benzamidine hydrochloride and glyoxal sodium hydrogen sulphite afford the phenylglyoxalinesulphonic acid,  $\text{N} \begin{smallmatrix} \text{CPh} \\ \text{CH} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{CH} \\ \text{CH} \end{smallmatrix} \text{SO}_3\text{H}$ , m. p. 109°.

H. BURTON.

**Dismutation of disulphides.** E. W. McCLELLAND and L. A. WARREN (J.C.S., 1930, 1095–1102).—Mol. wt. determinations of 2:2'-dithiodiphenyl-4:5-dihydroglyoxaline (I) (this vol., 95) in alcohol and benzene by the Menzies-Wright ebullioscopic method (A., 1921, ii, 622) gave low values which diminished with dilution, and were unaffected by boiling at any concentration. The apparent mol. wt. of the disulphide in alcohol to which 2-*o*-thiolphenyl-4:5-dihydroglyoxaline (II) had been added is higher than that in the pure solvent, and increases with increasing concentration of the thiol. Alcoholic solutions of I are thermochromic, and do not obey Beer's law (cf. Lecher, A., 1915, i, 532). These results are explained by the reversible dismutation of I into

II and the tricyclic compound III, which may be preceded by the formation of free radicals.



This view receives support from the formation in good yield of the disulphide I by treatment of an equimolecular mixture of the tricyclic hydrobromide and the thiol II with 1 equivalent of potassium hydroxide. Further, interaction of I in alcohol with methyl iodide at 100° afforded the hydriodide of III (identified as the hydrobromide, m. p. 257°), and 2-*o*-methylthiolphenyl-4:5-dihydroglyoxaline hydriodide, m. p. 206–208° (free base, m. p. 98–100°; picrate, m. p. 207°).

3:3'-Dithiobenzamide, m. p. 243°, prepared from 3:3'-dithiobenzoic acid, excess of thionyl chloride, and a little ferric chloride, followed by treatment with ammonia ( $d$  0.88) at 0°, yielded 3:3'-dithiobenzonitrile (IV), m. p. 102–103°, when boiled with phosphoric oxide in xylene. An alcoholic solution of IV and ethylenediamine saturated with hydrogen sulphide at –10°, and heated under pressure at 90–100° for 1.25 hrs. gave 2-*m*-thiolphenyl-4:5-dihydroglyoxaline, m. p. 225–228°, oxidised by alkaline potassium ferriocyanide to 2:2'-dithiodiphenyl-4:5-dihydroglyoxaline (V), m. p. 193° (normal mol. wt. in alcohol), and converted by heating with methyl iodide and alcohol into 2-*m*-methylthiolphenyl-4:5-dihydroglyoxaline hydriodide, m. p. 262–264° (decomp.) (base, m. p. 94–96°). The following *p*-compounds were similarly prepared from 4:4'-dithiobenzoic acid: 4:4'-dithiobenzamide, m. p. 278°; 4:4'-dithiobenzonitrile, m. p. 172–173°; 2-*p*-thiolphenyl-4:5-dihydroglyoxaline, m. p. 290° (decomp.); 2:2'-pp'-dithiodiphenyl-4:5-dihydroglyoxaline (VI), m. p. 213° (normal mol. wt. in alcohol); 2-*p*-methylthiolphenyl-4:5-dihydroglyoxaline, m. p. 155–156° (hydriodide, m. p. 237°).

Both the disulphides I and VI are reduced in hot alcohol by hydrogen sulphide to 2-*o*-, m. p. 242°, and 2-*p*-thiolphenyl-4:5-dihydroglyoxaline, m. p. 290°, respectively. The *m*-compound V is not reduced to the thiol under similar conditions. This variation in stability indicates that the dihydroglyoxaline nucleus tends to weaken the S·S linking when in the *o*- and *p*-position, but not in the *m*-position.

The conception of reversible dismutation is applied to explain various reactions of disulphides.

A. I. VOGEL.

**Pyrimidines. CXV. Alkylation on nitrogen of the pyrimidine ring by application of a new technique involving molecular rearrangements.** G. E. HILBERT and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 2001–2007).—When 2:6-dialkoxy- and 2-keto-6-alkoxy-3-alkyl-pyrimidines are heated, rearrangement into 1:3-dialkyluracils occurs. Partial rearrangement into monoalkyluracils has not been observed, but such derivatives can be prepared by hydrolysing 2-keto-6-alkoxy-3-alkylpyrimidines, formed from 2:6-dialkoxy-pyrimidines and alkyl iodide, with hydrochloric acid.

Treatment of 2:6-dichloropyrimidine with methanol alcoholic sodium methoxide gives 2:6-dimethoxy-

pyrimidine, b. p. 202°, m. p. 17.8° (lit. 10°), passing at 220—240° into 1:3-dimethyluracil. Treatment of the dimethoxy-derivative with methyl iodide furnishes 2-keto-6-methoxy-3-methylpyrimidine, m. p. 149—150°, converted also into 1:3-dimethyluracil. 2:6-Diethoxypyrimidine, b. p. 224—225°, m. p. 19—20°, and methyl iodide give 2-keto-6-ethoxy-3-methylpyrimidine, m. p. 136°, which when heated at 250° affords 3-methyl-1-ethyluracil, b. p. 140—141°/4 mm., m. p. 60—61°. Prolonged treatment of 2:6-diethoxypyrimidine with ethyl iodide yields 1:3-diethyluracil, b. p. 135°/4 mm., m. p. 14—15°, brominated in alcoholic solution to 5-bromo-1:3-diethyluracil, two forms, m. p. 71° and 80—81°. H. BURTON.

**Pyrazines.** V. C. GASTALDI and E. PRINCIVALLE. VI. E. PRINCIVALLE (Gazzetta, 1930, 60, 296—297, 297—301).—V. By determination of the number of *N*-methyl groups in the pre- and post-hydrolytic products of the transformation of 5-benzoyl-6-keto-1:2:5-trimethyl-1:6-dihydropyrazine (both contain two *N*-methyl groups), it is shown that the methyl group, which takes part in the transformation and is subsequently eliminated as acetophenone, is that occupying position 5 (cf. A., 1929, 196, 197).

VI. It is shown that hydroxypyrazines couple with diazonium salts through the tautomeric lactim form; thus 6-keto-1:2:5-trimethyl-1:6-dihydropyrazine (hydrochloride, m. p. 227°), obtained by heating the methiodide (A., 1928, 1027), in which the mobile hydrogen atom is substituted, does not couple in alkaline solution. 6-Hydroxypyrazine-3-carboxylic acids undergo coupling with elimination of the carboxyl group; 6-hydroxy-2:5-dimethylpyrazine-3-carboxylic acid (A., 1921, i, 602) with benzene- and *p*-toluene-diazonium chlorides affords 3-benzene- and 3-*p*-toluene-azo-6-hydroxy-2:5-dimethylpyrazines, m. p. 208° and 242°, respectively, identical with the products obtained directly from 6-hydroxy-2:5-dimethylpyrazine (A., 1929, 196, 197).

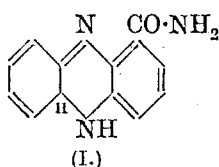
The transformation of 6-keto-1:2:5-trimethyl-1:6-dihydropyrazine methiodide by alkali hydroxides to give 6-keto-1:2:4-trimethyl-5-methylene-1:6:4:5-tetrahydropyrazine is not general for pyrazines possessing a methyl group  $\alpha$  to the quinquivalent nitrogen atom, and appears to depend on the presence of certain groups; thus 2:5-dimethylpyrazine methiodide (Stoehr, A., 1893, i, 486) when decomposed by alkali hydroxides does not give a methylenepyrazine. C. W. SHOPPEE.

**Transformation of *o*-aminoazo-derivatives into quinoxalines.** G. B. CRIPPA (Gazzetta, 1930, 60, 301—308).—The reaction between *o*-aminoazo-compounds and acetophenone (A., 1929, 1083) is a general one, and by use of other arylmethyl ketones affords quinoxalines which are otherwise inaccessible. *p*-Acetamidoacetophenone condenses with phenylazo- $\beta$ -naphthylamine in boiling xylene containing a trace of hydrochloric acid to give  $\beta$ -(*p*-acetamidophenyl)-1:2-naphthaquinoxaline, m. p. 235°, oxidised by chromic anhydride in acetic acid-acetic anhydride solution to  $\beta$ -(*p*-acetamidophenyl)-1:2-quinoxaline-3:4-naphthoquinone, m. p. 270°, which condenses with *o*-phenylenediamine to yield  $\beta$ -(*p*-acetamidophenyl)-1:2-quinoxaline-3:4-naphthazine, m. p.

above 335°. *p*-Benzamidoacetophenone, m. p. 200°, condenses under similar conditions with phenylazo- $\beta$ -naphthylamine to give  $\beta$ -(*p*-benzamido-phenyl)-1:2-naphthaquinoxaline, m. p. 246°, oxidised by chromic anhydride to  $\beta$ -(*p*-benzamido-phenyl)-1:2-quinoxaline-3:4-naphthoquinone, m. p. 286°, which with *p*-phenylenediamine yields  $\beta$ -(*p*-benzamido-phenyl)-1:2-quinoxaline-3:4-naphthazine, m. p. above 340°. *p*-Aminoacetophenone under similar conditions does not give the expected quinoxaline, but complicated autocondensation products.

Under the above conditions *p*-acetylphenylazo- $\beta$ -naphthylamine condenses with phenylazo- $\beta$ -naphthylamine to give  $\beta$ -[*p*-(2'-aminonaphthylazo)-phenyl]-1:2-naphthaquinoxaline, m. p. 258°, and aniline; a secondary reaction involving 2 mols. of *p*-acetylphenylazo- $\beta$ -naphthylamine occurs to yield the same quinoxaline and *p*-aminoacetophenone; traces of another substance, m. p. 172°, were also isolated. The quinoxaline by heating with copper powder in vaseline is converted into  $\beta$ -[*p*-(1':2'-triazolyl-*N*-phenyl)-1:2-naphthaquinoxaline, m. p. 299°, more readily obtained from phenylazo- $\beta$ -naphthylamine and *N*-*p*-acetylphenyl-1:2-naphthotriazole at 150—160° in the presence of a trace of hydrochloric acid. With *p*-acetylphenylazo- $\beta$ -naphthol phenylazo- $\beta$ -naphthylamine affords  $\beta$ -[*p*-(2'-hydroxynaphthylazo)-phenyl]-1:2-naphthaquinoxaline, m. p. 294°, whilst with 4-hydroxy-1-*p*-acetylphenylazonaphthalene, m. p. 219°, prepared by coupling  $\alpha$ -naphthol with diazotised *p*-aminoacetophenone,  $\beta$ -[*p*-(4'-hydroxynaphthylazo)-phenyl]-1:2-naphthaquinoxaline, m. p. above 310°, is obtained. C. W. SHOPPEE.

The green product of metabolism of *Bacillus chlororaphis*. F. KÖGL and J. J. POSTOVSKY (Annalen, 1930, 480, 280—297).—Chlororaphin,  $C_{26}H_{20}O_2N_6$  (cf. Lasseur, Thesis, Nancy, 1911), sublimes at 210° in absence of oxygen, and has m. p. about 225° in an atmosphere of nitrogen or hydrogen. Oxychlororaphin,  $C_{13}H_9ON_3$  (cf. loc. cit.), m. p. 241°, is not acetylated with acetic anhydride and pyridine. When heated with 33% potassium hydroxide solution, oxychlororaphin eliminates 1 mol. of ammonia; acidification of the resulting solution gives an acid,  $C_{13}H_8O_2N_2$ , m. p. 237°, which on distillation with soda-lime furnishes phenazine. Oxychlororaphin is shown to be phenazine-1-carboxylamide by the following synthesis. A mixture of anthranilic acid, nitrobenzene, and solid potassium hydroxide is heated at 145—160° (cf. Wohl and Aue, A., 1901, i, 612), whereby some phenazine-1-carboxylic acid, m. p. 239°, is obtained. This is converted by way of its chloride into the amide, m. p. 241°, identical with oxychlororaphin. Reduction of this amide with zinc dust and water affords chlororaphin, green (*M* in camphor 222—372, according to the concentration), but with zinc dust and acetic acid,



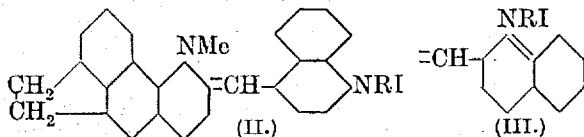
dihydrophenazine-1-carboxylamide (+AcOH), m. p. 192—194° with darkening, results. The intensely yellow colour of this dihydro-derivative indicates the structure I. Chlororaphin is probably a complex of molecular proportions of phenazine-1-carboxylamide and

I, since admixture of solutions of these in acetic acid with water precipitates the green compound.

H. BURTON.

**Cyanine dyes from quaternary salts of 2-methylacenaphthpyridine and 5-methylacridine.** (Miss) F. M. HAMER (J.C.S., 1930, 995—1003).—Condensation of 3-aminoacenaphthene (1 mol.) (best prepared by reduction of 3-nitroacenaphthene in 50% alcohol with sodium hyposulphite) with paraldehyde (2.5 mols.) in the presence of concentrated hydrochloric acid gave 2-methylacenaphthpyridine in 29% yield, converted by heating with methyl iodide at 100° into the *methiodide*, m. p. about 212°. This condenses with *p*-dimethylaminobenzaldehyde (1 mol.) in alcohol in the presence of piperidine to 2-*p*-dimethylaminostyrylacenaphthpyridine *methiodide*, m. p. 224° (decomp.), which is a sensitiser, and with *p*-nitrosodimethylaniline (1.25 mols.) under similar conditions to the *p*-dimethylaminoanil of acenaphthpyridine-2-aldehyde *methiodide*, m. p. 195° (decomp.), which is a desensitiser.

2-Methylacenaphthpyridine *methiodide* (I) (1 mol.) reacts with quinoline *methiodide* (2 mols.) in boiling absolute alcohol in the presence of sodium ethoxide to give the *isocyanine* (II), m. p. 220—240° (decomp.);



slow heating); with quinoline ethiodide the resultant *isocyanine* (II) has m. p. 217° (decomp.). I and 2-iodoquinoline *methiodide* react in aqueous solution in the presence of potassium hydroxide to give the *ψ*-cyanine (III), m. p. 236° (decomp.); with 2-iodoquinoline ethiodide, the resultant *ψ*-cyanine (III) has m. p. 201° (decomp.). These cyanines are sensitizers, and exhibit a shift in the absorption bands of 150 Å. towards the red as compared with the parent cyanines. I does not yield a carbocyanine by the ethyl orthoformate and pyridine method (A., 1928, 76).

5-Methylacridine, best prepared by heating acetyl-diphenylamine with zinc chloride at 220—240°, forms a *methiodide* (IV), m. p. 263° (decomp.) [lit.: 185° (decomp.); 273—275°; 235—245°], when heated with methyl iodide at 100°. This condenses with 2-iodoquinoline *methiodide* (1 mol.) in water at 100° in the presence of potassium hydroxide to give 1:1'-dimethyl-2:3(or 2':3')-benzisocyanine *iodide*, m. p. about 250—265° (decomp. at about 230°); 1(or 1')-methyl-1'(or 1)-ethyl-2:3(or 2':3')-benzisocyanine *iodide*, m. p. about 232°, was similarly obtained from 2-iodoquinoline ethiodide. IV does not condense with ethyl orthoformate and pyridine, or with quinoline *methiodide* in the presence of aqueous sodium hydroxide, or with *p*-dimethylaminobenzaldehyde or *p*-nitrosodimethylaniline in absolute alcohol in the presence of piperidine.

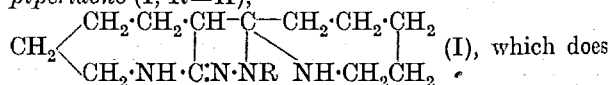
A. I. VOGEL.

**Oxidation of dihydrotetrazines.** H. ASPELUND (Ber., 1930, 63, [B], 1197—1199).—ββ-Diphenyl-ethylidenediphenylacethydrazide, CHPh<sub>2</sub>·CH·N·NH·CO·CHPh<sub>2</sub>, m. p. 216°, prepared from diphenylacethydrazide and diphenylacetalde-

hyde, is identical with the by-product obtained by Stollé and Schmidt (A., 1912, i, 980) during the oxidation of 3:6-dibenzhydryldihydrotetrazine by amyl nitrite in the presence of sodium carbonate. Treatment of 3-phenyl-6-benzhydryl- and 3:6-dibenzhydryl-dihydrotetrazine with amyl nitrite in presence of alcohol and sodium carbonate affords the corresponding tetrazines. It is suggested that Stollé's result may be due to the presence of sodium hydroxide in the sodium carbonate.

H. WREN.

**Derivatives of pyrazoline.** R. STOLLÉ (Ber., 1930, 63, [B], 1032—1037).—2-Hydrazino-Δ<sup>1</sup>-homopiperidine,  $\begin{matrix} \text{CH}_2\text{---CH}_2\text{---N} \\ \text{CH}_2\text{---CH}_2\text{---CH}_2 \end{matrix} \gg \text{C} \cdot \text{NH} \cdot \text{NH}_2$ , m. p. 112° (picrate, m. p. 136°), prepared by the action of hydrazine hydrate on 2-ethoxy-Δ<sup>1</sup>-homopiperidine at 40—50°, is very readily transformed by acids into Δ<sup>1</sup>-hydrazo-2:2'-Δ<sup>1</sup>-homopiperidine. It is converted by nitrous acid into pentamethylenetetrazole. Distillation of the hydrazo-compound in a high vacuum affords anhydro-2'-hydrazino-2'-homopiperidyl-3-homopiperidone (I, R=H),



(I), which does not react with diazomethane, methyl sulphate, methyl iodide, methyl *p*-toluenesulphonate, benzaldehyde, tolualdehyde, or *p*-nitrobenzaldehyde. It is transformed by benzenesulphonyl chloride and aqueous potassium hydroxide into the benzenesulphonyl derivative (I, R=Ph·SO<sub>2</sub>), m. p. 128°, by phenylcarbimide into the phenylcarbamate (I, R=·CO·NHPh), m. p. 160° (also obtained from hydrazo-2:2'-Δ<sup>1</sup>-homopiperidine), and by phenylthiocarbimide into the corresponding thiocarbamide (I, R=·CS·NHPh), m. p. 183°.

H. WREN.

**Extension of Michael's reaction.** I. Action of ethyl carbamate on esters of unsaturated acids. II. Action of ethyl carbamate on carbimides and thiocarbimides. T. N. GHOSH and P. C. GUHA (J. Indian Chem. Soc., 1930, 7, 263—273).—I. Treatment of an ethereal suspension of the sodium derivative of ethyl carbamate with ethyl cinnamate and acidification of the product formed with dilute hydrochloric acid affords ethyl β-carbethoxyamino-β-phenylpropionate, m. p. 70°, which on hydrolysis with 5% potassium hydroxide solution gives cinnamic acid. Ethyl β-carbethoxyamino-β-o-, -m-, and -p-nitrophenylpropionates have m. p. 210°, 195°, and above 280°, respectively. Similarly, methyl fumarate and ethyl carbamate afford a small amount of methyl α-carbethoxyaminosuccinate, m. p. 130° after shrinking at 110° (isolated through its copper derivative), whilst ethyl citraconate and mesaconate furnish brown, uncrystallisable oils. Treatment of the products formed from ethyl cinnamate and the sodium derivatives of acetamide and propionamide with dilute hydrochloric acid gives cinnamamide.

II. Phenylcarbimide and ethyl carbamate react as above, forming *s*-carbethoxyphenylcarbamide, NHPh·CO·NH·CO<sub>2</sub>Et, m. p. 106—107°. Phenylthiocarbimide furnishes 2-keto-4:6-dithion-3:5-diphenylhexahydro-s-triazine, NH<CO·NPh>CS, m. p. 248°

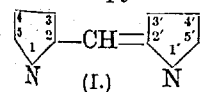


(methyl derivative, m. p. 220°, prepared by methylation with methyl iodide and sodium hydroxide solution; benzoyl derivative, m. p. 158—159°; bromo-derivative, m. p. 200° after softening at 140°), also formed from phenylthiocarbimide and the sodium derivative of *s*-carbethoxyphenylthiocarbamide (Doran, J.C.S., 1896, 69, 326) in ether. When the above methyl derivative is treated with mercuric oxide in alcohol, sulphur is eliminated and the compound  $C_{16}H_{13}O_2N_3S$ , m. p. 195°, results. Similarly, *o*- and *m*-tolyl- and *m*-4-xylyl-thiocarbimides furnish 2-keto-4:6-dithion-3:5-di-*o*-tolyl-, m. p. 280°, -di-*m*-tolyl-, m. p. 237° after shrinking at 226°, and -di-*m*-4-xylyl-hexahydro-*s*-triazines, m. p. 223—225°, respectively. Allylthiocarbimide (1 mol.) and the sodium derivative of ethyl carbamate (1 mol.) afford *s*-carbethoxyallylthiocarbamide, m. p. 57°. This reacts further with allylthiocarbimide, yielding 2-keto-4:6-dithion-3:5-diallylhexahydro-*s*-triazine, m. p. 133°. Using the requisite arylthiocarbimide and the *s*-carbethoxyarylthiocarbamide the following are prepared: 2-keto-4:6-dithion-3-phenyl-5-*o*-tolyl-, m. p. 244—245° (benzoyl derivative, m. p. 205°); -5-phenyl-3-*o*-tolyl-, m. p. 235—236° (benzoyl derivative, m. p. 155°); -3-phenyl-5-*p*-tolyl-, m. p. 251—252°; -3-*o*-tolyl-5-*p*-tolyl-, m. p. 224°; -5-*p*-tolyl-3-allyl-, m. p. 145°, and -5-*o*-tolyl-3-allyl-hexahydro-*s*-triazines, m. p. 136—137°.

Carbethoxythiocarbimide (Doran, *loc. cit.*) and the sodium derivative of ethyl carbamate react in toluene forming the sodium derivative of the unstable *s*-dicarbethoxythiocarbamide (copper derivative).

H. BURTON.

**Porphyrim syntheses. XXVIII. Syntheses of the chlorophyll porphyrins rhodo- and pyrroporphyrins, and pyrroaetioporphyrim.** H. FISCHER, H. BERG, and A. SCHORMÜLLER (Annalen, 1930, 480, 109—156).—Pyrrolypyrrolenylmethene is renamed pyrromethene; the numbering is as in I.



2:4-Dimethylpyrrolealdehyde and hæmopyrrole condense in presence of alcoholic hydrobromic acid, forming 3:5:4':5'-tetramethyl-3'-ethylpyrromethene hydrobromide, m. p. 203—206° (decomp.) [free base, m. p. 116° (copper salt, m. p. 197° after darkening and sintering at 100°)]. Fusion of a mixture of this methene and 5:5'-dibromo-3:3'-dimethyl-4:4'-diethylpyrromethene hydrobromide with methylsuccinic acid at 160—180° yields 1:3:6:7-tetramethyl-2:5:8-triethylporphyrin (pyrroaetioporphyrim 5), m. p. 284° (copper salt, m. p. 251°; hæmin derivative), together with some bromopyrroaetioporphyrim 5. The m. p. of the former is not depressed by the ætioporphyrim obtained from pyrroporphyrin (A., 1928, 1382).

Condensation of ethyl 2:4-dimethylpyrrole-3-carboxylate with 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid in presence of acetic and hydrobromic acids yields 5'-carboxy-4-carbethoxy-3:5:4'-trimethyl-3'-ethylpyrromethene hydrobromide, m. p. 224° with elimination of carbon dioxide [free base, m. p. 192°; 4:5'-dicarbethoxy-derivative, m. p. 172° (decomp.)]. Twofold crystallisation of this from hot acetic acid gives 4-carbethoxy-3:5:4'-trimethyl-3'-ethylpyrromethene hydrobromide, m. p. 197° (decomp.), whilst bromination affords a mixture (A) of unchanged methene and

perbromide. When a mixture of A, brominated 3:5:3'-trimethyl-4-ethyl-4'-β-carboxyethylpyrromethene hydrobromide and succinic acid is heated rapidly over a free flame for 30 sec., small amounts of mesoporphyrin V and the monoethyl ester of rhodoporphyrin 15 (cf. A., 1929, 1465) [dimethyl ester, m. p. 264° (corr.) (copper salt)] are obtained. Fusion of the rhodoporphyrin with resorcinol at 210° yields pyrroporphyrin, spectroscopically identical with the natural product (*loc. cit.*). Acetic-hydrobromic acid condensation of ethyl 5-aldehydo-2:3-dimethylpyrrole-4-carboxylate and 3-methyl-4-β-carboxyethylpyrrole-2-carboxylic acid furnishes 5'-carboxy-3-carbethoxy-4:5:4'-trimethyl-3'-β-carboxyethylpyrromethene hydrobromide, m. p. 192—193° (decomp.), brominated in acetic acid to a perbromide,  $C_{18}H_{23}O_4N_2Br_2$ , darkens about 225° and then decomposes gradually without melting. When a mixture of this perbromide, the methene from brominated hæmopyrrole, and methylsuccinic acid is heated at 180—190°, a small amount of rhodoporphyrin 15 is produced.

Acetic-hydrobromic acid condensation of 2:4-dimethylpyrrole and 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylic acid gives 5-carboxy-4:3':5'-trimethyl-3-ethylpyrromethene hydrobromide, decomp. 120° after blackening at 115°, brominated in acetic acid to 5-bromo-4:3':5'-trimethyl-3-ethylpyrromethene hydrobromide, darkens at 135°, not melted at 270°. Fusion of this and 5'-bromo-3:5:3'-trimethyl-4-ethyl-4'-β-carboxyethylpyrromethene hydrobromide, m. p. 224° (decomp.), with a mixture of succinic and methylsuccinic acids, first at 140—150° and then at 170°, affords a mixture of mesoporphyrin V, ætioporphyrim, bromopyrroporphyrin 15 [copper salt; methyl ester, m. p. 261° (copper salt, m. p. 229°)], and pyrroporphyrin 15 (copper salt). The methyl ester, m. p. 241° (corr.) (copper salt, m. p. 231°), of the last-named substance is identical (crystallographic data by STEINMETZ) with the natural product. Debromination of the bromoporphyrin (crystallographic data given) with hydrazine hydrate, palladised calcium carbonate, and 10% alcoholic potassium hydroxide solution gives the pyrroporphyrin. Hæmopyrrolecarboxylic acid and 4-bromo-5-aldehydo-3-methylpyrrole-2-carboxylic acid afford 3-bromo-5-carboxy-4:4':5'-trimethyl-3'-β-carboxyethylpyrromethene hydrobromide, decomp. 230° after blackening at 170°, brominated in acetic acid to 3:5-dibromo-4:4':5'-trimethyl-3'-β-carboxyethylpyrromethene hydrobromide, blackens at 205°, not melted at 270°. Fusion of the former of these methenes with methylsuccinic acid and 5-bromo-4:3'-dimethyl-3:4'-diethyl-5'-bromomethylpyrromethene hydrobromide at 150—170° yields a mixture of ætioporphyrim and the above pyrro- and bromopyrro-porphyrins.

Opsopyrrole and 2:4-dimethylpyrrole-5-aldehyde condense in presence of alcoholic hydrobromic acid, forming 3:5:3'-trimethyl-4'-ethylpyrromethene hydrobromide, decomp. 170°, brominated to the 4:5'-dibromo-derivative, decomp. 225°. Fusion of a mixture of this dibromo-compound and 5'-bromo-4:5:3'-trimethyl-3-ethyl-4'-β-carboxyethylpyrromethene hydrobromide with succinic and methylsuccinic acids at 145—170° furnishes a mixture of mesoporphyrin II, ætio- or deuteroætio-porphyrin, bromopyrroporphyrin 9 [copper salt; methyl ester, m. p. 243° (corr.) (copper

salt, m. p. 237° (corr.)], and *pyrroporphyrin* 9 [copper salt; *methyl ester*, m. p. 237° (corr.) (copper salt, m. p. 227°)]. These pyrro- and bromopyrro-porphyrins are spectroscopically identical with, but depress the m. p. of their isomerides. Spectrochemical data for most of the above porphyrins are recorded.

Condensation of butyl (or ethyl) butyrate with methyl propyl ketone in presence of ether and sodamide furnishes *dibutylmethane* (8%-diketononane), b. p. 83–84°/11 mm., m. p. –46°,  $d_4^{15}$  0.9181,  $n_D^{15}$  1.4629 (copper salt, m. p. 158°); this contains 90% of the monoenol. Addition of sodium nitrite to a solution of ethyl acetoacetate in acetic acid, and successive treatment of the product with the above diketone and zinc dust gives *ethyl 3-butyryl-4-methyl-2-propylpyrrole-5-carboxylate*, m. p. 104°. Thermal decomposition of the free acid, m. p. 160° (decomp.), isolated from the alkaline hydrolysis product, affords *3-butyryl-4-methyl-2-propylpyrrole*, m. p. 76° (p-sulphobenzene-azo-derivative, not melted at 240°), convertible by the Gattermann method into *3-butyryl-4-methyl-2-propylpyrrole-5-aldehyde*, m. p. 93° (oxime, m. p. 144–145°). Hydrolysis of the above ester with 63% sulphuric acid at 100° yields *4-methyl-2-propylpyrrole* (p-sulphobenzeneazo-derivative); the butyryl group is also eliminated on reduction. Treatment of 3-butyryl-4-methyl-2-propylpyrrole with aqueous-alcoholic formaldehyde furnishes *di-(4-butyryl-3-methyl-5-propyl-2-pyrrolyl)methane*, m. p. 149°, whilst with formic and hydrobromic acids *4:4'-dibutyryl-3:3'-dimethyl-5:5'-dipropylpyrromethene hydrobromide*, m. p. 172° (decomp.) (free base m. p. 92°; *perbromide*,  $C_{25}H_{37}O_2N_2Br_5$ , m. p. 178° after darkening at 170°), results. Treatment of ethyl 2:4-dimethylpyrrole-5-carboxylate with sulphuryl chloride in ether gives, after hydrolysis with water, *ethyl 3-chloro-2-aldehyde-4-methylpyrrole-5-carboxylate*, m. p. 131° (corr.) [azine, m. p. 232° (corr.); *phenylhydrazine*, m. p. 149° (corr.)]. Similarly, ethyl 3-bromo-2:4-dimethylpyrrole-5-carboxylate affords *ethyl 3-bromo-2-aldehyde-4-methylpyrrole-5-carboxylate*, m. p. 133° [free acid, not melted at 270°; *azine*, m. p. 226° (corr.); *phenylhydrazine*, m. p. 146° (corr.)]. Crystallographic data (by STEINMETZ) are given for the chloro- and bromo-aldehydes.

H. BURTON.

**Porphyrin syntheses. XXIX. Syntheses of phyllo- and phylloætioporphyryns and related compounds.** H. FISCHER and H. HELBERGER (Annalen, 1930, 480, 235–262).—Alcoholic hydrobromic acid condensation of xanthopyrrole and cryptopyrrolealdehyde furnishes *3:5:3'-trimethyl-4:5'-diethylpyrromethene hydrobromide*, m. p. 175° (the free base decomposes readily), which when heated with 5:5'-dibromo-4:4'-dimethyl-3:3'-diethylpyrromethene hydrobromide, succinic and methylsuccinic acids at 170° yields *isophylloætioporphyryn*, m. p. 285°, together with a pyrroætioporphyryn. Degradation of isoporphyryn with pyridine and methyl-alcoholic potassium hydroxide at 200° gives a porphyryn spectroscopically identical with pyrroporphyrin. Hæmopyrrolealdehyde and xanthopyrrole afford *4:5:3'-trimethyl-3:5'-diethylpyrromethene hydrobromide*, m. p. about 190° after sintering at 170°, which fusion at 140–160° with methylsuccinic acid and

5:5'-dibromo-3:3'-dimethyl-4:4'-diethylpyrromethene hydrobromide (I) affords *phylloætioporphyryn*, m. p. 261–263°, together with a pyrroætioporphyryn. *4:5:3'-Trimethyl-3-ethyl-5'-propylpyrromethene hydrobromide*, m. p. 188° (from hæmopyrrolealdehyde and 4-methyl-2-propylpyrrole), and I give, similarly, a *homologue*, m. p. 270°, of phylloætioporphyryn.

Xanthopyrrole and 2-aldehyde-3-methyl-4-ethylpyrrole-5-carboxylic acid give *5-carboxy-4:3'-dimethyl-3:5'-diethylpyrromethene hydrobromide*, m. p. 165° (decomp.), brominated in acetic acid to *5:4'-dibromo-4:3'-dimethyl-3:5'-diethylpyrromethene hydrobromide*. Condensation of this with 3:3':5'-trimethyl-4'-ethyl-4-β-carboxyethylpyrromethene hydrobromide (?) in presence of methylsuccinic acid at 140–160° produces a mixture of mesoporphyryn V, pyrroporphyrin, and *phylloporphyryn* [*methyl ester*, m. p. 230° (copper salt, m. p. 253°)]. The last-named porphyryn is spectroscopically identical with the natural product; crystallographic measurements (by STEINMETZ) show slight differences. The synthetic porphyryn is converted by treatment with 30% methyl-alcoholic potassium hydroxide and pyridine at 200° into pyrroporphyrin. Structural formulæ are suggested for phylloporphyryn.

Catalytic reduction (Adams) of various porphyrins and chlorins results in the absorption of 3 mols. of hydrogen by pyrro-, phyllo-, and meso-porphyrins (dimethyl ester). Chlorin *e* and its trimethyl ester absorb approximately 4 mols.; the leuco-compounds formed are oxidised by atmospheric oxygen to porphyrins. Phæophorbide *a* absorbs 3 mols. (cf. Conant and Hyde, this vol., 793); the leuco-compound is oxidised to a complicated mixture of porphyrins and chlorins.

H. BURTON.

**Chlorophyll. XI. Phæoporphyryn.** H. FISCHER and R. BAÜMLER (Annalen, 1930, 480, 197–234).—Treatment of phæoporphyryn *a*<sub>6</sub> (I) (A., 1929, 1185) with boiling 25% phosphoric acid for 24 hrs. and crystallisation of the residue from pyridine give *phæoporphyryn a*<sub>5</sub>,  $C_{34}H_{36}O_5N_4$ , m. p. 242° [*methyl ester*, m. p. 242° (not depressed by phæoporphyryn *a*<sub>6</sub> methyl ester)]. The same porphyryn is obtained when I is crystallised from alcoholic pyridine or extracted with chloroform. The ethoxyl (or methoxyl) content of phæoporphyryns *a*<sub>6</sub> and *a*<sub>4</sub> (*loc. cit.*) is less than that required for one alkoxy-group. Esterification of I with ethereal diazomethane gives a *methyl ester*,  $C_{34}H_{38}O_5N_4$ , m. p. 239°, whilst with methyl- and ethyl-alcoholic hydrogen chloride a *methyl ester*,  $C_{34}H_{36}O_5N_4$ , m. p. 226° (cf. *loc. cit.*), and an *ethyl ester*,  $C_{36}H_{40}O_5N_4$ , m. p. 211°, respectively, are formed; the m. p. of the second methyl ester rises to 243° after some weeks. Reduction of I with a 1% solution of hydrogen iodide in acetic acid in the cold yields a *compound*,  $C_{33}H_{34}O_5N_4$ , whilst treatment with boiling 95% formic acid produces a mixture of phylloporphyryn and *phæoporphyryn a*<sub>3</sub>,  $C_{33}H_{36}O_3N_4$  (iron and copper salts; *methyl ester*, m. p. 250°). When a crude specimen of I is used, *metaphæoporphyryn a*<sub>3</sub>,  $C_{31}H_{34}O_3N_4$  (*methyl ester*, m. p. 257°), is also produced.

Degradation of phæophytin with 95% formic acid at 150–160° furnishes a mixture of the above phæo- and *isophæo-porphyrin a*<sub>3</sub>,  $C_{33}H_{36}O_3N_4$  (*methyl ester*,

m. p. 258°; complex iron salt; copper salt; *phyllysins*, prepared by the action of magnesium methyl iodide and magnesium oxide in presence of 30% methyl-alcoholic potassium hydroxide, respectively). The last-named porphyrin is also obtained when phaeophorbide  $\alpha$  is treated with acetic and hydrobromic acids at 170—180°; with formic acid at 150—160°, phaeoporphyrin  $\alpha_3$  is almost the sole product. Phaeo- and isophaeoporphyrins are not affected by fuming sulphuric acid; the former is degraded by alkali to pyrro- and rhodoporphyrins, whilst the latter is unaffected. Degradation of phaeoporphyrin  $\alpha_5$  methyl ester with boiling formic acid affords a mixture of porphyrins, separable only with difficulty into the compounds,  $C_{34}H_{36}O_5N_4$ ,  $C_{32}H_{36}O_2N_4$  (methyl ester, m. p. 271°), and  $C_{33}H_{36}O_4N_4$ ; the residue from this contains an ester,  $C_{34}H_{36}O_4N_4$ , m. p. 265°.

Degradation of phaeophytin with iron powder and boiling formic acid gives a porphyrin,  $C_{32}H_{34}O_5N_4$ , whilst fusion with succinic acid at 265° yields a substance,  $C_{33}H_{34}O_3N_4$ . Phaeoporphyrin  $\alpha_6$  is oxidised by treatment with cold, fuming sulphuric acid to a compound,  $C_{33}H_{38}O_7N_4$ .

Phylloerythrin (+0.5CHCl<sub>3</sub>) (methyl ester, m. p. 263°) is unaffected by formic acid at 150—160°, but is decomposed by methyl-alcoholic potassium hydroxide in presence of magnesium oxide to pyrro- and rhodoporphyrins; in absence of the oxide, phylloporphyrin is formed.

The methyl ester, m. p. 268°, of phylloerythro-porphyrin (this vol., 634) does not depress the m. p. (268°) of the methyl ester of phylloerythrin.

Spectrochemical data are recorded for most of the above porphyrins.

H. BURTON.

**Pyrrole blacks.** A. ANGELI (Atti R. Accad. Lincei, 1930, [vi], 11, 439—442).—The author's earlier work (A., 1915, i, 991; 1916, i, 667; 1917, i, 413; 1918, i, 547; 1919, i, 134; 1920, i, 397, 886; 1921, i, 626; 1928, 89) is discussed in relation to that of Quilico and Freri (this vol., 793) and of Raper (A., 1927, 278, 1112).

T. H. POPE.

**isoOxazoline oxides.** IX. Reaction between triphenylisooxazoline oxide and organic magnesium compounds. E. P. KOHLER and N. K. RICHTMYER (J. Amer. Chem. Soc., 1930, 52, 2038—2046).—Short treatment of 3:4:5-triphenylisooxazoline oxide (A., 1924, i, 1239) with magnesium phenyl bromide affords an unstable compound, m. p. about 105°, converted by treatment with acetic acid into  $\alpha\beta\gamma$ -tetraphenylpropylene oxide, m. p. 162°. Treatment of this with methyl alcohol containing a small amount of acetyl chloride gives triphenylethylene and benzaldehyde. Ozonisation of triphenylethylene in chloroform solution yields benzophenone peroxide, (CPh<sub>2</sub>O)<sub>2</sub>, m. p. 200—220° according to the rate of heating. Triphenylisooxazoline oxide reacts with 3 mols. of magnesium methyl iodide, forming methane (1 mol.) and  $\beta$ -hydroxylamino- $\delta$ -hydroxy- $\beta\gamma\delta$ -triphenylpentane, m. p. 180—195° [acetoxylamino-derivative, melts to a colourless liquid which becomes yellow and then red between 135° and 155°; diacetate, m. p. about 172° (decomp.)]. The hydroxylamino-derivative is oxidised by potassium permanganate in cold acetone to acetophenone and  $\alpha$ -methylstilbene. Magnesium benzyl

chloride and the isooxazoline oxide afford dibenzyl and  $\gamma$ -oximino- $\alpha\beta\gamma$ -triphenylpropyl alcohol, m. p. 180—200° according to the rate of heating [copper derivative;  $\gamma$ -monoacetate, m. p. 100—110° (decomp.); diacetate, m. p. 131—132°, hydrolysed by shaking an ethereal solution with ammonia to the  $\alpha$ -monoacetate, m. p. 170—176° (decomp.)], which is identical with the compound previously described (*loc. cit.*) as 2-hydroxy-3:4:5-triphenylisooxazoline. The same oximino-derivative is also formed together with a compound,  $C_{23}H_{23}O_2N$ , m. p. 126°, from magnesium ethyl bromide and the isooxazoline oxide.

Reduction of the above oximino-alcohol with zinc dust and acetic acid gives  $\gamma$ -amino- $\alpha\beta\gamma$ -triphenylpropyl alcohol, two forms, m. p. 123° and 128—129° (hydrochloride, m. p. 232°; N-acetyl derivative, m. p. 142°; N-p-toluenesulphonyl derivative, m. p. 146—148°), converted by nitrous acid into triphenylisooxazoline oxide, and decomposed thermally to ammonia, stilbene, and benzaldehyde. Oxidation of the oximino-alcohol with chromic and acetic acids affords triphenylisooxazole, formed through the intermediate dibenzoylphenylmethane monoxime.

H. BURTON.

**cycloPropane series.** XIII. New type of cyclopropene derivative. E. P. KOHLER and S. F. DARLING (J. Amer. Chem. Soc., 1930, 52, 1174—1181).—The presumed intermediate formation of cyclopropene derivatives when nitrocyclopropane derivatives yield unsaturated open-chain compounds on treatment with alkalis has been confirmed by the preparation in this way of ethyl 1-phenyl-2-m-nitrophenyl- $\Delta^1$ -cyclopropenedicarboxylate, which is stable to alkalis. The stability of certain cyclopropenes is attributable to the absence of conjugation, as in this case, rather than to the presence of a characteristic mobile hydrogen atom (Goss, Hanhart, and Ingold, J.C.S., 1923, 123, 330).

The following series of compounds has been prepared by the methods used by Kohler and Barrett (A., 1926, 849) for the unsubstituted compounds: methyl  $\gamma$ -nitro- $\gamma$ -phenyl- $\beta$ -m-nitrophenylethylmalonate, m. p. 118—120°; the  $\alpha$ -bromo-derivative (I), m. p. 125°; methyl 3-phenyl-4-m-nitrophenylisooxazoline oxide-5:5-dicarboxylate (II), m. p. 173—174° [acid (+Et<sub>2</sub>O), melts with effervescence]. The constitution of the acid is shown by its conversion by boiling with water into 3-phenyl-4-m-nitrophenylisooxazole-5-carboxylic acid, decomp. about 300° (silver and copper salts; methyl ester, m. p. 133°). The ester (I) is converted by cold, concentrated sodium methoxide solution into 3-phenyl-4-m-nitrophenylisooxazoline oxide-5-carboxylic acid, m. p. about 190° (decomp.) (silver and sodium salts; methyl ester, m. p. 133°).

A stereoisomeride of I, m. p. 125—126°, is obtained when the sodio-derivative of methyl  $\gamma$ -nitro- $\gamma$ -phenyl- $\beta$ -m-nitrophenylethylmalonate is treated with bromine in methyl alcohol. This is converted by boiling with alcoholic potassium acetate into a mixture of methyl 1-nitro-1-phenyl-2-m-nitrophenylcyclopropane-3:3-dicarboxylate (III), m. p. 167—169°, with II and a little of the isooxazole-5-carboxylic acid. When III is heated with sodium methoxide solution it is converted into methyl 1-phenyl-2-m-nitrophenyl- $\Delta^1$ -cyclopropene-3:3-dicarboxylate (IV), m. p. 176—178°, which is

oxidised by potassium permanganate in alkaline solution to *m*-nitrodibenzoylmethane. Bromination of IV in sunlight in chloroform yields the *dibromide*, m. p. 144—145°, which slowly reacts with hot alcoholic potassium hydroxide to give the original *cyclopropene* compound.

R. K. CALLOW.

**Formation of phenoxazines.** O. L. BRADY and C. WALLER (J.C.S., 1930, 1218—1222).—Further investigation of the conversion by alkali of 2-nitro-2'-hydroxydiphenylamines into phenoxazines (Ullmann, A., 1909, i, 473; 1912, i, 104) confirms the earlier observation that the reaction takes place only when the 6-position is substituted. The nature of the substituent is apparently immaterial; a substituent in the 6'-position does not similarly facilitate ring closure. A steric explanation of these facts is offered.

2:6-Dinitro-3-methyl- (I), 2:4-dinitro-5-methyl-, and 2:6-dinitro-4-methyl-2'-hydroxydiphenylamine (II), prepared from 2:3:4-, 3:4:6-, or 3:4:5-trinitrotoluene and *o*-aminophenol, have m. p. 148°, 203°, and 152°, respectively; interaction of *o*-aminophenol with 3:4-dinitro-*o*-chlorotoluene or trinitroquinol dimethyl ether affords respectively 2-chloro-6-nitro-2'-hydroxy-3-methyl- (III), m. p. 106°, and 2:4-dinitro-2'-hydroxy-3:6-dimethoxy-diphenylamine (IV), m. p. 186°; 2:4-dinitro-2'-hydroxy-5:6'-dimethyl-, m. p. 173°, 2:6-dinitro-2'-hydroxy-4:6'-dimethyl- (V), m. p. 198° (decomp.), and 2:4:6-trinitro-2'-hydroxy-6'-methyl-diphenylamine (VI), m. p. 176°, are obtained from 3:4:6-, 3:4:5-trinitrotoluene, or picryl chloride, respectively, and 2-amino-*m*-cresol. The following phenoxazines are obtained by treating the necessary diphenylamine compound with 1% aqueous sodium hydroxide at 100°: 1-nitro-4-methyl-, m. p. 169° (from I), 1-nitro-3-methyl-, m. p. 165° (from II), 3-nitro-1:4-dimethoxy-, m. p. 173° (from IV), 1:3-dinitro-9-methyl-, m. p. 224° (from VI), and 1-nitro-3:9-dimethyl-phenoxazine, m. p. 162° (from V). 1-Nitro-4-methylphenoxazine is also obtained from III, the alternative synthesis showing that the reactive nitro-group of I is that in the *o*-position to the methyl group; 2:4-dinitro-2'-hydroxy-6'-methyl-diphenylamine and the other two diphenylamines mentioned above do not yield phenoxazines under similar conditions.

3-Bromo-4:6-dinitrotoluene, from 4:6-dinitro-m-tolylhydrazine and cupric bromide, has m. p. 101°. Reaction of 2:4-dinitrochlorobenzene with *N*-methyl-*o*-anisidine affords 2:4-dinitro-2'-methoxy-*N*-methyl-diphenylamine, m. p. 169°, the methoxyl group of which could not be demethylated by means of the usual reagents.

R. CHILD.

**Unsaturation and tautomeric mobility of heterocyclic compounds. II.  $\alpha$ - and  $\beta$ -Naphthathiazoles.** R. F. HUNTER and J. W. T. JONES (J.C.S., 1930, 941—949).—Naphthathiazoles are more readily formed by ring closure than are benzthiazoles.  $\beta$ -Naphthylthiocarbimide [best prepared by boiling *s*-di- $\beta$ -naphthylthiocarbamide (I part) with acetic anhydride (2 parts), followed by distillation in steam at 140°] and phosphorus pentachloride at 160—180° gave 1-chloro- $\alpha$ -naphthathiazole, m. p. 80°, b. p. 245—246°/13 mm., in 62% yield, converted by concentrated hydrochloric acid at 100° into 1-hydroxy- $\alpha$ -naphtha-

thiazole, m. p. 231°, and by heating with excess of ammonia (*d* 0.88) at 200° into 1-amino- $\alpha$ -naphthathiazole (I), m. p. 258° (acetyl derivative, m. p. 265°), identical with the substance erroneously described as 2-amino- $\alpha$ -naphthathiazole by Hunter (A., 1926, 850).  $\beta$ -Naphthylthiocarbamide, m. p. 194° (lit. 180°; 186°), and bromine in chloroform gave a *hydrotribromide* (sintering at 160—161°), reduced by sulphurous acid to I. Contrary to Hegershoff (A., 1900, i, 155), *s*-acetyl- $\beta$ -naphthylthiocarbamide (II), m. p. 171—172°, is the only product of dissolving  $\beta$ -naphthylthiocarbamide in excess of acetic anhydride at 80°. Acetamidonaphthathiazole, m. p. 264°, was obtained by the reduction with sulphurous acid of the bromo-additive compound, m. p. 154—156°, formed from II and bromine in chloroform.

Oxidation of  $\beta$ -naphthylthiourethane with alkaline potassium ferricyanide at 85° gave a 60% yield of 1-ethoxynaphthathiazole, m. p. 80°; 1-ethoxybenzthiazole was similarly produced in 40% yield from phenylthiourethane. 1- $\beta$ -Naphthylaminobenzthiazole, m. p. 191—192°, was obtained by heating together 1-chlorobenzthiazole and  $\beta$ -naphthylamine; 1-anilino- $\alpha$ -naphthathiazole, similarly prepared, had m. p. 211—212°.

Phenylthiocarbimide interacts with  $\beta$ -naphthylamine in alcohol to give *s*-phenyl- $\beta$ -naphthylthiocarbamide, m. p. 166—167° (lit. 157°; 165°), also produced from  $\beta$ -naphthylthiocarbimide and aniline in benzene solution. Wheeler's "phenylnaphthylthiocarbamide" (A., 1901, i, 487) is *s*-di- $\beta$ -naphthylthiocarbamide. Heating of *s*-phenyl- $\beta$ -naphthylthiocarbamide at 220—230° for 2 min. yielded *s*-di- $\beta$ -naphthylthiocarbamide, m. p. 191—193°. Treatment of *s*-phenyl- $\beta$ -naphthylthiocarbamide with bromine in chloroform, followed by reduction with sulphurous acid, afforded only 1-anilino- $\alpha$ -naphthathiazole, m. p. 211°. This could not be converted by bromine into 1-*p*-bromoanilino- $\alpha$ -naphthathiazole, m. p. 250°, which was prepared from 1-chloro- $\alpha$ -naphthathiazole and *p*-bromoaniline.

1-Imino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole (III), m. p. 178°, was the sole product obtained by heating 1-amino- $\alpha$ -naphthathiazole with methyl iodide at 100°, and was also formed from bromine and *as*- $\beta$ -naphthylmethylthiocarbamide, m. p. 170°, prepared from methyl- $\beta$ -naphthylamine, b. p. 189°/30 mm., hydrochloric acid, and potassium thiocyanate at 100°, followed by reduction with sulphurous acid.

Interaction in alcohol of  $\beta$ -naphthylthiocarbimide and methylamine gave *s*- $\beta$ -naphthylthiocarbamide, m. p. 130°. 1-Methylamino- $\alpha$ -naphthathiazole has m. p. 189°. 1- $\beta$ -Naphthylamino- $\alpha$ -naphthathiazole and methyl sulphate in the presence of chloroform gave 1- $\beta$ -naphthylimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole.

1-Methyl- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole, m. p. 235° (picrate, m. p. 281°), was formed either from methyl-*s*-di- $\beta$ -naphthylthiocarbamide, m. p. 178° (prepared from  $\beta$ -naphthylthiocarbimide and methyl- $\beta$ -naphthylamine in alcohol), and bromine followed by treatment with sulphurous acid or from 1-chloro- $\alpha$ -naphthathiazole and methyl- $\beta$ -naphthylamine.

1-Hydroxy- $\alpha$ -naphthathiazole and methyl sulphate in the presence of chloroform yielded 1-*keto*-2-methyl-1:2-dihydronaphthathiazole, m. p. 135—136°, also

prepared by prolonged heating of 1-nitrosoimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole (decomp. 165°), from III and nitrous acid, in xylene.

Interaction of 1-bromo- $\beta$ -naphthylamine and thio-carbonyl chloride in chloroform gave 1-bromo- $\beta$ -naphthylthiocarbimide, m. p. 90°, converted by alcoholic ammonia into 1-bromo- $\beta$ -naphthylthiocarbamide, m. p. 204°, and further by bromine in chloroform, and then sulphurous acid into 3-bromo-1-amino- $\beta$ - $\beta$ -naphthathiazole, m. p. 250° (acetyl derivative, m. p. 289°).

A. I. VOGEL.

**Nor-dl-ephedrine and nor-dl- $\psi$ -ephedrine.** D. H. HEY (J.C.S., 1930, 1232—1234).—Acetylphenylcarbinol, prepared by a modification of Wren's method (*ibid.*, 1909, 95, 1592) (semicarbazone, m. p. 194°; 2:4-dinitrophenylhydrazone, m. p. 170°), yields, with hydroxylamine, the oxime, m. p. 112.5°, and a small quantity of a compound, m. p. 231°, probably phenylmethylglyoxime (Borsche, A., 1907, i, 326). The former oxime, which is also obtained as a by-product of the reduction of isonitrosopropiophenone (cf. Rabe, A., 1912, i, 718; Hartung and Munch, A., 1929, 1066), is reduced by means of 3% sodium amalgam in dilute acetic acid to nor-dl-ephedrine (hydrochloride, m. p. 192°) and a small proportion of nor-dl- $\psi$ -ephedrine (hydrochloride, m. p. 169°),  $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NH}_2$ .

R. CHILD.

**Amino-alcohols. IV. Potentiometric measurements of certain homologues of ephedrine.** J. C. KRANTZ, jun., and W. H. HARTUNG (J. Amer. Pharm. Assoc., 1930, 19, 461—463).—Measurements of the hydrogen-ion concentration and degree of hydrolysis of 0.1M-solutions of the hydrochlorides of nine homologues (cf. Hartung and Munch, A., 1929, 1066) of ephedrine indicate that there is no marked relationship between these physical constants and the pharmacological behaviour of the compounds. The hydrochlorides of phenylethanolamine and diphenylethanolamine show a higher hydrogen-ion concentration than the hydrochlorides of those amines having a greater number of carbon atoms in the side-chain.

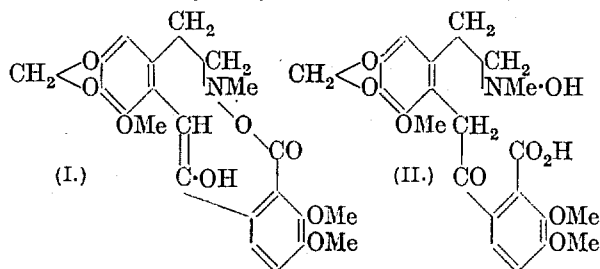
E. H. SHARPLES.

**Manufacture of cotarnine derivative.** E. MERCK etc.—See B., 1930, 586.

**Amine oxides of alkaloids. VI. N-Oxides of hydrastine and narcotine. VII. Conversion of the N-oxide of narcotine into a dialkylated hydroxylamine, N-hydroxynarceine.** M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1930, [iv], 47, 361—365, 365—380).—VI. In view of the influence of a free or esterified carboxyl group on the formation of amine oxides previously observed (A., 1926, 1160; 1927, 1208; 1928, 532), the influence of a lactone group in the vicinity of the basic ring has been examined. Pilocarpine yields no N-oxide, the methylglyoxaline ring giving no reaction with hydrogen peroxide under the conditions tried. Hydrastine and narcotine in acetic acid yield unstable amine oxides which redden with acetic anhydride and yield sulphuric esters with sulphur dioxide. Their salts are stable. The N-oxide of narcotine,  $[\alpha_D] +135^\circ$  in chloroform (cf. Drummond and McMillan, A., 1926, 1263) [hydrochloride, m. p. 193° (decomp.),  $[\alpha_D] +102^\circ$ ; picrate, m. p. 130° (decomp.); chloro-

platinate, m. p. 175°], on evaporation in chloroform yields a transformation product, insoluble in water, which is probably Drummond's amine oxide. The amine oxide of hydrastine,  $[\alpha_D] +90^\circ$  (chloroform), gives a hydrochloride, m. p. 187°,  $[\alpha_D] +160^\circ$ , hydriodide, m. p. 120°, picrate, m. p. 115° (decomp. at 128°), and a chloroplatinate, m. p. 178°.

VII. When boiled in dry neutral chloroform solution for 2 hrs., or more slowly in the cold on keeping in aqueous or chloroform solution (see above), the N-oxide of narcotine is converted, with progressive loss of water, basicity, and optical activity, into the neutral, inactive, anhydro-N-hydroxynarceine, m. p. 228°, identical with the product obtained by Drummond and McMillan (*loc. cit.*) except in optical inactivity. Since the substance is insoluble in alkali and does not react with methyl iodide, sulphur dioxide, or acetic anhydride it is assigned the disubstituted hydroxylamine structure (I). This



structure is supported by the conversion of anhydro-N-hydroxynarceine with bromine in chloroform into a neutral bromo-derivative  $\text{C}_{22}\text{H}_{23}\text{O}_8\text{NBr}$ , m. p. 186—187° (hydrobromide, m. p. 178°), and by hydrolysis with concentrated hydrochloric acid into N-hydroxynarceine (II), m. p. 191° (hydrochloride, m. p. 217°), hydrolysis of bromoanhydro-N-hydroxynarceine similarly yielding bromo-N-hydroxynarceine, m. p. 167°. N-Hydroxynarceine on reduction with ferrous sulphate in sodium hydroxide solution gives nornarceine, m. p. 226°, in 80% yield. Bromo-N-hydroxynarceine similarly yields bromo-narceine, m. p. 220°.

With hydrogen chloride in absolute alcohol anhydro-N-hydroxynarceine or N-hydroxynarceine yields an ethyl ester (III), m. p. 149—150° (hydrochloride, m. p. 195°) (the methyl ester, similarly obtained, has m. p. 135°), converted by sulphur dioxide in benzene into a stable sulphamic acid, m. p. 146°, yielding on hydrolysis N-hydroxynarceine sulphamic acid, m. p. 175°, also obtained from N-hydroxynarceine in hydrochloric acid solution. With methyl iodide and methyl alcohol in a sealed tube N-hydroxynarceine ethyl ether is converted into a mixture of the hydriodide, m. p. 210—211°, and methiodide of nornarceine ethyl ether.

R. BRIGHTMAN.

**Constitution of sinactine (l-tetrahydroepiberberine).** K. GOTO and Z. KITASATO (J.C.S., 1930, 1234—1237).—Sinactine, a subsidiary alkaloid

from *Sinomenium acutum* (this vol., 98), is  $C_{20}H_{21}O_4N$ ; on oxidation with iodine it affords a dehydrosinactine iodide, converted by silver chloride into the corresponding chloride. The latter is identical with *epiberberinium* chloride (Perkin, J.C.S., 1918, 113, 516), and on reduction yields *r*-sinactine, m. p. 168°, identical with *r*-tetrahydro*epiberberine* [hydrochloride, decomp. 286°; methosulphate, m. p. 257° (decomp.); methiodide, m. p. 275° (cf. Perkin, *loc. cit.*; Haworth and Perkin, A., 1926, 964).]

Sinactine is thus *l*-tetrahydro*epiberberine*.

R. CHILD.

**Strychnine alkaloids. IV. The degradation acids  $C_{17}H_{22}O_6N_2$  and  $C_{16}H_{20}O_4N_2$  from strychnine.** H. WIELAND and W. MÜNSTER (Annalen, 1930, 480, 39—48).—Oxidation of the acid  $C_{17}H_{22}O_6N_2$  (II) (*methyl ester dihydrochloride*, m. p. 205—210°) (obtained by chromic acid oxidation of strychnine or brucine; Cortese, this vol., 229 and references there cited) with three times the theoretical quantity of chromic acid and dilute sulphuric acid gives a 30% yield of the acid  $C_{16}H_{20}O_4N_2$  (I), which accompanies II in the original oxidation. Catalytic reduction of these two acids with hydrogen and a platinum oxide catalyst gives the corresponding saturated *dihydroacids*,  $C_{17}H_{22}O_5N_2 + 3H_2O$  (III), m. p. 224—227° (decomp.) (1 mol. of water being eliminated from the expected dihydro-acid, probably with the formation of a lactam ring), and  $C_{16}H_{20}O_4N_2$  (IV), decomp. 292—294°,  $[\alpha]_D^{25} -6.01^\circ$  in water, the latter being identical with a specimen obtained by similar oxidation of dihydrobrucine, m. p. 182° (solvent-free),  $[\alpha]_D^{25} +7.5^\circ$  in chloroform. Hence a double linking originally present in the alkaloid persists in acids I and II. When the acid II ( $\alpha$ -) is heated at 180° it loses 1 mol. of water, the product readily recombining with water to form, not the original  $\alpha$ -acid, but an isomeric  $\beta$ -acid,  $+5H_2O$ ,  $[\alpha]_D^{25} +39.8^\circ$  in water, which is not a polymorph of the  $\alpha$ -acid. Diazomethane converts I directly into the *methylbetaine*,  $C_{17}H_{22}O_6N_2$ , m. p. 250—252° (decomp.) (also  $+H_2O$ ),  $[\alpha]_D^{25} -92.6^\circ$ , which with alcoholic hydrogen iodide gives the same *methiodide*, decomp. 288—290°, as is obtained when I is heated with alcoholic methyl iodide in a sealed tube at 100° and, in turn, gives the *methylbetaine* when heated with moist silver oxide. This betaine loses carbon dioxide when heated at 180° and is, therefore, probably a  $\beta$ -betaine. The semicarbazone of the hydrobromide of II obtained by Leuchs and Hoffmann (this vol., 624) is converted by moist silver oxide into the *semicarbazone*  $+H_2O$ , not melting at 300°, of the free acid II. J. W. BAKER.

**Strychnos alkaloids. LV. Oxidation of strychnidine and experiments with the  $C_{17}$  and  $C_{19}$  acids from brucine, particularly the conversion of  $C_{17}H_{22}O_6N_2$  into the Hanssen acid,  $C_{16}H_{20}O_4N_2$ .** H. LEUCHS and F. KRÖHNKE (Ber., 1930, 63, [B], 1045—1056; cf. A., 1929, 1470).—Strychnidine is oxidised by chromic acid in dilute sulphuric acid at 60—75° to the base  $C_{17}H_{20}O_3N_2$ , m. p. 267—269° after softening,  $[\alpha]_D^{25} +55.6^\circ/d$  in water (also  $+1MeOH$  and  $1EtOH$ ); the *perchlorate* is described. It yields a *methiodide* of the hydrate,  $C_{17}H_{22}O_4N_2 \cdot MeI$ , not molten below 320°, whereas

the *methoperchlorate* corresponds with the anhydrous form. The *semicarbazone*, m. p. 303° (decomp.), and its *perchlorate*,  $C_{18}H_{23}O_5N_3 \cdot HClO_4$ , have been prepared. Oxidation with bromine water transforms the base into a basic substance,  $C_{17}H_{20}O_5N_2$ , isolated as the *perchlorate*.

The oxidation of brucine by chromic acid is described in detail. The yield of the acid  $C_{16}H_{20}O_4N_2$  (*perchlorate*,  $[\alpha]_D^{25} -94^\circ/d$  in water) always greatly exceeds that of the acid  $C_{17}H_{22}O_6N_2$ , the discrepancy becoming more marked with increasing amount of chromic acid. The *oxime hydrochloride*,  $C_{17}H_{21}O_5N_3 \cdot HCl$ , decomp. about 115°, *methyl ester hydrochloride*,  $C_{19}H_{26}O_6N_2 \cdot HCl$ , m. p. about 225° after softening at 120°, and *monoamide hydrochloride*,  $C_{17}H_{23}O_5N_3 \cdot HCl$ , darkening at 240° but not molten below 315°, of the  $C_{17}$  acid are described. The  $C_{17}$  acid is transformed into Hanssen's acid,  $C_{16}H_{20}O_4N_2$ , by hydrogen peroxide in presence of aqueous barium hydroxide or by chromic acid in dilute sulphuric acid. The connexion between the  $C_{17}$  and  $C_{16}$  series is further shown by the transformation of the acid  $C_{17}H_{20}O_8N_2$  derived from Wieland's acid into carbon dioxide and an amino-acid,  $C_{16}H_{20}O_7N_2$ , identical with that derived from the Hanssen acid  $C_{16}H_{20}O_4N_2$  by treatment with bromine and mercuric oxide. Reduction of the acid  $C_{17}H_{20}O_8N_2$  by sodium amalgam affords an acid  $C_{17}H_{22}O_8N_2$ .

Hanssen's acid  $C_{19}H_{22}O_6N_2$  is transformed by boiling acetic anhydride into the *anhydride*  $C_{19}H_{20}O_5N_2 \cdot 3AcOH$ ; the corresponding *perchlorate* is also obtained by the action of hot acetic anhydride on the *perchlorate* of Hanssen's  $C_{19}$  acid. The anhydride is transformed into the corresponding *monomethyl ester perchlorate* and *monoamide (hydrobromide)*. The reduced acid,  $C_{19}H_{24}O_6N_2$ , similarly yields an *anhydride*,  $C_{19}H_{22}O_5N_2$ , which darkens slowly above 250° and yields a crystalline *perchlorate*; it is converted by methyl alcohol and methyl-alcoholic ammonia, respectively, into the *monomethyl ester* and *monoamide (perchlorate)* of the acid  $C_{19}H_{24}O_6N_2$ . The dimethyl ester of the acid  $C_{19}H_{24}O_6N_2$  is transformed by acetic anhydride into the compound  $C_{21}H_{28}O_6N_2 \cdot AcOH$ , m. p. 184—186° (decomp.).

H. WREN.

**Tetrachloroiodides of alkaloids.** F. D. CHAT-TAWAY and G. D. PARKES (J.C.S., 1930, 1003—1005).—The tetrachloroiodides of alkaloids, and of hexamethylenetetramine, are formed by adding a solution in concentrated hydrochloric acid to a solution of tetrachloroiodic acid, prepared by saturating a suspension of iodine in concentrated hydrochloric acid with chlorine. They are decomposed to the free base by aqueous sodium sulphite, and on treatment with aqueous potassium iodide acidified with acetic acid iodine is quantitatively liberated. The tetrachloroiodides of quaternary bases were made by saturating a solution of the iodide in concentrated hydrochloric acid with chlorine. *Tetrachloroiodides* of the following are described: quinine, m. p. 114° (decomp.); cinchonine, m. p. 85° (decomp.); strychnine, m. p. 91° (decomp.); morphine, m. p. 78° (decomp.); codeine; cocaine, m. p. 141° (decomp.); hexamethylenetetramine m. p. 147° (decomp.); 1-methylpyridine-, m. p. 180° (decomp.);



1:2-dimethylpyridine, m. p. 185° (decomp.); 1:2:4:6-tetramethylpyridine, m. p. 130° (decomp.); 1-methylquinoline, m. p. 191°; 6-chloro-1-methylquinoline, m. p. 167°; 6-bromo-1-methylquinoline, m. p. 176°, and *N*-methylstrychnine (decomp.); also *NN*-dimethylnicotine bistetrachloroiodide, m. p. 145°.

A. I. VOGEL.

**New reaction for codeine and dionine [ethylmorphine].** G. DE HAAS (Pharm. Weekblad, 1930, 67, 508—510).—Addition of bromine water and ammonia gives a rose colour, easily distinguished from the brown or red colour obtained with morphine. The proportion of bromine is important, but the test may be employed over a considerable  $p_H$  range.

S. I. LEVY.

**Displacement of the elements of the fifth group from their phenyl derivatives by hydrogen.** V. IPATIEV and G. RAZUBAIEV (Ber., 1930, 63, [B], 1110—1114).—Comparative investigation of the strength of union of the element and the phenyl group is effected by heating equimolecular solutions of the triphenyl compounds of phosphorus, arsenic, antimony, and bismuth in xylene for 24 hrs. at varied temperatures and a constant pressure of 60 atm. of hydrogen. Reaction occurs according to the equation  $2RPh_3 + 3H_2 = 6C_6H_5 + R$  accompanied, particularly in the case of arsenic, by the pyrogenic decomposition  $2RPh_3 = 3Ph \cdot Ph + 2R$ . Phosphorus does not commence to separate below 350°, at which temperature triphenylphosphine itself decomposes; under similar conditions, separation of phosphorus does not occur in an atmosphere of nitrogen. Displacement of antimony takes place at a lower temperature and that of bismuth at a relatively low temperature, at which pyrogenic decomposition is slight. The influence of pressure on the amount of displaced metal is pronounced only with small pressures; above a certain limit, further increase in pressure has no effect. The duration of heating has a more profound influence, the quantity of separated antimony being almost directly proportional thereto. The affinity of the element to phenyl decreases sharply with increase in its metallic properties.

H. WREN.

**Aromatic amides of *N*-arylglycinearsinic acids.** G. W. RATZISS and LE R. W. CLEMENCE (J. Amer. Chem. Soc., 1930, 52, 2019—2023).—The following chloroacetamido-derivatives are prepared by treating the amine or its hydrochloride with chloroacetyl chloride in aqueous solution or suspension at about 0°: 4-chloroacetamidobenzoic acid, m. p. 248°; 4-nitro-*o*-chloroacet-toluidide, m. p. 151°; 5-chloroacetamidosalicylic acid, m. p. 242—244°; chloroacetamidantipyrin, m. p. 187°; chloroacetamidacriflavine, m. p. 215—220° (decomp.), and 4-chloroacetamidoguaiacol, m. p. 117°. Treatment of these with *p*-amino- and 4-amino-3-methylphenylarsinic acid in aqueous or alkaline medium gives 25—40% yields of the appropriate arsinic acid,  $NHR \cdot CO \cdot CH_2 \cdot NH \cdot C_6H_3R' \cdot AsO_3H_2$ . The following are described: *anilinoacet-p-carboxyanilide-4-arsinic acid*, m. p. 260—265° (decomp.) after darkening at 230°; *o-toluidinoacet-o-toluidide-4-arsinic acid*, m. p. 246° (decomp.); *anilinoacet-p-nitro-o-toluidide-*

*4-arsinic acid*, m. p. 115—120° (decomp.); *antipyrin*, m. p. 270° (decomp.), and *acriflavine* derivative, m. p. above 300° after darkening at 240°, of *anilinoacet-amide-4-arsinic acid*; *anilinoacet-p-hydroxy-m-methoxyanilide-4-arsinic acid*, m. p. 215—217°; *o-toluidinoacetanilide-4-arsinic acid*, m. p. above 275°; *o-toluidinoacet-p-carboxyanilide-4-arsinic acid*; *o-toluidinoacet-p-nitro-o-toluidide-4-arsinic acid*, m. p. 285—286° (decomp.); *o-toluidinoacet-p-acetamidolanilide-4-arsinic acid*; *anilino-*, m. p. 230—235° (decomp.) after darkening at 190°, and *o-toluidinoacet-m-carboxy-p-hydroxyanilide-4-arsinic acid*, m. p. 240—245° (decomp.); *o-toluidinoacet- $\alpha$ - and - $\beta$ -naphthylamide-4-arsinic acids*, m. p. 254—255° (decomp.) and 260—262° (decomp.), respectively; *o-toluidinoacet-piperidide-*, *-benzylamide-*, not melted at 275°, and *-o-carboxyanilide-4-arsinic acids*. Some of the above acids have a low toxicity, but their therapeutic effect is also small.

H. BURTON.

**Neoarsphenamine. II. Chemistry of sodium formaldehydesulphoxylate; structure of neoarsphenamine.** A. E. JURIST and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1930, 19, 464—467).—Sodium formaldehydesulphoxylate is stable in alkaline solution and its loss in reducing power is small. In acid solution the chief decomposition products are hydrogen sulphide, formic acid, and sulphur, and to account for these products at least two and possibly three forms of sodium formaldehydesulphoxylate appear to be necessary. The existence of these tautomeric forms indicates the existence of a corresponding number of forms of neoarsphenamine.

E. H. SHARPLES.

**[Arsenic] derivatives of pyridine. VII. Stability of quinquivalent arsenic in the pyridine ring.** A. BINZ, C. RÄTH, and H. MAIER-BODE (Annalen, 1930, 480, 172—182).—When 2-pyridone-5-arsinic (I) and 2-hydroxypyridine-5-arsinic acids (II) (this vol., 486) are heated with water at 170° for 8 hrs., the percentages of arsenic acid eliminated are 13.6 and a trace, respectively. The corresponding values for the *monosodium* salts are 10.5 and a trace; those for the *disodium* salts are 87.6 and 11, respectively. The sodium salts of I are more soluble in water than those of II. Bromination of I with 1 mol. of bromine gives the 3-bromo-derivative (A., 1927, 890); II affords a small amount of bromo-derivative (not separated). Bromination of I with 2 mols. of bromine furnishes 3:5-dibromo-2-pyridone, also formed in small amount from II. Nitration of II with nitric and sulphuric acids yields small amounts of 3-nitro-2-pyridone-5-arsinic acid (obtained also from I; cf. A., 1929, 1471) and 3-nitro-2-hydroxypyridine-5-arsinic acid, not melted at 250°. The last-named acid is isolated by reducing the mother-liquors from the nitration with hypophosphorous acid, and oxidising the arseno-compound formed with hydrogen peroxide.

5-Iodo- and 3-bromo-5-iodo-2-pyridones react with potassium arsenite in presence of a small amount of copper sulphate forming 30 and 25% of I and its 3-bromo-derivative, respectively.

H. BURTON.

**Quinoline compounds containing arsenic. I. Synthesis of 6-methoxyquinoline derivatives of aminophenylarsinic acids.** R. H. SLATER (J.C.S.,

1930, 1209—1215).—6-Methoxyquinolylaminophenylarsinic acids have been prepared for examination of their antimalarial activity.

4-Chloro-6-methoxy-2-methylquinoline (Conrad and Limpach, A., 1888, 853) could not be condensed directly with *o*- or *p*-aminophenylarsinic acid; condensation with *p*-phenylenediamine affords 4-*p*-aminoanilino-6-methoxy-2-methylquinoline (+H<sub>2</sub>O), m. p. 215° (acetyl derivative, m. p. 240°), which is converted normally into *p*-6'-methoxy-2'-methyl-4'-quinolylaminophenylarsinic acid, unmelted at 307°; 4-*m*-aminoanilino-6-methoxy-2-methylquinoline (from *m*-phenylenediamine), m. p. 230—231° (acetyl derivative, m. p. 269°), yields similarly *m*-6'-methoxy-2'-methyl-4'-quinolylaminophenylarsinic acid, darkens at 280°, unmelted at 300°, whilst 4-benzidino-6-methoxy-2-methylquinoline, m. p. 245° (from benzidine) (acetyl derivative, m. p. 159—160°), gives 4'-6''-methoxy-2''-methyl-4''-quinolylaminodiphenylarsinic acid, darkens at 290°, unmelted at 300°. Interaction of *pp'*-diaminodiphenylmethane and 4-chloro-6-methoxy-2-methylquinoline gives *pp'*-di-6'-methoxy-2'-methyl-4'-quinolylaminodiphenylmethane, m. p. 144°; similarly, no monoquinolyl derivative has been obtained from *o*-anisidine or *o*-toluidine.

Distinctive colour reactions of the above compounds with 0.001*N*-iodine are described and the tendency of several of them to form gels when dilute aqueous solutions of their salts are cooled is noticed.

R. CHILD.

**10-Chloro-5:10-dihydrophenarsazine and its derivatives.** XII. 1- and 3-Methyl derivatives. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1930, 1124—1128).—10-Chloro-3-methyl-5:10-dihydrophenarsazine, m. p. 215—216.5°, has been synthesised by an alternative method, in which the final cyclisation did not involve the arsenic atom, and shown to be identical with the 10-chloro-1-(and/or 3-)methyl-5:10-dihydrophenarsazine prepared by other methods (A., 1929, 710, 1090).

Diazotisation of 3-nitro-*p*-toluidine and interaction with *o*-bromophenylarsenious oxide affords 2'-bromo-2-nitro-4-methyldiphenylarsinic acid, m. p. 252—254°, converted by reduction with ferrous hydroxide into 2'-bromo-2-amino-4-methyldiphenylarsinic acid, darkens at 240°, decomp. 264—265°; the latter is converted (by way of the phenarsazinic acid) by the potassium carbonate-copper powder-boiling amyl alcohol method, followed by reduction, into 10-chloro-3-methyl-5:10-dihydrophenarsazine. The reduction product of 2'-bromo-2-nitro-6-methyldiphenylarsinic acid, softens 226°, decomp. 237—239° (from 3-nitro-*o*-toluidine as above), could not be purified or converted into 10-chloro-1-methyl-5:10-dihydrophenarsazine.

R. CHILD.

**Diphenyl series. II. Antimony derivatives of diphenyl.** D. E. WORRELL (J. Amer. Chem. Soc., 1930, 52, 2046—2050).—4-Chlorodiphenyl, sodium, and antimony trichloride in benzene give *tri*-4-diphenylstibine, m. p. 176.5—177.5° after softening [dichloride, m. p. 273—274°; dibromide, m. p. 259—260°; di-iodide, m. p. 176—178° (all decomp. after softening); dihydroxide, m. p. 210—211° (decomp.) after sintering at 205°; sulphide, m. p. 173° (decomp.)

after softening above 168°]. Treatment of the tertiary stibine with antimony trichloride in presence of xylene at 220—240° gives a mixture of *dichloro*-4-diphenylstibine, m. p. 132—133° after softening (oxide, m. p. 159—160° after softening above 155°), and *chlorodi*-4-diphenylstibine, m. p. 187—188° after softening above 150° [oxide, m. p. 120—121° after softening; dichloride, m. p. 210° after softening above 200°, hydrolysed by alcoholic ammonia to *di*-4-diphenylstibinic acid, m. p. 204—205° (decomp.) after softening above 201°]. 4-Diphenylstibinic acid, decomp. above 300°, is also described. Thermal decomposition of *tri*-4-diphenylstibine dichloride affords 4-chlorodiphenyl and traces of *chlorodi*-4-diphenylstibine. H. BURTON.

**Diphenyl polysulphides, thiodiselenides, and selenodisulphides.** A. BARONI (Atti R. Accad. Lincei, 1930, [vi], 11, 579—582; cf. A., 1929, 1039, 1270).—Diphenyl disulphide, Ph<sub>2</sub>S<sub>2</sub>, is obtained as a solid, m. p. 62°, by the action of sulphuryl chloride on an alkaline solution of thiophenol. The trisulphide, Ph<sub>2</sub>S<sub>3</sub>, m. p. 30°, is obtained by the action of sulphur chloride on thiophenol. Selenium and magnesium phenyl bromide give diphenyl diselenide, Ph<sub>2</sub>Se<sub>2</sub>, m. p. 59°, whilst the selenodisulphide, Ph<sub>2</sub>SeS<sub>2</sub>, m. p. 50—51°, results from the action of selenium chloride on a solution of thiophenol in carbon disulphide. The thiodiselenide, Ph<sub>2</sub>Se<sub>2</sub>S, m. p. 55°, is obtained from sulphur chloride and selenophenol in carbon disulphide solution. F. G. TRYHORN.

**Interaction of selenium tetrachloride with substances containing the reactive methylene group.** K. G. NAIK and R. K. TRIVEDI (J. Indian Chem. Soc., 1930, 7, 239—246).—Treatment of malonanilide (5 mols.) with selenium tetrachloride (4 mols.) in dry ether at 27—30°, affords a mixture of the *selenide* [(NHPh·CO)<sub>2</sub>CSe]<sub>2</sub>, m. p. 222—223° after darkening at 217°, and *malon-m-chloroanilide*, m. p. 175—176° (alkaline hydrolysis product *m*-chloroaniline). Reduction of the *selenide* with alkaline hydrosulphide affords the original anilide and hydrogen selenide, whilst treatment with bromine gives dibromomalonanilide and selenium bromide. Corresponding *selenides*, m. p. 218—219°, 210—211° after darkening at 205°, and 220°, respectively, are prepared similarly from malon-*p*- and -*m*-toluidides and -β-naphthylamide, respectively. Malon-heptylamide, -*m*-4-xylylide, and -*p*-xylylide when treated as above furnish *dichloromalon-heptylamide*, m. p. 90°, -*m*-4-xylylide, m. p. 136—137°, and -*p*-xylylide, m. p. 170°, respectively. Similar treatment of methylmalonanilide furnishes the *selenide* [(NHPh·CO)<sub>2</sub>CMe]<sub>2</sub>Se, m. p. 222—224°; the corresponding *selenides* from methylmalon-*p*-toluidide, -*m*-toluidide, and -β-naphthylamide have m. p. 224—225°, 221°, and 229—230°, respectively. No reaction occurs between selenium tetrachloride and malonamide, malon-α-naphthylamide, malonanilidic and malon-*p*-toluididic acids. Ethyl malonate gives resinous products.

H. BURTON.

**Organic derivatives of silicon.** XLII. *cyclo*-Hexyl derivatives of silicane and silicoethane. K. W. PALMER and F. S. KIPPING (J.C.S., 1930, 1020—1028).—When magnesium *cyclohexyl* bromide

(2.5 mols.) was added to silicon tetrachloride in dry ether at 0°, and the product distilled, first a little *cyclohexene* and then two fractions b. p. 120—135°/35 mm. (I) and 135—150°/35 mm. (II) were obtained, the residue decomposing on further distillation. Fraction I yielded *cyclohexylsilicon trichloride*, b. p. 208—211°, hydrolysed by water at 0° to *cyclohexylsiliconic acid*,  $(C_6H_{11}SiO \cdot OH)_n$  (sodium salt), converted by heating at 150° into the "anhydride,"  $[(C_6H_{11}SiO)_2O]$ . Fraction II yielded *dicyclohexylsilicon dichloride*, b. p. 140—145°, containing a little *dicyclohexyl*, hydrolysed to a mixture of condensation products of *dicyclohexylsilicanediol*, m. p. 140—145°/3—4 mm., which when kept or when heated at 100° afforded *anhydrodicyclohexylsilicanediol*,  $[(C_6H_{11})_2SiO]_7$ . The residue from the initial distillation when treated with ether yielded a soluble fraction, which on hydrolysis afforded first *tetracyclohexylsiliconethanediol* (soluble in ether), and then a substance,  $[(C_6H_{11})_2SiO]_7$ , and a mixture of compounds (insoluble in ether) containing  $R_2Si<$  and  $RSi\equiv$  groups, since alkali afforded *dicyclohexylsilicon oxide*.

It is inferred that the original reaction takes place normally giving *cyclohexylsilicic trichloride*, *dicyclohexylsilicon dichloride*, and probably some *tricyclohexylsilicic chloride*, these being mainly decomposed to *dicyclohexyl* and the products described above.

A. I. VOGEL.

**Organic derivatives of silicon. XLIII. Formation of tri- and tetra-phenylsilicane by action of sodium on triphenylsilicic chloride.** F. S. KIPPING and J. F. SHORT (J.C.S., 1930, 1029—1032).—From the interaction of phenylsilicon trichloride and sodium (4—4.5 atoms) in a nitrogen atmosphere at 190°, a poor yield of tri- (converted into triphenylsilicic oxide, m. p. 222°) and tetra-phenylsilicane, m. p. 229—230°, was obtained. Triphenylsilicon trichloride does not react when boiled with sodium hydride in the absence of air. It is assumed that the hydrogen of the triphenylsilicane is derived by the change:  $2 >SiPh_2 \longrightarrow >SiPh-C_6H_4-SiPh_2 + H$ .

A. I. VOGEL.

**Sturine.** K. FELIX and A. LANG (Z. physiol. Chem., 1930, 188, 96—106).—*Sturine methyl ester hydrochloride*, m. p. 250° (decomp.),  $[\alpha]_D^{20} -63.0^\circ$ , was prepared from the sulphate by way of the *picrate*, m. p. 235° (decomp.), and the constituent amino-acids were determined. It is composed as follows: 11 mols. of arginine, 3 mols. of lysine, 2 mols. of histidine, and 4 mols. of monoamino-acids. The ratio of monoamino-acids to hexone bases is 4:1. *Sturine* contains a preformed methyl group attached to nitrogen, 4 free amino-groups, and 2 esterifiable carboxyl groups for the smallest molecule. The oxygen content is higher than corresponds with the number of free carboxyl groups and peptide linkings. The groups containing oxygen can be benzoylated and are probably hydroxyl groups. *N-Methylsturine, benzoylsturine*, m. p. 258—260° (decomp.), corresponding with 28 benzoyl groups for the smallest molecule, and *methylbenzoylsturine*, m. p. 230° (decomp.), were prepared.

J. H. BIRKINSHAW.

Different samples of phosphotungstic acid are responsible for subsidiary variations in the nitrogen precipitated from gelatin hydrolysates by phosphotungstic acid. Heating a synthetic mixture of arginine, proline, and glycine with 5% sulphuric acid in the autoclave before precipitation destroys part of the precipitable diamino-nitrogen of arginine. The amount of nitrogen precipitated by phosphotungstic acid varies almost continuously with the concentration of nitrogen in the solution. Curves are given which show that treating gelatin with acid before hydrolysis profoundly affects the amount of nitrogen precipitated with phosphotungstic acid. A rapid method for the determination of amide-nitrogen is described.

S. S. ZILVA.

**Precipitation of the basic amino-acids of proteins with phosphotungstic acid.** K. V. THIMMANN (Biochem. J., 1930, 24, 368—377).—The precipitation of the individual amino-acids by phosphotungstic acid was determined at various nitrogen concentrations. The solubility of the phosphotungstates increases with nitrogen concentration and in the case of lysine there is evidence of the formation of a soluble double salt. Proline is precipitated only at high nitrogen concentrations. The minimum solubilities of the basic amino-acids in the final liquid are somewhat less than the solubility corrections given by Van Slyke. Acid flocculation of gelatin produces an increased amount of proline and lysine. The crystalline form of the phosphotungstates is described.

S. S. ZILVA.

**Solid protein hydrochlorides.** W. D. BANCROFT and C. E. BARNETT (Proc. Nat. Acad. Sci., 1930, 16, 118—123).—Equilibrium diagrams have been constructed for the adsorption of hydrogen chloride by zein, arachin, casein, edestin, fibrin, and gliadin. Zein forms no compound, but the other proteins form at least one, e.g., nine compounds at least are formed by gliadin unless polymerisation of the protein during adsorption is assumed, so that gliadin has  $M(2250)_x$ . The equivalent weights of arachin, casein, edestin, fibrin, and gliadin are respectively 280, 435, 330—405, 365, and 250.

F. G. TRYHORN.

**Adsorption of ammonia by proteins.** W. D. BANCROFT and C. E. BARNETT (Proc. Nat. Acad. Sci., 1930, 16, 135—139).—Stoichiometric relationships are found in the adsorption of ammonia by *p*-amino-benzoic acid, but not in the cases of glycine, arachin, casein, edestin, fibrin, gelatin, gliadin, and zein.

F. G. TRYHORN.

**Protein degradation.** O. FURTH. I. Formation of nitrogen from protein by the action of sodium hypobromite and its relationship to the arginine content. F. FROMM (Biochem. Z., 1930, 220, 69—81).—Caseinogen, gelatin, legumin, edestin, oryzanin, and zein on treatment with hypobromite form nitrogen in two phases, the first, a rapid one occurring in the first 10—20 min. and corresponding (with proteins rich in arginine) with half the arginine-nitrogen, and the second, a slow development corresponding with the lysine- and histidine-nitrogen content. Acetamide, the acidic group of asparagine, tryptophan, and the acyclic monoamino-acids give

**Gelatin. XI. Diamino-nitrogen of gelatin.** K. V. THIMMANN (Biochem. J., 1930, 24, 357—367).—

practically no nitrogen, whereas lysine and histidine give more than half their nitrogen.

P. W. CLUTTERBUCK.

**Structure of proteins from the basis of enzyme analysis.** E. WALDSCHMIDT-LEITZ (Chem. Weekblad, 1930, 27, 266—271).—A lecture summarising the broader aspects of the author's recent work.

S. I. LEVY.

**Proteins. VIII. Silk fibroin.** I. S. GOLDSCHMIDT and K. STRAUSS (Annalen, 1930, 480, 263—279).—The action of potassium hypobromite on silk fibroin (cf. A., 1927, 983; 1929, 937) reveals the presence of two components, one of which reacts much more rapidly than the other. The rate of reaction is decreased considerably by an increase in the excess of alkali hydroxide in the hypobromite. The initial degradation product (22—23% of the silk) is probably a polypeptide. It contains small amounts only of amino-nitrogen and potassium, and when boiled with barium hydroxide solution, eliminates only 1.2% of carbon dioxide; formic acid is also produced during the hydrolysis. When hydrolysed with 25% sulphuric acid, a mixture of alanine and glycine (mol. ratio about 3) is formed. The polypeptide reacts much more slowly with hypobromite than the original silk.

Röntgenographic examination of the silk and its degradation product indicates that the latter contains much less amorphous material. The Debye-Scherrer diagrams of both show the same number of interference rings, indicating that both contain the same crystalline substance.

H. BURTON.

**Physico-chemical studies on proteins. IV. Comparative study of the acid and alkali binding of native and deaminised proteins.** W. M. SANDSTROM (J. Physical Chem., 1930, 34, 1071—1101; cf. A., 1925, ii, 1011).—Edestin, arachin, and the globulin of the cantaloupe seed have been analysed for their nitrogen distribution by the method of Van Slyke. Edestin, arachin, casein, fibrin, and durummin have been deaminised and then similarly analysed. The acid- and alkali-binding powers have been determined potentiometrically at 30°. These proteins behave similarly to the prolamines studied by Hoffman and Gortner (A., 1925, i, 1479), and, with the exception of edestin, the amount of acid fixed by the proteins is approximately proportional to their lysine content. The acid-binding power is greatly decreased by deamination.

L. S. THEOBALD.

**Sources of error in organic elementary analysis. V. Oxygen, rubber, and various accessories.** J. LINDNER (Ber., 1930, 63, [B], 1123—1128; cf. this vol., 726).—The amount of carbonaceous impurity in oxygen is approximately constant, not very considerable but not without moment for the accuracy of the carbon determination. Generally, impurities imparted to the air or oxygen current by the rubber connexions have an approximately equal effect which is less considerable than usually assumed, and apparently depending on the nature of the rubber. If the free inner surface of the rubber is gradually increased by progressive separation of the ends of the glass tubes, the amount

of impurities evolved increases rapidly at first but soon attains a value which increases only slowly even with very long connexions. Under extreme conditions, the permeability of rubber tubing for carbon dioxide and coal gas can be demonstrated with a connexion without exposed inner surface. The recorded data do not deal with possible unusual impurities in oxygen or rubber. Asbestos as subsidiary tube filling and glass wool as support for phosphoric oxide can evolve carbon dioxide when heated or treated with acids unless they have been submitted to suitable preliminary purification. Silver gauze, after ignition in a current of oxygen, has no disadvantageous effect on the determination of carbon.

H. WREN.

**Rapid combustion of organic substances.** E. V. ZAPPI and A. MANINI (Anal. Assoc. Quím. Argentina, 1929, 17, 234—238).—The Liebig method is modified by supporting the boat in an expanded extension of the oxygen supply tube, outside of which a current of oxygen from a by-pass also passes. A more rapid current of oxygen may be used when combustion begins, and the analysis is completed in less than 1 hr.

R. K. CALLOW.

**Vanadium oxides as catalysts in [organic] elementary analysis.** J. MEYER and H. TISCHBIEREK (Z. anal. Chem., 1930, 80, 241—247).—The admixture of a little vanadium pentoxide with refractory substances such as electrode carbon greatly facilitates their combustion in oxygen, complete combustion being attained in 1 hr. provided that the temperature employed is above the m. p. of the oxide (i.e., above 658°). The action is apparently catalytic, the vanadium pentoxide functioning as a carrier of oxygen. Freshly-prepared vanadium tetroxide acts similarly, but a sample 5 days old had practically no effect; the reason for this has not been ascertained. A porcelain boat the interior of which had become stained after use with vanadium pentoxide as above was found on subsequent employment to be almost equally efficient in promoting the combustion of the carbon; the catalytic layer on the boat is considered to be probably potassium vanadate mixed with vanadium oxides.

H. F. HARWOOD.

**Micro-determination of halogens and metals in organic compounds.** H. H. WILLARD and J. J. THOMPSON (J. Amer. Chem. Soc., 1930, 52, 1893—1897).—The halogens are liberated by heating 15—25 mg. of the material with fuming sulphuric acid, potassium persulphate, and potassium permanganate (the second is omitted and the last replaced by hydrogen peroxide if iodine is being determined). The evolved halogen is absorbed in sodium arsenite and weighed as the silver halide (cf. Thompson and Oakdale, this vol., 799). Any quinquivalent arsenic or antimony in the residual sulphuric acid is reduced with sulphur dioxide and determined with 0.01N-potassium bromate. Selenic acid in the sulphuric acid is reduced with hydroxylamine hydrochloride and the selenium is determined gravimetrically.

J. G. A. GRIFFITHS.

**Capillary analysis and microchemistry. Detection of small quantities of formaldehyde with dimethyldihydroresorcinol.** L. KOFLER and H.

HILBECK (Mikrochem., 1930, 8, 117—120).—A piece of filter-paper 20×1 cm. having a constriction about 2—3 cm. from the lower end is moistened with a saturated alcoholic solution of the reagent at the narrow part and the lower end is immersed in 0.5—1 c.c. of the solution to be tested; by capillary attraction this solution rises up the filter-paper and at the narrow part "formaldimethone" is formed if the solution contains formaldehyde. The paper is washed once by capillarity, dried, and heated at 130° to sublime the dimethone, which is recognised by its crystal structure and m. p. (189°).

A. R. POWELL.

**Detection and determination of oxalic acid in stomach contents.** G. D. ELSDON and J. R. STUBBS (Analyst, 1930, 55, 321—322).—Evaporation to dryness and extraction with alcohol is unsatisfactory for the determination of oxalic acid, as is also extraction of the acid with ether. Dialysis methods are too slow. Precipitation with lead acetate solution, filtration, decomposition of the precipitate with hydrogen sulphide, filtration, and precipitation of the filtrate with calcium chloride solution is capable of giving accurate results, but digestion with hydrochloric acid, filtration, and precipitation of oxalates with ammonia and calcium chloride is preferable. The liquid is centrifuged and decanted, the residue is broken up, water to the original volume is added, and centrifuging repeated. The combined solutions and washings are mixed with 15—20% of concentrated hydrochloric acid, heated on the water-bath for 2 hrs., filtered, and the precipitate washed. The filtrate and washings are made alkaline with ammonia, acidified with acetic acid, and the oxalic acid precipitated in the usual way. Tartaric acid may be distinguished from oxalic acid in dilute solutions, since a 1% oxalic acid solution gives an immediate precipitate (a 0.01% solution a turbidity) in the cold with calcium chloride in presence of acetic acid, whilst tartaric acid is precipitated only on keeping or shaking.

D. G. HEWER.

**Influence of  $p_{H_2}$  on a colour reaction of adrenals.** H. BERRY and B. GOUZON (Compt. rend., 1930, 190, 1239—1241).—A steel needle dipping in an aqueous solution of adrenaline hydrochloride shows surface colours varying with the  $p_{H_2}$  as follows:  $p_{H_2} < 3$ , pale green;  $p_{H_2}$  3—7, bluish-violet;  $p_{H_2} > 7$ , reddish-violet. The reaction is due to the pyrocatechol nucleus. It is discernible with a concentration of 0.005%.

R. K. CALLOW.

**Detection of organic compounds. II. I. L. ROSENTHALER** (Pharm.-Ztg., 1930, 75, 650—652).—Chemical and microscopical tests are described for diocain, percain, dial, elbon, septacrol, lipiodin, atochinol, and coramin.

H. E. F. NORTON.

**Quinizarinsulphonic acid (rufanic acid) as precipitant.** W. ZIMMERMANN (Z. physiol. Chem., 1930, 188, 180—188).—Rufanic acid (1:4-dihydroxyanthraquinone-2-sulphonic acid) is proposed as a precipitant for organic bases. It is obtained by heating 5 g. of quinizarin dried at 130° with 10 c.c. of fuming sulphuric acid (20% of anhydride) for 2 hrs. in a bath at 130—150°. It forms sparingly soluble salts with creatinine, m. p. 290—300° (decomp.); histidine, m. p. 305° (decomp.); putrescine, m. p. 330—335° (decomp.); arginine, decomp. 290—300°; guanidine, not melted at 350°; methylguanidine, m. p. 297—300° (decomp.); betaine, m. p. 320° (decomp.); lysine, m. p. 327° (decomp.); cadaverine, m. p. 295° (decomp.); spermine, m. p. 275—279° (decomp.); ammonium, not melted at 355°; choline, m. p. 332° (decomp.). The monoamino-acids including proline and oxyproline form readily-soluble salts which can be precipitated by alcohol. The bases are regenerated by barium hydroxide, which gives an insoluble basic barium salt of rufanic acid.

J. H. BIRKINSHAW.

**Determination of diphenylchloroarsine and diphenylarsine oxide.** E. D. G. FRAHM and H. L. BOOGAERT (Rec. trav. chim., 1930, 49, 623—626).—Determination of diphenylchloroarsine and diphenylarsine oxide by Fleury's iodometric method (A., 1920, ii, 642) gives low results in alcoholic solution. Correct values are obtained using either chloroform or benzene in the former case, and only in benzene in the latter. Diphenylchloroarsine may also be accurately determined by decomposition of a solution of 0.6 g. in 25 c.c. of alcohol with 5 c.c. of a 15% sodium hydroxide solution, diluting with water after heating for a short time, acidifying with nitric acid, and determining the sodium chloride formed,  $2Ph_2AsCl + 2NaOH = (Ph_2As)_2O + 2NaCl + H_2O$ , by the Volhard method. By combination of the two methods both diphenylchloroarsine and diphenylarsine oxide may be determined in a mixture of the two. Determination of arsenic in either of these derivatives by the Meulen-Heslinga method gives high results if the deposited arsenic is weighed (probably owing to the occlusion of traces of naphthalene), better results being obtained if it is determined iodometrically.

J. W. BAKER.

## Biochemistry.

**Components of air in relation to animal life.** J. W. HERSHEY (Science, 1930, 71, 394—396).—Animals soon die in an atmosphere of pure oxygen; hæmorrhage and the development of certain bacteria occur under these conditions. The addition of 0.03% of carbon dioxide to the oxygen has little or no effect in prolonging life. Mice exist normally in a mixture of 79% of helium and 21% of oxygen and in one of 75% of argon and 25% of oxygen; higher

percentages of argon are harmful. The rare gases, together with carbon dioxide, appear to be essential to normal life in an atmosphere of 21% of oxygen and 78% of nitrogen. An increase in the percentage of oxygen up to 60 has little effect, but larger percentages had an adverse effect. In certain cases, artificial atmospheres supporting the life of white mice more effectively than normal air have been prepared.

L. S. THEOBALD.

The traces of combustible gases in human expired air. T. R. PARSONS (Biochem. J., 1930, 24, 585—588).—The slight diminution in volume when pure atmospheric air is submitted to combustion analysis is confirmed. This effect is obtained even when the air is passed over red-hot copper oxide. Air that has been rebreathed by a human subject contains traces of combustible gases in amounts that indicate a rate of production of about 0.02 c.c. per min., which is far too small to be of significance in determinations of total respiratory exchange.

S. S. ZILVA.

Source of expired carbon dioxide and the site of its retention. L. IRVING, J. K. W. FERGUSON, and F. B. PLEWES (J. Physiol., 1930, 69, 113—123).—The amounts of carbon dioxide expired in over-ventilation, and absorbed in ventilation with air rich in carbon dioxide, are much greater than can be accounted for by the capacity of the blood and muscles. It is suggested that bone is capable of retaining or evolving carbon dioxide in the body.

E. BOYLAND.

Gasometric determination of the relative affinity constant of carbon monoxide and oxygen in whole blood at 38°. J. I. SENDROY, S. H. LIU, and D. D. VAN SLYKE (Bull. Soc. Chim. biol., 1930, 12, 532).—The value of the relative affinity constant  $K = [\text{Hb CO}]/[\text{Hb O}_2] \times p_{\text{O}_2}/p_{\text{CO}}$  (where  $p_{\text{O}_2}$  and  $p_{\text{CO}}$  are the pressures of the gases respectively) is found to be for human blood 210 and for ox blood 179, the error being  $\pm 2.5\%$  of the mean.

W. O. KERMAK.

Hæmoglobin. A. B. MACALLUM and R. C. BRADLEY (Science, 1930, 71, 341).—The absorption band at 4100 Å. in oxyhæmoglobin and at 4300 Å. in hæmoglobin does not appear in washed corpuscle suspensions of horse and fowl hæmoglobins; the band at 2500 Å. in solutions of horse hæmoglobin is also absent in washed cell suspensions.

L. S. THEOBALD.

Blood-pigment. XII. Tryptic digestion of blood-pigment. F. HAUROWITZ (Z. physiol. Chem., 1930, 188, 161—179; cf. this vol., 489).—Oxyhæmoglobin, carbon monoxide-hæmoglobin, and reduced hæmoglobin are hydrolysed by trypsin with approximately equal rapidity. The hydrolysis is inhibited by putrefactive agents. In the tryptic digestion of blood-pigment the prosthetic group is unchanged, the labile linking between hæmin-iron and globin is broken. About 95% of the globin is disintegrated to dialysable fragments, about 5% remains combined with the total protohæmin molecules as hæminprotease. This can be precipitated from the digestion mixture with acetic acid. It contains 40—60% of hæmin. The mol. wt. of hæminprotease is greater than 20,000. The protein component is resistant to pepsin and trypsin. The linking between protein and hæmin components is hydrolysed by concentrated hydrochloric acid. The so-called tryptoporphyrin of Fränkel, Prinz, and Monasterio consists largely of a protein derivative.

J. H. BIRKINSHAW.

Preparation of some blood-pigment derivatives. J. ŠULA (Z. physiol. Chem., 1930, 188, 274—278).—Methods for the preparation of potassium

oxyhæmin, formylhæmin, acetylhæmin, and protoporphyrin directly from blood are described.

J. H. BIRKINSHAW.

Enzymes of leucocytes. V. Trypsin. R. WILLSTÄTTER, E. BAMANN, and M. ROHDEWALD (Z. physiol. Chem., 1930, 188, 107—123; cf. this vol., 629).—The freshly isolated leucocytes of horse's blood have practically no tryptic action, but suspension in glycerol gradually activates the trypsin present, whereas the leucocytes of dog's blood are active immediately on mixing with glycerol. The cell residues of horse's blood possess a much stronger tryptic action than the leucocytes, which contain an inhibitor. The leucocyte suspension is usually strongly activated by intestinal enterokinase. The system of trypsin activation and inhibition of the pancreatic gland is thus present in the blood-corpuscles.

J. H. BIRKINSHAW.

Catalase content of the blood of animals kept in air at low pressures. T. RADEFF (Biochem. Z., 1930, 220, 445—452).—White mice and rats were kept in air at 280 mm. for 1—2 weeks, some being brought abruptly into the low-pressure atmosphere, others gradually accustomed to it. Some of the animals were subsequently brought back to normal atmospheric pressure. The low pressure caused parallel increases in the catalase and hæmoglobin content and in the number of red corpuscles of the blood. Restoration to normal pressure caused the increased catalase content to decrease and the number of red corpuscles to decrease in proportion.

W. MCCARTNEY.

Determination of catalase. Importance of erythrocyte volume in determination of blood-catalase. A. BERNSTEIN (Zhur. exp. Biol. Med., 1929, 11, 18—21).—The catalase value of blood is untrustworthy unless expressed in terms of the volume of the cells.

CHEMICAL ABSTRACTS.

Determination of the quantity of free water in erythrocytes. C. KREVISKY (Biochem. J., 1930, 24, 815—819).—Determination of the maximum change of volume of blood-corpuscles in sodium chloride solutions of varying concentrations gives a value of 30—35% of the cell volume occupied by the free or osmotically transferable water contained in the corpuscle and 30—35% for the value of the bound water associated with the dispersed phase (hæmoglobin and lipins) confirming Gough's results (A., 1924, i, 583). Ege's high figure of 60% of free water in the cell (A., 1927, 892) is possibly due to sources of error such as washing cells in isotonic solutions, prolonged centrifuging, hæmolysis, and the use of Koeppé's criterion as an indication of true cell-volume.

S. S. ZILVA.

The  $p_{\text{H}}$  and buffering of the tissues and of the subcutaneous lymph in local venous hyperæmia. N. OKUNEV (Biochem. Z., 1930, 220, 164—176).—In venous hyperæmia, the buffering of the tissues of the frog's tongue is increased and the reaction displaced to the alkaline side. Then follows a period in which the buffering and the reaction are approximately normal and finally a slight acidosis accompanied by decreased buffering is observed. During venous hyperæmia the subcutaneous lymph of the frog's leg



shows considerable decrease of buffering and often considerable acidosis. The increased buffering and  $p_H$  are explained in terms of the simultaneously occurring passage of erythrocytes into the tissues.

P. W. CLUTTERBUCK.

**Comparison between the colorimetric and electrometric methods of measuring the  $p_H$  of blood.  $p_H$  of whole blood and plasma.** J. ERRERA, R. REDING, and A. SLOSSE (Bull. Soc. Chim. biol., 1930, 12, 470—481).—The  $p_H$  of oxalated human plasma has been determined electrometrically by the glass electrode and colorimetrically by the method of Hastings and Sendroy (A., 1924, ii, 869) and good agreement between the two methods is found.

W. O. KERMACK.

**Determination of protein in blood-serum.** F. KAYSER (Bull. Soc. Chim. biol., 1930, 12, 533—537).—Serum (5 c.c.) is added in small portions with agitation to a mixture of 25 c.c. of alcohol and 25 c.c. of acetone. The precipitated protein is collected, washed with alcohol, and weighed. For determination of globulin and albumin, the serum diluted with distilled water is precipitated with magnesium sulphate. The precipitated globulin is filtered off and an aliquot portion of the filtrate treated with formalin and acetic acid, boiled, and the precipitated albumin collected, washed, dried, and weighed; the globulin is found by difference. W. O. KERMACK.

**Chemical constitution of serum-proteins.** I. A. FISCHER and A. BLANKENSTEIN (Biochem. Z., 1930, 220, 380—393).—The proteins of ox-serum can be separated into various fractions by precipitation with neutral or acid solutions of ammonium and magnesium sulphates and of sodium and potassium chlorides. Determinations of the amounts of tryptophan, cystine, and tyrosine and of nitrogen in its various states of combination in the fractions show that the serum contains at least seven chemically different proteins. In human serum there are at least five such proteins.

W. MCCARTNEY.

**Precipitation of nitrogenous substances of serum in presence of formaldehyde.** M. MASCRÉ and M. HERBAIN (Compt. rend., 1930, 190, 1205—1207; cf. this vol., 103).—In presence of formaldehyde, sodium and magnesium sulphates and acetone precipitate considerably more nitrogenous substances from serum than when used alone. The amount precipitated by boiling alcohol is not affected by formaldehyde.

H. BURTON.

**Lipin-phosphorus accompanying globulins in blood-serum and serous fluids.** C. ACHARD and A. ARCAND (Compt. rend., 1930, 190, 1209—1212).—After extraction of lipins by acetone and ether, followed by grinding and extracting with ether, the proteins still contain residual lipins. This residue can be extracted by the prolonged application of Kumagawa's method. The low content of phosphorus indicates that it consists largely of sterols, with but little lecithin. The residue is almost entirely in the globulin fraction and it contains all the phosphorus of the latter.

R. K. CALLOW.

**Ultra-violet absorption spectra of serum-proteins. Specific extinction coefficient of serum-pseudoglobulin.** F. C. SMITH and J. R. MARRACK

(Proc. Roy. Soc., 1930, B, 106, 292—298).—Spectrophotometric observations have been made on a number of samples of pseudoglobulin prepared according to the methods of Smith (A., 1929, 431) and of Svedberg and Sjögren (A., 1929, 203) and the value of 12 for the specific extinction coefficient previously found by Marrack and Smith (this vol., 377) has been confirmed. The results are supported by observations on the absorption coefficients of blood-serum. Beer's law is valid for absorption by pseudoglobulin solutions.

W. O. KERMACK.

**Micro-distillation apparatus and methods for the determination of organic nitrogen, carbamide, acetone, and lactic acid [in blood].** H. J. FUCHS (Mikrochem., 1930, 8, 159—175).—Micro-forms of the Kjeldahl apparatus, apparatus for the fractional and steam distillation of liquids, and the double burette are described. In the micro-determination of nitrogen by the Kjeldahl method the excess of sulphuric acid over that required to combine with the ammonia is determined iodometrically after addition of potassium iodate and iodide. For the determination of carbamide 2 c.c. of oxalated blood are shaken with 22 c.c. of 2.5% trichloroacetic acid. After filtration, 8 c.c. of the clear solution are neutralised with 0.1N-sodium hydroxide, treated with 4 c.c. of urease solution (10 mg. of dry enzyme dissolved in 5 c.c. of phosphate buffer solution), and heated at 50—55° for 20 min. The solution is saturated with sodium chloride and treated with 5 c.c. of Nessler solution saturated with potassium chloride, the precipitate is collected on asbestos, and its nitrogen content determined by the micro-Kjeldahl method. Acetone derivatives are determined by removing the proteins with sodium tungstate from 3 c.c. of blood and distilling the filtrate with 1 c.c. of sulphuric acid into a mixture of 2 c.c. of 0.01N-iodine, 2 c.c. of 40% potassium hydroxide solution, and 5 c.c. of water; acidification of the distillate with sulphuric acid and titration of the excess of iodine gives a value for the acetoacetic acid content of the blood. The residue in the distillation flask is redistilled while a 2% acid solution of potassium dichromate is allowed to drop slowly into the liquid; the acetone that distills in this operation is determined as before and calculated to  $\beta$ -hydroxybutyric acid. Lactic acid is determined by treating 15—20 c.c. of blood with 4% hydrochloric acid saturated with sodium chloride, precipitating the proteins with 5% mercuric chloride solution, removing the mercury with hydrogen sulphide and the latter with a current of air, removing the sugars with copper sulphate and calcium hydroxide, distilling the filtrate with sulphuric acid and permanganate into 20 c.c. of 0.02N-sodium hydrogen sulphite, and titrating the excess with 0.01N-iodine.

A. R. POWELL.

**Determination of lactic acid in blood.** P. LOISELEUR and R. MOREL (Bull. Soc. Chim. biol., 1930, 12, 538—540).—Protein and dextrose are precipitated in one operation by adding calcium oxide (2 g.) to fluoridated plasma (3 c.c.) diluted with distilled water (21 c.c.), followed by a saturated solution (6 c.c.) of copper sulphate. After keeping for 1 hr. with occasional shaking, the mixture is centrifuged and a

clear liquid is obtained in which lactic acid is determined by the method of Furth and Charnass (cf. Clausen, A., 1922, ii, 593). W. O. KERMACK.

**Blood-sugar in the hare.** B. KISCH (Biochem. Z., 1930, 220, 378—379).—The sugar content of the blood of hares is very similar to that of rabbits.

W. MCCARTNEY.

**Critical blood-sugar.** H. ELIAS and B. FELL (Arch. exp. Path. Pharm., 1930, 150, 146—159).—The renal blood-sugar threshold, which is somewhat modified by the posture of the individual, averages normally about 0.16%. In a case of cholelithiasis the threshold was 0.205%. Administration of adrenaline does not affect it, but lordosis raises the threshold. Pilocarpine, pituitrin, and choline raise the threshold in varying degrees; sistomensin (fat-soluble ovarian hormone) and agomensin (water-soluble) both raise it to over 0.20%. Phytostigmine and choline also produce a definite rise in the renal sugar threshold of the dog.

P. G. MARSHALL.

**Glycolysis of red blood-corpuscles.** W. BURGER (Arch. exp. Path. Pharm., 1930, 150, 298—307).—The rates of anaërobic glycolysis of nucleated and non-nucleated red blood-cells are approximately equal, and although small compared with that of young or embryonic tissue are comparable with the latter if calculated on the weight of the stromata and not on that of the total corpuscle. The glycolytic activity of young corpuscles is especially high, and thus the glycolytic activity of the blood-cells is high in diseases or other conditions associated with blood regeneration.

W. O. KERMACK.

**Diffusibility of the calcium in blood-serum under normal and pathological conditions.** A. M. SNELL and F. WALES (Proc. Staff Mayo Clinic, 1930, 5, 17—20).—Normally, 45—55% of the serum-calcium is diffusible. The diffusibility depends on the protein content of the fluids, the  $p_H$ , and the chlorine content of the fluid against which it is dialysed. Observations on pathological conditions are recorded.

CHEMICAL ABSTRACTS.

**Determination of potassium in blood-serum.** F. H. L. TAYLOR (J. Biol. Chem., 1930, 87, 27—32).—Blood-serum is freed from protein with tungstic acid; 5 c.c. of the filtrate are evaporated to dryness in a centrifuge tube, the residue is dissolved in 50% alcohol, and the solution is treated with the cobalt-nitrite reagent of Briggs (A., 1924, ii, 132). The precipitate is separated, washed repeatedly with 30% alcohol, dissolved in dilute sodium hydroxide, and treated with sulphanilic acid and  $\alpha$ -naphthylamine in presence of acetic acid. The resulting colour is compared with that produced by similar treatment of a standard solution of potassium chloride. The error of the method is  $\pm 3\%$ .

C. R. HARRINGTON.

**Determination of potassium in blood-serum.** F. BREH and O. H. GAEBLER (J. Biol. Chem., 1930, 87, 81—89).—Blood-serum is freed from proteins with tungstic acid; the filtrate is treated with silver nitrate, and, after clearing on the centrifuge, with the cobalt-nitrite reagent of Kramer and Tisdall (A., 1921, ii, 412). The precipitate is separated, washed, and dissolved in dilute nitric acid, and the solution

is treated with an alcoholic solution of ammonium thiocyanate. The colour is compared with that produced by a standard solution of ammonium thiocyanate similarly treated. The method may also be utilised for the determination of small amounts of cobalt.

C. R. HARRINGTON.

**Determination of magnesium in serum.** M. N. KALLENIKOVA (Biochem. Z., 1930, 220, 278—282).—Calcium (which may also be determined) is removed from 1.0 c.c. of serum and the magnesium is precipitated as magnesium ammonium phosphate. The phosphorus content of this is determined by Samson's method (A., 1926, 328), the magnesium content being obtained then by calculation.

W. MCCARTNEY.

**Determination of phosphate in blood.** F. GRENDEL (Pharm. Weekblad, 1930, 67, 536—544).—A modified procedure based on Briggs' method is described. The much lower results obtained by Tisdall's method are traced to the fact that all the acid-soluble phosphate is not taken into solution; if the acid solution be heated before precipitation of the phosphates, the result obtained is increased by about 15%. The modified Briggs method gives accurate and consistent results.

S. I. LEVY.

**Coagulation of the blood.** S. OTAWARA (Nagasaki J. Med., 1928, 6, 63—88).—The relation  $k=tc^n$ , where  $t$  is the time of coagulation,  $c$  the concentration of thrombin solution, and  $k$  is a constant, holds generally.

CHEMICAL ABSTRACTS.

**Influence of some anticoagulants on the distribution between plasma and corpuscles of blood constituents. I. Migration of water and chlorine.** C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1930, 12, 491—503).—When various salts (fluoride, oxalate, and citrate) even in minimum concentrations are used as anticoagulants, water flows from the corpuscles into the plasma, the former in consequence being reduced in volume. In the case of fluorides this decrease may amount to 20%. In the case of citrate, the chlorine ions are displaced into the corpuscles, but with oxalates and fluorides in the opposite direction. When hirudin is not available, the anticoagulant is preferably sodium oxalate in amounts of 0.2% or less. Although the diffusible ions other than chlorine appear to be likewise affected by the presence of anticoagulants, the colloidal substances including the proteins are not displaced.

W. O. KERMACK.

**Phospholipin and hæmolysis.** Y. SUYEVOSH and K. OKAWA (Sei-i-kwai Med. J., 1929, 48, No. 9, Abstr., 3).—Rancid, but not pure, lecithin and cephalin exhibit hæmolytic action, the effect being inhibited by cholesterol.

CHEMICAL ABSTRACTS.

**Kinetics of hæmolytic systems. IV. Series of Ryvosh.** E. PONDER, G. SASLOW, and J. F. YEAGER (Biochem. J., 1930, 24, 805—814; cf. A., 1927, 271).—Ryvosh's observation that the resistance of red cells to hypotonic saline varies inversely with the resistance to saponin is not true of the cells of all mammals. Simultaneous chemical analyses and determinations of resistance to various lysins do not reveal any one substance the total quantity of which determines the

resistance of the cell. There is a different order of resistance when various lysins are used. This is in consonance with the theory on which studies of the kinetics of the hæmolytic reaction are based.

S. S. ZILVA.

**Oxygen-combining power of muscle-hæmoglobin.** M. N. J. DIRKEN and H. W. MOOK (J. Physiol., 1930, 69, 210—213).—Hæmoglobin extracted from muscle had an oxygen-combining power only 7—20% less than that of blood-hæmoglobin, so that it can be assumed that the true oxygen-combining powers of hæmoglobin from these two sources are identical.

E. BOYLAND.

**Isolation of histamine from the heart.** W. V. THORPE (Biochem. J., 1930, 24, 626—630).—Extracts of ox ventricles show a depressor activity corresponding with 8—18 mg. of histamine per kg. assayed biologically. Pure histamine has been isolated as the dipicrate from such an extract and is most probably responsible for the depressor activity and the cardiac stimulating effect of heart extracts attributed to a "heart hormone."

S. S. ZILVA.

**Protein sulphuric acid ester from the mucous membrane of the [pig's] stomach.** H. MATHIS (Biochem. Z., 1930, 220, 493—495; cf. Fränkel and Monasterio, A., 1929, 1329).—A substance similar to the protein sulphuric acid ester found in liver and in pituitary gland has been obtained from the mucous membrane of the pig's stomach. W. MCCARTNEY.

**Purines of rabbit muscle.** P. OSTERN (Biochem. Z., 1930, 221, 64—70).—The purine content of fresh rabbit muscle amounts to about 48 mg. of purine-nitrogen per 100 g., 39 mg. being contained in the extract and 9 mg. in the extracted muscle. The purines of the extract are present as nucleotides and scarcely any as nucleosides or free purines. Adenine is present as nucleotide or is united with protein and is never free or as nucleoside. In the extract a small amount of guanine nucleotide is present. Adenine nucleotide, on autolysis, is broken down to inosic acid and then to free and nucleoside hypoxanthine.

P. W. CLUTTERBUCK.

**Ammonia and purines in heat-coagulation of frog's muscle.** J. JAWORSKA (Biochem. Z., 1930, 221, 71—73).—The ammonia formed in the heat-coagulation of frog's muscle arises exclusively from adenine nucleotide. The inosic acid simultaneously formed is not further attacked in experiments lasting 2 hrs., but is decomposed during 24 hrs.' autolysis, giving free and nucleoside purines.

P. W. CLUTTERBUCK.

**Occurrence of methylguanidine in the animal organism.** IV. "Reineckate" of methylguanidine. I. A. SMORODINCEV (Z. physiol. Chem., 1930, 189, 7—10; cf. A., 1929, 839).—Reinecke salt,  $\text{Cr}(\text{NH}_3)_2\text{NH}_4(\text{SCN})_4$ , forms with methylguanidine a crystalline compound, m. p. 228—230°, solubility in water at 15°, 0.4311 g. in 100 g. It is 2.5 times as soluble as the corresponding creatinine salt, and cannot therefore be employed to separate the two bases.

J. H. BIRKINSHAW.

**Glutathione in Teleostei: methods of determination.** I. G. CANNICCI (Atti R. Accad. Lincei,

1930, [vi], 11, 509—515).—Of the two methods suggested for the determination of glutathione, the nitroprusside method (cf. Tunnicliffe, A., 1925, i, 752), especially as modified by Randoin and Fabre (A., 1927, 905), although not absolutely accurate, gives results sufficiently exact for physiological investigations.

T. H. POPE.

**Glutathione. III. Structure of glutathione.** E. C. KENDALL, H. L. MASON, and B. F. MCKENZIE (J. Biol. Chem., 1930, 87, 55—79).—Glutathione was oxidised to the corresponding sulphonic acid by means of bromine; treatment of the product with sodium hypobromite yielded 1 mol. of carbon dioxide and a substance from which, before or after further treatment with nitrous acid, succinic acid and glycine were liberated by hydrolysis with hydrochloric acid. Similar products were obtained after oxidation with "chloramine-T." In view of the previously-observed effects (this vol., 113) of treatment of glutathione with nitrous acid and with hydrogen peroxide, this indicates that the compound is either glutamylglycylcysteine or glutamylcysteinylglycine, the amino-group of the glutamic acid being in the  $\gamma$ -position to the amide linking. Since the product of interaction of glutathione ethyl ester hydrochloride with magnesium phenyl bromide yields, on hydrolysis, diphenylacetaldehyde, the latter alternative is the more probable.

Glutathione is slowly hydrolysed by crepsin; when it is kept for 14 days in sterile aqueous solution at 38°, 80% of the glutamic acid is liberated as pyrrolidonecarboxylic acid. For the preparation of glutathione from yeast the cuprous oxide precipitation of Hopkins (A., 1929, 1322) may be advantageously applied to the solution obtained by the authors on recovery from the lead precipitate (this vol., 113), precipitation with mercuric sulphate being omitted.

C. R. HARRINGTON.

**Glycogen ratio in the bundle of His and the cardiac muscle in man and the horse.** W. M. YATER, A. E. OSTERBERG, and H. W. HEFKE (Arch. Int. Med., 1930, 45, 760—771).—In man the bundle of His is quickly dissected from fresh hearts and the glycogen content determined with that of cardiac muscle. The average ratio of the glycogen content of cardiac muscle and the bundle of His is 1:0.9 in man, whilst in the horse (where the bundle of His contains a large amount of fibrous tissue) it is about 1:10.0. No explanation is offered of this discrepancy. Glycogen disappears only slowly from the tissues of the conduction system and the cardiac muscle after death. The total glycogen content of hearts shows wide variations.

P. G. MARSHALL.

**Occurrence of a new phosphorus compound in lecithin.** T. GASSMANN (Z. physiol. Chem., 1930, 189, 64).—The hypothesis of Embden that there is an "unknown" type of phosphorus in muscle and that of Sorg that there are two types of phosphorus in lecithin agree with the author's previously published view.

J. H. BIRKINSHAW.

**Cholesterol of protoplasm. II. Ox brain.** III. Ox erythrocytes. G. PFEIFFER (Biochem. Z., 1930, 220, 53—61, 210—216).—II. Of the total cholesterol of ox brain, cholesterol+oxycholesterol forms 72.38%, oxycholesterol 7.5%, cholesteryl ester

27.62%, cholesteryl oleate 0.22%, and oxycholesteryl oleate 27.4% (cf. A., 1929, 90). The amount of oxycholesterol (m. p. 110°) in mixtures with cholesterol (m. p. 146.5°) may be approximately (accuracy, 0.3%) deduced from the m. p., admixture of 1% of oxycholesterol lowering the m. p. of pure cholesterol by 0.365°.

III. Of the total cholesterol of ox erythrocytes, cholesterol+oxycholesterol form 90.86%, oxycholesterol 6.6%, cholesteryl ester 9.14%, and oxycholesteryl oleate 9.14%. The complete absence of ester is thus denied, being of the order of 10% in the winter months and somewhat higher in summer, especially in older animals on a green feed.

P. W. CLUTTERBUCK.

**Biology of aluminium.** C. MASSATSCH and H. STEUDEL (Biochem. Z., 1930, 220, 239—249).—Aluminium occurs in almost all animals and plants and may be necessary for maintenance of life. The metal, in the amounts likely to occur in foods, is quite harmless.

W. McCARTNEY.

**Water and phosphorus compounds of nerve on degeneration.** R. M. MAY (Compt. rend., 1930, 190, 1150—1151).—During the first month the water content of the degenerated sciatic nerve of the rabbit increases to 14% above the normal and thereafter falls to the normal value. The total phosphorus diminishes progressively during the first 2 months to a third of its normal value. The lipin-phosphorus decreases after 100 days to a tenth of its normal value, when histological examination shows complete reabsorption of the lipin products of the nerve. The alcohol-soluble and the protein phosphorus after an initial rise diminish to a third of the initial value, whilst the water-soluble phosphorus shows a steady increase up to 35% above the normal value after 6 months.

C. C. N. VASS.

**Mummification methods of the Egyptians.** M. WAGENAAR (Chem. Weekblad, 1930, 27, 348—355).—An examination of the mummy of Chonsoe Hotep, a priest of the 18th dynasty, and of the mummy windings, was made 40 years after the mummy had been partly exposed. A reddish-brown substance from between the ribs yielded hæmatin chloride, hæmochromogen, and hæmatoporphyrin, and contained iron and nitrogen in the same ratio as fresh blood. Microscopical examination between crossed Nicols revealed bundles of muscle-tissue and of flax fibre, with crystals of sodium chloride and potassium nitrate. From the brown resinous substance with which the windings were impregnated, catalase (and most probably protease), dextrose and lævulose, oxalic and citric acids, and calcium were extracted, and from these results, as well as from the importance of the fig tree in ancient Egypt, and from the evidence of old records and pictures, it is concluded that an extract of *Ficus Sycomorus* was the principal preservative employed in embalming bodies of important persons.

S. I. LEVY.

**Acid-base equilibrium of the ocular humours.** P. W. SALIT (Biochem. J., 1930, 24, 596—605).—Carbon dioxide content and capacity are identical for the vitreous humour. The amount decreases, with a few fluctuations, on the average from 58.7 vol.-% in a

calf 6 weeks old to 42.9 vol.-% in cattle 2 years old. Plasma exceeds the vitreous humour in carbon dioxide capacity by an average of 11 vol.-% in 2-year-old cattle. The vitreous humour in its natural state can be kept under oil in the refrigerator for about 1 week without loss of carbon dioxide. If, however, its structure is destroyed by mechanical liquefaction, it tends to lose its carbon dioxide much more readily. No dissolved oxygen could be demonstrated in the vitreous humour. The aqueous humour of cattle 1½—2 years old contained an average of 47.5 vol.-% of carbon dioxide. The aqueous humour loses its carbon dioxide very rapidly if disturbed, even under oil. The carbon dioxide content of the aqueous humour exceeds that of the vitreous by 3.8 vol.-% for cattle 1½—2 years old, the average figures being 47.5 vol.-% and 43.7 vol.-%, respectively. There is a distinct decrease in the hydrogen-ion concentration of the aqueous humour of cattle with advancing age. The relative  $p_H$  values increase from 7.23 in a 5-week-old calf to 7.40 in 2-year-old cattle. The relative  $p_H$  values of the vitreous humour of cattle increase on the average from 7.29 in 3-month-old calves to 7.50 in 2-year-old cattle.

S. S. ZILVA.

**Presence of citric acid in aqueous humour.** H. GRÖNVALL (Biochem. Z., 1930, 220, 82—83).—Aqueous humour of the eye of dog and pig contained 50  $\gamma$  per c.c. of citric acid as determined by Thunberg's citric-dehydrogenase method (A., 1929, 602). The human eye contained at least 30  $\gamma$  per c.c.

P. W. CLUTTERBUCK.

**Citric acid content of animal fluids (cerebrospinal, follicular, and amniotic fluids and aqueous humour).** I. NITZESCU and I. D. GEORGESCU (Compt. rend., 1930, 190, 1325—1327).—The citric acid content of the following animal fluids has been determined by Thunberg's methylene-blue test: human cerebrospinal fluid 0.075—0.080 g. per litre, of dog, 0.090—0.100 g. per litre; aqueous humour of oxen, 0.012 g. per litre; follicular fluid of cows, 0.040 g. per litre; human amniotic fluid, 0.025—0.027 g. per litre.

A. I. VOGEL.

**Biochemical investigation of the labyrinth and cerebrospinal fluids of the dog-fish.** J. KAIEDA (Z. physiol. Chem., 1930, 188, 193—202).—The physical properties, chemical composition, and enzymic action of the labyrinth (endolymph and perilymph) and cerebrospinal fluids of the dogfish (*Scoliodontus laticaudus*) were examined. The solids amount in all cases to 4—5%; the endolymph contains about 1.7% of sodium chloride. The total nitrogen is about 1.2%, present largely as carbamide in the endolymph; the perilymph and cerebrospinal fluid contain 1.3% and 0.8% of creatine, respectively. Amylase and esterase are found in all three fluids, trypsin only in the perilymph and cerebrospinal fluid. Pepsin and urease are absent.

J. H. BIRKINSHAW.

**Glycolysis and behaviour of lactic acid in normal and pathological cerebrospinal fluid.** H. FASOLD and H. A. SCHMIDT (Klin. Woch., 1929, 8, 1532—1535; Chem. Zentr., 1930, i, 248).—Cell-free cerebrospinal fluid shows no glycolysis. Decomposition of lactic acid does not take place in the normal or pathological fluid.

A. A. ELDRIDGE.

**Tributyrynase of the lymph. I. Properties compared with those of tributyrinases from blood and pancreas. II. Passage of enterally and parenterally introduced enzymes (tributyrynase and diastase) into the lymph. Tributyrinase of the urine.** S. TERASHIMA (Proc. Imp. Acad. Tokyo, 1930, 6, 179—180, 181—182).—I. Fasting lymph contains less tributyrinase than the blood. The optimum  $p_H$  of the enzyme from lymph and blood is 8.3—8.6, whilst that from pancreas is 7.16—7.97. In alkaline reaction cocaine inhibits the action of blood- and lymph-enzyme, whereas with pancreas-enzyme this inhibition does not occur at any reaction. Sodium fluoride behaves similarly, but quinine prevents the action of all three lipases. Lymph- and blood-enzymes from rabbits are strongly inhibited by atoxyl, but those from dogs are unaffected, as is the pancreas-lipase. The results indicate that lymph-tributyrynase has the same properties as serum-tributyrynase, whilst those of the pancreatic enzyme are different.

II. Diastase and tributyrinase readily pass through Chamberland filters. The reactions of blood-, lymph-, and pancreas-tributyrynase with poisons indicate that the method of Rona (A., 1927, 377; 1928, 1157) for lipase action is not very sensitive. Intravenous injection of a solution of both enzymes causes immediate increase in the enzyme concentration of the blood which persists for some hours. Diastase on intravenous injection passes very rapidly into the lymph. Tributyrinase behaves in the opposite manner. Intraperitoneal injection of diastase causes an increase in lymph-diastase, but does not affect the serum-diastase. Oral administration of the enzymes increases neither the lymph- nor the serum-enzyme content. Urine of fasting rabbits contains a higher concentration of diastase than the blood. Tributyrinase is not always present. The  $p_H$  optimum of urine-tributyrynase of rabbits is about 8.0. Intravenously introduced diastase and tributyrinase are excreted fairly rapidly in the urine.

F. O. HOWITT.

**Normal limits of variation of the methylene-blue reduction test [with milk].** A. C. FAY (J. Agric. Res., 1930, 40, 855—862).—Simplifications in measuring and variations in the amount of dye used have no serious effect on the reductase test used as a means of testing the desirability of a given source of milk. The differences in reduction time by using glassware boiled in water for 15 min. instead of bacteriologically sterile glassware are of no practical significance.

P. G. MARSHALL.

**Reduction of methylene-blue in milk. The influence of light.** H. R. WHITEHEAD (Biochem. J., 1930, 24, 579—584).—Methylene-blue is reduced by fresh milk, even if previously heated at 100° for 30 min., in a short time in the presence of sunlight at 37°. In darkness at 37° no decoloration occurs within 7 hrs. Milk from which the fat has been removed no longer reduces methylene-blue. The activity can be restored by the addition of sodium oleate, but not of sodium palmitate. Sunlight possibly catalyses an oxidation-reduction reaction in

which unsaturated fats and methylene-blue are involved.

S. S. ZILVA.

**Günzburg's reaction [gastric juice].** F. ERBEN (Biochem. Z., 1930, 220, 227—233).—In the Günzburg reaction, the  $p_H$  is not the only decisive factor causing the condensation of phloroglucinol and vanillin, since, besides the hydrochloric and other mineral acids, oxalic, malic, tartaric, and citric acids all give a positive reaction, whereas lactic and fatty acids give a negative reaction. The reaction as a test for free hydrochloric acid in gastric juice must therefore be used with care.

P. W. CLUTTERBUCK.

**Determination of sugar in urine.** H. SZANCER (Pharm. Zentr., 1930, 71, 321—327).—A review.

W. O. KERMAK.

**Lactose excretion in the puerperium, and isolation of sugars from urine and blood.** L. B. WINTER (J. Physiol., 1930, 69, Proc. viii—ix).—Lactose was isolated from the urine. No lactose was found in the urine obtained before parturition.

E. BOYLAND.

**Detection of acetone derivatives in urine.** P. HORKHEIMER (Pharm. Ztg., 1930, 75, 592—594).—A critical examination of the methods for detection and determination of acetone, acetoacetic acid, and  $\beta$ -hydroxybutyric acid. For diagnosis, the result of a qualitative examination for acetoacetic acid is most valuable, since where much is present acetone and  $\beta$ -hydroxybutyric acid are generally also present. If quantitative examination is necessary, determination of total acetone is recommended, since 90—95% of this is generally to be attributed to acetoacetic acid.

S. I. LEVY.

**Diacetyl and acetylmethylcarbinol in human urine?** H. SCHMALFUSS (Z. physiol. Chem., 1930, 188, 279—280).—Diacetyl and acetylmethylcarbinol (or homologues) were detected in various samples of human urine.

J. H. BIRKINSHAW.

**Substances which produce uræmia.** J. KLEEBERG and W. SCHLAPP (Z. physiol. Chem., 1930, 188, 81—95).—The effect of injection of substances adsorbed from urine by animal charcoal was examined. The adsorbate was recovered by elution with 80—85% alcohol containing 0.5% of hydrogen chloride. The effect of amino-acids and biogenic amine fractions obtained from the extracts and directly from urine was also investigated. Intravenous injection of the adsorbed substances into dogs produced a decrease of 15—60% in blood-pressure and an increase of 20—300% in amplitude. The only exception was in the case of the urine of sufferers from renal disease. The amino-acid and biogenic amine fractions gave indecisive results. Extracts obtained by means of acetic acid and alcohol were active.

Investigation of the blood of hypertonic patients indicated that there is a general parallelism between the guanidine content and the increased blood-pressure, but this does not hold in every case. Increased guanidine is usually accompanied by increased carbamide and uric acid. No definite change in blood-pressure was induced by guanidine injection. Dimethylguanidine was effective with young dogs. Deproteinised blood produced no increase in pressure.

J. H. BIRKINSHAW.

**Enzyme content of the faeces of domesticated animals.** F. W. KRZYWANIEK and BEDI-SCHAKIR (Biochem. Z., 1930, 220, 342—347).—The faeces of the horse, ox, sheep, goat, pig, and dog contain trypsin, erepsin, diastase, lipase, and, sometimes very small amounts of maltase and invertase, but neither pepsin nor nuclease. Lactase is present in the faeces of the pig when 1 month old, but not when 3 months old, and is absent from the faeces of calves 3—12 days old. The amount of enzymes in the faeces of the various animals can be related to the type of food on which they live. W. MCCARTNEY.

**Influence of fibre on nitrogen balance and on fat in human faeces.** J. WHITACRE, A. WILLARD, and K. BLUNT (J. Nutrition, 1929, 2, 187—195).—Diet rich in fibre tends to reduce the utilisation of nitrogen but not of fat; the action of proteolytic enzymes may be affected. CHEMICAL ABSTRACTS.

**Pathological variations of protein osmotic pressure and the protein composition of blood-serum.** C. ACHARD, A. GRIGAUT, and A. CODOUNIS (Bull. Soc. Chim. biol., 1930, 12, 417—440).—The colloidal osmotic pressure of the blood-serum in health and in disease has been measured. Considerable variations are found in pathological conditions, the total concentration of protein in the blood apparently being the most important factor. W. O. KERMACK.

**Globin of animals and of healthy and diseased human beings.** (Dynamic constitution of hæmoglobin.) E. G. SCHENCK (Arch. exp. Path. Pharm., 1930, 150, 160—172).—For preparation of the globin, the erythrocytes are washed several times with isotonic saline and then hæmolyzed by addition of 2 vols. of water. After centrifuging the hæmoglobin solution is run into 10—20 vols. of acetone containing 0.5% of hydrochloric acid. The methæmoglobin first formed decomposes and the globin settles as a white product, which is washed with acetone and further purified by reprecipitation. The globin of fowls' blood gives the strongest tryptophan reaction. Intravenous injection of 0.75 g. of globin proved fatal to a dog weighing 2.75 kg. Crystalline hæmoglobin contains the globin in denatured form. The different amino-acid fractions of the globin vary according to the species, and the synthesis of the globin is found to be partly dependent on the age of the erythrocytes. Abnormal synthesis of hæmoglobin occurs in hyperchromic anæmia. The monoamino-acid-nitrogen of the globin is increased in hypochromic anæmia. P. G. MARSHALL.

**Chemistry of cancer.** P. RONDINI (Giorn. Chim. Ind. Appl., 1930, 12, 163—169).—A lecture.

**Action of radium and X-rays on the fat metabolism of cancer patients.** K. KLAUS (Biochem. Z., 1930, 220, 204—209).—The author's observation (A., 1929, 91) of a considerable hypocholesterolaemia with normal fatty acid content is confirmed for cancer patients. After radium and X-ray treatment the unsaponifiable material and the cholesterol of the serum were increased in all cases, but the latter did not attain normal values. The fatty acids were increased above normal values. P. W. CLUTTERBUCK.

**Influence of arginine on the growth rate of a transplantable tumour in the mouse.** E. GILROY (Biochem. J., 1930, 24, 589—595).—Of the amino- and fatty acids arginine, histidine, glycine, alanine, cystine, cysteine, glutamic acid, and sodium valerate injected subcutaneously at some distance from the site of implantation, the first only exerted a definite effect on the rate of tumour growth. Histidine appeared to increase the percentage of "takes" of implanted "devitalised" tissue, but had no effect on the subsequent rate of growth, whereas arginine had a definitely stimulating effect. S. S. ZILVA.

**Phosphorus content of the blood of hens inoculated with infectious hen (Rous) sarcoma.** E. HAAM and R. STÖHR (Biochem. Z., 1930, 220, 399—419).—When hens are inoculated with the sarcoma the phosphorus quotient (phosphorus pentoxide content of 10 c.c. of blood divided by number of millions of erythrocytes) increases, but the increases are irregular and often they disappear. There is no relation between the course of the disease and the increase of the phosphorus quotient, this increase being a consequence rather than a cause of the formation of tumours. W. MCCARTNEY.

**Oral administration of insulin and diabetes mellitus in children.** M. OTTOW (Münch. med. Woch., 1929, 76, 1584—1585; Chem. Zentr., 1930, i, 245).—A clinical study. A. A. ELDRIDGE.

**Administration of lævulose and lævulose-insulin combinations in severe diabetic acidosis.** O. PUESKO (Münch. med. Woch., 1929, 76, 1755—1757; Chem. Zentr., 1930, i, 245).—A clinical study, with determinations of blood- and urinary sugar. A. A. ELDRIDGE.

**Residual carbon of human blood. II. Effect of insulin on the residual carbon in diabetes.** W. STEFF and J. SAUER (Deut. Arch. klin. Med., 1929, 165, 232—234; Chem. Zentr., 1930, i, 245—246).—In insulin treatment the blood-acetone substances are removed before the blood-sugar has been substantially lowered. A. A. ELDRIDGE.

**Calcium and phosphorus content of blood during the healing of fractures.** K. OHNO (Arch. Japan. Chir., 1929, 6, 1—61; J. Amer. Med. Assoc., 1929, 94, 374).—The serum-calcium is at first unchanged or slightly decreased; it then rises, gradually falling to a normal value during the seventh week. The serum-phosphorus exhibits similar changes. CHEMICAL ABSTRACTS.

**Serum-calcium in jaundice.** A. M. SNELL and C. H. GREENE (Amer. J. Physiol., 1930, 92, 630—638).—With biliary obstruction or with jaundice the calcium content of the blood appears to be very slightly lowered. E. BOYLAND.

**Oxygen capacity of the blood in mental disorders.** D. L. WOODHOUSE and F. A. PICKWORTH (Biochem. J., 1930, 24, 834—849).—In 28 cases out of 100 deficient oxygen capacity has been established. The difference between the active and total hæmoglobin varied from 2.5 to 12.5%. The presence of inactive pigment can in many instances be correlated with positive Widal agglutination reactions to organisms of the enteric group, and these infections



may prove of importance in the etiology of this pigment. A special form of Haldane apparatus yielding greater accuracy and trustworthiness is described; 0.5 c.c. of blood can be used with this apparatus. S. S. ZILVA.

**Lack of relationship between development and cure of rickets and concentration of inorganic phosphorus in the blood.** A. F. HESS, M. WEINSTOCK, H. RIVKIN, and J. GROSS (J. Biol. Chem., 1930, 87, 37—46).—The presence of active rickets may be accompanied by a normal concentration of inorganic phosphorus in the blood. If animals, on a rachitic diet containing milk, having a low concentration of inorganic phosphorus in the blood be treated with minimal amounts of irradiated ergosterol, the phosphorus of the blood may be increased without coincident healing of the rickets; if, on the other hand, the diet be supplemented with cod-liver oil the rickets may be cured while the phosphorus of the blood remains low. Association of rickets with reduction of inorganic phosphorus of the blood is thus by no means universal; the condition of rickets is to be viewed as the combination of a systemic disturbance with a local deficiency at the epiphyses which prevents the fixation of calcium and phosphorus. C. R. HARRINGTON.

**Lipocytic coefficient and resistance to hæmolysis of red blood-corpuscles in the course of experimental scurvy.** L. RANDOIN and A. MICHAUX (Compt. rend., 1930, 190, 1234—1236).—The red blood-corpuscles of the normal guinea-pig contain 0.34% of their dry weight of cholesterol, and 0.72% of fatty acids; the lipocytic coefficient ( $100 \times$  cholesterol/fatty acids) is 42. In the final stages of scurvy the content of fatty acids rises to 1%, and the lipocytic coefficient falls to 30. Simultaneously the range of variation of the resistance to hæmolysis increases. R. K. CALLOW.

**Chemical changes in the blood in experimental sunstroke.** R. SEKIGUCHI (Proc. Imp. Acad. Tokyo, 1930, 6, 183—185).—In rabbits exposed to sunlight until symptoms of sunstroke develop the blood-lactic acid increases threefold and the  $p_H$  is lowered. The carbon dioxide tension decreases considerably, the plasma-chloride remains at the same level, and there is a tendency towards hyperglycæmia. In sunstroke a condition of acidosis is set up. F. O. HOWITT.

**Iodine- and thiocyanate-combining power and lipid content of the serum-protein fractions in syphilis and Basedow's disease.** B. LUSTIG and G. BOTSTIBER (Biochem. Z., 1930, 220, 192—203).—The iodine-combining power of the serum-proteins in exophthalmic goitre is less and in syphilis is greater than normal. The phosphatide content and often the total lipids of the whole blood are increased in luetic sera. In these sera, the chief fraction of lipid, and especially of cholesterol, is combined with pseudoglobulin, whilst in normal serum the amount combined is in the order: with albumin > pseudoglobulin > euglobulin. Thiocyanate mainly combines with the pseudoglobulin fraction. P. W. CLUTTERBUCK.

**Oxidative-reductive power of the tissues.** R. FABRE and H. SIMONNET (Compt. rend., 1930,

190, 1233—1234; cf. A., 1928, 196).—When rabbit's liver is perfused with Ringer's solution containing methylene-blue or cystine, the latter are largely reduced. The same behaviour is shown by minced liver. The reducing substance is not destroyed at 120°, and may be related to the philothion of Rey-Pailhade. R. K. CALLOW.

**Significance of cytochrome in the physiology of cell respiration.** K. SHIBATA and H. TAMURA (Acta Phytochim., 1930, 5, 23—97).—The combination of cytochrome with oxygen is not an oxidation, nor is the removal of oxygen a reduction process. The oxygenated form of cytochrome is a ferrous compound and the oxygen bound is molecular; it functions as hydrogen acceptor in cell oxidation. The oxidation of cytochrome is inhibited by potassium cyanide and enhanced by low temperature. Cytochrome loses its power of fixing oxygen on boiling, drying, acetone treatment, etc., denatured hæmochromogen or hæmatinderivatives of the cytochrome being formed. The oxidation of these derivatives is not inhibited by potassium cyanide and they cannot be reconverted into cytochrome.

Cytochrome appears to be unnecessary for plants which grow aerobically, e.g., moulds; it is indispensable for submerged organisms. Since the velocity of oxidation of cytochrome is high, the rate is almost independent of the oxygen tension for yeasts; with the moulds it is otherwise. The respiration of moulds is not inhibited by carbon monoxide. From *Lactarius* a typical oxidase producing indophenol was isolated. This enzyme is inhibited by hydrogen sulphide, hydrogen cyanide, and acetone treatment, by warming to 70° or cooling to 0°, but not by carbon monoxide. Warburg's respiratory enzyme is probably cytochrome. J. H. BIRKINSHAW.

**Influence of "omega" and of benzoquinone on tissue respiration.** B. KISCH and J. LEIBOWITZ (Biochem. Z., 1930, 220, 97—116).—The respiration of kidney tissue, investigated by Warburg's method, was found in many animals (rats, guinea-pigs, rabbits, cats, and dogs) to give higher values for the female than for the male. Rats, guinea-pigs, and rabbits gave small, dogs, cats, and hares large variations of respiration. Using the medium at  $p_H$  7.4, the kidney respiration was in the order: rat > guinea-pig > hare > rabbit > dog > cat. An optimum respiration was obtained with rats and dogs at  $p_H$  7.1—7.4, with cats at  $p_H$  7.4, and with rabbits and hares at  $p_H$  7.7—8.1. Fresh adrenaline in concentrations of  $10^{-4}$  to  $10^{-14}$  had no effect when added to the medium. "Omega" (the autocatalysing oxidation product of adrenaline) added to the medium in concentrations  $10^{-4}$  to  $10^{-10}$  increased respiration considerably (up to 60%). Freshly-prepared *o*- and *p*-benzoquinone solutions inhibited respiration in high concentrations ( $10^{-4}$  to  $10^{-5}$ ), but increased it considerably in low concentrations ( $10^{-6}$  to  $10^{-11}$ ), whereas solutions of pyrocatechol and quinol of the same concentration were without effect. Solutions of "omega" and of benzoquinone lost their activity on keeping in presence of oxygen, especially in light. P. W. CLUTTERBUCK.

**Effect of carbon dioxide on nerve,** H. NECHELES and R. W. GERARD (Amer. J. Physiol., 1930, 93,

318—336).—Exposure to carbon dioxide may increase the action potential as much as fivefold, except in absence of oxygen, when the responses fall to zero in a few hours. On admitting oxygen the potential may be even more increased. The effect appears to vary with the rate of bubbling carbon dioxide through the chamber. Carbon dioxide increases the refractory period and reduces the chronaxic of nerve. The results are interpreted as causing a delay in the oxidative recovery of nerve. E. BOYLAND.

**Nerve metabolism. VI. Carbohydrate metabolism of active nerve.** E. G. HOLMES, R. W. GERARD, and E. I. SOLOMON (Amer. J. Physiol., 1930, 93, 342—352).—Frog nerves stimulated for periods of 3—9 hrs. in oxygen contain the same amounts of lactic acid, carbohydrate, and glycogen as similar resting nerves. The extra energy of the metabolism must be derived from some other source.

E. BOYLAND.

**Carbon dioxide dissociation curve of frog heart-muscle.** H. BRODY (Amer. J. Physiol., 1930, 93, 190—196).—Frog heart-muscle combines with only about two thirds as much carbon dioxide as does frog skeletal muscle.

E. BOYLAND.

**Effect of anaërobiosis on the oxygen consumption of muscles.** W. O. FENN (Amer. J. Physiol., 1930, 93, 124—137).—The non-irritability of unwashed muscle is accompanied by a very high oxygen consumption, but the normal irritability of muscle survives well in nitrogen. Minced muscle may have a high oxygen consumption which falls rapidly. Occasionally the oxygen consumption of unwashed muscles rises to four or five times that of washed muscle and the muscle is then found to be permanently non-irritable. Washing with Ringer solution may cause a decrease of oxygen consumption in addition to recovery of irritability. The shortening of muscle which occurs in anaërobiosis is accompanied by increase in oxygen consumption, and this may be concerned with rigor mortis.

E. BOYLAND.

**Biochemistry of the blood in neuromuscular fatigue.** A. K. PICKAT (Zhur. exp. Biol. Med., 1929, 12, 125—133).—Muscular work causes in rabbits a large rise in blood-sugar, even after insulinisation. In guinea-pigs fatigue is accompanied by hypoglycaemia following brief hyperglycaemia.

CHEMICAL ABSTRACTS.

**Alterations in lactic acid content of blood as a result of light exercise, and associated changes in the carbon dioxide combining power and alveolar carbon dioxide pressure.** W. H. OWLES (J. Physiol., 1930, 69, 214—237).—There is a critical metabolic level below which the blood-lactic acid does not increase with exercise, although the inorganic phosphate of the blood may increase. With more strenuous exercise in which the lactic acid of the blood increases the carbon dioxide combining power decreases. After the cessation of light exercise the carbon dioxide pressure of the alveolar air falls below the normal resting level.

E. BOYLAND.

**Chemistry of muscular hypertrophy and atrophy. I. Tension and relaxation of skeletal muscle.** H. WASSERMEYER and A. ROHRBACH

(Arch. exp. Path. Pharm., 1930, 150, 133—145).—Light extension of rabbit's quadriceps and sartorius muscles for 8—14 days produces an increase in weight of 10—25%. For the determinations of glycogen, ammonia, and phosphocreatine (phosphagen) the muscle is frozen in liquid air and finely powdered. Light stretching produces an immediate decrease in ammonia content, which returns almost to normal in about 2 hrs. Overstretching produces a loss in weight and an immediate increase in ammonia content. The glycogen content is not appreciably altered in light extension, but shows an average rise of 60—80% during recovery. The lactic acid content decreases during the recovery process to very variable extents.

P. G. MARSHALL.

**Chemistry of muscular hypertrophy and atrophy. II. Contraction and tension.** H. WASSERMEYER and K. DUTTE (Arch. exp. Path. Pharm., 1930, 150, 316—325).—Lactic acid is found in higher concentrations in human blood after a muscle has been fatigued by contraction than after it has been fatigued by being kept in strong tension.

W. O. KERMAK.

**Comparative rates of absorption of sugars from the human intestine.** R. A. McCANCE and K. MADDERS (Biochem. J., 1930, 24, 795—804).—The curves of excretion of rhamnose, arabinose, and xylose when injected intravenously in man are superimposable. In men and in rats if the rate of absorption of rhamnose=1 those of arabinose and xylose are 2.33 and 3.6, respectively. These sugars are all absorbed at the same level in the intestine and this level is high up in the small intestine. Lower down little or no absorption takes place. In normal man absorption of these sugars proceeds rapidly and at a linear rate for 1½ hrs. and then almost ceases even when large excess still remains in the intestine.

S. S. ZILVA.

**Intestinal absorption. I. Absorption of lactic acid.** G. T. CORI. **II. Absorption of ethyl alcohol.** C. F. CORI, E. L. VILLIAUME, and G. T. CORI (J. Biol. Chem., 1930, 87, 13—18, 19—25).—I. The rate of absorption of lactic acid from the intestine of rats at any time during a 4-hr. period after administration of sodium *dl*-lactate by stomach tube was approximately proportional to the concentration of lactic acid in the intestine, which, in turn, was kept low in some cases by slow emptying of the stomach. The absorption of lactic acid thus differs from that of amino-acids and of dextrose. Administration of mixtures of lactic acid and dextrose results in slower absorption of both constituents than when either is given alone.

**II.** The absorption of alcohol in rats is proportional to the rate at which it enters the intestine and hence to the amount given for solutions up to 20% concentration. Higher concentrations cause partial paralysis of the stomach, and the rate of absorption (in the resting condition) is diminished. After administration of alcohol the intestine retains a residual amount (12—56 mg.) which is independent of the amount administered, and disappears slowly. No accelerating effect of alcohol on the absorption of dextrose was observed (cf. Edkins and Murray, A., 1928, 1399).

C. R. HARRINGTON.

**Citric acid in urine: its origin.** H. FASOLD (Z. Biol., 1930, 90, 192—198).—The presence of citric acid in the ethereal extract of the organic acids of urine is detected by Denigès' reaction. The citric acid may be determined as pentabromoacetone by the method of Amberg and McClure (A., 1918, i, 141).

The urines of six children fed on a mixed or vegetarian diet contained almost equal amounts of citric acid, whereas when three of the subjects were put on a meat diet no precipitate of pentabromoacetone was obtained.

C. C. N. VASS.

**Conversion of pyruvic acid into lactic acid in the liver.** (MME.) Y. K. HOUVINE, E. AUBEL, and L. CHEVILLARD (Compt. rend., 1930, 190, 1243—1244; cf. this vol., 245).—The previous experiments have been repeated under aerobic conditions. An increased consumption of oxygen is observed under the influence of pyruvate. With an excess of pyruvate the lactic acid:carbon dioxide ratio is 1.97:1. The carbon dioxide is not diminished proportionately as the pyruvate decreases. The mechanism previously suggested is still possible on the assumption that the hydrogen liberated from dextrose is consumed by oxygen or compounds in the liver which are oxygenated under aerobic conditions.

R. K. CALLOW.

**$\beta$ -Oxidation of propionic acid. Formation of malonic acid.** L. KLING (Biochem. Z., 1930, 220, 117—121).—The oxidation of propionic acid with hydrogen peroxide in sulphuric acid solution in presence of an iron salt is followed quantitatively. The acid (9.45 g.) gave 2.63 g. of acetaldehyde, 2.7 g. of acetic acid, 0.425 g. of formic acid, 0.177 g. of malonic acid, and 6.9 g. of carbon dioxide, thus accounting for the whole of the carbon present. The formation of malonic acid is regarded as further evidence in support of the theory of  $\beta$ -oxidation.

P. W. CLUTTERBUCK.

**Influence of lecithin on carbohydrate metabolism.** G. IZAR and S. CONSTANTINO (Klin. Woch., 1929, 8, 1624; Chem. Zentr., 1929, ii, 2793).—The subcutaneous injection of 10 c.c. of "bioplastina," an emulsion of lecithin, lutein, and cholesteryl ester in physiological salt solution, brings about a constant increase in the blood-sugar of adults; this reaches a maximum 1—2 hrs. after injection and returns to normal after 5 hrs.

L. S. THEOBALD.

**Synthesis of cholesterol in the animal body.** H. DAM (Biochem. Z., 1930, 220, 158—163).—The cholesterol fraction of the egg and of the food supplied after hatching is not sufficient to account for the amount of cholesterol found in the 59-day-old chick. The sterol of the faeces consists chiefly of cholesterol.

P. W. CLUTTERBUCK.

**Distribution of ingested ergosterol in animal organs.** I. H. PAGE (Biochem. Z., 1930, 220, 420—431).—Solvents which contain chlorine and halogeno-acetic acids are the most favourable reagents for the production of colour in Rosenheim's colour test for ergosterol (A., 1929, 359), and for quantitative work dichloroethylene and trichloroacetic acid are most suitable. By means of the colour test the ergosterol content of the suprarenal capsules, brains, livers, muscles, spleens, kidneys, bones, lungs, hearts, testes, aorta, and lens of the eyes of rabbits which had

received over-doses of irradiated ergosterol for 36—164 days was determined. The sterol is stored chiefly in the three first-named organs. Spectrographic examination of extracts of rabbit brains showed that there is very probably more of the sterol in those of animals to which ergosterol had been fed than in those of others.

W. MCCARTNEY.

**Fat absorption by desaturation of fatty acids.** H. TANGL and N. BEREND (Biochem. Z., 1930, 220, 234—238).—Fat is converted in the small intestine by desaturation into water-soluble compounds which are dialysable and can then be absorbed.

P. W. CLUTTERBUCK.

**Factors influencing distribution and character of adipose tissue in the rat.** I. Influence of diet, weight, and sex on distribution of fat. F. YAMAGUCHI, W. E. ANDERSON, and L. B. MENDEL. II. Influence of diet, under-nutrition, fasting, and activity on distribution and character of fat. L. L. REED, W. E. ANDERSON, and L. B. MENDEL (J. Biol. Chem., 1930, 87, 147—155, 156—174).—I. Larger amounts of fat were stored by rats on a diet rich in fat than on one rich in carbohydrate, but the distribution of the fat was not affected by the diet. The proportion of subcutaneous fat was greatest in young rats; male rats deposited relatively large amounts of perirenal fat and females correspondingly large amounts in the genital fat depot. A general increase in the proportion of fat to body-weight was observed with increasing size of the rats.

II. Figures are given for the average distribution of fat in the female rat of 180 g. weight; the observation that this distribution is independent of the nature of the diet is confirmed. An increase in the proportion of intermuscular fat was observed in rats during periods of forced activity and of nocturnal activity; forced activity and under-nutrition brought about diminution in the genital fat of the rats on a carbohydrate diet. The differences in the iodine values of the fat of the various depots were small, but the iodine value of the stored fat as a whole was influenced by that of the food-fat.

C. R. HARINGTON.

**Protein ration and energy ration.** S. VISCO (Atti R. Accad. Lincei, 1930, [vi], 11, 522—527).—When supplied with a diet deficient in protein, rats lose weight and finally die, no matter what the amount of energy ration consumed. Hence, physiological and economic utilisation of the ternary substances absorbed is possible only with organisms satisfied as regards their need of protein.

T. H. POPE.

**Influence of nutrition on response to amino-acids.** II. Effect of fasting followed by diets high in carbohydrates. C. M. WILHELMJ and F. C. MANN (Amer. J. Physiol., 1930, 93, 258—266).—A high-carbohydrate diet fed to dogs which have been starved for 7 days causes a reduction of the specific dynamic action of intravenously injected amino-acids; it also increases the respiratory quotient measured after the injection of the amino-acids, although the total oxygen consumption is reduced. The toxic effect of intravenously injected glycine or alanine was also diminished by this diet.

E. BOYLAND.

**Rate of absorption of cystine from the gastrointestinal tract of the white rat.** R. H. WILSON (J. Biol. Chem., 1930, 87, 175—180).—Cystine was administered orally to rats after a fasting period of 24 hrs.; after 2 hrs. the contents of the stomach and intestines were analysed for residual cystine. After administration as the sodium salt, cystine was absorbed at an average maximum rate of 30.5 mg. per 100 g. body-weight per hr. After administration as the hydrochloride, absorption was slower. Cystine is thus less readily absorbed than any amino-acid hitherto studied. C. R. HARRINGTON.

**Origin of creatine and creatinine in the animal organism.** E. ABDERHALDEN and S. BUADZE (Z. physiol. Chem., 1930, 189, 65—79).—The feeding of considerable amounts of nucleic acid and histidine to dogs produces an increase in the total creatinine in the urine. Schumann (this vol., 243) found a similar increase after feeding nucleic acid, but not after histidine. His hypothesis that the increase is due to indirect action is rejected. The amount of histidine fed by Schumann was too small to give a positive result. J. H. BIRKINSHAW.

**High content of non-protein-nitrogen in insects.** A. COURTOIS (Compt. rend., 1930, 190, 1237—1239; cf. A., 1928, 437, 917).—The non-protein-nitrogen, which may reach 0.9% of the fresh tissue, has been determined in a number of insects, and the variation of the ratio of non-protein- to total nitrogen (18—36) in the stages of metamorphosis has been followed. In the chrysalis or nymph the ratio increases slowly as the proteins are demolished, and then falls fairly rapidly to nearly the original value during the more rapid process of building up the tissues of the imago. R. K. CALLOW.

**Changes of plasma-colloids at the stimulation of development of the sea-urchin egg.** J. RUNNSTRÖM (Protoplasma, 1929, 4, 388—514).

CHEMICAL ABSTRACTS.

**Metabolism of developing salmon eggs. I. Significance of hatching and rôle of water in development. II. Chemical changes during development.** F. R. HAYES (Biochem. J., 24, 723—734, 735—745).—I. The wet weight of a salmon egg increases slowly until a short time before hatching, then rapidly. In the larva the wet weight first increases and then decreases. The dry weight decreases rapidly after hatching. The enzyme which dissolves the shell has a very unfavourable effect on the embryo.

II. In the developing salmon the protein decreases in the earlier egg stages and increases before hatching. Embryonic protein contains 15.7 and yolk-protein 12.8% N. The fat content rises to two peaks, the first 10 days before hatching and the second 6 weeks after. The decreases after the maxima probably show a change from protein to fat as a source of energy. Variations in oxygen consumption indicate that metabolic processes drop to a low ebb before hatching and greatly increase in the free-swimming larva.

S. S. ZILVA.

**Embryochemical investigations with the injection method. IV. Glutathione formation in the organism of the hen's embryo.** J. SAGARA.

(Z. physiol. Chim., 1930, 188, 124—126; cf. this vol., 638).—Glutamic acid and taurine injected into hen's eggs increase the sulphydryl content (Tunncliffe's method for glutathione) after incubation. This is especially marked in the later stages of incubation.

J. H. BIRKINSHAW.

**Behaviour of the inorganic constituents on incubation of hen's eggs.** T. ISEKI (Z. physiol. Chem., 1930, 188, 189—192).—In the later stages of incubation of hen's eggs the calcium increases considerably in the egg contents, whilst that of the shell decreases. The shell-calcium is used to build up the embryo. The alkali chlorides and sulphates migrate from the white to the yolk during incubation and are then transferred to the embryo.

J. H. BIRKINSHAW.

**Distribution of blood-calcium in the circulation of laying hens.** G. D. BUCKNER, J. H. MARTIN, and F. E. HULL (Amer. J. Physiol., 1930, 93, 86—89).—The calcium content of the serum of a moulting hen was 11.2 mg. per 100 c.c., whilst that of laying hens was 22.4 mg. per 100 c.c. The blood going to the intestine had slightly less calcium than that coming from the intestine. E. BOYLAND.

**Metabolism of women. IV. Calcium and inorganic phosphorus in the blood of women at various stages of the monthly cycle.** R. OKEY, J. M. STEWART, and M. L. GREENWOOD (J. Biol. Chem., 1930, 87, 91—102).—Variations in the calcium of the blood-serum from day to day are more pronounced in women than in men. The calcium of women's blood is lowest in amount immediately before menstruation, and highest about 15 days after the commencement of menstruation. Generally similar, but less consistent changes were observed in the inorganic phosphorus of the blood-serum.

C. R. HARRINGTON.

**Definition and action of complex heavy metal compounds.** H. WEDEN (Arch. exp. Path. Pharm., 1930, 150, 332—353).—Observations have been made on the ability of various compounds, including various carboxylic acids, hydroxy-acids, alcohols, protein, peptone, and certain inorganic acids, to form complex compounds with ferrous and ferric ions, the effect of the compounds being observed on the precipitability of the metallic ions by hydroxyl, sulphide, and phosphate ions and by protein.

W. O. KERMAK.

**Fate of iron in the organism after administration of complex compounds containing iron organically and inorganically bound.** E. STAR-KESTEIN and H. WEDEN (Arch. exp. Path. Pharm., 1930, 150, 354—380).—The iron was determined in the blood and various organs of an animal killed after the administration of iron united to various compounds (see preceding abstract). The iron present in the ferric and ferrous states was also determined. In the case of sodium ferricitrate, ferrigluconate, and ferrocyanide the iron is rapidly excreted by the kidneys. The iron stored in the liver is in all cases present in a reduced form, insoluble in water, extractable only with hydrochloric acid. Only compounds containing iron in an anionic complex appear to exert an influence on the organism. The

ferrous iron compounds are oxidised in the blood, yielding complexes of ferric iron with protein.

W. O. KERMACK.

**Variation with age of the zinc content of animals. Influence of a milk diet.** G. BERTRAND and Y. BEAUZEMONT (Compt. rend., 1930, 190, 1089—1092).—Contrary to the results of Thompson, Marsh, and Drinker (A., 1927, 482) the zinc content of the rat, like that of the mouse and rabbit (A., 1921, i, 907), is highest at birth, decreases during suckling, but rises rapidly after weaning to an almost constant value of 3.5 mg. per 100 g. of tissue.

C. C. N. VASS.

**Comparative action of 5 and 10% carbon dioxide mixtures as respiratory stimulants in carbon monoxide poisoning.** D. P. MURPHY and C. K. DRINKER (J. Ind. Hygiene, 1930, 12, 92—98).—In the early stages of asphyxia, a 10% carbon dioxide mixture is more effective in stimulating lung ventilation than a 5% mixture. In acute asphyxia the use of such inhalation mixtures should be preceded by artificial respiration.

P. G. MARSHALL.

**Influence of mineral material on sugar metabolism.** E. STRANSKY (Biochem. Z., 1930, 221, 74—100).—In oxalate poisoning with lethal doses no change in the calcium content and calcium:magnesium ratio in rat's liver could be detected. In acute oxalate and fluoride poisoning, adrenaline hyperglycaemia is increased, fluoride having the greater effect. This lengthening of adrenaline hyperglycaemia is caused by an inhibition of glycolysis. The cations sodium, calcium, and ammonium and the anions chloride, sulphate, phosphate, citrate, and acetate have no influence on adrenaline hyperglycaemia and fasting blood-sugar. The action of insulin is not influenced by oxalate. Potassium often causes an increase of adrenaline hyperglycaemia, but does not inhibit blood glycolysis. "Parathormone" and "vigantol" do not affect adrenaline hyperglycaemia. Green food reduces sugar tolerance. Rabbits on green food show a greater adrenaline hyperglycaemia than when fed on oats.

P. W. CLUTTERBUCK.

**Influence of sympathetic nerves on muscle-glycogen.** S. W. BRITTON (Amer. J. Physiol., 1930, 93, 213—218).—Sympathectomy lowers the muscle-glycogen of cats. Regrowth of the thoracic sympathetic nerves was accompanied by a large increase in the muscle-glycogen of the fore-limbs.

E. BOYLAND.

**Chemical factors in ventricular fibrillation.** D. R. HOOKER (Amer. J. Physiol., 1930, 92, 639—647).—Change of concentration of hydrogen carbonate or calcium in the perfusing fluid may cause fibrillation.

E. BOYLAND.

**Blood-calcium in relation to sympathetic activity.** J. LAMELAS (Amer. J. Physiol., 1930, 93, 111—115).—Sympathectomy, section of splanchnic nerves, and injection of adrenaline had no effect on the blood-calcium of cats in amytal anaesthesia.

E. BOYLAND.

**Action of magnesium salts.** W. ZÖRKEN-DÖRFER (Biochem. Z., 1930, 221, 33—41).—The biological action of magnesium salts is explained in

terms of their tendency to form complex compounds. By electrometric titration, it is shown that in aqueous solution complex compounds are formed between magnesium salts and amino-acids. In presence of magnesium salts, insoluble calcium salts dissolve in water in considerable amounts, the calcium forming part of the complex ion.

P. W. CLUTTERBUCK.

**Influence of strontium salts on the movements of *Paramoecium caudatum*.** The rôle of calcium salts and of hydrogen-ion concentration. E. EISENBERG-HAMBURG (Acta Biol. Exp., Warsaw, 1930, 4, 261—277).—*P. caudatum* placed in dilute strontium chloride solutions executes rhythmic movements; this reaction increases as the concentration of salt rises from 0.000987 to 0.003912%, again falling at higher, toxic concentrations, and persists in sub-toxic concentrations during the entire duration of life of the infusoria. At a given concentration of strontium chloride the reaction is greater in acid or alkaline than in neutral solutions. A similar, although feebler reaction is given by dilute barium, rubidium, and caesium salts, but not by magnesium, calcium, sodium, potassium, and ferric chlorides, or by cadmium nitrate. The addition of calcium chloride abolishes the above reaction in strontium and barium solutions. A similar reaction is given also by *Colpidium*, *Stentor*, and *Spirostomum*.

R. TRUSZKOWSKI.

**Colloid chemistry of antiseptics and chemotherapy. III. Ultramicroscopic examination of neoarsphenamine and of certain antiseptics and their effects on protein solutions.** A. D. HIRSCHFELDER and H. N. WRIGHT (J. Pharm. Exp. Ther., 1930, 39, 13—37).—In aqueous solution acriflavine, rivanol, mercurochrome, and neoarsphenamine exist partly at least in a colloidal form, discrete particles being visible under the ultramicroscope. The triphenylmethane dyes, quinine, derivatives of hydrocoupreine, and "metaphen" appear to form ordinary crystalloidal solutions in water. Ultramicroscopic observations have been made on mixtures of these chemotherapeutic reagents with protein solutions, and the bearing on anaphylactoid and febrile reactions is discussed.

W. O. KERMACK.

**Colloid chemistry of antiseptics and chemotherapy. IV. Duplication *in vitro* of the interference phenomenon in combination chemotherapy.** H. N. WRIGHT and A. D. HIRSCHFELDER (J. Pharm. Exp. Ther., 1930, 39, 39—57).—The production of carbon dioxide by yeast in presence of various concentrations of acriflavine, basic fuchsin, brilliant-green, and methyl-violet has been investigated. Increasing concentrations of these dyes progressively depress the rate of production of carbon dioxide. This depressing action of one dye, e.g., methyl-violet, may be inhibited by suitable low concentrations of another dye, e.g., acriflavine. This mutual inhibition of toxic activity by two dyes is probably analogous to the interference phenomenon described by Browning and Gulbransen (J. Path. Bact., 1922, 395) and by Schnitzer in relation to chemotherapy. Certain pairs of dyes, e.g., acriflavine and basic fuchsin, do not exhibit the phenomenon with yeast.

W. O. KERMACK.

**Protective action of "Bayer 205" on proteins.** O. JIROVEC and V. KOCIAN (Biochem. Z., 1930, 220, 27—40).—Ovalbumin, serum-albumin, caseinogen, peptone, and "somatose" are protected by Bayer 205 (germanin) against precipitation by tannin and mercuric chloride. In acid solution the results are reversed, the reagent itself precipitating protein. Heat-coagulation of albumin is also inhibited by a sufficient concentration of "Bayer 205." The protective action of the substance against precipitation by heavy metal salts decreases with rise of temperature. Protective action against heat coagulation holds for the sera of both vertebrates and invertebrates. Thus centrifuged crab's blood mixed with an equal volume of 1% "Bayer 205" is not coagulated by heat.

P. W. CLUTTERBUCK.

**Toxicity of sodium salt of tetraiodophenolphthalein.** J. B. GOSÉ (Anal. Fis. Quim., 1930, 28, 281—289).—The average lethal dose of six samples injected intravenously into mice varied from 0.37 to 0.27 mg. per g. of body-weight. H. F. GILLBE.

**Detection of hexamethylenetetramine in the cerebrospinal fluid.** G. JUNG and K. VOIT (Münch. med. Woch., 1929, 76, 1511—1513; Chem. Zentr., 1929, ii, 2792).—The amounts of hexamethylenetetramine carried into the cerebrospinal fluid after oral and intravenous injection are extremely small and only by intravenous injection of large quantities could hexamethylenetetramine be regularly detected.

L. S. THEOBALD.

**Nephropathogenic action of cystine. II. Dietary control of cystine nephrosis.** G. J. COX and L. HUDSON (J. Nutrition, 1930, 2, 271—276).—Osborne and Wakeman's vitamin-B concentrate of yeast is preventive. The protective substance of yeast is probably distinct from known accessory food factors.

CHEMICAL ABSTRACTS.

**Chemical nature of allergic substances. IV.** L. F. LOEB (Biochem. Z., 1930, 220, 432—444; cf. A., 1929, 348).—Guinea-pigs can be sensitised against precipitates obtained from extract of goose-feathers with ammonium sulphate solutions of various concentrations. The active principle of pollen from *Dactylis glomerata* can be precipitated by alcohol and by ammonium sulphate. The precipitates and those similarly obtained from other pollens give positive protein reactions. The filtrates from alcohol precipitations are inactive. It is concluded that the active principle of allergic substances from pollen is either a protein or is combined with a protein.

W. MCCARTNEY.

**Action of iodoacetic acid on metabolic hydrolysis and oxidations.** E. LUNDSGAARD (Biochem. Z., 1930, 220, 8—18).—The utilisation of oxygen, the production of carbon dioxide aerobically and in hydrogen, the respiratory quotient, and the aerobic utilisation of sugar by normal yeast and yeast poisoned by addition of varying amounts of iodoacetic acid and also the oxygen utilisation of frogs before and after iodoacetic acid poisoning are investigated. In presence of this acid, oxidative processes are able to proceed after glycolysis is completely inhibited.

P. W. CLUTTERBUCK.

**Correlation of constitution with sweet taste in the furan series.** H. GILMAN and A. P. HEWLETT (Iowa State Coll. J. Sci., 1929, 4, No. 1, 27—33).—A record of the comparative sweetness of a number of furan derivatives. Generalisations are not made.

CHEMICAL ABSTRACTS.

**Pharmacology of the acid oxidation products of cholesterol and ergosterol.** H. SEEL (Arch. exp. Path. Pharm., 1930, 150, 198—220).—The toxicity of the following oxidation products of cholesterol is reported: a ketodicarboxylic acid  $C_{27}H_{42}O_5$ , an acid  $C_{27}H_{44}O_5$ , a tetracarboxylic acid  $C_{27}H_{44}O_8$ , a ketomonocarboxylic acid  $C_{26}H_{44}O_3$ , an acid  $C_{27}H_{40}O_5$ , a dicarboxylic acid  $C_{27}H_{44}O_4$ , a hydroxydicarboxylic acid  $C_{27}H_{46}O_5$ , and a chlorodicarboxylic acid  $C_{27}H_{45}O_4Cl$ . The most toxic derivative is the substance  $C_{27}H_{45}O_4Cl$ , whilst the substance  $C_{26}H_{44}O_3$  is the least toxic. Total hæmolysis of erythrocytes is produced by concentrations varying from 1:2000 to 1:200,000, the animal membrane being permeable to these acid derivatives. Irradiation of cholesterol or ergosterol in presence of oxygen gives rise to products which are in every way similar (as regards lethal dose in mice etc.) to those oxidation products which are produced by chemical means and are soluble in water.

P. G. MARSHALL.

**Effect of administration of ergosteryl acetate to rabbits.** I. H. PAGE and W. MENSCHICK (Biochem. Z., 1930, 221, 6—10).—Ergosteryl acetate fed in moderately large doses to rabbits is easily absorbed, has no toxic action, and the urine contains no ergosterol. The light-absorption curves of the brain-sterols show a greater storage of ergosterol than in feeding experiments with partly irradiated ergosterol.

P. W. CLUTTERBUCK.

**Toxicological investigation of some barbituric acid derivatives and their post-mortem transformation into thiocyanic acid.** G. VITTE (Bull. Soc. Chim. biol., 1930, 12, 524—531).—Methods for the detection of veronal and other barbituric acid derivatives in body-fluids and tissues are described. The presence of isothiocyanic acid in the blood and organs after veronal poisoning has been verified.

W. O. KERMACK.

**Pharmacological action of various aromatic-aliphatic lactones. II. Chemical constitution and pharmacological action.** W. F. VON OETTINGEN (J. Pharm. Exp. Ther., 1930, 39, 59—69).—The condensation products of  $\Delta^2$ -angelicalactone with resorcyllaldehyde, salicylaldehyde, anisaldehyde, vanillin, and piperonal exhibit a depressant action, increasing in the order given, on muscular and nervous tissue and are toxic to earth-worms.

W. O. KERMACK.

**Pharmacology of 23 isomeric octyl alcohols.** D. I. MACHT and H. P. LEACH (J. Pharm. Exp. Ther., 1930, 39, 71—97).—The pharmacological actions of 23 isomeric octyl alcohols have been studied on various animals and on *Lupinus albus*. No general conclusion can be reached with regard to their relative toxicity, as this differs according to the object used, but it appears that, subject to many exceptions, the primary alcohols are more active



pharmacologically than the secondary and the latter more than the tertiary. When two or more isomeric alcohols are applied simultaneously, synergistic effects are often observed.

W. O. KERMACK.

**Action of the parotid gland secretion of *Bufo regularis*.** D. EPSTEIN and J. W. C. GUNN (J. Pharm. Exp. Ther., 1930, 39, 1—11).—In the parotid secretion of the African toad *Bufo regularis*, there are probably two active principles, one possessing a digitalis-like action and the other similar to or identical with adrenaline.

W. O. KERMACK.

**Heart tonics. III. Relationships of calcium ions, hydrogen ions, and digitalis.** W. NYIRI and L. DUBOIS (J. Pharm. Exp. Ther., 1930, 39, 111—128).—The actions on the frog's heart of ouabain and digitalis on the one hand and of calcium ions on the other, although similar, are not essentially related or interdependent, the action of ouabain or digitalis occurring in the absence of calcium ions. The action of digitalis on the heart is not influenced by variation of the  $p_H$  from 5.2 to 7.6.

W. O. KERMACK.

**Action of Japan camphor on the heart. III.** K. TAMURA, G. KIHARA, and M. ISHIDATE (Proc. Imp. Acad. Tokyo, 1930, 6, 175—178).—Camphor itself does not exert any stimulating action on the isolated frog and rabbit heart. Only 6-ketocamphor amongst the common oxidation products of camphor has such an action, this being due to the presence of an optical isomeride (m. p. 200—201°,  $[\alpha]_D^{25} +81.6^\circ$ ) of the 6-ketocamphor of Bredt (A., 1924, i, 408), obtained by mild oxidation of 6-hydroxycamphor. The isomeride has a powerful cardiotonic action, whilst Bredt's substance is inactive. Camphor when absorbed in the body is excreted through the kidneys as 6- and 2-hydroxycamphorglycuronic acids.

F. O. HOWITT.

**Effect of surface tension on the activity of cinchona alkaloids.** R. N. CHOPRA and S. G. CHOUDHURY (Indian J. Med. Res., 1929, 17, 360—365).—The enhanced activity of cinchona alkaloids on the alkaline side is correlated with the decrease in surface tension of quinine solutions on the alkaline side.

CHEMICAL ABSTRACTS.

**Influence of light rays on the total cholesterol content of the skin.** S. KAWAGUCHI (Biochem. Z., 1930, 221, 232—240).—The total cholesterol contents of the skins of guinea-pigs of the same age and size are the same within narrow limits, but the cholesterol is not evenly distributed, the ventral surface containing more cholesterol than the dorsal. Intensive irradiation with sunlight increases considerably, and with ultra-violet rays not so greatly, the cholesterol content of the skin, but X-rays have no effect. The increase in cholesterol takes place, not only on the irradiated (dorsal) surface, but also on the non-irradiated (ventral). Histamine also appears in increased amounts during the irradiation of the skin.

P. W. CLUTTERBUCK.

**Behaviour of the total cholesterol of the blood.** S. KAWAGUCHI (Biochem. Z., 1930, 221, 241—246).—The blood-cholesterol of normal rabbits varies between 50 and 80 mg./100 c.c., the value being increased by three times in pregnancy and immediately after

parturition. Ligature of the pancreatic duct in 50% of cases caused decrease of cholesterol in the liver and increase in the blood, the increase being obtained chiefly in the red blood-corpuscles. Acetylcholine and adrenaline (both in small and large doses, 0.2—1.0 mg./kg.) are without action on the cholesterol content of blood.

P. W. CLUTTERBUCK.

**Magnesium content of irradiated rats.** J. S. McHARGUE and W. R. ROY (Amer. J. Physiol., 1930, 92, 651—655).—Irradiation with ultra-violet light caused a large decrease in the total magnesium content of rats, in addition to a slight increase in the total body-weight.

E. BOYLAND.

**Effect of radium rays on the carbohydrate content of the tissues.** A. KRONTOVSKI (Klin. Woch., 1929, 8, 1578; Chem. Zentr., 1929, ii, 2793).—Radium rays bring about significant changes in the carbohydrate content of the tissues. Exposure for 3—6 hrs. brought about a marked decrease in sugar consumption in certain tissues of rats and mice.

L. S. THEOBALD.

**Action of X-rays on tissue cultures *in vitro*.** L. DOLJANSKI, J. J. TRILLAT, and DU NOUY (Compt. rend., 1930, 190, 1147—1150).—The lethal dose for a pure culture of fibroblasts is reached after 5 min. exposure at 4 cm. from the copper anti-cathode ( $\lambda$  1.54 Å.) working at 28 kilowatts with a current of 30 milliamp. The destructive action of the X-rays is chiefly confined to the tissue and not to the medium.

C. C. N. VASS.

**Recent advances in the chemistry of enzymes.** R. H. HOPKINS (J. Inst. Brew., 1930, 36, 189—194).

**Inactivation of catalase by ultra-violet irradiation at different  $p_H$ .** S. MORGULIS (Biochem. Z., 1930, 221, 29—32).—The decrease of activity of catalase during irradiation is directly proportional to the time only at  $p_H$  6, 7, and 8. From  $p_H$  5.0 to 3.5 the inactivation is initially greater, but the loss in activity decreases in the later stages. This behaviour is even more pronounced at  $p_H$  9, 10, and 11 when the curves fall steeply only during the first few minutes of irradiation and then fall only very gradually.

P. W. CLUTTERBUCK.

**The two components of malt diastase, especially with regard to the mutarotation of the products formed in the hydrolysis of starch.** E. OHLSSON (Z. physiol. Chem., 1930, 189, 17—63).—Malt amylase is a mixture of two enzymes which are named dextrinogenamylase and saccharogenamylase, according to the nature of the principal products. In dialysis of a malt extract the dextrinogenamylase is practically completely destroyed at a time when the saccharogenamylase retains about half of its original activity. At low temperature and low  $p_H$  saccharogenamylase is more stable than the dextrinogenamylase, at alkaline reaction the reverse holds. Dextrinogenamylase is more stable at high temperature. If a malt extract at 0° is acidified with hydrochloric acid to  $p_H$  3.3 and after 15 min. restored to  $p_H$  6, the dextrinogenamylase is practically destroyed, whilst about 75% of the saccharogenamylase is unchanged. By heating a malt extract at  $p_H$  6—7 for 15 min. at 70°, the saccharogenamylase is destroyed and about 75% of the other

component remains. The optimum  $p_H$  zones for saccharogenamylase and dextrinogenamylase are 4—5.75 and 5.5—6, respectively.

Osmotic pressure measurements show that dextrinogenamylase breaks down the starch molecule into two or more dextrin molecules which then give smaller molecules until finally maltose is formed. Saccharogenamylase, on the other hand, gives one or more molecules of maltose and a dextrin residue which then breaks down further, yielding maltose and dextrin. Dextrinogen- and saccharogen-amylase correspond closely with the  $\alpha$ - and  $\beta$ -amylases of Kuhn, since the former produces  $\alpha$ -maltose and the latter  $\beta$ -maltose. These end-products are indicated by the mutarotation shown. J. H. BIRKINSHAW.

**Kinetics of ester hydrolysis by enzymes. II. Course of the reaction in the fission of mixtures of mandelic esters and ketocarboxylic esters by liver esterases.** E. BAMANN and M. SCHMELLER (Z. physiol. Chem., 1930, 188, 251—260; cf. A., 1929, 1197).—In the hydrolysis of methyl (or ethyl) mandelate by liver esterase of man and animals in presence of small amounts of methyl (or ethyl) benzoylformate there is a latent period of extremely slow hydrolysis followed by a normal rate of hydrolysis for mandelic ester (cf. Willstätter, Kuhn, Lind, and Memmen, A., 1927, 793). In presence of benzoylacetic esters, however, there is an initial speedy reaction followed by a reversion to the normal rate of hydrolysis. The two portions of the curve are linear in the case of both keto-acid esters. In both cases the keto-acid presumably combines with most of the enzyme, but the intermediate product decomposes in the first case slowly, in the second case rapidly. J. H. BIRKINSHAW.

**Glycolytic power of cerebral matter.** G. MARTINO (Arch. Farm. sperim., 1930, 28, 228—238, 255—267).—Measurements have been made of the decomposition of dextrose by minced rat and pig brains and by aqueous extracts. The grey matter is more active than the white matter. Glycolysis is maximal in a solution containing dextrose and sodium hydrogen carbonate in the proportion 1:10; the rate increases with rise of temperature (17—38°). In contrast with the behaviour of blood, tumours, and muscle, addition of cyanides decreases glycolysis by brain. Examination of the action of salts shows that the following cations have an accelerating effect in the order given:  $NH_4 > Ba > Na > Ca$ , whilst inhibitory effects are shown by potassium and less markedly by magnesium ions. Inhibitory effects are shown by anions in the order given:  $I > F > citrate > Cl > oxalate > Br > SO_4 > pyrophosphate > acetate$ , whilst phosphates have a marked accelerating action which may be connected with the known stimulating action of phosphates on the central nervous system. The variation of the rate of glycolysis ( $y$ ) with  $p_H$  is given by  $y = ax + bx^2 + cx^3$ , where  $x = p_H - 3$ , and is a maximum at  $p_H$  7. R. K. CALLOW.

**Enzymic experiments with mammary glands.** O. SVANBERG (Z. physiol. Chem., 1930, 188, 207—218).—Freshly extirpated minced udder parenchyma from cows in full milk in contact with solutions

containing sugar does not usually produce lactose. Various sugars (dextrose, galactose, and lactose) are more or less completely broken down, the chief but not the sole product being lactic acid. This degradation is usually accompanied by gas evolution. In one case where no gas was produced a synthesis of lactose from dextrose was observed. A test on milk showed it to be free from monoses.

J. H. BIRKINSHAW.

**Intracellular synthesis of protein.** A. TIMOFEEVA and O. STEPPUHN (Biochem. Z., 1930, 220, 133—137).—The intensity of autolysis of muscle pulp of mouse and rat was measured at  $p_H$  3.8 and 7.1 in terms of the disappearance of protein. Since the tissue has considerable power *in vivo* to synthesise protein and an intense autolytic power *in vitro* and since the synthetic and autolytic powers are much greater in growing than in adult animals, it is concluded that the two processes are related.

P. W. CLUTTERBUCK.

**Manometric determination of enzymic decomposition of proteins.** H. A. KREBS (Biochem. Z., 1930, 220, 283—288).—Directions are given for measuring the extent of enzymic hydrolysis of proteins, using the apparatus of Warburg ("Stoffwechsel der Tumoren," Berlin, 1926) for examining cell metabolism.

W. MCCARTNEY.

**Inactivation of trypsin by heat.** J. PACE (Biochem. J., 1930, 24, 606—614).—The inactivation of trypsin free from enterokinase and its pre-stage follows the unimolecular equation. The optimum stability is at about  $p_H$  6.5 and the rate of destruction increases markedly on either side of this point. The  $p_H$ -stability curve is similar in shape to that obtained for the effect of  $p_H$  on the rate of heat-denaturation of proteins. The critical increment is sensibly the same in the alkaline region, in the acid region, and in the region of optimum stability, and is of the order of 40,000 g.-cal. per molar unit of enzyme.

S. S. ZILVA.

**Sistoproteolytic action of serum-albumin.** L. UTKIN-LJUBOVZOV (Biochem. Z., 1930, 220, 138—153).—The sistoproteolytic (antitryptic) action of serum-albumin was examined both with trypsin and yeast protease at varying  $p_H$ . Although it was not possible to reach definite conclusions from the experiments with trypsin, with yeast protease it was shown that as the reaction of the medium approached the isoelectric point of the albumin, the sistoproteolytic action of the latter gradually decreased to null values. The direct decharging of albumin by the action of oppositely charged colloids decreases and treatment with acetone destroys the sistoproteolytic properties of serum with both trypsin and yeast protease (cf. A., 1928, 83, 662).

P. W. CLUTTERBUCK.

**Nature of proteases.** I. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1930, 12, 449—456).—Various preparations of pepsin have been analysed in respect of their content of total nitrogen and of amino- and carboxyl groups, and the surface tension, refractive index, and conductivity of their solutions have also been determined. The proteolytic activity appears to be correlated with the content of amino- and carboxyl groups and with the

ratio of these groups and also with the surface tension of the aqueous solution. W. O. KERMACK.

**Specificity of animal proteases. XIX. Aminopolypeptidases from intestinal mucous membrane.** E. WALDSCHMIDT-LEITZ and A. K. BALLS (Ber., 1930, 63, [B], 1203—1211).—The fall in activity of aminopolypeptidase towards leucylglycine between  $p_H$  7.2 and  $p_H$  8.0 is not attributable to the presence of dipeptidase; it depends on the concentration of the substrate. Among oxides and oxide hydrates the greatest general adsorptive power is found in colloidal materials with large surface and non-oriented structure, but most marked specific action is observed with crystalline materials; hæmatite and yellow ferric oxide,  $Fe_2O_3 \cdot H_2O$ , appear to have specific adsorptive power for dipeptidase. Examination of the behaviour of homogeneous aminopolypeptidase towards peptides and peptide derivatives shows that hydrolysis occurs only when a free amino-group is present in the substrate, whereas a carboxylic group is unnecessary; polypeptide esters but not acylated peptides are hydrolysed. Hydrolysis of polypeptides by animal aminopolypeptidase effects the removal of the amino-acid residue carrying the free amino-group and leads to the production of dipeptides. H. WREN.

#### Identity of cell-proteases of different sources.

X. UTKINA-LJUBOVZOVA and O. STEPPURN (Biochem. Z., 1930, 220, 41—52).—All the investigated animal, plant, bacterial, and yeast cells contain the same proteolytic enzymic system which against caseinogen shows the same three digestion optima at  $p_H$  3—4, 5—6, 7—7.5 (cf. A., 1929, 1338).

P. W. CLUTTERBUCK.

**Proteolytic enzymes of the spleen.** S. G. HEDIN (Z. physiol. Chem., 1930, 188, 261—273).—The existence in the spleen of two proteases ( $\alpha$  and  $\beta$ ), having  $p_H$  optima at 8.9 and 5.5, respectively, is demonstrated by a new method which excludes peptidase. The minced spleen is treated with very dilute acetic acid, the liquid is filtered and dialysed. The dialysate contains  $\beta$ - but very little  $\alpha$ -protease. The residue from the acetic acid extraction yields a mixture which normally contains the  $\alpha$ -protease in excess. Both enzymes are adsorbed by kaolin, the  $\alpha$ -protease more strongly. The  $\beta$ -enzyme is removed from the kaolin by caseinogen at weakly alkaline reaction at 37°. In presence of sodium chloride more  $\alpha$ -protease is adsorbed and when the kaolin is washed free from sodium chloride a little  $\alpha$ -protease is obtained by elution with water at 37°.

J. H. BIRKINSHAW.

**Proteolytic action of papain.** H. A. KREBS (Biochem. Z., 1930, 220, 289—303).—The proteolytic action of papain is reversibly inhibited by small amounts of the heavy metals of the first and second groups of the periodic system, and proteins such as caseinogen and gelatin usually contain sufficient of one of these metals (generally copper or zinc) to restrict or prevent proteolysis. Substances such as hydrocyanic acid, hydrogen sulphide, cysteine, pyrophosphoric and citric acids, 8-hydroxyquinoline, and even proteins themselves which form complexes with the metals, remove these from solution, and greatly

increase the proteolytic action. Citric and pyrophosphoric acids, however, form complexes with zinc and cadmium only and hence do not increase the action if one of the other metals is the inhibiting agent. The inhibitory action of the metals increases with increasing at. wt. and metals of the first group are more powerful than those of the second. Proteins of high mol. wt. form complexes with the metals more readily than do those of low mol. wt. and hence the action of papain on gelatin, for example, ceases as soon as the protein is broken down sufficiently. Bromelin (from pineapple) and cathepsin (from animal tissues) behave in the same way as does papain.

W. MCCARTNEY.

**Decomposition of purines under various conditions of autolysis.** J. M. ZDUNKIEWICZ (Acta Biol. Exp., Warsaw, 1930, 4, 241—260).—The oxidation of ox-liver purines takes place more rapidly when oxygen is passed through the tissue suspension than when hydrogen is passed. The end-product is allantoin, showing that the processes of anaërobic and aërobic purinolysis are essentially the same.

R. TRUSZKOWSKI.

**Action of pectase. I. Optimal conditions for pectase coagulation.** A. MEHLITZ (Biochem. Z., 1930, 221, 217—231).—A method is described for obtaining from lucerne a dry preparation of pectase which retains its activity for 4 months. A 10% aqueous solution loses its activity in 3 days. For optimal activity, 0.15% of calcium chloride, 1% of calcium pectate, and a  $p_H$  of 4.8—5 are used.

P. W. CLUTTERBUCK.

**Diffusion of yeast invertase through collodion membranes.** J. M. NELSON and A. H. PALMER (J. Biol. Chem., 1930, 87, 1—6).—At  $p_H$  6.7 about 13% of the enzyme contained in a solution of yeast invertase passes through a collodion membrane during 86 hrs. dialysis against distilled water. At  $p_H$  4.6 the diffusion of enzyme is negligible although the loss of enzyme from the solution inside the collodion bag is greater than in the first instance. The  $p_H$  of minimal diffusion corresponds with that of minimal ionisation of the invertase (cf. Michaelis and Davidsohn, A., 1911, i, 1052).

C. R. HARINGTON.

**Enzyme actions in filtered and dialysed maceration juice.** S. KOSTYTSHEV and S. KLUPP (Z. physiol. Chem., 1930, 189, 11—16).—Maceration juice after filtration through a Chamberland filter shows a large decrease in fermenting power. The action of carboxylase, mutase, invertase, and maltase of yeast is not affected by filtration. Zymase, carboxylase, and mutase do not diffuse through a collodion membrane, but yeast invertase and maltase are dialysable; malt amylase shows this power to a small extent. The pores of the Chamberland filter are too wide to hold back enzymes by adsorption. Only bacteria and zymase are retained.

J. H. BIRKINSHAW.

**Action of yeast enzyme on glyoxylic acid.** A. STEPANOV and A. KUSIN (Ber., 1930, 63, [B], 1147—1153).—The action of a maceration extract of beer bottom yeast prepared by Lebedev's method towards glyoxylic acid has been examined. The presence of a synthesising agent in the yeast is

established by the production of acetoin from pyruvic acid. The glyoxylic acid disappears with production of carbon dioxide, acetaldehyde, glycollaldehyde, glycollic, oxalic, hydroxyketosuccinic, and malic acids. The glycollaldehyde is identified as the *p*-nitrophenylhydrazone and osazone after distillation of the product with steam. Glycollic and oxalic acids are formed in equimolecular amount (15–21% of the glyoxylic acid used). The presence of formaldehyde, methyl alcohol, or pyruvic acid could not be detected.

H. WREN.

**Formation of methylglyoxal during the decomposition of sugar by maceration juice.** C. PIŠUŇER (Anal. Fís. Quím., 1930, 28, 270–280).—Methylglyoxal is formed during the decomposition of sugar by sterile dilute aqueous solutions of yeast-juice, even after removal of the co-enzyme. By allowing the decomposition to proceed at 37° for 24 hrs., the theoretical yield of methylglyoxal, isolated as 2:4-dinitrophenylhydrazone, may be obtained.

H. F. GILLBE.

**Methylglyoxal as an intermediary in fermentation.** J. O. GIRŠAVIČIUS (Nature, 1930, 125, 817–818).—The non-fermentation of methylglyoxal by yeast preparations is discussed.

L. S. THEOBALD.

**Phosphoric esters in alcoholic fermentation. III. Lag between phosphate esterification and carbon dioxide evolution. IV. Oxidation-reduction potentials of yeast preparations.** E. BOYLAND (Biochem. J., 1930, 24, 703–710).—The lag between phosphate esterification and carbon dioxide evolution in fermentation by yeast preparations is not removed by the addition of those hydrogen acceptors which reduce the time necessary for the attainment of the maximum phosphate rate of carbon dioxide production. The lag is accompanied by an increase in the amount of triose present. During the reaction of phosphate in fermentation the  $p_H$  of the solution saturated with carbon dioxide remains constant between 6.2 and 6.3. Those dyes which accelerate fermentation by acting as hydrogen acceptors or carriers have  $E_0'$  between 0 and 0.10 volt at  $p_H$  6.0. They are probably reduced by methylglyoxal and oxidised again by acetaldehyde.

S. S. ZILVA.

**Special behaviour of *d*-mannose in biochemical phosphorylation.** I. S. NEUBERG and C. OSTENDORF (Biochem. Z., 1930, 221, 154–165).—On phosphorylation by means of fresh yeast in presence of toluene, mannose gave less hexose-di- and more mono-phosphate than did dextrose.

P. W. CLUTTERBUCK.

**Alcoholic fermentation. XX. Action of poisons on living yeast, dried yeast, and maceration juice.** S. KOSTYTSHEV and V. BERG (Z. physiol. Chem., 1930, 188, 133–159; cf. A., 1929, 724).—The action of the inhibitors toluene, ether, chloroform, thymol, strychnine, cocaine, quinine, sodium fluoride, and mercuric chloride on fermentations by living yeast and by "cell-free" preparations was compared. It is not possible to inhibit completely fermentation by living yeast by means of toluene even when an excess is present. The sensitive-

ness of dried yeast and particularly of maceration juice to the inhibitors examined is as great as or greater than that of living yeast. In many cases the same stimulation is shown by minute amounts of these substances in supposed enzymic fermentation as with the living yeast. This is especially noticeable with ether, chloroform, and strychnine. So-called cell-free fermentation is inherently similar to that produced by living yeast. Thus the chief argument for the enzymic nature of zymase fails.

J. H. BIRKINSHAW.

**Action of iodoacetic acid on enzymic degradation of carbohydrates.** E. LUNDGAARD (Biochem. Z., 1930, 220, 1–7).—Iodoacetic acid (1/5000) completely inhibited alcoholic fermentation by living yeast (5–10%) and by zymase preparations, smaller concentrations also inhibiting completely when acting for longer times. When the fermentation was so inhibited hexosephosphate formation was not detected. Invertase, ptyalin, and catalase were not affected by considerably greater concentrations (1/300) of the acid.

P. W. CLUTTERBUCK.

**Specific effects of monochromatic light on the growth of yeast.** A. H. HUTCHINSON and D. NEWTON (Canad. J. Res., 1930, 2, 249–263).—Exposure of a strain of yeast to monochromatic light of varying wave-length causes a retardation in growth with blue and violet, and a stimulation with orange, yellow, and green. The near ultra-violet generally stimulates growth, whilst the far ultra-violet inhibits. It is suggested that the phenomena may be associated with resonance.

H. BURTON.

**Yeast-nucleic acid. VI.** H. STEUDEL (Z. physiol. Chem., 1930, 188, 203–206; cf. A., 1924, i, 104).—An old preparation of yeast-nucleic acid when exposed to 3.3% sodium hydroxide solution at 18° or 37° for 24 hrs. gave no sodium guanylate on addition of acetic acid; 2 hrs. at 100° was sufficient to produce the maximum yield. Of samples of yeast-nucleic acid obtained from two firms, one behaved similarly to the old sample and the other was completely hydrolysed in 18 hrs. at 19°.

J. H. BIRKINSHAW.

**Metabolism of *Nematospora gossypii* and related fungi with special reference to the source of nitrogen.** E. H. M. FARRIES and A. F. BELL (Ann. Bot., 1930, 44, 423–455).—The ability of various media to support *Spermophthora gossypii*, *N. coryli*, and *N. gossypii* (two strains) has been measured by the dry weights of the fungi obtained after 30 days growth on solid media. Optimum growth was obtained at  $p_H$  7. Dextrose, levulose, and mannose were favourable sources of carbon in a peptone medium, whilst rhamnose supported a slight growth of *S. gossypii* and *N. coryli*. Galactose and mannitol were valueless alone, but increased the growth when added to a dextrose medium. Good growth was obtained on sucrose or maltose, none on lactose, whilst *N. coryli* grew as well on a 2% soluble starch medium as on a 2% dextrose medium. None of the four fungi fermented sugary liquids.

All four fungi grew equally well on hydrolysed or unhydrolysed peptone media ( $N=0.3\%$ ) or "lemco." *N. gossypii* grew on hydrolysed egg-white, gluten,

caseinogen, and muscle-protein media but not at all on gelatin, hydrolysed or unhydrolysed, alone, or to which tyrosine, tryptophan, and cystine *separately* or together were added. No growth was obtained on a mixture of amino-acids designed to represent the hydrolytic products of a complete protein. Although asparagine and hydrolysed gelatin are unavailable by themselves as a source of nitrogen they are assimilated in the presence of peptone. The utilisation of egg-white by *N. gossypii* is conditional on a growth-promoting substance which can be removed by alcoholic precipitation. The growth-promoting substance appears to be a complex organic acid. Similar results were obtained with caseinogen. The active extracts prepared from egg-white and caseinogen induce the assimilation to some extent of such unavailable sources of nitrogen as asparagine, hydrolysed gelatin, and fibrin. C. C. N. VASS.

**Formation of kojic acid from carbohydrates by the action of *Aspergillus flavus*.** A. CORBELINI and B. GREGORINI (Gazzetta, 1930, 60, 244—256).—The fermentation of starch, inulin, sucrose, dextrose, laevulose, arabinose, xylose, or glycerol by *A. flavus* forms 3-hydroxy-6-hydroxymethyl- $\gamma$ -pyrone, which is identical with Yabuta's kojic acid (A., 1922, i, 939). The fact that this substance is formed from other compounds than dextrose renders improbable the suggestion of Haworth ("Constitution of Sugars," 1929) that the action of the enzymes of the mould consists of a simple oxidation and dehydration of the dextrose molecule. More probably the pyrone nucleus is formed by synthesis from three-carbon oxidation products of glycerol by a reaction analogous to that occurring with aldehydes under the action of carboligase. T. H. POPE.

**Enzymic deamination by *Aspergillus niger*.** K. SCHMALFUSS and K. MOTHES (Biochem. Z., 1930, 221, 134—153).—The decomposition of asparagine by *A. niger* is brought about by an enzyme which can be extracted from the mycelium by means of water or glycerol but is very sensitive to drying in a vacuum at the ordinary temperature and to treatment with alcohol, ether, and acetone. The enzyme is active between 0° and 60° (optimum, 33°) and over a  $pH$  range 6—10 (optimum, 7.7—7.8). The enzyme does not attack acetamide and oxamide. P. W. CLUTTERBUCK.

**Two new species of bacteria belonging to the genus *Chromobacterium*.** M. GRIMES (Sci. Proc. Roy. Dublin Soc., 1930, 19, 381—384).—From several surface waters *C. hibernicum*, and from an artesian well *C. cohaerens* have been isolated. The latter alone has diastatic action. Both are violet in habit, rodlike, aerobic, non-sporing, usually Gram-negative, and, unlike the usual chromobacter, reduce nitrates. They may be propagated at 21°, but show little growth at 35°. T. H. MORTON.

**Nitrogen metabolism of *B. mycoides*. III. Effect of dextrose in varying concentrations. IV. Effect of carbohydrates, polyhydric alcohols, and glucosides.** H. GLINKA-TSCHERNORUTZKI (Biochem. Z., 1930, 221, 113—124, 125—133).—Addition of dextrose in quantities greater than 0.1% or of

other available carbohydrates to cultures inhibits ammonia formation owing to its protein-sparing action. P. W. CLUTTERBUCK.

**Fermentation of gelatin.** J. A. LE BEL (Bull. Soc. chim., 1930, [iv], 47, 380—382).—A 2% gelatin solution seeded at 38—40° with faecal matter becomes strongly alkaline and the culture can be used to ferment 50 times its volume of 2% gelatin solution. Fermentation proceeds rapidly if the ammonia produced is neutralised with sulphuric acid, and the fermentation is complete when the production of ammonia ceases. The fermenting liquid readily dissolves a piece of gut, hemp being unattacked, an observation which indicates that the bacillus can attack the intestinal wall. The ferment need not be pure and a solid product which is rich in lactic ferment and is stable when dry can be obtained by fermenting a solution of lactose containing a little milk. The fermentation of gelatin affords ammonium carbonate, propionic and higher fatty acids, up to hexoic, the maximum amount of  $C_6$  acids being 2%, and higher alcohols up to active and inactive amyl alcohol. Hexyl alcohols were not formed. A small amount of the nitrogen is left in the form of base. R. BRIGHTMAN.

**Fermentative decomposition of creatinine.** F. LINNEWEEH (Z. Biol., 1930, 90, 109—112).—Creatinine is converted into methylhydantoin by putrefactive bacteria (cf. Ellinger and Matsuoka, A., 1914, i, 881). C. C. N. VASS.

**Formation of coprosterol.** H. BEUMER and G. BISCHOFF (Biochem. Z., 1930, 220, 154—157).—Neither allocholesterol nor egg-yolk is reduced during putrefaction *in vitro*. Dihydrocholesterol fed to mice is not stored. P. W. CLUTTERBUCK.

***Bacillus beriberi*.** S. MATSUMURA, G. KAKI-NUMA, K. KAWASHIMA, K. IANIKAWA, S. OCHIAI, R. MIYATA, K. FUJISAKI, R. KANAO, K. NOGUCHI, K. AOKI, T. SATO, K. ITO, and M. SUZUKI (Proc. Imp. Acad. Tokyo, 1930, 6, 126—129).—A Gram-negative bacillus, closely allied to the *typhus-coli* group, has been isolated from the stools of 74% of the cases of beriberi examined. Agglutinations with beriberi hen or human serums were observed. The *B. beriberi* has been further differentiated into Type A and Type B. C. C. N. VASS.

**Butyric acid fermentation.** P. ELIASBERG (Biochem. Z., 1930, 220, 259—277).—The "butyric acid" type of fermentation of dextrose in neutral solution by *Clostridium Pasteurianum* and by related organisms is changed to the "butyl alcohol" type if the fermentation proceeds in hydrogen at 65—120 atm. pressure with or without the addition of colloidal platinum or palladium. There is no proof that the butyl alcohol is formed by reduction of butyric acid or of intermediate products of fermentation, and the change in the type of this is not to the "acetone-butyl alcohol" type. Gaseous pressure, and especially pressure of hydrogen, although it reduces the yield of fermentation products, favours the change in the type of fermentation at least in the case of the bacteria used. W. MCCARTNEY.

**Reduction phenomena in lactic acid fermentation.** I. P. ZACHAROV (J. Russ. Phys. Chem. Soc., 1930, 62, 399—408).—Methylene-blue, sulphates, and nitrates added to cultures of *B. Delbrücki* in media containing dextrose undergo reduction, indicating the production of active hydrogen during the process of lactic acid fermentation. R. TRUSZKOWSKI.

**Formation of pyruvic acid in lactic acid fermentation.** S. KOSTYTSCHY, W. GWALADSE, and P. ELIASBERG (Z. physiol. Chem., 1930, 188, 127—132).—A method for isolating pyruvic acid in presence of sugar consists in treatment of the evaporated liquor, after removal of calcium carbonate, bacteria, and lactic acid, with phenylhydrazine and excess of hydrochloric acid. After 4 hrs. the phenylhydrazone is shaken out with ether, most of the latter is removed by distillation, and the remainder poured into benzene. The pyruvic acid phenylhydrazone which crystallises out is collected, washed, dissolved in a small excess of alkali hydroxide, and reprecipitated with mineral acid. By this means pyruvic acid was isolated in lactic acid fermentations by *B. Delbrücki*, *Streptococcus lacticus*, Kruse, and *B. caucasicum*.

J. H. BIRKINSHAW.

**Determination of sugar by means of *B. coli*.** K. P. JACOBSON (Biochem. Z., 1930, 220, 461—472).—The method of Rona and co-workers (A., 1927, 994) gives results which can only occasionally and by accident be correct, since during the fermentation various acids in addition to lactic acid are formed, carbon dioxide other than that formed by their action on the hydrogen carbonate is produced, hydrogen is liberated, and variations occur in the mechanism of the reaction as it is induced by various strains of the organism. W. MCCARTNEY.

**Metabolism of spirochaetes and trypanosomes.** B. VON FENYVESSY and G. SCHEFF (Biochem. Z., 1930, 221, 206—216).—During the metabolism of spirochaetes, oxygen utilisation could not be detected by Warburg's method, carbohydrate forming the sole source of energy. P. W. CLUTTERBUCK.

**Oxidation-reduction potentials of cultures of *C. diphtheriae*.** I. L. F. HEWITT (Biochem. J., 1930, 24, 669—675).—More highly-reducing conditions are developed in cultures of *C. diphtheriae* than with haemolytic streptococci, especially when the oxygen supply is most abundant. After the logarithmic phase of growth the electrode potentials do not rise. The potential-time curves of *C. diphtheriae* cultures are less susceptible to variation with cultural conditions than those of haemolytic streptococci. Serum possess an oxygen-carrying effect in *C. diphtheriae* cultures.

S. S. ZILVA.

**Oxidation-reduction potentials of staphylococcal cultures.** I. L. F. HEWITT (Biochem. J., 1930, 24, 676—681).—These cultures, like those of *C. diphtheriae* (see preceding abstract), maintain more intense reducing conditions when the oxygen supply is abundant than haemolytic streptococci. Their potential remains at a low level for a long period. In freshly-heated broth the potential falls more rapidly, as with streptococci. Serum has an oxygen-carrying effect in these cultures. The potential does not fall to as low a level in dextrose broth as in plain broth.

An abundant oxygen supply facilitates the utilisation of the acids liberated during the fermentation of the dextrose. Glycerol has little effect on the potential-time curve. S. S. ZILVA.

**Production of staphylococcal toxin.** F. M. BURNET (J. Path. Bact., 1930, 33, 1—16).—*S. aureus* in broth requires an atmosphere of carbon dioxide or the presence of a considerable number of *albus* variants for the production of appreciable quantities of haemolysin. CHEMICAL ABSTRACTS.

**Purification of anticarbuncle serum.** II. F. MODERN and R. WERNICKE (Anal. Assoc. Quim. Argentina, 1929, 17, 329—339; cf. A., 1929, 1493).—Felton's method of purification of antipneumococcus serum (J. Infect. Dis., 1928, 42, 259) is not applicable to anticarbuncle serum. The precipitate obtained by dilution of anticarbuncle serum with four volumes of distilled water (*loc. cit.*) contains all the precipitins, but only a small part of the substances which protect against infection. When the serum is diluted with distilled water successively to one third and one tenth of the initial concentration, the second precipitate is soluble in 2% sodium chloride solution and possesses all the protective power of the original serum with only 5% of the protein. R. K. CALLOW.

**Determination of bacteria in suspensions.** A. P. KRUEGER (J. Gen. Physiol., 1930, 13, 553—556).—A method is described for determining the cell concentration of bacterial suspensions by measurement of sediment columns after centrifuging in capillary tubes calibrated by suspensions standardised by direct count. F. O. HOWITT.

**Determination of bacteriophage.** A. P. KRUEGER (J. Gen. Physiol., 1930, 13, 557—564).—A definite relationship between concentration of antistaphylococcus phage and the time required to reduce a particular concentration of growing staphylococci (*S. aureus*) to an arbitrary turbidity end-point is given and its application to the determination of a bacteriophage described. F. O. HOWITT.

**Germicidal power of colloidal metallic silver and of ionic silver on *B. typhosus*.** K. SAMAN (Quart. J. Pharm., 1930, 3, 21—24).—In 0.02% and 0.05% solutions, colloidal silver, prepared in pure water by Bredig's method, is slightly less toxic to *B. typhosus* than is an equal weight of silver nitrate. The solutions are approximately equal in toxicity to 0.4% and 1% aqueous phenol, respectively.

H. E. F. NORTON.

**Influence of electrolytes on the bactericidal action of copper and silver salts.** Dependence of bactericidal action on the electrostatic charge of bacteria (explanation of the so-called salt inhibition of oligodynamic action). N. LEITNER (Biochem. Z., 1930, 221, 42—63).—Inhibition by electrolytes of the bactericidal action of copper and silver salts does not depend on a chemical or physico-chemical effect on the metallic ions, the concentration of which remains unchanged. The effect is due to an inhibition of the adsorptive union of metallic ion and bacterium. The greater the negative charge of the bacteria the stronger is the adsorption of metallic (electropositive)



ions. Inhibition by electrolytes depends on the decrease of the charge on the bacteria.

P. W. CLUTTERBUCK.

**Oligodynamy.** N. LEITNER (Klin. Woch., 1929, 8, 1952—1957; Chem. Zentr., 1930, i, 252).—The oligodynamic action of metals is due to, and identical with that of, metallic ions. A. A. ELDRIDGE.

**Vegetative-endocrine system as regulator of intermediary metabolism.** Rôle of adrenaline and the thyroid gland in regulation of the carbohydrate and fatty constituents of the blood. D. ALPERN, L. TUTKEVITSCH, and V. BESUGLOV (Klin. Woch., 1929, 8, 1719—1720; Chem. Zentr., 1929, ii, 2789—2790).—After administration of adrenaline to normal dogs a diminution of total and neutral blood-fat was observed, the values later becoming normal. The increase in ketonic substances was not always parallel with the diminution of fat. In hunger the effect of adrenaline was to increase the total fat. By thyroxine and hunger the curve of the blood-fat under the influence of adrenaline is usually not abruptly depressed by adrenaline, as for neutral fat. The ketonic substances are markedly increased by simultaneous administration of oleic acid. It is considered that adrenaline hyperglycemia increased by introduction of fat does not result from chemical metamorphosis, but from a change in the condition of the liver-carbohydrate caused by the penetration of colloidal substances. Removal of the thyroid gland depresses the hyperglycemic alimentary curve, changes the cause of alimentary lipæmia, and increases the biliary cholesterol. A. A. ELDRIDGE.

**Amino-alcohols.** III. Potentiation of the pressor action of adrenaline by arylpropanolamines. J. C. MUNCH and W. H. HARTUNG (J. Amer. Pharm. Assoc., 1930, 19, 356—361).—A study of the effect of a number of amino-alcohols on the pressor action of adrenaline. Phenylpropanolamine, its *p*-hydroxy- and *p*-methyl derivatives, and ephedrine given intravenously in doses of 1—3 mg. per kg. potentiated the pressor action of adrenaline. This effect is eliminated by increasing or decreasing the length of the aliphatic side-chain.

E. H. SHARPLES.

**Mechanism of adrenaline action.** VI. Changes in blood-sugar, lactic acid, and blood-pressure. C. F. CORI, G. T. CORI, and K. W. BUCHWALD (Amer. J. Physiol., 1930, 93, 273—283).—The minimum effective rate of injection of adrenaline into rabbits (0.00005 mg. per kg. body-weight per min.) produced an increase in lactic acid and in blood-sugar and the lactic acid curve followed the blood-sugar curve.

E. BOYLAND.

**Depletion of muscle-sugar by adrenaline.** F. BISCHOFF and M. L. LONG (J. Biol. Chem., 1930, 87, 47—53).—After injection of adrenaline into rabbits the sugar of the blood and muscles rises in concentration for 1½ hrs.; the blood-sugar continues to rise and reaches a maximum at 3 hrs., by which time, however, the muscle-sugar has fallen almost to the normal fasting level; subsequently the blood-sugar returns to normal whilst the muscle-sugar falls still further and remains abnormally low for 24 hrs. The results of Sahyun and Alsberg (A., 1929, 1107) are

therefore to be ascribed to diffusion of sugar into the muscle and fail to prove increased utilisation of sugar by the latter. C. R. HARRINGTON.

**Use of constant dextrose injections for the study of induced variations in carbohydrate metabolism.** III. Fate of retained sugar under normal conditions and after adrenaline and insulin. IV. Suppression of dextrose combustion by continuous prolonged adrenaline administration. A. R. COLWELL and E. M. BRIGHT (Amer. J. Physiol., 1930, 92, 543—554, 555—567).—III. Administration of dextrose causes glycogen to be stored at a constant rate and excess sugar is excreted in the urine. Insulin increases the combustion and storage of the sugar, whilst adrenaline increases the amount of sugar excreted.

IV. Adrenaline stops the oxidation of administered dextrose. It is possible that diabetes mellitus is due to excessive secretion of adrenaline which suppresses the action of insulin. E. BOYLAND.

**Influence of adrenaline on galactose assimilation of the liver.** J. BLÖCH (Klin. Woch., 1929, 8, 1707—1708; Chem. Zentr., 1930, ii, 2790).—Simultaneous introduction of adrenaline and galactose in cases of liver parenchyma injury brings about a lowering of the galactose tolerance.

L. S. THEOBALD.

**Bio-assay of adrenaline-procaine mixtures.** J. C. MUNCH and W. A. DECKERT (J. Amer. Pharm. Assoc., 1930, 19, 354—356).—By comparing the increases in blood-pressure produced by a series of injections of procaine-adrenaline mixtures with those produced by a previous series of injections of standard adrenaline it is possible to assay these mixtures by U.S.P. X. method for adrenaline.

E. H. SHARPLES.

**Preparation of insulin from alkaline aqueous extracts.** G. KAULBERSZ (Bull. Soc. Chim. biol., 1930, 12, 464—469).—A method for the preparation of insulin from ox pancreas is described in which the extraction is effected by 0.02N-sodium hydrogen-carbonate solution. W. O. KERMACK.

**Influence of insulin on distribution of glycogen in normal animals.** B. CORKILL (Biochem. J., 1930, 24, 779—794).—Goldblatt's observation (A., 1929, 357) that glycogen accumulates in the liver of young fasting rabbits as the result of injecting insulin is confirmed. The musculature loses at least as much glycogen as the liver gains. Other species, however, do not react in this way. Insulin causes no deposition of glycogen in the liver of the fasting chicken and prevents its deposition there as the result of giving dextrose, whilst causing its deposition in the muscles. In the ferret it causes formation of glycogen in the muscles and has little effect on that in the liver. In the mouse it causes rapid discharge of glycogen from the liver. When dextrose is also given, glycogen is deposited in the muscles but still disappears from the liver. Injections of adrenaline too small to cause glycosuria produce in the young fasting rabbit a change in glycogen distribution closely similar to that following injections of insulin.

S. S. ZILVA.

**Insulin and increase in weight of young animals.** J. J. R. MACLEOD, H. E. MAGEE, and W. MIDDLETON (Biochem. J., 1930, 24, 615—618).—Insulin injected subcutaneously in pigs in daily doses of 1.5—2 units per kg. body-weight had only a very slight accelerating effect on the rate of increase in weight. This increase was due to a correspondingly greater consumption of food. With marasmic pigs insulin had a more marked effect. S. S. ZILVA.

**Insulin inactivation by human blood-cells and plasma *in vitro*.** II. Effect of infection on insulin. S. KARELITZ, S. D. LEADER, and P. COHEN (Arch. Int. Med., 1930, 45, 690—701).—The inhibiting action of erythrocytes and plasma on insulin *in vitro* is enhanced in diabetes and cases of purulent infection. Blood from individuals with serum sickness following injection of diphtheria antitoxin shows marked insulin inactivation. Leucocytes show a greater inactivating power than erythrocytes. Pus cells from a patient with pneumococcus empyema exert a similar effect. Subcutaneous injection of typhoid vaccine in rabbits produced increased resistance to insulin lasting for 2—5 days. Paratyphoid-B vaccine gives inconclusive results. Heating for 1 hr. at 37° shows that the inactivating substance is thermolabile. The effect is most marked at a mildly alkaline reaction and is probably enzymic. P. G. MARSHALL.

**Hormone of the anterior pituitary lobe.** P. BOTSCHKAREV (Klin. Woch., 1929, 8, 1718; Chem. Zentr., 1929, ii, 2789).—Biological changes following the administration to mice of the hormone preparation are recorded. A. A. ELDRIDGE.

**Posterior pituitary lobe in diabetes insipidus and the mechanism of its action.** S. ISAAC and R. SIEGEL (Klin. Woch., 1929, 8, 1700—1704; Chem. Zentr., 1929, ii, 2789).—Experiments on the administration of "tonephin" and "orasthin" are recorded. The mobilisation of sodium chloride from the tissues is facilitated. A. A. ELDRIDGE.

**Parathyroid hormone and ergosterol hypercalcaemia.** G. BISCHOFF (Z. physiol. Chem., 1930, 188, 247—250).—Injection of the parathyroid hormone into dogs suffering from ergosterol hypercalcaemia produced a slight increase in serum-calcium followed by a considerable decrease. J. H. BIRKINSHAW.

**Action of thyroxine and acetylthyroxine on the metamorphosis of the axolotl.** A. A. TITAJEV and B. R. SUMM (Biochem. Z., 1930, 220, 62—68).—The following preparations are placed in order according to their degree of activity in causing the metamorphosis of the axolotl: thyroxine I, thyroxine II, acetylthyroxine II (monoacetyl), and acetylthyroxine I (diacetyl). Thyroxine I (0.1 mg.) is toxic and kills the axolotl in 5—6 days. With the same dose of the acetyl derivative, metamorphosis takes place smoothly during 38 days. The most suitable dose for comparative testing of the four preparations is 0.03 mg. An alcoholic solution of acetylthyroxine I is almost inactive. P. W. CLUTTERBUCK.

**Thyroxine, fat and lipid metabolism.** S. LEIRES (Biochem. Z., 1930, 221, 101—112).—

Subcutaneous injection of thyroxine decreases in dogs the alimentary lipaemia and ketonaemia obtained when feeding with olive oil, the effect being more pronounced in the male than in the female animal. Castration in males decreases the specific effect of thyroxine. P. W. CLUTTERBUCK.

**Œstrin in the urine of the pregnant cow.** A. LIPSCHÜTZ and S. VESHNJAKOV (Biochem. Z., 1930, 220, 456—460).—The urine of pregnant and non-pregnant cows contains small amounts of œstrin (about 800 mouse units per litre) which can be extracted in the same way as folliculin is obtained from the urine of pregnant women. No increase in the amount of œstrin in the urine occurs as pregnancy proceeds. Possibly the œstrin is derived from food. W. MCCARTNEY.

**Hormone balance after oral administration of ovarian hormone.** J. LUCHSINGER and H. E. VOSS (Klin. Woch., 1929, 8, 1577—1578; Chem. Zentr., 1929, ii, 2789).—Of 500 mouse units of "progynon" administered, 15 were found in the urine and faeces. A. A. ELDRIDGE.

**Occurrence of the female sexual hormone and the hormone of the anterior pituitary gland in the blood and urine of newly born infants.** R. BRUHL (Klin. Woch., 1929, 8, 1766—1767; Chem. Zentr., 1930, i, 242).—The amniotic fluid, the blood of the umbilical cord, and the urine of newly born infants contain female sexual hormone up to the fourth day; it is sometimes present in the milk. The anterior pituitary hormone was found in the urine up to the second day in half the cases examined, always in the blood of the umbilical cord, and only once in the milk. A. A. ELDRIDGE.

**Terminology of female sex-hormones.** A. LIPSCHÜTZ (Biochem. Z., 1930, 220, 453—455).—In the present state of knowledge the hormones are best named from their places of origin—folliculin, from the follicles, and luteohormone (possibly consisting of two substances,  $\alpha$ - and  $\beta$ -luteohormones, which act in opposite ways) from the corpus luteum. The origin of the material found in urine (and also in plants) is uncertain and a suitable name for it at present is œstrin. W. MCCARTNEY.

**Antimony trichloride reaction for vitamin-A.** II. Dilution curve of cod-liver oil with antimony trichloride reagent. E. R. NORRIS and A. E. CHURCH (J. Biol. Chem., 1930, 87, 139—146).—Further study of the dilution curves of various fish-liver oils confirms the previous conclusion (this vol., 379) that different curves are obtained with different oils, and that no linear relationship exists between intensity of colour and concentration of active material except at very high dilutions. Comparison of oils by this method is best made on the basis of the slope of the tangent to the dilution curve at the origin. C. R. HARRINGTON.

**Vitamin-A and carotene.** V. Absence of the liver-oil, vitamin-A from carotene. VI. Conversion of carotene into vitamin-A *in vivo*. T. MOORE (Biochem. J., 1930, 24, 692—702; cf. A., 1929, 1343).—The antimony trichloride colour reaction given by a minimal physiological dose of carotene at 590  $\mu$  is slightly less than that given by a

minimal physiological dose of the vitamin-A of liver oil at 610—630  $\mu\mu$  (cod-liver oil concentrates were used). The colour reaction of the former could, therefore, not mask the colour reaction due to the liver-oil vitamin-A in such amounts as would account for its physiological activity. Liver oils from rats suffering from vitamin-A deficiency do not give the reaction. On administration of purified carotene, m. p. 178° (uncorr.), red palm oil, or fresh carrots to the depleted animals traces of yellow pigment appeared in the liver oil, but the predominant chromogen was that associated with vitamin-A, i.e., showing a band at 610—630  $\mu\mu$  on addition of antimony trichloride. These liver oils also manifested intense biological activity and the development of an absorption band at 328  $\mu\mu$  in the untreated condition, an absorption characteristic of vitamin-A but not of carotene (cf. Capper, this vol., 822). Carotene, or some substance associated with it, behaves therefore *in vivo* as precursor of vitamin-A.

S. S. ZILVA.

**Metabolism of mineral substances of rabbits in hypervitaminosis-A.** T. MUNEHISA (Sei-i-kwai Med. J., 1929, 48, No. 10, 77—107).—The reason for the increased elimination of calcium and phosphorus by rabbits given excessive doses of "biosterol" is discussed.

CHEMICAL ABSTRACTS.

**Production of vitamin-B by *Bacillus vulgatus* (Flügge), Migula, and by *B. mesentericus* (Flügge), Lehm. et Neum.** M. SCHIEBLICH (Biochem. Z., 1930, 220, 394—398).—*B. mesentericus* produces much less vitamin-B in a vitamin-B-free medium than does *B. vulgatus* propagated in the same way. The alkalinity produced in the medium by *B. mesentericus* may partly account for this (cf. A., 1929, 726).

W. MCCARTNEY.

**Colorimetric determination of the anti-beriberi vitamin content of rice.** J. P. SPRUYT (Chem. Weekblad, 1930, 27, 298—304).—The whole rice grains are shaken with an aqueous solution of salicylic and sulphuric acids, to which toluene is added, in presence of norit, which adsorbs the non-vitamin constituents which are capable of giving a precipitate with phosphotungstic acid. The whole is filtered, and the vitamin precipitated by addition of phosphotungstic acid. The washed precipitate is dissolved in hydrochloric acid, reduced with zinc, and the colour developed compared with that of a standard plate. Results of the test applied to many samples of rice were found to be parallel with the results obtained by the rice-bird method.

S. I. LEVY.

**Localised lactic acidosis in brains of pigeons suffering from vitamin-B<sub>1</sub> deficiency.** H. W. KINNERSLEY and R. A. PETERS (J. Physiol., 1930, 69, Proc. xi).—The increase in lactic acid is most marked in the lower part of the brain.

E. BOYLAND.

**Carbohydrate metabolism in birds. II. Brain localisation of lactic acidosis in avitaminosis-B and its relation to the origin of symptoms.** H. W. KINNERSLEY and R. A. PETERS (Biochem. J., 1930, 24, 711—722).—The increased lactic acid found in brains of pigeons showing symptoms of opisthotonus due to vitamin-B<sub>1</sub> deficiency is

particularly marked in the lower part of the brain. This is also the case during the period in which the symptoms of opisthotonus are threatening. Severe exercise on the other hand causes a rise in the lactic acid content of the brain which is distributed evenly throughout the tissue. The symptoms of opisthotonus are due to the localised accumulation of lactic acid. The lowest lactic acid found in the brain of a normal pigeon was 24 mg. per 100 g. of tissue after death by injection of moniodoacetic acid. "Opisthotonus" birds killed in this way showed a higher lactic acid content and higher values were again observed in the lower part of the brain. Vitamin-B<sub>1</sub> is probably concerned with the oxidative removal of lactic acid.

S. S. ZILVA.

**Vitamins and tumor growth. III. Vitamin-B content of rat tumors.** W. NAKAHARA and E. SOMEKAWA (Proc. Imp. Acad. Tokyo, 1930, 6, 116—118).—Transplantable rat tumours, both sarcoma and carcinoma, contain only small amounts of vitamin-B.

C. C. N. VASS.

**Relationship of the water-soluble vitamins. II. Importance of alkaline hæmatin, the age of rats, and composition of diet in vitamin-B<sub>1</sub> deficiency.** W. KOLLATH (Arch. exp. Path. Pharm., 1930, 150, 236—255).—After administration of alkaline hæmatin 76% of young rats contract beriberi compared with 10% which contract it spontaneously. Deuterohæmin has a similar effect to alkaline hæmatin. Feeding of caseinogen, extracted with alcohol alone or containing 1.0% of hydrochloric acid, produced no intensification of the symptoms of beriberi caused by hæmatin. It is suggested that the importance of hæmatin as an accessory food factor is due to its catalytic effect on the anaërobic oxidation of unsaturated fatty acids. There is an increased liability to spontaneous contraction of beriberi in older rats.

P. G. MARSHALL.

**Importance of carbohydrates in the development of avitaminosis-B.** A. GOTTMACHER and I. I. LITVAK (Zhur. exp. Biol. Med., 1929, 11, 41—43).—Elimination of carbohydrates on a diet free from vitamin-B does not prevent the development of avitaminosis.

CHEMICAL ABSTRACTS.

**Fat-soluble vitamins of milk.** M. E. F. CRAWFORD, J. GOLDING, E. O. V. PERRY, and S. S. ZILVA (Biochem. J., 1930, 24, 682—691).—The entire vitamin-A and -D content of milk is associated with the milk-fat. These vitamins are not more concentrated in one fraction of milk-fat than in another, nor is there a significant loss in either vitamin due to separating or churning and consequently by testing the butters it is possible to obtain the relative potency of the milks from which they are prepared.

S. S. ZILVA.

**Relation of the fat-soluble vitamins (A and D) to the development of experimental rickets in rabbits.** A. R. MORITZ and C. KRENZ (J. Nutrition, 1930, 2, 257—263).—Rabbits, but not rats, failed to develop rickets when fed on a diet deficient only in the fat-soluble vitamins. Serum- and bone-calcium was diminished.

CHEMICAL ABSTRACTS.

**Fat-soluble vitamins. XXVIII. Effect of exposure of the cow to sunlight and to ultra-violet**

irradiation on antirachitic value of milk. H. STEENBOCK, E. B. HART, B. M. RIISING, C. A. HOPPERT, S. BASHEROV, and G. C. HUMPHREY. XXIX. Is antirachitic activity induced by ultra-violet irradiation a panacea for negative calcium balances? H. STEENBOCK, E. B. HART, B. M. RIISING, S. W. F. KLETZIEN, and H. T. SCOTT (J. Biol. Chem., 1930, 87, 103—126, 127—137).—XXVIII. No improvement in the quality of the milk, as regards either its content of fat or its antirachitic value, was observed as the result of daily exposure of cows to sunlight or to ultra-violet radiation.

XXIX. The antirachitic value of goat's milk was increased by exposure of the animal to ultra-violet radiation. In the early part of the period an increased retention of calcium was observed; subsequently the calcium balance became negative and the animal exhibited increasing irritability. Factors other than vitamin-D must therefore be concerned in the control of calcium excretion. C. R. HARRINGTON.

Antirachitic value of irradiated yeast. S. K. KON and M. MAYZNER (Lancet, 1930, i, 794—796).—Infantile rickets was cured in 6—8 weeks by feeding 0.75 g. of irradiated yeast per day; cure was accompanied by a definite rise in serum-calcium and -phosphorus. E. BOYLAND.

Absorption and excretion of calcium and phosphorus by rats receiving excessive doses of irradiated ergosterol. E. WATCHORN (Biochem. J., 1930, 24, 631—640).—The calcium and phosphorus retention is decreased by the consumption of excessive (0.05% level) doses of irradiated ergosterol. The urinary calcium is greatly increased but not the phosphorus. The faecal calcium and phosphorus decrease but not always in proportion to the intake. The disturbances in the retention and absorption persist during the recovery period even to a more marked extent. The retention and absorption of calcium and phosphorus decrease with the consumption of decreased quantities of a full synthetic diet without the addition of irradiated ergosterol.

S. S. ZILVA.

Phosphorus distribution in blood and calcium and phosphorus excretion during hypervitaminosis-D. C. A. ASHFORD (Biochem. J., 1930, 24, 661—668).—The increase in blood-inorganic phosphate obtained by feeding high quantities of irradiated ergosterol to rabbits is not associated with any change in the content of organic acid-soluble phosphorus compounds. There is an increase in the urinary excretion of inorganic phosphate. The urinary excretion of calcium is also greatly increased. The animals maintain this high phosphate and calcium excretion even after the other symptoms of the metabolic disturbance have disappeared. The rise in serum-calcium in hypervitaminosis is confirmed.

S. S. ZILVA.

Tree root activities. II. Factors which influence tree root respiration. G. H. HARRIS (Sci. Agric., 1930, 10, 564—585).—Apparatus for determining the rate of carbon dioxide production from root stocks is described. Ratios vary with different species. Among individuals of any one species, root injury causes an increase in carbon

dioxide production, whilst the bursting of buds results in a decrease. Root respiration increases at periods when leaf expansion and shoot extension is great.

A. G. POLLARD.

Biochemistry and histochemistry of fruits and seeds. I. A. NIETHAMMER (Biochem. Z., 1930, 220, 348—357).—As a result of increasing respiratory or enzymic activity the acetaldehyde content of oranges, lemons, pears, apples, bananas, dates, plums, and medlars increases as the fruits pass from the unripe to the ripe and over-ripe condition. The acetaldehyde is probably derived from carbohydrate. In the same fruits (dates and plums not examined), passing through the same conditions, uniform changes occur in the contents of oxalic, succinic, malic, citric, and tartaric acids. Some of the fruits contain phloroglucinol (or derivatives of it) and some contain glucosides. The amounts of these change as the fruits reach the over-ripe state. Seeds from some of the fruits mentioned and from certain other fruits also contain, at certain stages of development, organic acids, glucosides such as aesculin and saponarin, and phloroglucinol or its derivatives. W. MCCARTNEY.

Soil reaction and growth. Effect of phosphate solutions of varying hydrogen-ion concentration on the respiration and germination of seed. A. REIFENBERG and L. FRANKENTHAL (Biochem. Z., 1930, 220, 473—486).—Provided that the reaction is not strongly acid the production of carbon dioxide by peas, barley, and wheat is increased in the presence of phosphate, but this decreases both the uptake of oxygen and the production of carbon dioxide by oats. In the presence of phosphate the oxygen uptake of peas and of barley is increased only at neutral reaction and that of wheat only at faintly acid reaction, the optimum reactions for the process being at  $p_H$  6.5—7.2 for peas, 6.5—6.8 for barley, 5.2—6.9 for wheat, and 3.9—6.8 for oats. The respiratory quotient of peas is greatly increased by phosphate, whilst that of oats is maintained in the neighbourhood of unity and those of wheat (at  $p_H$  3.9—6.1) and barley (at  $p_H$  3.9—6.5) are maintained at 1.3—1.8. The germination of the seeds is unfavourably affected by phosphate, but there are zones of hydrogen-ion concentration ( $p_H$  6.1—6.5 for peas and wheat, 7.0 for barley, 3.9—6.5 for oats) within which the capability for germination is at its highest. In the presence of phosphate the optimum reactions for oxygen uptake are about the same as those for germination and coincide also with the optimum soil reactions for the plants concerned.

W. MCCARTNEY.

Physico-chemical regulation in the internal environment of some agricultural plants. J. CHAUSSIN and E. BLANCHARD (Compt. rend., 1930, 190, 1139—1141).—The concentrations of the water-soluble chlorides, sulphates, phosphates, silicates, and carbonates in the ash of the whole wheat plant and the leaves of the turnip and bean grown on different fertilisers have been evaluated as electro-chemical equivalents. In the wheat there is an antagonism between the concentrations of the carbonates and the sulphates when fertilised with sylvinit or potassium chloride. In the bean and the turnip grown on potassium sulphate, calcium sulphate.

or potassium chloride compensation is observed between the carbonates and the chlorides.

C. C. N. VASS.

**Comparative chemical evolution of the leaves of the vine taken from different heights on the branches.** H. LAGATU and L. MAUME (Compt. rend., 1930, 190, 1137—1139).—A comparison of the calcium and nitrogen contents of leaves taken from corresponding positions on the plants displays the same differences which are characteristic of the differing sources of nutrition.

C. C. N. VASS.

**Phosphorus in plants.** J. E. WEBSTER (Univ. Oklahoma Bull., 1929, 9, 47—49).—Plants, particularly the vegetative parts, contain significant amounts of inorganic phosphorus. Phosphorus is present chiefly as phytin. Starch contains approx. 0.09% P.

CHEMICAL ABSTRACTS.

**Rôle of magnesium in the ageing of plants.** B. F. LUTMAN and N. L. WALBRIDGE (Vermont Agric. Exp. Sta. Bull., 1929, No. 296, 1—48).—The percentage of magnesium in the ash of potato plants increases in the growing season, the ash of young leaves being richest. Only about 10% of the total magnesium exists in the chlorophyll. In culture experiments a low percentage of phosphorus in the solution led to a high magnesium content in the ash. Experiments were also conducted with Japanese millet. Lack of magnesium led to early chlorosis rather than to ageing.

CHEMICAL ABSTRACTS.

**Cell-sap concentration and transpiration related to age and development of cotton leaves.** F. M. EATON (J. Agric. Res., 1930, 40, 791—803).—In leaves of the Pima variety of Egyptian cotton the osmotic concentrations decrease with age, the f.p. depression falling from 1.57° for leaves 74 days old to 1.10° for leaves 10 days old. The electrical conductivity rises for leaves from 82 to 62 days old and then falls for progressively younger leaves.

P. G. MARSHALL.

**Transport of nitrogenous substances in the cotton plant. IV. Lability of the nitrogen compounds of the bark.** E. J. MASKELL and T. G. MASON (Ann. Bot., 1930, 44, 234—267; cf. this vol., 507).—The crystalloid-protein-nitrogen ratio of the bark, unlike that of the leaf, shows a marked lability. A diminished sugar concentration, produced by ringing, induces an increase in the proportion of crystalloid nitrogen in the bark, whilst desiccation causes a conversion of the crystalloid nitrogen into the protein-nitrogen but the concentration of the former does not diminish. When the initial concentration of the crystalloid nitrogen in the bark is greater than the average, a rapid conversion into protein-nitrogen generally occurs, mainly through the conversion of asparagine and the amino-acids in the inner and middle zones of the bark which are chiefly composed of sieve tubes and rays. A diurnal variation and the accumulation of total nitrogen in the bark, wood, and leaves above a ring are established. Unless rapid adjustments of the crystalloid-protein-nitrogen ratio occur in ringing experiments when the initial concentration of the crystalloid nitrogen is high, the resultant changes in the nitrogen concentrations are determined by the sugar concen-

trations. Radial spread from the sieve tubes into other tissues of the bark appears to be greater for nitrogen than for sugars.

C. C. N. VASS.

**Dynamics of carbohydrates in fruits in the course of development and ripening on the tree.** A. J. KOKIN (Biochem. Z., 1930, 221, 17—28).—Different fruits are characterised by a particular content of dextrose, laevulose, and sucrose. Thus peaches have a high sucrose (7.29 and 8.48% for Elberta and Champion respectively), a low dextrose (1.6%), and a mean laevulose content (2.32 and 4.5% respectively). Apples have a low sucrose (1.14%), low dextrose (1.62%), and a high laevulose content (9.26%). Ripe plums contain 7.6% of sucrose, 5.62% of dextrose, and 2.04% of laevulose. The dextrose content of peaches and apples decreases during ripening, but in plums it increases to 5.6%. The laevulose content of all the fruits examined increased during ripening. The sucrose content is very small in the early stages of development, but increases until it forms the chief sugar except for the apple, in which it never exceeds 1.5%.

P. W. CLUTTERBUCK.

**Effect of dormant pruning on the carbohydrate metabolism of *Vitis vinifera*.** A. J. WINKLER (Hilgardia, 1929, 4, 153—173).—The total carbohydrates of the vine normally exhibit maxima both in the dormant season and in the early summer. Data indicating the diminution in total and reducing sugars caused by pruning are recorded.

CHEMICAL ABSTRACTS.

**Selection characters as correlated with percentage of sucrose, weight, and sucrose content of sugar beet.** D. A. PACK (J. Agric. Res., 1930, 40, 523—546).—Examination of numerous beet samples revealed a negative and significant correlation between the percentage of sucrose and the weight of the beet, and a positive significant correlation between the percentage of sucrose and the sucrose content. Partial correlation coefficients for the weight of beet and percentage of sucrose with the more important selection characters were determined and discussed from the point of view of their use in the selective breeding of beet.

A. G. POLLARD.

**Inheritance of composition of Washington Navel oranges of various strains propagated as bud variants.** E. M. CHACE and C. G. CHURCH (U.S. Dept. Agric. Tech., Bull. 1930, No. 163, 22 pp.).—Differences in the chemical composition of different strains of the same variety of oranges exist and are inheritable; some are connected with physical differences. Variation usually occurs in the quantities of peel, oil, insoluble solids, and acid; less variation occurs in the d of the fruits, and in the soluble solids and sugar of the juice. Smooth-skinned strains usually contain small amounts of oil.

E. HOLMES.

**Polar permeability.** L. BRAUNER (Ber. deut. bot. Ges., 1930, 48, 109—118).—The permeability of the testa of horse chestnut (*Aesculus hippocastanum*) to water is examined and discussed.

F. O. HOWITT.

**Concentration effect with *Valonia*: potential differences with concentrated and diluted seawater.** E. B. DAMON and W. J. V. OSTERHOFF (J.

Gen. Physiol., 1930, **13**, 445—457).—An equation is given showing the *P.D.* between the interior of a cell and concentrated or diluted sea-water applied externally, and experiments with various concentrations of sea-water are recorded.

T. R. SESHADRI.

**Stempell's phenomenon in Liesegang rings.** W. W. SIEBERT (Biochem. Z., 1930, **220**, 487—492).—The distortion of Liesegang rings found by Stempell (Biol. Zentr., 1929, **49**, H. 10) to be produced by emanation from minced onion is also produced by substances which are volatile or emit volatile products (e.g., formaldehyde, acetaldehyde, garlic, asafœtida) and is a chemical, not a mitogenetic, phenomenon.

W. MCCARTNEY.

**Anatomical development of the apple and some observations on the "pectic constituents" of the cell walls.** U. TETLEY (J. Pomology, 1930, **8**, 153—172).—Micro-chemical examination of the cell walls of a number of varieties of apples, using a ruthenium-red stain, indicates that no direct staining is obtainable in the early stages of apple development, unless the tissues have been treated with sodium or potassium hydroxide. It is concluded that the discs, crescents, and bands of stained "pectic" material described by Carré and Horne (A., 1927, 704) are caused only by accumulations of this material round pits in the cell wall seen from different angles.

E. HOLMES.

**Pectin. V. Hydrolysis of pectin.** A. G. NORMAN and J. T. MARTIN (Biochim. J., 1930, **24**, 649—660).—Pectin hydrolyses rapidly at 100° with 0.5% or 0.2% alkali, the rupture of the pectin ring proceeding faster than the destruction of furfuraldehyde-yielding groups and apparent decarboxylation. The carbon dioxide yield is higher than can be accounted for from the uronic acids present. This may be due to the presence of certain dienolic fission products of sugars. Mild hydrolysis increases the furfuraldehyde yield due to simple decarboxylation of uronic acids with the production of pentose. Despite this decarboxylation an increase of carbon dioxide yield takes place, owing to the formation of non-uronic degradation products of unknown composition yielding carbon dioxide. A polyuronide derivative of pectin containing 57% of uronic anhydride was prepared by alkaline hydrolysis of pectin.

S. S. ZILVA.

**Seed of *Tetrapleura Thoningii*.** J. PIERAERTS and G. TANRET (Bull. Soc. Chim. biol., 1930, **12**, 457—463).—The seeds of *Tetrapleura Thoningii*, a leguminous tree of West Africa, consist of (1) a spermoderm containing cellulose and a small quantity of a pentosan (araban), (2) a horny layer containing galactomannan of various degrees of polymerisation, and (3) the embryo and cotyledons, free from starch, containing relatively large quantities of fat, some reducing sugar and considerable quantities of stachyose and sucrose.

W. O. KERMACK.

**Non-volatile constituents of *Mentha piperita*.** H. A. BRAUN (Amer. J. Pharm., 1930, **102**, 202—219).—Dried leaves of *Mentha piperita* contain water (6.2%), ash (6.8%), and pentosan (7.1%). Alcohol dissolves 26.2% of the leaves including 0.19% of volatile oil. The non-volatile portion of the extract

was separated into tar, resins, fatty oil, and water-soluble matter (A). The following were isolated from the fatty oil after alkaline hydrolysis: linolenic, oleic, palmitic, stearic, and melissic acids, an acid,  $C_{18}H_{36}O_2$ , m. p. 100—101° (silver salt), glycerol, a hydrocarbon, m. p. 69—69.5°, possibly hentriacontane, and phytosterol. The water-soluble matter (A) contained potassium nitrate, hesperidin, rhamnose, dextrose, betaine, tannin, a substance containing 39—40% of ash, a substance (29.2% of ash) which intumesced when heated, and a phytosterolin, m. p. 279° (acetate, m. p. 167—168°). The results are compared with those obtained for *Mentha aquatica* (Gordon, B., 1928, 799).

H. E. F. NOTTON.

**Essential oil of green violet leaves.** H. WALBAUM and A. ROSENTHAL (Ber. Schimmel, 1929, 209—218; Chem. Zentr., 1930, i, 298—299).—The oil had  $d^{20}_D$  0.9038,  $n^{20}_D$  1.47446,  $\alpha_D$   $-1^\circ 22'$ , acid value 2.8, saponif. value 71.0, and was probably nonadien-aldehyde.

A. A. ELDRIDGE.

**Mignonette oil.** H. WALBAUM and A. ROSENTHAL (Ber. Schimmel, 1929, 219—221; Chem. Zentr., 1930, i, 299).—Oil from the stems, leaves, and flowers contains sulphur; probably phenylethylthiocarbimide is present.

A. A. ELDRIDGE.

**Volatile oils in plant economy.** F. E. MARSH and W. K. MAUS (J. Amer. Pharm. Assoc., 1930, **19**, 344—348).—The germicidal action of 19 essential oils on *B. anthracis*, *B. typhosus*, *B. coli communis*, and *S. pyogenes albus* is described. There is only slight difference in the relative germicidal powers of oils from various plant organs; the fruit oils are the most germicidal, followed in order by those from leaves and flowering tops, leaves, and flower. The oils produced by glandular trichomes are relatively more germicidal than those produced by internal glands.

E. H. SHARPLES.

**Seeds of *Caesalpinia Bonducella*, Flem. I.** M. C. T. KATTI. **II. Fatty oil.** M. C. T. KATTI and S. V. PUNTAMBEKAR (J. Indian Chem. Soc., 1930, **7**, 207—220, 221—227).—I. The alcoholic extract of the kernels contains bonducin, a bitter, acid, resinous mixture of indefinite m. p. (cf. Bacon, A., 1907, ii, 500); palmitic, stearic, oleic, and linoleic acids, together with small amounts of unsaturated acids of lower mol. wt. than oleic acid, and (probably) lignoceric acid; ipuranol, m. p. 289—290°; and an unknown phytosterolin, m. p. 234—235°; sitosterol, m. p. 132—133°, and an unknown sterol, m. p. 122—123° (acetate, m. p. 109—111°); an unsaponifiable unsaturated oil; sucrose, saponin, and a little dextrose.

II. The oil obtained by extracting with light petroleum the residue from the extraction of the powdered kernels with alcohol contains, in addition to the glycerides found by Godbole, Paranjpe, and Shrikhande (A., 1929, 961), lignoceric acid, sitosterol, the sterol of m. p. 122—123° (see above), and heptacosane, m. p. 58—59° (cf. Power and Tutin, A., 1908, ii, 59).

H. A. PIGGOTT.

**Crystalline coloured wax.** R. KUHN, A. WINTERSTEIN, and W. KAUFMANN (Naturwiss., 1930, **18**, 418).—The crystalline red dye from the calyx of *Physalis* yields on alkaline saponification 2 mols. of



palmitic acid and 1 mol. of a polyene dye (m. p.  $202^{\circ}$ ), isomeric with xanthophyll, from which, by the action of 2 mols. of palmityl chloride in pyridine, the wax  $C_{75}H_{116}O_4$  (m. p.  $97^{\circ}$ ) is regenerated. It is conceivable that the physiological behaviour of carotene derivatives may be connected with the esterification of hydroxyl groups.

W. R. ANGUS.

**Biochemistry of plant fats.** S. IVANOV (Biol. Gen., 1929, 5, 579—586).—Determinations of iodine value showed that different species of the same genus of plants grown under similar climatic conditions showed a similar content of unsaturated fatty acids in the fatty oils. Oils containing glycerides of unsaturated acids with one double linking are indifferent to climatic changes, whilst in those with three double linkings the iodine value decreased with rise of temperature or more southerly location.

#### CHEMICAL ABSTRACTS.

**Amount of sorbitol in the rowan.** G. TANRET (Bull. Soc. Chim. biol., 1930, 12, 541—543).—The ripe fruit yields approximately 60—70 g. of sorbitol per kg. or about 30—40% of the total soluble matter. Unripe fruit contains less sorbitol.

W. O. KERMACK.

**Constituents of fruits of *Sorbus commixta*, Hedlund.** Y. ASAHINA and H. SHINODA (J. Pharm. Soc. Japan, 1930, 50, 1—7).—Sorbitol, a substance resembling sorbic acid, and probably phytosterol and wax are present.

#### CHEMICAL ABSTRACTS.

**Natural anthocyanin pigments. I. Magenta flower pigment of *Antirrhinum majus*. II. Magenta flower pigment of *Primula polyanthus*.** R. SCOTT-MONCREIFF (Biochem. J., 1930, 24, 753—766, 767—778).—I. The pigment *antirrhinin* was isolated by a modification of Willstätter and Zollinger's method (A., 1917, i, 45), the extraction being carried out with methyl-alcoholic hydrochloric acid. The pigment was purified by precipitation of the lead salt from the crude alcoholic extracts and subsequent decomposition with glacial acetic acid. The pure chloride of antirrhinin,  $C_{27}H_{31}O_5Cl$ , was obtained in four hydrates each possessing a characteristic crystalline form. The sugar-free pigment was identified as cyanidin chloride. Antirrhinin is a 3-rhamnoglycoside of cyanidin and is probably identical with the pigment keracyanin from the fruit of the cherry, but differs from sambucin from the elderberry. The identification of antirrhinin as a cyanidin compound contradicts the theory of a simple relationship between this pigment and the ivory flavone apigenin which is indicated by a study of the Mendelian factors for flower colour in *Antirrhinum*.

II. The pigment, *primulin*, was extracted with dilute hydrochloric acid and purified as the picrate (cf. Willstätter and Zollinger, A., 1915, i, 285). The chloride of primulin,  $C_{23}H_{25}O_{12}Cl$ , has been identified as 3-monoglucosidylmalvin chloride together with traces of a lower methylated compound. A comparison of the properties and reactions of the chlorides of primulin and cenin and of the sugar-free pigments primulin,  $C_{17}H_{35}O_7$ , cenin, and malvidin shows that although of nearly the same constitution the first two are not identical. Primulin furnishes the same aglucone as the pigments of *P. viscosa* and *P. integrifolia*,

but differs from them in the nature and position of attachment of its glucosidal residue. S. S. ZILVA.

**Constituents of derris and "cube" roots other than rotenone.** E. P. CLARK (Science, 1930, 71, 396).—A number of crystalline substances has been obtained from derris roots. Three compounds always predominate: they are toxicarol; a green compound, m. p.  $171^{\circ}$ , isomeric with rotenone; and a dimethoxy-compound,  $C_{23}H_{22}O_7$ , m. p.  $198^{\circ}$ , which may be tephrosine. "Cube" roots yield these two last-named compounds together with a yellow, crystalline, dimethoxy-compound,  $C_{22}H_{20}O_6$ , m. p.  $217^{\circ}$ . The yields of these compounds (4—5%) are much higher than that of rotenone. L. S. THEOBALD.

**Nitrogenous derivatives of piceoside.** J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 441—448).—The following derivatives of piceoside (see this vol., 258) are described: *phenylhydrazone*,  $C_{20}H_{24}O_6N_2$ , m. p.  $185^{\circ}$ ,  $[\alpha]_D -63.65^{\circ}$  in alcohol; *oxime*,  $C_{14}H_{19}O_7N$ , m. p.  $228^{\circ}$ ,  $[\alpha]_D -77.01^{\circ}$  in water; *semicarbazone*,  $C_{15}H_{21}O_7N_3$ , m. p.  $220^{\circ}$ ,  $[\alpha]_D -77.98^{\circ}$  in water. Experiments on the hydrolysis of these three compounds by dilute sulphuric acid and emulsin are recorded.

W. O. KERMACK.

**Chemical aspect of the drying of timber.** W. G. CAMPBELL and J. BOOTH (Biochem. J., 1930, 24, 641—648).—Air- and kiln-drying of wood decreases the total pentosans, but increases the cellulose-pentosans and the lignin. Oven-drying increases lignin and causes a slight amount of hydrolysis of the carbohydrate components which is more marked in the heartwood. Well-regulated kiln-drying treatment of timber is strictly comparable in effect to ordinary air-drying. Softwoods can be kiln-dried with greater ease than hardwoods because of their lower pentosan content.

S. S. ZILVA.

**Action of  $\alpha$ - and  $\beta$ -rays on protoplasm.** (FRL.) N. FEICHTINGER (Naturwiss., 1930, 18, 252—257).—Polonium and radium-E were employed as sources of  $\alpha$ - and  $\beta$ -rays, respectively. The radiating strengths of the  $\alpha$ - and  $\beta$ -rays were respectively equivalent to 0.0027 and 0.094  $\mu$ g. of radium: the period of irradiation was from 5 to 48 hrs. After irradiation of germinated seeds of *Crepis virens* some were fixed, stained with iron hæmatoxylin, and examined, whilst others were planted and their growth was compared with the growth of non-irradiated seeds planted at the same time. After 18 days the plants from seeds irradiated with  $\alpha$ -rays were much larger than the control plants, whilst the plants from the seeds irradiated with  $\beta$ -rays were very much smaller.

W. R. ANGUS.

**Action of ultra-violet rays on the germination of seeds and the growth of plants.** G. MEZZADROLI and E. VARETON (Atti R. Accad. Lincei, 1930, [vi], 11, 316—320).—Ultra-violet rays of wave-length less than 3000 Å. exert a harmful influence on the germination of seeds and on the growth of plants. Short exposures to the total rays from a quartz mercury-vapour lamp stimulate, but long exposures injure, germination and growth.

T. H. POPE.

**Prolonged effect on *Digitalis purpurea* of exposure under ultra-violet-transmitting glass.**

A. MCCREA (Science, 1930, **71**, 346).—Permanent benefit results from exposure during seedling development under glass affording increased transmission to ultra-violet radiation. L. S. THEOBALD.

Action exerted by ultra-short electromagnetic waves on the catalase activity of seeds. G. MEZZADROLI and E. VARETON (Atti R. Accad. Lincei, 1930, [vi], **11**, 429—432).—The ultra-short waves ( $\lambda$  2—3 metres) emitted by a radio-oscillator exert a favourable effect on the germination of barley and bean seeds, which show enhanced catalase activity during the early days of germination.

T. H. POPE.

X-Ray analysis of cotton fibres. G. L. CLARK, L. W. PICKETT, and W. K. FARR (Science, 1930, **71**, 293—294).—X-Ray investigation of the fibres of *Gossypium hirsutum* at various growth intervals (up to 55 days) by the diffraction method show that in all cases the patterns indicate a crystalline condition which, however, becomes more perfect with age. A progression in fibering, in micellar size, and in the dimensions of the unit crystal cell has been traced.

L. S. THEOBALD.

Relationship of environmental factors to growth and pathogenicity to sugar-cane of *Pythium* isolated from roots. H. H. FLOR (Phytopath., 1930, **20**, 319—328).—*Pythium* from sugar-cane grew well in culture solutions of  $pH$  5.3—9.2, but did not survive at  $pH$  4.6. *Pythium* injury increased with soil moisture content but decreased with rising temperature.

A. G. POLLARD.

Apparent destruction of coniferous wood by the larva of the common beetle (*Hylotrupes bajulus*, L.). R. FALCK (Cellulosechem., 1930, **11**, 89—91).—A piece of fir-wood, which had been attacked by this larva alone, was divided into two portions, the fine powder from the bore-holes and the wood surrounding these holes. Analyses showed that no lignin or resin, but about 21% of the combined cellulose and hemicellulose had been utilised by the larva. Since no discoloration or damage to structure had occurred, it is suggested that the lignin-cellulose complex, pre-existing in the original wood, remains unchanged.

T. H. MORTON.

Manometric determination of the carbon dioxide content of gas mixtures. H. A. KREBS (Biochem. Z., 1930, **220**, 250—252; cf. Warburg and Kubowitz, A., 1929, 109).—The carbon dioxide content of gas mixtures containing 0.10—10.0 vol.-% of carbon dioxide can be determined by means of an apparatus which consists of a specially-constructed flask connected to a manometer containing lead perchlorate solution. The gas is absorbed in the alkaline liquid resulting from the mixture of solutions of potassium permanganate and sodium iodide.

W. MCCARTNEY.

Use of the Barcroft apparatus for measuring tissue respiration. M. DIXON and K. A. C. ELLIOTT (Biochem. J., 1930, **24**, 820—833).—The usual method for absorbing the carbon dioxide evolved in respiration experiments in the Barcroft apparatus is not trustworthy because of the insufficient rate of absorption

of the carbon dioxide by the alkali present. A modification of the apparatus, overcoming this difficulty, is described which consists of the introduction of a sheaf of filter-paper moistened in alkali solution in the absorption tube. Experiments on the extent to which diffusion effects may limit the results obtained when the Barcroft apparatus is used for measuring velocities of oxygen uptake are described and discussed.

S. S. ZILVA.

Electron equilibria in biological systems. III. A vacuum-tube static voltmeter which eliminates minute polarisation currents. H. KAHLER, F. DE EDS, S. ROSENTHAL, and C. VOEGTLIN (Amer. J. Physiol., 1929, **91**, 225—237).—With a thin glass electrode the current is best measured with vacuum-tube voltmeter.

E. BOYLAND.

Apparatus for evaporation of liquids in a test-tube. M. A. LOGAN (J. Biol. Chem., 1930, **86**, 761—764).—Rapid evaporation of biological fluids is obtained by blowing a current of hot air on to the surface of the fluid which is contained in a test-tube and maintained close to the b. p.

C. R. HARRINGTON.

Testing of ampoule glass for alkalinity. C. STICH (Pharm.-Ztg., 1930, **75**, 482).—The ampoules are filled with very dilute hydrochloric acid containing methyl-red and heated in a boiling water-bath for 15 min., after which the colour of the acid is examined.

W. O. KERMACK.

Absorption ratios of biological stains. W. C. HOLMES and A. R. PETERSON (Stain Tech., 1930, **5**, 65—72).—The "absorption ratio" is the ratio of the extinction coefficients of a solution of a dye at two specific wave-lengths. If the wave-lengths are selected on opposite sides of the absorption maximum of the dye the absorption ratio defines the spectral position of the absorption band. If they are selected on the same side of the maximum the ratio defines the gradient of the slope of the band within the region of measurement. The absorption ratio affords a means of differentiating between different dyes, and the ratios of about 500 biological stains have been measured.

H. W. DUDLEY.

Electrometric determination of calcium-ion concentration. M. LE BLANC and O. HARNAPP (Z. Elektrochem., 1930, **36**, 116—117).—The combination  $Zn|ZnCl_2||CaCl_2|Ca|CaCl_2$  solution is not suitable for the determination of the calcium-ion concentration in blood; too long a time (7—8 weeks) is required for the establishment of equilibrium, and a slow replacement of calcium ions by zinc takes place; in 0.01—0.005N-solutions about 43% of the calcium ions are thus removed from the solution.

H. F. GILLBE.

Determination of organic nitrogen in liquids. R. B. SANDIN and N. M. STOVER (Canad. J. Res., 1930, **2**, 264—266).—The liquid (urine, milk, beer) is heated with a mixture of sodium and potassium hydroxides in a copper tube in a current of natural gas. The ammonia evolved is passed through a trap and absorbed in boric acid solution. The values found are almost identical with those obtained by the Kjeldahl method.

H. BURTON.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

AUGUST, 1930.

### General, Physical, and Inorganic Chemistry.

**Hydrogen atom in the Stark effect.** F. G. SLACK (Physical Rev., 1930, [ii], 35, 1170—1176; cf. A., 1927, 391).—Theoretical. Characteristics of the hydrogen atom wave function, which show the statistical distribution of electronic charge with respect to the nucleus and electric field, are computed for the first five quantum states; results are tabulated, and are represented graphically for one state. The average co-ordinates of the electronic charge are computed and tabulated.

N. M. BLIGH.

**Third order Stark effect for the hydrogen series lines  $H_\beta$  and  $H_\gamma$ .** R. GEBAUER and H. R. VON TRAUBENBERG (Z. Physik, 1930, 62, 289—299).—Hydrogen canal rays were exposed to the radiation of a strong perpendicular electric field of 947,600 volts/cm. The Stark effect for the hydrogen series lines  $H_\beta$  and  $H_\gamma$  was observed and measured. The results thus obtained were compared with those calculated by Schrödinger's theory. The accuracy of the method was so great that it was possible to compare the third order Stark effect in this way. For very strong fields in the neighbourhood of the limit of existence of excited atoms (about  $10^6$  volts per cm.) there was satisfactory agreement between theory and experiment for the lines considered. There were, however, certain systematic deviations from theory for the highest fields which can be explained by a Stark effect of the fourth order.

A. J. MEE.

**Ionisation of hydrogen by single electron impact.** W. BLEAKNEY (Physical Rev., 1930, [ii], 35, 1180—1186).—Available evidence on the ions produced by electron impact in hydrogen had failed to show that any ion other than  $H_2^+$  results from single electron impact. Using a method previously described (cf. A., 1929, 970) the primary ions in hydrogen were investigated. Results indicate the formation of  $H_2^+$  at  $15.4 \pm 0.1$ ,  $H^+$  at  $18.0 \pm 0.2$ , and  $H^+$  at 26—30 volts, the last having various amounts of kinetic energy, and are in agreement with an analysis of the theoretical potential energy curves (cf. Condon, A., 1929, 120). Curves showing the relative number of each of these types of ions indicate, at the higher velocities, about 92, 1, and 7%, respectively. A curve for the probability of ionisation for all types together as a function of the electron velocity shows a well-defined maximum at 60 volts.

N. M. BLIGH.

**Relation between the continuous and the many-lined spectra of hydrogen.** Y. HUKUMOTO

(Nature, 1930, 125, 975).—Certain band groups of the many-lined spectrum in the visible region are often strong when the continuous spectrum is intense. In the ordinary discharge tube this continuous spectrum is very intense at high pressure (5—8 cm. of mercury) and is accompanied by the band groups of the triplet system of the hydrogen molecule in greater intensity than the other many-lined spectrum.

L. S. THEOBALD.

**Combination series of helium.** Y. ISHIDA and T. TAMURA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 13, 115—134).—The positions of normally forbidden lines which appear in the presence of an electric field are determined. The lowest field at which any forbidden line appears is also determined. The intensity of this critical field decreases with increasing total quantum number. There is no obvious connexion between critical field strength and azimuthal quantum number, but a smooth curve is obtained if the critical field strength is plotted against change in azimuthal quantum number.

A. B. D. CASSIE.

**Application of the Stern-Gerlach experiment to the study of active nitrogen.** L. C. JACKSON and L. F. BROADWAY (Proc. Roy. Soc., 1930, A, 127, 678—689).—With the object of obtaining definite evidence as to the nature of the chemically active constituent of active nitrogen, a stream of active nitrogen was investigated by the Stern-Gerlach method. The nitrogen was activated by means of a condensed electric discharge and the presence of the beam recorded by the use of silver nitrate as indicator. The whole of the apparatus used, except for the electrodes and screen carrier, was constructed of pyrex glass. The results obtained indicated that the entity producing the trace on the silver nitrate screen had a magnetic moment such that the splitting was  $mg = \pm 1/3$ , and it is shown that this must be due to the nitrogen atom in the metastable  $2P_{1/2}$  state. No evidence was found for the presence of atoms or molecules in other states. The results support the theory of Cario and Kaplan (this vol., 124) that the production of the 11.5-volt excited nitrogen molecules of the after-glow is due to an interaction between a metastable molecule in the  $^3\Sigma$  state (8 volts) and a metastable nitrogen atom in the  $^2P$  state (3.5 volts). The fact that the  $^2P$  metastable state was recorded whether the discharge tube was run under conditions which gave the after-glow or in the glowless state when the walls were catalytically active indicates the correctness of the suggestion of Cario and Kaplan

(*loc. cit.*) that the absence of the after-glow is due to the deactivation of the metastable  $^3\Sigma$  molecules by the walls of the tube. L. L. BIRCUMSHAW.

**Zeeman effect of the lines of neon isotope Ne<sup>22</sup>.** H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1930, 6, 143—145).—A magnetic field which separates the normal components of the Ne<sup>20</sup> triplet line by half fringe intervals was used. When this magnetic field is applied, fringes due to triplet lines do not become more numerous, but are all displaced one half fringe interval. Fringes due to Ne<sup>22</sup> did not alter their position relative to Ne<sup>20</sup> fringes when this magnetic field was applied; *i.e.*, the Zeeman effect is the same for both isotopes.

A. B. D. CASSIE.

**Stark effect in the ultra-violet spectrum of neon.** Y. ISHIDA (Nature, 1930, 125, 970).—The principal changes accompanying the Stark effect in the ultra-violet spectrum of neon are recorded.

L. S. THEOBALD.

**Hyperfine structure in neutral manganese, Mn I.** H. E. WHITE and R. RITSCHL (Physical Rev., 1930, [ii], 35, 1146—1160).—The hyperfine structure patterns of about 40 lines in the Mn I spectrum were photographed, and results are tabulated. Vector diagrams are drawn for the space quantisation of each valency electron with respect to the nucleus, and hyperfine structure terms are computed (cf. this vol., 265). The normal  $^6S_{5/2}$  ( $3d^5 4s^2$ ) state is narrow, and the metastable  $^6D$  ( $3d^5 4s$ ) terms show the widest separations. The hyperfine structure is determined primarily by the coupling between the 4s electron and the nucleus, but the remaining valency electrons must be taken into account. The hyperfine structure formula (cf. Goudsmit, this vol., 265) is extended to include the spins of all the valency electrons and their *l* values; coupling constants for each electron are computed.

N. M. BLIGH.

**Change of wave-length and intensity in iron lines by disruptive discharge.** H. NAGAOKA, T. FUTAGAMI, and I. MACHIDA (Proc. Imp. Acad. Tokyo, 1930, 6, 146—149).—A condenser of 1.5 microfarads was charged until an air-gap of 1 cm. between wedge-shaped electrodes of electrolytic iron broke down. This gave an explosive discharge, the emitted radiation from which was examined by a concave grating. The iron lines are shifted from their normal wave-lengths, and their intensities are changed. Photographs showing these changes are reproduced.

A. B. D. CASSIE.

**Band spectra of zinc and cadmium vapours.** S. MROZOWSKI (Z. Physik, 1930, 62, 314—330).—The absorption spectra of zinc and cadmium vapours were investigated and compared with the spectrum of mercury. In the zinc spectrum a band series discovered by Mohler and Moore was confirmed and its convergence limit found. The effect of heat on the band fluorescence of cadmium vapour was also investigated and the best conditions for obtaining the band emission of zinc and cadmium vapours by electric discharge were found. The spectra were ordered by using data already available and by applying two general assumptions, *viz.*, that the formation of the bands is due to diatomic molecules

which possess a van der Waals linking, and that the selection rule for atomic transitions holds with approximate accuracy for these molecules. In this way the molecular levels can be calculated. Regularities appearing in the mercury spectrum were also found in the spectra of zinc and cadmium.

A. J. MEE.

**Mean lives of lines of mercury triplet  $2^3P_{012}$ — $2^3S_1$ .** R. H. RANDALL (Physical Rev., 1930, [ii], 35, 1161—1169).—The triplet was excited by simple electron impact at low voltages, and a specially designed potassium hydride photo-electric cell was used as the detecting system. Results agree with the assumption of exponential decay of radiation after impact. The lines  $\lambda 4047$  and  $\lambda 4358$  had the same life,  $5.75 \times 10^{-8}$  sec., supporting the assumption that lines from the same level have the same life. The life value for  $\lambda 5461$  was  $2.37 \times 10^{-7}$  sec., and it is suggested that this higher value may be explained by consideration of the fine structure of the  $2^3S_1$  level, in agreement with the anomalous fine structure found by Collins (cf. A., 1929, 112).

N. M. BLIGH.

**Possible origin of the band at 2540 in the spectrum of mercury vapour.** R. ROLLEFSON (Physical Rev., 1930, [ii], 35, 1177—1179).—Theoretical. The mercury 2540 Å. band can be explained on the basis of a molecule with low energy of dissociation, in agreement with the work of Koernicke (cf. A., 1925, ii, 848) on the heat of dissociation of Hg<sub>2</sub>. The high values for the heat of dissociation obtained by Mrozovski (cf. A., 1929, 860) are discussed.

N. M. BLIGH.

**Concentration of metastable mercury atoms.** E. GAVIOLA (Physical Rev., 1930, [ii], 35, 1226—1230; cf. this vol., 125).—Theoretical. The concentration of metastable atoms in presence of 3 mm. of nitrogen was recalculated from existing data, and taking into account the different statistical weights of the levels  $2^3P_1$  and  $2^3P_0$ . Corrected curves are given for the number of metastable atoms as functions of the foreign gas pressure for carbon monoxide, water vapour, nitrogen, argon, and helium.

N. M. BLIGH.

**Uniform positive column of an electric discharge in mercury vapour.** T. J. KILLIAN (Physical Rev., 1930, [ii], 35, 1238—1252).—The uniform positive column was investigated in a long cylindrical tube, using the Langmuir probe electrode method. Measurements were made of the space potentials, random electron current densities, and the electron temperatures along the axis and across a diameter of the tube at various vapour pressures. The mobility of the ions was obtained and the results are interpreted in terms of the mean free path of the electrons by Langevin's expression for mobility, the mean free paths being in fair agreement with those from angular scattering experiments. The rate of generation of positive ions was obtained and discussed. The ratio of the concentrations of electrons at any two points on a diameter satisfies the Boltzmann equation.

N. M. BLIGH.

**Absorption of resonance radiation in mercury vapour.** A. R. THOMAS (Physical Rev., 1930, [ii], 35, 1253—1261).—The theories of Malinovski and

of Wilson (cf. A., 1928, 567) for the absorption in mercury vapour of mercury resonance light of wavelength 2536.7 Å. are briefly reviewed. The absorption coefficient for resonance radiation increases as the number of absorbing atoms decreases, this being probably due to a Doppler effect in the radiating vapour. The resonance radiation from mercury vapour, used as a jet to diminish the influence of this effect, was investigated, and a series of absorption coefficient measurements of this light is given. The maximum atomic absorption coefficient is  $10.22 \times 10^{-13}$ , a value larger than has been previously observed. Malinowski's assumption that emission and absorption lines have the same width is not supported, the results favouring Wilson's theory, which regards the mercury atoms as behaving like simple linear oscillators.

N. M. BLIGH.

**Absorption of resonance lines in mercury vapour on admixture of foreign gases.** E. A. NEUMANN (Z. Physik, 1930, 62, 368—393).—The effect of the addition of different foreign gases (air, argon, helium, and hydrogen) on the total absorption of the mercury resonance lines in a layer of mercury vapour was found. The effect on the number of collisions was obtained by using the kinetic theory valuation of the diameter of the molecule of the foreign gas, and the diameter of the charged mercury atom calculated by Stuart. The diminution of the total absorption was used as a measure for the widening of the absorption lines. The collision number-absorption curves for air and argon were found to be within the experimental error, but those for helium and hydrogen deviated somewhat. An unsuccessful attempt was made to find a quantity other than the collision number into which the absorption could be brought into relationship. The differing effects of the different gases added appear to be due in some measure to the different mol. wt. either directly, or because of the resulting variations in the mean molecular velocities, and partly to the difference in field properties of the molecules.

A. J. MEE.

**Striated discharge.** D. A. KEYS and J. F. HEARD (Nature, 1930, 125, 971—972).—With discharge tubes filled with hydrogen, oxygen, helium, or neon, the variation of the striation separation,  $S$ , with the radius of the tube can be represented by the relation  $S = A + Cr^n$ , where  $A$  and  $C$  are constants depending on the nature of the gas. For hydrogen  $A$  is zero, whilst  $n$  and  $C$  appear to depend on the amount of mercury vapour present.

L. S. THEOBALD.

**Extension of Houston's and Slater's multiplet relations.** S. GOUDSMIT (Physical Rev., 1930, [ii], 35, 1325—1336; cf. Houston, A., 1929, 480; Slater, this vol., 126).—Theoretical. A simplified method is given for deriving expressions for the change in the positions of the energy levels with change in electron coupling. The type of equation for the first order perturbations to the energy is known from perturbation theory, and the coefficients are found from the known energies in extreme ( $j, j$ ), and extreme Russell-Saunders coupling. The method is illustrated for  $p^4$ ,  $p^2$ ,  $p^3$ ,  $3p+s$ ,  $d^2$ , and  $d^8$  configurations, and is extended to treatment of the Zeeman effect. The change in  $g$  values is discussed.

N. M. BLIGH.

**Resonance separations in configurations of type  $p^5s$  and  $d^9s$ .** O. LAPORTE and D. R. INGLIS (Physical Rev., 1930, [ii], 35, 1337—1341; cf. preceding abstract).—Theoretical. Houston's formulæ (cf. A., 1929, 480) are applied to the cases  $p^5s$  and  $d^9s$  with negative values of the interval factor and of the parameter describing the transition. Results of the application of the expressions thus obtained to the separations and  $g$  values of a number of spectra are satisfactory.

N. M. BLIGH.

**Singlet-triplet interval ratios for  $sp$ ,  $sd$ ,  $sf$ ,  $p^5s$ , and  $d^9s$  configurations.** E. U. CONDON and G. H. SHORTLEY (Physical Rev., 1930 [ii], 35, 1342—1346).—Theoretical. The accuracy of Houston's theory (cf. preceding abstracts, and A., 1929, 480) of the relation of the triplet interval ratio to the singlet-triplet interval for two electron configurations with one electron in an  $s$  state is examined by the application of available data, and good agreement with deviations from the Landé interval rule which accompany departure from Russell-Saunders coupling is shown. Various discrepancies are found, the most pronounced being for elements of high atomic number, and are attributed to the influence of second-order perturbations.

N. M. BLIGH.

**Properties of abnormal lines and series in atomic spectra.** H. DESLANDRES (Compt. rend., 1930, 190, 1250—1254).—A discussion of the nature and magnitude of the difference between the observed frequencies of the lines of atomic spectra and those calculated from the usual formulæ (Balmer, Rydberg, Ritz, Hicks), with special reference to magnesium, barium, helium, lithium, and sodium. The relation of the frequencies of these abnormal lines to the author's elemental frequency 1062.5 ( $d_1$ ) is indicated, and it is pointed out that the series associated with 6 multiples of  $d_1$  each include a more or less strong line which is almost a multiple of  $d_1$ , the other lines being multiples of  $d_1/2n$ , where  $n$  varies from 1 to 8. The frequencies of lines appear to change with their intensities.

J. GRANT.

**Ratio of the number of  $\text{Ca}^+$  atoms in the solar atmosphere over faculae and over corresponding parts of the solar surface near the limb.** P. KREMER (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 379—388).—Analysis of the  $H$  and  $K$  lines in the spectra of faculae by means of Unsöld's formulæ (A., 1928, 456) indicates that the number of  $\text{Ca}^+$  atoms over a facula is smaller than over a corresponding undisturbed part of the photosphere.

O. J. WALKER.

**Homochromatic spectrophotometry in the extreme ultra-violet.** G. R. HARRISON and P. A. LEIGHTON (J. Opt. Soc. Amer., 1930, 20, 313—330).—For spectrophotometry in the Schumann region plates may be rendered sensitive by coating them with fluorescent oils. Full details of the method are given and suggestions for the use of fluorescent materials for other problems of spectrophotometry are discussed.

C. W. GIBBY.

**Band spectrum of sulphur.** H. H. VAN IJDEKINGE (Nature, 1930, 125, 858).—The spectra obtained by passing a high-voltage discharge through hydrogen sulphide at a pressure of a few mm. showed the same

band spectrum in emission as was observed in absorption by Henri and by Rosen (A., 1928, 687) with the difference that the diffuse bands are absent. A second band system with maximum intensity at 2570 Å., apparently also due to  $S_2$ , has been observed.

L. S. THEOBALD.

**Scattering of X-rays by bound electrons.** B. B. RAY (Nature, 1930, 125, 856).—In passing through carbon, nitrogen, and oxygen, the copper  $K\alpha$  radiation produces the new, diffuse, and broad lines 1592, 1614, and 1643 X, which are attributed to scattering of the radiation by the elements concerned. A portion of the nickel  $K\alpha$  radiation in passing through carbon and nitrogen shows the new lines 1719 and 1746 X.

L. S. THEOBALD.

**Periodicity of elements in X-ray spectra.** V. DOLEJŠEK (Coll. Czech. Chem. Comm., 1930, 2, 380—382).—The difference between the observed and calculated values of  $\nu/R$  (cf. A., 1929, 225) for all elements is a periodic function of the atomic number, varying according to the periods of the periodic system,  $\nu$  being the characteristic X-ray frequency of the element. If the values are calculated for the highest valency forms instead of for the free elements, the periodic function becomes discontinuous, changing abruptly at the end of each period and at the transition elements.

C. W. GIBBY.

**Space-distribution of X-ray photo-electrons ejected from the  $K$  and  $L$  atomic energy levels.** C. D. ANDERSON (Physical Rev., 1930, [ii], 35, 1139—1145).—The space distribution and momentum of photo-electrons ejected from air, ethyl bromide, and methyl iodide by monochromatic X-rays were investigated by the expansion chamber method. A more isotropic space-distribution was found for electrons from the  $L$  than from the  $K$  level (cf. Auger, A., 1929, 367; Watson, this vol., 128). For a given radiation the average forward momentum of the  $K$  electrons decreased with increase in the binding energy of the parent atom, but was constant for a given velocity of ejection, and was lower than for the  $L$  energy level. Results for the  $K$  level are in fair agreement with quantum mechanics. N. M. BLIGH.

**Polarised and directed X-radiation from a crystal.** J. STARK (Naturwiss., 1930, 18, 531).—Support is obtained for the theory that the electrons in atoms even as simple as hydrogen and helium are definitely oriented with respect to some distinct axis, by observation of the secondary  $K$ -radiation from bromine atoms consequent on the absorption of primary X-radiation by monoclinic  $\gamma\gamma$ -dibromoanthracene crystals. At one position perpendicular to the axis of the crystal the intensity of the secondary  $K$ -radiation of the bromine atoms is greater than at smaller angles in other directions. This radiation is also polarised, in that the electric vector parallel to the axis is 20% greater than that perpendicular to it. It is concluded that the axes of the molecules in the dibromoanthracene crystals lie parallel to one another, that the valency axes of the bromine atoms are also parallel, and that the electrons of the first two shells in the bromine atom, to which the  $K$ -radiation is due, lie in a definite position with respect to one axis.

J. W. SMITH.

**Transmission of rapid corpuscular rays through matter.** H. BETHE (Ann. Physik, 1930, [v], 5, 325—400).—Theoretical. The inelastic collision of a rapidly moving charged particle (electron, proton, or  $\alpha$ -ray) with an atom is treated according to the wave-mechanics theory of Born. A very simple method for the evaluation of the matrix elements is given and the bearing on the intensity of the Compton effect is shown. A number of calculations were made. The collision with hydrogen atoms and with more complicated atoms was calculated as far as possible, and the following were deduced: the angular distribution of inelastic and elastic scattered particles, the excitation cross-section for the excitation of optical and X-ray levels by electronic collision, the total number of inelastic and elastic collisions, the number of primary and secondary ions formed, the velocity distribution of secondary electrons, and the deceleration of the colliding particles. Agreement with experiment is satisfactory.

A. J. MEE.

**$K$ -Ionisation capacity of rapidly moving electrons.** F. WISSHAK (Ann. Physik, 1930, [v], 5, 507—552).—The purpose of the work was to determine experimentally the number of atoms ionised in the  $K$  shell by the transmission of rapid electrons through matter. In this way, the number of atoms ionised in the  $K$  shell is obtained as a function of the energy of the colliding electrons and the atomic number of the atoms, and it may be obtained in absolute value from intensity measurements of the  $K\alpha$  lines of chromium, copper, molybdenum, and silver. The details of the apparatus and method are given. The result is compared with the theory of J. J. Thomson and an empirical formula due to Webster (A., 1928, 678, 691).

A. J. MEE.

**X-Ray spectrum of sulphur.** O. LUNDQVIST (Nature, 1930, 125, 925—926).—The results obtained with various sulphides and sulphates using aluminium as the anticathode are discussed and compared with those previously obtained with copper. Of the sulphides examined only copper sulphide maintains its characteristic  $\beta$ -doublet unchanged on the aluminium cathode, whilst of the sulphates only that of copper has the same structure on aluminium and copper anticathodes.

L. S. THEOBALD.

**Fluctuation in the ionisation of earth gases in Siberia over a period of years.** (FRL.) M. ORLOVA, G. HODALEVITSCH, and N. LJAMIN (Physikal. Z., 1930, 31, 585—589).—The work of Orlov in 1913 is compared with results which the authors have obtained during 1927—1928. The method of obtaining the gas and measuring the ionisation is discussed. In winter the ionisation is much higher than in summer. The dependence of ionisation on the pressure and temperature of the gas is considered.

W. R. ANGUS.

**Electronic conduction and ionisation in crossed electric and magnetic fields.** N. MINORSKY (J. Franklin Inst., 1930, 42, 757—775).—Mathematical.

W. E. DOWNEY.

**Photo-electric and thermionic properties of platinum-coated glass filaments.** A. K. BREWER (Physical Rev., 1930, [ii], 35, 1360—1366).—Using a



new method for the production and control of positive ions (cf. Cottrell and others, *J. Opt. Soc. Amer.*, 1930, 20, 152), the photo-electric and thermionic properties of platinum-sputtered glass filaments were investigated with special reference to temperature effect and to electrolysis of potassium through the glass to or from the sputtered coating. When electrolysis is away from the surface the photo-electric threshold is independent of the temperature up to  $450^{\circ}$ , and towards the surface up to  $260^{\circ}$ , its value being  $2720 \text{ \AA.}$ ; in the latter case it shifts towards the red with rise of temperature, reaching a maximum of about  $4300 \text{ \AA.}$  at  $410^{\circ}$ . Electrolysis produces identical effects on the photo-electric and thermionic emissivity for electrons, and also on positive ion emission, when, in addition, a maximum emissivity occurs for a specific electrolysis potential. Ultra-violet radiation has no effect on the thermionic emission of electrons or positive ions from this type of filament. N. M. BLIGH.

**Rôle of the core metal in oxide-coated filaments.** E. F. LOWRY (*Physical Rev.*, 1930, [ii], 35, 1367—1378).—Temperature-power relations were determined for oxide-coated filaments having cores of platinum-10% iridium, or of "Konel," an alloy of nickel, cobalt, iron, and titanium. Oxide-coated Konel was a much better radiator and yielded higher electron emissions; no activation was needed other than the decomposition of the alkaline-earth carbonate coatings to oxides in a vacuum. In view of the differences found for the two types of oxide filament a new theory of the mechanism of emission is suggested; it assumes that the source of emission is the composite layer formed by occlusion of alkaline-earth metal on the surface of the core, and that the electrons emitted diffuse through the interstices in the oxide coating into the vacuous space. A number of other phenomena are accounted for by this theory. N. M. BLIGH.

**Location of the *E.M.F.* in the photo-voltaic cell.** W. N. LOWRY (*Physical Rev.*, 1930, [ii], 35, 1270—1283; cf. Russell, A., 1928, 1306).—The *E.M.F.* of the photo-voltaic cell has been attributed to an illumination effect of the electrode-electrolyte boundary, or to a modification of the electrolyte with light. A modified form of the cell devised by Murdock (cf. *Trans. Faraday Soc.*, 1927, 23, 593) and a four-element vacuum tube, adapted to measure small *P.D.*, were used. The photo-voltaic *E.M.F.* appears to be due to a modification of the electrolyte; there was no evidence of any effect due to direct illumination of the electrode or the electrode-electrolyte boundary region. In certain circumstances the current cannot be regarded as proportional to the *E.M.F.*; this quantity increases with the concentration of the electrolyte. N. M. BLIGH.

**Energies of electrons in gases.** J. S. TOWNSEND (*Phil. Mag.*, 1930, [vii], 9, 1145—1173).—Recent experiments on the determination of the motion of electrons in gases with photo-electric currents (cf. A., 1923, ii, 721; Bailey, A., 1924, ii, 221; Hayman, *Phil. Mag.*, 1929, [vii], 6, 586) are discussed, and the results shown to be inconsistent with Franck and Hertz's laws of impact of an electron on a molecule

(cf. Atkinson, A., 1928, 809). In particular the suggestion that conductivity is due to impurities is regarded as untenable (cf. A., 1929, 969), and definite disagreement is demonstrated in the case of monatomic gases with the experimentally found properties of currents in wide tubes, and with the visible spectrum excited. On the assumption of the absence of any large losses of energy on collision (such as excite radiation), and neglecting variations in the amounts of such losses in other circumstances and in the mean free path, the motion of electrons due to diffusion is investigated mathematically. Wide differences in the velocities in the direction of the electric force and in amount of energy lost are shown to exist in different groups of electrons. These tend to disappear under the influence of that force. It is also shown that 18, 5, and 1% of the electrons have energies exceeding the mean by factors 1.5, 2, and 2.5, respectively.

C. A. SILBERRAD.

**Relation of electronic waves to light quanta and to Planck's law.** (SIR) J. J. THOMSON (*Phil. Mag.*, 1930, [vii], 9, 1185—1194).—An electron inside an atom consists of a core and a system of waves. Such a system if detached from the core would be a light quantum, which consists therefore of a system of electronic waves flowing round a closed circuit. It is quantised because of the necessity of having an integral number of wave-lengths round the circuit. In actual fact a light quantum is thrown off when an electron falls from a higher to a lower energy level, the excess of energy being thrown off as a separate wave system, leaving the core with the wave system appropriate to the lower level. The theory is discussed mathematically and shown to be consistent with Planck's law. C. A. SILBERRAD.

**Electron energy losses in mercury vapour.** C. W. FOARD (*Physical Rev.*, 1930, [ii], 35, 1187—1195; cf. Whitney, A., 1929, 1359).—Using an improved magnetic spectrum method giving increased sensitivity for slow electrons, and improved resolving power, the energy losses of slow electrons in mercury vapour were investigated, mainly for the region 0—25 volts. The energy losses found, below that required for ionisation, were: 4.9, 5.4, 6.7, 7.7, 8.8, and 9.8 volts, corresponding with the transitions of a valency electron from the basic 1S level up to each of the higher levels to 4P. A new loss was discovered of 11.07 volts, and it is suggested that this loss involves the simultaneous displacement of both valency electrons from their normal levels. N. M. BLIGH.

**Absorption coefficient for slow electrons in gases.** C. E. NORMAND (*Physical Rev.*, 1930, [ii], 35, 1217—1225).—In order to detect fine structure using an apparatus having a high-velocity resolving power, and to extend measurements into the low-velocity region, the absorption coefficients for 0.5—400-volt slow electrons in hydrogen, helium, argon, neon, nitrogen, and carbon monoxide were measured. Fine structure was found in each case. The absorption coefficient curves showed a minimum at velocities between 0.7 and 1.1 volts<sup>1</sup>. The discrepancy between the results and those of Ramsauer (cf. this vol., 7, 269) is explained. N. M. BLIGH.

**Electron diffraction at layers of gas adsorbed on metals.** E. RUPP (Ann. Physik, 1930, [v], 5, 453—474).—The diffraction of electrons at the surface layers of metals provides a new method for determining crystal structure. The differences between this method and the usual X-ray method are two, viz., that for slow electrons reflected from the surface layers only the first ten or so lattices come into play, and the interaction between electrons and the substance under investigation is much more intense than for X-rays. The experiments described deal with the space lattice of the top layer when hydrogen and nitrogen were adsorbed. No effect was found with argon on nickel. The following inner lattice potentials for the pure metals were found: nickel 16.5 volts, iron 14.5 volts, copper 12.8 volts, molybdenum 13.5 volts, and zirconium 10.2 volts. The inner lattice potential shows practically no change with electron velocity. If hydrogen is allowed to act on these metals they then show half-number order maxima. This occurs also with nitrogen on molybdenum, but not with the other metals, where nitrogen affects only the intensity of the maxima. A loosening of the lattice was found with the action of hydrogen on iron and nickel, and the time and temperature effects on this loosening were noted. The reaction between hydrogen and nitrogen on the surface of nickel and iron was followed. The work on copper shows that the half-number maxima for single copper crystals noted by Farnsworth (A., 1929, 861, 1212) disappear if the surface is covered with vaporised copper, but they reappear when the copper is treated with hydrogen. It is possible, therefore, that they were originally due to this cause. A. J. MEE.

**Scattering of electrons by atoms.** N. F. MOTT (Proc. Roy. Soc., 1930, A, 127, 658—665).—Mathematical. Formulæ for the scattering of electrons by atoms are deduced by methods similar to those used in calculating the scattering of X-rays by an atom, the atom being treated as a static distribution of electric charge, of density  $e|\psi(r)|^2$  at distance  $r$  from the nucleus. Good agreement between theory and experiment is found when the formula for the scattered intensity is compared with the experimental data given by Dymond and Watson for the scattering of a beam of 210-volt electrons by gaseous helium (A., 1929, 368), and by Thomson for the diffraction of 20,000-volt cathode rays by a gold foil (*ibid.*, 1209). It is considered probable that the formula gives the correct absolute magnitude of the scattering. For fast electrons and large angles it reduces to the Rutherford formula for the scattering of particles by a nucleus.

L. L. BIRCUMSHAW.

**Scattering of fast electrons and nuclear magnetic moments.** H. S. W. MASSEY (Proc. Roy. Soc., 1930, A, 127, 666—670).—Since the scattering formula obtained by Mott (A., 1929, 861) by using Dirac's wave equation is not in good agreement with experiment, the possibilities of other effects are considered. The effect of a nuclear magnetic moment is shown to be negligible, and the only explanation of the disagreement seems to be that it is due to the effect of radiation, as suggested by Mott.

L. L. BIRCUMSHAW.

**Motion of slow positive ions in gases.** J. S. THOMPSON (Physical Rev., 1930, [ii], 35, 1196—1216).—Using a modified positive-ray analysis apparatus, the motion of positive 3.5—600-volt cesium ions was investigated in hydrogen and helium. A retardation, proportional to the pressure, was found in all cases, and there is an approximate probability distribution of ion energies about an average retarded value. For  $\text{Cs}^+$  ions in helium the percentage loss of initial energy varies from 11.5 for 400- to 55 for 3.5-volt ions; results for hydrogen are similar. An interpretation of the absence of scattering and the retardation of the ions is given on the basis of elastic collisions between ions and gas molecules. The data on retardation give values of 1.78 Å. in helium and 3.09 Å. in hydrogen for the radius of the  $\text{Cs}^+$  ion. The retardation of the ions explains the large absorption of  $\text{Cs}^+$  ions in helium found by Ramsauer (cf. A., 1928, 1311). The absorption of  $\text{Li}^+$  ions for velocities of 20—900 volts was investigated by three methods; the coefficients of absorption, representing the effective absorbing cross-section, were determined by two methods (cf. Cox, this vol., 269). Results have led to the interpretation of scattering in which forces other than those due to elastic collisions are effective. No general retardation of the  $\text{Li}^+$  ions was found. It is concluded that no absolute significance can be attached to values of atomic radii determined from measurements of this kind.

N. M. BLIGH.

**Ions produced by discharges at liquid surfaces.** J. J. NOLAN and J. G. O'KEEFE (Nature, 1930, 125, 893).—Using water and various alcohols, only ions having mobilities similar to those produced in air by ionising radiations could be detected (cf. Zeleny, this vol., 654).

L. S. THEOBALD.

**Deceleration of hydrogen canal rays by transmission through solid bodies.** A. ECKARDT (Ann. Physik, 1930, [v], 5, 401—428).—The deceleration of homogeneous canal rays in celluloid and metallic foils was investigated. The experiments show that there is a definite deceleration in the passage of canal rays through the foils, which for canal rays of 30—50 kilovolts and foils of 15—350  $\mu$  thickness can be expressed by the formula  $\Delta v = c\sigma$ , where  $\sigma$  is the thickness and  $c$  a constant depending on the substance. Corresponding with the decrease in velocity there is a decrease in energy which increases with the velocity of the canal-ray particles. The dependence of the decrease in velocity on the distance traversed shows that for canal rays the kinetic energy of the single particles gradually becomes absorbed.

A. J. MEE.

**Recombination of ions in air and oxygen in relation to the nature of the gaseous ions.** O. LUHR (Physical Rev., 1930, [ii], 35, 1394—1404).—Using an improved form of Marshall's apparatus (cf. A., 1929, 1210) measurements of  $\alpha$ , the coefficient of recombination of ions in air and oxygen, were continued for longer time intervals with two different initial concentrations of ions. Values of  $\alpha$ , calculated by a new system, as a function of the age of the ions instead of the total time of recombination, are plotted and discussed. Results are explained by assuming that with increasing time heavy slow-

moving ions are formed by reaction with impurities present. Owing to disturbing factors an absolute value of  $\alpha$  in air cannot be arrived at; when the effect of the former is minimal  $\alpha$  has the value  $1.4 \pm 0.1 \times 10^{-6}$ . N. M. BLIGH.

**Primary and secondary ions in oxygen and carbon dioxide.** H. D. SMYTH and E. C. G. STUECKELBERG (Holv. phys. Acta, 1929, 2, 303—304; Chem. Zentr., 1930, i, 490).—Electron impact forms from oxygen molecules the ions  $O_2^+$  and  $O^+$ ; both possess the characteristics of primary ions. In mixtures with argon, secondary  $O_2^+$  ions appeared; neon and helium produced secondary  $O^+$  ions. The potential for the formation of  $O_2^+$  from  $O_2$  is less than 15.69 volts. Between 20 and 21.6 volts  $O_2$  affords  $O^+$  by a single process. By impacts at 14.2 volts,  $CO_2$  molecules yield  $CO_2^+$  ions, and at 15.5 volts  $CO^+$  ions; other ions, apparently  $C^+$ ,  $O^+$ , and  $O_2^+$ , were also produced. A. A. ELDRIDGE.

**Scattering of particles in strong fields.** G. BECK (Z. Physik, 1930, 62, 331—351).—Theoretical. A simple scheme is given which allows some problems concerning the scattering of particles in a strong field to be solved by consideration of a typical special case. The phenomenon of particle scattering can be regarded as a resonance phenomenon of the incident particles with virtual quantum states in the continuous spectrum, and is in some respects analogous to the optical phenomena at thin layers. The theory, when applied to the potential distribution in the atom as calculated by Hartree, leads to the Holtzmark theory of the Ramsauer effect. When it is applied to the potential distribution in the nucleus as derived by Gamow, it leads to the observed anomaly of  $\alpha$ -ray scattering, in qualitative agreement with the observed results of Rutherford. It thus appears that the Ramsauer effect and anomalous scattering of  $\alpha$ -rays have really the same origin, and they may be described as resonance phenomena in the continuous energy spectrum of a potential trough. The anomalies in  $\alpha$ -ray scattering especially correspond qualitatively with the deviations which would be found in a potential trough in the nucleus. The existence of such a trough is known independently from radioactive disintegration experiments. A. J. MEE.

**Relations between rotation, heat tone, and effective cross-section of reaction in elementary chemical processes.** H. BEUTLER and E. RABINOVITSON (Z. physikal. Chem., 1930, B, 8, 231—254; cf. A., 1929, 1353).—Theoretical. A more detailed treatment of work previously described. F. L. USHER.

**Oxygen isotope  $O^{18}$ .** E. RÜCHARDT (Naturwiss., 1930, 18, 534).—On analysis of positive rays from a mixture of carbon dioxide, air, and illuminating gas by the parabola method, 14 parabolas of the first order are observed, due to singly-ionised particles, and 4 parabolas of the second order due to doubly-ionised particles. Of the latter three are due to  $C^{++}$ ,  $N^{++}$ , and  $O^{++}$ , respectively, but the fourth, of apparent mass 9, cannot be ascribed to  $Al^{+++}$  or to  $H_2O^{++}$ . It is very weak and, it is suggested, may be due to  $O^{18++}$ . The four weakest of the first order parabolas correspond with apparent masses 20, 30, 34,

and 46 and may be due to  $H_2O^{18+}$ ,  $CO^{18+}$ ,  $O^{16}O^{18+}$ , and  $CO^{16}O^{18+}$ , respectively. Reasons for the exclusion of certain other possibilities are given.

J. W. SMITH.

**At. wt. of arsenic. I. Analysis of arsenic trichloride.** J. H. KŘEPELKA (Coll. Czech. Chem. Comm., 1930, 2, 255—265).—The mean value of the at. wt. of arsenic from eleven determinations of the ratio  $AsCl_3 : 3Ag$  is  $74.935 \pm 0.001$ , mean deviations  $\pm 0.005$ , and from two determinations of the ratio  $AsCl_3 : 3AgCl$   $74.936$ , mean deviation  $\pm 0.004$ . The mean of all the values is  $74.936 \pm 0.001$ , agreeing with Aston's value  $74.934$  (Nature, 1927, 120, 956). The arsenic trichloride was prepared from pure arsenic and pure chlorine, and the middle fraction taken after four fractional distillations. C. W. GIBBY.

**Revision of the at. wt. of tantalum. Determination of the ratios  $TaBr_5 : 5Ag : 5AgBr$  and  $TaCl_5 : 5Ag : 5AgCl$ .** K. R. KRISHNASWAMI (J.C.S., 1930, 1277—1292).—Tantalum was prepared by a modification of the Berzelius-Rose method. Oxidation experiments indicated that it contained 99.2% of free tantalum and, since spectrographic examination revealed no foreign metal, the remaining 0.8% was regarded as the oxide. The halides were prepared by direct union of the elements in an atmosphere of argon and purified by distillation and sublimation in a vacuum. They were analysed nephelometrically and gravimetrically by the Harvard methods as developed by Hönigschmid. Four series of determinations, involving twenty-four experiments with closely agreeing results, indicated an at. wt. for tantalum of 181.36. M. S. BURR.

**Radiations associated with the emission of  $\alpha$ -rays from polonium.** F. JOLIOT and (MME.) I. CURIE (Compt. rend., 1930, 190, 1292—1294).—Analysis of the radiations in the authors' experiments (this vol., 130) is facilitated by decreasing the residual natural  $H$ -radiations, as a result of the use of more intense sources of polonium prepared by volatilisation on supports of degassed metals. Absorption studies with aluminium and cellophane showed that a readily absorbed  $X$ -radiation,  $(\mu/\rho)_{Al} = 1000$ , is obtained from nickel or copper; it is not due to the  $L$ -radiations of these elements. Zirconium gives a highly-penetrating radiation  $(\mu/\rho)_{Al} = 17$ , identical with the polonium  $L$ -rays. The magnitudes of the excitation yields in quanta per  $10^4$   $\alpha$ -particles were  $M$ -rays 15,  $L$ -rays 4 (from polonium),  $L$ -rays (zirconium) 50,  $K$ -rays (nickel or copper) 9. The feeble  $\beta$ -radiation of polonium is less penetrating than that of radium- $E$ . No nuclear  $\gamma$ -radiation of polonium was observed. J. GRANT.

**Probability of fluctuations in the rate of emission of  $\alpha$ -particles.** L. F. CURTISS (Bur. Stand. J. Res., 1930, 4, 595—599).—Using a counting chamber and automatic recording apparatus the deviation from a simple probability distribution of the rate of emission of  $\alpha$ -particles from polonium was investigated. Sets of observations over 6 or 7 hrs. were made when the source was adjusted to give a count of about 60 particles per min. Results showed that a freshly prepared source exhibits a subnormal dispersion, becoming normal after about 35 days, and

are in agreement with the observations of Kutzner (cf. A., 1924, ii, 226). N. M. BLIGH.

**Relation between "filiation capacity" of radioactive atoms and the velocities of the  $\alpha$ -rays they emit.** G. FOURNIER (Compt. rend., 1930, 190, 1408—1410).—If the "filiation capacities" (A., 1929, 863) of radioelements ( $U$ ) are plotted as abscissæ against the velocities ( $v$  in  $10^9$  cm./sec.) of the  $\alpha$ -particles which they emit (cf. A., 1927, 393), a line corresponding with the expression  $v=0.0818(100-U)$  is obtained which gives values in good agreement with those obtained experimentally. The formula does not apply to atoms which also emit  $\beta$ -rays. The results obtained for elements of the actinium family indicate an at. wt. of 227 for this element. J. GRANT.

**Anomalous scattering of  $\alpha$ -particles from the quantum mechanical point of view.** H. S. W. MASSEY (Proc. Roy. Soc., 1930, A, 127, 671—677).—A consideration of the anomalous scattering of  $\alpha$ -particles by light nuclei from the point of view of wave mechanics leads to the conclusion that Bieler's (Proc. Camb. Phil. Soc., 1925, 28, 181) and Hardmeier and Debye's (A., 1926, 450) theories have little significance, the classical formulæ breaking down in the case of higher power laws. By applying Born's theory of collisions (Z. Physik, 1926, 28, 803) to scattering by higher power laws it appears that the anomalous scattering results obtained with magnesium are due to a spherically symmetrical field of force which is at first that of an inverse fifth or sixth power attractive force. A sudden rise of scattering occurs at a certain point, where it is possible that a higher power repulsive force may be coming into action. The radius of the neutral surface in the magnesium nucleus, taking the fifth power law, is calculated to be  $0.6 \times 10^{-13}$  cm., i.e., considerably smaller than the classical value of  $3.44 \times 10^{-13}$  cm. Aluminium appears to show no regularities of magnesium type. L. L. BIRCUMSHAW.

**Confirmation of the scattering formula of Klein and Nishina for short-wave  $\gamma$ -radiation.** L. MEITNER and H. H. HUFFELD (Naturwiss., 1930, 18, 534—535).—The scattering of  $\gamma$ -rays from thorium-B+C+C'' by aluminium, copper, silver, tungsten, and lead has been measured by means of a Geiger-Müller counter and the results have been compared with the respective theoretical values calculated according to the equations of Compton, Dirac, and Gordon, and of Klein and Nishina (cf. A., 1929, 373). The latter equation yields results in best agreement with the experimental values. J. W. SMITH.

**Mean life of ionium.** (MME.) P. CURIE and (MME.) S. COTELLE (Compt. rend., 1930, 190, 1289—1292).—A value of 119,000 years (cf. Soddy and Hitchens, A., 1924, ii, 446; Meyer and Schweidler, "Radioaktivität," 1927, 389), accurate to within 3%, was obtained from measurements of the amounts of radon produced in successive intervals of time from a solution in nitric acid of known quantities of oxides of thorium and ionium. J. GRANT.

**Magnetic spectrum of the rays of thorium-C.** S. ROSENBLUM (Rech. et Inv., 1929, 10, 199—202;

Chem. Zentr., 1930, i, 795).—A study of the deflexion of the  $\alpha$ -rays of thorium-C in a magnetic field of intensity 38,000 gauss. A. A. ELDRIDGE.

**Activation of matter by a surface discharge.** G. REBOUL and G. DÉCHÈNE (Compt. rend., 1930, 190, 1294—1296).—The activation of metallic plates produced by proximity to resistance cells (this vol., 129, 393) has been shown to be also produced by a luminous surface discharge generated by 20000—100,000 volts. The resulting activation curves correspond with the superposition of 3 exponentials with periods of 3 (radium-A), 27 (radium-B), and 20 min. (radium-C), and with a residual activity which decreases with a period of 10.6 hrs. (thorium-A). The activity appears to depend on the local atmospheric or geological conditions. J. GRANT.

**Disintegration of radioactive substances at very small concentrations and expulsion of  $\alpha$ -particles from radioactive nuclei exposed to short-wave radiation.** H. HERSZFINKIEL and H. DOBROWOLSKA (Z. Physik, 1930, 62, 432—434).—Polemical against Pokrovski (cf. this vol., 9, 393). A. J. MEE.

**Radioactivity of materials from roofs.** A. BOUTARIC and (MLLE.) M. ROY (Compt. rend., 1930, 190, 1410—1412; cf. this vol., 289).—Radioactive emanations were detected from glass tiles and slates from a roof 25 years old, from portions of lead guttering which had undergone various conditions of exposure, and from sand and charcoal which had been used for 30 years in an enclosed roof-filter for rain-water. The radioactivities increased to an extent corresponding approximately with the degree of exposure to rain-water, independently of exposure to sunlight. J. GRANT.

**Mechanics of photons.** V. FOCK (Compt. rend., 1930, 190, 1399—1401).—A mathematical development of the mechanics of a photon by treatment of Maxwell's equations in a manner corresponding with the wave-motion of a photon (light quantum). An equation for a single photon is deduced and extended to a number of photons by application of Dirac's method of "posterior" quantification. The reasoning may be applied to the deduction of Einstein's law of energy fluctuation, and to the laws of the interaction of matter and light. J. GRANT.

**Undulatory theory of quantum phenomena.** L. DÉCOMBE (Compt. rend., 1930, 190, 1385—1387).—The author's theory (A., 1929, 615) when applied to band spectra indicates that the Deslandres spectral term (this vol., 971) is attributable to ionic oscillations about the centre of gravity of the molecule. Assuming a constant  $H$  for the proton, analogous to the electronic quantum constant ( $h$ ), it is shown that there is resonance between the two rotatory frequencies of the spinning proton and electron. J. GRANT.

**Quantum mechanics of electrons in crystals.** P. M. MORSE (Physical Rev., 1930, [ii], 35, 1310—1324).—Mathematical. A general solution is developed for the motion of electrons in the potential field of the nuclei in a crystal lattice, neglecting the energy interaction terms due to nuclear vibration

and to the presence of other electrons. The solution, computed for a simple form of crystal lattice, gives results in agreement with the experimental results of Davisson and Germer (cf. A., 1928, 1173), but diverges for electrons of decreasing energy, and probably does not apply to tightly bound electrons in the inner atomic shells.

N. M. BLIGH.

**Interference measurements with single molecules.** P. DEBYE (Proc. Physical Soc., 1930, 42, 340—351).—A lecture.

J. W. SMITH.

**Richardson constants of distillation cathodes.** W. ESPE (Z. tech. Phys., 1929, 10, 489—495; Chem. Zentr., 1930, i, 802).

**Electronic theory of metals. II.** J. FRENKEL (Scientia, 1929, 46, 87—96; Chem. Zentr., 1930, i, 482).—A discussion.

A. A. ELDRIDGE.

**Most probable 1930 values of the electron and related constants.** R. A. MILLIKAN (Physical Rev., 1930, [ii], 35, 1231—1237).—Theoretical. Wilson's empirical oil-drop formula (cf. *ibid.*, 1929, [ii], 34, 1493) must be invalid. Eddington's spectroscopic fine structure constant (cf. A., 1929, 231; this vol., 518) is probably not a whole number, either 136 or 137. The most probable 1930 values of  $e$ ,  $N$ , and  $h$  are those of 1917 corrected for the velocity of light and the absolute value of the ohm, and are  $e = (4.770 \pm 0.005) \times 10^{-10}$ ,  $h = (6.547 \pm 0.011) \times 10^{-27}$ ,  $N = (6.064 \pm 0.006) \times 10^{23}$ .

N. M. BLIGH.

**Atomic dimensions.** B. B. RAY and B. C. MUKHERJEE (Indian J. Physics, 1930, 4, 467—476).—Metals and non-metals are differentiated on the hypothesis that in the former the crystals are so arranged that the sum of the atomic radii is equal to the distance between two atomic centres, the valency shells of all the atoms being deformed and forming a large equipotential surface in the crystal in which an electron can travel freely. In non-metals the distance between the neighbouring atomic centres is greater than their atomic radii, and hence the valency electrons are attached to the atom to which they belong. Atomic and ionic radii are calculated according to the methods of Bragg and Saha. The calculated results indicate that all alkali halide crystals should be non-conductors, a result which is in accordance with experimental observation, but at variance with the empirical relations of Bragg (A., 1910, ii, 919) and of Davey (A., 1923, ii, 847).

J. W. SMITH.

**Absorption band spectrum of chlorine. II.** A. ELLIOTT (Proc. Roy. Soc., 1930, A, 127, 638—657; cf. A., 1929, 624).—An analysis has been made of the rotation structures of four bands assigned to  $\text{Cl}^{35}\text{Cl}^{35}$  and two assigned to  $\text{Cl}^{35}\text{Cl}^{37}$ . As before, only  $P$  and  $R$  branches are found, and from these, term differences are obtained for the upper and lower states ( $\Delta F'$  and  $\Delta F''$ , respectively). Tables of vibration and rotation constants are given, and probable extrapolations for these constants are made for the lowest vibrational state in both electronic levels. The values calculated for the vibrational isotopic separators demand a revision of the vibrational quantum numbers for both the normal and excited states, the former being decreased by 1 and the latter by 6. The  $B'_v-v'$  curve for the excited

state appears to consist of two linear portions with a discontinuity at the point  $v'=8.5$ . This may have a connexion with the point of discontinuity in the  $w'_v-v'$  curves found by Birge for certain molecules, including the halogens (this vol., 3). From intensity measurements carried out on a large number of lines, a lower limit of 1.3:1 is derived for the alternating intensity ratio, but it is considered probable that the true ratio is nearer 1.4:1, the theoretical value corresponding with a nuclear spin of  $5/2$ . An estimate, from intensity measurements, of the relative abundance of the molecules  $\text{Cl}^{35}\text{Cl}^{35}$  and  $\text{Cl}^{35}\text{Cl}^{37}$  leads to the value 1.45:1, which is considerably below the value 1.67 calculated from Aston's value for the isotope ratio. This may be due to experimental error, but might also be caused by a greater absorption coefficient for the non-symmetrical molecule  $\text{Cl}^{35}\text{Cl}^{37}$ .

L. L. BIRUMSHAW.

**Spectrophotometry of aqueous chlorine and bromine solutions, and a method for their analysis.** E. S. SOKOLOVA and P. I. SOKOLOV (J. Russ. Phys. Chem. Soc., 1930, 62, 319—331).—The extinction coefficients of chlorine and bromine are for  $\lambda$  436, 454, and 463  $\mu\mu$  little different for gaseous mixtures than for aqueous solutions. The value of the extinction coefficient of bromine vapour more nearly approaches that found in aqueous solution as the temperature of the vapour is raised; thus  $\epsilon_N$  is 72.9 at 66°, 55.7 at 320°, and 54.9 at 620°, whilst in aqueous solution it is 40.9. Beer's law is followed by aqueous solutions of both halogens. Dilute bromine water is quite stable during the time of measurement, no difference in  $\epsilon_N$  being found before 60 min. of illumination. A method for the determination of chlorine and bromine together in water and of bromine in aqueous solution, based on the spectrophotometric determination of  $\epsilon_N$ , is described and experimentally verified for various solutions.

R. TRUSZKOWSKI.

**Manometric and spectroscopic study of the thermal dissociation of pyrites  $\text{FeS}_2$ .** L. D'OR (Compt. rend., 1930, 190, 1296—1298).—The partial pressure ( $p$  in mm. Hg) of  $\text{S}_2$  is related to the temperature  $T$  (Abs.) for the range studied (548—676°) by the equation  $\log p = [14.964(T-892)/T] + \log T + 2.8205$ . The equation  $2\text{FeS}_2 \rightarrow 2\text{FeS} + \text{S}_2 - 61,000$  g.-cal. was established, the energy of fixation of the first sulphur atom ( $\text{FeS}$ ) being 90,500 and that of the second  $\text{S}_2$ , 500 g.-cal. No absorption was observed below 548°; at 548—685° the bands were characteristic of  $\text{S}_2$ , and at 664—687° the bands attributed to  $\text{S}_6$  by Henri were observed.

J. GRANT.

**Fluorescence of mercury vapour in the far ultra-violet.** M. ELIASHEVICH and A. TERENIN (Nature, 1930, 125, 856).—The re-emission of the aluminium line at 1854 Å. previously observed in the fluorescence spectrum of mercury vapour (A., 1926, 776) has been confirmed. Using a fluorite spectrograph, re-emission is conspicuous at a vapour pressure of 10 mm., and on raising the pressure of the vapour the aluminium lines at 1862, 1935, and 1990 Å. appear in succession. A continuous background from 1854 to 2345 Å. accompanies the fluorescence spectrum. Heating the vapour at 800° quenches the

whole spectrum, but the presence of traces of gases does not have the strong quenching effect occurring with the near ultra-violet and visible fluorescence.

L. S. THEOBALD.

**Absorption spectrum of sodium hydride.** T. HORI (Z. Physik, 1930, 62, 352—367).—A new absorption spectrum for sodium hydride was found in the neighbourhood of 3680—4450 Å. It resembles the absorption spectrum of lithium hydride recently found by Nakamura (cf. A., 1929, 625; this vol., 124), and belongs to a transition of the type  $^1\Sigma \rightarrow ^1\Sigma$ . The excited  $^1\Sigma$  state is characterised throughout by the fact that its nuclear oscillation levels are not given by the theoretical formula as ordinarily used. An anomaly of a similar kind occurs also in the dependence of rotational energy in the excited state on the oscillation quantum number.

A. J. MEE.

**Intensities of vibration-rotation bands with special reference to those of hydrogen chloride.** J. L. DUNHAM (Physical Rev., 1930, [ii], 35, 1347—1354).—Theoretical. The intensity formulæ obtained from the potential function about the equilibrium point and from the potential function due to Morse (cf. A., 1929, 975) give results in close agreement. Formulæ are given for the fundamental and first harmonic vibration bands, and for the ratio of the intensity of the first two harmonic bands to that of the fundamental. Using the experimental data of Meyer and Levin (cf. A., 1929, 974), the results are applied to hydrogen chloride (cf. *ibid.*, 1126), and lead to an ambiguity of coefficients.

N. M. BLIGH.

**Infra-red frequencies of the diamond.** F. SIMON (Nature, 1930, 125, 855).—It is suggested that the diffuse Raman line observed by Ramaswamy agrees with a band observed by Reinkober at  $14\ \mu$  and with Simon's value of 0 in the modified Debye formula for the specific heat of diamond (cf. Robertson and Fox, also Ramaswamy, this vol., 662).

**Dispersion formula and Raman effect for the symmetrical top.** M. MUSKAT (Physical Rev., 1930, [ii], 35, 1262—1269).—Mathematical. Schrödinger's theory of dispersion is applied to the symmetrical top. An expression is derived for the index of refraction of a gas composed of symmetrical tops, as a function of the frequency of the incident light. The moments for the Raman effect transitions for the symmetrical top and the polarisation of the Raman variations are computed.

N. M. BLIGH.

**Chemical constitution and the Raman effect: the acetylenic linking.** M. BOURGUEL and P. DAURE (Compt. rend., 1930, 190, 1298—1299).—The frequencies of the Raman lines characteristic of unsaturated compounds have been studied. For compounds of the type  $RC\equiv CH$ , one line of frequency 2110—2120  $\text{cm}^{-1}$  is obtained, for the linking  $CR\equiv CR'$  one or two lines between 2200 and 2300, whilst acetylene gives the lines 1960 and 3320, the last-named being weak and characteristic of all true acetylenic compounds (i.e., of the linking  $\equiv CH$ ). The saturated and ethylenic linkings are characterised by lines of frequencies 1450 and 1600—1700, respectively. Substitution of a hydrogen atom in a triple linking by

Me, Cl, or OAc increases the characteristic frequency of the linking.

J. GRANT.

**Raman spectra and molecular structure.** K. W. F. KOHLRAUSCH (Naturwiss., 1930, 18, 527—528).—Monosubstituted methane derivatives exhibit one Raman frequency lower than the characteristic frequency at 3000  $\text{cm}^{-1}$ ; di- and tri-substituted derivatives show respectively three and four such frequencies. For mono-derivatives a linear model is postulated, and for di- and tri-derivatives, respectively, an isosceles triangle and a tetrahedron with the alkyl group at the apex in each case. From the relation  $f = (4\pi c^2 v_1^2 / L) [mM / (m + M)]$ , the elasticity,  $f$ , of the alkyl-halogen and halogen-halogen linkings is calculated. The theoretical deductions of Bjerrum and Demison give relations whereby the "valency angles" can be computed. The value for the elasticity of the alkyl-halogen linking diminishes as the number and the weight of substituent groups increase. Further work is in progress, but the results already obtained are in good agreement with stereochemical conceptions and observations of the dipole moment of these compounds.

W. R. ANGUS.

**Raman effect of sulphuric acid.** R. M. BELL and W. R. FREDRICKSON (Nature, 1930, 125, 892—893).—Pure sulphuric acid gives Raman lines at 4585, 4566, 4542, 4470, 4438, 4276, 4252, 4224, 4203, 4171, and 4142 Å. These lines decrease in number and intensity down to 30% sulphuric acid, at which concentration they disappear.

L. S. THEOBALD.

**Raman effect in metallic halides.** P. KRISHNAMURTI (Nature, 1930, 125, 892).—Mercurous and mercuric chlorides and the solid trichlorides of antimony and bismuth give strong Raman lines; auric chloride, cadmium iodide, and anhydrous zinc chloride give feeble lines, whilst the chlorides of lithium, barium, and thorium give no effect. Stannic chloride, unlike the stannous compound, gives a strong Raman spectrum. A covalent linking appears to favour the production of the Raman effect.

L. S. THEOBALD.

**Raman effect in gaseous hydrogen chloride.** R. W. WOOD and G. H. DREKE (Physical Rev., 1930, [ii], 35, 1355—1359; cf. A., 1929, 241, 378, 627).—Improved spectrograms of the Raman effect in hydrogen chloride have been obtained; wave-lengths, frequency differences with the exciting  $\lambda$  4358 mercury line, rotational transitions, and comparison with infra-red data are tabulated. The results are in exact agreement with the predictions of the dispersion theory.

N. M. BLIGH.

**Mode of action of boric acid on the phosphorescence of zinc sulphides prepared by the explosion method.** F. PREVET (Compt. rend., 1930, 190, 1402—1403).—Since substitution of boric acid by silica, silicates, chlorides, sulphates, boron, or alkali borates fails to produce phosphorescence in zinc sulphide prepared by the author's method (A., 1929, 489, 524), and since the phosphorescence is produced by ammonium borate, and is independent of the state of division of boric acid, it is concluded that the phenomenon is due to decomposition by the heat of reaction with the production of boric anhydride (cf. following abstract).

J. GRANT.



**Poisons and phosphorogens for phosphorescent zinc sulphide.** R. COUSTAL (Compt. rend., 1930, 190, 1403—1405).—Observations of the effects of additions of various compounds in the preparation of phosphorescent zinc sulphide by the explosion method (cf. A., 1929, 489, and preceding abstract) show that these are dependent on the procedure used and on the method of observation of the phosphorescence (e.g., excitation by daylight, incandescence, electric light, mercury arc, etc.). Thus, a brilliant phosphorescence was obtained in the absence of any phosphorogen, whilst manganese and copper, which are the phosphorogens usually employed, acted as poisons in the light of the mercury arc, although in the latter case the phosphorescence was doubled in the light of an incandescence lamp. Other metals immediately preceding zinc in atomic number (e.g., iron, cobalt, nickel) are highly active poisons or phosphorogens, whilst the metalloids are almost inactive.

J. GRANT.

**Polarisation of sensitised fluorescence.** A. C. G. MITCHELL (J. Franklin Inst., 1930, 209, 747—756).—The problem of carrying over of polarisation on collision between two atoms has been investigated using the 3261 Å. cadmium line. In a tube containing cadmium at a pressure of 0.5 mm., mercury at 0.001 mm., and helium at 2 mm. no polarisation of the cadmium 3261 Å. line occurs, whereas it does occur with the 2537 Å. mercury line. It is concluded, therefore, that polarisation is not carried over on collision.

W. E. DOWNEY.

**Absorption of light by alkali halide phosphors.** W. KOCH and R. W. POHL (Nachr. Ges. Wiss. Göttingen, 1929, 6—8; Chem. Zentr., 1930, i, 943).—Thallous chloride crystals show an absorption band at 216  $\mu$ , potassium chloride phosphor with addition of thallous chloride at 208  $\mu$ , and thallous chloride in dilute aqueous solution at 213  $\mu$ . Similar results were obtained with lead chloride and phosphors containing it.

A. A. ELDRIDGE.

**Mutual behaviour of two kinds of polar molecules in benzene solution and the applicability of dipole liquids in the determination of electric moments.** O. HASSEL and A. H. UHL (Z. physikal. Chem., 1930, B, 8, 187—206; cf. this vol., 523).—An elaboration of work previously abstracted. The conclusions reached are essentially the same.

F. L. USHER.

**General character and form of the formula for the dielectric constant of non-homogeneous mixtures.** A. PIEKARA (Physikal. Z., 1930, 31, 579—584).—Two general hypotheses and Wiener's postulate of proportionality give a general formula for the dielectric constant of a mixture. This formula does not follow the additive rule. Experimental determinations of the dielectric constant of water-alcohol, mercury-paraffin oil, and mercury-vaseline mixtures are used to make the formula more definite.

A. B. D. CASSE.

**Ionisation during the formation of ozone.** R. RUYSSSEN (Natuurwetensch. Tijds., 1930, 12, 86—90).—Theoretical considerations relating to the occurrence of ionisation during the formation of ozone are discussed.

H. F. GILLBE.

**Significance of dipole measurements in the stereochemistry of carbon compounds.** E. BERGMANN and L. ENGEL (Z. physikal. Chem., 1930, B, 8, 111—137).—Theoretical. The calculation of dipole moments and the determination of the characteristic moments of substituents from molecular models are discussed. It is shown that, in some cases, e.g., *o*-substituted compounds, there are discrepancies between calculated and observed moments which are to be ascribed to steric influences. In this connexion also, ethylene and ethylenic compounds, diphenyl derivatives, and compounds of the ethane type are discussed. Arguments in favour of the fumaroid structure of succinic acid are given. The probability of valency tautomerism in compounds of the ethylene type is considered.

M. S. BURR.

**Dipole moments of some alcohols and esters.** H. L. DONLE and K. L. WOLF (Z. physikal. Chem., 1930, B, 8, 55—59; cf. A., 1929, 244; this vol., 523).—The following values of  $\mu \times 10^{18}$  have been obtained at 22°: menthyl formate 2.06 and acetate 1.83, bornyl formate 2.04, acetate 1.87, and propionate 1.84, *l*-menthol 1.58, and *l*-borneol 1.56. If the infra-red term of the molecular polarisation is neglected the numbers for menthol and borneol are 1.68 and 1.66, respectively, so that the moments are practically the same as for aliphatic alcohols, and the ring system makes no appreciable difference. Within the limits of experimental error the esters show the same variation with the length of the acid chain as the corresponding acids themselves.

M. S. BURR.

**Dipole moments and ultra-violet absorption of organic molecules.** H. L. DONLE and G. VOLKERT (Z. physikal. Chem., 1930, B, 8, 60—71).—Dipole moments of a number of alicyclic ketones have been obtained at 22° and the following values are given for  $\mu \times 10^{18}$ : cyclopentanone 3.00, menthone 2.80, camphor 2.95, and fenchone 2.92. Comparison with one another and with the value for cyclohexanone, 2.75 (Wolf, A., 1929, 244), indicates the influence of positive ring tension, due to the presence of a five- or fewer-membered ring, on the dipole moment. This influence is more marked than in the case of the alicyclic alcohols (cf. preceding abstract) because of the presence of the strongly polar ketone groups. The following further determinations make evident the difference in the moments of the ketone and thioketone groups: anisole 1.23, dianisylmethane 1.61, benzophenone 2.95, dianisyl ketone 3.90, and dianisyl thioketone 4.44. The difference is attributed to the difference in the structure of the two groups. This view is supported by determinations of the ultra-violet absorption bands, the thioketone having an additional band which does not resemble in position and intensity those found in the related compounds. In general, the measurements of the absorption bands of the alicyclic ketones in different solvents confirm the regularities observed in the case of aliphatic ketones.

M. S. BURR.

**Spectrochemistry of compounds containing nitrogen.** III. K. VON AUWERS and W. SUSEMHL (Z. physikal. Chem., 1930, 148, 125—147; cf. A., 1926, 994).—The investigation of the refractivity and dispersivity of organic nitrogen compounds has been

continued. Examination of the substitution products of dimethylaniline has confirmed the observation that the *o*-derivatives of *NN*-dialkylanilines have much smaller molecular refractivities and dispersivities than the corresponding *m*- and *p*-derivatives, this effect being, indeed, so marked that the *o*-compounds are easily recognised, although it is not possible to distinguish between the *m*- and *p*-compounds in the same way. In the substitution products of aniline and the *N*-alkylanilines with an active conjugation in the molecule it is, however, the *p*-derivatives which are unique, their exaltations being greater than those of either of the other derivatives. Introduction of hydroxyl or alkoxyl into the end groups of a conjugated system increases the exaltation, and the amino- and alkylamino-groups have a similar, but more pronounced, action. The optical depression shown by pyridine is reduced or even converted into exaltation by introduction of an active conjugation, and in the case of 2-imino-1-methylpyridine the optical data confirm the structure suggested by Tschitschibabin and others (A., 1921, i, 450). Indole and its methyl derivatives closely resemble optically the indenenes, cumarones, and thionaphthenes. In no case has the introduction of a methyl group into either ring any appreciable optical effect, which indicates that the molecules of these compounds must be regarded as consisting, not of two parts of different character, but of a single system with a special degree of saturation. *Ethyl p*-dimethylaminobenzoate, m. p. 65°, has been prepared. R. CUTHILL.

**Atomic refractions of nitrogen.** K. VON AUWERS (Z. physikal. Chem., 1930, 147, 436—460).—From a survey of refractivity data for organic compounds containing the N:C and N:CO groups values for the atomic refraction of nitrogen in the groups O:N:C, C:N:C, H:N:C, N:N:C, N:CO-R, and N:CO-OR have been deduced. Conjugation in the molecule of an azine causes exaltation of the refractivity, but has little effect on the dispersion. By condensation of isobutaldehyde with propylamine and isoamylamine, isobutylidenepropylamine, b. p. 114—115°, and isobutylideneisoamylamine, b. p. 158—160°, have been prepared. R. CUTHILL.

**Molecular configuration and optical activity.** F. M. JAEGER (Coll. Czech. Chem. Comm., 1930, 2, 330—343).—A lecture. C. W. GIBBY.

**Dependence of molecular polarisation on temperature, especially in the case of substances with groups capable of free rotation.** L. MEYER (Z. physikal. Chem., 1930, B, 8, 27—54; cf. A., 1929, 980).—The extent to which the capacity for free rotation is hindered by the potential due to opposed moments of rotation has been investigated mathematically and experimentally. Calculation shows that, when the inner molecular potential exceeds  $kT/10$ , rotation should be checked, and the total moment should decrease with falling temperature. The molecular polarisation would then be no longer a linear function of  $1/T$ . The dependence on temperature of the molecular polarisation of ethylene chloride in benzene and hexane, and of quinol dimethyl ether in benzene, has been determined by a method of which the details are given. Although in both

cases the inner molecular potential is a multiple of  $kT$ , yet in the benzene solutions, for the temperature interval 5—50°, the moment is independent of temperature within the limits of experimental error. For ethylene chloride in hexane from -75° to 40° there is a rise in the moment of about 10%, and the polarisation does not bear a linear relationship towards  $1/T$ . It has also been shown that benzene alone, which has no dipole, shows a slight rise of molecular polarisation with temperature. This is explained as due to increased mobility of the electrons with rise of temperature, since there is, at the same time, practically a parallel increase in molecular refraction.

M. S. BURR.

**Magneto-rotatory behaviour of some optically active substances in solution.** S. S. BHATNAGAR, K. N. MATHUR, and B. D. JAIN (Indian J. Physics, 1930, 4, 503—513).—For any particular solvent the magnetic field producing magnetic rotation just sufficient to balance the optical rotation is proportional to the optical rotation itself. Unlike optical rotation, the magnetic rotation of an optically active solution of a substance is independent of the concentration so long as the latter is comparatively low. In the case of solutions of optically active liquids in inactive liquids, where high concentrations of the former could be taken, the magnetic rotation changes with the concentration and seems to depend on the relative volume concentrations. These results agree with the conclusions of Perkin (J.C.S., 1896, 69, 1025) and of Schivers (Compt. rend., 1912, 155, 398) but not with those of Calcagni (A., 1928, 6, 461). J. W. SMITH.

**Measurement and interpretation of rotatory dispersion of simple substances.** W. KUHN and E. BRAUN (Z. physikal. Chem., 1930, B, 8, 281—313).—From measurements of the absorption and rotatory dispersion of the dimethylamide and methyl ester of  $\alpha$ -azidopropionic acid in alcoholic and in ethereal solution it has been shown that the azido-group has a characteristic absorption band at about 2900 Å. Deviations from Drude's formula for rotatory dispersion similar to those recorded by Lowry and Cutter (A., 1925, ii, 356) have been observed. Absorption and dispersion data for the ethyl ester and dimethylamide of  $\alpha$ -bromopropionic acid are also recorded. From the results the anisotropic factors of the various absorption bands are calculated. It appears that the vicinal actions (cf. this vol., 276) of chemically similar substituents are approximately equivalent, originating in strong Schumann bands.

R. CUTHILL.

**Optical rotatory power.** T. M. LOWRY (Trans. Faraday Soc., 1930, 26, 266—271).—A review of the progress during the last sixteen years in the elucidation of problems of optical rotatory power. The lines along which progress may be expected in the near future are indicated. F. G. TRYHORN.

**Wave mechanics of optical rotation and of optically active molecules.** G. TEMPLE (Trans. Faraday Soc., 1930, 26, 272—280).—The principles of wave mechanics are applied in an analysis of the action of polarised light on optically active gas molecules. Equations are derived for the induced moments due to the action of light on molecules, and

by considering the energy distribution in an assembly of molecules an equation is obtained for the rotatory power for a given wave-length.

From a consideration of a one-dimensional model of an active molecule, an expression is deduced for the separation of the energy levels in the isomeric forms. The limitations of the theories proposed are discussed.

F. G. TRYHORN.

**Molecular theory and the calculation of natural rotatory power.** R. DE MALLEMANN (Trans. Faraday Soc., 1930, 26, 281—292).—A discussion of the correlation of optical activity and structure on the basis of the molecular theory. From a review of recent work on this subject it is shown that qualitative correlation has been achieved, but that the numerical calculation of rotatory power is still uncertain and inexact.

F. G. TRYHORN.

**Physical significance of optical rotatory power.** W. KUHN (Trans. Faraday Soc., 1930, 26, 293—308).—A presentation of the author's theory that rotatory power arises from the dissymmetric coupling of vibrations with different characteristic frequencies. Examples are given of the application of the theory to a number of problems of optical rotatory power.

F. G. TRYHORN.

**General physical aspects of natural optical activity.** P. P. EWALD (Trans. Faraday Soc., 1930, 26, 308—310).—An attempt to deduce the nature of optical rotatory power, independently of any specialised type of molecular model, from the relationship between the theories of refraction and rotation.

F. G. TRYHORN.

**Atomic linkings in elements.** W. STÄCKEL (Z. Elektrochem., 1930, 36, 375—376).—The following approximation rule is advanced. The energy of dissociation of a non-polar linking of similar kinds of atoms possessing the same number of shells of electrons is a constant, the latter being a multiple of a common constant. This rule is applied to a few of the elements and compared with the heat of dissociation found experimentally.

H. I. DOWNES.

**Chemical affinity and the principle of symmetry.** A. KAPUSTINSKI (Z. physikal. Chem., 1930, B, 8, 72—80).—Theoretical. Regarding the molecule as a collection of spheres representing the spheres of action of single atoms or groups of atoms, it is shown that a higher degree of symmetry is obtained with even than with uneven numbers of spheres, except in the case of 10, which gives a minimum degree. The requirements for compactness of structure are found to correspond with the requirements for minimum potential energy, and hence it can be shown that the higher is the symmetry the greater is the stability of the compound. In the case of complexes, many more compounds with even co-ordination numbers are found to exist than compounds with uneven co-ordination numbers.

M. S. BURR.

**Co-ordination properties of halides near the volatility limit, and determination of structure of the halides  $AX_4$ .** H. HANSEN (Z. physikal. Chem., 1930, B, 8, 1—26).—From consideration of the data for the crystal structure and energy relationships of the halides it is shown that the compounds of

low volatility have an ionic structure, whilst those of high volatility have a lattice structure consisting of individual molecular groups, the energy required to break up the lattice structure being smaller than the energy of dissociation of the molecular groups. Halides of the former type give a vapour consisting of simple molecules, e.g., KCl, whilst the vapour of halides of the latter type contains polymerised molecules, e.g.,  $Al_2Cl_6$  and  $Fe_2Cl_6$ . The energy relationships in the crystal lattice of halides of the composition  $AX_4$  are discussed. X-Ray investigations of the crystal structure of zirconium and uranium tetrachlorides have been made by the powder method, since it was expected that these might have a definite co-ordination lattice of a type not observed hitherto. The structure of zirconium chloride, however, is of the stannic iodide type,  $D_{2h}$ , and uranium chloride has another type of structure which could not be definitely determined.

M. S. BURR.

**Spontaneous disintegration of diatomic molecules.** R. DE L. KRONIG (Z. Physik, 1930, 62, 300—310).—Theoretical. The recently developed theories of the spontaneous disintegration of diatomic molecules are discussed and grouped, being dealt with from a single viewpoint. Certain unproved results of the theory are shown to be in agreement with experiment.

A. J. MEE.

**B. p. and chemical constitution. III. Monopolar open-chain organic compounds.** B. NEKRASSOV (Z. physikal. Chem., 1930, 148, 216—226; cf. A., 1929, 872).—A better empirical equation,  $T = KM^{3/2}/\Sigma$ , for the b. p. (Abs.),  $T$ , of a liquid has been devised. In this equation  $M$  is the mol. wt.,  $K$  is a quantity which is constant for all the compounds of a particular class, and  $\Sigma$  is the algebraic sum of the refractivity constants of the active (polar) groups present and those of the other atoms together with a quantity,  $\Delta$ , characteristic of each active group. For the normal saturated hydrocarbons from  $C_4$  to  $C_{10}$  the equation reduces to  $T = K\sqrt{M}/R$ , where  $R$  is the specific refractivity. The values of  $K$  and  $\Delta$  for a given class of compounds may be calculated from the b. p. of two members of the series, and values for the principal types of aliphatic compound are tabulated. Of 1500 b. p. calculated by means of the new equation, 80% were within  $5^\circ$  of the experimental value.

R. CUTHILL.

**Diamagnetism and molecular structure.** (SIR) C. V. RAMAN (Proc. Physical Soc., 1930, 42, 309—320).—A lecture.

J. W. SMITH.

**Theory of liquid crystals.** W. OSTWALD (Z. Krist., 1929, 71, 131—134; Chem. Zentr., 1930, i, 933—934).—Polemical.

A. A. ELDRIDGE.

**Theory of liquid crystals.** E. ALEXANDER and K. HERRMANN (Z. Krist., 1929, 71, 134; Chem. Zentr., 1930, i, 934).—Polemical (cf. preceding abstract).

A. A. ELDRIDGE.

**Magnetic moments of alloys and measurement of mean atomic moments.** R. FORRER (Compt. rend., 1930, 190, 1284—1287).—If in a binary alloy a certain number of atoms of one of the constituents is replaced by those of the other, their moments being different, there will be a linear vari-

ation of mean atomic moment over the whole interval for which the substitution is of the same character. This "principle of substitution" is applied to nickel-copper, nickel-cobalt, iron-nickel, and iron-cobalt alloys, and verified, and the significance of the sub-multiple 5 of the Bohr magneton is indicated.

J. GRANT.

Value of the Weiss magneton deduced from paramagnetic bodies. B. CARRERA (Anal. Fis. Quim., 1930, 28, 431—447).—The quantity  $\mu_0$  in the equation  $\mu_0 = \sqrt{3RC}$ , where  $R$  is the gas constant and  $C$  the Curie constant, has been calculated from a large number of magnetic data; the mean value is  $1125.0 \pm 0.3$ .

H. F. GILLBE.

Binding energy of some organic compounds. L. S. KASSEL (Nature, 1930, 125, 926).—The older and lower values for the C-C and C-H linkings in higher hydrocarbons are preferred to the higher values suggested by Mecke (this vol., 702). The complete dissociation of such hydrocarbons will then yield carbon atoms in the normal  $^3P$  state.

L. S. THEOBALD.

Rotation heat of hydrogen at low temperatures. S. DÄUMICHEN (Z. Physik, 1930, 62, 414—418).—According to the theory of wave mechanics, hydrogen consists of two modifications, a symmetrical and an anti-symmetrical form. The rotation heat of both forms as well as that of their inter-combination is calculated, and the rotation heat of ordinary hydrogen in the temperature range 0—300° Abs. is derived.

A. J. MEE.

Complete spectral diagrams of crystals. H. SEEMANN, O. KANTOROWICZ, and K. F. SCHOTZKY (Nature, 1930, 125, 853).—Spectral diagrams more complete than those of Linnik (*ibid.*, 1929, 124, 946) are obtained by reflexion at the surface of a rock-salt crystal backwards by using a broad conical X-ray pencil. Diagrams are reproduced.

L. S. THEOBALD.

Complete spectral diagram of a single crystal. H. SEEMANN and O. KANTOROWICZ (Naturwiss., 1930, 18, 526—527).—The X-ray spectral diagrams obtained with rock-salt oriented in different directions with respect to the direction of the incident radiation are illustrated and discussed.

J. W. SMITH.

Phenomena in X-ray tubes. A. IANITZKY (J. Phys. Radium, 1930, [vii], 1, 153—162).—When the anode of an ionic X-ray tube is completely degassed the current ceases to pass (cf. Z. Physik, 1922, 11, 22; 1925, 35, 27). If two pieces of metal (e.g., platinum), precisely similar, save that one has been completely degassed, are placed in contact the gas passes from the undegassed piece to the other in the form of positive ions, and it is concluded that the gas dissolved in the metal is dissociated into positive ions and electrons (cf. *ibid.*, 1925, 31, 277). This hypothesis is now supported by experiments showing that when the electrodes of a tube are maintained at high P.D. gas is driven out only from the anode. This explains several phenomena, including the initial ionisation in an ionic X-ray tube; the reversal of current in certain tubes with small anode, and the fact that in a Coolidge tube if the anode is thoroughly degassed the pressure of gas in the tube may then be substantially higher

than that usually determining ionisation without the tube ceasing to function electronically.

C. A. SILBERRAD.

Scattering powers of the atoms in magnesium oxide for X-rays and some related properties. G. W. BRINDLEY (Phil. Mag., 1930, [vii], 9, 1081—1094).—In view of the uncertainty of the method of Fourier analysis for determining the relation between the scattering power of an atom and the number and distribution of its electrons, an alternative method has been devised, based on the radial distribution of charges in the atom and a temperature factor to correct for thermal vibration (cf. James and others, A., 1928, 112, 462; 1929, 14). Scattering (i.e.,  $F \sin \theta/\lambda$ ) curves have in this way been calculated for O, O<sup>-2</sup>, Mg, and Mg<sup>+2</sup> from the experimental data of Wyckoff and Armstrong (Z. Krist., 1930, 72, 433). The curves for O and O<sup>-2</sup> are similar, but the experimental results agree better with that for non-ionised oxygen. A marked decrease of  $F$  for large values of  $\sin \theta/\lambda$  seems connected with the use of powdered crystals, as it did not occur in the case of a single crystal of aluminium (cf. A., 1929, 1367). The curves for Mg and Mg<sup>+2</sup> are identical save for values of  $\sin \theta/\lambda$  below those for which experimental results are available. The amplitude of vibration of the atom in the lattice is estimated as 0.09 Å. for oxygen and 0.11 Å. for magnesium.

C. A. SILBERRAD.

Absorption of long wave-length X-rays of 2—10 Å. by light elements. B. WOERNLE (Ann. Physik, 1930, [v], 5, 475—506).—Absorption measurements in the long wave-length X-ray region were made by means of a vacuum ionisation spectrometer, a null method being used to obtain greater accuracy. The absorption coefficients of air, nitrogen, oxygen, neon, argon, sulphur dioxide, and the vapours of pentane and carbon tetrachloride were determined over the wave-length range 2.3—9.9 Å. From the values for the compounds, the coefficients of carbon, sulphur, and chlorine were obtained. Jönsson (A., 1928, 340, and Diss., Upsala, 1928) has formulated a law for absorption of long wave-length X-rays stating that the electronic absorption coefficient is a pure function of the product  $Z\lambda$ . This is not strictly accurate for light elements, there being systematic deviations. For sulphur, chlorine, and argon the  $K$ -level absorption energy change was found. Its value was found to be approximately equal to the ratio of the energy values of the  $K$  and  $L_1$  levels, in agreement with an empirical relationship put forward by Jönsson.

A. J. MEE.

Influence of foreign matter in suspension in the mother-liquor on the habit of crystals. P. GAUBERT (Compt. rend., 1930, 190, 1230—1232).—It has already been shown (cf. A., 1925, ii, 271) that lead nitrate crystallises from a cold solution saturated with methylene-blue in cubes instead of the usual octahedra. From a hot saturated solution containing some undissolved dye it forms thin plates several cm. across but only about 0.2 mm. thick—apparently rhombohedral crystals flattened along (111). They are thinner and of deeper colour as the amount of dye is increased. From a similar solution of rosolic acid the salt crystallises in long, slender, quadratic

prisms apparently of rhombic symmetry. These are coloured by inclusions of the dye. These variations are attributed to the action of concentration currents the directions of which are influenced by the dye.

C. A. SILBERRAD.

**Crystal structure of krypton.** G. NATTA and A. G. NASINI (*Nature*, 1930, 125, 889).—Solid krypton examined by the method used for xenon (this vol., 528) showed 14 lines, 4 of which belonged to the  $K\beta$  radiation, corresponding with a face-centred cubic structure. The elementary cell of four atoms has a 5.78 Å., the volume is  $193 \times 10^{-24}$  c.c.;  $d_{\text{calc.}}$  2.83 g./c.c.; the calculated atomic radius is 2.04 Å.

L. S. THEOBALD.

**Crystal structure of krypton.** W. H. KEESOM and H. H. MOOR (*Nature*, 1930, 125, 889).—Solid krypton has a face-centred cubic lattice,  $a$  5.59 Å., and  $d_{\text{calc.}}$  3.13; the distance between the atomic centres is 3.96 Å.

L. S. THEOBALD.

**Twin crystals.** V. BILLIET (*Natuurwetensch. Tijds.*, 1930, 12, 73–85).—The types of twinning which may occur are described, and the theory is developed that the possible twinning groups are symmetrical or pseudosymmetrical groups of a single or multiple lattice of the crystal. H. F. GILLBE.

**Crystal structure of niobium.** K. MEISEL (*Z. anorg. Chem.*, 1930, 190, 237–240; cf. von Olshausen, *A.*, 1926, 228).—The investigations of von Olshausen have been repeated with three different specimens of highly purified niobium. The crystal structure found by him (face-centred cubic, tungsten type) has been confirmed, but the mean lattice constant is different, viz.,  $3.31 \text{ Å.} \pm 1.5\%$ . It is assumed that the earlier work was done with impure niobium or with mixed crystals of niobium and aluminium.

F. L. USHER.

**Energy of crystal lattices.** H. JONES (*Proc. Roy. Soc.*, 1930, A, 127, 689–703).—Mathematical. Heitler's method (*Z. Physik*, 1928, 46, 47) of determining the mean first order energy of a crystal lattice is criticised and the perturbation calculation is made without assuming that the initial wave functions form an orthogonal set. It is shown that the mean energy of the crystal depends to a much greater extent on the simple electrostatic potential energy given by the interlapping of the Schrödinger space charge, and to a much smaller extent on the interchange integral, than does the binding energy in a diatomic molecule. For the case of a collection of hydrogen atoms arranged in a simple cubic lattice it is found that the mean energy of the crystal is of the same order of magnitude as that of the same number of atoms forming a diatomic gas; the simple calculation assuming orthogonal functions would make it much less. When the atom possesses a closed shell lying behind the single valency electron, the value of the interchange integral is much reduced and the potential energy of the crystal form always lies lower than that of the same number of atoms arranged as a diatomic gas.

L. L. BIRCUMSHAW.

**Colour and fine structure of alloys. IV. Iron-carbon alloys.** M. CHIKASHIGE and D. UNO (*Z. anorg. Chem.*, 1930, 190, 303–312; cf. *A.*, 1928, 698, 717).—The light-reflecting power of various iron-

carbon alloys has been examined over a wide range of composition. The colour of the reflected light is independent of the carbon content and of the previous heat treatment, but its intensity varies. The formation of patterns on the blades of Japanese swords is determined by the degree of polishing and by differences in the reflecting power and corrodibility of the structural constituents of the steel. F. L. USHER.

**X-Ray diffraction in liquid hexamethylbenzene.** P. KRISHNAMURTI (*Indian J. Physics*, 1930, 4, 449–455).—A comparison has been made of the positions and intensities of the haloes in the X-ray patterns of powdered and liquid hexamethylbenzene. The liquid pattern consists of a strong inner halo (spacing 8.2 Å.) and a weak outer ring (4.2 Å.), roughly corresponding respectively with the (100) and (001) reflexions of the crystal powder with spacings 7.7 and 3.7 Å. Analogy with Lonsdale's analysis (*A.*, 1929, 750) favours the assumption that the 4.2 Å. spacing of the liquid is caused by the thickness of the molecule, whilst the 8.2 Å. spacing represents periodicities in the plane of the benzene ring. An approximate calculation of the density of the liquid on these assumptions leads to a value of 0.95 at 175°. The considerable diminution in the intensity of the outer halo in the liquid as compared with the crystal is attributable to the diminished structure factor for the (001) spacing caused by the thermal agitation of the molecules in the liquid. The thickness of the molecule of other substituted benzene derivatives (as mesitylene) previously investigated (*A.*, 1928, 691; 1929, 246) corresponds with the spacings of the outer rings and not with those of the inner.

J. W. SMITH.

**Crystals of paratophan.** J. HENRIOT (*Bull. Soc. chim. Belg.*, 1930, 39, 229–230).—Paratophan [2-phenyl-6-methylquinoline-4-carboxylic acid] forms clinohedral crystals,  $a : b : c = 0.61280 : 1 : 0.63147$ ;  $n$  1.6–1.7,  $H$  2.5.

C. W. GIBBY.

**Lattice structure of some simple sugars.** J. HENGSTENBERG and H. MARK (*Z. Krist.*, 1929, 72, 301–308; *Chem. Zentr.*, 1930, i, 313–314).—The unit cell of *d*-glucose contains 4 mols.;  $a$  10.40,  $b$  14.89,  $c$  4.99 Å.; space-group  $V^4$ ; that of *d*-cellobiose contains 2 mols.;  $a$  5.00,  $b$  13.2,  $c$  11.1 Å.,  $\beta$  90 ± 0.5°; space-group  $C_2^2$ ; that of *d*-lævulose contains 4 mols.;  $a$  8.06,  $b$  10.6,  $c$  9.12 Å.; space-group  $V^4$ .

A. A. ELDRIDGE.

**Crystal structure of rubidium azide.** L. PAULING (*Z. physikal. Chem.*, 1930, B, 8, 326–328).—The structure proposed for rubidium azide by Günther, Porger, and Rosbaud (this vol., 401) is inconsistent with known values of atomic radii. It seems much more probable that the structure is similar to that of potassium azide (*A.*, 1926, 113).

R. CUTHILL.

[Crystal structure of rubidium azide.] P. GÜNTHER and P. ROSBAUD (*Z. physikal. Chem.*, 1930, B, 8, 329).—A reply to Pauling (cf. preceding abstract).

R. CUTHILL.

**Goethite, stainerite, diasporite, and heterogenite.** W. F. DE JONG (*Natuurwetensch. Tijds.*, 1930, 12, 69–71).—X-Ray analysis indicates that stainerite is not isomorphous with goethite, and that although diasporite has probably the same lattice

structure as goethite, that of manganite is different. The following lattice constants have been determined for goethite, diasporite, and manganite, respectively:  $a$  4.55, 4.35, 4.46;  $b$  9.90, 9.35, 5.28;  $c$  3.01, 2.82, 2.88 Å.

H. F. GILLBE.

**Structure of analcime.** W. HARTWIG (Naturwiss., 1930, 18, 601; cf. Zentr. Min., 1928, A, 380).—Possible spatial arrangements of the atoms in the analcime ( $\text{NaAlSi}_2\text{O}_6$ ) crystal are listed and discussed in relation to the X-ray diagram and the valencies of the atoms concerned.

J. W. SMITH.

**X-Ray study of heulandite.** WYART (Compt. rend., 1930, 190, 1564—1566).—The structure of heulandite has been determined by means of Laue and rotation photographs. The unit cell has  $a$  7.45,  $b$  17.80,  $c$  15.85 Å., equivalent to  $a:b:c=0.418:1:0.890$  (crystallographically,  $0.4025:1:0.4293$ ). The space-group is  $C_{2h}^2$ . From the foregoing and the densities of three samples the numbers of atoms (excluding water) in the unit cell are: O 35.45—35.94, Si 13.31—13.67, Al 4.17—4.52, Ca 1.45—1.75, K 0.13—0.96, Na 0.27—0.91, Mg 0—0.03; and of water molecules 12.20—13.19. It is concluded that the unit cell varies, consisting of a fixed scaffolding of 36 oxygen atoms with the other atoms fitted in between, one metal replacing another in the different cells in electrically equivalent amounts. The structure is not compact, the volume occupied by an oxygen atom being  $28.9 \times 10^{-24}$  cm.<sup>3</sup> as compared with  $13.9 \times 10^{-24}$  cm.<sup>3</sup> in many compounds. The water molecules occupy the vacant space, thus affording an explanation of the peculiar nature of the zeolites.

C. A. SILBERRAD.

**Partial breakdown of solid insulators.** A. WALTHER and L. INGE (Naturwiss., 1930, 18, 528—529).—When a plate of homogeneous insulating material of about 1 mm. thickness is fixed between electrodes and immersed in oil there is a marked increase in the breakdown potential when the potential is applied for periods less than  $10^{-3}$  to  $10^{-6}$  sec. This is due to the circumstance that the breakdown voltage has insufficient time to build up. There are two critical potentials, the initial potential at which the first discharge occurs, and the true breakdown potential. The former remains unchanged up to periods of  $3 \times 10^{-8}$  sec. and is identical with the maximum breakdown potential for alternating currents. Photographs show the partial discharge preceding breakdown in glass and rock-salt plates. In the latter case the discharge course is oriented along the crystal cleavage planes.

J. W. SMITH.

**Passage of electricity through solid dielectrics.** D. NASLEDV and P. SCHARAVSKI (Ann. Physik, 1930, [v], 5, 429—452).—The passage of electricity through solid dielectrics is considered mainly from the point of view of polarisation phenomena. The solid examined was paraffin wax. If a solid is subjected to the action of an electric field a polarisation is set up in it, and on short-circuiting the ionisation chamber, a current opposite to the charging current flows, a certain amount of electricity being thereby furnished by the dielectric. This amount varies with the time for which the dielectric is subjected to the action of the

field, increasing with the time, but approaching asymptotically a limiting value. Ionised dielectric gives up a greater quantity of electricity than the non-ionised. A method of measuring the polarisation is given, and experiments show that the polarisation potential is very high, but an ionised dielectric has a smaller polarisation potential than one not ionised. Within the range 325—1600 volts there is proportionality between the applied potential and the polarisation. The observations can best be explained on the theory of ionic conductivity.

A. J. MEE.

**Surface-resistivity measurements on solid dielectrics.** L. HARTSHORN (Proc. Physical Soc., 1930, 42, 300—308).—A new form of metal strip electrode suitable for surface-resistivity measurements on insulating materials in sheet form is described. It gives good contact along the whole length, and is less likely to contaminate a surface than mercury or graphite. The method of determining the volume-resistivity correction is described and illustrations are given of the value of this correction for electrodes of various forms. The surface resistivities of common insulating materials have been measured. Ebonite initially has a very high surface resistivity, but deteriorates very rapidly on exposure to light, whereas the leakage resistances of "bakelite" and "keramot" are almost unaffected by exposure to light. Little difference is observed between the values for polished and matt surfaces.

J. W. SMITH.

**Ferromagnetism of alloys of nickel and of chromium.** C. SADRON (Compt. rend., 1930, 190, 1339—1340).—The saturation magnetisation ( $\sigma$ ) of nickel-chromium alloys in a particular field varies with the temperature ( $T$  Abs.) between  $110^\circ$  and  $150^\circ$  Å. according to the relation  $\sigma_T = \sigma_0(1 - AT^2)$  (cf. Weiss and Forrer, this vol., 22). Values of  $\sigma_0$  accurate to within 0.5% were thence obtained by extrapolation, and were shown to decrease linearly, from 57.87 for pure nickel (*loc. cit.*), with increase in chromium content up to 6% when the heterogeneity of the alloy influences its saturation. The Curie point falls from  $628^\circ$  Abs. for pure nickel to  $130^\circ$  Abs. for an alloy containing 10% Cr, and is zero (by extrapolation) for 12% Cr.

J. GRANT.

**Alteration in the electrical conductivity of ferromagnetic substances in longitudinal magnetic fields.** O. STIERSTADT (Physikal. Z., 1930, 31, 561—574).—Iron and nickel were investigated, as cobalt wire was not available. The effects of a longitudinal magnetic field on the electrical resistance is in the direction of an increase. Fields up to 250 gauss were used. The resistance "hysteresis" curves show that the change in resistance is a function of the field strength, marked by the appearance of phenomena similar to hysteresis loops, resistance remanence, and coercivity. By the use of magnetisation curves it is shown that the change in resistance is dependent on the magnetisation. The change in resistance is a function of the resultant induction, and, to a first approximation, is equal to its third or fourth power. This relation also gives rise to a loop, but not of the hysteresis type. It is suggested that this is due to a fundamental change in structure produced by magnetostriiction or the like,



but it cannot be excluded as being due possibly to a small error in the method. J. FARQUHARSON.

**Dependence of electrical conductivity of metals on pressure at low temperatures.** U. FISCHER (Z. physikal. Chem., 1930, B, 8, 207—217).—The dependence of the electrical conductivity of lead, tungsten, molybdenum, copper, iron, and constantan on pressure has been investigated down to the temperature of liquid hydrogen. The pressure coefficient of resistance of the pure metals increases with falling temperature, and this increase sets in at temperatures which are the higher, the higher is the characteristic temperature of the substance. The change is considerable; the pressure coefficient of resistance of tungsten or molybdenum at 20° Abs. is about four times the value at the ordinary temperature. On the other hand, the pressure coefficient of resistance of constantan decreases to a flat minimum at 145° Abs., and at the temperature of liquid hydrogen reaches approximately the value at the ordinary temperature. The main conclusions are in agreement with those reached by Seemann (A., 1929, 633).

F. L. USHER.

**Dependence of the electrical resistance of single crystals of bismuth on the purity of the metal.** L. SCHUBNIKOV and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 350—362).—The resistance of single crystals of bismuth is dependent greatly on the purity of the metal. By careful purification crystals of bismuth were prepared with a resistance at 20° Abs. one third of that of the purest metal of Hilger and one twelfth of that of Kahlbaum's pure metal.

O. J. WALKER.

**Change of resistance of bismuth crystals in the magnetic field at the temperature of liquid hydrogen.** L. SCHUBNIKOV and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 363—378; cf. this vol., 675).—The variation of the resistance of single crystals of bismuth with  $\phi$  has been determined for various magnetic fields, where  $\phi$  is the angle between a binary axis and the direction of the field. The change of resistance of the single crystals with the magnetic field does not obey the laws for an ideal crystal suggested by Kapitza (A., 1928, 825), whose conclusions are derived from resistance measurements with polycrystalline wires and not with single crystals.

O. J. WALKER.

**Electrical resistance of gold in magnetic fields at low temperatures.** W. MEISSNER and H. SCHEFFERS (Physikal. Z., 1930, 31, 574—578; cf. this vol., 142).—Polemical against Kapitza (this vol., 531).

J. FARQUHARSON.

**Thomson effect in metal crystals.** H. VERLEGER (Physikal. Z., 1930, 31, 590).—The Thomson effect in different zinc crystals was measured at various temperatures. The observed values are of the same order as those of Ware (this vol., 844), but his large temperature coefficient was not found.

A. B. D. CASSIE.

**Variation of the *E.M.F.* of zinc under the action of light.** A. SCHUKAREV and L. VERESCHTHAGIN (Physikal. Z., 1930, 31, 590).—The *E.M.F.* across a zinc-calomel electrode cell depends on the exposure

of zinc to radiation. The variation of this *E.M.F.* with the irradiating wave-length is given.

A. B. D. CASSIE.

**Thermoelectric properties of ferromagnetics.** E. C. STONER (Nature, 1930, 125, 973).—Theoretical. The results obtained suggest that less than one electron per atom is required to produce a non-ferromagnetic state and that the ferromagnetic properties of nickel are to be traced to a deficiency of electrons from complete groups.

L. S. THEOBALD.

**Experiments with moistened rock-salt crystals.** E. SCHMID and O. VAUPEL (Z. Physik, 1930, 62, 311—313; cf. A., 1929, 989).—In previous work results were obtained which conflicted with those of Joffe. It was supposed that the increased solidity of moistened crystals was due to water that had been forced into the lattice. The density, lattice constant, and hardness have been determined, and it is found that the first two are practically unaltered by the treatment. Hence it would appear that the increased solidity is not due to any alteration of the lattice. The hardness, however, increases considerably.

A. J. MEE.

**Effect of cold-working on Young's modulus.** T. KAWAI (Sci. Rep. Tôhoku, 1930, 19, 209—234).—Young's modulus for Armeo iron, mild steel, and nickel steel decreases asymptotically with cold-working. For copper, aluminium, and nickel it passes through a minimum. On annealing cold-worked iron and steel Young's modulus increases at first rapidly and then slowly up to 450°, when recrystallisation begins; it reaches its original value at 900°. Young's modulus for copper, aluminium, and nickel passes through maxima at 300°, 200°, and 350°, respectively, on annealing. It is considered that the changes are the result of two opposing factors, internal stress, which decreases the modulus, and rotation of the microcrystals, which increases it.

C. W. GIBBY.

**Hardness of metals and their alloys at various temperatures.** V. P. SCHSCHOKIN (J. Appl. Chem., Russia, 1929, 2, 675—688).—For tin, lead, thallium, cadmium, bismuth, and zinc the Brinell hardness,  $H = ke^{-\alpha t}$ , where  $k$  and  $\alpha$  are constants; for pure metals  $\alpha$  is smaller than for their alloys. Inflexions were observed as follows: cadmium 115—131°, thallium 100° (approx.) and 225—235°, zinc 175—185°, lead 115° (approx.), these temperatures usually corresponding with known transition temperatures of the allotropic forms.

CHEMICAL ABSTRACTS.

**Production by annealing of the two states of pure iron stable at ordinary temperature.** R. FORRER and J. SCHNEIDER (Compt. rend., 1930, 190, 1391—1393).—Iron in the two states corresponding with the two values (0.5 and 0.7) of the ratio of the residual to the saturation magnetisation has been produced by annealing in hydrogen at 300° and 650°, respectively. The latter state is characteristic of a dissymmetric triplet, and once attained is stable at the lower temperature. Its formation is favoured by presence of impurities.

J. GRANT.

**Polymorphism of cyclohexane-1:4-diol.** C. GAUDEFEY (Bull. Soc. Franç. Min., 1929, 52, 55—

59; Chem. Zentr., 1930, i, 977).—The substance, m. p.  $102^{\circ}$ , crystallises from aqueous or alcoholic solution in triclinic prisms,  $n$  1.517. On cooling after fusion there are produced isotropic (small octahedra), uniaxial (needles, tetragonal), and biaxial (triclinic) crystals. The last-named form is stable at the ordinary temperature; the two unstable forms have a low m. p., approx.  $88$ – $92^{\circ}$ . A. A. ELDRIDGE.

**Mol. wt., determined by the dynamic method, of substances exhibiting the phenomenon of superfusion.** E. BOVALINI and A. BANCHETTI (Gazzetta, 1930, 60, 399–408).—Anethole (m. p.  $20.6^{\circ}$ ) shows the Moerschini effect at  $20.7^{\circ}$  (A., 1900, ii, 465), but its viscosity increases almost linearly and without discontinuity as the temperature is lowered. Determinations have been made of the mol. wt. of anethole by measuring the lowering of the vapour pressure of benzene by dissolved anethole, the dynamic method (Ostwald and Luther, "Physiko-chemische Messungen," 4th Ed., 351) being used. This method, which has not given good results in the hands of other experimenters, has proved most satisfactory and seems worthy of more extended application, especially as it may be employed to determine mol. wt. at various temperatures. The results now obtained for anethole give mol. wt. about 10% below the theoretical value if calculated by means of Ostwald's first formula, but good agreement is shown if the third formula is used. The mol. wt. furnished by either formula diminish as the temperature rises, to reach a sharp minimum at  $21.5^{\circ}$ . T. H. POPE.

**Theory of superconductivity of elements. I. Thermo-elastic characteristics of superconductors.** Z. A. EPSTEIN (Z. Physik, 1930, 62, 401–411).—Taken on the whole, the Onnes superconductors have relatively high values for their compressibility coefficients, compared with those for elements which are not superconducting. The idea of an inter-atomic compressibility coefficient is introduced, and the approximate constancy of the inter-atomic tension coefficient for superconductors is shown. For the recently discovered superconductors the same regularities are found as far as the constants are known. The theoretical explanation of the superconductivity of the gold-bismuth eutectic is specially dealt with, and the analogy between a group of superconductors and the ferromagnetic elements is mentioned. A. J. MEE.

**M. p. and vapour pressures of krypton and xenon.** K. PETERS and K. WEIL (Z. physikal. Chem., 1930, 148, 27–35).—The m. p. of krypton and xenon have been found to be  $-157.0^{\circ}$  and  $-112.0^{\circ}$ , respectively, and the values of 2313.9 and 3270.7 g.-cal., respectively, for the molecular heat of vaporisation have been calculated from the b. p. Vapour-pressure measurements have been made with krypton at  $-192^{\circ}$  to  $-151^{\circ}$ , and with xenon at  $-178^{\circ}$  to  $-109^{\circ}$ . Solid krypton apparently has a transition point at about  $-185^{\circ}$ . R. CUTHILL.

**M. p. of pure tellurium.** A. ŠIMEK and B. ŠTEHLÍK (Coll. Czech. Chem. Comm., 1930, 2, 304–313).—The m. p. of tellurium purified by fractional distillation is  $452.0^{\circ}$  (vac.), and is lowered in hydrogen

and carbon dioxide by  $0.15^{\circ}$  and  $0.2^{\circ}$ , respectively, which is to be explained if the gas dissolves in the molten metal. C. W. GIBBY.

**M. p. of oxygen difluoride and of nitrogen trifluoride.** O. RUFF and K. CLUSIUS (Z. anorg. Chem., 1930, 190, 267–269).—Apparatus is described in which the low m. p. of the above compounds can be determined. Oxygen difluoride melted very sharply at  $-223.8^{\circ}$ . The greater part of the nitrogen trifluoride, which was less pure, melted at  $-216.6^{\circ}$ , and this value is provisionally taken as a lower limit. F. L. USHER.

**Additivity of specific heats of crystalline compounds.** G. TAMMANN and A. ROHMANN (Z. anorg. Chem., 1930, 190, 227–236).—The relation of the specific heats of crystalline compounds to the sum of the specific heats of their components is discussed from the point of view of crystal structure. Whilst only slight deviations from strict additivity are to be observed in the specific heats, these may be considerable if the heat capacities over wide temperature intervals are taken into account. Tables are given showing the heat capacities of a number of metals and of intermetallic compounds for intervals of  $100^{\circ}$  from  $-200^{\circ}$  to  $500^{\circ}$ . In 14 out of 25 compounds studied the total heat capacity of the compound is smaller, and in 8 greater, than the sum of the heat capacities of the components, and in 3 the difference changes in sign with change of temperature. Deviations from Kopp's law are not necessarily associated with differences in lattice type between compound and components, nor are such deviations always absent when the lattice type is unchanged. In three instances where contraction of volume occurs on combination a diminution in heat capacity is also observed, as is to be expected if the compound possesses a higher internal pressure. F. L. USHER.

**Thermally excited quantum jumps in solids. IV. Measurement of thermal expansion in anomalous region.** F. SIMON and (FRL.) R. BERGMANN (Z. physikal. Chem., 1930, B, 8, 255–280; cf. A., 1929, 119).—Measurements have been made of the coefficients of linear expansion of various metals from about  $-180^{\circ}$  to the ordinary temperature and of ammonium salts from about  $-70^{\circ}$  to the ordinary temperature. For lithium the Grüneisen law is valid over the whole temperature range provided that the specific heat is calculated by means of a Debye function with a characteristic temperature of  $510^{\circ}$ . Actually, however, the experimentally determined values of the specific heat do not agree with this characteristic temperature, but the deviation indicates the occurrence of an internal rearrangement within the atom, which has no effect on the thermal expansion. The expansion coefficients of iron, steel, and nickel exhibit an anomalous behaviour, remaining approximately constant from  $-100^{\circ}$  to  $-30^{\circ}$ . The values for copper cannot be represented by a Debye function. In the temperature region of abnormal specific heat ammonium salts have abnormally high positive or even negative coefficients of expansion, the value for ammonium chloride with a fibrous structure being different according as it is measured parallel to or perpendicular to the fibres. R. CUTHILL.

**Constant of molecular field. Magneto-thermal equation of state.** P. WEISS (J. Phys. Radium, 1930, [vii], 1, 163—175; cf. this vol., 141).—The phenomena hitherto explained as due to the internal or molecular field are held to be of two kinds according as they are connected with (i) the ferromagnetic equation of state  $\sigma = \mathcal{L}(H + h_m)/T$  ( $\sigma$  is the intensity of magnetisation,  $H$  the external and  $h_m$  the molecular field), and (ii) calorimetric properties due to a field  $H_M = dU/d\sigma$  ( $U$  is the energy of the substance under consideration). Various hypotheses connected with this theory are discussed, and the relations  $H_M = h_m + T\partial h_m/\partial T$ , and  $h_m = n\sigma$  ( $n$  is a constant) deduced. The fact that  $h-\sigma$  curves for nickel (cf. A., 1926, 339) are not straight lines is attributed to that metal consisting of varying amounts of 3-magneton and 8-magneton nickel. This is supported by deductions from specific heat measurements (cf. A., 1928, 827), and is in agreement with Bauer's hypothesis (cf. this vol., 22). C. A. SILBERRAD.

**"Reaction-isochore" equation for ionisation within metals.** E. H. HALL (Proc. Nat. Acad. Sci., 1930, 16, 371—373; cf. this vol., 531).—If it is assumed that an equation of the form  $U = RT^2 d \log_e k/dT$  holds for the breaking up of atoms into ions and free electrons, the factor ( $f/k$ ) must be substituted for  $R$ , where  $k$  is the Boltzmann constant for a single molecule, and  $f$  is an empirical factor ranging between 1.33 and 3.13. J. R. I. HEPBURN.

**Compressibility of carbon monoxide at 0° and ordinary temperature between 50 and 130 atm.** S. GOIG (J. Chim. phys., 1930, 27, 212—235).—The compressibilities of carbon monoxide have been determined at 0°, 12.44°, and 20.22° and at pressures greater than 50 atm. The isotherms obtained are in good agreement with the results of Amagat (1880) and confirm the analogy between the physical properties of this gas and nitrogen. The coefficients of variation from Boyle's law indicate that whilst carbon monoxide behaves normally with respect to its compressibility, it tends to polymerise under the influence of pressure. It is suggested that the electronic configuration of this gas is that of a stable molecule, which is possibly in equilibrium with an active form, responsible for its ability to take part in additive reactions. J. A. V. BUTLER.

**Viscosity of compressed gases.** J. H. BOYD, jun. (Physical Rev., 1930, [ii], 35, 1284—1297).—Using the transpiration method, viscosity measurements were made for nitrogen, hydrogen, and nitrogen-hydrogen mixtures at a number of pressures and temperatures. Results corrected for "end effects" are tabulated. A new theory for the viscosity of compressed gases is based on an analogy between the kinetic pressure and viscosity of a gas, and is derived from a Lorentz type equation of state. The theory is supported by recalculation of data on the variation with the pressure of Reynolds' criterion, which is shown to be constant, and is the first direct proof of the validity of the separate treatment of the kinetic and cohesive pressures in the equation of state. N. M. BLIGH.

**Internal friction of gases and vapours. III. Effect of dipole moment on magnitude of**

**Sutherland's constant.** H. BRAUNE and R. LINKE (Z. physikal. Chem., 1930, 148, 195—215; cf. A., 1929, 24).—The viscosities in the gaseous state of ammonia, water, hydrogen cyanide, chlorine, iodine, methyl chloride, methylene chloride, chloroform, carbon tetrachloride, mercuric chloride, bromide, and iodide, and stannic chloride and bromide have been determined over a wide temperature range. Calculation of the molecular diameter,  $\sigma$ , from the results shows that the volume of the methane molecule increases by equal amounts as the hydrogen atoms are successively replaced by chlorine. The observed values of Sutherland's constant,  $C$ , do not in general correspond with the values calculated from the dipole moment,  $\mu$ , the polarisability,  $\alpha$ , and  $\sigma$  by means of the equation  $C = 16\pi\mu^2/3k\sigma^6$  (Falkenhagen, Physikal. Z., 1922, 23, 87), where  $k$  is Boltzmann's constant. This discrepancy is probably due to the fact that Falkenhagen took into account only the dipole moment of the molecules in deriving his equation, whereas in general the quadrupole effect cannot be neglected. If both dipole and quadrupole effects are taken into consideration, Debye's theory of dipoles leads to the conclusion that the observed and calculated values of  $C$  will be approximately equal only when  $\mu^2/\sigma^3$  has a high value, a deduction which is in agreement with the experimental data. R. CUTHILL.

**Vapour and liquid compositions in binary systems. II. Acetone-water at 25°.** W. G. BEARE, G. A. McVICAR, and J. B. FERGUSON (J. Physical Chem., 1930, 34, 1310—1318).—The formula weight of acetone vapour at various pressures and the vapour pressure of dried and moist acetone at 20°, 25°, 30°, and 35° have been determined. The liquid and vapour compositions for the system at 25°, and the total pressures at 25° are recorded. L. S. THEOBALD.

**Azeotropic data for calculating general properties of binary systems.** C. ALLEN (Ind. Eng. Chem., 1930, 22, 608—609).—Theoretical. L. S. THEOBALD.

**Structure of copper-zinc alloys.** W. BRONIEWSKI and J. STRASBURGER (Compt. rend., 1930, 190, 1412—1415).—The curves connecting the composition of the alloys with the electrical conductivity, the dilatation coefficient at 0°, the thermo-electric effect and its temperature coefficient, the maximum *E.M.F.* of solution, and Brinell hardness show breaks corresponding with the compounds CuZn, CuZn<sub>2</sub>, and CuZn<sub>5</sub>, the existence of which was confirmed micrographically. There is no evidence of Cu<sub>2</sub>Zn<sub>3</sub>, and this composition appears to correspond with the limit of solid solutions of copper in CuZn<sub>2</sub>. No transition point is apparent between 20° and 400°. J. GRANT.

**Age-hardening lead-calcium alloys.** E. E. SCHUMACHER and G. M. BOUTON (Met. and Alloys, 1930, 1, 405—409).—The conductivity curve of the alloys aged for 18 months at 30° shows a break at 0.01% Ca, indicating a solid solubility at least as small as that at 30°. Hardness data are recorded.

CHEMICAL ABSTRACTS.

**X-Ray investigation of iron and manganese alloys.** A. ŌSAWA (Sci. Rep. Tōhoku, 1930, 19, 247—264).—X-Ray analyses of the complete range of iron-manganese alloys have been made, together

with hardness and density measurements up to 50% Mn. Four phases have been found:  $\alpha$ - and  $\beta$ -manganese,  $\alpha$ -iron, and  $\text{Fe}_3\text{Mn}$ . The lattice constants of manganese decrease with increasing iron content and those of iron increase with increasing manganese content.

C. W. GIBBY.

**X-Ray investigation of the iron-manganese system.** E. ÖRMAN (Z. physikal. Chem., 1930, B, 8, 81—110).—Powder photograms of the iron-manganese system have been obtained and from these data a new phase diagram has been constructed. The face-centred cubic  $\gamma$ -iron phase and the face-centred tetragonal  $\gamma$ -manganese phase probably form an unbroken series of mixed crystals, although there may be a small miscibility gap in the neighbourhood of 70 at.-% Mn, where the cubic structure passes into the tetragonal. The atomic volume is a linear function of the composition and increases from 11.32 Å.<sup>3</sup> for pure  $\gamma$ -iron to 12.56 Å.<sup>3</sup> for pure  $\gamma$ -manganese. For pure  $\gamma$ -iron  $a=3.562\pm0.003$  Å., whence the distance between atomic centres is 2.52 Å. The solubility of iron in  $\beta$ -manganese increases from 0% at 1191°, the transition point of  $\gamma$ -manganese to  $\beta$ -manganese, to about 35% at 730°. By saturation with iron  $a$  changes from 6.305 to 6.251 Å. The transition point of  $\beta$ - to  $\alpha$ -manganese is very little affected by the presence of iron. The solubility of iron in  $\alpha$ -manganese diminishes slightly from 37% at 490° to 34% at 690°. By the dissolution of 36 at.-% of iron  $a$  is diminished from 8.904 to 8.864 Å. The atomic volume of  $\beta$ -manganese is 12.53 Å.<sup>3</sup> and of  $\alpha$ -manganese 12.17 Å.<sup>3</sup>. The miscibility gap between  $\alpha$ -manganese and  $\gamma$ -iron extends over a concentration range of approximately 15% between about 500° and 700°, whilst between  $\beta$ -manganese and  $\gamma$ -iron it is about 4 at.-% at 800°. The existence of the  $\epsilon$ -phase with a hexagonal close-packed structure observed by Schmidt (this vol., 148) has been confirmed in quenched samples containing between 12 and 23 at.-% of manganese. It is not stable above 500°. In alloys of 22.9 at.-% of manganese the  $\epsilon$ -phase has the lattice dimensions  $a$  2.541 Å.,  $c$  4.106 Å. The formation of the  $\epsilon$ -phase from  $\gamma$ -iron is accompanied by a considerable decrease in volume. The solubility of manganese in  $\alpha$ -iron is very small. The miscibility gap between  $\gamma$ -iron and the  $\alpha$ -iron phase increases rapidly with falling temperature until it has a range of 30% Mn at 500°. It has not been followed below this temperature.

M. S. BURR.

**Iron-silicon equilibrium diagram.** B. STOUGHTON and E. S. GREINER (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 309, 3—33).—There is evidence of the existence of the compounds  $\text{Fe}_3\text{Si}$ ,  $\text{FeSi}_2$ ,  $\text{FeSi}$ , and  $\text{Fe}_3\text{Si}_2$ . Discontinuities are shown by the temperature-electrical resistance curves which correspond with the line of critical ductility in Pilling's diagram. A new tentative equilibrium diagram is presented.

CHEMICAL ABSTRACTS.

**System iron-vanadium.** M. ÔYA (Sci. Rep. Tôhoku, 1930, 19, 235—245).—Metallic vanadium 98.4% pure has been prepared by the thermite process, using less than the theoretical amount of aluminium and sodium carbonate as a flux. By thermal and magnetic analysis it is shown that a continuous

series of solid solutions is formed. On addition of vanadium the A4 point of iron is lowered, and the A3 point raised. The A2 point passes through a maximum at 15% V and then falls until it reaches the ordinary temperature at 35% V.

C. W. GIBBY.

**Formation of the violet copper alloy  $\text{Cu}_2\text{Sb}$ .** G. ARRIVAUT (Compt. rend., 1930, 190, 1506—1507).—The alloy  $\text{Cu}_2\text{Sb}$  was prepared by digesting pure, finely-divided reduced copper with 10% antimony chloride solution and a little hydrochloric acid on the water-bath in the absence of air. After 2 days the powder was washed, dried with alcohol and ether out of contact with air, and the alloy obtained as a stable, violet crystalline powder,  $d$  7.35.

J. GRANT.

**Influence of recovery on the resistivity and resistance to shear of tempered silicon-aluminium alloys.** L. GUILLET and M. BALLAY (Compt. rend., 1930, 190, 1473—1475).—The experiments (B., 1930, 717) have been extended to alloys containing 0.4% Fe, which were heated for 45 min., tempered in water at 500—600°, and allowed to recover at 20—450° during periods of 7 days to 30 min. The resistivity is diminished to an extent which increases with rise of temperature of recovery up to a maximum at 350° (30 min.), and then decreases until the original value is again reached. Recovery at 150—200° after tempering at 600° increases resistance to shear, an effect which is not obtained after tempering at 525°.

J. GRANT.

**Retardation of dissolution of zinc [in acid] by alloying with cadmium.** M. STRAUMANIS [with M. DRUJANS] (Z. physikal. Chem., 1930, 148, 112—124).—The rate of dissolution of alloys of zinc with platinum, nickel, or iron in 2*N*-sulphuric acid at 25° is much reduced by the presence of a small amount of cadmium, and for the alloys of zinc with gold and copper the effect is particularly pronounced. From metallographic observations it seems probable that the cadmium acts partly by extracting the less electro-positive metal from the molten alloys during solidification and partly by increasing its overvoltage. The protective action of aluminium, magnesium, lead, thallium, cadmium, and mercury on zinc-gold alloys increases in this order. With pure zinc, mercury, cadmium, thallium, and lead have no accelerating effect, and the action of arsenic and silver is only slight.

R. CUTHILL.

**System cyclohexanol and water.** N. V. SIDGWICK and L. E. SUTTON (J.C.S., 1930, 1323—1331).—The miscibility of cyclohexanol and water has been determined over a range of concentration of 0—93% by weight of the alcohol. This includes the two-liquid-phase region and most of the ice line. The two-liquid phase shows reversed solubility in water between approximately 3 and 5% cyclohexanol. The solid separating out below 5% and above 88% appears to be ice, and the results give no indication of the existence of the hydrate  $\text{C}_6\text{H}_{12}\text{O} \cdot 0.5\text{H}_2\text{O}$  suggested by de Forcrand (A., 1912, i, 694). The existence of the reverse solubility curve, however, makes it probable that there is some combination in solution.

M. S. BURR.

**Ternary systems water, *tert.*-butyl alcohol, and salts at 30°.** P. M. GINNINGS and D. ROBBINS (J. Amer. Chem. Soc., 1930, 52, 2282—2286).—The miscibility of *tert.*-butyl alcohol and water has been examined in the presence of inorganic salts at 30°. The binodal curve approaches most closely to the water axis in the case of sodium carbonate, and potassium carbonate and fluoride have the greatest salting-out effects. For potassium halides, this effect is an inverse function of the mol. wt. J. G. A. GRIFFITHS.

**Solubility of lead sulphate, chromate, and molybdate in nitric acid and in perchloric acid.** H. H. WILLARD and J. L. KASSNER (J. Amer. Chem. Soc., 1930, 52, 2402—2408).—The recorded solubilities refer to 25° and acid solutions ranging from 0.1 to 5.0*M*, with and without the addition of the common ions. The salts are much less soluble in perchloric acid than in nitric acid of equivalent concentration. The solubilities of lead sulphate and chromate in perchloric acid pass through maxima in approximately 2.0 and 4.0*M*-acid, respectively.

J. G. A. GRIFFITHS.

**Effect of several factors on the solubility of tartrates.** P. H. RICHERT (J. Amer. Chem. Soc., 1930, 52, 2241—2244).—The solubility of potassium hydrogen tartrate is markedly diminished by the addition of potassium tartrate, especially at low concentrations. Tartaric acid has a much smaller effect which is independent of the concentration when this is greater than 0.01*M*. Invert-sugar has a slight solvent action. J. G. A. GRIFFITHS.

**Solubilities of nitrophenols in aqueous ethyl-alcoholic solutions.** J. C. DUFF and E. J. BILLS (J.C.S., 1930, 1331—1338; cf. this vol., 149).—The solubility of *o*-nitrophenol in aqueous ethyl-alcoholic solutions (100% water to 100% alcohol) has been determined at 25°, that of *m*- and *p*-nitrophenol at 0°, 12.5°, and 25°, and of *p*-nitrophenol at 40° also. A smooth curve, with no unusual features, is obtained for *o*-nitrophenol. No oily phase is formed. The curve for *m*-nitrophenol is unbroken at 0°, but there is a straight portion between 33 and 90% of alcohol. At the higher temperatures, however, two liquid phases are formed for concentration ranges of alcohol which increase with rising temperature. At 25° *m*-nitrophenol shows a maximum solubility at approximately 63% alcohol. Two liquid phases are obtained in the case of *p*-nitrophenol at all the temperatures employed, the range of alcohol concentration through which the two phases coexist increasing with rising temperature. Maximum solubilities are also obtained at all the temperatures, the corresponding alcohol concentrations varying with temperature. There is no evidence for the existence of alcohol hydrates in solution, but it is suggested that both *m*- and *p*-nitrophenols are capable of association with the solvent. M. S. BURR.

**Solubility of oxygen in solid iron. II.** W. KRINGS and J. KEMPENS (Z. anorg. Chem., 1930, 190, 313—320; cf. A., 1929, 1230).—The solubility of oxygen in solid iron has been found by the synthetic kinetic method previously described to be  $0.095 \pm 0.010\%$  at 800°, as compared with  $0.11 \pm 0.015\%$  at 715°. In view of the small difference

between the two values no conclusion can be reached with regard to the temperature coefficient of solubility. An approximation to this value of the solubility is obtained when mixtures of hydrogen and water vapour are passed over heated ferric oxide made by carefully oxidising electrolytic iron in oxygen, but not with commercial ferric oxide. F. L. USHER.

**Salting-out action. I.** P. GROSS and K. SCHWARZ. **II.** P. GROSS and M. ISEK (Monatsh., 1930, 55, 287—306, 329—337).—The electrostatic theory of the salting-out effect is supported by the action of a number of salts on solutions of acetone and of hydrocyanic acid. With few exceptions the theoretically expected reversal of the effect with hydrocyanic acid is observed. The exceptions are not in contradiction to the theory. The salting-out effects of different salts are of the same order at equal ionic concentrations. It is only slightly dependent on the temperature and on the concentration of the substance salted out, and is generally approximately proportional to the concentration of the salt, but the latter is not true for the reversed effect with hydrocyanic acid. J. W. SMITH.

**Influence of alkali chlorides on the solubility of calcium iodate.** P. GROSS and S. S. KLINGHOFFER (Monatsh., 1930, 55, 338—341).—The solubility of calcium iodate hexahydrate in pure water and in solutions of lithium, sodium, potassium, and ammonium chlorides of concentrations between 0.05 and 2.0*M* has been measured. From the data the activity coefficient of the calcium iodate in these solutions is calculated. J. W. SMITH.

**Absorption of gas from a current of air.** M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1930, 62, 683—692).—A mathematical exposition of the relations involved in the removal by an adsorbent of a gaseous admixture from a current of air. R. TRUSZKOWSKI.

**General equation for the velocity of simple adsorption.** S. TOŁŁOCZKO (Coll. Czech. Chem. Comm., 1930, 2, 344—345).—Theoretical. During the course of adsorption or desorption the degree of saturation  $a_t$  of an adsorbent by a given substance is given by  $a_t = \alpha P^{1/n} (1 - e^{-kt})^{1/n}$ , where  $\alpha$ ,  $1/n$ , and  $k$  are constants, and  $P$  is the initial maximum value of the pressure of the substance. C. W. GIBBY.

**Adsorption experiments with the heavier inert gases.** K. PETERS and K. WEIL (Z. physikal. Chem., 1930, 148, 1—26).—The quantitative separation of mixtures of argon, xenon, and krypton by adsorbing on activated carbon and pumping off the adsorbed gas at various temperatures is described. From an investigation of the adsorption of the pure gases at -80°, -18°, and 0° the constants of the Freundlich adsorption isotherm have been obtained and these are used to determine the optimum pressures, temperatures, and amounts of adsorbent for the purpose of separation. Radium emanation in solution in liquid air is completely removed by silica gel. R. CUTHILL.

**Adsorption of the vapours of methane and its chlorine derivatives by activated charcoal.** J. N. PEARCE and H. F. JOHNSTONE (J. Physical Chem., 1930, 34, 1260—1279).—The adsorption of methane

and its chlorine derivatives by activated charcoal has been investigated over the widest possible temperature range. In general, the results are in agreement with Póányi's theory that the adsorbed layer is more than one molecule thick. Except in the case of carbon tetrachloride, the isosteres are practically linear and parallel, indicating that the heats of adsorption change but little with either temperature or composition; the isosteres for carbon tetrachloride tend to show a reversal of curvature. The calculated heats of adsorption,  $\Delta H$ , are for methane  $-3750$ , methyl chloride  $-8300$ , methylene chloride  $-10,450$ , chloroform  $-10,700$ , and carbon tetrachloride  $-8900$  g.-cal., respectively. Carbon tetrachloride decomposes in the presence of charcoal at temperatures as low as the b. p.

L. S. THEOBALD.

**Nature of sorption by charcoal of gases and vapours under great pressure.** J. W. MCBAIN and G. T. BRITTON (J. Amer. Chem. Soc., 1930, 52, 2198—2222).—The sorption of nitrogen for pressures between 1 and 61 atm. and at  $-77^\circ$  and  $20^\circ$ , of nitrous oxide at 0.6—51 atm. and  $20^\circ$ ,  $45^\circ$ , and  $67^\circ$ , and of ethylene at 2.5—43 atm. at  $0^\circ$ ,  $20^\circ$ , and  $45^\circ$  by air- and steam-activated sugar charcoal has been determined. The curves for gases and vapours are similar and no special difference in the behaviour of ethylene and nitrous oxide above and below their critical points is observed, and therefore capillary condensation plays no part in these cases. The sorption phenomena are reversible and except for the sorption of nitrogen at  $20^\circ$  by air-activated charcoal saturation values are reached. The density of carbon is assumed to be 1.8 or 2.0. The data are adequately represented by the Langmuir formula, but by others only for a limited range.

The compressed film theory of Póányi requires a decrease in sorption with increase of pressure, but actually the sorption of nitrogen by charcoal increases greatly with pressure. It is suggested that the dissemination of sorbed molecules between the carbon atoms is closely similar to a true solid solution.

J. G. A. GRIFFITHS.

**Adsorption of hydrogen by nickel at low temperatures.** A. F. BENTON and T. A. WHITE (J. Amer. Chem. Soc., 1930, 52, 2325—2336).—The adsorption of hydrogen by reduced nickel has been investigated at pressures between 0 and 1 atm., and at temperatures between  $-210^\circ$  and  $110^\circ$ . The isotherms exhibit no hysteresis, and those for  $-191^\circ$  and  $-183^\circ$ , but not other temperatures, exhibit discontinuities. At constant pressure, the adsorption increases with fall of temperature to about  $-100^\circ$  and then decreases to a minimum at  $-175^\circ$  to  $-200^\circ$ , followed by a sharp increase at still lower temperatures. At 600 mm., the adsorption is constant between  $0^\circ$  and  $-110^\circ$ , and this is attributed to the formation of a single saturated layer on the surface. Contrary to expectation, hydrogen adsorbed at  $0^\circ$  is not partly desorbed on cooling to  $-191^\circ$ , but additional quantities of gas can be adsorbed reversibly.

It is suggested that the hydrogen is adsorbed in two different ways characterised at higher temperatures by a strong binding which is associated with activation of the gas and at the lowest temperatures by a looser type of binding. J. G. A. GRIFFITHS.

**Adsorption of water vapour and carbon dioxide by manganese dioxide and hopcalite catalysts.** C. E. LANNING (J. Amer. Chem. Soc., 1930, 52, 2411—2415).—The adsorption of water vapour at  $35^\circ$  and carbon dioxide at  $0^\circ$  by finely powdered manganese dioxide has been investigated. Compound formation does not occur, and adsorbed alkali, which reduces catalytic activity, has no effect.

J. G. A. GRIFFITHS.

**Adsorption of water and benzene vapours by manganese dioxide.** H. W. FOOTE and J. K. DIXON (J. Amer. Chem. Soc., 1930, 52, 2170—2179).—Adsorption isotherms have been determined for water vapour at  $-17.5^\circ$ ,  $0^\circ$ ,  $25^\circ$ , and  $40^\circ$ , and for benzene vapour at  $0^\circ$  and  $25^\circ$  with manganese dioxide as adsorbent. The effect of permanent gases and the temperature of outgassing has been investigated. A sharp break in each curve indicates a transition from surface adsorption to condensation. The data are in agreement with Póányi's theory of adsorption, and a pore radius of 10—40 Å. is calculated. The isotherms exhibit hysteresis which is not attributable to false equilibrium or the adsorption of permanent gases. Carbon monoxide and dioxide, but not oxygen, are adsorbed and diminish the adsorption of water vapour, but not the surface condensation. The composition of the oxide is changed to  $Mn_2O_3$  and the surface structure is altered (pore radius 54 Å.) by raising the temperature of outgassing from  $190^\circ$  to  $475^\circ$ . Hysteresis is small and adsorption is markedly diminished owing to the destruction of active adsorption patches. J. G. A. GRIFFITHS.

**Adsorption of gases by glass walls. VII. Ethylene.** M. CRESPI and E. MOLES (Anal. Fis. Quim., 1930, 28, 448—460).—The adsorption of ethylene by a glass surface is in accord with the Freundlich equation, but the Schmidt and Perrin-Langmuir equations yield widely different values. The coefficient of adsorption at 1 atm., referred to 1 litre of gas, is  $0.38 \times 10^{-4}$  g.

H. F. GILLBE.

**Sorption of water vapour by cellulose and derivatives. II. Kinetics of sorption.** S. E. SIEPPARD and P. T. NEWSOME (J. Physical Chem., 1930, 34, 1158—1165).—The actual and the derived curves obtained for the sorption of water vapour by sheets of cellulose acetate and nitrate show that the rate of sorption is primarily dependent on diffusion; since, however, diffusivity and density both vary with thickness, a structure factor of porosity must also be taken into account. The rate of transpiration of water is independent of the hydrostatic head applied. The results support previous views (this vol., 28) of the nature of the sorption process.

L. S. THEOBALD.

**Adsorption of chlorine on silica gel.** A. MAGNUS and A. MÜLLER (Z. physikal. Chem., 1930, 148, 241—260).—An accurate method is described for determining the adsorption isotherms of chlorine on silica gel at  $0^\circ$ ,  $20^\circ$ , and  $40^\circ$  and at pressures of 1—760 mm. The apparatus used in earlier investigations (cf. this vol., 150) is unsuitable owing to the action of chlorine on the mercury and tap grease, and the authors have employed one constructed entirely of glass without taps or mercury. The heats of adsorp-



tion calculated from the isotherms by means of the Clausius-Clapeyron equation decrease with rising temperature or increasing gas pressure. The theory of Magnus (A., 1929, 1139), which gives a quantitative explanation of the adsorption of carbon dioxide on charcoal, cannot be applied to the present system without modification. Comparison of the isotherms shows that the difference lies in the adsorbent rather than in the adsorbed gas. Adsorption on silica gel is a complex process. F. L. USHER.

**Adsorption of complex ammonium ions by silica gel.** G. W. SMITH and L. H. REYERSON (J. Amer. Chem. Soc., 1930, 52, 2584—2585; cf. Latshaw and Reyerson, A., 1925, ii, 412).—Complex ammonium salts of platinum and palladium are easily reduced to the metals on silica gel by adsorbed hydrogen. The complex ammonium ions of copper and nickel are strongly adsorbed by silica gel, and the passage of hydrogen over the dried products yields good deposits of metal. J. G. A. GRIFFITHS.

**Adsorption phenomena in solutions. XIX. "Gas-free" carbon as adsorbent.** N. SCHILOV and K. TSCHMUTOV (Z. physikal. Chem., 1930, 148, 233—236; cf. A., 1929, 1140).—Experiments on the adsorption of hydrochloric acid from aqueous solution by gas-free carbon in presence of oxygen at various pressures have shown that as the oxygen pressure increases the amount of acid adsorbed increases very slowly until the pressure reaches about 2 mm., when a rapid increase begins, a second period of approximate constancy ultimately being reached, however. In explanation of these observations it is suggested that at very low oxygen pressures and even in a high vacuum there is present on the surface of the carbon a complete film of active oxide, which cannot be removed either by evacuation or by heating, and that under these conditions the amount of acid adsorbed is constant, independent of the oxygen pressure, since it depends only on the amount of oxide. When the gas pressure exceeds about 2 mm., however, a new active oxide is formed, and at the same time the amount of acid adsorbed rises rapidly.

R. CUTHILL.

**Adsorption of mineral colours by wool fibre from aqueous suspension.** M. A. ILJINSKI and V. V. KOZLOV (J. Russ. Phys. Chem. Soc., 1930, 62, 665—672).—One g. of wool adsorbs 50% of the pigment from 50 c.c. of 0.5% lead chromate suspension in 1 min., and 82.3% in 30 min. Maximal adsorption takes place from 0.41% suspensions. The degree of adsorption is little affected by temperature. Adsorption is diminished by the addition of sodium chloride to the suspension. The percentage adsorption gradually diminishes as the dilution is increased from 5 to 100 c.c. The adsorbed lead chromate content is reduced from 1.29 to 0.88% by shaking three times with water, showing that adsorption is only partly reversible. Adsorption is enhanced by 13—25% by the addition of sulphuric acid. R. TRUSZKOWSKI.

**Adsorption of radioactive by inactive substances.** A. N. PILKOV (J. Russ. Phys. Chem. Soc., 1930, 62, 617—629).—Methods are described for the preparation of ionium and thorium adsorbates on cerium oxalate, and radium-D, -F, and -G adsorbates

on bismuth and lead oxides, from Fergansk radioactive minerals. Thorium and cerium nitrates are completely insoluble in ether. R. TRUSZKOWSKI.

**Adsorption phenomena in systems of several constituents.** H. CASSEL (Z. physikal. Chem., 1930, 148, 95—96).—The results of Wagner for the adsorption at the surface of mixed aqueous solutions of phenol and aniline (A., 1929, 1231) are in good agreement with the theory of adsorption previously developed (A., 1926, 127). R. CUTHILL.

**Influence of adsorption on the growth of crystal surfaces.** K. F. HERZFELD (Coll. Symp. Ann., 1930, 7, 51—57).—Consideration of the influence of adsorption on surface tension leads to a formula for the free surface energy of a crystal. In macroscopic, but probably not in microscopic, crystals the external form does not correspond with the form of minimum surface energy. CHEMICAL ABSTRACTS.

**Crystal structure and adsorption from solution.** W. G. FRANCE (Coll. Symp. Ann., 1930, 7, 59—87).—Adsorption by a growing crystal depends on the residual valency force fields of the crystal faces, the interionic distances between the faces, and the presence and distribution of polar groups in the adsorbed material. Adsorbed dyes are not necessarily colloidal in solution. The quantity adsorbed depends on the concentration and adsorbing area. The minimum concentration of dye which will yield a saturated surface is less than that required for a unimolecular layer. Adsorption by growing crystals of ammonium, caesium, or potassium alum or lead nitrate occurs at those faces having the strongest electric force fields. CHEMICAL ABSTRACTS.

**Drop-weight method for determination of surface tension. Effect of inclination of the tip on the drop weight.** D. M. GANS and W. D. HARKINS (J. Amer. Chem. Soc., 1930, 52, 2287—2289).—The weight of the drop is independent of the tilt of the dropping surface if this deviates less than 3° from the horizontal. J. G. A. GRIFFITHS.

**Surface tension of aqueous solutions of *p*-toluidine.** D. M. GANS and W. D. HARKINS (J. Amer. Chem. Soc., 1930, 52, 2289—2295).—The measurements made at 20° by an improved drop-weight method agree with those of Frumkin and others (A., 1926, 1092) and are higher than those of Edwards (A., 1925, ii, 387). *p*-Toluidine is very surface-active, and a molecule in the surface region of the nearly saturated solution is computed to occupy an area of 28 sq. Å. J. G. A. GRIFFITHS.

**Shrinking force of metallic leaves at high temperature.** I. SAWAI and M. NISHIDA (Z. anorg. Chem., 1930, 190, 375—383).—The shrinking of metallic leaves at high temperature due to the surface tension (cf. Schottky, A., 1912, ii, 630) has been studied in the case of silver and gold by measuring the load required to be placed on the leaf, suspended in an atmosphere of nitrogen, to keep it in equilibrium when heated above 600°. The leaves were shown by means of X-rays to have no regular microcrystalline structure, and no change in structure was brought about by the shrinking. From the load measurements the value of the shrinking force  $\alpha$ , in

mg. per min., has been calculated. The value of  $\alpha$  is always smaller than the surface tension, and increases with rise in temperature even although the surface tension decreases. O. J. WALKER.

**Micro-method for determination of angle of contact.** D. TALMUD and N. M. LUBMAN (*Z. physikal. Chem.*, 1930, **148**, 227—232).—The method described depends on the fact that if a drop of liquid is placed on a horizontal solid surface and is not deformed by gravity it will assume the form of a segment of a sphere; from the radius of the plane face and the height the angle of contact can be calculated. In practice, the effect of gravity may be sufficiently diminished by placing the surface in a liquid of approximately the same density as the drop and immiscible with it, and using a very small drop. With liquids of very high surface tension, such as mercury, the angle of contact liquid-air-solid may be obtained in the same way. The results of determinations made with various liquids are recorded.

R. CUTHILL.

**Stability of soap films.** A. S. C. LAWRENCE (*Nature*, 1930, **125**, 970—971).—The stratification theory of Green (*ibid.*, 815) is criticised and the author's view that the films consist of a pair of surface layers adsorbed at the liquid-air interface enclosing a layer of liquid (cf. this vol., 413) is further developed.

L. S. TREOBALD.

**Osmosis in systems containing also liquids with constant compositions.** I. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 344—349).—Mathematical.

O. J. WALKER.

**Densities and specific heats of unit volumes of solutions of sodium, calcium, and magnesium chlorides at low and moderate temperatures.** W. KOCH (*Z. ges. Kälte-Ind.*, 1924, **31**, 105—108; *Chem. Zentr.*, 1930, i, 804).—Data are tabulated.

A. A. ELDRIDGE.

**Volume changes in reactions of neutralisation.** I. I. ZASLAVSKI and E. G. SHTANDEL (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 653—664).—In the neutralisation of sodium or potassium hydroxide solutions the volume of the system reaches a maximum at neutrality, whilst for ammonia solution the volume is minimal at this point. In the former case the magnitude of the volume change attains a maximum for 9—10*N*-solutions, but in the latter it increases linearly with concentration. For a given concentration of alkali the magnitude of the volume changes is connected with the dissociation constant of the acid used. The volume changes observed vary within the limits −9 to +6.5%.

R. TRUSZKOWSKI.

**Extinction coefficients of the mixtures of chromates and dichromates.** N. R. TAWDE and G. R. PARANJPE (*Indian J. Physics*, 1930, **4**, 533—538).—The extinction coefficients of solutions of chromates, dichromates, and mixtures of these have been measured. The results obtained are used to determine the percentages of chromate and dichromate in presence of each other. J. W. SMITH.

**Optical measurement of electrolytic dissociation in very dilute ethyl-alcoholic solution.** P. GROSS and A. GOLDSTERN (*Monatsh.*, 1930, **55**,

316—328).—Measurements have been made of the extinction coefficients at a wave-length of 4360 Å. for very dilute ethyl-alcoholic solutions of lithium picrate alone and in the presence of lithium chloride, and of picric acid alone and with the addition of lithium chloride, sodium chloride, sodium bromide, and hydrogen chloride. The extinction coefficient of lithium picrate is almost constant at concentrations between  $2 \times 10^{-5}$  and  $1.5 \times 10^{-3}$  mol. per litre, but at higher concentrations increases with the concentration of the salt. On the other hand, the extinction coefficient of picric acid increases with increasing acid concentration over the range  $3.3 \times 10^{-6}$  to  $7.0 \times 10^{-3}$  mols. per litre. Assuming the extinction of the undissociated acid to be zero, the degree of dissociation of picric acid is calculated. The dissociation constant is independent of the nature of the added salt up to an ionic concentration of about  $10^{-3}$ , except in the case of hydrogen chloride, when secondary effects appear. The logarithm of the activity coefficient, however, is greater than would be expected on Debye's theory. J. W. SMITH.

**Measurement of the magnetisation coefficient of aqueous solutions by the falling-drop method.** L. ABONNENC (*Compt. rend.*, 1930, **190**, 1395—1397).—The method (*Ann. Physique*, 1925, **3**, 161) measures the change in weight ( $\Delta m$ ) of a drop of liquid formed on the end of a vertical cylinder in a non-uniform magnetic field, and thence the magnetic susceptibility, which is proportional to  $\Delta m/m$ . Measurements at 20° for the halogen acids (compared with pure water), when corrected for the apparent paramagnetism, give values for the diamagnetism of the halogen ions in close agreement with those of other workers. J. GRANT.

**Frictional motion of solid bodies in a liquid.** H. BENNDORF (*Physikal. Z.*, 1930, **31**, 593—610).—Exner's formula (*ibid.*, 1929, **30**, 458), derived from energy considerations, is said to be based on a wrong assumption. The limiting velocity of a sphere under the influence of a constant force is calculated and an expression is derived for the influence of temperature and pressure of the medium on the magnitude of the limiting velocity. The retardation of a sphere by a liquid is discussed. If the resistance function is known, the equations deduced for a sphere are applicable to all bodies irrespective of shape.

W. R. ANGUS.

**Polyatomic hydroxy-compound method of synthesis of hydrosols. II.** A. V. DUMANSKI and B. G. ZAPROMETOV (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 747—767).—The ternary systems *N*-cobaltous chloride or nickelous nitrate-*N*-sodium tartrate or 0.5*N*-mannitol-*N*-sodium hydroxide have been examined for gel and sol formation, and the results are represented graphically in a three-co-ordinate system. Cobaltous hydroxide adsorbs more sodium tartrate than does nickelous hydroxide, but less sodium succinate.

R. TRUSZKOWSKI.

**Degree of dispersity of solutions of cadmium in cadmium chloride ("pyrosols").** E. HEYMANN and E. FRIEDLÄNDER (*Z. physikal. Chem.*, 1930, **148**, 177—194).—From measurements of the distribution ratio of cadmium between molten bismuth

and molten cadmium chloride at 590° and 690° and of the effect of bismuth on the solubility of cadmium in the chloride, it appears that cadmium is present in solution in molten cadmium chloride as monatomic molecules, and therefore the system is a molecular dispersion. This conclusion is further substantiated by the fact that the concentration of metal in molten cadmium chloride in equilibrium with molten cadmium is independent of the amount of metal phase (cf. Ostwald, A., 1927, 310). It is probable, however, that the dissolved metal is solvated (cf. Eitel and Lange, A., 1928, 700). Cadmium may be determined even in presence of a large excess of bismuth by precipitating the hydroxides from the solution of the nitrates, then dissolving the cadmium hydroxide by adding excess of potassium cyanide, and depositing the metal by electrolysis of the solution with a current of 1 amp. at 4.8–5 volts at 40°. R. CUTBILL.

**Viscosity of mixtures of hydrophilic sols.** H. G. B. DE JONG and O. S. GWAN (Biochem. Z., 1930, 221, 166–181).—The viscosity of mixtures of hydrophilic sols shows additive relations (see A., 1929, 1382) only under special conditions. Both sols must follow Poiseuille's law; the particles of both sols must retain their individuality in the mixture; the viscosity values must be either small or, if large, must not be far removed from one another, and the medium of the two sols must be of the same composition. When soluble starch sol is added to gum arabic sol, additive viscosity values are obtained, but when the starch sol contains small amounts of electrolytes, additive relations are destroyed, the viscosity values of the mixtures being up to 47% less than those calculated from the mixture rule. Additivity is restored if the electrolyte is added to both sols before mixing. P. W. CLUTTERBUCK.

**Influence of radium emanation on the viscosity of aqueous solutions of gelatin.** I. I. SHUKOV and V. A. UNKOVSKAYA (J. Russ. Phys. Chem. Soc., 1930, 62, 581–600).—The time-viscosity curves of aqueous solutions of gelatin exposed to  $\beta$ - and  $\gamma$ -radiation of radon rise to a maximum during the second day; the viscosity of solutions exposed to  $\alpha$ -radiation falls linearly with time, attaining that of water on the fourth day of exposure. An insoluble gel is deposited from solution, giving highly refractive crystals on prolonged boiling with water. When acid or alkaline solutions of gelatin were used, their viscosity fell asymptotically, practically constant values being obtained after 8 days of exposure; at the same time the  $p_H$  of the solutions diminished from 10.6 to 7.5 in four days, from 2.4 to 1.85 in 14 days, and from 5.0 to 3.3 in 4 days. R. TRUSZKOWSKI.

**Behaviour of silicic, vanadic, tungstic, molybdic, antimonie, and telluric acids in the colloidal state.** S. GHOSH and N. R. DHAR (Z. anorg. Chem., 1930, 190, 421–427).—The viscosity of a silicic acid sol is increased by small amounts of hydroxyl ion up to a maximum concentration, beyond which the viscosity decreases. Traces of hydrogen ion diminish the viscosity. Vanadic and tungstic acid sols behave similarly. The stability of antimonie acid sols is only slightly increased by traces of hydroxyl ion, and is not altered by small amounts

of hydrogen ion. In general, the colloidal behaviour of sols of the above acids is very similar.

O. J. WALKER.

**Hysteresis in the electrical conductance of colloidal solutions.** S. VISCO (Atti R. Accad. Lincei, 1930, [vi], 11, 583–586).—The values found for the conductance of gelatin solutions are lower when the temperature of measurement is approached by cooling than when it is reached by heating. The hysteresis is greatest in the neighbourhood of 50°, and the curves obtained are closely paralleled by the viscosity curves for the solutions. The hysteresis in the conductance is attributed to the effect of the viscosity hysteresis on the ionic mobilities of the solutions. F. G. TRYHORN.

**Stabilisers of colloidal systems. II.** S. I. DIJATSKHOVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 763–769).—Silicic acid sols occasionally exhibit levorotation; this phenomenon appears shortly before coagulation of the sol, and is ascribed to transient formation of crystalline products. The stability of sols prepared by addition of sodium silicate to hydrochloric acid solution is enhanced by dialysis. The specific conductivity of dialysed sols at first increases with dilution, and then falls; in the case of undialysed sols two points of maximum conductivity are observed. R. TRUSZKOWSKI.

**Mutual flocculation of sols of ferric hydroxide having granules of opposite signs.** A. BOUTARIC and (MLLE.) G. PERREAU (J. Chim. phys., 1930, 27, 250–255).—The flocculation produced when a dilute positive ferric hydroxide sol is mixed with a similar negative sol of the same concentration (prepared by dilution of a concentrated positive sol with an equal volume of a solution of suitable concentration of an electrolyte having a multivalent anion) is dependent on the electrolyte used. The effect of dilution due to mixing is to carry the concentration of the electrolyte beyond the value for which it cannot produce flocculation, to a lower value at which flocculation is possible. J. GRANT.

**Gel formation from silicic acid sols by means of acids.** K. WOLF and M. PRAETORIUS (Kolloid-Z., 1930, 52, 103–107).—See this vol., 857.

**Structure of cellulose gels. I. Mechanism of gelation. II. Syneresis of viscose.** K. ATSUKI and H. SOBUE (Proc. Imp. Acad. Tokyo, 1930, 6, 161–164, 165–167).—I. The spontaneous coagulation of viscose is assumed to be due to electric discharge and dehydration of the disperse phase by the alkali and salts which are either present initially or separate spontaneously from the dilute solution of sodium cellulose xanthate employed. The interfacial tension between the disperse phase and the medium has also some influence on the coagulation. Observations are recorded which show that the interfacial tension increases with the dilution of the sol and that the structure of the resulting gel is affected by syneresis.

II. Experiments have been carried out on the syneresis of viscose; the results can be expressed by Liepatov's formula (A., 1925, ii, 685).

W. R. ANGUS.

**Measurement of the hydration of gelatin and similar materials and the relation of hydration to swelling.** H. A. NEVILLE and E. R. THEIS (Coll. Symp. Ann., 1930, 7, 41—49).—The contraction of the total volume of the system gelatin-water was measured. Although equilibrium is reached more quickly at higher temperatures, the final contraction and therefore the hydration increases as the temperature falls from 36.3° to 1°. The total contraction at equilibrium diminishes with rising temperature. Minimum contraction occurred at  $p_H$  1.5, and maximum contraction at  $p_H$  6. Salts also decrease the contraction. Swelling and change of volume are probably largely independent phenomena. The treatment of hides is discussed. CHEMICAL ABSTRACTS.

**Complex coacervation. II. Serum-albumin and gum arabic.** H. G. B. DE JONG and O. S. GWAN (Biochem. Z., 1930, 221, 182—205; cf. this vol., 158).—Colloidal particles of only one kind take part in the formation of simple coacervates (colloid-rich phases), and of two or more kinds in compound coacervates. Compound coacervates are further divided into mixed coacervates (when each of the colloidal components under the given conditions gives simple coacervates which are miscible) and complex coacervates (when each of the colloidal components under the given conditions would if present singly be found as the stable sol). Using isohydric 0.64% serum-albumin and 0.5 or 0.33% gum arabic sols at 26°, it is found that above  $p_H$  4.2 the optimal coacervation does not coincide with the minimum of the additivity curve. The position of optimal coacervation, if the protein is feebly positively and the gum arabic strongly negatively charged, lies completely on the serum-albumin side, whereas with decrease of  $p_H$  it is displaced completely to the gum arabic side. Multivalent cations tend to displace the mixture proportions for optimal coacervation to the gum arabic side and multivalent anions to the albumin side. Serum-albumin of complex coacervate is gradually denatured. Whereas potassium chloride and sulphate divide the complex coacervate into two sols, potassium ferriocyanide divides it into sol and simple coacervate.

P. W. CLUTTERBUCK.

**Diffusion rings of silver dichromate and chromate in gelatin and agar-agar.** F. PANNAOH (Chem. Erde, 1930, 4, 598—631).—A continuation of the work of Linck (A., 1929, 134) on the rates of diffusion of potassium dichromate or chromate and silver nitrate in gelatin etc., and on the form of the resulting precipitates.

L. J. SPENCER.

**Colloidal platinum. VII. Effect of electrolytes on the cataphoretic velocity of platinum particles, and its bearing on stability.** S. W. PENNYQUICK (J.C.S., 1930, 1447—1458).—Determinations of the cataphoretic velocity of platinum sols have been made in the presence of hydrochloric acid, barium, calcium, ferric, sodium, and potassium chlorides, potassium cyanide, and sodium and barium hydroxides. The intermicellar fluid, obtained by freezing out the colloid particles, was used as the over-lying liquid after adjusting to the correct conductivity. In spite of a similarity in the method of preparation, the cataphoretic velocities of the pure

sols exhibited variations in the value of  $u \times 10^5$  from 27.8 to 37.0 cm./sec. per unit potential gradient, and no simple relationship appears to hold between velocity and concentration of acid as measured by the conductivity assumed to be due to  $H_2Pt(OH)_6$ . Addition of hydrochloric acid diminishes the velocity, and this is interpreted as due to direct repression of the ionic atmosphere. The linear relationship of Debye and Hückel between the decrease in cataphoretic velocity and the square root of the acid concentration holds. Univalent bases, and potassium cyanide which acts as a weak base, react with the surface oxide to form fresh stabilising ionogens, and the cataphoretic velocity passes through a pronounced maximum at low concentrations. This accounts for the peptising action of univalent bases previously observed (A., 1929, 643). Bivalent bases have an insignificant maximum, owing to the high coagulating power of the bivalent ion. Univalent salts also exhibit a maximum. With hydrochloric acid, barium hydroxide, and barium, calcium, and ferric chlorides coagulation takes place between velocities of  $10 \times 10^{-5}$  and  $15 \times 10^{-5}$  cm./sec. and critical potential 0.020—0.030 volt. The velocity of coagulation, under the influence of poor coagulants such as univalent bases and salts, is much higher, as is also the corresponding potential. With sodium hydroxide the velocity at coagulation is greater than that of the pure sol. Ferric chloride has two critical velocities, one negative and the other positive. The nature of the coagulation process is discussed.

M. S. BURR.

**Chemical mechanics.** A. SKRABAL (Monatsh., 1930, 55, 225—286).—Mathematical. The classical laws of chemical mechanics, i.e., the partition law and the static and kinetic mass action law, are generalised so as to apply not only to a known constant medium, but also to any variable medium. J. W. SMITH.

**Thermal dissociation of carbon tetrachloride.** M. BODENSTEIN and P. GÜNTHER (Z. angew. Chem., 1930, 43, 423—425).—The dissociation of carbon tetrachloride vapour in a silica tube at 400—580° in presence of activated carbon has been studied and the degree of dissociation in the equilibrium state at each temperature obtained by extrapolation. The dissociation at the lower temperatures of the range is less than that indicated by the heat of formation and the Nernst formula. At higher temperatures the values approach the theoretical. Traces of solid by-products (hexachlorobenzene?) were noticed in the reaction tube.

C. IRWIN.

**Water-gas equilibrium under the influence of the electric discharge at reduced pressure.** K. PETERS and H. KÜSTER (Z. physikal. Chem., 1930, 148, 284—303; cf. B., 1930, 594).—The conditions of the interaction of carbon dioxide and hydrogen when the mixture is subjected to an electric discharge at pressures between 20 and 50 mm. have been systematically studied. The percentage decomposition increases rapidly to a constant value with increasing current density. The steady value is independent of the distance separating the electrodes and of their temperature, but increases with an increase of the proportion of hydrogen in the mixture. The decomposition is not influenced by variation in the velocity

of flow of the gas between 25 and 710 litres per hour. The percentage decomposition reaches a maximum when the ratio  $H_2:CO_2$  is initially 3:1, but the efficiency is highest with equimolecular proportions. The temperature in the path of the discharge lies between  $800^\circ$  and  $1000^\circ$  according to the rate of flow of the mixture, its composition, and its pressure. The average temperature of the discharge tube is  $300^\circ$ . The temperatures measured during discharge with a load of 1.2 kilowatts agree approximately with those calculated from Nernst's law when the composition is  $ICO_2:2H_2$ , but are appreciably higher with larger proportions of hydrogen, whilst with mixtures rich in carbon dioxide or with pure carbon dioxide the calculated temperatures are from  $200^\circ$  to  $1000^\circ$  higher than those measured. The discordance between observed and calculated temperatures indicates that the decomposition is not purely thermal, but that electrical effects are important. The stages in the reaction are:  $CO_2=CO+O-86.5$  kg.-cal.;  $H_2=H+H-100$  kg.-cal.;  $H+H+O=H_2O+176.1$  kg.-cal.

F. L. USHER.

**Chemical equilibrium between phosphine, phosphorus, and hydrogen.** V. N. IPATIEV and A. W. FROST (Ber., 1930, 63, [B], 1104—1110).—The dried mixture of phosphine and hydrogen, obtained by the action of water on red phosphorus, was passed at varying rates through a quartz tube filled with quartz powder at  $340^\circ$ . With diminishing rate of flow the value of  $\log K_p$  in the expression  $\log K_p = \log P_{PH_3}^2/P_P \times P_{H_2}^2$  diminishes continuously, falling for minimal rates much below the values recorded by Drummond (A., 1927, 940). Attempts to approach the equilibrium from the other side by passing hydrogen and phosphorus vapour through the heated tube were frustrated by the slowness with which the equilibrium is attained. Experiments are therefore described in which violet phosphorus was heated with hydrogen or a mixture of phosphine and hydrogen in a silvered autoclave at constant temperatures between  $349^\circ$  and  $498^\circ$  until equilibrium was attained. Within the limits of experimental error the results agree with the expression  $\log K_p = -A/T + B$  ( $A = -4956$ ;  $B = -18.68$ ). The heat of formation of phosphine from solid white phosphorus and hydrogen is calculated to be 2355 g.-cal.

H. WREN.

**Dissociation of strong electrolytes. II. Two-phase equilibria. Heats of neutralisation.** M. B. JACOBS and C. V. KING (J. Physical Chem., 1930, 34, 1303—1309; cf. this vol., 859).—A discussion of data relating to vapour pressure of dilute aqueous solutions of the hydrogen halides, the extraction of silver perchlorate from benzene by water, and the heats of neutralisation of strong acids and bases; these data do not support a theory of complete in preference to one of partial dissociation.

L. S. THEOBALD.

**Incomplete dissociation of typical binary salts and validity of dilution law for non-aqueous solutions of such salts.** P. WALDEN (Z. physikal. Chem., 1930, 148, 45—94).—A comprehensive survey of the ionisation relations of binary salts in non-aqueous solution, as indicated by the degree of dissociation obtained from the conductivity ratio, shows

that the ionisation process is intimately dependent on the chemical nature of solvent and solute. No theory of ionisation which takes into consideration only physical factors, such as viscosity and dielectric constant, is adequate to account for the experimental data, and in fact the values of  $(1-\alpha)\sqrt{v}$  calculated from the Onsager equation often deviate by as much as 2000% from the experimental values (cf. this vol., 703). Similarly, two electrolytes which are approximately equally dissociated at a particular dilution in a given solvent may have widely divergent degrees of dissociation in another solvent of almost the same dielectric constant. Thus many salts which are strong electrolytes in aqueous solution behave like typical weak electrolytes even in non-aqueous solvents of relatively high dissociating power, and obey the Ostwald dilution law over a wide range of concentration. In solvents of very low dielectric constant, indeed, practically all the strong electrolytes become weak. From these observations it seems necessary to conclude that undissociated molecules may be present to an appreciable extent even in solutions of strong electrolytes.

R. CUTHILL.

**Dissociation of carbonic acid and its action on metallic nickel under pressure.** E. MÜLLER and A. LUBER (Z. anorg. Chem., 1930, 190, 427).—In the calculation of the affinity constant for the first stage of dissociation of carbonic acid (this vol., 440) the total concentration of acid was erroneously used instead of the concentration of the undissociated acid. The correct value for the affinity constant is  $3.06 \times 10^{-4}$ .

O. J. WALKER.

**Complex ions having extremely small instability constants.** A. PRINS (Chem. Weekblad, 1930, 27, 191—193).—Feigl's observations (cf. this vol., 724) on nickel potassium cyanide are shown to be invalid. The velocity of the reaction between the sulphide ion and silver potassium cyanide solution is discussed in reference to the rate of transference of electric charges, and it is shown that reactions with relatively stable complex ions are governed primarily by conditions within the complex.

H. F. GILLBE.

**Diethylbarbiturate buffer.** L. MICHAELIS (J. Biol. Chem., 1930, 87, 33—35).—Sodium diethylbarbiturate forms a suitable buffer substance over the range  $p_H$  6.8—9.6.

C. R. HARRINGTON.

**Solubility of acids in salt solutions. II. Solubility of benzoic acid and activity coefficient of its molecules in aqueous benzoate solutions.** E. LARSSON (Z. physikal. Chem., 1930, 148, 148—155; cf. A., 1927, 829).—The solubility at  $18^\circ$  of benzoic acid in 0.01—1.0*N*-solutions of sodium benzoate and 0.05—0.23*N*-solutions of potassium benzoate has been determined, and the activity coefficient,  $f$ , of the undissociated acid in these solutions calculated from the results. For the sodium benzoate solutions the relation  $\log f = -0.40\alpha$ , where  $\alpha$  is the benzoate concentration, holds over the whole range of concentration. The dissociation constant of the acid is calculated to be  $5.9 \times 10^{-5}$  at  $18^\circ$ .

R. CUTHILL.

**Solubility of acids in salt solutions. III. Solubility of benzoic acid and the activity**

coefficient of its molecule in solutions of sodium chloride and of potassium chloride. E. LARSSON (Z. physikal. Chem., 1930, 148, 304—317; cf. A., 1927, 829).—The activity coefficient of a sparingly soluble acid like benzoic in solutions of sodium or potassium chloride can be obtained from measurements of its solubility by correcting for its dissociation. Three ways of allowing for the dissociation have been worked out, viz., an experimental (electrometric), a graphical, and a mathematical method. The concordance of the results obtained by the three methods is satisfactory. In the first the hydrogen-ion activity of the solution is directly measured, but since up to the present the activity coefficient of the hydrogen ion is known with sufficient accuracy only in solutions of sodium and potassium chloride the applicability of the method is limited. In the graphical method sodium benzoate is added to the solution in such quantity that the amount of benzoic acid dissociated becomes negligible and the activity coefficient is measured directly. By extrapolation of the curve representing the relation between the activity coefficient and the concentration of sodium benzoate the value of the former in a benzoate-free solution is obtained. In the third method the extrapolation is performed mathematically and fewer experiments are required. The concentration of the sodium and potassium chloride solutions used varied between 0.2*M* and 3.0*M*. The dependence of the activity coefficient (*f*) of the benzoic acid molecule on the salt concentration (*c*) is given by the equation  $\log f = 0.177c (\text{NaCl}) = 0.137c (\text{KCl})$ . F. L. USHER.

**Activity coefficients of sodium, potassium, and lithium chlorides and hydrochloric acid at infinite dilution in water-methyl alcohol mixtures.** G. ÅKERLÖF (J. Amer. Chem. Soc., 1930, 52, 2353—2368; cf. Harned, A., 1929, 513).—The *E.M.F.* at 25° of the cell  $\text{Ag}|\text{AgCl}|\text{MCl}_{\text{aq}}(c_1)|\text{M}_x\text{Hg}|\text{MCl}(c_2)|\text{aq. alcohol}(c_2)|\text{AgCl}|\text{Ag}$  and of the cell  $\text{Ag}|\text{AgCl}|\text{HCl}(c_1)|\text{aq. alcohol}(c_2)|\text{H}_2$  has been determined, where *M*=K, Na, Li,  $c_1=0.02$ —1.0 molal, and  $c_2=10$ —90 wt.-% alcohol. Activity coefficients have been calculated, but except in the case of the hydrogen chloride solutions, theoretical values of the constant, *a*, of the Debye limiting equation for dilute solutions cannot be used, and differences between the empirical and theoretical values of *a* increase rapidly with increasing concentration of alcohol. The equation of Gronwall, La Mer, and Sandved (A., 1928, 841) is not applicable. The logarithm of the activity coefficient at infinite dilution is approximately inversely proportional to the dielectric constant of the pure water-alcohol mixtures, as predicted by theory.

J. G. A. GRIFFITHS.

**Thermal dissociation of pyrites.** L. D'OR (J. Chim. phys., 1930, 27, 239—249).—Details of the author's method (this vol., 977) are provided. Changes in the absorption capacity of pyrites at 540°, 625°, and 660° indicate that the dissociation is reversible. There are indications that the pyrites used contained a sulphide of iron poorer in sulphur than  $\text{FeS}_2$ , and that neither pure pyrites nor the quartz walls of the tube can adsorb sulphur.

J. GRANT.

**Iron-nitrogen system; X-ray investigation.** O. EISENHUT and E. KAUPP (Z. Elektrochem., 1930, 36, 392—403).—The equilibrium relations characterising the iron-nitrogen system are determined from X-ray observations. Between the temperatures 350° and 750° four homogeneous phases exist: (1)  $\alpha$ -phase: a solid solution of nitrogen in  $\alpha$ -iron (0—0.5% N), (2)  $\gamma$ -phase: a solid solution of nitrogen in  $\gamma$ -iron (observed between 1 and 2.7% N), (3)  $\gamma'$ -phase: mixed crystals of  $\text{Fe}_4\text{N}$  and iron (between 5.5 and 6.0% N), and (4)  $\epsilon$ -phase: observed between 4.5 and 11% N. There is a continuous absorption of nitrogen in these different phases with a corresponding regular change of the crystal lattice constants.

H. I. DOWNES.

**Iron-hydrogen-ammonia equilibrium.** E. LEHRER (Z. Elektrochem., 1930, 36, 383—392).—Data are recorded for the iron-hydrogen-ammonia equilibrium between 350° and 750°. The four phases  $\alpha$ ,  $\gamma$ ,  $\gamma'$ , and  $\epsilon$  (cf. preceding abstract) are associated with five bivariant equilibria and two univariant equilibria; in the latter the solid phases are  $\alpha$ ,  $\gamma$ ,  $\gamma'$  and  $\gamma$ ,  $\gamma'$ ,  $\epsilon$ , respectively. The dissociation pressures of these phases are calculated with the aid of Haber's data for the ammonia equilibrium, and the possibility of their production from pure iron and molecular nitrogen is discussed. The  $\epsilon$ -phase cannot be obtained directly in this way, and the  $\gamma'$ -phase is obtained most readily at high pressures and low temperatures.

H. I. DOWNES.

**Borate-alkali halide fusion systems.** B. STÅLHANE (Z. Elektrochem., 1930, 36, 404—408).—The equilibrium relations of the potassium halide-borate fusion system are entirely similar to those of the corresponding sodium system, but the solubilities are somewhat smaller. Conductivity measurements show (1) that the conductivity of a borax-sodium chloride (or sodium fluoride) fused mass increases continuously with the content of sodium halide, whilst the temperature coefficient decreases, and (2) that the conductivity of the sodium borates increases with the  $\text{Na}_2\text{O}$  content, whilst the temperature coefficient decreases. It is assumed that the conductivity is directly proportional to the concentration of metal ions and inversely proportional to the viscosity, which two factors increase and decrease respectively with increase of the  $\text{Na}_2\text{O}$  content. Deviations from this relation are found at points on the curve corresponding with compounds of the type  $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  etc.

H. I. DOWNES.

**Oxide hydrates. XXVI. System cadmium oxide-water.** G. F. HÜTTIG and R. MYTYZEK. **XXVII. System beryllium oxide-water.** G. F. HÜTTIG and K. TOISCHER (Z. anorg. Chem., 1930, 190, 353—363, 364—374; cf. this vol., 700).—XXVI. Isobaric dehydration curves and X-ray diagrams of differently aged preparations of cadmium oxide have been determined and compared. The crystal lattice of all preparations is either that of the monohydrate or of the anhydrous oxide. No amorphous solid phase was found. During the formation of larger crystalline aggregates in the ageing process the water content in excess of that corresponding with the monohydrate is given off continuously. The monohydrate is stable over a limited temperature range.



The preparations of well-formed crystals, which are obtained by dissolving cadmium iodide in excess of concentrated potassium hydroxide and then diluting with water, have almost exactly the composition  $\text{CdO} \cdot \text{H}_2\text{O}$  ( $d^{25} = 4.810 \pm 0.004$ ).

**XXVII.** The system beryllium oxide-water has been investigated by similar means. Freshly prepared specimens of the hydrated oxide, obtained by precipitation of beryllium salts with ammonia solution, are amorphous. The newest specimens contained 1.5 mol.  $\text{H}_2\text{O}$  for 1 mol.  $\text{BeO}$ . The water in excess of the composition  $\text{BeO} \cdot \text{H}_2\text{O}$  is given off continuously with rise in temperature. When the dehydration has reached the monohydrate stage it ceases to be continuous, and the appearance of two solid phases is probable. At  $\text{BeO} \cdot 0.4\text{H}_2\text{O}$  there is only one solid phase, which again loses water continuously.

O. J. WALKER.

**Equilibria in natural soda lakes. Ternary system sodium sulphate-sodium carbonate-water.** N. S. KURNAKOV and S. Z. MAKAROV (Ann. Inst. Anal. Phys. Chem., 1930, 4, 307-363).—The crystals separating from sodium carbonate solution also containing sodium sulphate are solid solutions of the two salts; the concentration of sulphate in the solid phase increases with the sum of the concentrations of the salts in solution. The proportion of sulphate in the crystals attains a maximum value of 2% at temperatures between 25° and 30°. At temperatures above 28.4° hanksite separates from solution. Hanksite is a solid solution of sodium sulphate in carbonate of variable composition, containing also sodium and potassium chlorides; these chlorides stabilise the solid solutions, which are unstable below 28.4°.

R. TRUSZKOWSKI.

**Solubility phenomena in the system sodium chloride-magnesium sulphate.** N. S. KURNAKOV and M. A. OPICHTINA (Ann. Inst. Anal. Phys. Chem., 1930, 4, 365-374).—The compositions of the saturated solutions which characterise this system have been determined.

R. TRUSZKOWSKI.

**Heats of dilution of sodium nitrate, chlorate, bromate, and iodate at high dilution at 25.0°.** E. LANGE and A. L. ROBINSON (Z. physikal. Chem., 1930, 148, 97-111).—The integral and differential heats of dilution of the above salts at concentrations of 0.0001-0.1 mol./litre have been determined at 25°. At concentrations below about 0.0025 mol./litre the integral heat of dilution,  $V_m$ , is related to the concentration,  $m$ , by the equation  $V_m = k\sqrt{m}$ , the constant  $k$  having the value 393 for the chlorate and bromate and 297 for the nitrate and iodate. From these figures the ionic diameter is calculated to have the value of approximately 1.5 Å. for the chlorate and bromate and approximately 5 Å. for the nitrate and iodate (cf. A., 1929, 1389). At higher concentrations the experimental results deviate from the above equation, indicating possibly the presence of non-ionised molecules in solution, although the experimental data do not permit any definite conclusion.

R. CUTHILL.

**Integral and theoretical heats of dissolution.** D. I. KOMPANSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 555-579).—Bertrand's formula is applicable to the

calculation of the heat of vaporisation of saturated solutions. Values for the integral heat of dissolution of anhydrous sodium sulphate or of its decahydrate cannot be calculated with any close approximation to accuracy from Kirchhoff's formula. Speranski's formula (A., 1914, ii, 31) gives satisfactory values for the b. p. of saturated sodium sulphate solutions. The Dupré-Hertz formula is applicable to the calculation of the vapour pressure of saturated sodium sulphate solutions.

R. TRUSZKOWSKI.

**Heat of combustion of carbon.** W. B. PLUMMER (Ind. Eng. Chem., 1930, 22, 630-632).—The heats of combustion of various types of carbon degassed in a vacuum at 1000° and protected from air during subsequent operations are 0.9-1.5% higher than previous values. The accepted value for the heat of combustion of graphite is 1% low.

L. S. THEOBALD.

**Reliability of heat data as a factor in calculating equilibria involving methyl alcohol.** D. F. SMITH and L. L. HIRST (Ind. Eng. Chem., 1930, 22, 634-635).—A discussion.

L. S. THEOBALD.

**Calorimetric researches on geometrical isomerism. I. Preliminary studies on oleic and elaidic acids and esters from a comparison of their heats of combustion.** L. J. P. KEFFLER (J. Physical Chem., 1930, 34, 1319-1325).—The heats of combustion of elaidic and oleic acids and their methyl esters have been determined. The larger value obtained for oleic acid confirms the view that it is the *cis*-isomeride; the difference between the values for the esters is too small to be of significance. Oleic acid is unstable, the value of the heat of combustion falling rapidly during the first few days after redistillation to an equilibrium value attained after a longer time.

L. S. THEOBALD.

**Incompatibility between any theory of complete dissociation and migration data.** J. W. MCBAIN and P. J. VAN RYSELBERGE (J. Amer. Chem. Soc., 1930, 52, 2336-2347; cf. A., 1929, 143).—Observations on the ionic transport in solutions which contain magnesium and rubidium sulphates with one of the metals in large excess show that the metal present in small concentration migrates from the cathode towards the anode. The addition of a suitable excess of potassium iodide to ammonium iodide almost suppresses the migration of ammonium ions. In mixtures of potassium chloride with excess of sodium chloride (ratios 1:49, 24, or 9), or of potassium nitrate with excess of sodium nitrate, the migration of the potassium is much reduced and the alteration is approximately that required by the Nernst theory.

J. G. A. GRIFFITHS.

**Accurate method for comparing electrolytic resistances at high frequencies.** A. DEUBNER (Ann. Physik, 1930, [v], 5, 305-324).—An apparatus for determining the conductivity of neutral electrolytes for current of frequency  $10^7$  per sec. with an accuracy of 0.3 in 1000 is described. The sources of error are discussed and attention is directed to the elimination of errors due to alterations in the dielectric constant of the electrolyte. This is effected by making use of a special property of the oscillation apparatus. The results for calcium sulphate show

that the Debye-Falkenhagen relaxation phenomena for ionic atmospheres are confirmed. There are, however, definite small deviations from the theory. Copper sulphate solution gave almost the same curve as calcium sulphate. For hydrochloric acid quantitative agreement with the theory could be obtained only at relatively high concentrations; at lower concentrations chemical effects play too large a part. Some mixed electrolytes were also investigated. 0.01*N*-Solutions of sodium chloride and copper sulphate, which are approximately equally good conductors, give, on mixing, an increase in conductivity of about 5% for the lower frequencies. A. J. MEE.

**Electrical conductance of aqueous solutions of barium chloride as a function of concentration.** G. JONES and M. DOLE (J. Amer. Chem. Soc., 1930, 52, 2245—2256; cf. A., 1929, 767, 1385).—The molal conductance,  $\Lambda$ , at 25° of barium chloride solutions varying in concentration from 0.001 to 1.0*M* has been determined by the method previously described (A., 1928, 595), using 1100 or 2500 cycles and cells giving more than 1000 ohms resistance. The results are reproduced with an average deviation of 0.014% by the equation  $\Lambda - 282.13 + 31.13c = -636.3\sqrt{c}/(1 + 4.628\sqrt{c})$ . The factors affecting the magnitude of the viscosity correction to be applied to conductance data are discussed. The density of the above solutions is given by the equation  $d = 0.99707 + 0.18224c - 0.00421c^2$ . J. G. A. GRIFFITHS.

**Electrochemical examination of solutions of antimony trichloride in bromine.** V. A. PLOTNIKOV and O. K. KUDRA (J. Russ. Phys. Chem. Soc., 1930, 62, 365—373).—Solutions of antimony trichloride in bromine do not conduct electricity at concentrations below 10%  $\text{SbCl}_3$ ; the specific conductance attains a maximum value of  $1.34 \times 10^{-4}$  at 97%  $\text{SbCl}_3$ . The molecular conductivity at first rises with dilution, and then again falls at dilutions greater than 90 c.c. A mixture of bromine and chlorine is produced at the anode during electrolysis. The solutions follow Ohm's law. Electrolytic dissociation consists in the processes:  $\text{Sb}_2\text{Cl}_6 \rightleftharpoons \text{Sb}_2\text{Cl}_5^+ + \text{Cl}^- \rightleftharpoons \text{intermediate products} \rightleftharpoons \text{Sb}_2\text{Cl}_3^{\dots} + 3\text{Cl}^-$ . The expression  $\kappa\phi^2 = \text{constant}$ , where  $\kappa$  is the specific conductance and  $\phi$  the dilution, is derived and verified experimentally. R. TRUSZKOWSKI.

**Electrode potential of indium against indium chloride solutions.** S. HAKOMORI (J. Amer. Chem. Soc., 1930, 52, 2372—2376).—The *E.M.F.* of the cell  $\text{In(s)}|\text{InCl}_3(0.0015-0.0274M) + 0.02M\text{HCl}|\text{AgCl(s)} + \text{Ag(s)}$  has been determined at 25°, whence that of the cell  $\text{In(s)}|\text{I}^-(1M)|\text{Cl}^-(1M)|\text{AgCl(s)} + \text{Ag(s)}$  is computed to be 0.55S volt. The electrode potential of  $\text{In(s)}|\text{In}^{\dots}$  is therefore +0.336 volt referred to the hydrogen electrode. J. G. A. GRIFFITHS.

**Electrode potential of hopcalite.** E. BAUR (Z. Elektrochem., 1930, 36, 410—414).—The electrode potential of hopcalite ( $\text{MnO}_2 + x\text{CuO}$ ) is measured and the discharge curves for a hopcalite cell are compared with those for a similar Leclanché cell. It is inferred that in using hopcalite for the oxidation of carbon monoxide, the copper oxide acts as oxidising agent, the manganese dioxide serving only to regenerate the

former. Oxygen consumption measurements of a Leclanché and graphite electrode show that regeneration of reduced manganese dioxide in contact with air takes place only very slowly. H. I. DOWNES.

**Oxygen electrode: an adsorption potential.** H. V. TARTAR and M. WALKER (J. Amer. Chem. Soc., 1930, 52, 2256—2264).—The influence of several factors on the *E.M.F.* of the cell  $\text{Pt-O}_2|\text{electrolyte}||N\text{-KCl}||M\text{-H}^+|\text{H}_2\text{-Pt}$ , at 25° is recorded. It is suggested that an electrode absorbs ions preferentially from the electrolyte and that these do not form two distinct double layers ("electrical double layer") at the surface, but are arranged so that the concentration of each ion gradually changes with increasing distance from the electrode until electrical neutrality is attained in the bulk of the electrolyte. In the oxygen electrode, the gas is adsorbed and causes a change in the adsorption of the ions.

The potentials of the oxygen electrode in acid, neutral, and alkaline electrolytes drift with time and approach steady values (cf. A., 1928, 1097), but mechanical vibration causes disturbance. Bright platinum electrodes and electrodes which are gas-free, or charged with hydrogen or nitrogen, show similar phenomena. Fine sand, agar jelly, and substances which decrease interfacial tension have a stabilising influence. J. G. A. GRIFFITHS.

**Measurements of *E.M.F.* of the calomel electrode against the hydrogen electrode at low concentrations of hydrochloric acid.** J. MUKHERJEE and K. K. KUMAR (J. Amer. Chem. Soc., 1930, 52, 2179—2184).—*E.M.F.* measurements at 35° with the cell  $\text{Hg, HgCl}|\text{HCl}(c_1)|\text{HCl}(c_2)|\text{H}_2(\text{Pt})$  ( $c_1$  and  $c_2$ , 0.1085—0.0034*N*) show that the variation of *E.M.F.* is almost completely attributable to a decrease in the concentration of the acid in the calomel electrode vessel. This is due to reaction between hydrochloric acid and mercury in the presence of oxygen. J. G. A. GRIFFITHS.

***E.M.F.* measurements with calcium chloride solutions.** G. SCATCHARD and R. F. TEFFT (J. Amer. Chem. Soc., 1930, 52, 2265—2271; cf. Foshbinder, A., 1929, 769).—The *E.M.F.* of the cells  $\text{Ag, AgCl}|\text{CaCl}_2(0.1M, \text{aq.})|\text{CaHg}(x), \text{CaCl}_2(c)|\text{AgCl, Ag}$ , and  $\text{CaHg}(x)|\text{CaCl}_2(0.1M, \text{aq.})|\text{AgCl, Ag}$  have been determined at 25° with the dropping calcium amalgam electrode, where  $c = 0.01-0.97M$  in water and in 25 mol.-% alcohol, and  $x = 0.02-0.05\%$  Ca. The potential of the electrode decreases slightly with increasing rate of flow and more rapidly at higher rates, possibly due to adsorption of calcium at the interface and failure to attain equilibrium between the interface and bulk phase. The *E.M.F.* with aqueous alcohol increases rapidly with rate of flow, rendering accurate determinations impossible with 50 mol.-% alcohol. The data are in approximate agreement with the requirements of the Debye-Hückel theory. J. G. A. GRIFFITHS.

***E.M.F.* measurements on cells containing zinc chloride.** Activity coefficients of chlorides of bivalent metals. G. SCATCHARD and R. F. TEFFT (J. Amer. Chem. Soc., 1930, 52, 2272—2281).—The *E.M.F.* of the cell  $\text{ZnHg}(2 \text{ phase})|\text{ZnCl}_2(0.003-1.48M)|\text{AgCl, Ag}$  has been determined at 25°. The

elimination of oxygen affords reproducible results. The data are in accord with calculations by the Debye-Hückel equation except at low concentrations. However, by assuming incomplete dissociation of the primary ion, the data for zinc, lead, and cadmium chlorides may be fitted to the equation. Standard cell potentials and activity coefficients are computed.

J. G. A. GRIFFITHS.

**Polarographic studies with the dropping mercury cathode. XI. Overpotential of mercury deposited from mercuric salt solutions.** W. KEMULA (Coll. Czech. Chem. Comm., 1930, 2, 347—362).—Polarograms have been obtained for the electrolysis of mercuric cyanide solutions containing potassium chloride, hydroxide, iodide, nitrate, and cyanide, and hydrochloric acid, and the deposition potentials calculated; also for mercuric chloride in the presence of various electrolytes and saturated solutions of mercuric oxide containing potassium hydroxide. The influence of temperature, rate of dropping, concentration of mercuric salt, and of the added electrolyte has been investigated. The overpotential in the electrolysis of mercuric cyanide depends only on the concentration of the latter, being given approximately by the expression  $(RT/F) \log_e [\text{Hg}(\text{CN})_2]$ . It is suggested that the overpotential is caused by the slowness of ionisation of the mercuric cyanide.

C. W. GIBBY.

**Polarographic studies with the dropping mercury cathode. XII. Commencement of the decomposition of sucrose.** K. ŠANDERA (Coll. Czech. Chem. Comm., 1930, 2, 363—369).—The maximum on the current-voltage curves, due to the reduction of atmospheric oxygen at a dropping mercury cathode in a 0.002*M*-solution of potassium sulphate containing sucrose is very sensitive to impurities in the latter, traces of surface-active matter causing considerable depression. Substances depressing the maximum are produced by heating pure sucrose. The changes occurring at the beginning of the decomposition have been followed polarographically. A reversible decomposition starts on heating at 100° for 10 min., the effect disappearing on prolonged heating. Heating for 3 hrs. at 100° causes an irreversible decomposition, producing a permanent suppression of the maximum in the voltage-current curve.

C. W. GIBBY.

**Polarographic studies with the dropping mercury cathode. XIII. Effect of proteins.** J. HEYROVSKÝ and J. BABIČKA (Coll. Czech. Chem. Comm., 1930, 2, 370—379).—Protein can be detected in concentrations as small as 0.0001% in solutions of blood-serum, flours, milk, beer, and urine by determining current-voltage curves with a dropping mercury cathode. On adding an ammonium salt an increase of current is found at a potential about 0.2 volt more positive than that due to the deposition of ammonium ions. With excess of ammonium salt the limiting height reached by the wave on the current-voltage curve is proportional to the protein content.

C. W. GIBBY.

**Passivity of metals. V. Potential-time curves of some iron alloys.** L. C. BANNISTER and U. R. EVANS (J.C.S., 1930, 1361—1374).—The method

previously employed for determining potential-time curves at metal surfaces in various stages of passivity (A., 1929, 270) has been improved by preventing access of the liquid to the cut edges of the metal and by increasing the sensitivity of the method of potential measurement. The behaviour of iron, iron alloys, and aluminium, after various abrasive, chemical, and thermal treatments, has been studied in potassium chloride and chromate solutions. The results point to the existence of an oxide film in various stages of discontinuity. The more complete is the protection afforded by the film the higher is the potential, so that a potential which rises with time indicates that the film is extending and the metal becoming more immune from further attack, and conversely. Treatments such as high polishing increase resistance to attack and raise the potential; those favouring corrosion, e.g., coarse abrasion, lower it. The presence of a second phase favours the breakdown of the protective film, as illustrated by the fact that, under comparable surface conditions, the homogeneous (austenitic) alloys yield higher potentials than the duplex (hardenable) materials. The character of the potential-time curves probably indicates the "liability to corrosion" rather than the velocity of corrosion when fully developed, and gives information regarding the protective character of the film such as velocity measurements cannot afford.

M. S. BURR.

**Theoretical significance of the passivity of metals.** W. J. MÜLLER (Z. Elektrochem., 1930, 36, 365—371).—The criticism of Smits (cf. this vol., 299) is discussed and the author's views (cf. A., 1929, 886, 1241; this vol., 165, 298) are elaborated.

H. I. DOWNES.

**Theoretical significance of the passivity of metals.** A. SMITS (Z. Elektrochem., 1930, 36, 371—375).—A reply to Müller (cf. preceding abstract).

H. I. DOWNES.

**Electro-osmose theory of the electrolytic rectifier.** A. DOBIAŠ, L. KRAMP, and O. LEBEDINSKAJA (Z. Physik, 1930, 61, 852—872).—The behaviour of the aluminium rectifier has been investigated with the aid of the Siemens oscillograph. Its action can be explained by the occurrence of electrical endosmosis of the electrolyte in the pores of the oxide film formed on the electrode. This is supported by the observation that if two identical platinum electrodes are taken and one of them is covered with a thick layer of paper, then the system acts as a rectifier when placed in various electrolytes. An oxide film was applied to an aluminium electrode by preliminary treatment in sodium hydrogen carbonate solution, and then its rectifying action investigated in various solutions. In solutions of aluminium chloride, hydrochloric or nitric acid an inverse rectifying effect was observed, and this is correlated with the reverse endosmosis of these electrolytes. The effect in a solution of borax in water is compared with that of borax in glycerol, and it is shown that the more viscous liquid causes a delay in development of the active phase. The rectifying action in 0.01*M*-sodium hydrogen carbonate solution is shown to be greater than that in 0.1*M*-solution, in spite of the greater resistance of the dilute solution which would

in general lead to a decrease in the rectifying action. Reverse rectifying action could not be obtained with tantalum electrodes, and this is explained by the acidic nature of the film preventing the occurrence of reverse endosmosis. H. A. JAHN.

**Rule for the investigation of chain reactions.** G. M. SCHWAB (Z. physikal. Chem., 1930, B, 8, 141—146).—A general rule for determining the mechanism of chain reactions is deduced. It is limited to chains of which the partial reactions of intermediate substances are of the first order only. M. S. BURR.

**Energy of activation of bimolecular reactions.** H. J. SCHUMACHER (Z. physikal. Chem., 1930, B, 8, 218—220).—Polemical against Eyring (this vol., 546). The rule proposed is insufficiently supported by experiment. F. L. USHER.

**Kinetics of the recombination of atomic hydrogen.** J. F. HAVILČEK (Naturwiss., 1930, 18, 531—532).—The decrease in volume concentration with time of atomic hydrogen at atmospheric pressure follows an exponential law  $C_t = C_0 \times e^{-at}$ , where  $a$  is independent of the hydrogen concentration at constant temperature. The reaction is therefore unimolecular, and this is confirmed by the fact that in agreement with Arrhenius' rule the logarithm of the reciprocal of the half-life period is inversely proportional to the absolute temperature.

J. W. SMITH.

**Interaction of oxygen with nitrogen after collision with electrons.** O. H. WANSBROUGH-JONES (Proc. Roy. Soc., 1930, A, 127, 511—529).—The combustion of nitrogen and its dependence on ionisation, investigated in the apparatus previously described (Caress and Rideal, A., 1927, 943), depends on the activation or ionisation of the nitrogen, activation of the oxygen playing no part. At pressures low enough for the electronic oxidation to be studied and at 1800° Abs. the thermal oxidation at the surface of the platinum wire was too slow to affect the results. Full details are given of the experimental arrangements. The rate of the reaction, obtained from the rate of fall of pressure, is constant for a particular voltage over the range 180—130 bars. The conditions necessary for obtaining reproducible results are noted. The mean rates of reaction are plotted against the applied electron voltages; no reaction occurs unless the electron has an energy greater than 17 volts. There are well-defined breaks at 17 and 23 volts, and there is a rapid, regular rise above 30 volts with no breaks. No breaks are observed at any of the reported critical potentials of oxygen. Details are given of experiments made (a) with oxygen in excess, and (b) with nitrogen in excess, and the method of examining the products of the reaction (chiefly nitrogen peroxide) is described. It is calculated that 70% of the electrons emitted will possess their full energy in the grid anode space where the reaction occurs. A table is given showing the approximate number of electrons which must be emitted from the filament to give one ion at various voltages. Below 24 volts one ion readily forms two molecules of nitrogen peroxide. The results are compared with those obtained by previous investigators. The two principal reactions are considered to be  $N_2^+ + O_2 = 2NO$ , and  $N^+ + O_2 = NO_2$ , or

$N_2^+ + O_2 \rightarrow NO_2 + N$ , and the independent production of either of these gases is established.

L. L. BIRCUMSHAW.

**Formation of ozone from oxygen after collision with electrons.** O. H. WANSBROUGH-JONES (Proc. Roy. Soc., 1930, A, 127, 530—539).—A detailed study has been made of the behaviour of oxygen in the apparatus used for investigating the reaction between nitrogen and oxygen after collision with electrons (cf. preceding abstract). Experiments carried out to determine if the slow removal of oxygen in the low-voltage arc, noted previously, was connected with ozone formation gave negative results. The removal of oxygen in these experiments depends primarily on the state of the glass walls; a chemical process, not necessarily connected with ion-formation, takes place between the oxygen and the glass. Further attempts to detect small amounts of ozone by means of a "flow" apparatus, using concentrated sulphuric acid as an absorbent, were successful. The amount of ozone produced depended on the rate of flow, the pressure, and the applied potential. The quantity of ozone increased by about 20% when the rate of flow was increased five times; it increased regularly with the applied potential, none being detected unless at least 25 volts were applied, and it decreased with decreasing pressure, none being formed below 0.8 mm. It is concluded that for dry ozone the mode of formation is by collision between a neutral molecule and an active ion, the life of the ion being of the order of  $10^{-7}$  sec. Collision between an ion and an atom would be rare, and although giving efficiencies of the same order as those found, would not show the same dependence on pressure.

L. L. BIRCUMSHAW.

**Speed of initial uniform movement of the flame in hydrocarbon-air mixtures.** Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 109—110b).—The initial uniform velocity of propagation of the flame through air containing a mixture of dimethylcyclopentane (43%) and isoheptane (57%) has been determined as a function of the concentration of the hydrocarbon vapour. The maximum velocity occurs when the hydrocarbon concentration is about 2.5 mol.-%, and the fact that this exceeds the concentration required for complete combustion is ascribed to the dissociation of carbon dioxide at high temperatures.

H. F. GILLBE.

**Law of flame speeds. I. General condition required for application of the law.** Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 110—113b).—Payman's law of the velocity of propagation of flames is valid for all mixtures of which the component gases have the same theoretical flame propagation temperature, and is independent of the heat conductivities of the components. If this condition does not hold the law does not apply.

H. F. GILLBE.

**Chain characteristics of ethylene-oxygen reaction.** R. SPENCE and H. S. TAYLOR (J. Amer. Chem. Soc., 1930, 52, 2399—2402; cf. Thompson and Hinshelwood, A., 1929, 1243).—The oxidation of ethylene with oxygen and with ozonised oxygen at temperatures between 260° and 440° has been investigated by a flow method. The total reaction

is greatly increased in the presence of small quantities of ozone, which is therefore an initiator of reaction chains of short length. The presence of ozone renders the reactants liable to explode at 400°.

J. G. A. GRIFFITHS.

**Non-stationary explosion of carbon disulphide vapour with oxygen.** H. W. THOMPSON (*Naturwiss.*, 1930, 18, 530—531).—A mixture of 1 vol. of carbon disulphide vapour with 3 vols. of oxygen at a temperature below 200° exhibits the same phenomenon as electrolytic gas (cf. Hinshelwood and Thompson, A., 1928, 483; Kopp, Kowalsky, Sagulin, and Semenov, this vol., 299) in that at constant temperature there is a pressure threshold at which the immeasurably slow reaction changes into an explosion, and similarly there is a threshold temperature at constant pressure. The pressures required are higher than with electrolytic gas. When gaseous carbon disulphide and oxygen impinge in free space no explosion is observed below 200°. On continuous use without cleaning the quartz vessel the carbon disulphide-oxygen explosion exhibits an induction period.

J. W. SMITH.

**Homogeneous decomposition of gaseous acetaldehyde.** L. S. KASSEL (*J. Physical Chem.*, 1930, 34, 1166—1173).—The homogeneous decomposition of acetaldehyde vapour has been studied over a wide range of pressure. The initial rates of reaction are well represented by an equation of the five-thirds order, but the rate during a single decomposition decreases faster than such an equation demands and is best expressed by a second order equation.

L. S. THEOBALD.

**Velocity of oxidation of hydrogen iodide with arsenic acid in presence of acids and salts.** M. BOBTELSKI and R. ROSOVSKAJA-ROSSIENSKAJA (*Z. anorg. Chem.*, 1930, 190, 346—352).—The velocity of liberation of iodine from hydrogen iodide by arsenic acid at 30° is measurable only in presence of fairly large amounts of free acid. The action of the acid is not catalytic, but a neutral electrolyte effect. The addition of further quantities of an acid accelerates the reaction to a greater extent than the addition of a salt with the same ion. The accelerating effect of neutral chlorides is much greater than that of the corresponding sulphates. The same rule holds as in the oxidation with chromic acid (cf. following abstract) with regard to the effect of the nature and valency of the cation on the velocity of oxidation. Bromide ion has the same effect as chloride ion. In the case of chlorides and sulphates, if the hydrogen ion is replaced by another cation the retarding effect can be represented by a coefficient which is characteristic for the particular cation for a given concentration.

O. J. WALKER.

**Velocity of reaction of chromic acid and hydrogen iodide in presence of neutral electrolytes.** M. BOBTELSKI (*Z. anorg. Chem.*, 1930, 190, 337—345; cf. A., 1929, 1149).—The reaction between chromic acid and hydriodic acid is very sensitive towards hydrogen ions. In presence of small quantities of hydrogen chloride the action is very rapid, in presence of sulphuric acid slower. Neutral sulphates all have a retarding effect, the strongest effect being that due to aluminium sulphate. Chlorides, particularly

lithium and magnesium chlorides, accelerate the reaction. With cations having a simple structure the velocity of the reaction is affected only by the specific character and not by the valency of the cation, whereas with cations having a more complex nucleus (e.g., Ni<sup>++</sup>, Co<sup>++</sup>, Mn<sup>++</sup>) the influence of the valency of the cation is strong. If acetic acid instead of sulphuric acid is added the effects of neutral salts on the velocity of the reaction are not in general altered, except that in this case potassium bromide has a marked accelerating effect. Potassium thiocyanate has an accelerating effect on the velocity of the oxidation reaction, which increases to a maximum and then decreases with increasing concentration of thiocyanate.

O. J. WALKER.

**Kinetics of hydrogen peroxide decomposition by porphyrin-metal complex salts.** K. ZEILE (*Z. physiol. Chem.*, 1930, 189, 127—147).—Various hæmin types, including hæmin (alkali and phosphate solutions), hæmatin, mesohæmin, deuterohæmin, hæmatohæmin, isourhæmin, and coprohæmin, are able to decompose hydrogen peroxide. The effect of  $p_H$  and of potassium cyanide on the reaction was studied. Natural hæmin alone showed a relatively constant activity owing to its stability towards hydrogen peroxide. A typical potassium cyanide inhibition of the hydrogen peroxide decomposition catalysed by "alkali-hæmins" was observed only below  $p_H$  8 in presence of a large excess of potassium cyanide (0.01*M*). The copper complex salts of proto- and meso-porphyrin were catalytically inactive.

J. H. BIRKINSHAW.

**Velocity of reduction of potassium ferricyanide by dextrose in alkaline solution.** W. NITOSEWSKA (*Rocz. Chem.*, 1930, 10, 349—364).—Iodine does not at 25° react with either dextrose or its oxidation products, and potassium hydroxide is without action on ferricyanide. The reducing power of dextrose is diminished only to a small extent by the action of 10% potassium hydroxide at 25°. The curves expressing velocity of reduction of ferricyanide are linear when 0.15*N*-alkali is used, becoming increasingly concave in contour as the concentration of potassium hydroxide is increased; the shape of the curves is also affected by changes in concentration of dextrose and of ferricyanide. The reaction is bimolecular with respect to dextrose and ferricyanide. The velocity coefficient, calculated on the assumption that 3 atoms of oxygen are used per mol. of dextrose, remains constant for systems containing about 0.5*N*-alkali; with higher alkalinities a satisfactory coefficient can be obtained by assuming that 9 atoms of oxygen are required per mol. of dextrose. The probable products of the reaction in feebly and strongly alkaline solutions are respectively dibasic acids and carbon dioxide. As the reaction approaches completion decomposition of ferricyanide commences.

R. TRUSZKOWSKI.

**Velocity of inversion of sucrose. II. Influence of temperature and of ultra-violet rays.** N. TAKETOMI and K. MIURA (*J. Soc. Chem. Ind. Japan*, 1930, 33, 99—101b).—The constant *A* in the Arrhenius equation  $K_1 = K_0 e^{A(T_1 - T_2)/T_1 T_2}$  for the inversion of sucrose is for oxalic acid 12,650, hydrochloric acid 12,820, sulphuric acid 12,440, acetic acid 12,500, and

lactic acid 12,460. At temperatures between 25° and 65°, exposure of a sucrose solution to radiation from a quartz mercury-vapour lamp for 6 hrs. produces no appreciable change of polarisation, but at 70° inversion becomes perceptible and thereafter increases with rise of temperature. H. F. GILLBE.

**Reduction of metal oxides by hydrogen.** G. B. TAYLOR and H. W. STARKWEATHER (J. Amer. Chem. Soc., 1930, 52, 2314—2325).—The rates of reduction by hydrogen of nickel, copper, iron, and zinc oxides and certain mixtures have been investigated at temperatures below 500° by determining the volume of hydrogen consumed. Copper oxide in the form of wire showed autocatalytic reduction. Ferric oxide gel is reduced to  $\text{Fe}_3\text{O}_4$  at 250—350° and to the metal at 450°. The ignited oxide is not reduced at 350°, but yields the metal at 450°. Ferric oxide gels glow in hydrogen at fairly low temperatures, but not in air or a vacuum. The exothermic reduction of ferric oxide to  $\text{Fe}_3\text{O}_4$  is too slow to account for the phenomenon.

The reduction at 450° of ferric oxide coprecipitated with nickel, copper, or silver oxides shows that the latter metals accelerate the production of iron. Coprecipitation, unlike mechanical mixing of the ferric oxide with aluminium or chromium oxides, retards the reduction at 450°. Zinc oxide has no effect.

Thermodynamic calculations show that hydrogen will reduce zinc oxide if the pressure of water vapour is maintained sufficiently small. In the presence of copper the compound  $\text{Cu}_2\text{Zn}_3$  can be formed, and thus a much higher equilibrium pressure of water vapour (0.15 mm. at 419°) is permissible. This explains the formation of  $\alpha$ -brass by the reduction of a mixture of zinc and copper oxides. J. G. A. GRIFFITHS.

**Passivation of metal surfaces by bombarding electrons.** F. GOLDMANN and E. RUPP (Z. physikal. Chem., 1930, B, 8, 180—186).—The impact of electrons (whether slowly moving or from a Coolidge tube) on non-evacuated surfaces of silver or copper causes them to become passive, so that the bombarded surface is not attacked by iodine vapour, whilst the protected parts are quickly covered with a violet film, which is thickest near the boundary. Positive ions or the prolonged action of ultra-violet light produce the same effect. Since passivation does not occur when the surfaces are evacuated or when the evacuated surfaces are subsequently brought into contact with hydrogen, but is pronounced if oxygen is introduced, it is considered to be due to the formation of an oxide film on the exposed part of the metal. Work on the photo-electric effect or on the alteration of surfaces by electrons should be carried out with completely evacuated surfaces in order to avoid complications due to passivation. F. L. USHER.

**Effect of the magnetic field on the rate of dissolution of iron in cupric chloride solution.** H. FORESTIER (Compt. rend., 1930, 190, 1421—1423).—The rate of dissolution of iron (99.86%) immersed during 10 min. in 2—12% cuprous chloride solutions at 15° increases rapidly with the magnetic field up to 4500—5000 gauss, after which it remains constant. The rate of dissolution is tripled for 2% solutions, but the stimulating effect of the field decreases as the

concentration of reagent increases up to 8%, and then remains approximately constant. Copper sulphate produces similar but less pronounced effects, which are attributed to the formation of a protecting layer of copper. J. GRANT.

**Velocity of dissolution of tin in aqueous stannic chloride solution.** E. BÉKIER and A. BASINSKI (J. Chim. phys., 1930, 27, 256—265).—See this vol., 549.

**Measurement of the corrosion of metals.** G. GOLLNOW (Chim. et Ind., 1930, 23, 1359—1360).—See B., 1930, 379.

**Corrosion and protective films.** A. C. HANSON. —See B., 1930, 667.

**Explosive reactions and negative catalysis.** W. P. JORISSEN (Coll. Czech. Chem. Coll., 1930, 2, 288—291; cf. B., 1929, 841).—A preliminary account of work now in progress. 1.75% of isobutyl chloride vapour prevents a 10% methane-air mixture from being exploded by a spark, but renders an otherwise non-inflammable 2.2% methane-air mixture inflammable. Propyl bromide, silicon tetrachloride, and sulphuryl chloride behave similarly.

C. W. GIBBY.  
**Oxidation processes in motor fuels. III.** E. BERL and K. WINNACKER (Z. physikal. Chem., 1930, 148, 36—44; cf. this vol., 168).—From the theory of combustion of hydrocarbons previously advanced (B., 1929, 158) it is inferred that as the symmetry of a combustible molecule decreases owing to combination with oxygen it becomes more and more easily oxidised. In accordance with this view it is found that the period of induction which occurs in the oxidation of hexane in oxygen (Brunner and Rideal, A., 1928, 731) is reduced and violent reaction sets in sooner if the hexane is first partly oxidised so as to contain small amounts of aldehydes and acids, the unsymmetrical molecules of which presumably add oxygen more readily than the symmetrical hydrocarbon molecule, and act as autoxidisers towards the hydrocarbon molecules. The anti-knock action of ethyl alcohol is explained similarly. R. CUTHILL.

**Oxidation processes in motor fuels. IV. Autoxidation of benzaldehyde.** E. BERL and K. WINNACKER (Z. physikal. Chem., 1930, 148, 261—283; cf. this vol., 168, and preceding abstract).—Results of previous work on the effect of various substances (including the so-called anti-detonators) in arresting the oxidation of hydrocarbons by interrupting the reaction "chains" or by forming intermediate compounds with the hydrocarbon peroxide are summarised. The authors have investigated the effect of the same substances on the autoxidation of liquid benzaldehyde at the ordinary temperature; the reaction can be followed by direct measurement of the rate of absorption of oxygen. Under the conditions imposed the oxidation of benzaldehyde proceeded at a rapidly increasing rate after the expiration of a period of induction in which presumably a positive catalyst of the nature of a peroxide was being formed. Addition of benzoic acid prolonged the period of induction and diminished the maximum reaction velocity attained, whilst benzoyl



peroxide had the opposite effect. Organic liquids retard the reaction either by preventing the formation of peroxide or by destroying it, and the effect increases in the order: benzene, hexane, acetone, *cyclohexane*, ether, *cyclohexene*, ethyl alcohol, benzyl alcohol, lead tetraethyl. The sols resulting from the dispersion of lead, iron, or tin in benzaldehyde (cf. this vol., 155) give rise to a diminished capacity for oxidation which is not due to a rearrangement of the benzaldehyde molecule in the electric field, since the velocity of oxidation in a similarly prepared sol of graphite is unchanged. F. L. USHER.

**Mechanism of antioxygenic action.** G. DUPONT and J. ALLARD (Compt. rend., 1930, 190, 1419—1421).—Spectroscopic and other evidence of the nature of the influence of cobalt and quinol on the oxidation of abietic acid supports an analogy between positive and negative catalysts. Both form complexes with the active agent of autocatalysis, but these are active and inactive, respectively. Positive catalysts therefore activate, and negative catalysts poison, the normal agent of autocatalysis. J. GRANT.

**Catalytic decomposition of potassium chlorate by dust (smoke) particles of manganese dioxide.** S. ROGINSKI and E. SCHULZ (Sci. Mag. Chem. Catheder Katerinoslav, 1926, 189—206; Chem. Zentr., 1930, i, 481).—Acceleration of the decomposition of potassium chlorate by passing gases through it is due to the presence of dust particles. A. A. ELDRIDGE.

**Electronic nature of the catalytic decomposition of potassium chlorate by oxides and metals.** L. PISARSHEVSKI (Sci. Mag. Chem. Catheder Katerinoslav, 1926, 165—169; Chem. Zentr., 1930, i, 480).—It is supposed that the absorbed gases are ionised by impact of electrons of the catalyst, and thereafter act upon the salt. A. A. ELDRIDGE.

**Catalytic phenomena in the decomposition of potassium chlorate.** M. BELENJKI (Sci. Mag. Chem. Catheder Katerinoslav, 1926, 171—173; Chem. Zentr., 1930, i, 480).—In presence of manganese dioxide (2 : 1) or uranium oxide,  $U_3O_8$  (3 : 1), decomposition commences at 75° or 100°, respectively. Moisture increases the rate of decomposition. Palladium, osmium, ruthenium, and uranium are good, and iridium, rhodium, molybdenum, tungsten, vanadium, chromium, and niobium are poor, catalysts. A. A. ELDRIDGE.

**Heterogeneous decompositions. III. Decomposition of methyl alcohol on zinc oxide.** H. DONSE (Z. physikal. Chem., 1930, B, 8, 159—179; cf. this vol., 431).—The decomposition of methyl alcohol on zinc oxide consists of two consecutive unimolecular reactions. The final products are carbon monoxide and water, formaldehyde being formed in the first stage. Both velocity coefficients have been determined and found to decrease slowly during the course of an experiment. The heat of activation calculated from the dependence of the velocity coefficients on temperature is 22.5 kg.-cal. for the first stage and 35.0 kg.-cal. for the second. The latter value agrees with that found experimentally for the decomposition of formaldehyde on the same catalyst. F. L. USHER.

**[Catalytic] synthesis of the higher hydrocarbons from water-gas at atmospheric pressure.** E. BERL and K. JÜNGLING.—Sec B., 1930, 650.

**Dependence of the catalytic activity of vanadium pentoxide on its mode of combination with silica.** I. E. ADADUROV and G. K. BORESKOV.—Sec B., 1930, 659.

**Vanadium compounds as catalysts for the oxidation of sulphur dioxide.** H. N. HOLMES and A. L. ELDER.—Sec B., 1930, 659.

**Decomposition reactions in the process of catalytic hydrogenation in presence of nickel. Rôle of the catalyst in heterogeneous catalysis.** A. A. BALANDIN (J. Russ. Phys. Chem. Soc., 1930, 62, 703—728).—An empirical rule is given, the use of which allows the products of catalytic hydrogen of organic substances to be predicted. If the values 1, 2, 3, and 4 be assigned to the elements halogen, oxygen, nitrogen, and carbon, and if  $\pi$  be taken to represent the product of the numbers assigned to any pair of these elements, then the facility with which the linking between the two elements is broken in the catalytic hydrogenation of the compound is inversely proportional to the value of  $\pi$ . This rule is shown to hold for a large number of compounds; the most frequent exceptions to it are to be found amongst compounds containing the carbonyl group, which often eliminate carbon monoxide without reduction, and amongst heterocyclic compounds possessing nitrogen in the ring. The explanation of the above rule is not to be found in the energy change associated with the formation of the linkings in question, or in the affinity between hydrogen and the respective atoms of a given pair. The same order is found for the above four elements for a series expressing facility of replacement of the given element from its compound with nickel by a different element in combination with hydrogen. The readiness with which an atomic group is separated during the catalytic hydrogenation of a compound is the greater the greater is its affinity to the catalyst, and is the smaller the greater is its affinity to the remainder of the molecule; for this reason the stability of a given linking in the absence of a catalyst need not be the same as in its presence. R. TRUSZKOWSKI.

**Chemical action in the glow discharge. IV. Synthesis of ozone.** A. K. BREWER and J. W. WESTHAVER (J. Physical Chem., 1930, 34, 1280—1293; cf. this vol., 553).—The synthesis of ozone in the positive column of the glow discharge has been investigated by the methods previously used (this vol., 304). The rate of synthesis is proportional to the length of the column immersed in liquid air and to the power input for low pressures and current densities, but at a constant current is practically independent of pressure over the range 0.3—15 mm. The amount of ozone synthesised is proportional to the number of positive ions formed and the maximum yield obtained is 1 mol. per 11.9 electron volts. This is equivalent to a minimum  $M/N$  ratio of 1.19 ozone molecules per  $O_2^+$  ion. No synthesis attributable to neutral oxygen atoms or to radiation produced in the discharge could be detected. The presence of foreign gases decreases the yield. Nitrogen has the most marked effect,

argon decreases the yield approximately in proportion to the amount present, but small percentages of helium slightly increase the yield.

L. S. THEOBALD.

**Preparation of metal powders by electrolysis of fused salts. I. Ductile uranium.** F. H. DRIGGS and W. C. LILLIENDAHL.—*See B.*, 1930, 668.

**Electro-deposition of beryllium.** H. S. BOOTH and G. G. TORREY (*J. Amer. Chem. Soc.*, 1930, 52, 2581—2582).—Beryllium salts can be dehydrated by heating in fused ammonium salts, and the product, on electrolysis in liquid ammonia, yields pure beryllium. Organic and other inorganic non-aqueous solvents may be used. J. G. A. GRIFFITHS.

**Photochemically sensitised oxidation of hydrogen at normal temperature.** H. KLINKHARDT and W. FRANKENBURGER (*Z. physikal. Chem.*, 1930, B, 8, 138—140).—Determinations have been made of the quantum efficiency of the formation of hydrogen peroxide through the oxidation of atomic hydrogen produced by the action of the mercury resonance line 2537 Å. on molecular hydrogen containing 1—2% of oxygen. The value obtained was 1—1.5. Hence, contrary to the opinion of Marshall (*A.*, 1926, 252), this is probably not a chain reaction. The following mechanism is suggested: (1)  $\text{H} + \text{O}_2 + \text{H}_2 = \text{OH} + \text{H}_2\text{O}$ ; (2)  $2\text{OH} + \text{M} = \text{H}_2\text{O}_2 + \text{M}$ , where M represents the partner in the threefold collision which carries away the reaction energy, e.g., a hydrogen molecule or the wall of the containing vessel. These two processes represent a quantum efficiency of 1, since two hydrogen atoms produced by one quantum give one molecule of hydrogen peroxide. In addition, however, the water formed at the same time may also take part in the production of hydrogen peroxide and give rise to the reactions (3)  $\text{H} + \text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_2 + \text{OH}$ ; (4)  $2\text{OH} + \text{M} = \text{H}_2\text{O}_2 + \text{M}$ . The quantum efficiency of this process is 3. The actual quantum efficiency, therefore, will lie between 1 and 3. Similarly, in the formation of aldehydes from atomic hydrogen and carbon monoxide, chain reactions do not appear to be involved. M. S. BURR.

**Molecular mechanism of some photosensitised reactions. Energy of dissociation of water.** E. GAVIOLA (*Temas de quim.*, 1929, 2, 173—183).—In presence of excited mercury atoms, water vapour is decomposed into hydrogen atoms and hydroxyl groups; the latter are normal, but become excited by reaction with excited mercury atoms and then give rise to the lines ascribed to hydroxyl. The heat of decomposition of water into atoms is 240 kg.-cal.

CHEMICAL ABSTRACTS.

**Mechanism of photochemical decomposition of ozone.** H. J. SCHUMACHER (*J. Amer. Chem. Soc.*, 1930, 52, 2377—2391).—A theory of the direct photochemical decomposition of ozone is formulated, and is shown to be in accord with existing data and hitherto unpublished results of Kistiakowsky. In red light, the following reactions are postulated: (1)  $\text{O}_3 + h\nu = \text{O}_2 + \text{O}$ , (2)  $\text{O} + \text{O}_3 = 2\text{O}_2^*$ , (3)  $\text{O} + \text{O}_2 + \text{M} = \text{O}_3 + \text{M}$ , whence the rate of decomposition of ozone is given by  $-d[\text{O}_3]/dt = I_{\text{abs}} \cdot 2k_2[\text{O}_3]/(k_2[\text{O}_3] + k_3[\text{O}_2][\text{M}])$ , where M designates a third substance (oxygen, or added nitrogen or helium) which removes the excess of

energy. At low total pressures and very small oxygen concentrations, the quantum efficiency is greater than 2, since the initiation of reaction chains by the activated oxygen molecules from reaction (2) is favoured. With hydrogen, the predominant reaction is  $\text{O} + \text{O}_2 + \text{H}_2 = \text{H}_2\text{O} + \text{O}_2$ .

The high quantum efficiency of the decomposition in ultra-violet light is attributed to the production of an excited oxygen atom in reaction (1) and hence reaction (2) will occur much more frequently than once in  $2 \times 10^3$  collisions. J. G. A. GRIFFITHS.

**Influence of intensity and wave-length of the incident radiation on the photochemical reaction between hydrogen and chlorine.** N. R. DHAR and W. V. BHAGWAT (*Z. anorg. Chem.*, 1930, 190, 415—420).—From an examination of the data on the relation between the velocity of the photochemical reaction between hydrogen and chlorine and the intensity of the incident radiation (I) it is shown that when the reaction is strongly accelerated by ultra-violet light the velocity is proportional to  $I^{1/4}$  or  $I^{1/3}$ . When, on the other hand, the reaction is only feebly accelerated by radiation which is not greatly absorbed by the mixture, the velocity is proportional to  $I^{3/2}$ . The reaction can occur with radiation of wave-lengths 5750—5800 and 6650 Å., and very slowly at 7304 Å. All radiations below 10,000 Å. apparently accelerate the reaction. O. J. WALKER.

**Photochemical decomposition of nitrogen peroxide.** H. J. SCHUMACHER (*J. Amer. Chem. Soc.*, 1930, 52, 2584).—Mixtures of nitrogen peroxide with hydrogen or hydrogen and oxygen, or with carbon monoxide and oxygen have been exposed to light of various wave-lengths. Water and carbon dioxide are produced in light of wave-lengths less than 3700 Å., and hence the photo-decomposition of nitrogen peroxide in the regions of predissociation bands yields oxygen atoms (cf. Henri, this vol., 272). The probability of the reaction  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$  is  $10^{-4}$  that of  $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ , but the yield of water is higher with light of shorter wave-length. For each hydrogen atom produced, less than two molecules of water are formed.

J. G. A. GRIFFITHS.

**Reaction between nitrogen and hydrogen in presence of mercury vapour and resonance radiation of mercury.** W. A. NOYES, jun. (*J. Amer. Chem. Soc.*, 1930, 52, 2418—2419).—The production of atomic nitrogen by collision of molecules with doubly-activated mercury atoms (Bentler and Rabinovitsch, this vol., 126) affords an explanation of the synthesis of ammonia from nitrogen and hydrogen at high pressures in the presence of mercury vapour and the resonance radiation of mercury (*A.*, 1925, ii, 573). The high pressure favours the formation of nitrogen atoms which may react thus: (1)  $\text{N} + \text{H} + \text{wall or third body} \rightarrow \text{NH}$  or (2)  $\text{N} + \text{H}_2 \rightarrow \text{NH} + \text{H}$ , followed by  $\text{NH} + \text{H}_2 \rightarrow \text{NH}_2 + \text{H}$  and  $\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}$ . J. G. A. GRIFFITHS.

**Photochlorination of chloroform.** G. M. SCHWAB and U. HEYDE (*Z. physikal. Chem.*, 1930, B, 8, 147—158).—The mechanism and quantum efficiency of the formation of carbon tetrachloride by the chlorination of chloroform in carbon tetrachloride

solution, under the influence of light of wave-length approximately 5000 Å., has been investigated. The velocity increases with the chlorine and chloroform concentrations, and with the light intensity. As the mean molecular concentration of chlorine increases from approximately 0.5 to 4 the mean quantum efficiency varies from approximately 4 to 10. Hydrogen chloride has an inhibiting action. It is suggested that the following chain of reactions takes place (cf. this vol., 1000): (1)  $\text{Cl}_2 + E = 2\text{Cl}$ . (2)  $\text{Cl} + \text{CHCl}_3 = \text{CCl}_3 + \text{HCl}$ . (3)  $\text{CCl}_3 + \text{Cl}_2 = \text{CCl}_4 + \text{Cl}$ . (4)  $\text{CCl}_3 + \text{HCl} = \text{CHCl}_3 + \text{Cl}$ . (5)  $\text{Cl} = 0.5\text{Cl}_2$ . It is shown that this mechanism is possible when the energy of the different reactions is taken into account.

M. S. BURR.

**Photo-conductance phenomena in the silver halides, and the latent photographic image.** I, II. F. C. TOY and G. B. HARRISON (Proc. Roy. Soc., 1930, A, 127, 613—628, 629—637).—I. The photo-current observed by applying a *P.D.* to the silver halide appears to be due to the same mechanism as that which brings about photochemical decomposition. Experiments are described in which the relation between the photo-conductance effect in silver bromide and the time of exposure and light intensity are studied under different conditions of crystallisation and over a range of temperature from 20° to -180°. Provided silver bromide is exposed in such a way that no permanent decomposition can take place, the photo-current starts instantaneously on illumination and rises within about 0.07 sec. to a constant final value which is strictly proportional to the light intensity. The dark conductance varies rapidly with temperature, being practically exponential in form; the relation found can be expressed by the formula  $\log \sigma = A - B/T$ , where  $\sigma$  is the conductance,  $T$  the absolute temperature, and  $A$  and  $B$  are constants. The variation of the photo-conductance with temperature is in sharp contrast to that of the dark conductance, the shape of the former curve depending on the conditions of crystallisation and in all cases being different from that expressing the relation between dark conductance and temperature. Moreover, whilst at atmospheric temperature the effect of annealing the silver bromide is to decrease the dark conductance, it increases the photo-conductance to a remarkable extent.

II. The experimental results are discussed and an interpretation is suggested. The photo-current is probably largely, if not entirely, electronic. If any part of it is ionic, that part is presumably carried by the same kind of silver ion as that which carries the dark current, and should decrease rapidly with falling temperature. Since, however, the sensitivity of a photographic plate at the temperature of boiling liquid oxygen is still a considerable fraction of its sensitivity at atmospheric temperature, the conclusion is reached that the formation of the latent image does not depend on the transport of silver by elementary electrolytic currents. It is considered more probable that in light some of the bromide ions are momentarily changed into free bromine atoms, which are not present in the dark; these can readily react with other atoms or molecules, such as those in the surrounding gelatin. A permanent change thus

takes place, with metallic silver as one of the resulting products.

L. L. BIRCUMSHAW.

**Colour-selectivity, a new property of the latent photographic image.** F. WEIGERT and J. SHIDEI (Naturwiss., 1930, 18, 532—533; cf. A., 1929, 871, 894).—The relation between the relative dichroism and the time of excitation for a photographic plate, using monochromatic polarised light of wave-length from 6800 to 4800 Å., has been investigated. With linearly polarised light a much greater difference in the photographic activity of light of different colours is observed than that normally obtained. The results support the previously developed micellar theory of the latent image (cf. A., 1929, 1248).

J. W. SMITH.

**Photochemical analogue to the three-colour mixture rule.** F. WEIGERT (Naturwiss., 1930, 18, 533—534).—The curve showing the relation between the relative dichroism and the time of excitation for a photographic plate (cf. preceding abstract) for any wave-length of incident polarised light can be described additively in terms of the curves for red, green, and blue light, thus yielding an analogue to the well-known colour mixture rule.

J. W. SMITH.

**Formation of vitamin-D by monochromatic light.** A. L. MARSHALL and A. KNUDSON (J. Amer. Chem. Soc., 1930, 52, 2304—2314).—Relative energy distributions of light sources are graphed. The development of antirachitic potency in alcoholic ergosterol irradiated with monochromatic light of wave-lengths between 2300 and 3022 Å. shows that the rate of production of vitamin-D is directly proportional to the first power of the light intensity and to the quanta absorbed by the ergosterol, and is independent of the wave-length. The quantum efficiency is about 0.3. Vitamin-D absorbs, and is destroyed by, light in the same spectral region as that absorbed by ergosterol, and hence the maximum concentration of the vitamin is 35%.

J. G. A. GRIFFITHS.

**Ultra-violet irradiation of ergosterol.** A. WINDAUS, K. WESTPHAL, F. VON WERDER, and O. RYGH (Nachr. Ges. Wiss. Göttingen, 1929, 45—58; Chem. Zentr., 1930, i, 404).—A summary.

A. A. ELDRIDGE.

**Metallic oxides and sodium hydroxide.** J. D'ANS and J. LÖFFLER (Ber., 1930, 63, [B], 1446—1455).—The reaction between metallic oxides and sodium hydroxide,  $x\text{RO}_y + 2\text{NaOH} \rightarrow \text{Na}_2\text{R}_x\text{O}_{xy+1} + \text{H}_2\text{O}$ , is followed by determination of the water formed and, by means of suitable dissolution, establishment of the quantity of metallic oxide which has entered into the change. If in different experiments an excess of alkali hydroxide and of metallic oxide is used, it can be established with a large measure of certainty if one or more compounds of oxide and alkali can exist in the molten mass. Double compounds cannot be detected by this method if they are very sensitive to moisture and the equilibrium is displaced greatly towards the left side. Only the double oxides richest and poorest in alkali are detected with certainty, the elucidation of intermediate compounds depending on their individual properties. The molten masses are dissolved in cold water and the

solubility of the residual oxides in suitable acids is investigated. In nearly every case it is possible to find conditions under which the original oxide is insoluble, whereas a second portion, invariably simply related to the amount of water evolved, becomes dissolved. The method fails only in the case of silicic acid. The existence of the following compounds is established:  $\text{Na}_4\text{SiO}_4$ ;  $\text{Na}_2\text{ZrO}_3$ ;  $\text{Na}_4\text{TiO}_4$ ;  $\text{Na}_8\text{Ti}_5\text{O}_{14}$ ;  $(?)\text{Na}_2\text{Ti}_5\text{O}_{11}$ ;  $\text{Na}_2\text{CeO}_3$ ;  $\text{Na}_2\text{Al}_2\text{O}_4$ ;  $\text{Na}_2\text{Fe}_2\text{O}_4$ ;  $\text{Na}_2\text{FeO}_4$ ;  $(?)\text{Na}_2\text{Cr}_2\text{O}_4$ ;  $\text{Na}_2\text{CrO}_4$ ;  $\text{Na}_2\text{Cr}_2\text{O}_7$ . Evidence of definite compounds is not obtained in the systems  $\text{Na}_2\text{O}-\text{ThO}_2$ ,  $\text{Na}_2\text{O}-\text{ZnO}$ , and  $\text{Na}_2\text{O}-\text{MgO}$ . The method of investigation is applicable to ternary systems; thus, zirconium silicate affords the compound  $\text{Na}_2\text{ZrSiO}_5$ .

Examination of the action of zirconium and titanium oxides with sodium carbonate shows that at  $850^\circ$  the formation of metazirconate is completely reversed by carbon dioxide under 1 atm. and that the formation of orthotitanate does not take place. A mixture of sodium metasilicate and metazirconate is converted by carbon dioxide at  $850^\circ$  into sodium carbonate and sodium zirconosilicate.

H. WREN.

**Reduction of sodium hydroxide by hydrogen.** P. VILLARD (Compt. rend., 1930, 190, 1329—1331).—A layer of sodium hydroxide deposited by fusion inside a glass tube and heated in a stream of moisture- and oxygen-free commercial hydrogen passing at the rate of 1 m./sec. is reduced at about  $900^\circ$  to water and metallic sodium (cf. B., 1929, 394). The vapours recombine on condensation and regenerate sodium hydroxide.

J. GRANT.

**[Preparation of] basic salts, particularly "ol" salts of copper.** J. V. DUBSKÝ and E. TESAŘÍK (Pub. Fac. Sci. Univ. Masaryk, 1929, No. 115, 17—29).—The preparation of some of the "ol" salts noted in the following abstract is described.

**Basic salts, particularly the hydroxy-salts of copper.** J. V. DUBSKÝ, E. TESAŘÍK, and A. OKÁČ (Coll. Czech. Chem. Comm., 1930, 2, 266—287).—The following compounds have been prepared:  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3]\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3]\text{Br}_2$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3]\text{I}_2 \cdot 9\text{H}_2\text{O}$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3]\text{SO}_4 \cdot \text{H}_2\text{O}$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3](\text{NO}_3)_2$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3](\text{NO}_3)_2$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3]\text{CO}_3$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3](\text{OAc})_2 \cdot \text{H}_2\text{O}$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3](\text{OH})_2$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_3]\text{CrO}_4 \cdot 1.5\text{H}_2\text{O}$ ;  $[\text{Cu}\{(\text{OH})_2\text{Cu}\}_2]_2(\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ .

C. W. GIBBY.

**Antimony pentasulphide.** E. SCHÜRMANN and W. BÖHM.—See B., 1930, 710.

**Reaction between magnesium and water at high temperatures.** G. PICCARDI (Gazzetta, 1930, 60, 337—351).—The arc spectrum of magnesium, burning in an atmosphere of water vapour, contains bands of the hydride  $\text{MgH}$  and oxide, the intensity of these bands increasing as the concentration of the water vapour increases; the oxide bands are always of lower intensity than those of the hydride. The spectrum shows also the bands of the hydroxyl group and the atomic hydrogen band  $\text{H}_\alpha$ , which is more intense at low than at high pressures. The intensity of the atomic magnesium bands belonging to the

principal series (in the ultra-violet) diminishes as the concentration of the water vapour increases. These results are in complete agreement with thermochemical considerations. Thus, at high temperatures and in a homogeneous system, the reaction between magnesium and water not merely consists in formation of magnesium oxide with displacement of hydrogen, but also gives a system of equilibria resulting in the simultaneous formation of magnesium oxide and hydride.

T. H. POPE.

**Hydrates of the alkaline-earth peroxides. I.** C. NOGAREDA (Anal. Fis. Quim., 1930, 28, 461—478).—The conflict of data in the literature relating to calcium, strontium, and barium peroxides is ascribed to the use of impure materials prepared by unsatisfactory methods. The pure substances may be obtained by treating the hydroxides with hydrogen peroxide in an atmosphere free from carbon dioxide, and after washing with water and alcohol, drying at the ordinary temperature in a current of air free from carbon dioxide. In each case the product has the formula  $\text{MO}_2 \cdot 8\text{H}_2\text{O}$ , and is stable for many months.

H. F. GILBE.

**Reactions in the solid state at high temperatures. VI. Acid exchange with some tungstates and molybdates.** W. JANDER (Z. anorg. Chem., 1930, 190, 397—406; cf. this vol., 873).—The following reactions have been investigated in the solid state:  $\text{CdO} + \text{ZnWO}_4 = \text{ZnO} + \text{CdWO}_4$ ;  $\text{CdO} + \text{ZnMoO}_4 = \text{CdMoO}_4 + \text{ZnO}$ ;  $\text{MgO} + \text{ZnWO}_4 = \text{MgWO}_4 + \text{ZnO}$ ;  $\text{MgO} + \text{ZnMoO}_4 = \text{MgMoO}_4 + \text{ZnO}$ ;  $\text{MgO} + \text{CdWO}_4 = \text{MgWO}_4 + \text{CdO}$ ;  $\text{MgO} + \text{MnWO}_4 = \text{MgWO}_4 + \text{MnO}$ . In the systems  $\text{MgO} + \text{MWO}_4$  and  $\text{MgO} + \text{MMoO}_4$  ( $\text{M} = \text{Zn, Cd, Mn}$ ) the mechanism of the reaction consists in the transfer of the acid anhydride ( $\text{WO}_3$  or  $\text{MoO}_3$ ) from one metallic oxide to the other. In the reactions in which cadmium oxide takes part it is not certain whether double decomposition or interchange of acidic oxide takes place.

O. J. WALKER.

**Preparation of mercurammonium bromides and chlorides.** Crystalline dimercurammonium bromide and chloride. M. FRANÇOIS (Compt. rend., 1930, 190, 1507—1509).—Dimercurammonium bromide,  $\text{Hg}_2\text{NBr}$  (14 g.), is prepared by shaking together daily for 1 month 25 g. of the freshly powdered compound  $\text{HgBr}_2 \cdot 2\text{NH}_3$  and 10 litres of ammonia solution ( $d$  0.922). A white compound ( $\text{HgH}_2\text{NBr}$ ) is first formed and is slowly transformed into the yellow  $\text{Hg}_2\text{NBr}$ , which is shaken with 1 litre of fresh ammonia solution, collected without washing after 15 days, dried over sulphuric acid, and obtained as hexagonal prisms terminated by hexagonal pyramids. The compounds  $\text{HgBr}_2 \cdot 2\text{NH}_3$ ,  $\text{HgCl}_2 \cdot 2\text{NH}_3$  (fusible white precipitate),  $\text{HgH}_2\text{NCl}$  (infusible white precipitate), and  $\text{Hg}_2\text{NCl} \cdot \text{H}_2\text{O}$  (yellowish-green, sandy octahedra, prepared in the dark) were obtained analogously.

J. GRANT.

**Action of sulphuric acid on mercury at the ordinary temperature.** F. TABOURY (Compt. rend., 1930, 190, 1428—1430).—At  $20^\circ$  mercury reacts with sulphuric acid liberating sulphur dioxide only, and forming transparent crystals of the com-

position  $\text{Hg}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4$ . The substance is readily decomposed by water, and blackens superficially on exposure to air and light. J. GRANT.

**Spinel. II.** The compounds  $\text{CuAl}_2\text{O}_4$ ,  $\text{MgAl}_2\text{O}_4$ ,  $\text{MgFe}_2\text{O}_4$ ,  $\text{ZnAl}_2\text{O}_4$ ,  $\text{ZnCr}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{MnFe}_2\text{O}_4$ . L. PASSERINI (Gazzetta, 1930, 60, 389—399; cf. A., 1929, 673).—The first six of these compounds were prepared by evaporating solutions containing the two nitrates and calcining the residue at about  $800^\circ$ ; the last-named was obtained by precipitating the two hydroxides together and calcining at about  $800^\circ$ . Comparison of the observed intensities of the X-ray lines with the calculated values shows that all crystallise in the cubic system with a structure of the spinel type. The powder method was used, the side of the unit cell (Å.) and the calculated density being:  $\text{CuAl}_2\text{O}_4$ ,  $8.055 \pm 0.005$ , 4.625;  $\text{MgAl}_2\text{O}_4$ ,  $8.050 \pm 0.005$ , 3.63;  $\text{MgFe}_2\text{O}_4$ ,  $8.360 \pm 0.005$ , 4.436;  $\text{ZnAl}_2\text{O}_4$ ,  $8.050 \pm 0.005$ , 4.68;  $\text{ZnCr}_2\text{O}_4$ ,  $8.280 \pm 0.005$ , 5.47;  $\text{ZnFe}_2\text{O}_4$ ,  $8.350 \pm 0.005$ , 5.50;  $\text{MnFe}_2\text{O}_4$ ,  $8.515 \pm 0.005$ , 4.965. For  $\text{CuAl}_2\text{O}_4$  and  $\text{MgFe}_2\text{O}_4$ , the experimental values of  $d^{15}$ , not previously recorded, are 4.532 and 4.436, respectively. T. H. POPE.

**Forms of silicon.** W. MANCHOT and H. FUNK (Ber., 1930, 63, [B], 1441—1446).—Mainly a reply to Bedel (A., 1929, 756, 997, 1399) and Sanfourche (*ibid.*, 1030, 1251). Ignition of silicon does not appear to occur below  $500^\circ$ . Preparation of finely-divided silicon, such as is obtained by rapidly cooling its dilute solutions in molten metals, by mechanical means appears exceedingly difficult. When subjected to prolonged grinding in an agate mortar, the material suffers considerable oxidation which causes it to be partly soluble in hydrofluoric acid without evolution of considerable quantities of hydrogen. H. WREN.

**Potassium fluotitanate,  $\text{K}_2\text{TiF}_6$ , and the preparation of an oxyfluoride of hydrofluotitanic acid.** I. H. GINSBERG and G. HOLDER (Z. anorg. Chem., 1930, 190, 407—414).—From a review of the literature it is shown that the data regarding the preparation of potassium fluotitanate are conflicting and uncertain. The monohydrate could not be obtained by crystallisation either from aqueous solution or from solutions containing hydrofluoric acid. By careful evaporation and cooling of potassium fluotitanate solutions a hydrate was obtained containing  $1/3$  mol.  $\text{H}_2\text{O}$  per mol., which is retained up to  $50^\circ$ . Above this temperature the hydrate is hydrolysed. The anhydrous salt can be obtained by crystallisation at  $40$ – $60^\circ$  from the saturated solution and drying. From solutions which are highly concentrated with respect to hydrofluoric acid a compound  $\text{K}_2\text{TiF}_6 \cdot \text{HF}$ , which is stable up to  $300^\circ$ , is obtained. From a study of the loss in weight on heating the hydrated and anhydrous fluotitanate the existence of an oxyfluoride,  $\text{K}_2\text{TiOF}_4$ , stable up to  $500^\circ$ , appears probable.

O. J. WALKER.

**Germanium. XXIX.** Germanium monohydride. L. M. DENNIS and N. A. SKOW (J. Amer. Chem. Soc., 1930, 52, 2369—2372).—The reaction between sodium germanide and cold water yields germanium monohydride, a dark brown powder which decomposes with a slight explosion when dried in air. In a vacuum or an inert gas dissociation of the com-

pound into hydrogen and germanium is slow below  $165^\circ$ . Dissolution in solvents is accompanied by chemical change. Hydrogen chloride and concentrated alkali have no action, but oxidising agents yield germanium dioxide. Halogens yield the corresponding germanium tetrahalides.

J. C. A. GRIFFITHS.

**Compounds of cerium.** J. ŠTĚRBA-BŮHM and A. PÍSAŘÍČEK (Coll. Czech. Chem. Comm., 1930, 2, 244—254).—The following salts of cerium have been prepared:  $\text{NH}_4\text{Ce}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{KCe}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{K}_4\text{Ce}_2(\text{C}_2\text{O}_4)_9 \cdot 9\text{H}_2\text{O}$ ,  $\text{NaCe}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_4\text{Ce}_2(\text{C}_2\text{O}_4)_9 \cdot 10\text{H}_2\text{O}$ ,  $\text{LiCe}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{LiCe}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ . Cerous sulphate (2 g.) can be oxidised quantitatively to the ceric salt by gradual addition to boiling 30% sulphuric acid containing lead peroxide. C. W. GIBBY.

**Preparation and properties of lead perchlorate.** H. H. WILLARD and J. L. KASSNER (J. Amer. Chem. Soc., 1930, 52, 2391—2396).—Normal lead perchlorate is prepared by heating lead nitrate with perchloric acid until fuming occurs; the excess of perchloric acid is removed at  $160^\circ$  by a stream of moist air. The trihydrate (m. p.  $83$ – $84^\circ$ ); when dehydrated in a vacuum at  $60$ – $120^\circ$ , gave the anhydrous salt, m. p.  $270$ – $275^\circ$  (decomp.). The substance is excessively hygroscopic, yielding the monohydrate, m. p.  $153$ – $155^\circ$ , and the trihydrate. The solubility of anhydrous lead perchlorate at  $25^\circ$  is 81.472 g. per 100 g. of solution;  $d_4^{25}$  2.7753. The anhydrous salt is soluble in organic solvents. The solution in anhydrous methyl alcohol is explosive.

J. G. A. GRIFFITHS.

**Irreversible reduction of nitrogen oxides by sulphurous acid.** A. SANFOURCHE and L. RONDIER (Compt. rend., 1930, 190, 1555—1557).—To a mixture of nitrogen and oxygen in the ratio 84.85 : 8.65 was added sulphur dioxide to produce a mixture containing (a) 6.5 and (b) 2.0% thereof. To this was added 0.8% of nitric oxide and the mixed gases were bubbled through dilute sulphuric acid of concentration varying from 48.4 to 78.0%  $\text{H}_2\text{SO}_4$ , at temperatures from  $20^\circ$  to  $175^\circ$ . The gases were then passed through and collected over dilute hydrogen peroxide solution, and the amount of nitrogen oxides was determined. The coefficient of irreversible reduction thus determined (allowance being made for a loss of 2.5% indicated by a blank experiment) showed in both (a) and (b) maxima of decreasing amount and occurring at a higher temperature as the concentration of the acid increased. This maximum was higher for (a) than for (b); e.g., for (a) it is 41 at  $70^\circ$  for 48.4% acid and 13 at  $150^\circ$  for 78%; for (b) 31 at  $90^\circ$  for 48.4% acid and 19 at  $120^\circ$  for 70%.

C. A. SILBERRAD.

**Nitrosyl perchlorate and nitrosyl sulphate, and their coloured reduction products.** A. HANTZSCH and K. BERGER (Z. anorg. Chem., 1930, 190, 321—336).—Nitrosyl perchlorate does not exist as a hydrate. From its conductivity in nitromethane it is shown to be a normal electrolyte like the nitracidium perchlorates (cf. A., 1928, 855), and its constitution corresponds with that of anhydronitrosocidium perchlorate,  $[\text{ClO}_4][\text{NO}]$ . The so-called nitrosylsulphuric acid is also a salt and can be repre-

sented by the formula  $[\text{HO}\cdot\text{SO}_3][\text{NO}]$ ; the nitrosulphonic acid structure  $\text{O}_2\text{N}\cdot\text{SO}_3\text{H}$  is incorrect. Nitrosyl sulphate dissolves in pure sulphuric acid without decomposition and acts as a nitrosating agent only. The nitrating action of aqueous solutions is due to hydrolysis of the nitrosyl sulphate with formation of oxides of nitrogen. Nitrosyl perchlorate forms a blue reduction product very similar to the blue reduction product of nitrosyl sulphate. The blue compounds are probably hydronitrosylium salts,  $[\text{NOH}]\cdot\text{SO}_4\text{H}$  and  $[\text{NOH}]\cdot\text{ClO}_4$ . They form violet copper derivatives which are not true copper salts, but complex compounds in which the copper is linked to the nitrogen oxide.

O. J. WALKER.

**Double oxalates of bismuth and sodium.** S. ŠKRAMOVSKÝ (Coll. Czech. Chem. Comm., 1930, 2, 292—299).—The compound,  $\text{NaBi}(\text{C}_2\text{O}_4)_2\cdot 5\text{H}_2\text{O}$ , *d* 2.685, has been prepared by heating excess of bismuth oxalate with a 3% solution of sodium oxalate on a water-bath for 0.5 hr. A lower hydrate,  $\text{NaBi}(\text{C}_2\text{O}_4)_2\cdot 2.5\text{H}_2\text{O}$ , *d* 3.221, has been obtained by adding 4 g. of basic bismuth nitrate to a boiling solution of 20 g. of sodium oxalate. The double salts  $\text{Na}_4\text{Bi}_2(\text{C}_2\text{O}_4)_5\cdot 4\text{H}_2\text{O}$  and  $\text{LiBi}(\text{C}_2\text{O}_4)_2\cdot 5\text{H}_2\text{O}$  also exist.

C. W. GIBBY.

**[Preparation and properties of] hydrogen disulphide.** K. H. BUTLER and O. MAASS (J. Amer. Chem. Soc., 1930, 52, 2184—2198; cf. Walton and Parsons, A., 1922, ii, 281).—Optimal conditions are described for the preparation of hydrogen disulphide by the method previously recorded (*loc. cit.*). The pure disulphide (m. p.  $-89.6^\circ$ , b. p.  $70.7^\circ/760$  mm.,  $n_D^{20}$  1.6322) is stable in specially cleaned quartz apparatus, and the physical properties have been investigated. The density at temperatures between  $-32^\circ$  and  $51^\circ$  has been determined (*d*<sub>4</sub><sup>20</sup> 1.3615, *d*<sub>4</sub><sup>25</sup> 1.327), and the surface tension,  $\gamma$ , by capillary rise in the range  $-33^\circ$  to  $20.5^\circ$ , is given by  $96.3 = \gamma + T(d\gamma/dT)$ , where  $d\gamma/dT = -0.1695$ . From vapour-pressure determinations in the range  $0-45^\circ$ , the latent heat of vaporisation (129.2 g.-cal. per g.) is calculated, whence Trouton's constant is 24.9 and hence the liquid is associated. Ramsay and Shields' constant is 1.78. The parachor (130.0) proves the absence of a double or co-ordinated valency linking in the molecule. The specific heat of the liquid is 0.333 g.-cal. per g., that of the solid 0.142, and the latent heat of fusion is 27.3.

The f.-p. curve of the system sulphur-hydrogen disulphide has no break corresponding with the composition  $\text{H}_2\text{S}_2\cdot\text{S}$ , and the f. p. of this solution is much higher than that of hydrogen trisulphide; hence the latter is not a molecular compound of sulphur and hydrogen disulphide.

J. G. A. GRIFFITHS.

**Cyanogen iodide as impurity in iodine.** Its detection and elimination. S. MORRIS, E. B. CALLAGHAN, and L. DUNLAP (J. Amer. Chem. Soc., 1930, 52, 2415—2417).—The passage of hydrogen sulphide through aqueous iodine and cyanogen iodide produces hydrogen iodide and hydrogen cyanide. The latter passes over in the first fractions when the liquid is distilled. By further concentration, 0.00015% CN in iodine can be detected by the Prussian-blue test.

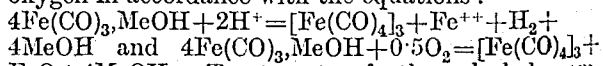
J. G. A. GRIFFITHS.

**Production and properties of large iron crystals.** N. A. ZIEGLER (Amer. Inst. Min. Met. Eng. Tech. Pub., 1930, No. 273, 3—17).—Single crystals were produced in strips of decarburised Armco iron which were heated at  $950^\circ$  in moist hydrogen for 24 hrs., strained to 2.25—2.5% elongation, and reannealed for 72 hrs. in dry hydrogen at  $850^\circ$ . The magnetic permeability of single-crystal iron is many times as great as that of polycrystalline iron.

CHEMICAL ABSTRACTS.

**Metallic carbonyls. VIII. Iron tetracarbonyl and its chemical behaviour.** W. HIEBER and E. BECKER (Ber., 1930, 63, [B], 1405—1417; cf. this vol., 875).—Iron tetracarbonyl is obtained in 40% yield by the action of alkali alkoxide on iron pentacarbonyl and shown by cryoscopic examination in the pentacarbonyl to have the trimeric structure  $[\text{Fe}(\text{CO})_4]_3$ . It reacts vigorously with pyridine, evolving carbon monoxide in relatively small amount and yielding primarily the compound  $\text{Fe}(\text{CO})_3\cdot\text{C}_5\text{H}_5\text{N}$  and iron pentacarbonyl. Prolongation of the reaction or use of a higher temperature causes conversion of the tricarbonyl compound into the substance  $\text{Fe}_2(\text{CO})_4\cdot 3\text{C}_5\text{H}_5\text{N}$ . Both pyridine compounds absorb carbon monoxide with formation of iron pentacarbonyl. With iodine in pyridine, the substance  $\text{Fe}(\text{CO})_2\text{I}_2\cdot 2\text{C}_5\text{H}_5\text{N}$  is produced. With ethylenediamine in pyridine the product

$\text{Fe}(\text{CO})_3\text{en}\cdot 1.5\text{C}_5\text{H}_5\text{N}$  is initially formed, and passes when washed with anhydrous ether into the compound  $\text{Fe}(\text{CO})_3\text{en}$ ; when treated with pyridine the last-named substance yields successively the compounds  $\text{Fe}(\text{CO})_2\cdot x\text{C}_5\text{H}_5\text{N}$  and  $\text{Fe}_2(\text{CO})_5\text{en}\cdot x\text{C}_5\text{H}_5\text{N}$ . Decomposition of the tricarbonyl compound by dilute acid occurs strictly in accordance with the scheme:  $2\text{Fe}(\text{CO})_3\cdot\text{C}_5\text{H}_5\text{N} + 4\text{H}^+ = \text{Fe}^{++} + \text{Fe}(\text{CO})_4$  [polymerised]  $+ 2\text{CO} + \text{H}_2 + 2\text{C}_5\text{H}_5\text{NH}^+$ . The reaction of iron tetracarbonyl with methyl alcohol is, in principle, analogous with that of pyridine, giving carbon monoxide, iron pentacarbonyl, and the substance  $\text{Fe}(\text{CO})_3\cdot\text{MeOH}$ , which is soluble in water and indifferent organic media, in which it exists in the monomeric form. It is decomposed by acids and oxygen in accordance with the equations:



Treatment of the alcohol compound with boiling methyl alcohol causes reaction according to the schemes  $3\text{Fe}(\text{CO})_3 \rightleftharpoons \text{Fe}(\text{CO})_5 + 2\text{Fe}(\text{CO})_2$  and  $\text{Fe}(\text{CO})_2 + 2\text{MeOH} = \text{Fe}(\text{OMe})_2 + \text{H}_2 + 2\text{CO}$ . The phenomenon of carbon monoxide exchange during carbonyl reactions is very widespread. Thus tricarbonyl and pentacarbonyl react according to the scheme  $\text{Fe}(\text{CO})_3\text{M} + \text{Fe}(\text{CO})_5 = 2\text{Fe}(\text{CO})_4$  [polymerised]  $+ \text{M}$  (M = neutral molecule). Iron tetracarbonyl decomposes at about  $140^\circ$  into the pentacarbonyl and non-uniform products.

In the metallic carbonyls and their derivatives, carbon monoxide unites two chemical functions. It is present as a neutral molecule and, as such, can be substituted by other neutral components such as ammonia, amines, and alcohols. On the other hand, without electronegative charge, it behaves as anion. As a consequence of very strong polarisation, a



fusion of the electron arrangements of metallic atom and carbon monoxide has occurred. There exists, therefore, a non-polar union between the metallic atom and the carbon atom of the monoxide somewhat comparable with the atomic union of halogen, for example of iodine in cuprous iodide. H. WREN.

**New compounds and reactions in the nitroprusside series.** R. BRUNNER (Z. anorg. Chem., 1930, 190, 384—396).—By the action of formaldehyde on an alkaline solution of sodium nitroprusside a compound,

$\text{Na}_4\text{Fe}(\text{CN})_5\text{N}(\text{OH})\text{C}(\text{OH})\text{NO}(\text{CN})_5\text{FeNa}_4 \cdot 19\text{H}_2\text{O}$ , is obtained; its properties are described. When an aqueous solution of this substance is hydrolysed sodium nitritopentaferrocyanide is formed together with another compound which is probably sodium isocyanopentaferrocyanide,  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NC}]$ . This differs from the isomeric sodium ferrocyanide in the fact that a concentrated solution is not precipitated by a concentrated solution of calcium and potassium chlorides. Sodium sulphitopentaferrocyanide can be obtained by the action of sodium thiosulphate on an alkaline solution of sodium nitroprusside. Attempts to prepare a tetracyano-compound by the action of sodium oxalate on sodium aquoferrocyanide were unsuccessful. By the action of sodium thiocyanate on the latter compound a yellow substance, which is a mixture of  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{CNS}]$  and sodium ferrocyanide, was formed. The formation of coloured products from resorcinol and sodium nitroprusside is described. O. J. WALKER.

**Hexamminecobaltic sulphate.** II. P. B. SARKAR and T. P. BARAT (J. Indian Chem. Soc., 1930, 7, 199—206; cf. this vol., 702).—A study of the solubility of hexamminecobaltic sulphate (I) in aqueous sulphuric acid of concentrations between zero and 80% confirms the existence of the three acid salts previously described, viz., (I),  $\text{H}_2\text{SO}_4$  (Jørgensen, A., 1938, ii, 592); (I),  $2\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  and (I),  $5\text{H}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (Klobb, A., 1902, ii, 23). They may be prepared by crystallisation of I from aqueous sulphuric acid of concentrations 2.1—16.1%, 16.1—60.3%, and above 60.3%, respectively. The second, contrary to the statements of Benrath and Würzburger (A., 1924, ii, 557), is definitely hydrated. These acid salts may be analysed for free acid and sulphate ion by conductometric titration with baryta, there being a very definite break at neutrality and a less definite break when all sulphate has been precipitated. H. A. PIGCOTT.

**Separation of nickel and cobalt by means of hypochlorite.** F. H. RHODES and H. J. HOSKING. —See B., 1930, 667.

**Nickel and cobalt nitrites.** J. J. HERRERA (Anal. Fis. Quim., 1930, 28, 358—361).—Duval's method of preparation of the compound  $\text{Ni}(\text{NO}_2)_2 \cdot 4\text{NH}_3$  has been repeated. The stability of the compound is greater than that reported by Duval; ammonia is not lost on heating at  $100^\circ$ , but is completely removed at  $135$ — $140^\circ$ , the green residue having the composition of a basic nitrate. Attempts to produce the corresponding cobalt compound by Duval's procedure led to the formation of compounds of indefinite composition, which always contained acetate. H. F. GILLBE.

**Glass electrode system.** C. MORTON (J. Sci. Instr., 1930, 7, 187—190).—N-Hydrochloric acid saturated with quinhydrone is contained in a bulb of high-conductivity glass, made by fusing pure silica (60), anhydrous sodium carbonate (30), and calcium carbonate (10) at  $1500^\circ$  until evolution of gas ceases. The bulb dips in the solution of which the  $p_{\text{H}}$  is to be determined. The  $E.M.F.$ - $p_{\text{H}}$  relationship of the glass is linear to within 1 millivolt up to  $p_{\text{H}}$  10, above which it deviates rapidly. The  $E.M.F.$  is measured by a ballistic method, and determinations can be made in less than a minute with an accuracy of  $\pm 0.01 p_{\text{H}}$ . C. W. GIBBY.

**Protected hydrogen electrode.** A. THIEL and G. SCHULZ (Z. Elektrochem., 1930, 36, 408—410).—The poisoning effect of colloids in the measurement of  $p_{\text{H}}$  values with a hydrogen electrode is obviated as follows. The cleaned electrode, preferably of unpolished iridium, is immersed in an acetate collodion solution (8%); the latter is coagulated on the electrode by water, and repeatedly washed. Such a membrane is permeable to the molecular-disperse phase, complete equilibrium being obtained within 3 hrs., but not to colloids such as casein.

H. I. DOWNES.

**Possible sources of error in  $p_{\text{H}}$  determination.** L. FLETCHER and J. B. WESTWOOD (J.S.C.I., 1930, 49, 201—203T).—The importance of an exact temperature control of all parts of the apparatus used in the electrolytic determination of hydrogen-ion concentration is emphasised and details are given of a procedure which gives entire satisfaction. A description of the method employed by the authors for platinising electrodes is also given. Some difficulties found in using hydrogen from various sources are described. A method for the rapid electrometric titration of beer or wort to any  $p_{\text{H}}$  value desired, using a pair of hydrogen electrodes, has been elaborated and a specially designed hydrogen electrode vessel is illustrated.

**Azo-indicators.** E. E. HARRIS, H. W. HAUGEN, and B. E. FAHL (J. Amer. Chem. Soc., 1930, 52, 2397—2399).—The influence of constitutional factors on the  $p_{\text{H}}$  at which azo-indicators change colour has been investigated. The  $p_{\text{H}}$  is lowered progressively by moving the acid group from *o*- to *p*- to *m*-. The introduction of methyl groups has little effect, but strongly negative groups (e.g., nitro-) lower the  $p_{\text{H}}$ .

J. G. A. GRIFFITHS.

**"More perfect indicators" and some other misapprehensions in the realm of volumetric analysis.** F. L. HAHN (Z. anal. Chem., 1930, 80, 321—330).—Attention is directed to a number of incorrect statements in current literature dealing with the use of indicators in acidimetry and alkalimetry and this subject is discussed theoretically. In every case where a new indicator is proposed for use, the following data respecting it should be given: the limiting  $p_{\text{H}}$  values between which a recognisable colour change takes place, and the sensitivity, as measured by the employment of suitable buffer solutions. H. F. HARWOOD.

**Use of potassium titanium oxalate for the preparation of a standard titanium solution**

for colorimetry. W. M. THORNTON, jun., and R. ROSEMAN (Amer. J. Sci., 1930, [v], 20, 14—16).—A satisfactory standard titanium solution has been prepared in a short time by mixing potassium titanium oxalate with ammonium sulphate, heating gradually with concentrated sulphuric acid, and boiling for a few minutes. C. W. GIBBY.

Diphenylamine-blue as indicator in the precipitation volumetric determination of the chlorine, bromine, and silver ion in acid solution. R. LANG and J. MESSINGER (Ber., 1930, 63, [B], 1429—1431).—The 0.5—5*N*-sulphuric acid solution containing 0.015—0.17 g. of chloride chlorine, the total volume, not exceeding 40 c.c., is mixed with 10 c.c. of freshly-prepared diphenylamine-blue solution and titrated with 0.1*N*-silver nitrate solution with vigorous agitation until the liquid just acquires a permanent violet tint. If the volume of the solution lies between 40 and 150 c.c., 0.5 g. of dissolved barium nitrate is added previously to titration. The indicator is made by mixing 3 drops of a solution of 1 g. of diphenylamine in 100 c.c. of sulphuric or phosphoric acid with 10 c.c. of 5*N*-sulphuric acid and 1 c.c. of 0.1*N*-potassium dichromate. If less indicator is used, the process is available in 0.01*N*-solution. Titration can be effected in the presence of nitric, perchloric, phosphoric, hydrofluoric, oxalic, and iodic acids and of alkaline-earth, manganese, aluminium, and ferric salts. Titration of silver in nitric acid solution by alkali chloride is possible if less indicator is used and agitation is very vigorous towards the end-point. Bromide can be treated similarly, particularly if further addition of indicator is made immediately before precipitation is complete. Iodine, thiocyanate, and cyanide cannot be determined analogously. H. WREN.

Adsorptional method of titration. N. P. RUDENKO (J. Russ. Phys. Chem. Soc., 1930, 62, 505—548).—The end-point obtained in Fajans and Wolff's method (A., 1924, ii, 776) for argentometric titration of halides using rose-Bengal as indicator is much sharper in solutions acidified with acetic acid; with erythrosin excess of group I or II metal nitrates should be added. The presence of even large concentrations of group I or II metals does not affect the accuracy of the above method; in group III the following equivalent concentrations of cation per equivalent of halide should not be exceeded: aluminium 5, zinc 5, manganese 20, nickel 0.5 with uranyl, 10 with eosin, cobalt 0.5 with uranyl, 5 with eosin, uranyl 2. A satisfactory end-point cannot be obtained in the simultaneous presence of chromic and chromous ions, of ferric and ferrous ions, and of nickel and cobalt ions. Of the fourth analytical group, only cadmium in amount not exceeding 5 equiv. per equiv. of halide can be present without affecting the accuracy of the results obtained. R. TRUSZKOWSKI.

Micro-iodometry. R. V. TEISS (J. Russ. Phys. Chem. Soc., 1930, 62, 601—606).—The greatest accuracy in the iodometric titration of various solutions is obtained by using 0.002*N*-iodine solution. R. TRUSZKOWSKI.

Determination of nitrogen in gaseous mixtures. Z. N. BLYUMSHTEIN (J. Appl. Chem., Russia, 1929, 2,

801—807).—Lidov's method (J. Russ. Phys. Chem. Soc., 42, 42) is modified. CHEMICAL ABSTRACTS.

Direct determination of nitric nitrogen in colloidal [explosive] powders. H. MURAUER.—See B., 1930, 687.

Determination of nitrates [in water]. G. W. BURKE, M. LEVINE, and G. H. NELSON.—See B., 1930, 688.

Determination of phosphorous acid. A. P. DUNAIEV (Min. Suir. Tsvet. Met., 1929, 424—429).—A saturated solution of sodium hydrogen carbonate (30 c.c.) is added to the neutral solution containing 0.1—0.15 g. of phosphorous acid, followed by 5—6 c.c. of 0.1*N*-bromine solution in excess of that required to produce a yellow colour. After 2—3 min. 5% potassium iodide solution (10 c.c.) and 4*N*-sulphuric acid (10 c.c.) are added, the mixture being titrated after 5 min. with 0.05*N*-sodium thiosulphate.

CHEMICAL ABSTRACTS.

Determination of arsenic [in foods etc.].—See B., 1930, 638.

Decomposition of aluminous silicates for chemical analysis. A. N. FINN and J. F. KLEKOTKA (Bur. Stand. J. Res., 1930, 4, 809—813).—The difficulties introduced into silicate analysis by the presence of large quantities of sodium salts used in the original decomposition of the substance by fusion with sodium carbonate may be avoided by working as follows: 0.5 g. of the finely-powdered substance is intimately mixed with 0.6 g. of sodium carbonate in a platinum crucible and the mixture is heated at 875° in an electric muffle for 2 hrs. After cooling, the mass is digested with 1—2 c.c. of water for 10 min., broken up by stirring with a glass rod, and rinsed into a beaker with not more than 50 c.c. of water. The whole is heated to boiling, 20 c.c. of hydrochloric acid (*d* 1.19) are added rapidly with constant stirring, and the solution is evaporated to dryness. The residue is heated at 105—110° for 1 hr. to dehydrate the silica, moistened with 20 c.c. of hydrochloric acid (*d* 1.19), and boiled with 100 c.c. of water. The silica is collected and the analysis finished in the usual way. A. R. POWELL.

Volumetric determination of alkali metals in glass. N. A. TANANAEV and A. K. BABKO.—See B., 1930, 663.

Sodium sulphite for analysis. HOLZVERKOHLEUNGS-IND. A.-G. (Chem.-Ztg., 1930, 54, 502).—Contrary to earlier statements, pure sodium sulphite does not yield alkaline solutions and the faint blue colour with thymolphthalein is destroyed by one drop of 0.1*N*-hydrochloric acid. In the use of sodium sulphite for the determination of formaldehyde, the grade "pro analysi" is not essential because reasonable proportions of neutral saline impurities, such as sodium sulphate, do not affect the titration; sodium carbonate must, however, be absent. D. F. TWISS.

Microchemical detection of silver as azide. R. UZEL (Coll. Czech. Chem. Comm., 1930, 2, 300—303).—Silver may be detected microchemically as azide by adding a solution of sodium azide to a neutral solution of a silver salt on a microscope slide. The

precipitate is dissolved in one drop of 10% ammonia solution and left to crystallise. The azide is dimorphous, crystallising either in needles or in plates.

C. W. GIBBY.

**Micro-determination of calcium ions.** M. MOUSSERON and N. BOUVISSOU (Bull. Soc. Chim. biol., 1930, 12, 482—490).—The calcium is precipitated by sodium tungstate and the precipitate after being separated by centrifuging and washing with distilled water is treated with dilute hydrochloric acid to remove the calcium, the tungstic oxide remaining behind. This is dissolved in potassium hydroxide solution, the mixture exactly neutralised, and then treated with titanium chloride solution after a definite quantity of dilute hydrochloric acid has been added. The blue colour developed is compared with a standard. The application of the method to solutions in which iron and phosphorus are present is also described.

W. O. KERMACK.

**Micro-analysis of calcium ion.** A. ASTRUC and M. MOUSSERON (Compt. rend., 1930, 190, 1558—1559; cf. this vol., 443).—An amount of the liquid for analysis containing about 0.5 mg. of calcium is mixed with 5 c.c. of the potassium nickelnitrite reagent (the preparation of which is to be described later). After 5 hrs. the mixture is centrifuged, the precipitated calcium potassium nickelnitrite,  $\text{CaK}_2\text{Ni}(\text{NO}_2)_6$ , washed successively with 20% acetone and alcohol-ether, and the nitrogen reduced to ammonia with aluminium and sodium hydroxide, the ammonia then being determined alkalimetrically. The method is recommended for biological analyses, as the reagent, whilst precipitating the alkaline-earth metals, of which practically only calcium occurs in such analyses, does not precipitate copper, manganese, aluminium, iron, zinc, or magnesium.

C. A. SILBERRAD.

**Assay of calcium carbide.** R. VONDRAČEK.—See B., 1930, 659.

**Analysis of calcium hypochlorite solutions.** E. FABRIZI.—See B., 1930, 658.

**Titrimetric determination of magnesium.** J. S. PIERCE and M. B. GEIGER.—See B., 1930, 659.

**Rapid electrotitrimetric determination of zinc in a mineral.** N. JOASSART and E. LECLERC (Bull. Soc. chim. Belg., 1930, 39, 231—238).—A solution containing 0.05—0.12 g. of zinc is made just acid with hydrochloric acid and diluted to 300 c.c. It is then titrated, while boiling, with a solution of potassium ferrocyanide containing a little potassium ferricyanide. One electrode is a coil of platinum wire, the other is a carbon block. The current falls rapidly when the end-point is approached.

C. W. GIBBY.

**Detection of copper and Feigl's rhodanine test for silver.** I. M. KOLTHOFF (J. Amer. Chem. Soc., 1930, 52, 2222—2226).—The rhodanine (Feigl, A., 1928, 1108) under suitable conditions is a very sensitive test for mercury and copper. 10 C.c. of aqueous mercurous or strongly dissociated mercuric salt give a red precipitate or coloration on the addition of 0.5 c.c. of 4*N*-nitric acid and 0.3 c.c. of reagent (saturated alcoholic rhodanine). 0.5 Mg. of mercurous ion per litre can be detected and 0.2 mg. of mercuric

in the absence of halide. Cupric salts give a brownish-orange coloration in neutral solution (sensitivity: 0.3 mg.  $\text{Cu}^{++}$  per litre). Cuprous ions in dilute acid solution give a violet precipitate (Funakoshi, A., 1929, 901) or orange-brown coloration (sensitivity: 0.1 mg.). Cupric ions in the presence of many metallic ions are detected as cuprous after reduction with hydrazine sulphate and ammonia.

As little as 0.1 mg. of copper per litre may be determined in the presence of alkali chloride, but in the absence of other metals, by a modification of the method of Clarke and Jones (A., 1929, 900). 1 C.c. of saturated potassium iodate is added to 10 c.c. of copper solution containing 0.2—0.3 c.c. of 0.1% dimethylglyoxime. The colour is maximal after 5 min.

J. G. A. GRIFFITHS.

**Cuprous sulphide as gravimetric form.** F. L. HAHN (Ber., 1930, 63, [B], 1616—1617).—The conversion of cupric into cuprous sulphide is quantitatively effected in 2—3 min. by heating the product to bright redness in a current of sulphur vapour introduced by a stream of carbon dioxide charged with the vapour of methyl alcohol. For this purpose a short tube is fixed in the lid of the Rose crucible, one end of which projects into the crucible and the other end into a bulb blown at the end of a silica tube. The bulb contains coarsely crushed sulphur and the silica tube serves for the introduction of the carbon dioxide.

H. WREN.

**Electrometric determination of copper. III. Application of bi-metallic electrodes.** M. E. PRING and J. F. SPENCER (Analyst, 1930, 55, 375—382).—The bi-metallic electrode system of Foulk and Bawden (A., 1926, 927) may be successfully used for the titration of iodine liberated by the action of cupric salts on potassium iodide, using either sodium thiosulphate or sodium arsenite. With the former all concentrations of copper down to 0.004*N* may be used, but solutions more dilute than 0.01*N* could not be determined with sodium arsenite. The concentration of acetic acid and potassium iodide may be varied over a wide range, and copper may be determined electrometrically using thiosulphate in the presence of nickel, bismuth, aluminium, zinc, lead, silver, and stannic tin, with as sharp an end-point as in their absence. It may also be determined in the presence of ferric iron if sufficient sodium pyrophosphate is present to convert the ferric ion into a complex ferric pyrophosphate anion, but the amount of iodine liberated from potassium iodide by a mixture of ferric and cupric salts always falls short of the calculated quantity.

D. G. HEWER.

**Determination and separation of mercury by means of cupferron.** A. PINKUS and (MLLE.) M. KATZENSTEIN (Bull. Soc. chim. Belg., 1930, 39, 179—195).—Cupferron precipitates mercurous ions quantitatively from nitric acid solutions containing free acid less concentrated than 0.5*N*. The metal is determined by dissolving the precipitate in hot *N*-nitric acid and electrolysis the solution. This method permits the separation of mercury from silver, lead, cadmium, aluminium, chromic, manganous, nickel, cobalt, and zinc ions, which are not precipitated by cupferron in acid solution. A separation of

mercurous from mercuric mercury is not possible by this method, since mercuric ion is partly precipitated by cupferron in moderately acid solution. A nephelometric method of determining mercury, based on the formation of hydrosols of metallic cupferron compounds (cf. A., 1927, 639), which is much superior to the colorimetric sulphide method, has been developed.

F. G. TRYHORN.

**Ceric sulphate in volumetric analysis. VIII. Use of methyl-red, erio-glaurin, and erio-green indicators in the reaction between ceric and ferrous ions.** N. H. FURMAN and J. H. WALLACE, jun. (J. Amer. Chem. Soc., 1930, 52, 2347—2352).—The end-point of the titration of acid ferrous sulphate with ceric sulphate is determined by methyl-red, which changes to brown or yellow (small end correction). In the reverse titration, the indicator, together with phosphoric acid, is added just before the end-point (colour change, yellow to violet). Erio-glaurin A and alkali-fast (erio-)green A (Knop, A., 1929, 670) are reversible indicators in the above titrations (colours: yellow in ferric and pale rose in ceric solutions). Hydrochloric acid, calomel, and mercuric chloride do not interfere. J. G. A. GRIFFITHS.

**Gravimetric quantitative separation of aluminium and phosphate ions from manganous, ferrous, calcium, and magnesium ions.** B. SOLAJA (Z. anal. Chem., 1930, 80, 334—351).—The author's method of precipitation by means of "fusible white precipitate" (A., 1923, ii, 583; 1925, ii, 602) has been extended to a number of separations. Satisfactory separations of alumina and phosphoric acid from manganese, calcium, and magnesium can be accomplished by the addition of a suspension of "fusible white precipitate" in water to a solution of the above metals, of  $p_H$  5.0—6.5, provided that the ratio of the alumina to the phosphoric acid present is not less than 3:1. Alumina and phosphoric acid can be separated from iron under similar conditions by precipitation of the two first-named with "fusible white precipitate" in the presence of hydroxylamine; a double precipitation is advisable if the iron is present in large excess. H. F. HARWOOD.

**Determination of manganese, iron, and aluminium in presence of phosphoric acid.** J. S. TELETOV and N. N. ANDRONIKOVA (Z. anal. Chem., 1930, 80, 351—357).—The solution containing the above substances is diluted to 200 c.c., and treated with 12 c.c. of 12% sodium hydroxide solution, followed by 1—1.5 c.c. of 30% hydrogen peroxide. The whole is boiled for 30 min. and filtered, manganese and iron being precipitated, whilst aluminium and phosphoric acid pass into the filtrate. The precipitate is dissolved in a known amount of 0.1N-oxalic acid in the presence of 15 c.c. of sulphuric acid (1:4), and the manganese is first determined by titration of the excess of oxalic acid with 0.02N-potassium permanganate. The iron in solution is then reduced to the ferrous condition by passage through a filter tube packed with electrolytic cadmium, and determined volumetrically. The aluminium and phosphoric acid in the original alkaline filtrate may be separated by almost neutralising the liquid with

hydrochloric acid, adding barium nitrate, and keeping hot for some time. The whole of the phosphoric acid is precipitated as barium phosphate, and after filtration the aluminium in the filtrate can be determined as usual by precipitation with ammonia. An alternative method of treatment consists in acidifying the solution with nitric acid and precipitating the phosphoric acid with ammonium molybdate; the aluminium in the filtrate can then be directly precipitated with ammonia. The above procedure yields excellent results provided that the amount of manganous oxide present does not exceed 0.04 g.; with larger quantities the results are inaccurate.

H. F. HARWOOD.

**Thiocyanate method of determining iron. Influence of different classes of phosphates.** G. W. LEEPER (Analyst, 1930, 55, 370—371).—The danger of interference by orthophosphate in the colour formation of ferric thiocyanate appears to have been exaggerated, and the effects may often have been due to dehydrated phosphoric acids, mainly pyrophosphates. With regard to orthophosphates the equilibrium  $FePO_4 + 3CNS' \rightleftharpoons Fe(CNS)_3 + PO_4'''$ , should be pushed as much as possible to the right, and a high concentration of thiocyanate maintained. Working with a solution containing 10 c.c. of 2N-sulphuric acid, 1 c.c. of M/2000-ferric sulphate solution, and 5 c.c. of 2.5M-ammonium thiocyanate, diluted to 50 c.c., the minimum amount of  $P_2O_5$  as various types of phosphates which produce interference are:  $NaPO_3$ , 0.08 mg.;  $Na_4P_2O_7$ , 0.40; and  $H_3PO_4$ ,  $Na_2HPO_4$ , and  $KH_2PO_4$ , 100—120 mg. However, differences in concentration of acid and thiocyanate lead to a lower level of toleration. 0.02 Mg. of iron may be conveniently determined in this way, and the thiocyanate method is safe for all biological material [with the possible exception of milk, for which the method of Marriott and Wolf is recommended (A., 1906, ii, 582)] provided that the amount of phosphoric anhydride in the Nessler tube does not exceed 100 mg. and that precautions are used, such as due time being allowed during digestion of the ashed material with acid for any pyrophosphate to be reconverted into orthophosphate.

D. G. HEWER.

**Determination of chromium and vanadium [in steel].** I. M. KOLTHOFF and E. B. SANDELL.—See B., 1930, 666.

**Entrainment of polonium. Insoluble derivatives thereof as colloidal centrifugable precipitates.** M. GUILLOT (Compt. rend., 1930, 190, 1553—1555).—When the polonium is separated as sulphide (by hydrogen sulphide from N-hydrochloric acid solution), as metal (by stannous chloride from the same), or as diethyldithiocarbamate (cf. this vol., 308, 405; Escher-Desrivieres, A., 1926, 879; Brennan, A., 1925, ii, 770), the entrainment of the polonium by a precipitate of another compound is due to the insolubility of the polonium compound and is independent of adsorption. On the other hand, such separation as occurs from a strongly alkaline medium, and in some cases (e.g., as hydroxide) from an acid one, is apparently due to selective adsorption of the soluble ionised polonium. Polonium hydroxide more

closely resembles tellurous acid than bismuth hydr-oxide. C. A. SILBERRAD.

**Determination of tantalum, tungsten, vanadium, and molybdenum in steel.** K. SWOBODA and R. HORNÝ.—See B., 1930, 667.

**Detection of traces of gold chloride in photographic salts.** L. SETTIMI.—See B., 1930, 641.

**Potentiometric determination of gold and platinum.** E. MÜLLER and W. STEIN (Z. Elektrochem., 1930, 36, 376—383).—Gold in solution is determined potentiometrically by titration with titanous chloride (cf. this vol., 728), and also with stannous chloride. High values obtained with the former are due to slight decomposition of the titanous chloride in the presence of gold; the error may be determined and allowed for. Accurate results are obtained with stannous chloride. By means of titanous chloride gold and platinum may each be determined in the same solution with an error of about 2% by effecting the first part of the titration at the ordinary temperature and the latter part at 50°. Only the sum of the two elements may be found with stannous chloride. The standardisation of the stannous chloride by a potentiometric titration against dichromate is accurate only under specific conditions. H. I. DOWNES.

**Ultramicroscope allowing the direct projection of ultramicroscopic tests and Brownian movement.** A. TURPAIN and R. DE BONY DE LAVERGNE (Compt. rend., 1930, 190, 1398—1399).—Concentric circles of black paper (9 cm. diameter) are attached to the parallel bases of two glass hemispheres so as to cut off the central portion of a beam of light from an electric arc. By means of suitable projection apparatus an image of particles in Brownian movement in a drop of liquid 5 mm. in diameter may be obtained at 1 m. from the apparatus. J. GRANT.

**Photo-electric cell for the ultra-violet. Mechanism of sensitisation.** H. HULUBEI (Compt. rend., 1930, 190, 1549—1552).—For researches in the region 2800—2850 Å. a palladium photo-electric cell having a quartz window, central anode, and cathode of "black body enclosure" form has been devised. The palladium is deposited on a silver support by a slow discharge (maximum voltage 1200) in hydrogen at a few tenths of a mm. pressure. An osmo-regulator addition is advisable. The accelerating potential should be 120—480 volts according to the pressure of hydrogen. Such a cell works satisfactorily to the limits of transparency of quartz and shows satisfactory stability. The mechanism of the sensitisation of photo-electric cells by making the metal the cathode for a discharge in an atmosphere of hydrogen is discussed, and preliminary experiments with palladium and potassium suggest that the effect is at least mainly due to active hydrogen, and but slightly, if at all, to mechanical action. C. A. SILBERRAD.

**Leonard Hill acetone-methylene-blue actinometer.** T. W. B. OSBORN and A. D. STAMMERS (Brit. J. Actinother., 1930, 5, 68—69).—Exclusion of air is essential for securing reproducible results. C. W. GIBBY.

**Laboratory apparatus. [Desiccators and drying ovens.]** F. W. HORST (Chem. Fabr., 1930, 250—252).—Pumice used with sulphuric acid in desiccators may contain chlorides which, if present in more than traces, should be removed with dilute sulphuric acid before use. The feet of porcelain crucible stands for desiccators are advantageously secured by copper wire to a framework. The door of a drying oven is usually not quite tight and in exact determinations of moisture errors may be introduced by the entrance of moist outside air around the door. It is desirable to evacuate the oven by means of a filter pump, to place the sample to be dried in the back of the oven, and to turn off the gas a quarter of an hour before the sample is due for removal. C. IRWIN.

**Non-isothermal adiabatic calorimetry. II. Measurement of temperature changes of less than 0.1° with an accuracy of  $\pm 0.0001^\circ$ .** E. LANGE and K. P. MIŠČENKO (Z. physikal. Chem., 1930, 148, 161—176; cf. A., 1929, 1233).—The construction and manipulation of an adiabatic calorimeter are described. By means of a Beckmann thermometer graduated in 0.001° temperature changes of less than 0.1° can be measured with an accuracy of  $\pm 0.0001^\circ$ . R. CUTHILL.

**Gas analysis pipette for difficult absorptions.** M. SHEPHERD (Bur. Stand. J. Res., 1930, 4, 747—752).—The gas inlet tube of the bubbling pipette is turned slightly upwards and opened out to form an inclined flat dish-shaped end which is closed with a sealed-in platinum disc 0.05 cm. thick and 20 mm. in diameter perforated with 212 holes 0.06 mm. in diameter spaced 1 mm. apart and extending to within 2 mm. of the outer edge of the disc. A pressure of 30 mm. of mercury is required to force the gas through the perforations. Thorough contact with the absorption liquid is ensured by this arrangement, which renders it possible to remove oxygen completely from air by passing it three times through alkaline pyrogallol, whereas ten treatments are necessary in the ordinary type of absorption pipette. A. R. POWELL.

**New principle of nephelometric comparison.** F. L. HAHN (Ber., 1930, 63, [B], 1543—1545).—The liquids under comparison contained in glass tubes are placed in a blackened case. Light from a uniform source (window etc.) passes through a filter near the bottom of the case and is reflected upwards through the solution. A second filter in the side of the case permits the light to fall directly on to the solution. The two filters preferably allow lights of complementary colours to pass. Greater accuracy is obtained by this method, since differences of transparency are transformed into differences of colour tone to which the eye is more sensitive. H. WREN.

**Inorganic lubricants. I. Amalgams.** W. A. BOUGHTON (J. Amer. Chem. Soc., 1930, 52, 2421—2422).—Satisfactory lubrication of taps with amalgams is accomplished by previously heavily silvering the glass surfaces. Deterioration occurs after a few days and is immediate in the presence of acid gases or aqueous solutions of many salts. J. G. A. GRIFFITHS.

**Calculation of surface tension from measurements of capillary rise.** A. W. PORTER (*J. Sci. Instr.*, 1930, 7, 197—198).—A table is given to facilitate the calculation of capillary constants from the rise of liquids in narrow tubes. The ratio of radius of tube to capillary rise is tabulated against the difference from  $h/2r+1/6$ , for values of  $r/h$  between 0.01 and 0.34. C. W. GIBBY.

**Preparation of mirrors by sputtering metals on to glass surfaces.** A. C. G. BEACH (*J. Sci. Instr.*, 1930, 7, 193—195).—Experimental details are given for the preparation of mirrors of silver and nickel by sputtering. C. W. GIBBY.

**Constant-temperature preheater.** S. T. BOWDEN (*J.S.C.I.*, 1930, 49, 257—258r).—Water is passed over a 300-watt electrical heater fixed centrally in a cylindrical Dewar flask. Equilibration of the temperature of the issuing water is effected by means of a thick layer of soft copper gauze. Rough adjustment of the temperature of the water is made by altering the rate of flow through the apparatus, and final adjustment by means of a variable resistance in series with the electrical heater.

**Viscosimeter.** A. KÄMPF and O. SCHRENK (*Kunstseide*, 1929, 11, 376—381; *Chem. Zentr.*, 1930, i, 751).—A viscosimeter suitable for use with moderately and highly viscous materials is described. A. A. ELDRIDGE.

**Apparatus for catalytic hydrogenation.** J. FREJKA (*Coll. Czech. Chem. Comm.*, 1930, 2, 433—439).—An apparatus in which hydrogen can be generated and stored at a given pressure and with which the volume used in hydrogenation can be measured is described. C. W. GIBBY.

**Sensitive and manometric flames.** R. C. COLWELL (*Rev. Sci. Instr.*, 1930, [ii], 1, 347—350).—Designs of special burners for producing sensitive flames with natural gas are described. C. W. GIBBY.

**Sensitive method for determining refractive indices.** S. A. KORFF and J. Q. STEWART (*Rev. Sci. Instr.*, 1930, [ii], 1, 341—346).—The fringes produced by a Michelson interferometer are measured with a spectrometer. C. W. GIBBY.

**Current-temperature relations in tungsten pyrometric filaments.** G. RIBAUD (*J. Phys. Radium*, 1930, [vii], 1, 176—184).—In a pyrometer of disappearing-filament type with tungsten filament, in a vacuum, of sufficient length for the central

portion to be at constant and maximum temperature the values of  $1/I \times dI/dT$  and of  $1/I \times dI/dS$ , where  $I$  is the current,  $T$  the true, and  $S$  the apparent temperature (temperature of brightness) are independent of the shape and dimensions of the filament. Based on results previously obtained (*Ann. Physique*, 1927, [x], 7, 5) the above ratios and connected data are calculated and a curve connecting  $1/I \times dI/dS$  and  $S$  (for  $\lambda=0.655 \mu$ ) is drawn. With a filament 0.06 mm. diam. the current variations at the m. p. of gold and palladium are respectively 0.00033 and 0.00045 amp. per  $1^\circ$ . The necessary modifications for absorbing glasses and for short filaments are detailed, with  $S/I$  curves for three different short-length filaments, showing their gradual approximation to a similar curve for a long filament which is almost a straight line. C. A. SILBERRAD.

**Connecting flask for vacuum distillation.** K. H. SLOTTA (*Chem. Fabr.*, 1930, 183).—A Woulff bottle such as is commonly used between the distillation flask and water pump in vacuum distillation is a source of leakage and occupies space. It may be replaced by a closed cylindrical glass bulb clamped to the side of the bench and having four glass connexions. These lead to the pump, to the flask, to the manometer, and, as a safety release, to air. The arrangement is clean and compact. C. IRWIN.

**Differential fractional distillation.** P. M. GINNINGS (*J. Amer. Chem. Soc.*, 1930, 2420—2421).—A method of graphing results to yield a sharp maximum at the b. p. of each component is suggested. J. G. A. GRIFFITHS.

**Nomogram for reduction of gas volumes to N.T.P.** G. BARR (*J.S.C.I.*, 1930, 49, 21—23r).—Equations are given and numerical values of co-ordinates tabulated for the construction of a nomogram for the calculation of reduction factors for the volumes of dry or of moist gases. There are uniformly divided linear scales for barometric pressure and factor, and a non-uniform straight or curved scale for temperature. The factor may be read to  $\pm 0.0001$ . By the addition of an extra scale actual volume corrections may be determined, with some sacrifice both of accuracy and of simplicity.

**Was Mendeléev's system known prior to 1869?** G. ELSÉN (*Chem. Weekblad*, 1930, 27, 378—379).—A historical survey. The classification of the elements into seven groups was proposed by Cooke in 1854. H. F. GILLBE.

## Geochemistry.

**Sea-water near Puget Sound Biological Station during the summer of 1927.** T. G. THOMPSON, R. C. MILLER, G. H. HITCHINS, and S. P. TODD (*Pub. Puget Sound Biol. Sta.*, 1929, 7, 65—99). CHEMICAL ABSTRACTS.

**Chemical character of the hot springs of Arkansas and Virginia.** M. D. FOSTER (*Ind. Eng. Chem.*, 1930, 22, 632—633).—A series of analyses shows that the mineral matter in the hot springs of

Arkansas, about 200 in  $10^6$ , consists almost entirely of calcium hydrogen carbonate and silica. The water of the hot springs of Virginia contains much more sulphate and a trace of hydrogen sulphide. Seasonal changes are most evident in the cooler and shallower springs and are of concentration only. C. IRWIN.

**Radioactivity and chemical composition of some New Zealand thermal waters.** F. J. T. GRIGG and M. N. ROGERS (*New Zealand J. Sci.*



Tech., 1929, 11, 216—219).—The amounts of radium emanation in 22 samples of thermal waters varied from 0 to 3.6 mg. per million litres of water, whilst the amounts of radium in 9 samples varied from 0.0025 to 0.0300 mg. per million litres. E. HOLMES.

Iodine in the air, dew, soil, and water in Salta [Argentina]. Iodine in food in Salta. P. MAZZOCCO. Iodine content of the thyroid of sheep in Salta and at the coast. P. MAZZOCCO and C. A. ARANDA. Iodine metabolism and prophylaxis of goitre in Salta. P. MAZZOCCO (Semana méd., 1930, 37, 358—364, 364—366, 366—370, 370—373).—Air contained 0—0.0008 mg. per m.<sup>3</sup>, and dew 0—0.003 mg. per m.<sup>2</sup>. Soil of the Buenos Aires and Salta districts contains 0.0018—0.0028 and 0.14—0.67 mg. per kg., respectively. Iodine in vegetables varies from 0.005—0.085 mg. per kg., the values in non-goitrous districts being 0.016—0.115 mg. Meat contained 0.008—0.025, milk 0.025—0.035, and eggs 0.065—0.080 mg. of iodine, values for non-goitrous districts being 0.040—0.045, 0.15—0.18, and 0.20—0.22 mg., respectively. The iodine content of the sheep's fresh thyroid gland (which decreases with the weight of the gland) was: 0.019—0.049% (Salta), 0.095—0.231% (Buenos Aires), 0.115% (Santa Fé). The average daily intake of iodine per person in Salta is below 0.04 mg., and is inadequate.

#### CHEMICAL ABSTRACTS.

Physico-chemical study of the water and mud of salt lakes of the Ukraine and of the Kuban district. E. S. BURKSER (Ann. Inst. Anal. Phys. Chem., 1930, 4, 133—162).—The results of the chemical, physical, and radiological analysis of the water and mud of a number of salt lakes in the Odessa district, and in the vicinity of the Black Sea and of the Sea of Azov are given.

R. TRUSZKOWSKI.

Mud deposits of Lake Saki. S. A. SCHUKAREV, S. K. KOSMAN, and O. M. KOSMAN (Ann. Inst. Anal. Phys. Chem., 1930, 4, 163—195).—Analyses are given of sludge taken from various parts of the bottom of Lake Saki. R. TRUSZKOWSKI.

Chemical and petrographic examination of the therapeutic sludges taken from Lake Saki. P. T. IVANOV (Ann. Inst. Anal. Phys. Chem., 1930, 4, 197—206).—The composition and structure of vertical sections of Lake Saki mud deposits are not homogeneous. White strata contain chiefly gypsum and sand, with an inconsiderable admixture of carbonates and aluminosilicates, whilst black strata are composed of clay containing sand, calcite, magnesite, dolomite, gypsum, and organic debris; the entire mass of the black strata is permeated by hydrotroilite, which gives it its colour. R. TRUSZKOWSKI.

Review of work of the research laboratory of the Health Insurance Board sanatoria in Eupatoria. [Sludge of salt lakes.] A. F. SAGAI-DATSCHEI (Ann. Inst. Anal. Phys. Chem., 1930, 4, 207—216).—The composition of the sludge forming in salt lakes depends on reactions taking place between clay and salts, and varies with the concentration of the latter. The components of sludge insoluble in dilute hydrochloric acid are, together with hydrated oxides of iron and aluminium and ferrous hydro-

sulphide, responsible for its colloidal properties. The formation of fresh layers of sludge is due exclusively to fresh suspension of soil being discharged into the waters of the lake. R. TRUSZKOWSKI.

Physico-chemical properties of the Baskuntschak salt lake. A. P. NIKOLAEVSKI (Ann. Inst. Anal. Phys. Chem., 1930, 4, 217—276).—Seasonal variations in the physical constants and the chemical composition of the water of Lake Baskuntschak, and of the deposits separating from it, are recorded. R. TRUSZKOWSKI.

Chemical composition of the Solikamsk salt deposits. J. V. MORATSCHEVSKI (Ann. Inst. Anal. Phys. Chem., 1930, 4, 113—132).—The results of a detailed chemical analysis of potassium minerals from the Solikamsk deposits are given. R. TRUSZKOWSKI.

Bromine content of Solikamsk carnallites. N. N. EFREMOV and A. A. VESELOVSKI (Ann. Inst. Anal. Phys. Chem., 1930, 4, 99—112).—The bromine content of Solikamsk carnallite is little inferior to that of the Stassfurt deposits. The preparation on a technical scale of bromides presents no difficulties, and can be accomplished by using the cold method of extraction of potassium chloride. Bromides remain in the mother-liquors after crystallisation of potassium chloride, chiefly as magnesium bromide; the loss of bromides under these conditions does not exceed 5—10%. R. TRUSZKOWSKI.

Mineralogical composition of certain samples of Solikamsk salts. I. V. POIRÉ (Ann. Inst. Anal. Phys. Chem., 1930, 4, 85—98).—The three varieties of carnallite found in the Solikamsk deposits, viz., colourless, red, and opalescent yellow carnallite, differ from one another in the nature of the included oxides of iron. These are absent from colourless carnallite, are present as spherical reddish-brown granules in red carnallite, and as needles, threads, and platelets in the last-named variety. In addition to these, very finely-divided particles of iron oxide are present in all varieties of carnallite examined, with the exception of a lemon-yellow variety. The coloration of sylvite is due to the same causes as is that of carnallite. Opalescence is due to the presence of minute bubbles of gas. The deposition of sodium chloride took place before that of other salts at Solikamsk, as the sodium chloride crystals found in the layers of carnallite have rounded edges, pointing to their partial subsequent dissolution. The deposition of sodium chloride and of sylvite was in all probability simultaneous, as numerous cases of inclusions of halite in sylvite crystals and *vice versa* have been found. Anhydrite and sodium carbonate appear as well-developed crystals, often in association with clay seams and pockets. These are probably of secondary formation. Halite and sylvine crystals contain numerous rhythmically distributed inclusions; these are due to periodic rapid crystallisation occasioned by influx of fresh supersaturated solution. Solikamsk carnallite is often strongly doubly refractive, as a result of pressure to which the crystals had been subjected. R. TRUSZKOWSKI.

Order of deposition of the Solikamsk potassium salts from the point of view of the course of

**crystallisation of the quaternary system: KCl-NaCl-MgCl<sub>2</sub>-H<sub>2</sub>O.** G. G. URAZOV (Ann. Inst. Anal. Phys. Chem., 1930, 4, 41—83).—A study of the crystallisation field of sodium chloride in the quaternary system KCl-NaCl-MgCl<sub>2</sub>-H<sub>2</sub>O shows that sodium chloride crystallises out first, then sylvite, and finally carnallite. The same order is observed in the Solikamsk deposits, indicating that no secondary action has taken place since the deposition of these salts. The presence of layers of sodium chloride in the sylvite and carnallite strata is due to the influx of sodium chloride solution to the lake at some period subsequent to the formation of the main deposits, whilst the presence of sylvite above carnallite is due to redissolution of the former salt with subsequent redeposition in a different location.

R. TRUSZKOWSKI.

**Eruptive rocks of the Oberwiesenthal, Erzgebirge.** R. HERRE (Chem. Erde, 1930, 4, 632—665).—Petrographical descriptions with chemical analyses are given of phonolites and basalts from this locality in Saxony.

L. J. SPENCER.

**Formulisation of silicates.** W. KUNITZ (Chem. Erde, 1930, 4, 549—550).—A further discussion of the chemical formula of tourmaline, with comparison of the views of the author (A., 1929, 905) and of Machatschki (this vol., 315). To conform with the determination that the unit cell contains three molecules, the empirical formula may be multiplied by 3/2 or 9/4.

L. J. SPENCER.

**Iron and manganese hydroxide sols in relation to the black coating on rocks and the formation of laterite.** W. KNAUST (Chem. Erde, 1930, 4, 529—548).—Sols of the hydroxides were prepared with phosphoric acid as a peptising agent, and various experiments were made to determine the conditions for their coagulation. The bearing of these experiments on the deposition of iron and manganese oxides as a coating on rocks and on the formation of laterite is discussed.

L. J. SPENCER.

**Origin, weathering, and artificial colouring of agate.** H. HEINZ (Chem. Erde, 1930, 4, 501—525).—The different layers in agates were examined chemically, optically, and by X-rays. Analyses are given of the white weathered crust and of the fresh agates: e.g., flint from the English Chalk gave I for the inner black portion, and II for the white chalk-like crust.

	SiO <sub>2</sub> .	(Fe,Al) <sub>2</sub> O <sub>3</sub> .	(Mg,Mn)O.	CaO.	Ign.	d.
I.	97.93	0.27	0.20	0.59	1.25	2.596
II.	96.72	0.28	0.09	1.71	1.68	2.501

The portion soluble in 10% potassium hydroxide solution, taken to represent admixed opal, varies in different bands from 5.02 to 30.69%, with a corresponding range in density from 2.620 to 2.601. Artificial colouring, by soaking in sugar solution for 14 days and then in concentrated sulphuric acid, was effected in the finer-grained layers containing more opal, rather than in porous weathered layers. Banded and tubular structures, similar to those seen in agates, were obtained experimentally by the interaction of silicic acid sols and salt solutions.

L. J. SPENCER.

**Agate.** G. LINCK and H. HEINZ (Chem. Erde, 1930, 4, 526—528).—A discussion of the preceding paper. The banding of agate is attributed to the alternating action of solutions of silicic acid and of salts, the former during the dry season and the latter during the wet season of the year. L. J. SPENCER.

**Occurrence of magnetite and ilmenite in sand from the banks of the River Gallego.** I. PARRA and D. LORENZO (Anal. Fis. Quím., 1930, 28, 353—357).—Analysis of sands from 42 places on the north-west coast of Spain indicates that ilmenite is in general present to a much greater extent than is magnetite; four samples contained 81, 58, 25, and 17% of ilmenite, and 0.2, 0.1, 0.6, and 0.9% of magnetite respectively. Magnetic separation of the two minerals is easily effected, since the sands are of non-volcanic origin and are therefore free from titanomagnetite.

H. F. GILLBE.

**Mineralogical study of the soil of the Vercelli district.** E. REROSSI (Atti R. Accad. Sci. Torino, 1929, 64, 335—358; Chem. Zentr., 1930, i, 425).

**Chloritoids.** F. CORIN (Bull. Acad. roy. Belg., 1929, [v], 15, 928—931).—A stereographic projection has been constructed according to the method of Federov after an examination of a number of specimens of chloritoids.

F. G. TRYHORN.

**Geochemistry of Galician rocks.** I. P. PONDAL (Anal. Fis. Quím., 1930, 28, 488—489).—From a general study of Galician rocks it appears that the content of nickel, chromium, and vanadium is very much greater in basic rocks than in acidic rocks. The samples investigated contained V<sub>2</sub>O<sub>5</sub> 0.005—0.083%, Cr<sub>2</sub>O<sub>3</sub> 0.002—0.32%, and NiO 0.0—0.42%.

H. F. GILLBE.

**Nepheline-gneiss complex near Egan Chute, Dugannon Township, and its bearing on the origin of the nepheline syenite.** F. F. OSBORNE (Amer. J. Sci., 1930, [v], 20, 33—60).—Analyses are given of ijolites, hornblende nepheline syenite, vesuvianite, and nepheline garnet rock from the locality named.

C. W. GIBBY.

**Self-electrification of sulphide ore bodies.** A. MATSUBARA (Japan. J. Geol., 1930, 7, 59—73).—A local surface P.D. of an ore is due to difference in composition of the surrounding ground water. Natural sulphide ore converts the hydrogen ions (imparting a higher surface potential) into hydrogen sulphide ions (imparting a lower surface potential), whilst atmospheric oxidation produces the former at the expense of the latter ions. Surface potential is greater in the upper part of the ore.

CHEMICAL ABSTRACTS.

**Brazilian diamond fields.** A. P. L. BÉTIM (Bull. Soc. Franç. Min., 1929, 52, 51—55; Chem. Zentr., 1930, i, 958).—The matrix is a breccia with a siliceous agglutinant containing Al<sub>2</sub>O<sub>3</sub> 26.68—28.56, MgO 2.33—3.3, K<sub>2</sub>O 4.72—9.90, Na<sub>2</sub>O 2.54—4.75%.

A. A. ELDRIDGE.

**Constitution of mica.** VIII. J. JAKOB (Z. Krist., 1929, 72, 327—380; Chem. Zentr., 1930, i, 957—958).—To the muscovite group belong muscovite, sericite, phengite, fuchsite, lepidolite, zinnwaldite, lithionite, and polyolithionite; the members

are classified according to the ratios  $K_2O + H_2O + MgO : Al_2O_3 : SiO_2/2$ , and their structure from the units  $Al_6(SiO_3, SiO_2)_3$ ,  $Al_6K_2H_4(SiO_6, SiO_2)_3$ ,  $Al_3KH_2(SiO_4, SiO_2)_3$ ,  $Al_3KH_8(SiO_5, SiO_2)_3$ , and  $Al_3KH_{14}(SiO_6, SiO_2)_3$  is discussed. A continuous series of mixed crystals does not occur in nature.

A. A. ELDRIDGE.

**Heulandite.** P. GAUBERT (Bull. Soc. Franç. Min., 1929, 52, 14—42; Chem. Zentr., 1930, i, 958).

**Fusion of algodonite and whitneyite.** F. MACHATSCHKI (Zentr. Min. Geol., 1929, A, 371—373; Chem. Zentr., 1930, i, 957).—X-Ray studies support Borgström's view (Geol. För. Forh., 38, 96) that copper and the compound  $Cu_3As$  are formed.

A. A. ELDRIDGE.

**Essential constituent of Japanese acid clay and a theory of its reactions.** N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1930, 33, 92—95B).

—The essential constituent of the Japanese acid clay crystal is regarded as being an aluminosilicic acid of the probable formula  $Al_2O_3 \cdot 6SiO_2 \cdot H_2O$ . By assuming a face-centred cubic arrangement of the oxygen atoms, calculations based on the density indicate a relatively loose packing of the oxygen atoms, which is consistent with the observed refractive index of the material. The acidity of the clay is ascribed to the valencies of the surface atoms not being completely saturated, so that the surface hydrogen atoms are readily replaced. Interaction of the clay with a neutral salt solution primarily liberates free acid, but this in turn removes aluminium atoms from the surface of the clay and yields a solution which although containing no free acid has an acid reaction on account of hydrolysis of the aluminium salt. The restricted action of the acid on the clay is due to

an initial removal of the surface aluminium atoms which leaves a surface containing only silicic acid. The marked adsorptive power of the clay is ascribed to its polar properties, and calculations of the ultimate particle size for the adsorption of indophenol, regarding the latter as a monoacid base, yield results in good agreement with those obtained by direct measurement. Combined water is expelled at about 500° and at a temperature between 500° and 600° the power of reversibly adsorbing water is lost, and the X-ray diagram alters.

H. F. GILLBE.

**Graphite from Koschary-Alexandrov.** N. S. LAVROVITSCH (Min. Syrje Zwetnyje Met., 1929, 4, 57—68; Chem. Zentr., 1930, i, 661).—Analyses of two samples are recorded.

A. A. ELDRIDGE.

**Graphite from Troitzkoje.** I. A. SCHAPIRO (Min. Syrje Zwetnyje Met., 1929, 4, 69—84; Chem. Zentr., 1930, i, 661).—An analysis is given.

A. A. ELDRIDGE.

[Lignin theory of the origin of coal.] H. BODE, also R. LIESKE (Brennstoff-Chem., 1930, 11, 160—163; cf. this vol., 570).—Polemical.

A. B. MANNING.

**Soils derived from the glacial boulder-marl in the Hamburg district.** E. SCHMIDT (Chem. Erde, 1930, 4, 475—500).—Determinations of the amount of calcium carbonate, of the size of particles, and of the heavy minerals present in the boulder-clay and the overlying soils are recorded.

L. J. SPENCER.

**Soils of Anatolia and eastern Thrace.** F. GIESECKE (Chem. Erde, 1930, 4, 551—597).—A description of the various types of soils, with partial mechanical and chemical analyses. A soil map of Anatolia is given.

L. J. SPENCER.

## Organic Chemistry.

**Polymerisation. XIII. Depolymerisation of the polymeric forms of isobutylene.** S. V. LEBEDEV and G. G. KOBLIANSKI (Ber., 1930, 63, [B], 1432—1441; cf. this vol., 316).—Insight into the mechanism of the polymerisation of isobutylene is sought by an examination of the reverse process, since the change is regarded as balanced. The individual polymeride is either heated with floridin in a distillation flask or, preferably, is passed over the catalyst heated at 200° in a glass tube. The pentameride decomposes into tri- and di-meride, the tetrameride into 2 mols. of dimeride, the trimeride into di- and mono-meride, and the dimeride into 2 mols. of isobutylene. In all cases some monomeric isobutylene is produced, attributed in the cases of the tetra- and penta-merides to progressive dissociation of the initial di- and tri-meric forms. The study of the decomposition of the hexa- and hepta-merides has been prevented by lack of material, but a higher fraction (mean mol. wt. 840) is found to yield triisobutylene in more than 30% yield.

Prolonged contact of the polymeric forms with floridin at a high temperature causes the production of stable forms of high mol. wt. Diisobutylene is the most stable polymeric variety. With increasing

mol. wt. the stability rapidly decreases. Depolymerisation of individual polymeric varieties or of the crude polymerised product is recommended as a preparative process for diisobutylene.

H. WREN.

**Oxidation of "diisobutene" by ozone.** R. J. McCUBBIN and H. ADKINS (J. Amer. Chem. Soc., 1930, 52, 2547—2550).—Treatment of "diisobutene" (Edgar, Ind. Eng. Chem., 1927, 19, 746) with ozonised oxygen in acetic acid containing about 1% of acetic anhydride, and subsequent decomposition of the ozonide by the addition of water and zinc dust, affords acetone (1 part), trimethylacetaldehyde (1 part), and methyl *tert.*-butylmethyl ketone (3·7 parts) [semicarbazone, m. p. 176° (corr.)]. The original hydrocarbon mixture contains  $\beta\delta\delta$ -trimethyl- $\Delta^2$ - and - $\Delta^3$ -pentenes, the former predominating.

H. BURTON.

**Periodicity.** P. PETRENKO-KRITSCHENKO (J. pr. Chem., 1930, [ii], 126, 287—295).—A summary and theoretical discussion of results previously published (A., 1929, 537).

J. W. BAKER.

**Trichloromethyl perchlorate.** L. BIRCKENBACH and J. GOUBEAU (Naturwiss., 1930, 18, 530).—In presence of a little hydrogen chloride, carbon

tetrachloride reacts with silver perchlorate at the ordinary temperature, yielding trichloromethyl perchlorate,  $\text{CCl}_3\text{ClO}_4$ , in 60–70% yield. By repeated fractionation in a vacuum in absence of moisture this can be obtained as a colourless liquid which solidifies at about  $-55^\circ$  to colourless crystals. With water it yields perchloric acid and liberates iodine with iodides. With alcohol and other organic substances, e.g., tap grease, it reacts at the ordinary temperature with detonation. When heated it explodes, liberating chlorine. J. W. SMITH.

**Preparation of *s*-bromiodoethylene.** H. VAN DE WALLE and V. DE LANDSBERG (Bull. Acad. Roy. Belg., 1930, [v], 16, 369–393; cf. A., 1926, 496).—The preparation of *s*-bromiodoethylene by the action of acetylene on a mixture of bromine and iodine in aqueous, hydrochloric acid, alcoholic, and chloroform solution, and isolation of the product by simple fractionation or by distillation with *n*-butyl alcohol, has been investigated in detail. When a mixture of bromine (75%) and iodine (25%) under water is used the products are bromiodoethylene 24%, diiodoethylene 1%, and tetrabromoethane 36%, which are obtained by distillation with *n*-butyl alcohol, the following azeotropic mixtures being produced: *n*-butyl alcohol with *n*-butyl bromide (87.2%), b. p.  $98.0^\circ$ ,  $d_4^{20}$  1.1881, and with *n*-butyl iodide (59.0%), b. p.  $113.8^\circ$ ,  $d_4^{20}$  1.1343, and the ternary mixture *n*-butyl alcohol–*n*-butyl butyrate (15%)–*s*-bromiodoethylene (22.1%), b. p.  $116.9^\circ$ ,  $d_4^{20}$  0.9522. Removal of the alcohol with water and distillation of the residue affords an azeotropic mixture of *s*-bromiodoethylene (55.5%) with *n*-butyl butyrate, b. p.  $141.0^\circ/748$  mm.,  $d_4^{20}$  1.2822, from which the ethylene derivative cannot be separated. Direct distillation of the original crude reaction product causes decomposition of the tetrabromoethane into di- and tri-bromoethylenes with liberation of hydrogen bromide and bromine which displaces iodine from the bromiodoethylene originally present. Direct fractional distillation of the product obtained by the action of acetylene on an equimolecular mixture of bromine and iodine in concentrated hydrochloric acid solution affords only 15% of *s*-bromiodoethylene, but distillation with *n*-butyl alcohol affords chlorobromo-2.8%, dibromo-4.7%, chloriodo-27.3% (azeotropic mixture with 25% of *n*-butyl alcohol, b. p.  $108.5$ – $108.8^\circ$ ,  $d_4^{20}$  1.534), bromiodo-38.8% (azeotropic mixture with 68% of *n*-butyl alcohol, b. p.  $117.2$ – $117.4^\circ$ ,  $d_4^{20}$  1.043) and diiodo-11% ethylene. When the reaction is carried out in ethyl alcohol or chloroform solution and, after evaporation of the solvent, the crude product is separated from *s*-diiodoethylene (50%) by steam-distillation, 38 and 27%, respectively, of *s*-bromiodoethylene may be obtained by distillation. In all cases only one stereoisomeride (probably *cis*) of *s*-bromiodoethylene, b. p.  $149$ – $149.1^\circ$ , m. p.  $16.55^\circ \pm 0.05^\circ$ ,  $d_4^{20}$   $2.6396 \pm 0.0004$ ,  $n_D^{20}$  1.63259,  $\epsilon$  3.09 (Errata), azeotropic mixtures (in addition to those above) with 59.5% of acetic acid, b. p.  $115.6^\circ$ , and with 34.8% of propionic acid, b. p.  $135.3^\circ$ , is obtained and all attempts to isomerise it were unsuccessful. It is unstable in light, whilst bromine converts it into *s*-dibromoethylene in 80% yield. J. W. BAKER.

**Ethyl alcohol, a product of high-pressure synthesis.** G. T. MORGAN and R. TAYLOR (Nature, 1930, 125, 889).—Ethyl alcohol has been synthesised from carbon monoxide and hydrogen.

L. S. THEOBALD.

**[Preparation of] heptan- $\beta$ -ol.** F. C. WHITMORE and T. OTTERBACHER (Organic Syntheses, 1930, 10, 60–61).

**Composition and acidity of glycol-boric acids.** J. BÖESEKEN, N. VERMAAS, and A. T. KÜCHLIN (Rec. trav. chim., 1930, 49, 711–716).—The acid complexes formed between boric acid and glycols are shown by methods not involving their separation from solution to have the composition  $\text{HBD}_2$ , D representing the diol residue (cf. Hermans, A., 1925, i, 500; Böeseken and others, A., 1925, i, 911; 1927, 132). The first method is based on hydrogen-ion determinations on aqueous solutions of boric acid and diol in various proportions, consideration of the equilibria involved giving a relation  $-\Delta p_H = (n/2) \log a$ , connecting the difference of  $p_H$  of two solutions and the ratio,  $a$ , of the amounts of diol present in each,  $n$  being the number of molecules of diol combining with 1 mol. of boric acid. The second method involves a consideration of the partition of hydroxyl ions between the acid complex and free boric acid during neutralisation, and the third is a cryoscopic method.

The structure and mode of ionisation of these complexes are shown by the general formula

$$\left[ \begin{array}{c} \text{:}\ddot{\text{O}}\text{:} > \text{B} < \text{O} < \ddot{\text{O}}\text{:} \\ \text{:}\ddot{\text{O}}\text{:} > \text{B} < \text{O} < \ddot{\text{O}}\text{:} \end{array} \right]^- \text{H}^+.$$

R. CHILD.

**Colour reaction of glycerol with alkali thiosulphates.** D. GANASSINI (Arch. Ist. Biochim. Ital., 1930, 2, 239–242).—Most of the colour reactions of glycerol are due to its products of oxidation or dehydration. Of these, acetaldehyde, which is formed by heating with potassium hydrogen sulphate (or boric or phosphoric anhydride) either glycerol or its derivatives, may be identified by spontaneous conversion of its phenylhydrazone into phenylpyrazoline, this giving an intense violet coloration in presence of oxidising agents in acid solution. Powdered sodium thiosulphate dissolves in very concentrated glycerol solution, with slight heating, to a colourless solution, which becomes sky-blue and then deep indigo when heated to boiling. This reaction is not given by carbohydrates in general, but a much less intense coloration is obtained with the polyhydric alcohols. To separate glycerol from organic liquids and tissues, the material is mixed with water and filtered, the filtrate being treated with a slight excess of basic lead acetate and filtered. After removal of the lead as sulphide, the liquid is evaporated to dryness with milk of lime, the residue being extracted with a mixture of 95% alcohol (2 parts) and ether (1 part) and the solution evaporated to a syrup, to which the above test is applied. To extract glycerol present as glycerides, glycerophosphate, or lecithin, the material must be first hydrolysed with sodium hydroxide. The coloration given with thiosulphate appears to be due to the transitory formation of the unstable blue modification of sulphur. The test may be used also for the detection of thiosulphate. T. H. POPE.

**Action of chromium halides on ethyl ether and complex derivatives of chromium dihalide alkoxides.** F. HEIN [with H. FARL and H. BÄR] (Ber., 1930, 63, [B], 1418—1429).—Technical chromium trichloride is somewhat soluble or completely insoluble in anhydrous ether in which the purified product does not dissolve. Solubility is due to the presence of chromous chloride as established by the behaviour of the products prepared by partial chlorination of chromium or incomplete reduction of chromic chloride. Chromous chloride gives brownish-violet to olive-green solutions in ether. The ratio Cr:Cl in the solutions is 1:2, but the extracts have no reducing power and do not evolve hydrogen when treated with hydrochloric acid and palladium chloride. The behaviour towards iodine and permanganate establishes the absence of the chromous ion. The composition of the product cannot be ascertained by direct analysis, but examination of its complex derivatives (see later) establishes the presence of the substance  $\text{CrCl}_2 \cdot \text{OEt}$ . The mode of formation has not been definitely ascertained. The ethereal solutions are non-conductors of electricity and hence the halogen atoms are in direct, non-ionic union, as shown also by the formation of chromium phenyl compounds with magnesium phenyl bromide. Mixtures of chromous and chromic bromide and homogeneous chromous bromide give coloured solutions in ether which contain mainly the *dibromide ethoxide*. Chromium iodide mixtures yield brown extracts containing the substance  $\text{CrI}_2 \cdot \text{OEt}$  in addition to iodine and other chromium compounds. Dioxan and benzyl ethyl ether behave similarly to diethyl ether, whereas anisole and phenetole are indifferent.

Treatment of an ethereal solution of chromium dichloride ethoxide with ammonia yields the substance,  $\text{CrCl}_2 \cdot \text{OEt} \cdot 3\text{NH}_3$ , which retains ether and dissolves in water when freshly prepared. It is slowly transformed in cold solution into chromium hydroxide. When heated in an atmosphere of nitrogen, the salt decomposes according to the scheme:  $\text{CrCl}_2 \cdot \text{OEt} \cdot 3\text{NH}_3 \rightarrow \text{CrOCl} + 2\text{NH}_3 + \text{NH}_4\text{Cl} + \text{C}_2\text{H}_4$ . The corresponding *bromide*,  $\text{CrBr}_2 \cdot \text{OEt} \cdot 3\text{NH}_3 \cdot 0.5\text{Et}_2\text{O}$ , and *iodide*,  $\text{CrI}_2 \cdot \text{OEt} \cdot 3\text{NH}_3$ , are described. With aniline the following substances are prepared:

$(\text{CrCl}_2 \cdot \text{OEt} \cdot \text{PhNH}_2)_2$ ;  $\text{CrCl}_2 \cdot \text{OEt} \cdot 2\text{PhNH}_2$ ;

$\text{CrBr}_2 \cdot \text{OEt} \cdot \text{PhNH}_2$ ;  $\text{CrBr}_2 \cdot \text{OEt} \cdot 2\text{PhNH}_2$ ;

$\text{CrI}_2 \cdot \text{OEt} \cdot 2\text{PhNH}_2 \cdot 0.5\text{Et}_2\text{O}$ . They are distinguished by their stability and solubility in water. Pyridine and piperidine yield the compounds,  $\text{CrCl}_2 \cdot \text{OEt} \cdot 2\text{C}_5\text{H}_5\text{N}$  and  $\text{CrCl}_2 \cdot \text{OEt} \cdot 2\text{C}_5\text{H}_{11}\text{N}$ . H. WREN.

**Cyclic acetals.** J. D. VAN ROON (Rec. trav. chim., 1930, 49, 662—664).—Polemical. The author's results on the isomeric ethylideneglycerols (A., 1929, 291) are amplified and compared with those of Hill, Hill, and Hibbert (A., 1928, 1114, 1213). Priority for the idea of the formation of isomeric cyclic acetals is claimed for Böeseken and his co-workers.

R. CHILD.

**Esters of chlorinated alcohols. II.** V. V. NEKRASSOV and N. N. MELNIKOV (J. Russ. Phys. Chem. Soc., 1930, 62, 631—642).—Trichloromethyl chloroformate reacts with methyl alcohol to yield methyl trichloromethyl carbonate, and with ethyl

and *isoamyl* alcohols to yield respectively the corresponding *ethyl* ester, b. p.  $78^\circ/19$  mm.,  $d_4^{20}$  1.4205, and the *isoamyl* ester, b. p.  $120^\circ/23$  mm.,  $d_4^{20}$  1.2644. The above carbonates when heated yield carbonyl chloride and the corresponding alkyl chloroformate; in the presence of excess of alcohol they give a mixture of dialkyl carbonate and alkylformate. With aniline they yield diphenylcarbamide, hydrogen chloride, alkyl chloroformate, and *N*-methyl, ethyl, or *isoamyl phenylurethane*, m. p.  $55$ — $56^\circ$ , b. p.  $174^\circ/17$  mm. In all cases the reactivity of the esters rises with the mol. wt. of the alkyl radical. Sodium phenoxide reacts with methyl trichloromethyl carbonate to yield diphenyl carbonate and phenyl methyl carbonate, and with trichloromethyl chloroformate to yield phenyl trichloromethyl carbonate, m. p.  $70.5^\circ$ ; this, on heating, yields diphenylcarbamide and phenyl chloroformate. With *isoamyl* alcohol, di*isoamyl* carbonate and phenyl *isoamyl* carbonate are obtained; with aniline or sodium phenoxide the products are respectively diphenylcarbamide and *N*-phenylphenylurethane, and diphenyl carbonate. The products of reaction of trichloromethyl carbonate with *isoamyl* alcohol are *isoamyl* chloroformate and *isoamyl* trichloromethyl carbonate, whilst with aniline the only product isolated is diphenylcarbamide. With sodium phenoxide diphenyl carbonate is produced.

R. TRUSZKOWSKI.

**Lower trialkyl orthophosphates. I.** D. P. EVANS, W. C. DAVIES, and W. J. JONES (J.C.S., 1930, 1310—1313).—*Tri-n-butyl*, b. p.  $289^\circ/760$  mm.,  $d_4^{25}$  0.9727,  $n_D^{25}$  1.4224, and *tri-n-amyl orthophosphates*, b. p.  $225^\circ/50$  mm.,  $d_4^{25}$  0.9497,  $n_D^{25}$  1.4283, were prepared by the action of phosphoryl chloride on the sodium alkoxides. New determinations of the b. p. at 50, 100, 150, 150, and 760 mm.,  $d_4^{25}$ ,  $d_4^{40}$ , and  $n_D^{25}$  for the *F*, *D*, and *C* lines are recorded for methyl (b. p.  $196^\circ/760$  mm.,  $d_4^{25}$  1.2052,  $n_D^{25}$  1.3950), ethyl (b. p.  $215^\circ/760$  mm.,  $d_4^{25}$  1.0637,  $n_D^{25}$  1.4039), *n*-propyl (b. p.  $252^\circ/760$  mm.,  $d_4^{25}$  1.0023,  $n_D^{25}$  1.4136), *n*-butyl (b. p.  $289^\circ/760$  mm.,  $d_4^{25}$  0.9727,  $n_D^{25}$  1.4224), *isobutyl* (b. p.  $264^\circ/760$  mm.,  $d_4^{25}$  0.9617,  $n_D^{25}$  1.4173), and *tri-n-amyl* orthophosphates. The b. p. at different pressures of the series of esters may be calculated from the equation  $a - \log p = b/(t + 273)$ . A mean value of 10.902 is derived for the molecular refractivity of " $[\nu_L]_D$ " of the  $\text{PO}_4$  group. H. A. PIGGOTT.

**Hydrolysis of sulphuric acid esters.** K. H. BAUER and W. POETHKE (J. pr. Chem., 1930, [ii], 126, 296—303).—The hydrolysis of sodium ethyl, amyl, and octadecyl sulphates with boiling *N*-hydrochloric or *N*-sulphuric acid has been studied quantitatively under varied conditions of concentration and time of heating. With either acid, hydrolysis is ultimately complete, although the velocity of hydrolysis with hydrochloric acid is approximately twice that with sulphuric acid, the mean values of the velocity coefficient  $10^3k$  for hydrolysis of the first two esters with these acids being 630 and 333, and 285 and 141, respectively. Under comparable conditions the velocity of hydrolysis of sodium amyl sulphate is only 75% of that of the ethyl compound, whilst that of sodium octadecyl sulphate is 2.8—3.9 times as great and the process is complete

after heating over a free flame for 1 hr. These results suggest that Herbig's observations (Lehnes, *Färber-Ztg.*, 1912, 91) concerning the incomplete hydrolysis of organically bound sulphuric acid in Turkey-red oils are incorrect (cf. Bauer, B., 1928, 273, 935).

J. W. BAKER.

**Complexes of mercuric iodide with alkylsulphonium iodides.** P. C. RAY and N. ADHIKARY (J. Indian Chem. Soc., 1930, 7, 297—303).—Treatment of an equimolecular mixtures of methyl sulphide and mercuric iodide with an excess of methyl iodide in cold acetone gives the compound  $\text{Me}_3\text{S}\cdot\text{HgI}_3$ , m. p. 163°, also formed from molecular proportions of trimethylsulphonium and mercuric iodides. The same compound is also produced by heating a mixture of methyl sulphide (1 mol.); mercuric iodide (1 mol.), and an excess of methyl iodide. When dimethyl disulphide (2 mols.) or dimethyl trisulphide (1 mol.) is heated with mercuric iodide (1 mol.) and methyl iodide, the substance  $[\text{Me}_2\text{S}]_2\text{HgI}_4$ , m. p. 189°, is formed. The same substance also results from 2 mols. of trimethylsulphonium iodide and 1 mol. of mercuric iodide. Ethyl sulphide, mercuric and ethyl iodides afford the compound (I),  $[\text{Et}_2\text{S}]\text{HgI}_3$ , m. p. 110°, whilst with diethyl disulphide a mixture of this and the complex  $[\text{Et}_2\text{S}]_2\text{HgI}_4$ , m. p. 148°, results. The last-named substance is also formed from diethyl trisulphide. The molar conductivity of I in acetone at 25.6° increases with dilution, and is of the same order as that of potassium mercuric iodide. The conductivity of methylethylphenacylthetine mercuric iodide, m. p. 129° (Pope and Neville, J.C.S., 1902, 81, 1560), in acetone at 18.4° is of the same order as that of potassium iodide.

H. BURTON.

**Preparation of monochloroacetic acid; hydrolysis of trichloroethylene.** C. TORRES and L. SOCIAS (Anal. Fis. Quim., 1930, 28, 490—494).—An apparatus is described whereby an 80% yield of monochloroacetic acid may be obtained by passing the vapour of trichloroethylene into 90% sulphuric acid at 185—200°.

H. F. GILLBE.

**Preparation and bactericidal properties of certain penta-, hepta-, and nona-decoic acids.**

**XIX.** C. M. GREER and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 2540—2543).—The following ethyl di-*n*-alkylmalonates are described: *methyldeacyl*, b. p. 161—164°/1.5—2.5 mm.,  $d_4^{20}$  0.9217,  $n_D^{20}$  1.4412; *ethylundecyl*, b. p. 150—154°/0.2—1 mm.,  $d_4^{20}$  0.9262,  $n_D^{20}$  1.4420; *propyldecyl*, b. p. 143—148°/0.1—1 mm.,  $d_4^{20}$  0.9256,  $n_D^{20}$  1.4416; *butylnonyl*, b. p. 143—147°/0.1—1 mm.,  $d_4^{20}$  0.9241,  $n_D^{20}$  1.4420; *amylloctyl*, b. p. 142—146°/0.1—1 mm.; *hexylheptyl*, b. p. 146—152°/0.1—1 mm.,  $d_4^{20}$  0.9231,  $n_D^{20}$  1.4412; *methyltetradecyl*, b. p. 172—176°/0.5—1 mm.,  $d_4^{20}$  0.9164,  $n_D^{20}$  1.4436; *ethyltridecyl*, b. p. 178—181°/0.8—2 mm.,  $d_4^{20}$  0.9207,  $n_D^{20}$  1.4435; *propyldodecyl*, b. p. 173—177°/0.5—1 mm.,  $d_4^{20}$  0.9191,  $n_D^{20}$  1.4438; *butylundecyl*, b. p. 171—176°/0.5—1 mm.,  $d_4^{20}$  0.9173,  $n_D^{20}$  1.4439; *amyldecyl*, b. p. 148—154°/0.1—0.8 mm.; *hexylnonyl*, b. p. 170—174°/0.5—1.5 mm.,  $d_4^{20}$  0.9178,  $n_D^{20}$  1.4441; *heptyloctyl*, b. p. 157—161°/0.2—1 mm.,  $d_4^{20}$  0.9171,  $n_D^{20}$  1.4436; *propyltetradecyl*, b. p. 180—184°/0.2—1 mm.,  $d_4^{20}$  0.9141,  $n_D^{20}$  1.4459; *amyldeacyl*, b. p. 178—181°/0.2—1 mm.,  $d_4^{20}$  0.9112,  $n_D^{20}$  1.4460; *heptyldecyl*, b. p.

182—186°/0.2—1 mm.,  $d_4^{20}$  0.9116,  $n_D^{20}$  1.4459. These are converted by the usual method into  $\alpha$ -alkyl-*n*-fatty acids, the following being described:  $\alpha$ -methyltetradecoic, b. p. 172—175°/2—3 mm., m. p. 34—36°;  $\alpha$ -ethyltridecoic, b. p. 160—163°/2—3 mm.,  $d_4^{20}$  0.8821,  $n_D^{20}$  1.4455;  $\alpha$ -propyldodecoic, b. p. 164—167°/2—3 mm.,  $d_4^{20}$  0.8819,  $n_D^{20}$  1.4450;  $\alpha$ -butylundecoic, b. p. 159—162°/2—3 mm.,  $d_4^{20}$  0.8824,  $n_D^{20}$  1.4459;  $\alpha$ -amyldecoic, b. p. 161—164°/2—3 mm.;  $\alpha$ -hexylnonoic, b. p. 156—159°/1—2 mm.,  $d_4^{20}$  0.8806,  $n_D^{20}$  1.4450;  $\alpha$ -methylhexadecoic, b. p. 174—177°/1—2 mm., m. p. 45.5—47.5° (lit. 54°);  $\alpha$ -ethylpentadecoic, b. p. 164—168°/1—2 mm.,  $d_4^{20}$  0.8810,  $n_D^{20}$  1.4480;  $\alpha$ -propyltetradecoic, b. p. 183—187°/2.5—3.5 mm.,  $d_4^{20}$  0.8827,  $n_D^{20}$  1.4483;  $\alpha$ -butyltridecoic, b. p. 174—177°/2—3 mm.,  $d_4^{20}$  0.8783,  $n_D^{20}$  1.4484;  $\alpha$ -amyldecoic, b. p. 177—182°/2—3 mm.;  $\alpha$ -hexylundecoic, b. p. 182—185°/2—3 mm.,  $d_4^{20}$  0.8821,  $n_D^{20}$  1.4489;  $\alpha$ -heptyldecoic, b. p. 184—187°/2—3 mm.,  $d_4^{20}$  0.8780,  $n_D^{20}$  1.4483;  $\alpha$ -propylhexadecoic, b. p. 182—185°/0.5—1.5 mm., m. p. 35—37°;  $\alpha$ -amyltetradecoic, b. p. 184—188°/0.5—1.5 mm.,  $d_4^{20}$  0.8752,  $n_D^{20}$  1.4508;  $\alpha$ -heptyldecoic, b. p. 180—184°/0.5—1.5 mm., m. p. 31.5—33.5°. The  $\text{C}_{15}$  and  $\text{C}_{17}$  acids possess some bactericidal action towards *B. lepræ*, but they are not so active as the  $\text{C}_{16}$  acids (this vol., 741, 772). The acids containing 19 carbon atoms have only a very slight action.

H. BURTON.

**Quantitative oxidation of double linkings in oils and fats by peracetic acid; a new method for determining degree of unsaturation.** W. C. SMITH (Rec. trav. chim., 1930, 49, 691—696; cf. A., 1929, 910).—To 5 c.c. of peracetic acid solution (see below) is added such an amount of the substance under examination that the excess of oxidising agent is about 100% and the mixture is kept at the ordinary temperature for 20 hrs.; excess of potassium iodide and 4*N*-sulphuric acid are added and after shaking for an hour the solution is titrated with 0.1*N*-thiosulphate. A blank determination is carried out in the same manner. The reagent is prepared by adding gradually 4.5 parts of acetic anhydride containing 1% of sulphuric acid, at 0°, to 1 part of 30% hydrogen peroxide, the temperature being kept below 10°. Only small amounts of hydrogen peroxide and diacetyl peroxide are present in the solution so prepared, which contains 2—3 equivalents of oxygen; it is diluted with glacial acetic acid to about normality.

Results given for oleic acid and for linoleic acid and its ethyl ester, as well as for some natural oils, are in agreement with the Wijs iodine values; the method gives more concordant results than the perbenzoic acid method of Nametkin and Abakumovski (B., 1927, 179).

R. CHILD.

**Action of peracids on linoleic acids and on some other unsaturated fatty acids. Influence of composition and configuration of isomeric unsaturated fatty acids on the rate of oxidation by peracetic acid.** W. C. SMITH (Rec. trav. chim., 1930, 49, 675—685, 686—691).—See A., 1929, 910.

**Preparation of the thiocyanates of the unsaturated fatty acids.** D. HOLDE (Chem. Umschau, 1930, 37, 173—174).—*Linoleic acid dithiocyanate*, a viscous pale yellow oil, and *erucic thiocyanate*, a viscous yellow oil setting at -4° to a salve-like solid,



are described. Elaidic thiocyanate, m. p. 79—79.5°, and brassidic thiocyanate, m. p. 57—57.5° (cf. Kaufmann, this vol., 741; Kimura, B., 1930, 429), were prepared. A nitrogen (Kjeldahl) determination is a desirable check on the sulphur determination in the analysis of these products. E. LEWKOWITSCH.

**Salt formation of ethyl acetoacetate and of acetylacetone.** A. HANTZSCH and W. KRÖBER (Z. physikal. Chem., 1930, 147, 293—301).—The formula  $\text{COMe}\cdot\text{CH}\cdot\text{C}(\text{ONa})\cdot\text{OEt}$  for sodium acetoacetate and the existence of dienol salts with the group  $\cdot\text{C}(\text{ONa})\cdot\text{C}(\text{ONa})\cdot$  proposed by Grossmann (A., 1924, i, 834) are considered to be incorrect. Titration of alkaline solutions of ethyl acetoacetate and of acetylacetone with bromine solutions shows that the excess of bromine taken up by the enolic compound varies with the concentration of the bromine solution and is due to secondary reactions. Measurements of the amount of hydrogen liberated by the action of acetylacetone and of benzoylacetone on sodium or potassium suspended in benzene or xylene show that only one atom of the alkali metal is taken up by the enol. O. J. WALKER.

**Preparation of anhydrous oxalic acid.** E. I. JOHNSON and J. R. PARTINGTON (J.C.S., 1930, 1510—1511; cf. Adams, "Organic Syntheses," 1921, 1, 67).—The hydrated acid is distilled with excess of toluene until all water is expelled, and the product removed from the residual liquid by filtration and kept over wax in a vacuum desiccator for 12 hrs.

H. A. PIGGOTT.

**Action of dilute mineral acids on uronic acids.** K. P. LINK and C. NIEMANN (J. Amer. Chem. Soc., 1930, 52, 2474—2480).—*d*-Glycuronic and *d*-galacturonic acids are partly decarboxylated by heating with 2% hydrochloric or 2.5% (or *N*) sulphuric acid at 135—140°. This decarboxylation accounts for the poor yields of uronic acids isolated from natural sources such as gum arabic. The products formed during decarboxylation are furfuraldehyde and an unidentified furan derivative. The method commonly used for the determination of pectin and hemicellulose is shown to be inaccurate by the above observations.

H. BURTON.

**Synthesis of  $\alpha$ -ketoerythronic acid.** A. T. KÜCHLIN (Rec. trav. chim., 1930, 49, 705—710).—Ethyl  $\alpha$ -hydroxy- $\Delta^2$ -butenoate (van der Sleen, A., 1901, i, 499) is converted by addition of bromine into ethyl  $\beta$ -dibromo- $\alpha$ -hydroxybutyrate, which on oxidation by means of dichromate yields ethyl  $\beta$ -dibromo- $\alpha$ -ketobutyrate, a colourless oil (phenylhydrazine and other reagents eliminate hydrogen bromide). Treatment of the latter with barium carbonate, followed by hydrolysis with barium hydroxide, affords barium  $\alpha$ -keto- $\beta$ -dihydroxybutyrate (+1.5H<sub>2</sub>O), from which an impure phenylhydrazone and osazone have been prepared.

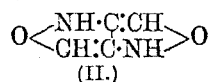
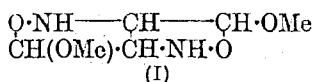
R. CHILD.

**Dissociation constants of alkylthiolacetic acids.** E. LARSSON (Ber., 1930, 63, [B], 1347—1352).—The action of sodium hydroxide and the necessary alkyl halide on thiolacetic acid affords methylthiolacetic, b. p. 130—131°/27 mm.,  $d_{20}^{25}$  1.223,  $n_D^{25}$  1.495, *n*-propylthiolacetic, b. p. 132°/15 mm.,  $d_{20}^{25}$  1.109,  $n_D^{25}$  1.483, iso-

propylthiolacetic, b. p. 128°/13 mm., *n*-butylthiolacetic, b. p. 153°/20 mm., and benzylthiolacetic, b. p. 204°/20 mm., m. p. 64°, acids. Triphenylmethylthiolacetic acid, m. p. 162°, is obtained from triphenylcarbinol and thiolacetic acid at 110°. The dissociation constants ( $\times 10^4$ ) of the acids  $\text{OR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  and  $\text{SR}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  at 25° are as follows: R=H, 1.52, 2.14; R=Me, 2.94, 1.92; R=Et, 2.50, 1.83; R=Pr, 2.21, 1.68; R=Pr <sup>$\beta$</sup> , —, 1.9; R=Bu <sup>$\alpha$</sup> , 2.19, 1.54; R=Ph, 7.6, 3.0; R=CH<sub>2</sub>Ph, —, 1.87; R=CPh<sub>3</sub>, —, 0.5.

H. WREN.

**Derivatives of asparaginedialdehyde.** I. A. WOHL and E. BERNREUTHER (Annalen, 1930, 481, 1—29).—*Acetylenedialdehyde tetramethylacetal*, b. p. 97.5°/11 mm.,  $d_4^{20}$  1.0328,  $n_D^{20}$  1.43447 (from methyl orthoformate and dimagnesium acetylene dibromide; cf. A., 1912, i, 162), like the tetraethylacetal, could not be caused to react with ammonia or phenylhydrazine (cf. A., 1921, i, 304), but combines with hydroxylamine to form *oximinosuccindialdehyde tetramethylacetal*, b. p. 102—108°/0.02 mm., which forms a *methyl ether*, b. p. 65—67°/0.02 mm., does not reduce ammoniacal silver or Fehling's solution, and could not be reduced to the aminoacetal. A compound, C<sub>6</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub> (? I), m. p. 137.5°, is formed as a by-product in the above reaction with hydroxylamine, and on treatment with concentrated hydrochloric acid is converted into a compound, C<sub>4</sub>H<sub>4</sub>O<sub>2</sub>N<sub>2</sub> (? II), m. p. 151°.



Catalytic reduction of the above acetylenic acetal affords *maleindialdehyde tetramethylacetal*, b. p. 78°/10 mm.,  $d_4^{20}$  1.0047,  $n_D^{20}$  1.42817 (the free aldehyde, not isolated, readily yields pyridazine on treatment with hydrazine hydrate). The latter adds hydrogen bromide (excess over one mol. being removed by means of methyl orthoformate) to give bromosuccindialdehyde tetramethylacetal, not purified, but used directly for the following condensations: heated under pressure with excess of methyl-alcoholic ammonia it yields *asparaginedialdehyde tetramethylacetal* (III), b. p. 108—110°/10 mm., purified through the oxalate [chloroplatinate, m. p. 150.5° (decomp.)], methylation of which with methyl iodide followed by treatment with silver chloride affords the quaternary chloride of *trimethylasparaginedialdehyde tetramethylacetal* (IV), very hygroscopic, m. p. 125° (corresponding chloroplatinate, m. p. 148—150°); similar condensation with piperidine converts the bromoacetal into *piperidinosuccindialdehyde tetramethylacetal* (V), b. p. 144—145°/14 mm.; trimethylamine and dimethylamine, however, remove hydrogen bromide with re-formation of the maleinacetal.

Attempts were made to convert the foregoing acetals into the corresponding aldehydes. Treatment of III with concentrated hydrochloric acid at 0° gives a solution of the hydrochloride of asparaginedialdehyde, which could not be crystallised nor could a dioxime or a disemicarbazone be prepared; *asparaginedialdehydebis-p-nitrophenylhydrazone hydrochloride* (+1H<sub>2</sub>O), decomp. 240—242° after darkening. A solution of the free aldehyde is unstable and after a few hours deposits a brownish-yellow condensation

product. From V is similarly obtained *piperidino-succindialdehydebis-p-nitrophenylhydrazone hydrochloride* (chloroplatinate, m. p. 168—170°, decomp.). When hydrolysed IV readily loses trimethylamine and is converted into maleindialdehyde, isolated as the *bis-p-nitrophenylhydrazone*, m. p. 238—240° (decomp.); hydrolysis in presence of hydroxylamine affords a compound,  $C_4H_6O_2N_2$  m. p. 193° (explodes; darkens at 185°), not identical with the maleindialdoxime of Wohl and Mylo (A., 1912, i, 162) or the fumardialdoxime of Marquis (A., 1905, i, 225). This compound, for which the constitution  $\begin{array}{c} N-O \\ | \quad | \\ CH-CH_2 \end{array} > CH \cdot CH \cdot N \cdot OH$  is suggested, is converted by acetic anhydride into a substance, m. p. 193° (decomp., darkens 165°, sinters 187°), probably  $OAc \cdot N \cdot CH \cdot CH_2 \cdot CH(OAc) \cdot CN$ .

R. CHILD.

**Space configuration of the trithioacetaldehydes.** F. D. CHATTAWAY and E. G. KELLET (J.C.S., 1930, 1352—1356).— $\beta$ -Trithioacetaldehyde on oxidation with hydrogen peroxide in acetic acid gives a single *monosulphoxide*, m. p. 118.5°, which on further oxidation with neutral permanganate gives  $\beta$ -trithioacetaldehyde *monosulphone*, m. p. 190°. Oxidation of  $\alpha$ -trithioacetaldehyde with hydrogen peroxide yields a mixture of  $\alpha$ -trithioacetaldehyde  $\alpha$ -monosulphoxide, m. p. 136°, and  $\beta$ -monosulphoxide, m. p. 93°; the latter can be reduced by nascent hydrogen to  $\alpha$ -trithioacetaldehyde. The crude solution of  $\alpha$ - and  $\beta$ -monosulphoxides gives on further oxidation  $\alpha$ -trithioacetaldehyde  $\alpha$ -monosulphone, which exists in two distinct crystalline modifications, both having m. p. 157.5°, and  $\alpha$ -trithioacetaldehyde  $\beta$ -monosulphone, m. p. 115—116°. As  $\alpha$ -trithioacetaldehyde produces two sulphones, and the  $\beta$ -variety one, it is concluded that the former is the *trans*-, and the latter the *cis*-modification.

H. A. PIGGOTT.

**Condensation of ketones.** V. GRIGNARD and J. COLOGNE (Compt. rend., 1930, 190, 1349—1353).—Optimal conditions for the condensation of ketones by hydrogen chloride are obtained when the molecular ratio of acid to ketone is 2 : 3. With the exception of methyl ethyl ketone the reaction is confined to the methyl group of one molecule and the ketonic group of the second molecule. Methyl ethyl ketone yields  $\gamma$ -chloro- $\gamma\delta$ -dimethylhexan- $\beta$ -one, b. p. 108—110°/55 mm.,  $d_4^{20}$  0.988,  $n_D^{20}$  1.4481,  $R_m$  44.07, which with alkalis furnishes  $\gamma\delta$ -dimethyl- $\Delta^7$ -hexen- $\beta$ -one, b. p. 157—159° (semicarbazones, m. p. 182° and 142°; cf. Abbott, Kon, and Satchell, A., 1928, 1218). Methyl ethyl ketone with magnesium butoxybromide gives  $\gamma$ -methyl-*n*-heptan- $\gamma$ -ol- $\epsilon$ -one, b. p. 72—73°/6 mm. (semicarbazone, m. p. 124°), dehydration of which yields  $\gamma$ -methyl- $\Delta^7$ -hepten- $\epsilon$ -one, b. p. 162—164°/737 mm. (semicarbazone, m. p. 116°) (cf. Grignard and Fluchaire, A., 1928, 396).

Hydrogen bromide and hydrogen iodide used in the same molecular ratio of acid to ketone furnish higher yields; moreover they facilitate the condensation of methyl ketones with secondary carbon groups, but do not condense ketones with a tertiary group. Methyl *sec*.-butyl ketone condenses in 40% yield with hydrogen bromide to give  $\gamma\delta\eta$ -trimethyl- $\Delta^8$ -nonen- $\zeta$ -one, b. p. 218—220°,  $d_4^{20}$  0.856,  $n_D^{20}$  1.4522,  $R_m$

57.37. Phenyl ethyl ketone furnishes in 22% yield  $\alpha\gamma$ -diphenyl- $\beta$ -methyl- $\Delta^8$ -penten- $\alpha$ -one slightly impure, m. p. 75°. C. C. N. VASS.

**Action of methylglyoxal on acetoacetic acid.** I. M. HENZE (Z. physiol. Chem., 1930, 189, 121—126).—Methylglyoxal reacts with sodium acetoacetate giving a product, b. p. 98—99.5°/10 mm., lowest mol. wt. 118 by titration, which reduces Benedict's solution strongly. It does not appear to contain a carboxyl group. Crystalline derivatives were obtained with semicarbazide, m. p. 255° (decomp.), and *p*-bromophenylhydrazine, m. p. 181°.

J. H. BIRKINSHAW.

**Oxidative decomposition of sugars. IX. Formation of trioses from sugars under pressure.** K. BERNHAUER and H. WOLF (Biochem. Z., 1930, 221, 11—16).—When sucrose is autoclaved at 105—120°, 57%, whereas with invert-sugar 27%, with dextrose 33%, and with laevulose 23% of the sugar is converted into trioses.

P. W. CLUTTERBUCK.

**Reducing equivalents of rare sugars determined by colorimetric methods.** C. F. POE and D. KLEMM (J. Biol. Chem., 1930, 87, 7—12).—Figures are given for the reducing equivalents of *d*- and *l*-arabinose, xylose, laevulose, galactose, mannose, lactose, maltose, cellobiose, fucose, glucoheptose,  $\beta$ -*d*-glucose, glucosamine, and rhamnose as determined by all the recognised colorimetric methods, the reducing value of dextrose being taken as the standard.

C. R. HARRINGTON.

**Influence of sulphite and hydrogen sulphite solutions on sugars at high temperatures. III.** E. HÄGGLUND, T. JOHNSON, and H. URBAN (Ber., 1930, 63, [B], 1387—1395; cf. A., 1929, 428, 1280).—The mechanism of the reaction between dextrose and acid hydrogen sulphite solutions is discussed at length. Occasionally a *disulphonic acid* is produced which is hydrolysed by boiling, dilute sulphuric acid exclusively to gluconic acid; it is converted by phenylhydrazine with loss of a sulphonc acid group into a non-crystalline phenylhydrazone. When dextrose is treated with neutral sulphite solutions, a *sulphonic acid* not identical with any of those obtained in an acid medium is produced. It is stable towards hot, dilute mineral acid and cold alkali hydroxide. Boiling alkali hydroxide causes slow removal of the sulphonyl group. It is not oxidised by bromine in aqueous solution. The *barium* salt affords a crystalline *phenylhydrazone*, but not a *phenylosazone*. The product appears to contain the  $\cdot CO \cdot$ ,  $\cdot CO_2H$ , and  $\cdot SO_3H$  groups in a manner as yet unexplained.

H. WREN.

**Carbohydrates. IX. Derivatives of the aldehydic form of dextrose.** P. BRIGL and H. MÜHLSCHLEGEL (Ber., 1930, 63, [B], 1551—1557; cf. A., 1929, 1043).—Benzoylation of glucose diethylmercaptal in presence of sodium hydroxide yields the *tetrabenzoate*, m. p. 166°, whereas with benzoyl chloride and pyridine the *pentabenzoate*,  $OBz \cdot CH_2 \cdot [CH(OBz)]_4 \cdot CH(SET)_2$ , m. p. 97—98°,  $[z]_D^{20} +49.6^\circ$  in chloroform, is produced. Removal of the mercaptal groups without affecting the benzoyl

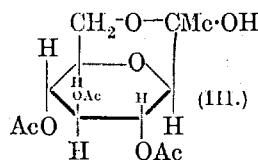
radical is difficult and is best effected by distilling the compound with 95–98% formic acid which is renewed as it is volatilised. The *semiactal*,  $\text{OBz}\cdot\text{CH}_2\cdot[\text{CH}\cdot\text{OBz}]_4\cdot\text{CH}(\text{OH})\cdot\text{OEt}$ , m. p. 76–82°,  $[\alpha]_D^{25} +37.1^\circ$  in alcohol, is obtained by treating the product with alcohol. The crystals lose alcohol quantitatively in a high vacuum at 50°, leaving a glassy mass which softens at 62° and melts at 71–81°. The aldehydic nature of the product is established by the formation of a crystalline sodium hydrogen sulphite derivative,  $\text{C}_{41}\text{H}_{35}\text{O}_{11}\cdot\text{NaHSO}_3$ , m. p. 108–114° after softening at 103°, and by its conversion by ethyl mercaptan and hydrogen chloride into the initial diethylmercaptan. H. WREN.

**Glucosides. III. Abnormal replacement of halogen in glucosyl halides: formation of  $\beta$ -glucosides from  $\beta$ -glucosyl chlorides.** W. J. HICKINBOTTOM (J.C.S., 1930, 1338–1348).—The action of 1 equivalent of sodium methoxide in methyl-alcoholic solution on 2-trichloroacetyl-3:4:6-triacetyl- $\beta$ -glucosyl chloride gives 3:4:6-triacetyl- $\beta$ -methylglucoside, the trichloroacetyl group being removed by hydrolysis. The reaction, which was followed polarimetrically, is rapid, and deacetylation of the crude product gives  $\beta$ - and  $\alpha$ -methylglucosides, the latter being about 14–19% of the mixture. If a slight excess of sodium methoxide is used extensive deacetylation occurs and the main product is monoacetyl- $\beta$ -methylglucoside. Sodium ethoxide behaves similarly. The phenoxide, however, in dry acetone gives a product from which, after acetylation, 64% of 2:3:4:6-tetra-acetyl- $\alpha$ -phenylglucoside and 36% of the corresponding  $\beta$ -derivative may be isolated. 3:4:6-Triacetyl- $\beta$ -glucosyl chloride gives with sodium methoxide a solution from which  $\beta$ -methylglucoside may be isolated, but with sodium phenoxide and phenol the  $\beta$ - and  $\alpha$ -glucosides are in the ratio 65:35. 2:3:4:6-Tetra-acetyl- $\alpha$ -glucosyl bromide when heated with sodium methoxide yields mainly the  $\beta$ -glucoside.

3:4:6-Triacetyl-2-trichloroacetyl- $\beta$ -glucosyl chloride is stable in acetone in the presence of a little sodium methoxide or hydroxide, or hydrochloric acid, and is not affected by solid sodium methoxide in the absence of methyl alcohol. This resistance to isomeric change does not support the isomerisation hypothesis of Fischer and Armstrong (A., 1901, i, 671) in view of the rapidity of glucoside formation; it is suggested that addition occurs first, and that the subsequent behaviour of the additive compound is determined by the nature of the reacting system. H. A. PIGGOTT.

**Conversion of 1:2:3:4-tetra-acetyl- $\beta$ -D-glucose into 2:3:4:6-tetra-acetyl- $\beta$ -methylglucoside.** W. N. HAWORTH, E. L. HIRST, and E. G. TEECE (J.C.S., 1930, 1405–1409).—The non-identity of 1:2:3:4- (I), m. p. 127° (Helferich and Klein, A., 1927, 135), 2:3:4:6- (II), m. p. 135° (Fischer and Delbrück, A., 1909, i, 633), and 1:2:3:6-tetra-acetyl- $\beta$ -D-glucose (III), m. p. 135° (Helferich and Klein, A., 1927, 858), is confirmed by mixed-m. p. determinations. On methylation with methyl iodide and silver oxide I and II both give 2:3:4:6-tetra-

acetyl- $\beta$ -methylglucoside, m. p. 104–105°,  $[\alpha]_D^{25} -18.2^\circ$  in chloroform, thus behaving exactly as III (Helferich), which is known to exist in equilibrium with I in alkaline solution. The migration of groups between the 1 and 6 positions is tentatively explained by assigning the orthocarbonic ester formula (annexed) to III (cf. Fischer, A., 1920, i, 808).



H. A. PIGGOTT.

**Action of titanium tetrachloride on derivatives of sugars. II. Preparation of tetra-acetyl- $\beta$ -n-hexylglucoside and its transformation into the  $\alpha$ -form. III. Transformation of tetra-acetyl- $\beta$ -cyclohexylglucoside into the  $\alpha$ -form and preparation of  $\alpha$ -cyclohexylglucoside. IV. Transformation of hepta-acetyl- $\beta$ -methylcellobioside into the  $\alpha$ -form and preparation of  $\alpha$ -methylcellobioside.** E. PACSU (J. Amer. Chem. Soc., 1930, 52, 2563–2567, 2568–2571, 2571–2575).—II. *Tetra-acetyl- $\beta$ -n-hexylglucoside*, m. p. 51.5°,  $[\alpha]_D^{25} -19.9^\circ$  in chloroform, prepared from n-hexyl alcohol, bromotetra-acetylglucose, and silver oxide in ether, is transformed by treatment with titanium tetrachloride in chloroform (A., 1928, 1118) into *tetra-acetyl- $\alpha$ -n-hexylglucoside*, m. p. 61°,  $[\alpha]_D^{25} +116.6^\circ$  in chloroform. Application of Hudson's isorotation rule indicates that the two forms contain the same (1:5) oxide ring.

III. *Tetra-acetyl- $\alpha$ -cyclohexylglucoside*, m. p. 40–41°,  $[\alpha]_D^{25} +121.7^\circ$  in chloroform, is prepared from the  $\beta$ -form by the abovemethod, and hydrolysed by methyl-alcoholic sodium methoxide in chloroform to  $\alpha$ -cyclohexylglucoside, m. p. 125–126°,  $[\alpha]_D^{25} +133.2^\circ$  in chloroform. These glucosides all possess the 1:5-ring structure.

IV. *Hepta-acetyl- $\alpha$ -methylcellobioside*, m. p. 185°,  $[\alpha]_D^{25} +55.7^\circ$  in chloroform, is hydrolysed as above to  $\alpha$ -methylcellobioside, m. p. 144–145°,  $[\alpha]_D^{25} +96.8^\circ$  in water. A substance, m. p. 174°,  $[\alpha]_D^{25} +23.8^\circ$  in chloroform, is formed as a by-product during the treatment with titanium tetrachloride: when hydrolysed, it gives dextrose as the sole product. The primary ring in these cellobiosides is deduced to be 1:5.

H. BURTON.

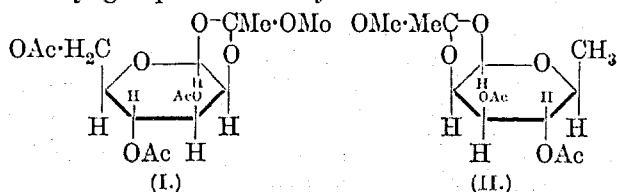
**Relations between rotatory power and structure in the sugar group. XXX.  $\alpha$ - and  $\beta$ -Methyl-D-galactosides and their tetra-acetates.** J. K. DALE and C. S. HUDSON (J. Amer. Chem. Soc., 1930, 52, 2534–2537).—Acetylation of  $\alpha$ -methyl-D-galactoside with acetic anhydride and pyridine in the cold gives the corresponding *tetra-acetate*, m. p. 87° (corr.),  $[\alpha]_D^{25} +133.0^\circ$  in chloroform.  $\beta$ -Methyl-D-galactoside is acetylated with acetic anhydride and sodium acetate at 100°; the *tetra-acetate* has  $[\alpha]_D^{25} -14.05^\circ$  in chloroform. The rotations of solutions of  $\alpha$ - and  $\beta$ -methylglucosides, -galactosides, -xylosides, -arabinosides, and -gentiobiosides, and their acetyl derivatives show that the rules of isorotation hold in all these cases.

H. BURTON.

**Fifth penta-acetate of galactose, its alcoholate and hydrate.** M. L. WOLFROM (J. Amer. Chem. Soc., 1930, 52, 2464–2473).—Treatment of the *penta-acetate*, m. p. 77–78°,  $[\alpha]_D^{25} +9.8^\circ$  in chloroform (all rotations quoted are in this solvent), of galactose ethyl

mercaptal (improved method of preparation given) with cadmium carbonate and mercuric chloride in aqueous acetone (cf. A., 1929, 1043), and dissolution of the product formed in alcohol, gives (aldehyde) *galactose alcoholate penta-acetate*, m. p. 133—134°,  $[\alpha]_D^{25} -0.9^\circ$  after 1.5 min.  $\rightarrow +18.8^\circ$  after 50 hrs.; the mutarotation is ascribed to dissociation of the alcohol. Crystallisation of the alcoholate from water affords (aldehyde) *galactose hydrate penta-acetate*, m. p. 124—126°,  $[\alpha]_D^{25} +18.2^\circ$  after 2 min.  $\rightarrow -14.2^\circ$  after 8 hrs.  $\rightarrow +8.7^\circ$  after 47 hrs., whilst crystallisation from toluene furnishes (aldehyde) *galactose penta-acetate*, m. p. 120—121°,  $[\alpha]_D^{25} -22.0^\circ$  after 3 min.  $\rightarrow +10.5^\circ$  after 22 hrs. This change in rotation may be due to the presence of alcohol in the chloroform used; the rotation is constant ( $[\alpha]_D^{25} -16.1^\circ$ ) in *s*-tetrachloroethane. The galactose penta-acetate differs from the known four modifications, gives a positive Schiff's reaction, furnishes a *semicarbazone*, m. p. 200—201° (corr.; decomp.), and when oxidised with nitric acid yields mucic acid. H. BURTON.

**Novel form of isomerism in the sugar series.**  
**II. Third variety of tetra-acetylmethylmannoside.** H. G. BOTT, W. N. HAWORTH, and E. L. HIRST (J.C.S., 1930, 1395—1405).—The third or " $\gamma$ -" variety of tetra-acetylmethylmannoside (I), m. p. 105°,  $[\alpha]_D^{25} -26.6^\circ$  in chloroform, is shown to be strictly analogous to  $\gamma$ -triacetylmethylrhamnoside (II) (this vol., 68). The resistance of the acetyl group in position 2 in these compounds to alkaline but not to acid hydrolysis, which in the case of derivatives of I at least removes both this and the 1-methyl group, is now explained by the *ortho*-ester formulæ (below) involving the union of the 1-methyl and the 2-acetyl groups to form a cyclic structure.



" $\gamma$ -" Monoacetylmethylmannoside,  $[\alpha]_D^{25} -6^\circ$  in water, is conveniently prepared by the hydrolysis of  $\gamma$ -tetra-acetylmethylmannoside with cold dilute alcoholic sodium hydroxide. It is not further hydrolysed by 15% aqueous alkali at 80°, but is very readily hydrolysed by dilute acids with the loss of both the methyl and acetyl groups. On acetylation it is readily reconverted into the  $\gamma$ -tetra-acetyl compound, and on methylation, either with silver oxide and methyl iodide or with methyl sulphate, gives *monoacetyltrimethylmethylmannoside*, b. p. about 120°/0.1 mm.,  $n_D^{25} 1.4594$ ,  $[\alpha]_D^{25} -20^\circ$  in water,  $-11^\circ$  in chloroform. This compound is not hydrolysed by dilute alkali, but very readily by 0.01*N*-hydrochloric acid at 20°,  $[\alpha]_D^{25}$  changing from  $-25^\circ$  to  $+2^\circ$  (constant) in 1 hr.; for the complete removal of the acetyl group 0.5*N*-acid at 90° is needed and gives *d*-3 : 4 : 6-trimethyl- $\alpha$ -mannopyranose, m. p. 101—102°,  $[\alpha]_D^{25} +36^\circ$  in methyl alcohol,  $+21^\circ$  in water, falling to  $+8.2^\circ$  in 90 min. Methylation with methyl iodide and silver oxide gives tetramethyl- $\beta$ -methylmannopyranoside, m. p. 36—37°,  $[\alpha]_D^{25} -78^\circ$  in water (identified by mixed

m. p.), and oxidation with bromine yields *d*-3 : 4 : 6-trimethyl- $\delta$ -mannonolactone, m. p. 96—97°,  $[\alpha]_D^{25} +167.5^\circ \rightarrow 110^\circ$  in 74 hrs. (hydrolysis), converted by phenylhydrazine into the phenylhydrazone of *d*-3 : 4 : 6-trimethylmannonic acid, m. p. 137—139°. These properties correspond exactly with those of the corresponding *l*-isomerides (Haworth and Peat, A., 1929, 425) except that the rotation is opposite in sign. Proof is thus afforded of the pyranose structure of trimethylmannopyranose, and hence also of the  $\gamma$ -acetylmethylmannosides.  $\gamma$ -Tetra-acetylmethylmannoside is simultaneously deacetylated and methylated by methyl sulphate and alkali, but not by methyl iodide and silver oxide in the presence of solid sodium hydroxide, to give tetramethylmethylmannoside, identified by hydrolysis to tetramethylmannopyranose (anilide, m. p. 140—142°). The latter reagent gives mainly monoacetyltrimethylmethylmannoside.

H. A. PIGGOTT.

**Relations between rotatory power and structure in sugar group. XXIX. Preparation of crystalline turanose.** C. S. HUDSON and E. PACSU (J. Amer. Chem. Soc., 1930, 52, 2519—2524).—Hydrolysis of melezitose with dilute sulphuric acid, neutralisation of the solution with calcium carbonate, removal of the dextrose formed (by fermentation or oxidation with bromine water), evaporation in a vacuum, and dissolution of the residual syrup in methyl alcohol gives turanose, m. p. 157° (cf. Tanret, A., 1906, i, 560). The sugar is non-hygroscopic and aqueous solutions exhibit mutarotation ( $[\alpha]_D^{25} +53.5^\circ$  after 4 min.  $\rightarrow +75.3^\circ$  after 25 hrs.); the initial value of  $[\alpha]_D^{25}$  (by extrapolation) is  $+22.0^\circ$ . H. BURTON.

**Structure of "gum levan."** H. HIBBERT and R. S. TIPSON (J. Amer. Chem. Soc., 1930, 52, 2582).—"Gum levan," formed by the action of *B. mesentericus* on sucrose, is a polymerised anhydrofructofuranose. Methylation of the gum affords a trimethyl derivative, hydrolysed to 1 : 3 : 4-trimethylfructofuranose, m. p. 63°. When acted on by *B. xylinum*, it gives a more highly polymerised product. H. BURTON.

**Uzarin.** A. WINDAUS and E. HAACK (Ber., 1930, 63, [B], 1377—1380; cf. Hennig, A., 1918, i, 94; Wolff, Diss., Marburg, 1925).—Uzarin, probably  $\text{C}_{35}\text{H}_{56}\text{O}_{16}$ , m. p. 268—270°,  $[\alpha]_D^{25} -27^\circ$  in pyridine, is prepared by extraction of *Gomphocarpus* root with methyl alcohol and purification of the evaporated extract by treatment with glycol methyl ether, chloroform, and water. It behaves as a lactone, gives the Legal test, and becomes isomerised when warmed with alkalis. It is only slowly and incompletely decomposed by dilute acids, whereas boiling acid causes the elimination of two mols. of dextrose. The residue from the hydrolysis which is insoluble in water is non-homogeneous, but consists mainly of *anhydrouzarin* (?),  $\text{C}_{23}\text{H}_{30}\text{O}_9$ , m. p. 247—248°,  $[\alpha]_D^{25} -53.6^\circ$  in chloroform, which behaves as a lactone; it is trebly unsaturated, and yields an *acetyl* derivative, m. p. 175°, and a *p*-nitrobenzoyl compound, m. p. 246°. Hydrogenation of the acetate in presence of spongy platinum affords *perhydroanhydrouzarin acetate*,  $\text{C}_{23}\text{H}_{38}\text{O}_9$ , m. p. 225—226°. Uzarin appears to be very closely related to the digitalis glucosides.

H. WREN.

**Constitution of daphnin.** F. WESSELY and K. STURM (Ber., 1930, 63, [B], 1299—1301).—If natural daphnin is methylated and the sugar group is then removed, the *monomethyldaphnetin* [7-hydroxy-8-methoxycoumarin], m. p. 185.5°, is not identical with the synthetic hydroxymethoxycoumarin of Wessely and Sturm (A., 1929, 298). Natural daphnin therefore contains the sugar residue in position 7 and is not identical with the product obtained by Leone (A., 1925, i, 1283) from  $\beta$ -acetobromoglucose and 7 : 8-dihydroxycoumarin. This conclusion is confirmed by the observation that the same 8-methoxy-7-ethoxycoumarin, m. p. 81°, is obtained from daphnin by successive methylation, hydrolysis, and ethylation, and from synthetic glucosidodaphnetin by successive ethylation, hydrolysis, and methylation. Similarly, 7-methoxy-8-ethoxycoumarin, m. p. 85.5°, is obtained from the natural product by successive ethylation, hydrolysis, and methylation and from the synthetic material by successive methylation, hydrolysis, and ethylation. H. WREN.

**Supposed depolymerisation of inulin.** E. BERNER (Ber., 1930, 63, [B], 1356—1362).—The preparation of specimens of inulin of apparently low mol. wt. can be effected, in addition to treatment with hot glycerol or acetamide, by means of glycerol at the ordinary temperature or, more conveniently, by ethylene glycol. The effect is not due to depolymerisation, but to a physico-chemical process caused by the adsorption of various organic substances, whereby solubility in water is conferred. The extent of such adsorption depends on the completeness with which adherent water has been previously removed. Inulin "depolymerised" in glycerol and precipitated with alcohol retains both media after desiccation in a vacuum over calcium chloride. A sample of "inulan" obtained by means of acetamide with an apparent mol. wt. of 245, increasing to 319 after further desiccation, is found to retain 10.2% of alcohol and 2.1% of acetamide; after making allowance for the effect of these substances on the cryoscopic measurements, the value 3300 is found for the mol. wt. of "inulan" approximating closely to that of homogeneous inulin. Most specimens of inulin contain alcohol in considerable amount, which cannot be removed completely by desiccation at 78°/vac.; it is lost by protracted heating at 110°/vac. When inulin is obtained by freezing its aqueous solutions containing small amounts of alcohol, the latter is adsorbed. H. WREN.

**Kinetics of the degradation of multimolecular chains.** W. KUHN (Ber., 1930, 63, [B], 1503—1509).—Mathematical. Consideration is devoted to the amount of possible fragments produced by the successive rupture of long chains and the alteration of degree of fission with time, (a) if all linkings are resolved independently of one another and have the same reaction coefficient, (b) if all linkings with the exception of those of the small fragments react similarly, whereas those of the fragments are more readily resolved, (c) if the coefficients per unresolved linking are the same for fragments of differing magnitude, whereas all other linkings have a different but constant value, (d) if two components from a cyclic structure so that two linkings must be ruptured to yield the simple

unit, and (e) if two types of linking are present in the chain which react independently and simultaneously but with differing coefficients. H. WREN.

**Lignin and cellulose. XIV. Hydrolysis of polysaccharides.** K. FREUDENBERG, W. KUHN, W. DÜRR, F. BOLZ, and G. STEINBRUNN (Ber., 1930, 63, [B], 1510—1529).—The hydrolysis of cellulose, cellobextrin, cellobiose, starch, and maltose by 50% sulphuric acid at 18° and 30° has been followed by the method of Willstätter and Schudel and also polarimetrically (determination with copper is not applicable) and the results are evaluated in the light of the deductions of Kuhn (preceding abstract).

If the rotations of equimolecular solutions of the equilibrium forms of cellobiose and maltose are added and halved, an approximation is obtained for the activity of a 4- $\alpha$ -glucosidylglucose, thus a maltose or cellobiose inactive at the disaccharide linking. The rotation of cellulose is displaced almost as much towards the left as is that of starch towards the right of this value and, although the equality in magnitude is accidental, it is certain that cellulose is composed uniformly of  $\beta$ - and starch of  $\alpha$ -glucosidic residues.

The initial consumption of iodine is greater with cellobextrin than with cellulose, and it is estimated that the cellobextrin molecule contains 30—40 glucose residues with mean mol. wt. 5000—7000. On the bases of initial iodine consumption the cellulose chain is computed to contain fifty glucose residues as average. Dextrin can be regarded as cellulose degraded to the extent of about 1%. By reason of the smallness of this difference a distinction in the course of the reaction cannot be detected. With the exception of the copper number and iodine value, an indication of the aldehydic termination of the cellulose chains has not been observed. When the possibility of the presence of minute amounts of lower carbohydrates in native cellulose is taken into consideration, it appears feasible to conceive cellulose chains with hundreds of glucose residues and long chains alternating with shorter portions, so that an interruption occurring for every 60—100 glucose residues would fulfil the requirements of the Röntgen investigation. When judged from the iodine value, the starch molecule appears to have a mean chain length of 25—30 glucose residues.

The observations now recorded are reconcilable with the chain structure, and their uniform interpretation is possible only along these lines. This structure has been established for cellulose by structure-chemical experiments and is now deduced for starch and inulin. H. WREN.

**[Hydrolysis of polysaccharides.]** K. H. MEYER, H. HOFF, and H. MARK (Ber., 1930, 63, [B], 1531).—The authors concur with the views of Kuhn and of Freudenberg and co-workers (preceding abstracts). H. WREN.

**Constitution of lignin. XII. Quantitative composition of the lignin in various plants.** P. KLASON (Ber., 1930, 63, [B], 1548—1551; cf. this vol., 751).—Analysis of the naphthylamine salts of lignosulphonic acid from various *Coniferae* are recorded. Xylose is regarded as the parent substance of lignin and its partial methylation is effected by

the formaldehyde formed in the leaves; coniferyl alcohol is therefore formed according to the scheme  $C_5H_{11}O_5 + C_5H_9O_5Me = C_{10}H_{12}O_3 + CO_2 + 5H_2O$ . The mechanism of ring closure is discussed. The aliphatic propylene glycol group suffers auto-oxidation to the corresponding aldehyde, which is autopolymerised to lignin. The naphthylamine salt of the lignosulphonic acid from birch, beech, oak, etc. conforms to the formula  $3(C_{10}H_{10}O_3 + O), H_2SO_3, C_{10}H_9N, H_2O$ , and the lignin appears therefore to be a polymeric form of a hydroxyguaiaicolpropyleneglycollaldehyde. The initial change in the formaldehyde is conversion into methyl alcohol and formic acid, the latter behaving as an oxidising agent in the action between pentose and methylpentose:  $C_5H_{10}O_5 + C_5H_9O_5Me + H \cdot CO_2H = C_{10}H_{12}O_4 \cdot H \cdot CHO + CO_2 + 5H_2O$ . H. WREN.

**Action of ammonia and amines on aliphatic and aromatic hydroxymethylene ketones.** E. BENARY (Ber., 1930, 63, [B], 1573—1577; cf. A., 1929, 68).—The sodium salt of hydroxymethyleneacetone is converted by ammonium chloride and alcohol into  $\beta$ -acetylvinylamine,  $CHAc:CH \cdot NH_2$ , b. p. 94—96°/14 mm. With the requisite amine hydrochloride the following compounds are similarly prepared:  $\beta$ -acetyl-N-methylvinylamine,  $CHAc:CH \cdot NHMe$ , b. p. 90—93°/17 mm.;  $\beta$ -acetyl-N-dimethylvinylamine, b. p. 118°/19 mm.; piperidinomethyleneacetone,  $CH_3 \cdot CO \cdot CH:CH \cdot NC_5H_{10}$ , b. p. 160—162°/16 mm.  $\beta$ -Acetyl- $\Delta^a$ -propenylamine, m. p. 112°, is prepared by the action of alcoholic ammonia on  $\beta$ -keto- $\gamma$ -hydroxymethylenebutane. N-Methyl- $\beta$ -acetyl- $\Delta^a$ -propenylamine, m. p. 58°, N-dimethyl- $\beta$ -acetyl- $\Delta^a$ -propenylamine, b. p. 135—139°/23 mm., m. p. 55°, N-diethyl- $\beta$ -acetyl- $\Delta^a$ -propenylamine, b. p. 140°/14 mm., and  $\alpha$ -piperidino- $\beta$ -acetyl- $\Delta^a$ -propene, b. p. 155—158°/16 mm., are described. Ethylenedi- $\beta$ -acetyl- $\Delta^a$ -propenylamine,  $(CAcMe:CH \cdot NH \cdot CH_2)_2$ , decomposes at about 235° after darkening at 220°. The following compounds are derived from the requisite hydroxymethylene ketone and appropriate amine hydrochloride: diethyl- $\beta$ -n-butylvinylamine, b. p. 137°/15 mm.; dimethyl- $\beta$ -isobutylvinylamine, b. p. 132—134°/16 mm.; dimethyl- $\beta$ -trimethylacetylvinylamine, b. p. 132—135°/15 mm.; dimethyl  $\beta$ - $\beta'$ -methyl- $\Delta^a$ -butenylvinylamine, m. p. 104°; methyl- $\beta$ -benzoylvinylamine, m. p. 138°; dimethyl- $\beta$ -benzoylvinylamine, m. p. 90—92°; piperidinomethyleneacetophenone,  $CHBz:CH \cdot NC_5H_{10}$ , m. p. 80—81°; ethylenedi- $\beta$ -benzoyl- $\Delta^a$ -propenylamine, m. p. 141—142°. The sodium derivative of hydroxymethyleneacetophenone and ammonium chloride in methyl alcohol yield 5-benzoyl-2-phenylpyridine. H. WREN.

**Ability of glycine to form salts.** J. V. DUBSKY and A. RABAS (Pub. Fac. Sci. Univ. Masaryk, 1929, 115, 12—16).—By hydrolysis of the normal zinc salt of glycine the salt  $R_2Zn \cdot 3RH \cdot H_2O$ , decomp. 245°, is formed ( $R = NH_2 \cdot CH_2 \cdot CO_2$ ). The following salts are also described:  $ZnCl_2 \cdot 2RH \cdot 2H_2O$ , m. p. 100°, decomp. 230°;  $ZnCl_2 \cdot 3RH \cdot 2H_2O$ , decomp. 228°;  $ZnBr_2 \cdot 2RH \cdot 2H_2O$ , m. p. 98°, decomp. 335°;  $ZnSO_4 \cdot RH \cdot 5H_2O$ , m. p. 82°, decomp. 320°;  $CuCl_2 \cdot R_2Cu \cdot 2H_2O$ , decomp. 195°;  $CuCl_2 \cdot R_2Cu \cdot HCl$ , decomp. 190°;  $CuCl_2 \cdot 2RH \cdot 2HCl \cdot 2H_2O$ , m. p. 96°,

decomp. 120°. Analogous compounds of cobaltous, nickel, and stannic chlorides could not be prepared.

O. J. WALKER.

**Compound amino-acids.** S. MIYAMOTO and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 87, 327—337).—Titration curves are given for mixtures of arginine, lysine, and histidine with aspartic and glutamic acids. The data are subjected to mathematical treatment and indicate that, in such mixtures, actual formation of compound amino-acids takes place.

C. R. HARRINGTON.

**Optical activity of *d*-arginine.** H. K. MILLER and J. C. ANDREWS (J. Biol. Chem., 1930, 87, 435—439).—Figures are given for the optical rotation of *d*-arginine in presence of varying amounts of acid or base. Calculation of the dissociation constants of arginine from the data by the method of Levene and others (A., 1927, 625) gives results in approximate agreement with those of direct titration.

C. R. HARRINGTON.

**Synthesis of methionine.** W. WINDUS and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 2575—2578).— $\beta$ -Methylthioethyl chloride and ethyl sodium-malonate afford ethyl  $\beta$ -methylthioethylmalonate, b. p. 166—167°/30 mm.,  $d_4^{20}$  1.081,  $n_D^{20}$  1.4675. Bromination of the free acid, m. p. 92—93°, in ethereal solution, treatment of the reaction mixture with an excess of aqueous ammonia, neutralisation of the aqueous solution with hydrobromic acid, and subsequent evaporation gives methionine, m. p. 272° (cf. Barger and Coyne, A., 1929, 175).

H. BURTON.

**Oxidation-reduction potentials of sulphhydryl compounds.** J. W. WILLIAMS and E. M. DRISSSEN (J. Biol. Chem., 1930, 87, 441—451).—Electrometric titrations of cysteine at varying  $p_H$  were made with potassium iodate, potassium dichromate, and iodine. Curves of the normal type were obtained. The calculated values of  $E_0$  agreed well for any one oxidising agent, but differed as between the various agents employed, which indicates the formation of more than one oxidation product of cysteine. The potentials observed are regarded as resulting from the presence not only of cysteine and cystine, but also of an intermediate oxidation product of the former. Similar results were obtained with thiolacetic acid.

C. R. HARRINGTON.

**Mercury derivatives of cysteine.** J. C. ANDREWS and P. D. WYMAN (J. Biol. Chem., 1930, 87, 427—433).—The precipitate formed by addition of mercuric sulphate to a solution of cystine is apparently analogous in constitution to the silver compound of Vickery and Leavenworth (this vol., 754) and is regarded as a mercuric mercaptide of cysteine in combination with mercuric sulphate or mercuric hydroxide. The hypothesis is confirmed by the facts that the mother-liquor from the precipitation is dextrorotatory, owing presumably to the presence of cysteic acid, that recovery of cysteine from the precipitate by treatment with hydrogen sulphide is not accompanied by liberation of sulphur, and that the electrometric titration curve of cystine with mercuric sulphate shows a break at the ratio 1 mol. mercuric sulphate : 1 mol. cystine (2 mols. cysteine).

C. R. HARRINGTON.



**Constitution of disodium cyanamide.** R. STOLLÉ (J. pr. Chem., 1930, [ii], 126, 304).—Since sodium cyanamide by the action of nitrous oxide at 300–400° followed by acid hydrolysis affords a 25% yield of azoimide its structure is definitely fixed as  $\text{NNa}_2\cdot\text{C}\cdot\text{N}$ . J. W. BAKER.

**Mechanism of formation of thiuram and xanthogen monosulphides, and observations on thiocarbamyl thiocyanates.** A. CAMBRON (Canad. J. Res., 1930, 2, 341–356).—Evidence is adduced for the following mechanism of the formation of dialkyl sulphurdicarbothionate,  $(\text{OR}\cdot\text{CS})_2\text{S}$ , and of the thiuram derivative,  $(\text{NR}_2\cdot\text{CS})_2\text{S}$ , from the corresponding dialkyl disulphurdicarbothionates,  $(\text{OR}\cdot\text{CS})_2\text{S}_2$ , and thiuram derivatives,  $(\text{NR}_2\cdot\text{CS})_2\text{S}_2$ , and alkali cyanide:

$\text{X}\cdot\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{X} + \text{KCN} \rightarrow \text{X}\cdot\text{CS}\cdot\text{SCN} + \text{KS}\cdot\text{CS}\cdot\text{X}$ ;  
 $\text{X}\cdot\text{CS}\cdot\text{SCN} + \text{KS}\cdot\text{CS}\cdot\text{X} \rightarrow \text{X}\cdot\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{X} + \text{KSCN}$  ( $\text{X} = \text{RO}$  or  $\text{NR}_2$ ). Thus ethylphenylthiocarbamyl thiocyanate, m. p. 75.5–76°, from ethylphenylthiocarbamyl chloride and potassium thiocyanate in absolute alcohol solution, reacts with sodium isopropylxanthate in alcohol to give ethylphenylthiocarbamyl isopropylxanthyl sulphide, m. p. 39.5–40°, also prepared, m. p. 41°, from ethylphenylthiocarbamyl chloride and sodium isopropylxanthate. Methylphenylthiocarbamyl isopropylxanthyl sulphide, m. p. 42°, was similarly obtained from methylphenylthiocarbamyl chloride and sodium isopropylxanthate. Sodium methylphenyldithiocarbamate, from sodium sulphide (1 mol.) and methylphenylthiocarbamyl thiocyanate (1), m. p. 114°, in alcohol, reacts with I (1 mol.) to produce s-dimethyldiphenylthiuram monosulphide, m. p. 196–197° (90% yield); s-dimethyldi-p-tolylthiuram monosulphide, m. p. 143.5–144°, is analogously prepared from methyl-p-tolylthiocarbamyl thiocyanate, m. p. 116.5°. Ethyl o- and p-tolylthiocarbamyl chlorides have m. p. 69° and 53–54°, respectively.

Xanthogen monosulphides are formed from alkyl chloroformates and potassium ethylxanthate as follows:  $\text{RO}\cdot\text{CS}\cdot\text{SK} + \text{Cl}\cdot\text{CO}\cdot\text{OR}' \rightarrow \text{RO}\cdot\text{CS}\cdot\text{S}\cdot\text{CO}\cdot\text{OR}' + \text{KCl}$ ;  $\text{RO}\cdot\text{CS}\cdot\text{S}\cdot\text{CO}\cdot\text{OR}' + \text{KS}\cdot\text{CS}\cdot\text{OR} \rightarrow \text{KS}\cdot\text{CO}\cdot\text{OR}' + \text{RO}\cdot\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{OR}$ . Interaction of ethyl chloroformate and sodium isopropylxanthate in dry acetone at –5° affords the mixed anhydride,  $\text{OEt}\cdot\text{CO}\cdot\text{S}\cdot\text{CS}\cdot\text{OPr}^i$ ,  $n_D^{25}$  1.5110, converted by sodium isopropylxanthate (1 mol.) in alcohol into diisopropyl monoxanthogen, m. p. 55–55.5°, in 69% yield, also produced from the thio-anhydride of ethylthioformic acid and sodium isopropylxanthate. Sodium ethylxanthate (2 mols.) and benzoyl chloride in acetone solution yield ethyl xanthogen monosulphide: the mother-liquors on treatment with sodium tetrathionate (cf. Cambron and Whitby, this vol., 579) afforded benzoyl disulphide, m. p. 127°, proving that sodium thiobenzoate is a by-product of the reaction.

When I is heated at 100–110° for 10 min. and the product treated in benzene solution with aniline,  $\alpha$ -methylphenyl- $\alpha'$ -phenyldithiobiuret, m. p. 123°, is produced. A. I. VOGEL.

**Action of electrical discharges on thiocyanic acid.** W. GLUUD and C. DIECKMANN (Ber., 1930, 63, [B], 1374–1376).—Aqueous ammonium thiocyanate solution is decomposed by sulphuric acid in

the presence of ammonium sulphate and the moist thiocyanic acid vapour is passed at 20–25 mm. pressure through the discharge tube. Under the influence of the silent discharge, about 80% of the thiocyanic acid suffers decomposition and 95–100% of the decomposed acid is isolated as hydrogen cyanide. Varying amounts of sulphur dioxide, hydrogen sulphide, and sulphur are also produced.

H. WREN.

**Constitution of cyanogen halides. I. Reactions of cyanogen chloride and iodide.** E. V. ZAPPI (Bull. Soc. chim., 1930, [iv], 47, 453–456).—Cyanogen chloride, obtained by Held's method, using 4 mols. of potassium cyanide to 1 mol. of zinc sulphate, does not give chlorine with hydrochloric acid or chlorate or cyanate with potassium hydroxide. 3% Cyanogen chloride solutions in water, alcohol, ether, or chloroform yield an immediate precipitate of silver chloride, the alcoholic solutions being more active than the aqueous and older solutions precipitating more rapidly. Neither fresh nor old solutions of cyanogen chloride in water, alcohol, ether, or chloroform yield a precipitate of Prussian-blue with potassium hydroxide and ferrous-ferric mixture. Since cyanogen iodide, m. p. 140° (sealed tube), in the same solvents yields no precipitate with silver nitrate, but an immediate precipitate of Prussian-blue, the cyanogen halides are regarded as having the structures  $\text{I}\cdot\text{C}\cdot\text{N}$  and  $\text{Cl}\cdot\text{N}\cdot\text{C}$  or  $\text{Cl}\cdot\text{N}\cdot\text{C}$  respectively.

R. BRIGHTMAN.

**Preparation of diazomethane.** F. ARNDT and J. AMENDE (Z. angew. Chem., 1930, 43, 444–446).—The most convenient source of diazomethane is nitrosomethylcarbamide, readily obtained from technical methylamine hydrochloride or ammonia and methyl sulphate by treatment with potassium cyanate and subsequently with sodium nitrite and sulphuric acid. Suitable treatment of the carbamide with potassium hydroxide affords diazomethane, obtained as a solution in ether, benzene, or acetone with or without intermediate formation of the gaseous phase.

C. IRWIN.

**Methylethylloxarsylacetic acid.** N. WIGREN (J. pr. chem., 1930, [ii], 126, 246–249).—Methyl ethylarsine oxide,  $(\text{AsMeEt})_2\text{O}$ , reacts with sodium monochloroacetate in 10N-sodium hydroxide at 0° to give the sodium salt of methylethylloxarsylacetic acid,  $\text{O}\cdot\text{AsMeEt}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 137° (decomp., specimen put into bath at 130°) (silver salt). This acid is converted, in 90–95° yield, by the action of hydrogen sulphide on its methyl-alcoholic solution into methylethylsulpharsylacetic acid, m. p. 82° (brucine salt, +EtOH and solvent-free). J. W. BAKER.

**Halogen derivatives of trimethylstibine.** T. M. LOWRY and J. H. SIMONS (Ber., 1930, 63, [B], 1595–1602).—The dihalogeno-derivatives of trimethylstibine have been examined for comparison with the tellurium dimethyl dihalides. The colourless trimethylstibine di-iodide does not exhibit an absorption band in the ultra-violet and is therefore most suitably represented as a completely ionised, tertiary electrolyte  $\text{I}^-\text{[SbMe}_3\text{]}^+\text{I}^-$ . The molecular conductivities of the dihalides in acetonitrile show that the substances are weak electrolytes only if their hydro-

lysis is prevented by absence of water. The colourless hydroxychloride has all the properties of a strong, binary electrolyte and can be represented by the formula  $[\text{SbM}_2(\text{OH})]^+\text{Cl}^-$ ; hydrogen chloride is liberated from it in the presence of a very large excess of water. It has only a very slight tendency towards the elimination of hydroxyl ions, since its solution has an acid, not a basic reaction. The colourless base is a very weak electrolyte, although both hydroxyl groups can be replaced if sufficient acid is added to precipitate the dihalide. Possible causes of the anomalous properties of these and the corresponding tellurium compounds are discussed in detail.

*Trimethylstibine hexaiodide*, m. p.  $68-70^\circ$ , is incidentally described. H. WREN.

**Stereochemistry of tellurium.** T. M. LOWRY (Ber., 1930, 63, [B], 1590—1595).—A lecture.

H. WREN.

**Magnesium di-*n*-butyl.** H. GILMAN and R. E. BROWN (Rec. trav. chim., 1930, 49, 724—725).—Magnesium di-*n*-butyl is obtained from mercury di-*n*-butyl and magnesium (cf. Fleck, A., 1893, i, 622). It is non-distillable in a high vacuum, and is identified by conversion into *n*-valero- $\alpha$ -naphthalide by means of  $\alpha$ -naphthylcarbimide (A., 1928, 660). R. CHILD.

**Preparation of magnesium phenyl chloride.** H. GILMAN and N. B. ST. JOHN (Rec. trav. chim., 1930, 49, 717—723).—Conditions leading to satisfactory yields are described. Iodine is employed as a catalyst, the use of activated magnesium-copper alloy (A., 1928, 253) being then unnecessary. The effect of varying amounts of iodine on the time required to start the reaction is described. R. CHILD.

**Reaction of molybdenum with xanthates. Molybdenyl ion.** R. MONTEQUI (Anal. Fis. Quím., 1930, 28, 479—487).—Pure molybdenyl ethylxanthate, m. p.  $106^\circ$ , has been prepared by gradually acidifying a solution containing ammonium molybdate and potassium ethylxanthate, separating and drying over sulphuric acid the tar which separates, extracting with chloroform, and inducing crystallisation by gradually mixing with benzene. The isoamyl compound, m. p.  $98^\circ$ , is similar. The formulæ are of the type  $(\text{OR}\cdot\text{CS}_2)_4\text{Mo}_2\text{O}_3$ , thus confirming the author's previous result for the isobutyl compound (cf. A., 1917, i, 249; 1918, i, 249). Various colour reactions of the molybdenyl ion are described. H. F. GILLBE.

**Synthesis of cyclooctane and its behaviour when catalytically dehydrogenated.** N. D. ZELINSKI and M. G. FRIEMANN (Ber., 1930, 63, [B], 1485—1488).—*cyclo*Octanone, b. p.  $73-74^\circ/12$  mm., m. p.  $27-28^\circ$ , obtained by heating thorium azelaate, is converted into the *hydrazone*, b. p.  $121^\circ/17$  mm., from which *cyclo*octane, b. p.  $148.5-149.5^\circ/749$  mm.,  $d_4^{20}$  0.8349,  $n_D^{20}$  1.4586, is obtained by heating with solid potassium hydroxide. When passed over platinised charcoal at  $300^\circ$  it is converted into a mixture of *dicyclo*-[0 : 3 : 3]-octane and methyl*cyclo*heptane, whereas it is unchanged by wood charcoal at  $300^\circ$ . The observations are in harmony with the hypothesis of Balandin (A., 1929, 519, 890, 1245). H. WREN.

**Structure of aromatic rings in the light of orientation phenomena.** J. OBERMILLER (J. pr.

Chem., 1930, [ii], 126, 257—286).—A theoretical paper in which the author summarises and extends his views ("Die orientierenden Einflüsse und der Benzolkern," Leipzig, 1909) and represents all organic nuclei by the diagonal formulæ in which the *p*-positions are united but in a manner different from the normal union of the *o*-positions. In the case of naphthalene it is concluded that the  $\alpha$ -carbon atom is united in a similar manner to carbon atoms of the benzene ring, but the union between the 2 : 6- and 3 : 7-positions causes the naphthalene ring to behave formally as if the 2 : 3- and 6 : 7-positions were not united. The diagonal type of formula is also held to apply to pyridine and quinoline, whilst in anthraquinone two true benzene rings are united by carbonyl groups in the *o*-position. J. W. BAKER.

**Parallelism between the mobility of hydrogen in the benzene nucleus and that of chlorine in the side-chain.** S. C. J. OLIVIER (Rec. trav. chim., 1930, 49, 697—704; cf. A., 1923, i, 908).—Since previous observations may have been influenced by alcoholysis, the reaction velocities of the hydrolysis in acetone solution of a number of substituted benzyl chlorides have been determined at  $30.4^\circ$  and  $60^\circ$ . The reaction has only one fifth the velocity of that in aqueous alcohol (A., 1922, i, 646; 1923, i, 197, 769, 908) but the effect of the nature and position of the various substituents remains the same, with the exception that *o*- and *p*-nitrobenzyl chlorides change places in the series.

The observed rates of hydrolysis of benzyl chloride were ( $k \times 10^3$ ) 0.0225 at  $30.4^\circ$  and 0.46 at  $60^\circ$ ; the rates for *o*-, *m*-, and *p*-methyl-, chloro-, bromo-, iodo-, -nitro-, and *m*- and *p*-carboxy-benzyl chlorides at  $30.4^\circ$  were (benzyl chloride=1) 4.36, 1.24, 7.7, 0.271, 0.177, 0.56, 0.244, 0.173, 0.489, 0.258, 0.176, 0.444, 0.072, 0.095, 0.088, 0.244, and 0.174 respectively; and at  $60^\circ$ , 4.11, 1.20, 8.7, 0.298, 0.202, 0.58, 0.280, 0.202, 0.51, 0.267, 0.193, 0.467, 0.098, 0.111, 0.100, 0.287, and 0.187, respectively. R. CHILD.

**Action of aluminium chloride on benzotrichloride.** A. WOHL and E. WESTPOROCH (Annalen, 1930, 481, 30—42).—The intermediate products of the reaction are best obtained by using 0.1 mol. of aluminium chloride at  $50-60^\circ$  for 4 hrs.;  $\frac{2}{3}$ —1 mol. of hydrogen chloride is evolved and fractionation of the resulting mixture at 0.04—0.05 mm. affords, besides unchanged benzotrichloride, *m*-trichloromethyl*diphenyldichloromethane* (I),  $\text{CCl}_3\cdot\text{C}_6\text{H}_4\cdot\text{CPhCl}_2$ , b. p.  $123-125^\circ/0.005$  mm., m. p.  $59-61^\circ$  (gives on hydrolysis by ferric chloride followed by addition of water, by sulphuric or nitric acid, or by water under pressure, *m*-benzoylbenzoic acid); *m*-(*m*-trichloromethyl*dichlorobenzyl*)*diphenyldichloromethane* (II), b. p.  $249^\circ/0.2$  mm.,  $d_4^{21}$  1.472, a viscous oil [not attacked by water under pressure; yields with sulphuric acid *m*-benzoyl-*m*-benzoylbenzoic acid, m. p.  $195^\circ$  (barium salt), and with nitric acid a nitro-derivative of the latter, m. p.  $178-179^\circ$  (barium salt); the nitro-acid is converted by chromium trioxide into 5-nitroisophthalic acid], which also results from the interaction of I with benzotrichloride in presence of aluminium chloride, but not from I alone; and a dark, brittle residue,  $\text{C}_{17}\text{H}_{10}\text{Cl}_4$ , m. p. about  $120^\circ$ , converted by

sulphuric or nitric acid into alkali-insoluble products containing chlorine.

Anhydrous zinc chloride, or tin or silicon tetrachloride has no action on benzotrichloride at its b. p., beryllium chloride has a slight action at 140°, whilst the reaction with ferric chloride is more complex than with aluminium chloride.

Although *ortho*-substituted compounds have not been obtained in the above condensation, benzotrichloride and benzene react in presence of aluminium chloride to give 9:9':10:10'-tetraphenyldihydroanthracene, m. p. 159°; since the latter is not obtained by further condensation of phenyl-substituted chloromethanes, their formation as intermediates cannot be postulated. With benzene and aluminium chloride I gives a substance,  $C_{31}H_{26}O_3Cl_2$ , apparently not homogeneous, whilst II gives only carbonised products.

R. CHILD.

**Action of chlorosulphonic acid on cyclic hydrocarbons.** J. POLLAK, M. HEIMBERG-KRAUSS, E. KATSCHER, and O. LUSTIG (Monatsh., 1930, 55, 358—378).—The action of chlorosulphonic acid on various aromatic hydrocarbons, chloro- and nitrobenzenes, *p*-chloronitrobenzene, thiophenetole, and ethyl phenylxanthate is studied.

[By O. LUSTIG, K. FREY, and L. RINK].—Addition of benzene to chlorosulphonic acid (10 parts) and subsequent heating of the mixture at 150—160° (bath) affords benzene-1:3-disulphonyl chloride (main product), diphenylsulphonedisulphonyl chloride, m. p. 175° (Otto, A., 1886, 1031; 1887, 263), and benzene-1:4-disulphonyl chloride (trace). When a larger amount of chlorosulphonic acid is used, the sulphonedisulphonyl chloride is the main product.

[By O. LUSTIG and L. RINK].—Toluene and chlorosulphonic acid (8 parts) at 140—150° give toluene-2:4-disulphonyl chloride. When equimolecular quantities are heated to boiling and the resulting sulphone is then treated with an excess of the acid at 150—160°, *di-p*-tolylsulphone-3:3'-disulphonyl chloride, m. p. 177—178° (corresponding *dianilide*, m. p. 325—330°), is obtained in 95% yield. Oxidation of the corresponding diamide, m. p. 268°, with alkaline potassium permanganate affords a small amount of the saccharin derivative,  $SO_2(C_6H_3<\overset{CO}{\underset{SO_2}{\text{N}}})_2$ .

Di-*m*- and di-*p*-xylylsulphones are prepared from approximately molecular quantities of the xylene and chlorosulphonic acid at the b. p. The *p*-sulphone is converted by the general method into a *disulphonyl chloride*, m. p. 190° (corresponding *amide*, m. p. above 325°). Similarly, phenyl ethyl sulphone gives the *3-sulphonyl chloride*, m. p. 93.5°, whilst thiophenetole and ethyl phenylxanthate both furnish *pentachlorophenyl ethyl sulphide*.

[By O. LUSTIG and R. EHRENZWEIG].—Sodium *o*-xylenesulphonate and chlorosulphonic acid at 150—160° afford *o*-xylene-3:5-disulphonyl chloride. Similar treatment of technical *o*-xylene gives an uncrystallisable oil, which with aniline yields a mixture of *o*-xylene-3:5-disulphonanilide, m. p. 199—200°, *m*-xylene-4:6-disulphonanilide, m. p. 196°, and *p*-xylene-2:6-disulphonanilide, m. p. 174°, separable by crystallisation from 50% alcohol. *p*-Xylene-3:6-disulphon-

*anilide* has m. p. 223°. Reduction of *o*-xylene-3:5-disulphonyl chloride with tin and hydrochloric acid or zinc dust and 30% sulphuric acid furnishes 3:5-dithiol-*o*-xylene, b. p. 150—151°/13 mm. [*diacetyl derivative*, m. p. 47—49°; *dimethyl ether*, m. p. 39°; *dicarbethoxy-derivative*, b. p. 206—209°/14 mm.; *di(thiolacetic acid)*, m. p. 161—162°; *dipicryl derivative*, decomp. 202—203°].

[By E. KATSCHER].—Successive treatment of chlorobenzene with chlorosulphonic acid at 100° and 150—180° gives the 2:4-disulphonyl chloride, which on hydrolysis with cold alcoholic potassium hydroxide affords a considerable amount of ether. *p*-Chloronitrobenzene affords 1-chloro-4-nitrobenzene-2-sulphonyl chloride, and potassium 1-chloro-2:6-dinitrobenzene-4-sulphonate furnishes the 4-sulphonyl chloride. Nitrobenzene-2:5-disulphonic acid is converted by chlorosulphonic acid or phosphorus pentachloride into a mixture of products from which 1-chloro-2-nitrobenzene-4-sulphonyl chloride, m. p. 59—60°, is isolated; replacement of the sulphonic acid grouping by chlorine occurs. Nitration of potassium chlorobenzene-4:6-disulphonate with fuming nitric and sulphuric acids yields *potassium hydrogen 1-chloro-2-nitrobenzene-4:6-disulphonate*, convertible into 1-chloro-2-nitrobenzene-4:6-disulphonyl chloride, m. p. 98°, by treatment with chlorosulphonic acid at 140—160°. *Potassium 2-nitrodiphenylamine-4:6-disulphonate* is also described. Nitrobenzene is oxidised and chlorinated by prolonged treatment with chlorosulphonic acid forming chloranil.

[By M. HEIMBERG-KRAUSS and S. ILSE].—Equimolecular quantities of diphenyl and chlorosulphonic acid react in tetrachloroethane at 50° forming diphenylsulphonic acid, m. p. 138° [*barium salt*; *amide*, m. p. 228° (lit. 227—230°); *anilide*, m. p. 125°]. The same acid is obtained in better yield from diphenyl and sulphuric acid in presence of nitrobenzene at 50°. Diphenyl-4:4'-disulphonyl chloride and *diphenylene-2:2'-sulphone-4:4'-disulphonyl chloride*, m. p. 236° (corresponding *anilide*, m. p. 207°), are also prepared from diphenyl and chlorosulphonic acid under various conditions.

[With R. KOLM, Z. RUDICH, and F. BECKER].—Naphthalene and chlorosulphonic acid (10 parts) react at about 0° yielding naphthalene-1:5-disulphonyl chloride [*nitro-derivative*, m. p. 163—164°, obtained by the action of boiling nitric acid (*d* 1.5)].

H. BURTON.

**[Preparation of] benzenesulphonyl chloride.** H. T. CLARKE, G. S. BABCOCK, and T. F. MURRAY (Organic Syntheses, 1930, 10, 6—8).

**Phenylthiosulphuric acid.** P. BAUMGARTEN (Ber., 1930, 63, [B], 1330—1335).—Thiophenol is converted by *N*-pyridiniumsulphonic acid into *pyridine phenylthiosulphate*,  $SPh \cdot SO_3H \cdot C_5H_5N$ , m. p. 89—91°. Treatment of a saturated alcoholic solution of this salt with the equivalent amount of the alkali alkoxide yields *potassium* and *sodium phenylthiosulphates*. The alkali salts are very stable in neutral, alcoholic solution. In acid solution, particularly when concentrated, they become decomposed into thiophenol and sulphuric acid. In alkaline solution they decompose very readily into diphenyl disulphide, sulphurous acid, and benzene-

sulphinic acid; the intermediate production of benzenesulphinic acid is assumed. H. WREN.

**Preparation of compounds analogous in structure to sulphinic acids but containing *p*-toluenesulphonimido-groups in place of oxygen atoms. Phenyl- and methyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines.** S. G. CLARKE, J. KENYON, and H. PHILLIPS (J.C.S., 1930, 1225—1232).—Compounds of the type described in the title,

$C_6H_5 \cdot SO_2 \cdot N^{\oplus} SR \cdot NH \cdot SO_2 \cdot C_6H_5$  (I), are obtained by the action of "chloramine-T" on an alkaline solution of ethyl and phenyl mercaptans and thus are obtained *ethyl*-, m. p. 189° (decomp.) (I, R=Et), and *phenyl*-, (I, R=Ph), m. p. 152—153° (sodium, m. p. 227—228°, and silver salts), -*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine. Thus "chloramine-T" must dissociate to give a neutral *p*-toluenesulphonimido-

radical,  $C_6H_5 \cdot SO_2 \cdot \dot{N} ClNa = C_6H_5 \cdot SO_2 \cdot N^{\oplus} + NaCl$ , a deduction which receives support from the fact that a larger yield of the above phenyl compound is obtained in the anhydrous solvents acetic acid or pyridine than in aqueous solution in which the hydrolytic action,  $C_6H_5 \cdot SO_2 \cdot \dot{N} ClNa + H_2O =$

$C_6H_5 \cdot SO_2 \cdot NH_2 + NaOCl$ , is favoured. The same two compounds (I) are also obtained by the action of "chloramine-T" on an alkaline solution of ethyl- [accompanied, in this case, by a substance, m. p. 128° (decomp. to a substance, m. p. 108—112°)] and phenylthiolacetic acid, respectively. Oxidation of these compounds (I) with alkaline potassium permanganate converts them, respectively, into the acids EtX, m. p. 275—276° (decomp.), and PhX, m. p. 201° (decomp.)

(X=CO<sub>2</sub>H·C<sub>6</sub>H<sub>4</sub>·SO<sub>2</sub>·N<sup>+</sup>·SO<sup>+</sup>·NH·SO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H), which yield *p*-sulphonamidobenzoic acid on hydrolysis. The imido-hydrogen atom in the original substances cannot be replaced by methyl groups by any of the ordinary methylation processes, the only products isolated by the action of sodium hydroxide and methyl sulphate on the ethyl compound being *p*-toluenesulphonodimethylamide, m. p. 78—79° (also by methylation of *p*-toluenesulphonamide), and *ethyl-p*-toluenesulphonylsulphinamide,

$EtSO \cdot NH \cdot SO_2 \cdot C_6H_5$ , m. p. 120°. With the phenyl compound, mono- and di-methyl derivatives of *p*-toluenesulphonamide and diphenyl sulphide were the only products identified. J. W. BAKER.

**Nitration of toluene in the side-chain.** P. P. SCHORIGIN and A. M. SOKOLOVA (J. Russ. Phys. Chem. Soc., 1930, 62, 673—681).—3—5% Yields of phenylnitromethane are obtained by heating toluene in a sealed tube with aqueous nitric acid, whilst 14% yields are obtained by nitration in glacial acetic acid solution. Acetic anhydride protects the side-chain from substitution, as do also mercury salts; the latter, however, catalyse substitution in the nucleus. Irradiation with a tungsten-filament or a mercury-vapour lamp is without effect on the reaction in acetic acid solution. Ethylbenzene can be more readily nitrated in the side-chain than toluene.

R. TRUSZKOWSKI.

**Action of the system Mg+MgBr<sub>2</sub> on triphenylcarbinol, triphenylmethyl bromide, and triphenylmethyl.** M. GOMBERG and W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 2455—2461).—Magnesium (1 atom) and triphenylmethyl bromide react readily in a mixture of ether and benzene forming magnesium triphenylmethyl bromide (crystalline etherate). With 0.5 atom of the metal, no Grignard reagent is present at the end of the reaction; the products formed are triphenylmethyl and magnesium bromide, which probably result from the reaction  $CPh_3 \cdot MgBr + CPh_3 \cdot Br = 2CPh_3 + MgBr_2$ . Addition of a further 0.5 atom of magnesium to the reaction mixture gives the Grignard reagent, also prepared from pure triphenylmethyl, magnesium, and magnesium bromide in ethereal benzene. When triphenylcarbinol is heated with magnesium bromide, the following reaction occurs:  $CPh_3 \cdot OH + MgBr_2 = CPh_3 \cdot Br + MgBr \cdot OH$ . H. BURTON.

**Synthesis of indene derivatives.** E. BERGMANN and H. WEISS (Annalen, 1930, 480, 64—75; cf. this vol., 901, 902).—1-Hydroxy-1:2:3-triphenylindene methyl ether is converted by the consecutive action of metallic sodium and methyl iodide into the non-crystalline 1:2:3-triphenyl-1-methylindene, reduced by sodium and boiling amyl alcohol to 1:2:3-triphenyl-1-methylhydrindene, m. p. 163—164°. Condensation of ethyl α-bromopropionate with benzophenone and zinc affords *ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate*, m. p. 102—103°, dehydrated by heating with 85% formic acid at 150° to *ethyl β-phenyl-α-methylcinnamate*, m. p. 84°. This reacts with magnesium phenyl bromide to give *ααγγ-tetraphenyl-β-methyl-Δ<sup>2</sup>-propen-α-ol*, m. p. 119°, which readily undergoes ring closure when treated with alcoholic sulphuric acid to give 1:1:3-triphenyl-2-methylindene, m. p. 150°, reduced catalytically in propyl alcohol to 1:1:3-triphenyl-2-methylhydrindene, m. p. 165°. 3-Phenyl-2-benzylindene, prepared from tribenzylcarbinol [acetate, m. p. 186° (decomp. with formation of dibenzylethylene, an improved method for the preparation of which is described)] by Oréchoff's method (A., 1914, i, 265), is converted by amyl nitrite and alcoholic sodium ethoxide into the *oxime*, m. p. 174—176°, of 3-phenyl-2-benzylindone, m. p. 113—114°, the ketone being liberated by the action of hydrogen bromide in acetic acid. Magnesium phenyl bromide converts the indone into 1-hydroxy-1:3-diphenyl-2-benzylindene, m. p. 109—112°. Reduction of this with red phosphorus and hydriodic acid (d 1.7) gives two of the three possible stereoisomeric forms, m. p. 121—122.5° and 117—118°, respectively, of 1:3-diphenyl-2-benzylhydrindene. 1:2-Diphenylindene (Oréchoff, *loc. cit.*) is similarly converted into 1:2-diphenyl-3-benzylhydrindene, m. p. 115° (only one stereoisomeride being obtained in this case), and 3-phenyl-2-methylindone (prepared by the action of concentrated sulphuric acid on ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate) into 3-phenyl-1-benzyl-2-methylhydrindene, b. p. 242—245°/16 mm. (probably a mixture of stereoisomerides). Reduction of 2:3-diphenylindene (prepared from α-benzylstilbene; Oréchoff, *loc. cit.*) with red phosphorus and hydrogen iodide in boiling acetic acid gives only one stereo-

isomeride of 1:2-diphenylhydrindene, m. p. 123—124.5°, but when reduction is effected with sodium and boiling amyl alcohol, this form is accompanied by a second stereoisomeric form, m. p. 89°.

J. W. BAKER.

#### Stereochemistry of aromatic ring systems.

III. E. BERGMANN (Ber., 1930, 63, [B], 1617—1631; cf. A., 1929, 688).—The supposed  $\beta$ -forms of 9-benzylidene- and 9-anisylidene-fluorene are not isomerides of the  $\alpha$ -compounds, but vinylenes homologues. Whereas hydrogenation of  $\alpha$ -benzylidene-fluorene affords 9-benzylfluorene, m. p. 131—132°, similar treatment of the  $\beta$ -compound [9-cinnamylidene-fluorene] yields 9- $\gamma$ -phenylpropylfluorene, m. p. 75—76°; the last-named compound is prepared synthetically from  $\gamma$ -phenylpropyl bromide and lithium fluorene. Condensation of *p*-methoxycinnamaldehyde with fluorene in presence of sodium ethoxide gives 9-*p*-methoxycinnamylidene-fluorene, m. p. 142°, identical with  $\beta$ -9-anisylidene-fluorene. The production of these compounds is attributed to partial dehydrogenation of ethyl alcohol to acetaldehyde during the prolonged condensation and condensation of the aliphatic with the aromatic aldehyde.

The red 9-tetramethyldiaminodiphenylmethylenefluorene is reduced by sodium and amyl alcohol to 9-tetramethyldiaminodiphenylmethylfluorene, m. p. 237—238°, identical with the "ethylene" of Rodd and Linch.

The author considers that the discussion of the non-planar constitution of aromatic ring systems is not yet closed and cites the following instances. During the action of sodium diphenylmethyl on 9-chlorofluorene a second benzhydrylfluorene, m. p. 187°, is invariably produced in addition to the benzhydrylfluorene, m. p. 217°, and tetraphenylethane. It appears to be completely homogeneous and cannot be composed of mixed crystals of the compound, m. p. 217°, and tetraphenylethane. The condensation of lithium fluorene with phenyldiphenylmethyl chloride or of sodium phenyldiphenylmethyl with 9-chlorofluorene, however, gives a single  $\beta$ -phenyl- $\beta$ -diphenyl- $\alpha$ -diphenylene-ethane, m. p. 253—254°; during the latter condensation the stereoisomeric  $\alpha$ -diphenyldidiphenylethanes, m. p. 245—246° and 202—203°, respectively, are also obtained. Phenyl-diphenylmethyl chloride, m. p. 70—72°, and *p*-phenylbenzhydryl methyl ether, m. p. 80°, are incidentally described. The  $\alpha$ - and  $\beta$ -9-methoxyfluorene-9-carboxylic acids do not appear to be identical, since they differ from one another in crystalline form and electrical conductivity. Differences in the last-named property are not exhibited by the  $\alpha$ - and  $\beta$ -fluorene-9-carboxylic acids, but although the two forms melt separately without softening at 230—232°, a mixture of them softens distinctly at 215°. Further, the varieties differ in crystalline habit and, in solution, the  $\alpha$ -form is much more readily auto-oxidised than the  $\beta$ -variety.

A polymeric form of diphenyl-9-fluorenylcarbinol, m. p. 218—219°, is obtained by very slow crystallisation of the normal variety from light petroleum.

H. WREN.

[Isomerism of 9-fluorene derivatives.] A. KLEGL, F. WENG, and G. WIEST (Ber., 1930, 63,

[B], 1631—1632; cf. this vol., 918).—The identity of " $\beta$ -benzylidene-fluorene" with 9-cinnamylidene-fluorene and of " $\beta$ -anisylidene-fluorene" with 9-*p*-methoxycinnamylidene-fluorene is established.

H. WREN.

Sources of error in organic elementary analysis. VI. Determination of hydrogen; action of copper oxide and lead peroxide. J. LINDNER [with F. HERNLER] (Ber., 1930, 63, [B], 1396—1405; cf. this vol., 726).—The importance of a more accurate determination of hydrogen is emphasised and the conditions which exert influence are discussed. Granular copper oxide does not adsorb significant amounts of water at a red heat, whereas appreciable quantities are retained at 350°. With lead peroxide, the formation of water on heating cannot quite be reduced to zero. With carefully pre-treated specimens the amounts are not quite unimportant, but fall into the background relatively to the adsorption phenomena. Formation of water can be caused even by the combustion of volatile adsorbed organic compounds. Careful purification and intensive desiccation of the peroxide cause a more pronounced effect of adsorption in comparison with contrary influences.

H. WREN.

Experiments with dibenzylidenedihydroanthracene. E. BERGMANN and S. FUJISE (Annalen, 1930, 480, 188—196).—Reduction of 9:10-dibenzylanthracene with sodium and amyl alcohol gives 9:10-dibenzyl-9:10-dihydroanthracene (I), m. p. 118°, also obtained by the successive action of sodium and alcohol on the original hydrocarbon. Decomposition of the product from dibenzylanthracene and lithium with carbon dioxide affords 9:10-dibenzyl-9:10-dihydroanthracene-9:10-dicarboxylic acid, m. p. 280° (decomp.). Bromination of dibenzylanthracene with 2 mols. of bromine gives an impure dibromo-derivative, which when boiled with xylene yields 9:10-dibenzylidene-9:10-dihydroanthracene, m. p. 199—200°. This is converted into I by reduction with sodium and amyl alcohol, or by successive treatment with lithium and alcohol; in the last case, addition of the metal across the double linkings occurs.

Reduction of 9:9-dibenzylanthracene with sodium and amyl alcohol gives 9:9-dibenzyl-9:10-dihydroanthracene, m. p. 178°, but with red phosphorus and hydriodic acid at 130°, 9-benzyl-9:10-dihydroanthracene, m. p. 118° (lit. 110°), results (cf. Hallgarten, A., 1888, 1202, who describes it as the dibenzyl derivative). Benzylidenexanthene and 9:9-diphenyl-10-benzylidene-9:10-dihydroanthracene form normal additive compounds with sodium, decomposed by alcohol to benzylxanthene, m. p. 80°, and 9:9-diphenyl-10-benzyl-9:10-dihydroanthracene, m. p. 192°, respectively.

9-Benzylanthracene, m. p. 133° (lit. 119°), formed as a by-product in the preparation of dibenzylanthracene, is oxidised by chromic oxide in acetic acid first to 9-benzylxanthene and then to anthraquinone and benzoic acid.

H. BURTON.

Phenylurethane anaesthetics. T. H. RIDER (J. Amer. Chem. Soc., 1930, 52, 2583).—The hydrochlorides of the phenylcarbimide derivatives of  $\gamma$ -di-*n*-butylaminopropyl and  $\beta$ -diethylaminoethyl

alcohols have m. p. 123—124° and 138—139°, respectively. These salts produce anaesthetics of longer duration than do the hydrochlorides of the *p*-amino-benzoates of the same alcohols. H. BURTON.

**Nitroamines. I. Nitrophenylnitroamines.** E. MACCIORTA (Gazzetta, 1930, 60, 408—414).—When treated with nitric acid (*d* 1.52) and fuming sulphuric acid (30% SO<sub>3</sub>), while cooled with ice and salt, *m*-nitroaniline gives first the nitrate, which, by anhydri-fication, passes into the nitroamine, this process being continued, as described by Flürscheim and Holmes (A., 1929, 57). The final product thus obtained is not, however, tetranitroaniline but 2:3:4:6-tetranitrophenylnitroamine, NO<sub>2</sub>·NH·C<sub>6</sub>H(NO<sub>2</sub>)<sub>4</sub>, decomposing at 104—105°, which, even when pure, soon decomposes giving tetranitroaniline and nitrous acid. The nitroamine always yields aniline derivatives when treated with chemical reagents, but small quantities of the ammonium salt of 2:4:6-trinitro-3-aminophenyl-nitroamine, decomp. at about 180°, were obtained by treatment with ammonia solution, and of the unstable 2:3:4:6-tetranitrophenylnitroacetamide by the action of acetyl chloride. No nitroamines were obtainable under similar conditions from *o*- and *p*-nitroanilines, which yielded only 2:6-dinitroaniline and 2:4:6-trinitroaniline, respectively; nitration of the latter compound gave only small proportions of its nitrate. It is concluded that absence of the nitro-group from the *meta*-position annuls the stability of the nitroamines and prevents their formation, so that only the nitrate of the base is obtained as final product. Greater facility of substitution in both *ortho*-positions than in the *para*-position seems also indicated.

T. H. POPE.

**Preparation of *o*- and *p*-xenyamines (aminodiphenyls).** G. T. MORGAN and L. P. WALLS.—See B., 1930, 600.

**Azotriphenylcarbinol dyes.** R. N. SEN and A. K. SEN.—See B., 1930, 653.

**Nitridation. I. Introduction. II. Mercuric and bismuth nitrides as nitridising agents.** I. SCHURMAN and W. C. FERNELIUS (J. Amer. Chem. Soc., 1930, 52, 2425—2430).—Details are given for the preparation of bismuth and mercuric nitrides from the corresponding iodides and potassamide in liquid ammonia. Treatment of hydrazobenzene and hydrazo-*p*-toluene with iodine or either of the above nitrides in liquid ammonia gives azobenzene and azo-*p*-toluene, respectively. The reaction with mercuric nitride is: 3(NHPh)<sub>2</sub> + Hg<sub>3</sub>N<sub>2</sub> = 3(NPh)<sub>2</sub> + 3Hg + 2NH<sub>3</sub>. When hydrazobenzene is treated with potassamide or potassium hydroxide in liquid ammonia, a deep reddish-brown coloration is produced owing to alkali metal salt formation. The colour is discharged by the addition of ammonium nitrate. Mercuric nitride does not react with hexamethylenetetramine, amylene, styrene, or azoxybenzene under the above conditions.

H. BURTON.

**Structure of diazo-compounds.** A. ANGELI (Gazzetta, 1930, 60, 352—388).—A summary is given of the numerous investigations carried out during the past few decades by the author and his collaborators on azoxy-derivatives and their relations to diazo-compounds.

T. H. POPE.

**Constitution and reactions of the isomeric diazo-hydrates.** A. HANTZSCH (Ber., 1930, 63, [B], 1270—1283).—A reply to Angeli and others (A., 1929, 548, 1290) and Swientoslawski (*ibid.*, 1290). The structures assigned to the normal and *iso*-diazo-hydrates and diazotates by the authors and by Cambi on the basis of purely chemical experiment and analogy are shown to be untenable. The constitution of tautomeric and isomeric compounds containing inorganic atomic complexes cannot be determined solely by chemical means. The calorimetric observations of Swientoslawski prove only that a single physical method can lead to false conclusions when applied to compounds without regard to their chemical behaviour. The constitution and configuration of the isomeric diazo-hydrates and diazotates remain unaffected. H. WREN.

**Pyrolysis of diazoamino-*p*-toluene.** G. T. MORGAN and L. P. WALLS (J.C.S., 1930, 1502—1509).—To the pyrolytic products of diazoaminobenzene at 150° (Hirsch, A., 1892, i, 1198) azobenzene should be added. A quantitative study of the pyrolysis of diazoamino-*p*-toluene dissolved in *p*-toluidine at 150° (cf. Heusler, A., 1891, i, 555; Hirsch, *loc. cit.*) has been made; the more volatile products are toluene (0.5 mol.) ammonia (0.02 mol.), and nitrogen (0.94 mol.), whilst hydrogen, either free or combined, could not be detected. The less volatile products, obtained by distillation under reduced pressure (b. p. 155—170°/4 mm.) are azo-*p*-toluene, *p*-ditolylamine, and small quantities of 6-amino-3:4'-dimethylazobenzene, m. p. 118° (hydrochloride, m. p. 174°), which is the chief product in the transformation of diazoamino-*p*-toluene by concentrated acid. The considerable quantity of tarry matter which remains consists largely of acid-soluble resins. The main pyrolytic products are nitrogen and toluene; the proportion of aminoditolyis is about 15% of the calculated possible amount. One of the isomeric aminoditolyis (hydrochloride, m. p. 175—177°; hydrochloride monohydrate, m. p. 172°; acetyl derivative, m. p. 169.5—170.5°; azo-β-naphthol derivative, m. p. 188—189.5°) is obtained in very small amount only, and has not been oriented. The more plentiful isomeride is 2-amino-4':5-dimethyldiphenyl (4':5-dimethyl-2-xenyamine), b. p. 165—167°/4 mm. [hydrochloride, 216—226° (decomp.); acetyl derivative, m. p. 104°; azo-β-naphthol derivative, m. p. 179.5°; triazo-compound, oily], converted pyrogenically (cf. Blank, A., 1891, i, 591) into 2:6-dimethylcarbazole, m. p. 224°, identical with the product described as 3:7-dimethylcarbazole obtained by Ullmann (A., 1898, i, 591) from hydrazo-*p*-toluene, and with the product, m. p. 208—209°, described by Borsche, Witte, and Bothe (A., 1908, i, 365); in the preparation of Borsche's product both *r*- (giving a liquid *p*-tolylhydrazone) and *d*-3-methylcyclohexanone (giving a *p*-tolylhydrazone, m. p. 90°) were employed and yielded the same dimethyltetrahydrocarbazole, m. p. 147°. Purified 2:6-dimethylcarbazole gives no blue fluorescence in alcoholic solution (cf. Borsche, *loc. cit.*). A comparison of the properties of carbazole, 2:6-, and 3:6-dimethylcarbazole, m. p. 219° (Taüber and Löwenberg, A., 1891, 834, 1491), in tabular form is given; their picrates have m. p. 187°, 162°, and



192°, respectively, and their 9-nitroso-derivatives, 82°, 113°, and 106°, respectively. C. W. SHOPPEE.

**Mechanism of the rearrangement of diazoaminobenzene into aminoazobenzene.** E. ROSENHAUER (Ber., 1930, 63, [B], 1056—1058).—The observation of Yokojima (A., 1928, 749) that conversion of diazoaminobenzene into aminoazobenzene takes place in the presence of aniline alone could not be confirmed, thus invalidating his conclusions with regard to a transformation hypothesis. Aminoazobenzene or diazoaminobenzene could not be obtained by the action of aniline on *p*-nitrodiazoaminobenzene. Condensation between diazoamino-compound and aniline cannot therefore be assumed. The addition of hydrogen chloride to the imino-group of diazoaminobenzene must be regarded as a preliminary step in the fission into diazonium chloride and aniline, and not as a prelude to its isomerisation. H. WREN.

**Nitration. I. Nitrosation of phenol. II. Nitration of phenol.** S. VIEBEL (Ber., 1930, 63, 1577—1582; 1582—1589).—I. The action of nitrous acid on phenol at 0°, 25°, and 40° has been studied in aqueous solution by addition of phenol to acid, of acid to phenol, and in mixtures of acid and phenol. The total nitrosophenol is determined by titration with titanium trichloride. *o*-Nitrosophenol is removed from another portion of the solution by steam and the residual *p*-nitrosophenol is determined by the same method. It is thus established that *o*-nitrosophenol is actually formed during the process. This is shown qualitatively to be the case also with *o*- and *m*-cresol.

II. The interaction of nitric acid and phenol in aqueous solution has been investigated at 25° under such conditions that the concentration of nitric acid is the only variable factor (all other factors such as temperature and initial concentration of nitrous acid being maintained constant), and so great an excess of acid is used that its concentration may be regarded as constant. Conditions are chosen so that exclusively mononitration occurs. *o*-Nitrophenol is removed from the product by distillation with steam and determined in the distillate by titration with titanium trichloride and with bromine. The residue from the steam distillation is diluted with water to dissolve the *p*-nitrophenol, the mixture is filtered, and the *p*-nitrophenol in the filtrate is determined by bromine. It is found that approximately equal amounts of *o*- and *p*-nitrophenol are obtained by nitration of phenol at 25° with *N*- to 3*N*-nitric acid. The ratio *o/p* appears to increase somewhat with increasing concentration of acid. H. WREN.

**Reactivity of aromatic hydroxyl groups. I.** H. L. BASSETT (J.C.S., 1930, 1313—1315).—The reaction between phenols and acetyl bromide in ethyl acetate solution at 0° has been used to compare the reactivities of various phenols. From the time-titration curves the half-periods of the reactions are obtained; the reciprocals of these half-periods, taking phenol as unity, are: phenol 1, *o*-cresol 0.574, *m*-cresol 1.71, *p*-cresol 2.35, thymol 0.468, carvacrol 0.725. Whilst changes in the concentration of the phenol affect the velocity of the reaction, the concentration of acetyl bromide may be varied within wide limits; the ratio of the half-periods remains unchanged

in solutions of half the concentration of those used. It is suggested that the reaction measured is the breakdown of a first formed additive compound of the phenol and acetyl bromide; this is supported by the effect produced by the addition of a small quantity of water to the reaction mixture, when the formation of phenyl acetate proceeds almost to completion and is followed by a slower hydrolysis. C. W. SHOPPEE.

**Sulphonation of *m*-chlorophenol and some new halogenophenols.** H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 1419—1425).—Sulphonation of *m*-chlorophenol with concentrated sulphuric acid at 15° or 100° gives almost entirely 3-chlorophenol-6-sulphonic acid (*potassium, sodium, ammonium, barium, strontium, lead salts; calcium salt monohydrate*); the solubilities of the salts are in the order Ca>Sr>Ba, and Na>K. By treatment with the theoretical quantity of barium hypochlorite solution, barium 3-chlorophenol-6-sulphonate gives barium 2:3:4-*trichlorophenol-6-sulphonate (dihydrate)*, hydrolysed by 80% sulphuric acid to 2:3:4-*trichlorophenol*, m. p. 79°, from which 2:3:4-*trichloroanisole*, m. p. 69.5°, is obtained by methylation with methyl sulphate. With bromine barium 3-chlorophenol-6-sulphonate in aqueous solution affords 3-chloro-2:4-*dibromophenol-6-sulphonic acid* as the barium salt *dihydrate* (*sodium and potassium salts*); the free acid, but not the salts, is readily hydrolysed to give 3-chloro-2:4-*dibromophenol*, m. p. 88° (direct preparation from 3-chlorophenol, together with some 3-chloro-2:4:6-*tribromophenol*, described), which by nitration in glacial acetic acid with nitric acid (*d* 1.5) yields 3-chloro-2:4-*dibromo-6-nitrophenol*, m. p. 90°, identical with the product obtained by bromination of 3-chloro-6-nitrophenol in glacial acetic acid. 3-Chloro-2:4-*dibromoanisole*, m. p. 92°, by bromination in glacial acetic acid gives 3-chloro-2:4:6-*tribromoanisole*, m. p. 92°, which is also obtained by methylation of the corresponding phenol. Barium 3-chlorophenol-6-sulphonate by treatment with iodine and mercuric oxide in aqueous-alcoholic solution affords the barium salt *tetrahydrate* of 3-chloro-2:4-*diiodophenol-6-sulphonic acid*, m. p. 167° (decomp.), hydrolysed to 3-chloro-2:4-*diiodophenol*, m. p. 111.5°, from which 3-chloro-2:4-*diiodoanisole*, m. p. 105°, is readily obtained.

By treatment with oleum (27% SO<sub>3</sub>) 3-chlorophenol after addition of barium carbonate yields barium 3-chlorophenol-4:6-*disulphonate tetrahydrate*, which with the theoretical quantity of barium hypochlorite solution furnishes barium 2:3-*dichlorophenol-4:6-disulphonate tetrahydrate*, hydrolysed in 70% yield to 2:3-*dichlorophenol*, b. p. 206°, m. p. 58°, directly dibrominated to give 2:3-*dichloro-4:6-dibromophenol*, m. p. 90°; 2:3-*dichloro-4:6-dibromoanisole* has m. p. 82°. 3-Chlorophenol by disulphonation as above, bromination, and treatment of the resulting solution with barium carbonate gives barium 3-chloro-2-bromophenol-4:6-*disulphonate tetrahydrate*, from which a 75% yield of 3-chloro-2-bromophenol, m. p. 55.5°, b. p. 225°, is obtained by hydrolysis; the last-named with methyl sulphate and sodium hydroxide affords 3-chloro-2-bromoanisole, m. p. 50° (cf. A., 1929, 1062). By nitration with nitric acid (*d* 1.5) in ice-cold glacial acetic acid solution 3-chloro-2-bromophenol yields a

mixture of 3-chloro-2-bromo-6-, m. p. 98.5°, and 4-nitrophenol, m. p. 136°, separated by steam distillation, the latter being non-volatile. Iodination of barium 3-chlorophenol-4:6-disulphonate with iodine and mercuric oxide in aqueous-alcoholic solution gives barium 3-chloro-2-iodophenol-4:6-disulphonate tetrahydrate, hydrolysed to 3-chloro-2-iodophenol, m. p. 56°, also obtained by the action of potassium iodide on diazotised 3-chloro-2-aminophenol.

3-Chloro-2:4-dibromo-6-nitrophenol is obtained in two crystalline forms according to which of the two methods, described above, is used for its preparation. Though interconvertible, each form can be crystallised from alcohol without change of habit; it is tentatively suggested that the two forms are an example of Kekulé's *ortho*-isomerism.

The colour reactions of the 3-chlorophenol mono- and di-sulphonic acids and their derivatives with ferric chloride in aqueous solution are briefly described.

C. W. SHOPPEE.

**Bromodi-iodophenols. Symmetrical trihalogeno-compounds.** P. BRENANS and K. YEU (Compt. rend., 1930, 190, 1560—1561).—Bromination in cold acetic acid of 2:4-di-iodophenol (A., 1901, i, 322) gives 6-bromo-2:4-di-iodophenol, m. p. 128° (acetate, m. p. 121°; benzoate, m. p. 118°; ethyl ether, m. p. 76°). 4-Bromo-2:6-di-iodophenol (A., 1928, 631) (benzoate, m. p. 124°) is similarly obtained from 2:6-di-iodophenol.

R. CHILD.

**Bromination of 2-nitro- and 2-acetamidodiphenyl ether.** H. McCOMBIE, W. G. MACMILLAN, and H. A. SCARBOROUGH (J.C.S., 1930, 1202—1208).—2-Nitrodiphenyl ether is brominated in acetic acid solution to 4-bromo-2'-nitrodiphenyl ether, m. p. 72°; both of the foregoing are converted by excess of bromine in diffused light into 2:4-dibromo-2'-nitrodiphenyl ether, m. p. 80° (also obtained by bromination in acetic acid of 2-bromo-2'-nitrodiphenyl ether, b. p. 250°/20 mm., m. p. 54°). Excess of bromine converts all the above and 4-bromo-2-nitrodiphenyl ether, b. p. 210°/15 mm. (which yields 4:4'-dibromo-2-nitrodiphenyl ether, m. p. 94° on monobromination in acetic acid), into 2:4:4'-tribromo-2'-nitrodiphenyl ether, m. p. 102°. The structures of the foregoing mono- and di-bromo-compounds are established by synthesis from appropriate halogenonitrobenzenes and sodium or potassium halogenophenoxides; that of the tribromoderivative follows from its formation.

5-Bromo-2-nitrodiphenyl ether, m. p. 108°, is successively brominated in acetic acid to 4:5'-dibromo-2'-nitrodiphenyl ether, m. p. 99°, and (with excess of bromine in sunlight) to 2:4:4':5'-tetrabromo-2'-nitrodiphenyl ether, m. p. 170°.

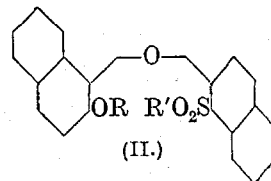
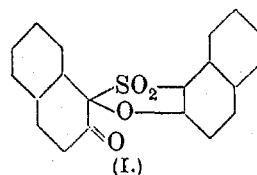
Bromination of 2-acetamidodiphenyl ether in acetic acid affords 5-bromo-2-acetamidodiphenyl ether, m. p. 146° (also obtained by reduction and acetylation of the corresponding nitro-compound, the structure of which is established by synthesis; free amine, m. p. 46°; hydrochloride, m. p. 186°); similarly 2-bromo-2'-acetamidodiphenyl ether, m. p. 95° (from the corresponding nitro-ether; free base, m. p. 60°; diacetyl compound, m. p. 105°), gives 2:5'-dibromo-2'-acetamidodiphenyl ether, m. p. 112°, and 4-bromo-2'-acetamidodiphenyl ether, m. p. 106° (base, b. p. 211°/15 mm.), gives 4:5'-

dibromo-2'-acetamidodiphenyl ether, m. p. 144° (base, m. p. 82°; hydrochloride, m. p. 202°), also obtained by reduction and acetylation of 4:5'-dibromo-2'-nitrodiphenyl ether, the orientation of which is thus established. 2:5'- and 2:4-Dibromo-2'-acetamidodiphenyl ether, m. p. 117° (base, an oil; hydrochloride, m. p. 180°), yield the same 2:4:5'-tribromo-2'-acetamidodiphenyl ether, m. p. 147°. 4:4'-Dibromo-2'-acetamidodiphenyl ether, m. p. 142° (base, m. p. 70°), gives 4:4':5'-tribromo-2'-acetamidodiphenyl ether, m. p. 167° (base, m. p. 120°; hydrochloride, m. p. 222°), and 2:4:4'-tribromo-2'-acetamidodiphenyl ether, m. p. 127° (base, m. p. 83°), gives 2:4:4':5'-tetrabromo-2'-acetamidodiphenyl ether, m. p. 210° (also from 2:4:4':5'-tetrabromo-2'-nitrodiphenyl ether by reduction and acetylation). The acetyl derivative of 4-bromo-2-aminodiphenyl ether, m. p. 54°, could not be crystallised.

The theoretical bearing of the results is discussed.

R. CHILD.

**Dehydro-2-naphtholsulphone.** L. A. WARREN and S. SMILES (J.C.S., 1930, 1327—1331; cf. this vol., 908).—Experiments are described which further elucidate the structures of the dehydro- and *iso*-2-naphtholsulphones derived from 2-naphtholsulphone and their relationship to the corresponding derivatives of 2-naphthol 1-sulphide. Dehydro-2-naphthol-1-sulphone (I), m. p. 245° (preparative details given), by reduction with sodium sulphide yields *iso*-2-naphtholsulphone (II: R and R' = H), which is therefore to be regarded as 2-hydroxy-1:2'-dinaphthyl ether 1'-sulphinic acid, converted by methyl sulphate and sodium hydroxide into the dimethyl ether, m. p. 144° (II: R and R' = Me), also obtained by methylation of



2-hydroxy-1:2'-dinaphthyl ether 1'-methylsulphone and from 2-methoxy-1'-methylthiol-1:2'-dinaphthyl ether by oxidation with hydrogen peroxide in acetic acid solution at 100°. Reduction of I with zinc dust in boiling acetic and hydrochloric acids gave 77% of *iso*-β-naphthol sulphide (i.e., 2-hydroxy-1'-thiol-1:2'-dinaphthyl ether; *loc. cit.*), also obtained from *iso*-2-naphtholsulphone by treatment with zinc and hydrochloric acid in boiling alcohol. Reduction of I with zinc and acetic acid (90% yield) or by sodium amalgam in warm aqueous-alcoholic solution affords 2-hydroxy-1:2'-dinaphthyl ether, m. p. 197°, also obtained from *iso*-2-naphtholsulphone with these reagents; it was identified by conversion into 2-methoxy-1:2'-dinaphthyl ether, m. p. 161°, also obtained by reduction of *iso*-2-naphtholsulphone dimethyl ether with sodium amalgam in aqueous-alcohol.

C. W. SHOPPEE.

**Catalytic partial decomposition of cyclohexanediols with iodine and bromine.** S. SABBETAY and J. BLÉGER (Bull. Soc. chim., 1930, [iv], 47, 463—467).—When distilled below 175° in presence

of iodine or, better, of bromine, 1 : 3- and 1 : 4-*cyclohexanediols* are converted into *cyclohexadiene* and 50—60% of  $\Delta^3$ -*cyclohexenol*, b. p. 160—164°/761 mm. (phenylurethane, m. p. 81°), which probably contains a little  $\Delta^2$ -*cyclohexenol*. A similar dehydration is effected in presence of a few drops of fuming hydrobromic acid. 1 : 2-*cyclohexanediol* in presence of bromine similarly affords an unsaturated distillate, b. p. 150—157°,  $n_D^{20}$  1.4570. R. BRIGHTMAN.

**Conversion of hydroaromatic into aromatic compounds. IV. Influence of the nitro-group in nitrophenyldihydroresorcinols.** L. E. HINKEL and J. F. J. DUFFY (J.C.S., 1930, 1387—1390).—3-Nitrostyryl methyl ketone, m. p. 102°, for which an improved preparation is described, condenses with ethyl malonate to give ethyl *m*-nitrophenyldihydroresorcylate, m. p. 169° (decomp.) (cf. lit.), hydrolysed by 4% aqueous sodium hydroxide to 5-*m*-nitrophenyldihydroresorcinol, m. p. 188° (decomp.). In a similar way 4-nitrostyryl methyl ketone yields 5-*p*-nitrophenyldihydroresorcinol [monohydrate, m. p. 190—191° (decomp.)]. Neither of the nitrophenyldihydroresorcinols reacts with phosphorus trichloride, and phosphoryl chloride is without action on *m*-nitrophenyldihydroresorcinol, but reacts with the *p*-compound in chloroform on the water-bath to give a small quantity of 3 : 5-dichloro-1-*p*-nitrophenyl- $\Delta^{2:4}$ -*cyclohexadiene*, m. p. 81°. Phosphorus pentachloride converts *m*-nitrophenyldihydroresorcinol into 3 : 5-dichloro-1-*m*-nitrophenyl- $\Delta^{2:4}$ -*cyclohexadiene*, m. p. 66—68°, together with a small quantity of 3 : 5-dichloro-3'-nitrodiphenyl, m. p. 162°, reduced by stannous chloride and hydrogen chloride to 3 : 5-dichloro-3'-aminodiphenyl (acetyl derivative, m. p. 168°). The low reactivity of the nitrophenyldihydroresorcinols towards the chlorides of phosphorus is attributed to the recognised electron-affinity of the nitro-group. The effect of the nitrophenyl group on the properties of the dichlorocyclohexadienes is not markedly different from that of the phenyl group. By treatment with 1 mol. of chlorine below 0° in chloroform, 3 : 5-dichloro-1-*m*-nitrophenyl- $\Delta^{2:4}$ -*cyclohexadiene* affords 3 : 5-dichloro-3'-nitrodiphenyl, whilst with excess of chlorine at -10° 2 : 3 : 5(?)-trichloro-3'-nitrodiphenyl, m. p. 116°, is obtained; excess of chlorine at the ordinary temperature yields 3 : 5-dichloro-3'-nitrodiphenyl. C. W. SHOPPEE.

**Derivatives of cresorcinol [2 : 4-dihydroxytoluene].** F. HENRICH and O. FLEISCHMANN (Ber., 1930, 63, [B], 1335—1341).—2 : 4-Dihydroxytoluene is converted by fuming nitric acid in absolute ether at -10° into a mixture of 3-nitro-2 : 4-dihydroxytoluene, m. p. 112°, and 5-nitro-2 : 4-dihydroxytoluene, m. p. 125°, volatile and non-volatile with steam, respectively. The nitro-compounds are reduced by stannous chloride and hydrochloric acid to the corresponding amines. 5-Amino-2 : 4-dihydroxytoluene hydrochloride in absolute alcohol is oxidised by dry air to hydroxydimethylphenoxazone, whereas under similar conditions the free base in an individual experiment gave the indophenol, (OH)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>Me·N:C<sub>6</sub>H<sub>2</sub>Me·O, in good yield. The base is not transformed into the corresponding quinoneimine by silver oxide in ether. 2 : 4-Dihydroxytoluene is converted by methyl

sulphate and sodium hydroxide into the dimethyl ether and a mixture of monomethyl ethers, b. p. 249—250°/743 mm. Nitration of the mixture in ether followed by distillation of the product with steam leads to the isolation of the volatile 3-nitro-4-methoxy-*o*-cresol, m. p. 116° (sodium salt), and the non-volatile 5-nitro-4-methoxy-*o*-cresol, m. p. 184—185°. The preparation of 3-amino-4-methoxy-*o*-cresol, m. p. 155—156° (hydrochloride; sulphate), is described. Treatment of the base with silver oxide in ether appears to yield the quinoneimine, C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>N, m. p. 169—170° after darkening at 80°. 5-Amino-4-methoxy-*o*-cresol, m. p. 215—216°, is converted by silver oxide into 3-methoxy-6-methylbenzoquinone-monoimine, m. p. 146° after darkening at 110°. Oxidation of 5-amino-4-methoxy-*o*-cresol hydrochloride with potassium dichromate and sulphuric acid yields the quinone, C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>, m. p. 173° after darkening at 85°. H. WREN.

**Action of oxygen on 1 : 4-dimethylcyclohexane.** G. CHAVANNE and (Mlle.) E. BODE (Bull. Soc. chim. Belg., 1930, 39, 206—228).—See this vol., 768.

**Manufacture of esters of *O*-arylated or *O*-aralkylated bivalent [dihydric] alcohols.** O. Y. IMRAY. From I. G. FARBENIND. A.-G.—See B., 1930, 603.

**Oxidation of inositol with nitric acid.** O. GELORMINI and N. E. ARTZ (J. Amer. Chem. Soc., 1930, 52, 2483—2494; cf. Maquenne, A., 1887, 459; Contardi, Gazzetta, 1921, 51, 1, 107).—The following compounds have been isolated from the product obtained by oxidising *i*-inositol with nitric acid (*d* 1.5) : hexahydroxybenzene, tetrahydroxy-*p*-benzoquinone (green disodium salt), rhodizonic acid (violet dipotassium salt), and croconic acid (dipotassium salt). Triquinoyl and leuconic acid are also probably formed, but they have not been isolated. Oxidation of the sodium salt of tetrahydroxy-*p*-benzoquinone and potassium rhodizonate affords the corresponding salts of croconic acid; carbon dioxide is produced, and the initial six-membered rings become five-rings.

H. BURTON.

**Action of stannous chloride on aromatic carbinols.** A. WANSCHIEDT and B. MOLDAVSKI (Ber., 1930, 63, [B], 1362—1369).—Addition of stannous chloride in concentrated hydrochloric acid to a solution of carbinols in glacial acetic acid causes conversion into the corresponding chlorides and thence into complex salts [R<sub>3</sub>C]SnCl<sub>3</sub>. The latter substances are frequently stable, particularly in the case of strongly basic carbinols. In other cases they decompose with production of stannic chloride and radicals, which become either dimerised to stable substances or reduced to triarylmethanes. Triphenylcarbinol becomes converted into *p*-benzhydryl-tetraphenylmethane, m. p. 228° (corr.), and triphenylmethane. 9-Phenylfluorenol yields diphenylbis-diphenylene-ethane, m. p. 254°, whilst 9-chloro-9-*p*-anisylfluorene gives di-*p*-anisylbisdiphenylene-ethane, m. p. 229° (corr.). 9- $\alpha$ -Naphthylfluorenol is converted by hydrogen chloride and ether into 9-chloro-9- $\alpha$ -naphthylfluorene, m. p. 149—150° (corr.), and by hydrobromic and glacial acetic acids into 9-bromo-9- $\alpha$ -naphthylfluorene, m. p. 194—195° (corr.).

The last-named compound is converted by molecular silver or copper powder followed by oxygen into *di-α-naphthylfluorenyl peroxide*, m. p. 185–186°, and by stannous chloride into impure bisdiphenylene-*di-α-naphthylethane* and 9-*α-naphthylfluorene*. Xanthhydrol with stannous chloride gives dixanthyl, m. p. 201–202°, whereas 9-phenylxanthenol yields a complex salt.

H. WREN.

**Reduction of triphenylcarbinols.** D. I. ROBERTS and S. T. BOWDEN (Rec. trav. chim., 1930, 49, 665–674).—The rate of reduction of a number of methoxy-substituted triphenylcarbinols to the corresponding triarylmethanes has been investigated by a modification of the method of Kauffmann and Pannwitz (A., 1912, i, 351) using formic acid at 100°. This reduction involves the thermal decomposition of the triaryl-methyl formate first formed, and it is therefore not surprising that reducibility does not run parallel with basicity, which is a measure of the stability of the salts towards hydrolysis. *meta*-Methoxy-groups exert an inhibitory effect.

The following new compounds are described: 2:2':3''-trimethoxytriphenylcarbinol (from methyl *m*-anisate and magnesium *o*-anisyl iodide), m. p. 112°, reduced to 2:2':3''-trimethoxytriphenylmethane, m. p. 97°; 2:2'-dimethoxydiphenylpiperonyl-carbinol (as above, and using methyl piperonylate), m. p. 128°, *-methane*, m. p. 158°.

The basicities of these carbinols confirm the rule of Baeyer and Villiger (A., 1902, i, 380, 769) connecting basicity with number and position of methoxyl groups, and show that it can be extended to include the dioxymethylene ring.

R. CHILD.

**Autocatalysts of the oxidation of adrenaline.** B. KISCH (Biochem. Z., 1930, 220, 84–91).—The production of a red pigment during the oxidation of adrenaline is accelerated by light, by rise of temperature, and decrease of hydrogen-ion concentration and is autocatalysed by some oxidation product of adrenaline itself which can still be detected in dilutions as great as 1 in 10<sup>10</sup>. Solutions of this substance when exposed to light and oxygen or heated for a long time lose their activity. It is adsorbed by animal charcoal and eluted with aqueous alcohol and has no pressor effect on animals, but produces hyperglycemia. Freshly prepared solutions of *p*-benzoquinone in concentrations of 1 in 10<sup>10</sup> also cause acceleration of the oxidation of adrenaline.

P. W. CLUTTERBUCK.

**Catalysis of the oxidation of dihydroxyphenylalanine by "omega" [the autocatalysing oxidation product of adrenaline].** B. KISCH (Biochem. Z., 1930, 220, 92–96).—The spontaneous oxidation of dihydroxyphenylalanine is accelerated by rise of temperature, by decrease of hydrogen-ion concentration, and by light. Addition of "omega" accelerates both in the dark and in faintly acid solution, whereas adrenaline, pyrocatechol, "dopa," and the oxidation products when pyrocatechol and "dopa" are kept in air do not show this action. In absence of oxygen the pigmentation of "dopa" is not obtained. Addition of 0.001*M*-potassium cyanide does not inhibit "omega" catalysis of "dopa" oxidation in acid medium. Heating decreases the autocatalysing

action of "omega." *p*-Benzoquinone (1 in 10<sup>6</sup>) accelerates "dopa" oxidation considerably.

P. W. CLUTTERBUCK.

**Constitution of cholesterol.** XI. E. MONTIGNIE (Bull. Soc. chim., 1930, [iv], 47, 467–469).—Gaseous formaldehyde does not react with cholesterol in ether; in concentrated sulphuric acid (Nastjukov's reaction; A., 1904, i, 801) formaldehyde gives a viscous mass. By addition of sulphuric acid to a solution of cholesterol in ether and formaldehyde the formal, CH<sub>2</sub>(OC<sub>27</sub>H<sub>45</sub>)<sub>2</sub>, m. p. 139° (*bromide*, m. p. 87°), is obtained; this is hydrolysed by dilute hydrochloric acid. When lævulose is used instead of rhamnose in Neuberg's reaction (A., 1906, ii, 497) a bluish-violet coloration is obtained with cholesterol and rose colorations with ergosterol and phyto-sterol; with xylose, cholesterol yields a rose and then a red coloration, and ergosterol a pale rose; similarly with lactose cholesterol gives a red and ergosterol a brownish-red. Phytosterol gives no coloration in either case, and none of the sterols gives colorations when dextrose, arabinose, galactose, or mannitol is used in this test.

R. BRIGHTMAN.

**Preparation and antirachitic activation of derivatives of ergosterol and cholesterol.** D. W. MACCORQUODALE, H. STEENBOCK, and H. ADKINS (J. Amer. Chem. Soc., 1930, 52, 2512–2518).—Hydrolysis of the product formed from ergosterol, bromotetra-acetylglucose, and silver oxide in dry ether with alcoholic potassium hydroxide gives *ergosterol-d-glucoside*, m. p. 308° (decomp.), [α]<sub>D</sub><sup>25</sup> –98.5° in pyridine (*tetra-acetate*, m. p. 167°, [α]<sub>D</sub><sup>25</sup> –43° in chloroform). *Cholesteryl hippurate*, m. p. 153–154°, [α]<sub>D</sub><sup>25</sup> –30.5° in chloroform, and *ergosteryl hippurate*, m. p. 166–167°, [α]<sub>D</sub><sup>25</sup> –67.5° in chloroform, are prepared from the sterols and hippuryl chloride in chloroform. The above ergosterol derivatives are activated by exposure to ultra-violet light, although to a smaller degree than ergosterol. *α*-Ergosterol and its acetate are probably activated, but *isoergosterol* and its acetate, *cholesterol-d-glucoside*, and *cholesteryl hippurate* are not.

When cholesterol is shaken with acetbromamide in a mixture of chloroform and water, *cholesterol bromohydrin*, C<sub>27</sub>H<sub>47</sub>O<sub>2</sub>Br, m. p. about 85° (all m. p. except this are corr.), is produced. Similar treatment of ergosterol causes extensive decomposition.

H. BURTON.

**Existence of optically active cinnamic acid.** A. MCKENZIE and A. G. MITCHELL (Biochem. Z., 1930, 221, 1–5).—No evidence could be obtained for the existence of optically active modifications of cinnamic acid.

P. W. CLUTTERBUCK.

***α*-Phenylethylallylacetic acid and its cyclisation to a tetrahydronaphthalene derivative.** Preparation of 1:4-dimethylnaphthalene. G. DARZENS (Compt. rend., 1930, 190, 1562–1564; cf. A., 1927, 242; this vol., 1037).—Ethyl *α*-phenylethylmalonate, b. p. 146–148°/6 mm. (Fischer and Schmitz, A., 1906, i, 182, 584, give 185–187°/24 mm.; Kohler, A., 1905, i, 701, 230–235°/15 mm.), is converted by the action of allyl bromide on its sodium derivative into *ethyl α-phenylethylallylmalonate*, b. p. 174–176°/12 mm.; the corresponding

acid loses carbon dioxide at 150—160°, and on distillation yields  $\alpha$ -phenylethylallylacetic acid ( $\beta$ -phenyl- $\Delta^4$ -hexene- $\gamma$ -carboxylic acid), not isolable, and the isomeric  $\alpha$ -( $\alpha$ -phenylethyl)- $\gamma$ -valerolactone, b. p. 126—128°. The latter on prolonged warming with 64% sulphuric acid (cf. benzylvalerolactone, *infra*) is isomerised to 1:4-dimethyl-1:2:3:4-tetrahydro-2-naphthoic acid, viscous, b. p. 160—165°/8 mm., dehydrogenated with sulphur to 1:4-dimethyl-2-naphthoic acid, m. p. 167°. Decarboxylation of this with lime affords 1:4-dimethylnaphthalene (picrate, m. p. 139—140°) (Cannizzaro, A., 1883, 79).

R. CHILD.

Metallic compounds of the enolic forms of monocarbonyl compounds. **XI. Condensation reactions of ethyl potassiophenylacetate.** H. SCHEIBLER, A. EMDEN, and R. NEUBNER. **XII. Substitution reactions of ethyl potassiophenylacetate.** H. SCHEIBLER, A. EMDEN, and W. KRABBE (Ber., 1930, 63, [B], 1557—1562, 1562—1573; cf. A., 1927, 1167).—**XI.** Ethyl acetate reacts with an ethereal suspension of ethyl potassiophenylacetate to form ethyl  $\alpha$ -phenylacetoacetate, whereas ethyl benzoate affords ethyl  $\alpha$ -phenylbenzoylacetate, m. p. 89—90°. Ethyl potassiophenylacetate and ethyl crotonate yield ethyl  $\alpha$ -phenyl- $\beta$ -methylglutarate, m. p. 140° (corresponding acid), and ethyl  $\alpha$ - $\gamma$ -diphenylacetoacetate, m. p. 79°; the intermediate production of a tetramethylene derivative is assumed. Similarly, ethyl  $\alpha$ -phenyl- $\beta$ - $\gamma$ -dimethylglutarate, m. p. 140·5°, is derived from ethyl tiglate. Ethyl crotonate does not condense with ethyl benzoate in presence of sodium ethoxide; this reagent causes auto-condensation of the crotonate to ethyl dicrotonate, hydrolysed to dicrotonic [ $\beta$ -methyl- $\alpha$ -ethylideneglutaric] acid, m. p. 128—129°. Ethyl tiglate is unaffected by sodium ethoxide.

**XII.** Benzyl chloride converts ethyl potassiophenylacetate suspended in ether into ethyl  $\alpha$ - $\beta$ -diphenylpropionate, whilst ethyl chloroacetate affords ethyl phenylsuccinate. In each case, *C*-substitution is exclusively observed. With acid chlorides, however, the reaction is not homogeneous. From acetyl chloride and ethyl potassiophenylacetate, ethyl  $\alpha$ -phenylacetoacetate is isolated, identified as the phenylbenzylhydrazone and by hydrolysis to phenylacetic acid. The action of benzoyl chloride on ethyl potassiophenylacetate followed by treatment of the product with ether gives phenylketen benzoyl ethylacetal, CHPh:C(OEt)·OBz, m. p. 103°. It does not react with phenylhydrazine in boiling, glacial acetic acid. It is converted by alcoholic potassium hydroxide into potassium benzoate and phenylacetate and by bromine into ethyl  $\alpha$ -bromophenylacetate and benzoyl bromide. It is isomerised by sodium ethoxide in boiling benzene into ethyl phenylbenzoylacetate. Ethyl  $\alpha$ -phenylbenzoylacetate, m. p. 88—90° (phenylhydrazone, m. p. 194—196°), is isolated from the filtrate from the acetal (see above); it is hydrolysed to deoxybenzoin and brominated to ethyl  $\alpha$ -bromo- $\alpha$ -phenylbenzoylacetate. The mother-liquors from the isolation of the ester yield deoxybenzoin and the benzoyl derivative of the enolic form of  $\beta$ -hydroxy- $\beta$ -benzylidene- $\alpha$ -phenylpropiolactone,

CHPh:C(O)  
CPh C·OBz, m. p. 202° (corr.), also

prepared by heating the phenylketen acetal with copper-bronze at 300—305°. It is hydrolysed to benzoic and phenylacetic acids. H. WREN.

**Salts of nitriles. IV. Sodio- $\alpha$ -phenylbutyronitrile.** M. M. RISING and E. W. LOWE (J. Amer. Chem. Soc., 1930, 52, 2524—2527).—Sodio- $\alpha$ -phenylbutyronitrile (corresponding *potassio*-derivative), sodium cyanide, and propylbenzene are obtained from sodium and  $\alpha$ -phenylbutyronitrile in dry ether in an atmosphere of nitrogen:  $2\text{CHEtPh}\cdot\text{CN} + 2\text{Na} = [\text{C}(\text{EtPh})\cdot\text{C}\cdot\text{N}]\text{Na} + \text{NaCN} + \text{Ph}\cdot\text{Pr}$  (cf. this vol., 772). Ethereal solutions of the sodio-derivative decompose slowly, forming sodium cyanide; exposure of the salt to air causes spontaneous ignition. Treatment of an ethereal solution of the salt with ethyl iodide yields  $\alpha$ -phenyl- $\alpha$ -ethylbutyronitrile, *C*-alkylation taking place. H. BURTON.

**Isomerisation of benzylvalerolactone to methyl-tetrahydronaphthalenecarboxylic acid.** G. DARZENS (Compt. rend., 1930, 190, 1305—1306).—Contrary to a previous statement (A., 1927, 40),  $\alpha$ -benzylvalero- $\gamma$ -lactone (1 part) is converted by heating with 64·5% sulphuric acid at 120—125° for 8 days into 1-methyl-1:2:3:4-tetrahydronaphthalene-3-carboxylic acid. The latter is directly produced in quantitative yield from  $\beta$ -phenyl- $\alpha$ -allylpropionic acid (cf. A., 1926, 1239). A. I. VOGEL.

**4-Sulpho-3-hydroxybenzoic acid.** M. S. SHAH (J.C.S., 1930, 1293—1301).—4-Sulpho-3-hydroxybenzoic acid (I) (hydrate +  $2\frac{1}{2}\text{H}_2\text{O}$ , m. p. 206°, giving by desiccation a monohydrate, m. p. 213°: sodium hydrogen salt +  $1\frac{1}{2}\text{H}_2\text{O}$ , potassium hydrogen salt +  $\text{H}_2\text{O}$ , and ammonium hydrogen salt) obtained by an improved method from *m*-hydroxybenzoic acid (Barth, Annalen, 1868, 148, 38; A., 1871, 829), and 4-sulpho-3-methoxybenzoic acid (II) (dihydrate, m. p. 228°, potassium hydrogen salt +  $\text{H}_2\text{O}$ , sodium hydrogen salt, and barium salt +  $4\text{H}_2\text{O}$ ), prepared from I by methylation with methyl sulphate, by fusion with potassium hydroxide give protocatechuic acid only (cf. Barth, *loc. cit.*).

The potassium hydrogen salt of the acid II with phosphorus pentachloride at 100° affords 4-chlorosulphonyl-3-methoxybenzoyl chloride, m. p. 87°, slowly hydrolysed by cold water to 4-chlorosulphonyl-3-methoxybenzoic acid (III), m. p. 214°, and quantitatively converted by heating with ammonia (*d* 0·88) into 4-sulphonamido-3-methoxybenzamide (IV), m. p. 255°, hydrolysed by hot concentrated hydrochloric acid to 4-sulphonamido-3-methoxybenzoic acid (V), m. p. 290° (decomp.). The substance IV appears to be identical with that described by Haworth and Lapworth (J.C.S., 1923, 123, 2982; A., 1924, i, 848) as 4-sulphonamido-3-methoxybenzoic acid. Repetition of the preparation of these authors has given products identical with IV and V.

The position of the sulphonic group at 4 was confirmed by two methods: (a) by reduction with tin and hydrochloric acid, III gave 4-thiol-3-methoxybenzoic acid (monothiovanillic acid), m. p. 180°, converted by methylation into 4-methylthiol-3-methoxybenzoic acid, m. p. 193°, which by oxidation with alkaline permanganate yielded 2-methoxyphenylmethylsulphone-4-carboxylic acid, m. p. 227°; (b) 3-methoxytoluene-4-sulphinic acid, m. p. 111°, prepared by the

method of Haworth and Lapworth, was oxidised as the barium salt with 1% barium permanganate solution to give, after treatment with potassium carbonate, potassium hydrogen 4-sulpho-3-methoxybenzoate, from which products identical with IV and V were obtained, whilst by reduction by Gattermann's method the sulphinic acid afforded 4-thiol-3-methoxytoluene, b. p. 254° (lead derivative; benzoyl derivative, m. p. 76°), methylated to give 4-methylthiol-3-methoxytoluene, b. p. 269—270°, converted by hot 5% alkaline permanganate into the foregoing sulphone, m. p. 227°.

The acid III by reduction with zinc dust and hydrochloric acid in the cold, followed by treatment with solid ferric chloride in the presence of hydrochloric acid, gives 3-methoxybenzoic acid 4-disulphide, m. p. 270°; 4-thiol-3-methoxytoluene by oxidation with iodine in potassium iodide solution in the presence of sodium hydroxide furnishes 3-methoxytoluene 4-disulphide, m. p. 83°. By oxidation with 5% potassium permanganate, 3-methoxytoluene-4-sulphonamide yields 4-sulphonamido-3-methoxybenzoic acid.

C. W. SHOPPEE.

**Manufacture of *o*-(aminoaroyl)benzoic acids and inner anhydrides thereof.** I. G. FARBERIND. A.-G.—See B., 1930, 603.

**Manufacture of [6-amino-]derivatives of 2:3-hydroxynaphthoic acid.** O. Y. IMRAY. From I. G. FARBERIND. A.-G.—See B., 1930, 604.

**Arylsulphonyl derivatives of [amides and imides of] dibasic acids.** T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, 52, 2531—2533).—When phthalic anhydride is heated with arylsulphonamides and phosphoryl chloride at 100°, *N*-arylsulphonphthalimides are produced. The following are thus prepared: benzenesulphon-, *p*-bromobenzenesulphon-, m. p. 246°; *o*- and *p*-toluenesulphon-, and 3-nitro-*p*-toluenesulphon-phthalimides. Phthalyl and succinyl chlorides react with sulphonamides at 150—200° (or in boiling toluene) (cf. this vol., 213), forming imides. The following are new: *N*-benzenesulphon-, m. p. 161°; *N*-*p*-bromobenzenesulphon-, m. p. 181°; *N*-*o*- and -*p*-toluenesulphon-, m. p. 136° and 184°, respectively; *N*-3-nitro-*p*-toluenesulphon-, m. p. 212—213°, and *N*-naphthalene-2-sulphon-succinimides, m. p. 175—176°, and naphthalene-2-sulphonphthalimide, m. p. 216°. Succinic anhydride and sulphonamides react in presence of phosphoryl chloride forming succin-sulphonamides, except with *p*-toluenesulphonamide (the succinimide derivative is produced in this case). Succin-benzenesulphonamide, m. p. 235—237°; *p*-bromobenzenesulphonamide, m. p. 231°; *o*-toluenesulphonamide, m. p. 231—232°, and 3-nitro-*p*-toluenesulphonamide, m. p. 236°, are described.

Maleicbenzenesulphonamide, m. p. 258°, is prepared from maleic acid and benzenesulphonamide in presence of phosphoryl chloride at 100°. H. BURTON.

**Syntheses of lactones resembling santonin.** H. BERGS (Ber., 1930, 63, [B], 1285—1298).— $\beta$ -Phenylethylmalonic acid is readily converted by bromine in ether at 30° into bromo- $\beta$ -phenylethylmalonic acid, m. p. about 158° (decomp.), which passes at 160—165° into  $\alpha$ -bromo- $\gamma$ -phenyl-*n*-butyric acid. It is converted through the chloride, b. p. 140—145°/14 mm. (slight decomp.), into 2-bromo-1-keto-1:2:3:4-

tetrahydronaphthalene (oxime, m. p. 137°), which is more readily prepared by bromination of homogeneous 1-keto-1:2:3:4-tetrahydronaphthalene in glacial acetic acid. Treatment of the bromo-ketone with ethyl sodiomalonate in ether and subsequent hydrolysis affords 1-ketotetrahydronaphthalene-2-malonic acid, m. p. 168° (calcium and barium salts), converted at 170° into 1-keto-1:2:3:4-tetrahydronaphthalene-2-acetic acid, m. p. 109—110°.

Ethyl  $\beta$ -phenylethylmalonate and ethyl chloroacetate in presence of alcoholic sodium ethoxide afford ethyl  $\delta$ -phenylbutane- $\alpha\beta$ -tricarboxylate, b. p. 206—211°/12 mm., obtained less advantageously from phenylethyl bromide or chloride and ethyl ethanetricarboxylate. Hydrolysis of the ester gives  $\delta$ -phenylbutane- $\alpha\beta\beta$ -tricarboxylic acid, m. p. about 95° (sodium, calcium, and barium salts), transformed at 135° into  $\beta$ -phenylethylsuccinic acid, m. p. 136° (*p*-toluidide, m. p. 146°). Attempted ring closure of the acid by sulphuric acid or of its anhydride or chloride with aluminium chloride did not proceed satisfactorily.

Ethyl 1-keto-1:2:3:4-tetrahydronaphthalene-2-carboxylate, sodium ethoxide, and ethyl chloroacetate yield ethyl 1-keto-1:2:3:4-tetrahydronaphthalene-2-carboxylate-2-acetate, b. p. 205—210°/12 mm. (slight decomp.), hydrolysed by boiling aqueous sodium hydroxide to 1-ketotetrahydronaphthalene-2-acetic acid, m. p. 109—110°. Analogously, ethyl  $\alpha$ -bromopropionate affords a non-crystalline ester which decomposes when distilled and is hydrolysed to a mixture of 1-keto-1:2:3:4-tetrahydronaphthalene-2-carboxylic-2- $\alpha$ -propionic acid, m. p. 135.5° (decomp.) (sodium salt sparingly soluble in water), and 1-keto-1:2:3:4-tetrahydronaphthalene-2- $\alpha$ -propionic acid, m. p. 135°. The dibasic acid is very stable towards alkali, but passes into 1-ketotetrahydronaphthalene when boiled alone or with acidified water or alcohol. Ethyl  $\alpha$ -bromo-*n*-butyrate appears to yield little dicarboxylic acid, the main product being the mixture of racemic monocarboxylic acids of which 1-keto-1:2:3:4-tetrahydronaphthalene-2- $\alpha$ -*n*-butyric acid, m. p. 153—154°, is described. 1-Keto-1:2:3:4-tetrahydronaphthalene-2-phenylacetic acid, m. p. 155—156°, is obtained by use of ethyl  $\alpha$ -bromophenylacetate. Reduction of the respective acids or their salts by sodium amalgam in aqueous solution affords 1-hydroxy-1:2:3:4-tetrahydronaphthalene-2-acetolactone, m. p. 104—105°, 2-propionolactone, m. p. 97° (which with alcoholic potassium hydroxide give the red colour characteristic of santonin), 2- $\alpha$ -*n*-butyrolactone, m. p. 99—100°, and 2-phenylacetolactone, m. p. 134—135°. H. WREN.

**Monophenyl ethers of glyceric acid.** C. F. KOELSCH (J. Amer. Chem. Soc., 1930, 52, 2430—2436).— $\beta$ -Chloro- $\alpha$ -hydroxypropionic acid and sodium phenoxide react in aqueous solution forming mainly  $\alpha$ -hydroxy- $\beta$ -phenoxypropionic acid, m. p. 157.5—159° (silver salt; methyl ester, b. p. 168—170°/17 mm.,  $d_{20}^{25}$  1.1934,  $n_D^{20}$  1.5190; ethyl ester, b. p. 173—175°/17 mm., m. p. 71—72°; acid amide, m. p. 149—150°; anilide, m. p. 122—123°), together with 1% of  $\beta$ -hydroxy- $\alpha$ -phenoxypropionic acid, m. p. 107—109° (silver salt; methyl ester, b. p. 168—169°/14 mm.,  $d_{20}^{25}$  1.1966,  $n_D^{20}$  1.5213; ethyl ester, b. p. 174—175°/16 mm.,  $d_{20}^{25}$  1.1545,



$n_D^{20}$  1.5117; acid *amide*, m. p. 137—139°; *anilide*, m. p. 129—131° after sintering at 122°). Both the above acids are converted by hydriodic acid ( $d$  1.96) at 120—125° into a mixture of phenol and  $\beta$ -iodopropionic acid. The initial reaction between the chlorohydroxy-acid and the phenoxide is probably the formation of  $\alpha\beta$ -oxidopropionic acid; addition of phenol then occurs in two ways.

Ethyl formate and phenoxyacetate condense in presence of sodium and ether yielding *ethyl β-hydroxy-α-phenoxyacrylate*, b. p. 148—150°/11 mm.,  $d_{25}^{25}$  1.1637,  $n_D^{25}$  1.5210 (*benzoate*, m. p. 76—77°). This is reduced by hydrogen in presence of a nickel catalyst and alcohol at 100°/150 atm. to *ethyl β-hydroxy-α-phenoxypropionate*. Elimination of phenol occurs when the unsaturated ester is reduced with zinc dust or amalgamated zinc and acetic acid, or aluminium amalgam in ether. *Methyl*, b. p. 153—154°/16 mm.,  $d_{25}^{25}$  1.2177,  $n_D^{25}$  1.5166, and *ethyl α-chloro-β-phenoxypropionate*, b. p. 165—167°/16 mm.,  $d_{25}^{25}$  1.1812,  $n_D^{25}$  1.5091, are prepared from the corresponding α-hydroxy-esters by Darzens' method. Ethyl β-phenoxypropionate is obtained when the α-chloro-ester is treated with zinc dust and a small amount of copper carbonate in alcoholic acetic acid.

H. BURTON.

**Preparation of depsides with the aid of acid azides.** R. O. PEPE (J. pr. Chem., 1930, [ii], 126, 241—245).—Various phenolic esters of substituted gallic acids have been prepared by the action of the phenol on the acid azide. Thus methyl trimethoxybenzoate is converted by boiling with hydrazine hydrate into its *hydrazide*, m. p. 159°, which with sodium nitrite in 0.4*N*-nitric acid solution affords the *azide*, m. p. 85°. The latter reacts in acetone with a solution of the appropriate phenol in 3*N*-sodium hydroxide to give *phenyl trimethoxybenzoate*, m. p. 103°, *quinol trimethoxybenzoate*, m. p. 218°, and *p*-*trimethoxybenzoyloxybenzoic acid*, m. p. 210°, in 65, 50, and 70% yields, respectively. The hydrazide of gallic acid forms a *compound*, m. p. 206°, with acetone.

Two isomeric *p*-benzoquinonedithioglycollic acids. E. GEBAUER-FÜLNEGG and H. JARSCH (J. Amer. Chem. Soc., 1930, 52, 2451—2454).—*p*-Benzoquinone and thioglycollic acid react in chloroform solution forming a mixture of *p*-benzoquinone-2:3-dithioglycollic acid, violet-black, m. p. 205°, and *p*-benzoquinone-2:5(6?)-dithioglycollic acid (+H<sub>2</sub>O), violet-black, anhydrous, red and brown modifications, m. p. 171°. When the 2:5-acid is heated with an excess of chlorosulphonic acid at 50—70°, a violet thioindigoid dye is produced; this dyes wool and cotton (vat) with a greenish-blue shade. The 2:3-acid does not give a dye with chlorosulphonic acid. H. BURTON.

**Scymnol.** A. WINDAUS, W. BERGMANN, and G. KÖNIG (Z. physiol. Chem., 1930, **189**, 148—154).—Scymnol,  $C_{27}H_{46}O_5$ , crystallised from aqueous acetone has m. p.  $115^\circ$  [contains water of crystallisation; from ethyl acetate, m. p.  $187^\circ$  (anhydrous)]. With acetic anhydride in pyridine it forms *tetra-acetylscymnol*, m. p.  $148^\circ$ . With hydrogen chloride in acetone it gives a *hydrochloride*, m. p.  $196^\circ$ , with hydrochloric acid a second *hydrochloride*, m. p.  $126^\circ$ , containing water of

crystallisation. Oxidised with chromic anhydride in acetic acid it yields an *acid*,  $C_{27}H_{38}O_6$ , m. p.  $236^\circ$ , which with hydroxylamine gives a *trioxime*, decomp.  $240-250^\circ$ . When heated at  $180^\circ$  with hydriodic acid, scymnol gives an oily *hydrocarbon*, apparently  $C_{27}H_{46}$ .

J. H. BIRKINSHAW.

Graphite and graphitic acid. H. THIELE.—  
See this vol., 875.

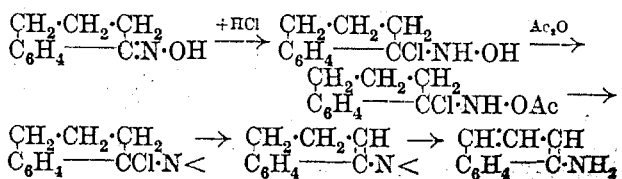
**Swelling of graphite and formation of graphitic acid.** U. HOFMANN and A. FRENZEL.—See this vol., 875.

Decomposition of divinyl [ethylene] glycol by various catalysts:  $\Delta^1$ -cyclopentene-1-aldehyde. URION (Compt. rend., 1930, **190**, 1512—1514).—When the vapour of  $\Delta^{\alpha}$ -hexadiene- $\gamma\delta$ -diol is passed over alumina at 280°,  $\Delta^1$ -cyclopentene-1-aldehyde, b. p. 146°/756 mm., 48°/11 mm., m. p. about -32°,  $d_4^{20}$  0.970,  $n_D^{20}$  1.4828 (p-nitrophenylhydrazone, m. p. 198°), is obtained in 60% yield. Oxidation of the aldehyde with silver oxide gives  $\Delta^1$ -cyclopentene-1-carboxylic acid, b. p. 210°/760 mm., m. p. 121° (dibromide, m. p. 133°), oxidised by potassium permanganate to glutaric acid. Reaction probably occurs by way of the intermediate  $\Delta^{\alpha}$ -hexadiene- $\alpha\zeta$ -diol (the dienol form of adipic aldehyde). The recovered glycol from an experiment with a pumice catalyst contains a small amount of adipic aldehyde, indicating the above mechanism to be correct. H. BURTON.

Photochemical reactions among derivatives of *o*-nitrobenzylideneacetals. V. Tri-*o*-nitrobenzylidenesorbitol. I. TANASESCU and E. MACOVSKY (Bull. Soc. chim., 1930, [iv], 47, 457—463).— Sorbitol and *o*-nitrobenzaldehyde in presence of 75% sulphuric acid yield two isomeric forms of tri-*o*-nitrobenzylidenesorbitol, m. p. 142—146° and 212—215°; the isomeride, m. p. 142—146°, is converted into the isomeride, m. p. 212—215°, by prolonged boiling. A structure is suggested in which the acetalisation is effected between two adjacent *trans*-hydroxyl groups. On insolation, either in benzene or in chloroform, both isomerides are converted into the same dioximinoderivative, m. p. 144°, which yields a *dibenzoate*, m. p. 124° (decomp.), and on hydrolysis with nitric acid and addition of acetone yields an indigo. The isomeride, m. p. 142—146°, isomerises much more rapidly than the isomeride, m. p. 212—215°, to the dioximinoderivative.

R. BRIGHTMAN.

**Oxime transformations in the ketotetrahydronaphthalene series.** G. SCHROETER [with A. GLUSCHKE, S. GÖTZKY, J. HUANG, G. IRMISCH, E. LAYES, O. SCHRADER, and G. STIER] (Ber., 1930, **63**, [B], 1308—1329; cf. A., 1909, i, 617, 773; 1911, i, 505).—The conversion of oximes or oxime acetates of 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalenes into naphthylamines is considered to occur in accordance with the scheme :



If a substituent is present in the 5 or 8 position the change is replaced by a Beckmann re-arrangement involving the production of a lactam; the intermediate production of a "gap molecule" with univalent nitrogen atom is again postulated. In the case of the arylsulphonyl derivatives of the oximes, the Beckmann re-arrangement is also observed, the difference in behaviour of the acetates and arylsulphonates being attributed to the widely differing strengths of the acids.

1-Oximino-1:2:3:4-tetrahydronaphthalene is converted by hydrogen chloride in presence of acetic anhydride and glacial acetic acid into a mixture of  $\alpha$ -naphthylamine and acet- $\alpha$ -naphthalide. 1-Keto-1:2:3:4-tetrahydronaphthalene is transformed by a mixture of nitric and sulphuric acids into 7-nitro-, m. p. 106°, and 5-nitro-1-keto-1:2:3:4-tetrahydronaphthalene, m. p. 102.5°. The oxime, m. p. 150° (acetate, m. p. 115°), of the former compound is transformed into 7-nitro- $\alpha$ -naphthylamine, m. p. 133—134° (hydrochloride), oriented by conversion into 1:7-naphthylendiamine, m. p. 117° (diacetyl derivative, m. p. 213°). The oxime, m. p. 170°, of the latter compound yields an acetate, m. p. 115°, transformed into 5-nitro- $\alpha$ -naphthylamine and 5-nitro-1-acetamidonaphthalene, m. p. 218°. Chlorination of tetrahydronaphthalene and oxidation of the product gives a mixture of much 6-chloro-1-ketotetrahydronaphthalene, m. p. 30—31°, and little 7-chloro-1-ketotetrahydronaphthalene, m. p. 96—97°. The oxime, m. p. 145°, of the 6-chloro-compound (or its acetate, m. p. 85—87°) is converted into 6-chloro- $\alpha$ -naphthylamine, m. p. 63—64° (hydrochloride), oriented by conversion into 1:6-dichloronaphthalene. The oxime acetate, m. p. 101—102° (oxime, m. p. 120°), of the 7-chloro-compound yields 7-chloro- $\alpha$ -naphthylamine. From chlorotetralone mixtures a third chloroketotetrahydronaphthalene, m. p. 65—67° (oxime, m. p. 121°; oxime acetate, m. p. 133—134°), has been isolated, yielding a chloro-naphthylamine, m. p. 71—71.5°. 6-Methoxy-1-keto-1:2:3:4-tetrahydronaphthalene, m. p. 80°, yields an oxime, m. p. 139—140°, and an oxime acetate, m. p. 92°, transformed into 1-acetamido-6-methoxynaphthalene, m. p. 140—141°. 1-Oximino-octahydrophenanthrene is converted into 1-amino-5:6:7:8-tetrahydrophenanthrene, m. p. 112—113° (hydrochloride; sulphate; acetyl derivatives, m. p. 183.5°). Diazotisation and treatment with water or, preferably, hydrolysis with hydrochloric acid converts the amine into 1-hydroxy-5:6:7:8-tetrahydrophenanthrene, m. p. 125—126°. 1-Methoxy-5:6:7:8-tetrahydrophenanthrene, b. p. 212°/15 mm., m. p. 49—50° (picrate, m. p. 149—150°), is dehydrogenated by sulphur to 1-methoxyphenanthrene, m. p. 104°. 1-Keto-octahydrophenanthrene is transformed successively into its 9-nitro-derivative, m. p. 165°, and its oxime, m. p. 195—196°. The acetate, m. p. 172—173°, of the last-named compound is converted into 9-nitro-1-aminotetrahydrophenanthrene, m. p. 176° (hydrochloride, decomp. 224—227°).

1-Keto-5:8-dimethyl-1:2:3:4-tetrahydronaphthalene, m. p. 23—34°, from  $\gamma$ -2:5-dimethylphenyl-*n*-butyryl chloride, yields an oxime, m. p. 143—144°, and oxime acetate, m. p. 60—61.5°, which is converted into  $\gamma$ -6-amino-2:5-dimethylphenyl-*n*-butyrolactam,

$\text{C}_6\text{H}_2\text{Me}_2 \begin{smallmatrix} \text{CH}_2\text{---CH}_2 \\ \text{NH---CO} \end{smallmatrix} \text{CH}_2$ , m. p. 158—160°, hydrolysed to  $\gamma$ -6-amino-2:5-dimethylphenyl-*n*-butyric acid, m. p. 124—124.5°. 4-Oximino-octahydrophenanthrene acetate, m. p. 49—50° (corresponding oxime, m. p. 167—169°), gives 1-aminotetrahydronaphthalene-2-*n*-butyrolactone (see later). 4-Keto-10-methoxyoctahydrophenanthrene, m. p. 58°, is transformed successively into the corresponding oxime, m. p. 144°, oxime acetate, m. p. 132°, and 4-amino-2-methoxytetrahydronaphthalene-3-butyrolactam, m. p. 170—171° [4-amino-2-methoxytetrahydronaphthalene-3-*n*-butyric acid, m. p. 145—146°, and its hydrochloride, m. p. 210° (decomp.)]. 1-Oximino-tetrahydronaphthalene is converted by *p*-toluenesulphonyl chloride in acetone into the oxime hydrochloride, m. p. 169—170° (decomp.), and the *p*-toluenesulphonyl derivative, m. p. 98°. The last-named compound passes when warmed with the requisite alcohol into methyl or ethyl  $\gamma$ -o-aminophenyl-*n*-butyrate *p*-toluenesulphonate, m. p. 141—142° and 115—116°, respectively, whereas with phenol it affords the lactim ether salt,

$\text{CH}_2 \begin{smallmatrix} \text{C}_6\text{H}_4\text{---N} \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix} \text{C} \cdot \text{OPh} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ , m. p. 172° (free ether, m. p. 71—72°).  $\gamma$ -o-Aminophenyl-*n*-butyric acid, m. p. 125—126°, its hydrochloride, m. p. 200° (decomp.), *p*-toluenesulphonate, m. p. 177—178°, sulphate, and  $\gamma$ -o-aminophenylbutyrolactam, m. p. 139—140°, are described. 1-Oximino-6-methoxy-1:2:3:4-tetrahydronaphthalene *p*-toluenesulphonate, m. p. 140° (corresponding hydrochloride, m. p. 178°), affords methyl  $\gamma$ -2-amino-5-methoxyphenyl-*n*-butyrate *p*-toluenesulphonate, m. p. 148.5°, whence  $\gamma$ -2-amino-5-methoxyphenyl-*n*-butyric acid, m. p. 128°, and 2-amino-5-methoxyphenyl-*n*-butyrolactam, m. p. 144—146°. The conversion of 1-oximino-5:8-dimethyltetrahydronaphthalene *p*-toluenesulphonate into  $\gamma$ -6-amino-2:5-dimethylphenyl-*n*-butyric acid (see above) is described. 1-Oximino-octahydroanthracene *p*-toluenesulphonate, m. p. 146—147°, yields methyl 6-aminotetrahydronaphthyl-7-butyrate *p*-toluenesulphonate, m. p. 179—180° [free ester, m. p. 60—61°, and its sulphate, m. p. 174° (decomp.)], whence 6-aminotetrahydronaphthyl-7-butyric acid, m. p. 106—107° [sulphate, m. p. 167—168° (decomp.)], and aminotetrahydronaphthylbutyrolactam, m. p. 208—209°. Diazotisation of the amino-acid results in the formation of 6-hydroxytetrahydronaphthyl-7-butyric acid, m. p. 83—84°, whence the corresponding lactone, m. p. 113—114°. The oxime *p*-toluenesulphonate and phenol yield the *p*-toluenesulphonate of the lactim phenyl ether.

$\text{CH}_2 \begin{smallmatrix} \text{C}_{10}\text{H}_{10}\text{---N} \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix} \text{C} \cdot \text{OPh} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$ , m. p. 187—188° (free ether, m. p. 72—73°, and its hydrochloride, m. p. 137—138°), converted by boiling water or sodium hydroxide into phenol, *p*-toluenesulphonic acid, and 6-aminotetrahydronaphthyl-7-butyrolactam; the *p*-toluenesulphonyl ester of the lactim, m. p. 132—133°, is described. 1-Oximino-octahydrophenanthrene *p*-toluenesulphonate, m. p. 132—133°, gives methyl 7-aminotetrahydronaphthyl-8-butyrate *p*-toluenesulphonate, m. p. 184—185° [free ester, m. p. 39—40°, and its sulphate, m. p. 155—156° (decomp.)]. Ethyl 7-aminotetrahydronaphthyl-8-butyrate, m. p. 34.5—35.5° (hydrochloride; acetyl derivative, m. p. 102°), 3-amino-

tetrahydronaphthyl-4-butyric acid, m. p. 128.5—129.5°, and aminotetrahydronaphthylbutyrolactam, m. p. 201—202°, are described. 7-Hydroxytetrahydronaphthyl-8-butyric acid, m. p. 136—137°, passes when distilled into the corresponding lactone, m. p. 90°. 9-Nitro-1-oximino-octahydrophenanthrene p-toluenesulphonate, m. p. 164—165°, does not become transformed when heated with alcohols. 9-Amino-1-keto-octahydrophenanthrene, m. p. 159—160°, is converted into the 9-acetamido-compound, m. p. 234°, the oxime, m. p. 253°, of which yields a p-toluenesulphonate, m. p. 215—220°, transformed by methyl alcohol at 100° into methyl 7-amino-5-acetamidotetrahydronaphthyl-8-butyrate p-toluenesulphonate, m. p. 188—189°; the corresponding free ester, m. p. 166—167°, is described. 4-Oximino-octahydrophenanthrene p-toluenesulphonate, m. p. 117—118°, yields methyl 8-aminotetrahydronaphthyl-7-butyrate p-toluenesulphonate, m. p. 153—154°. The free ester, m. p. 37—39°, 8-aminotetrahydronaphthyl-7-butyric acid, m. p. 114.5—115.5°, aminotetrahydronaphthylbutyrolactam, and 8-hydroxytetrahydronaphthyl-7-butyric acid, m. p. 100—101.5°, are described. H. WREN.

**Phenyl styryl ketones. II. Decomposition by alkali.** R. L. SHRINER and T. KUROSAWA (J. Amer. Chem. Soc., 1930, 52, 2538—2540).—4-Hydroxyphenyl styryl ketone is decomposed by boiling with 50% potassium hydroxide solution to benzaldehyde and p-hydroxyacetophenone. Phenyl 4-hydroxystyryl ketone, m. p. 183—184°, regenerates acetophenone and p-hydroxybenzaldehyde when boiled with 33% potassium hydroxide solution. The yields of the decomposition products are 25—50% of the theoretical. H. BURTON.

**Brazilin and hæmatoxylin. X. Compounds of the  $\alpha$ -phenoxy- $\alpha'$ -phenylacetone series.** P. PFEIFFER, K. QUEHL, and F. TAPPERMANN (Ber., 1930, 63, [B], 1301—1308; cf. A., 1929, 822).—Methylation of vanillin is followed by condensation with hippuric acid and degradation of the product to 3:4-dimethoxyphenylpyruvic acid, the oxime of which when heated with sulphuric acid at 155° gives 3:4-dimethoxyphenylacetone, m. p. 48—51°, possibly dimorphous with the compound described by Kaufmann and Müller (A., 1918, i, 178). The compound condenses with ethyl m-methoxyphenoxyacetate in presence of alcoholic sodium ethoxide to form  $\gamma$ -cyano- $\alpha$ -3-methoxyphenoxy- $\gamma$ -3:4-dimethoxyphenylacetone, m. p. 95° after softening at 92° (copper salt). The ketonitrile is converted by glacial acetic acid and fuming hydrochloric acid into the corresponding amide,  $C_{19}H_{21}O_6N$ , m. p. 186°, transformed by boiling aqueous hydrochloric acid into  $\alpha$ -3-methoxyphenoxy- $\gamma$ -3:4-dimethoxyphenylacetone, b. p. 217°/0.7 mm., m. p. 69° after softening at 67°. Addition of anhydrous hydrocyanic acid to the ketone in ether affords  $\alpha$ -hydroxy- $\beta$ -3-methoxyphenoxy- $\beta'$ -3:4-dimethoxyphenylisobutyronitrile, m. p. 90° after softening at 83°. Condensation of 3:4-dimethoxyphenylacetone with ethyl 2:3-dimethoxyphenoxyacetate, b. p. 180—182°/18 mm., yields  $\gamma$ -cyano- $\alpha$ -2:3-dimethoxyphenoxy-3:4-dimethoxyphenylacetone, m. p. 91° [sodium salt, m. p. 243° (decomp.)], which is transformed into the corresponding amide, m. p. 164.5°, and thence into

2:3-dimethoxyphenoxy-3:4-dimethoxyphenylacetone, m. p. 92°; the corresponding cyanohydrin,  $C_{20}H_{23}O_6N$ , has m. p. 99°. Phenylacetone nitrile, ethyl m-methoxyphenoxyacetate, and sodium ethoxide give  $\gamma$ -cyano- $\gamma$ -phenyl- $\alpha$ -m-methoxyphenylacetone, m. p. 75° after softening at 72° (copper salt), and thence the amide,  $C_{17}H_{17}O_4N$ , m. p. 140—142°.  $\gamma$ -Cyano- $\alpha$ -2:3-dimethoxyphenoxy- $\gamma$ -phenylacetone monohydrate, m. p. 107° (decomp.), is described. H. WREN.

**Affinity of the piperonyl radical.** M. TIFFE-NEAU and (Mlle.) J. LÉVY (Compt. rend., 1930, 190, 1510—1512).—Dehydration of the carbinol formed from magnesium benzyl chloride and piperonal affords  $\alpha$ -phenyl- $\beta$ -3:4-methylenedioxyphenylethylene, m. p. 94—95°. Distillation of the oxide from this under ordinary pressure gives phenyl 3:4-methylenedioxybenzyl ketone, m. p. 71—72°, indicating that the affinity of the methylenedioxyphenyl group is greater than that of phenyl. The same conclusion is reached from the following experiments. The iodohydrin from  $\alpha$ -3:4-methylenedioxyphenyl- $\beta\beta$ -dimethylethylene, b. p. 136—137°/10 mm., and hypiodous acid is converted by dry potassium hydroxide into  $\alpha$ -3:4-methylenedioxyphenyl- $\alpha$ -methylpropaldehyde, b. p. 148—150°/12 mm., also formed by dehydration of  $\alpha$ -3:4-methylenedioxyphenyl- $\beta$ -methylpropane- $\alpha\beta$ -diol, m. p. 107—108°, with dilute sulphuric acid.  $\alpha$ -3:4-methylenedioxyphenyl- $\beta\beta$ -dimethylethylene oxide, b. p. 142—145°/12 mm., is isomerised by distillation to  $\alpha$ -3:4-methylenedioxyphenylethyl methyl ketone, b. p. 150°/12 mm.; the 3:4-methylenedioxyphenyl group behaves as the p-tolyl and o-anisyl groups (cf. A., 1927, 769). The affinity of the 3:4-methylenedioxyphenyl group is of the same order as that of the p-tolyl and o-anisyl groups, but less than that of anisyl. H. BURTON.

**Synthesis of meso-alkyl and meso-aryl anthracene derivatives. VII.** E. DE B. BARNETT and N. F. GOODWAY (J.C.S., 1930, 1348—1352).—2-Chloro- and 3-chloro-9-anthrone (for the latter of which an improved preparation is described) condense with benzyl chloride in the presence of potassium hydroxide to give respectively 2-chloro-, m. p. 185°, and 3-chloro-10:10-dibenzylanthrone, m. p. 174°. By condensation of the appropriate chlorinated anthrone with benzhydryl chloride under similar conditions the following 10-benzhydrylanthrones are obtained: 1-chloro-, m. p. 204°; 2-chloro-, m. p. 171°; 4-chloro-, m. p. 175°; 1:4-dichloro-, m. p. 191°; 1:8-dichloro-, m. p. 242°; 4:5-dichloro-10-benzhydrylanthrone, m. p. 224°; a crystalline product could not be obtained from 3-chloro-9-anthrone. The foregoing products are colourless and when boiled with alcoholic alkali hydroxide give a distinct colour only when there is no chlorine atom in position 4 or 5; by interaction with magnesium benzyl chloride they afford the following 9-benzyl-10-benzhydryl-9:10-dihydro-9-anthranols: 1-chloro-, an oil; 2-chloro-, m. p. 166°; 4-chloro-, m. p. 208°; 1:4-dichloro-, m. p. 199°; 4:5-dichloro-, m. p. 186°; 1:8-dichloro-9-benzyl-10-benzhydryl-9:10-dihydro-9-anthranol, m. p. 190°. All these, except the last-named, by treatment with hydrochloric acid in glacial acetic acid undergo transannular loss of benzhydryl to yield the corresponding chlorinated 9-benzylanthracene; 1:8-dichloro-9-benzyl-10-benzhydryl-

9 : 10-dihydro-9-anthranol, on the contrary, by transannular loss of water gives 1 : 8-dichloro-9-benzyl-10-benzhydrylanthracene, m. p. 139°. It is inferred that co-ordination of the *meso*-hydrogen atom cannot be the factor which determines the type of transannular loss (Barnett and Wiltshire, this vol., 202; with Goodway, *ibid.*, 465).

1 : 8- and 4 : 5-Dichloro-9-anthrone differ markedly from anthrone itself (cf. Padova, A., 1906, i, 741; 1909, i, 167, 655) in their behaviour towards benzo-phenone chloride, and are merely oxidised to the corresponding dianthrones; these give no colour with boiling alcoholic alkali hydroxide, although the latter, but not the former, is enolised by boiling in pyridine solution to give a red colour with sodium hydroxide. 1 : 4-Dichloro-9-anthrone condenses with benzyl chloride in the presence of sodium hydroxide to yield 1 : 4-dichloro-10-benzyl-9-anthrone, m. p. 123°, which reacts with magnesium benzyl chloride to furnish 1 : 4-dichloro-9 : 10-dibenzyl-9 : 10-dihydroanthranol, m. p. 165°; dehydration of the last-named with hydrochloric acid in glacial acetic acid affords 1 : 4-dichloro-10-benzylidene-9 : 10-dihydroanthracene, m. p. 186°. This result agrees with the suggestion that the *meso*-hydrogen atom forms a chelate ring with the chlorine atom in the *peri*-position. Further evidence is furnished by the failure of 1 : 4-dichloro-10-benzyl-9-anthrone to undergo enolisation when boiled with alcoholic sodium hydroxide solution.

C. W. SHOPPEE.

**Benzanthrone series.** F. MAYER, E. FLECKENSTEIN, and H. GÜNTHER (Ber., 1930, 63, [B], 1464—1472).—Contrary to Mayer and Sieglitz (A., 1922, i, 740), the methylbenzanthrone obtained by treatment with aluminium chloride of phenyl 4-methylnaphthyl ketone, m. p. 68—70°, is identical with that derived similarly from phenyl 2-methylnaphthyl ketone, b. p. 240—245°/15 mm., m. p. 68—70°, or from 2-methylantraquinone, glycerol, and sulphuric acid. The compound is identified as 2-methylbenzanthrone by oxidation to 2-methylanthraquinone-1-carboxylic acid, m. p. 268° (and thence to anthraquinone-1 : 2-dicarboxylic acid), which is prepared synthetically as follows. 1-Amino-2-methylanthraquinone is transformed in the usual manner into 1-cyano-2-methylanthraquinone, m. p. 270°, which is hydrolysed by boiling 80% sulphuric acid. The methyl group of phenyl 2-methylnaphthyl ketone therefore wanders during treatment with aluminium chloride.

The formation of three different ketones from naphthalene and the three toluoyl chlorides and their conversion into three different methylbenzanthrone are described. The methylbenzanthrone from *o*- and *m*-toluoyl chlorides are shown to be identical, and since the product has been proved to be 6-methylbenzanthrone, a further instance of methyl migration is afforded. The methylbenzanthrone from *p*-toluoyl chloride is oxidised to an unknown methylanthraquinonecarboxylic acid, m. p. 312—314° (suggesting the possible identity with the acid derived from methylaceanthrenequinone, which, however, is proved to be 2-methylanthraquinone-1-carboxylic acid). 3-Tolyl 4-methylnaphthyl ketone, b. p. 240—245°/20 mm., and 3-tolyl 2-methylnaphthyl ketone, b. p. 240—245°/20 mm., m. p. 104—105°, yield the same di-

methylbenzanthrone, m. p. 158°, regarded as the 2 : 6-dimethyl compound on the basis of analogy (see above) and on its production from 2 : 6-dimethylantraquinone, aniline sulphate, glycerol, and sulphuric acid. 3-Tolyl 4-methylnaphthyl ketone, b. p. 250—255°/20 mm., m. p. 58—59°, yields 2 : 7-dimethylbenzanthrone, m. p. 168°, not identical with the product, m. p. 158° (? 3 : 6-dimethylbenzanthrone), obtained from 2 : 7-dimethylantraquinone by means of sulphuric acid and glycerol. *p*-Tolyl 2-methylnaphthyl ketone, m. p. 105—106°, affords two dimethylbenzanthrone, m. p. 144° and 192°, respectively, in amount too small for further investigation.

H. WREN.

**2 : 7-Dimethylantraquinone.** F. MAYER and H. GÜNTHER (Ber., 1930, 63, [B], 1455—1464).—Ozonisation of 2 : 6- or 2 : 7-dimethylnaphthalene yields 5-methylphthalic acid in small amount, but the method is useless for preparative purposes. The acid is obtained by the following processes in 45% yield. 3-Nitro-*p*-toluidine is transformed into the corresponding nitrile, which by successive reduction and hydrolysis is converted into 2-amino-*p*-toluic acid. The last-named substance is esterified, after which the amino-group is replaced by the cyano-group. Subsequent hydrolysis affords 5-methylphthalic acid, which passes at 165° into the anhydride, m. p. 92°. Condensation of 5-methylphthalic anhydride with toluene in presence of aluminium chloride gives a non-separable mixture of acids with which ring closure is effected by concentrated sulphuric acid. The dimethylantraquinones thus produced are separated from one another by 96% alcohol or light petroleum, thus giving 2 : 7-dimethylantraquinone, m. p. 162°, and 2 : 6-dimethylantraquinone, m. p. 236—237°. Treatment of these substances in glacial acetic acid with tin and hydrochloric acid gives 2 : 6-dimethylanthrone, m. p. 149°, and 2 : 7-dimethylanthrone, m. p. 171° after softening at 164°, whereas zinc dust and ammonia convert the 2 : 7-derivative into 2 : 7-dimethylanthrone, m. p. 231—232°. Anthraquinone-2 : 7-dicarboxylic acid, m. p. above 360° (sodium salt), is described. Nitration of 2 : 7-dimethylantraquinone gives 1 : 8-dinitro-2 : 7-dimethylantraquinone, m. p. above 360°, reduced by sodium sulphide to 1 : 8-diamino-2 : 7-dimethylantraquinone, m. p. 271° (dibenzoyl derivative, m. p. 269°). Treatment of 2 : 6-dimethylantraquinone with aniline in boiling nitrobenzene gives the dianil of anthraquinone-2 : 6-dialdehyde, m. p. 247°, hydrolysed by hydrochloric acid in glacial acetic acid to anthraquinone-2 : 6-dialdehyde, m. p. 281° (phenylhydrazone). 1 : 8-Diaminoanthraquinone-2 : 7-dialdehyde, m. p. above 300° (phenylhydrazone), and the corresponding dianil, m. p. 214°, are described.

Condensation of 5-methylphthalic anhydride with pyrocatechol in presence of a mixture of aluminium and sodium chlorides yields 5 : 6 (or 7 : 8)-dihydroxy-2-methylantraquinone, m. p. 217°, and 6 : 7-dihydroxy-2-methylantraquinone, m. p. 330—340°. 6 : 8-Dihydroxy-2-methylantraquinone, m. p. 297°, and 5 : 8-dihydroxy-2-methylantraquinone, m. p. 175°, are obtained similarly from resorcinol and quinol respectively. Treatment of the 5 : 8-dihydroxy-compound with glacial acetic acid and lead tetra-

acetate followed by warming with acetic anhydride containing a little concentrated sulphuric acid affords 5:6:8-triacetoxy-2-methylanthraquinone, m. p. 196—197° after softening at 191°, hydrolysed to 5:6:8-trihydroxy-2-methylanthraquinone, m. p. 243°, obtained also from 5-methylphthalic anhydride and hydroxyquinol. Treatment of the trihydroxy-compound with ammonia and sodium hyposulphite yields 6:8-dihydroxy-2-methylanthraquinone, m. p. 297°, identical with that prepared from resorcinol. H. WREN.

**Halogenoquinizarins.** H. WALDMANN and (in part) H. MATHIOWETZ (J. pr. Chem., 1930, [ii], 126, 250—256).—Halogenated quinizarins are best obtained by condensation of the appropriate halogenophthalic anhydride and quinol at 200—220° in the presence of sodium aluminium chloride (Zahn and Ochwat, A., 1928, 891). Thus 3:6-dichlorophthalic anhydride is converted in 84% yield into 5:8-dichloroquinizarin, m. p. 275.5° (Frey, A., 1912, i, 477, gives m. p. 266°) (diacetyl derivative, m. p. 180°), converted by heating with methyl *p*-toluenesulphonate and potassium carbonate in boiling *p*-dichlorobenzene into 5:8-dichloro-1:4-dimethoxyanthraquinone, m. p. 313.5°. Similarly, from the appropriate substituted phthalic anhydride are obtained 6:7-dichloroquinizarin, m. p. 295.5° (80% yield) (also by condensation of 4-chlorophthalic anhydride obtained by chlorination of phthalic anhydride, some of the 4:5-dichloro-compound also being produced), converted into 6:7-dichloro-1:4-dimethoxyanthraquinone, m. p. 239°; 6-chloro-, m. p. 188° (95% yield) (diacetyl derivative, m. p. 213°), and 6-bromo-, m. p. 185.5° (diacetyl derivative, m. p. 220.5°), quinizarin, converted into 6-chloro-, m. p. 168.5°, and 6-bromo-, m. p. 176.5°, 1:4-dimethoxyanthraquinone. J. W. BAKER.

**Nuclear hydrogenation of polynuclear quinones.**  
**III. Phenanthraquinone, 1:4-naphthaquinone, and 1:4-anthraquinone.** A. SKITA and W. ROHRMANN (Ber., 1930, 63, [B], 1473—1484).—Hydrogenation of phenanthraquinone in the presence of various catalysts does not come to a pause at any stage of the operation, so that the optimal conditions for the preparation of 9:10-dihydroxy-1:2:3:4:9:10-hexahydrophenanthrene can be determined only empirically. Since the glycol and the quinone derived from it could not be obtained analytically pure by this method, the following process is preferred. Phenanthraquinone is hydrogenated in glacial acetic acid in presence of colloidal platinum and gelatin and the product is transformed into 9:10-diacetoxy-1:2:3:4:9:10-hexahydrophenanthrene, m. p. 172—173°, converted by successive hydrolysis and oxidation with ferric chloride into 1:2:3:4-tetrahydro-9:10-phenanthraquinone, decomp. 120—130° according to the rate of heating [corresponding phenazine,  $C_{20}H_{16}O_2$ , m. p. (indef.) 190—196°; quinhydrone].

1:4-Naphthaquinone is very smoothly hydrogenated to 5:6:7:8-tetrahydro-1:4-naphthaquinol, m. p. 176—177° or, in an individual case, m. p. 180—181° (the cause of variation of the m. p. is not definitely established). It is oxidised by ferric chloride to 5:6:7:8-tetrahydro-1:4-naphthaquinone, m. p. 55—56°. 5:6:7:8-Tetrahydro-1:4-naphthaquin-

hydrone has m. p. 118°. Acetylation of the quinol gives 1:4-diacetoxy-5:6:7:8-tetrahydronaphthalene, m. p. 186—187°, also prepared by catalytic hydrogenation of 1:4-diacetoxynaphthalene. 2-Anilino-5:6:7:8-tetrahydro-1:4-naphthaquinone has m. p. 164—165°. Tetrahydronaphthaquinone in ether is converted by chlorine into 2:3-dichloro-1:4-diketo- $\Delta^9$ -octahydronaphthalene, m. p. 191—191.5°, transformed by sodium acetate in glacial acetic acid into 2-chloro-5:6:7:8-tetrahydro-1:4-naphthaquinone, m. p. 62—63°, from which 2:3-dichloro-5:6:7:8-tetrahydro-1:4-naphthaquinone, m. p. 145—147°, is derived. 2:3-Dibromo-5:6:7:8-tetrahydro-1:4-naphthaquinone has m. p. 176—177°. 3-Chloro-2-anilino-5:6:7:8-tetrahydro-1:4-naphthaquinone, m. p. 175.5—176°, is described. Tetrahydronaphthaquinone, acetic anhydride, and sulphuric acid yield 1:2:4-triacetoxy-5:6:7:8-tetrahydronaphthalene, m. p. 142—143°, converted by successive hydrolysis and oxidation into 4-hydroxy-5:6:7:8-tetrahydro-1:2-naphthaquinone, m. p. 137—139° (corresponding phenazine,  $C_{16}H_{14}ON_2$ , m. p. above 300°). The substance is also prepared from 4-hydroxy-1:2-naphthaquinone (a simplified method of preparing  $\beta$ -naphthaquinone from  $\beta$ -naphthol is given).

2-Acetamido-1:4-naphthaquinone is converted by catalytic hydrogenation followed by acetylation into 2-acetamido-1:4-diacetoxy-5:6:7:8-tetrahydronaphthalene, m. p. 193—194°. Treatment of 2-acetamido-5:6:7:8-tetrahydro-1:4-naphthaquinone with acetic anhydride, sodium acetate, and zinc dust gives an isomeric 2-acetamido-1:4-diacetoxy-5:6:7:8-tetrahydronaphthalene, m. p. 106—107°, converted into the variety, m. p. 193—194°, by alcohol containing a little hydrochloric acid. Reduction and subsequent oxidation with ferric chloride converts 2-acetamido-1:4-naphthaquinone into 2-acetamido-5:6:7:8-tetrahydro-1:4-naphthaquinone, m. p. 124—128°. 2-Amino-1:4-diacetoxy-5:6:7:8-tetrahydronaphthalene, m. p. 202—203°, and 2-amino-5:6:7:8-tetrahydro-1:4-naphthaquinone, m. p. (indef.) 139—140°, are described.

1:4-Anthraquinone is hydrogenated and subsequently acetylated to 1:4-diacetoxy-5:6:7:8-tetrahydroanthracene, m. p. 191.5—192°; 5:6:7:8-tetrahydro-1:4-anthraquinone, m. p. 138—139°, is described.

H. WREN.

**Preparation of *o*-(*p*-sulphobenzoyl)benzoic acid derivatives and anthraquinone compounds derivable therefrom.** I. GUBELMANN, H. J. WEILAND, and O. STALLMANN.—See B., 1930, 603.

**Friedel-Crafts reactions, naphthalene series.**  
**I. Preparation of naphthantraquinone.** P. H. GROGGINS and H. P. NEWTON.—See B., 1930, 601.

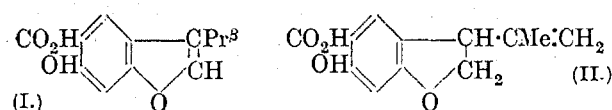
**Solubility of rotenone.** I. Solubility and optical rotation in organic solvents at 20°. H. A. JONES and C. M. SMITH (J. Amer. Chem. Soc., 1930, 52, 2554—2562).—The solubility of rotenone has been determined in 21 organic solvents and found to be 0.2—33%. The specific rotation varies from  $-66^\circ$  to  $-230^\circ$  in the same solvents. H. BURTON.

**Rotenone. V. Identity of isotubaic and rotenic acids.** H. L. HALLER and F. B. LAFORGE (J. Amer. Chem. Soc., 1930, 52, 2480—2483).—When

isorotenone (A., 1929, 1181) is heated with dilute alcoholic potassium hydroxide solution, isotubaic acid, m. p.  $186^{\circ}$ , is produced. This acid is also formed by heating tubaic acid with 50% sulphuric acid, and is identical with rotenic acid (cf. Butenandt and Hildebrandt, this vol., 477; Takei, Koide, and Miyajima, *ibid.*, 609). The change occurring when rotenone is converted into isorotenone involves the same groupings as in the production of rotenic acid from tubaic acid.

H. BURTON.

**Rotenone, the active compound of the *Derris* root. V. Constitution of rotenic acid.** S. TAKEI, M. KOIDE, and S. MIYAJIMA (Ber., 1930, 63, [B], 1369—1373; cf. this vol., 609).—Decarboxylation of rotenic acid followed by treatment of the rotenol thus produced with potassium hydroxide at  $270$ – $280^{\circ}$  affords resorcinol and isovaleric acid, thus establishing the constitution I for rotenic acid without, however,



proving the position of the substituents in the benzene nucleus. In furtherance of the work of Butenandt and Hildebrandt (this vol., 477), rotenic acid has been converted by energetic catalytic hydrogenation in glacial acetic acid into dihydrototenic acid, which is shown by the mixed m.-p. method applied to the acid and its brucine salt to be identical with dihydrotubaic acid. Dihydrototenic acid is readily resolved into its optical antipodes by means of brucine. The specific rotation of *l*-dihydrototenic acid is in good agreement with that of dihydrotubaic acid; *d*-dihydrototenic acid,  $[\alpha]_D^{25} +76.74^{\circ}$  in chloroform, is its optical antipode. The constitution II is assigned to tubaic acid, dihydrotubaic acid having the side-chain saturated.

H. WREN.

**Sapogenin of the sugar-beet. V. PRELOG** (Coll. Czech. Chem. Comm., 1930, 2, 413—423).—The sapogenin,  $C_{31}H_{50}O_3$  (cf. Haar, A., 1928, 68, and Rehorst, A., 1929, 568), m. p.  $303^{\circ}$ ,  $[\alpha]_D +79.4^{\circ}$  in chloroform, isolated from the sugar-beet, probably contains unreactive double linkings, since, although it is not reduced by sodium and *n*-butyl alcohol, it gives a yellow colour with tetranitromethane. The carboxyl group is probably united to a tertiary carbon atom, since it readily loses carbon monoxide under the influence of concentrated sulphuric acid at  $80$ – $130^{\circ}$ . Oxidation with chromic and acetic acids converts it into a ketonic acid  $C_{31}H_{48}O_3$ , softening at  $160^{\circ}$ , not melting completely until  $200^{\circ}$  (also gives carbon monoxide with sulphuric acid), which could not be obtained pure but gives a pure semicarbazone, m. p.  $270^{\circ}$  (decomp.), and methyl ester, m. p.  $184$ – $185^{\circ}$ ,  $[\alpha]_D +88.4^{\circ}$  in 96% alcohol (semicarbazone, m. p.  $236^{\circ}$ ). Hence a secondary alcohol group is present. Further oxidation of the ketonic acid or of the original sapogenin gives the hydroxy-ketonic lactone  $C_{31}H_{46}O_4$ , m. p.  $272$ – $273^{\circ}$ ,  $[\alpha]_D +29.0^{\circ}$  in 96% alcohol (one hydroxyl group by the Zerevitinoff method), which, since the lactone ring is readily opened by boiling 0.1*N*-potassium hydroxide and the lactone re-formed on acidification, is probably a  $\gamma$ -lactone. Hence the sapogenin must contain two readily oxidisable tertiary

carbon atoms, one of which is in the  $\gamma$ -position to the carboxyl group.

J. W. BAKER.

**Conjugated double linkings. XII. Physalis dyes.** R. KUHN, A. WINTERSTEIN, and W. KAUFMANN (Ber., 1930, 63, [B], 1489—1497; cf. A., 1929, 1456).—Improvement in the isolation of physalien (cf. Kuhn and Wiegand, A., 1929, 823) is effected by precipitating the benzene extracts with acetone in place of alcohol. It has m. p.  $98.5$ – $99.5^{\circ}$  (corr.),  $[\alpha]_D^{25} -30^{\circ}$  in chloroform. It is oxidised by permanganate to acetic and palmitic acids and hydrolysed by cold, alcoholic potassium hydroxide to 2 mols. of palmitic acid and 1 mol. of zeaxanthin. Physalien is therefore the dipalmityl ester of zeaxanthin and has the composition  $C_{72}H_{116}O_4$ . Hydrogenation of physalien in a mixture of hexane and glacial acetic acid in presence of platinum oxide causes absorption of 11 mols. of the gas and formation of the colourless, partly crystalline perhydrophysalien,  $[\alpha]_D^{25} -16.5^{\circ}$  in chloroform. Hydrolysis of the hydrogenated product gives palmitic acid and perhydrozeaxanthin,  $[\alpha]_D^{25} -25.5^{\circ}$  in chloroform (maximum observed). Zeaxanthin when hydrogenated becomes almost colourless after absorption of 8–9 mols. of hydrogen, whereas complete decolorisation requires 10.8 mols.; the product,  $C_{40}H_{78}O_2$ , has  $[\alpha]_D^{25} -24.5^{\circ}$  in chloroform (maximum observed). Physalien is synthesised by the action of palmityl chloride on zeaxanthin in pyridine; the synthetic differs from the natural product only in undergoing auto-oxidation with greater readiness. The dialauryl ester of zeaxanthin,  $C_{64}H_{100}O_4$ , m. p.  $104^{\circ}$ , is less readily auto-oxidised.

H. WREN.

**Colouring matter of boxthorn berries and the occurrence of chemically combined carotinoids in nature.** L. ZECHMEISTER and L. VON CHOLNOKY (Annalen, 1930, 481, 42—56).—The dried skins of berries of the boxthorn (*Lycium halimifolium*, Mill.; *Solanaceae*) yield by extraction with ether or carbon disulphide a colouring matter identified with physalien from alkekengi (Kuhn and Wiegand, A., 1929, 823); the substance (new formula  $C_{72}H_{116}O_4$ ) has m. p.  $99^{\circ}$  (corr., block), is laevorotatory, and possesses absorption bands at  $523$ – $505$ ,  $490$ – $471$ , and  $457$ – $444 \mu$ ; it takes up 8 atoms of bromine in chloroform, and on treatment with perbenzoic acid (cf. Pummerer and others, A., 1928, 765; 1929, 906) 8 atoms of oxygen; catalytic hydrogenation gives the colourless perhydrophysalien (Kuhn and Wiegand, *loc. cit.*) (new formula  $C_{72}H_{138}O_4$ ). Hydrolysis of physalien (from *Lycium*) by cold methyl-alcoholic potassium hydroxide gives two molecules of palmitic acid and an isomeride,  $C_{40}H_{56}O_2$ , of xanthophyll, m. p.  $204$ – $205^{\circ}$  (corr.; block); the latter, also obtained by direct alkaline extraction of the skins, is identified with zeaxanthin from maize (Karrer and others, A., 1929, 1077). The original pigment is thus the dipalmitate of zeaxanthin, the presence in which of two hydroxyl groups is confirmed.

Perhydrophysalien is similarly hydrolysed to palmitic acid and perhydrozeaxanthin, a laevorotatory oil (cf. preceding abstract).

R. CHILD.

**$\alpha$ - $\Delta^3$ -Carene oxide.** B. A. ARBUSOV and B. M. MICHAÏLOV (J. Russ. Phys. Chem. Soc., 1930, 62,



607—615).— $\alpha$ - $\Delta^3$ -Carene oxide, b. p. 126—127°/103 mm.,  $[\alpha]_D^{20} +13.05^\circ$ ,  $d_4^{20}$  0.9464, prepared by the action of benzoyl peroxide differs physically and chemically from that described by Simonsen (B., 1928, 274). The oxide is readily converted by aqueous sulphuric acid into  $\Delta^3$ -carene  $\beta$ -glycol, identical with that of Simonsen. The oxide combines with bromine to yield an uncrystallisable tribromide.

R. TRUSZKOWSKI.

Action of substituted aromatic amines on camphoric anhydride. Hydroxy-, methoxy-, and ethoxy-camphoranilic acids and camphoromethoxy- and -ethoxy-phenylimides. M. SINGH and R. SINGH (J.C.S., 1920, 1301—1304).—Condensation of camphoric anhydride with the appropriate hydroxy- or alkoxy-aniline (cf. A., 1928, 1377) gives the following camphoranilic acids and camphorophenylimides, the values for  $[M]_D$  in each case being in methyl alcohol, ethyl alcohol, acetone, and methyl ethyl ketone, respectively. 2'-Hydroxy-, m. p. 183° (shrinks at 159°),  $[M]_D$  -37°, -47°, -45°, -53°; 4'-hydroxy-, m. p. 241—242° (Wootton, J.C.S., 1910, 97, 405, gives m. p. 239°),  $[M]_D$  +246°, +266°, +154°, +203°; 2'-methoxy-, m. p. 152° (shrinks at 141°),  $[M]_D$  +30°, +28°, -16°, -10°; 4'-methoxy-, m. p. 204°,  $[M]_D$  +163°, +152°, +122°, +99°; 2'-ethoxy-, m. p. 146—147°,  $[M]_D$  -50°, -62°, -90°, -89°; 4'-ethoxy-, m. p. 202—203°,  $[M]_D$  +180°, +154°, +116°, +104°; -camphoranilic acid; camphoro-o-, m. p. 136°,  $[M]_D$  +49°, +43°, +40°, +44°, and -p-, m. p. 122—123°,  $[M]_D$  +84°, +63°, +49°, +34°; -methoxy-; -o-, m. p. 138°,  $[M]_D$  +115°, +98°, +80°, +77°, and -p-, m. p. 122°,  $[M]_D$  +86°, +47°, +53°, +39°, -ethoxy-phenylimide. The relative rotatory power of these derivatives is discussed.

J. W. BAKER.

Reaction between bromine and  $\gamma$ -diketones in hydrobromic acid solution. I. A. TREFILEV and E. A. GOROSCHKO (J. Russ. Phys. Chem. Soc., 1930, 62, 643—652).— $\alpha\beta$ -Diacetylcane yields with bromine in hydrobromic acid 2:5-dimethylpentabromofuran, m. p. 180°, which may also be produced under similar conditions from dimethylfuran.

R. TRUSZKOWSKI.

Nitrofurfuraldehyde and nitrofurylacrylic acid. H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1930, 52, 2550—2554).—Treatment of furfuraldehyde diacetate with nitric acid (*d* 1.5) in acetic anhydride below -5° affords the open-chain compound,  $\text{OAc}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{CH}(\text{OAc})_2$ , m. p. 106—107°, which on dissolution in pyridine is converted quantitatively into 5(?)-nitrofurfuraldehyde diacetate, m. p. 92.5°; the intermediate need not be isolated. Hydrolysis of the diacetate with 33% sulphuric acid in an atmosphere of carbon dioxide gives nitrofurfuraldehyde, b. p. 128—132°/10 mm., m. p. 35—36° (oximes, m. p. 121° and 153°). The diacetate reacts with acetic anhydride and fused sodium acetate in presence of a drop of pyridine at 142°, forming nitrofurylacrylic acid, m. p. 235—236° (ethyl ester, m. p. 125°), also obtained by nitration of furylacrylic acid with nitric acid (*d* 1.5) in acetic anhydride at -5°. The stability of the furan ring is increased by the introduction of a nitro-group.

H. BURTON.

Influence of substituents on the stability of cyclic compounds. M. GIUA and G. RACCUI (Atti R. Accad. Sci. Torino, 1929, 64, 331—334; Chem. Zentr., 1930, i, 224).—With excess of alcoholic hydrazine, 4:5-benzocoumaran-2:3-dione gives the hydrazone-hydrazide of  $\beta$ -hydroxy- $\alpha$ -naphthylglyoxylic acid,  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_4$ , m. p. 195—196° (decomp.). When gently heated with acetic anhydride this affords the 3-acetylhydrazone, of 4:5-benzocoumaran-2:3-dione,  $\text{C}_{14}\text{H}_{10}\text{O}_3\text{N}_2$ , m. p. 244°.

A. A. ELDRIDGE.

Action of ammonia on 3-hydroxythionaphthen. W. KÖNIG and G. HAMPRECHT (Ber., 1930, 63, [B], 1546—1548).—Dithionaphthenylamine accompanied by very small amounts of 3-aminothionaphthen is obtained by the action of calcium or zinc chloride and ammonia, or zinc oxide and ammonia or ammonium sulphite on 3-hydroxythionaphthen. It is mainly formed, in addition to 3-acetamidothionaphthen, from 3-hydroxythionaphthen and acetamide in acetic acid. The conditions most favourable to the production of 3-amino- from 3-hydroxy-thionaphthen consist in the use of 50% ammonia at 130° for 5 hrs.

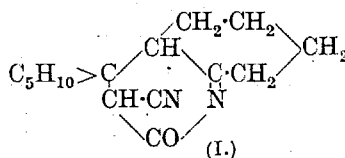
H. WREN.

Formation of pyrrolidine from halogenobutylphthalimides. W. KEIL (Ber., 1930, 63, [B], 1614—1615).—Potassium phthalimide is transformed by  $\alpha\delta$ -dichlorobutane into  $\delta$ -chlorobutylphthalimide, converted by boiling 30% potassium hydroxide into pyrrolidine;  $\alpha\delta$ -diaminobutane does not appear to be formed.

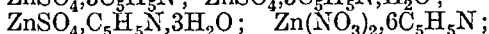
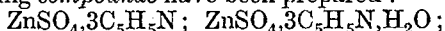
H. WREN.

Heterocyclic compounds. V. Condensation of cyclohexylidenecyclohexanone with cyanoacetamide. H. K. SEN and N. C. NEOGI (J. Indian Chem. Soc., 1930, 7, 305—308).—2-cyclohexylidenecyclohexanone condenses with cyanoacetamide in presence of alcoholic sodium ethoxide forming the quinolone (I), m. p. 340—341°. The corresponding quinolones obtained similarly from 2,4'-methylcyclohexylidene-4-methylcyclohexanone and 2,3'-methylcyclohexylidene-5-methylcyclohexanone(?) have m. p. 285—287° and 326—328°, respectively. Amyl formate and 2-cyclohexylidenecyclohexanone react in presence of sodium wire and ether forming hydroxymethylenecyclohexylidenecyclohexanone, b. p. 170—172°/15 mm. (copper salt, m. p. 174—175°; pyrazole derivative, m. p. 258°, formed by the action of semicarbazide acetate), which condenses with cyanoacetamide in presence of piperidine (cf. Sen, J.C.S., 1915, 107, 1351) yielding a substance,  $\text{C}_{16}\text{H}_{18}\text{ON}_2$ , m. p. 230—232°. The hydroxymethylene derivative, b. p. 180°/11 mm. (pyrazole derivative, m. p. 262—263°), from 2,4'-methylcyclohexylidene-4-methylcyclohexanone(?) and acetamide afford a compound,  $\text{C}_{18}\text{H}_{22}\text{ON}_2$ , m. p. 243—244°. Ethyl acetate condenses with cyclohexylidenecyclohexanone in presence of sodium affording an impure product, b. p. 170—175°/20 mm., which condenses with cyanoacetamide in presence of piperidine forming an unsaturated compound, m. p. 245—246°. When condensation is effected with sodium ethoxide a mixture of this and I is produced.

H. BURTON.



**Additive compounds of organic bases with zinc salts.** J. V. DUBSKY and A. RABAS (Pub. Fac. Sci. Univ. Masaryk, 1929, 115, 3—11).—By the addition of pyridine to zinc sulphate or nitrate the following compounds have been prepared:



$\text{Zn}(\text{NO}_3)_2 \cdot 4\text{C}_5\text{H}_5\text{N}$ , and  $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}$ . These compounds are soluble in water and can be represented by structures of the type  $[\text{Zn} \cdot 6\text{C}_5\text{H}_5\text{N}](\text{NO}_3)_2$  and  $[\text{Zn} \cdot 3\text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{O}]\text{SO}_4$ . O. J. WALKER.

**Quinoline syntheses.** W. L. BARR (J. Amer. Chem. Soc., 1930, 52, 2422—2425).— $\beta$ -Chloropropaldehyde diethylacetal (1 mol.) reacts with aniline (2.5 mols.) in dry ether forming an impure product, which on acid hydrolysis gives polymerised  $\beta$ -anilino-propaldehyde. The product could not be condensed with aniline in presence of hydrochloric or 70% sulphuric acid. These results afford no evidence for the constitution of the intermediate in the Skraup reaction. Treatment of allylaniline with sulphuric acid and nitrobenzene (or arsenic oxide) furnishes about 1% of quinoline. H. BURTON.

**Preparation of compounds for therapeutic trial.** I. Amino-alcohols. II. Derivatives of atophan. III. Derivatives of carbostyryl. IV. Quinoline derivatives and arsenicals. E. FOURNEAU, J. TRÉFOUEL, (MME.) J. TRÉFOUEL, and (Mlle.) G. BENOIT (Ann. Inst. Pasteur, 1930, 44, 719—751).—I. The following substituted isopropyl alcohols were prepared by the methods previously described (A., 1920, i, 672; 1928, 635):  $\alpha$ -piperidinoyl-*xylyl*-, b. p. 205—206°/24 mm. (hydrochloride);  $\alpha$ -*m*-anisidino- $\gamma$ -dimethylamino-, b. p. 210—215°/15 mm.;  $\alpha$ -*p*-anisidino- $\gamma$ -dimethylamino-, b. p. 218—223°/25 mm., m. p. 73° (hydrochloride, m. p. 114°);  $\alpha$ -*o*- and -*m*-phenetidino- $\gamma$ -dimethylamino-, m. p. 82° and b. p. 220—225°/15 mm. (hydrochloride, m. p. 123—124°), respectively;  $\alpha$ -*o*- and -*m*-toluidino- $\gamma$ -dimethylamino-, b. p. 205—210°/33 mm. and m. p. 66°, respectively;  $\alpha$ -1- and -2-naphthylamino- $\gamma$ -dimethylamino-, m. p. 79° and 101—102°, respectively (hydrochlorides, m. p. 162° and 135°, respectively);  $\alpha$ -*benz*-idino- $\gamma$ -*bis*dimethylamino-;  $\alpha$ -*p*-carbethoxyanilino- $\gamma$ -dimethylamino-, m. p. 79—80° (hydrochloride, m. p. 152—153°);  $\alpha$ -benzylamino- $\gamma$ -dimethylamino-, b. p. 173—176°/16 mm. (hydrochloride, m. p. 203°);  $\alpha$ -methylbenzylamino- $\gamma$ -dimethylamino-, b. p. 177°/20 mm. (hydrochloride, m. p. 220°);  $\alpha$ -*p*-phenetidino- $\gamma$ -piperazino-, b. p. 220—225°/0.5 mm., m. p. 85° (hydrochloride, m. p. 187°);  $\alpha$ -piperazino- $\gamma$ -butoxy-, b. p. 185—188°/30 mm. (hydrochloride, m. p. 108—109°);  $\alpha$ -*p*-phenetidino- $\gamma$ -phenoxy-, m. p. 103°;  $\alpha$ -*p*-phenetidino- $\gamma$ -benzylamino-, b. p. 225°/0.5 mm., m. p. 95° (hydrochloride, m. p. 178°);  $\alpha$ -benzylamino- $\gamma$ -phenoxy-, m. p. 78°, isopropyl alcohol.

II. Magnesium ethyl bromide and ethyl 2-phenylcinchoninate afford 2-phenyl-4- $\alpha$ -hydroxy- $\alpha$ -ethylpropylquinoline, m. p. 153° (the 6-methyl derivative is obtained similarly from ethyl 2-phenyl-6-methylcinchoninate, m. p. 80°). Condensation of methoxyisatin and acetophenone gives 6-methoxy-2-phenylcinchoninic acid, m. p. 234° (ethyl ester, m. p. 110°), whilst isatin and *p*-aminoacetophenone furnish 2-*p*-aminophenyl-

cinchoninic acid, m. p. 165° (ethyl ester). 6-Methoxy-2-*p*-aminophenylcinchoninic acid, m. p. 221° (decomp.), and ethyl 2-*p*-hydroxyphenylcinchoninate are described.

III. The following quinoline derivatives were prepared from 2-chloroquinoline and the appropriate base, usually in presence of benzene at 135—150°; 2- $\beta$ -aminoethylamino- (hydrochloride); 2:2'-ethylene-diamino- (hydrochloride); 2-diethylamino- (hydrochloride, m. p. 165—170° after decomp. about 155°). 6-Amino-3-methoxycinnamic acid, m. p. 181°, is converted by 50% sulphuric acid at 150—160° into 6-methoxycarbostyryl, m. p. 210° after subliming at about 197° (the m. p. falls to 187° when the substance is kept in a desiccator). This is converted by phosphoryl chloride into 2-chloro-6-methoxyquinoline, m. p. 92°, which with diethylamine yields the 2-diethylamino-derivative (hydrochloride, m. p. 170—175° after decomp. about 160°). 6-Chloro-2-diethylaminoquinoline hydrochloride, m. p. 180° after decomp. about 165°, is obtained similarly from 2:6-dichloroquinoline, m. p. 156° (sublimes about 144°), which is prepared from 6-chlorocarbostyryl, m. p. 256° (sublimes at about 240°). 3-Chloro-6-aminocinnamic acid has m. p. 220° (sublimes at about 180°).

IV. 8-Chloro-5-nitroquinoline and ethylenediamine (5 parts) at 140° give 5-nitro-8- $\beta$ -aminoethylaminoquinoline, m. p. 115°; the hydrochloride (decomp. above 220°) of this is reduced by stannous chloride and hydrochloric acid to the corresponding amino-derivative hydrochloride, m. p. 238—240°. 8-Nitro-7- $\beta$ -aminoethylaminoquinoline, m. p. 135—145° (hydrochloride, m. p. 240°), is reduced similarly to the 8-amino-derivative (hydrochloride, m. p. about 235°). 8-Nitro-7-aminoquinoline, m. p. 194° (from the chloronitroquinoline and ammonia at 160°), is converted by the Bart reaction into 8-nitroquinoline-7-arsinic acid (sodium salt). The following are obtained by methods similar to the above: 8-nitro-5- $\beta$ -aminoethylaminoquinoline, m. p. 175° (hydrochloride, m. p. 248—250°); 8-amino-derivative hydrochloride, m. p. 245—247°; 8-nitro-5- $\beta$ -aminoethylamino-6-methoxyquinoline hydrochloride, chars from 210°; 6-methoxyquinoline-8-arsinic acid [sodium salt (+3H<sub>2</sub>O)]; 8-methoxyquinoline-6-arsinic acid; 6-ethoxyquinoline-8-arsinic acid (sodium salt).

5-Chloro-8-nitro-6-methoxyquinoline, m. p. 204° after partial sublimation about 195°, is prepared by the usual method from 2-chloro-5-nitro-4-aminoanisole, m. p. 139°, the acetyl derivative, m. p. 159°, of which results by nitrating 2-chloro-4-acetamidooanisole. 6-Amino-8-methoxyquinoline, m. p. 168° [hydrochloride, m. p. about 250° (decomp.)], 8-amino-6-methoxyquinoline, an oil, and 8-amino-6-ethoxyquinoline (hydrochloride, m. p. about 190°) are all prepared by reduction of the corresponding nitro-derivatives.

H. BURTON.

**Preparation of ketones of the pyridine and quinoline series.** A. BOEHRINGER.—See B., 1930, 640.

**Manufacture of hydroxycarboxylic acids of carbazole.** I. G. FARBENIND.—See B., 1930, 603.

**Heterocyclic compounds. VI. Synthesis of tetrahydroacridones.** H. K. SEN and U. BASU

(J. Indian Chem. Soc., 1930, 7, 435—441).—Ethyl cyclohexan-2-one-1-carboxylate is converted by aniline at the ordinary temperature into *ethyl 2-anilino- $\Delta^1$ -cyclohexene-1-carboxylate*, m. p. 58.5°, transformed at 260° into 1 : 2 : 3 : 4-tetrahydroacridone, m. p. 357—358°. Similarly, the non-crystalline *ethyl 2-p-toluidino- $\Delta^1$ -cyclohexenecarboxylate* affords 7-methyl-1 : 2 : 3 : 4-tetrahydroacridone, m. p. 340°, and *ethyl 2-m-xylidino- $\Delta^1$ -cyclohexenecarboxylate* gives 7 : 9-dimethyl-1 : 2 : 3 : 4-tetrahydroacridone, m. p. 316—318°. *Ethyl 2-p-acetamidoanilino- $\Delta^1$ -cyclohexenecarboxylate*, m. p. 191.5°, could not be transformed into the corresponding acridone.

2-Hydroxymethylenecyclohexanone is converted by aqueous ammonia into the corresponding amine,  $C_6H_{11}ON$ , m. p. 112°, transformed by hydroxylamine hydrochloride and an excess of sodium hydroxide into 2-cyanocyclohexanoneoxime, m. p. 118°, probably owing to hydrolysis of the amine to the original hydroxymethylene ketone. Condensation of the amine with cyanoacetamide at 130—140° gives the quinoline derivative,  $CH_2 \cdot CH_2 \cdot C(OH) \cdot NH \cdot CO$   
 $CH_2 \cdot CH_2 \cdot CH = CH \cdot C \cdot CN$ , m. p. 301—302°, hydrolysed by 80% sulphuric acid to the corresponding acid, m. p. 266°. H. WREN.

**Acridine derivatives.** Synthesis of isomerides of proflavine and of neutral acriflavine. M. T. BOGERT, A. D. HIRSCHFELDER, and P. G. I. LAUFFER (Coll. Czech. Chem. Comm., 1930, 2, 383—395).—When 2-chloro-5-nitrobenzoic acid [prepared in only 35% yield by nitration of *o*-chlorobenzoic acid with mixed acids at 50—55°; Hübner's yield of 95% (A., 1884, 599) could not be obtained] is fused with *p*-nitroaniline at 160°, a 33% yield (allowing for recovered starting material) of 2-*p*-nitroanilino-5-nitrobenzoic acid, m. p. 293°, is obtained. This is converted by heating with 17 parts of concentrated sulphuric acid at 88° into 3 : 7-dinitroacridone, not melting at 370° (sodium salt), reduced, in 61% yield, by sodium sulphide and alcohol to 3 : 7-diaminoacridone, m. p. 325° (also +H<sub>2</sub>O) (dibenzylidene and diacetyl derivatives), which, in turn, is reduced by sodium amalgam in alkaline solution at 80° to 3 : 7-diaminoacridine, m. p. 318° [monohydrochloride; dibenzylidene derivative, m. p. 208°; diacetyl derivative, m. p. 344° (hydrochloride)]. The diacetyl derivative is converted by methyl sulphate in boiling nitrobenzene into 3 : 7-diacetamidomethylacridinium methosulphate (chloride), hydrolysed to 3 : 7-diamino-N-methylacridinium chloride. When 3 : 7-diaminoacridine is heated with 25% hydrochloric acid in a sealed tube at 250°, 3 : 7-dihydroxyacridine, m. p. 324° (hydrochloride), is obtained. The bactericidal properties of 3 : 7-diaminoacridine are inferior to those of proflavine and acriflavine. All attempts to condense 2-nitro-6-aminobenzoic acid with *o*- or *p*-chloronitrobenzene or with 2-chloro-4-nitrotoluene were unsuccessful. The following corrected m. p. data are given : 5-methylacridine (Bernthsen, A., 1884, 1356), m. p. 119°; *o*-(5-acridyl)benzoic acid, darkens at 293°, not melting completely below 375° [loc. cit., m. p. 163° (decomp.)]; acridylaldehyde, m. p. 146.5—147° (Bernthsen and Muhlert, A., 1887, 849, give m. p. 139—140°). All m. p. are corrected.

J. W. BAKER.

**Synthesis of the polypeptide hydantoin, 5-*p*-hydroxybenzyl-3-methylhydantoin-1- $\alpha$ -phenylacetic acid.** D. A. HAHN and E. DYER (J. Amer. Chem. Soc., 1930, 52, 2494—2504).—Ethyl  $\alpha$ -bromophenylacetate reacts with the sodium derivative of 5-anisylidene-3-methylhydantoin in alcohol, forming *ethyl 5-anisylidene-3-methylhydantoin-1- $\alpha$ -phenylacetate*, m. p. 119—120.5°, converted by treatment with alcoholic hydrogen chloride into an isomeric ester, m. p. 100.5—101.5°. Reduction of either of these esters with hydrogen in presence of colloidal palladium and alcohol affords two isomeric *ethyl 5-anisyl-3-methylhydantoin-1- $\alpha$ -phenylacetates*, m. p. 112—113° (I) and 64—65° (II), respectively. Hydrolysis of I with alcoholic potassium hydroxide and sodium ethoxide gives *potassium*, m. p. 109—110°, and *sodium 5-anisyl-3-methylhydantoin-1- $\alpha$ -phenylacetates*, m. p. 178° (decomp.), respectively. The free acid has been obtained in five modifications : (a) +H<sub>2</sub>O, m. p. 92—94°, which loses water above 100° yielding (b), m. p. 114.5—116°, (c) +Et<sub>2</sub>O, m. p. 76—78° with loss of ether, (d), m. p. 67—69° (obtained when c or e is fused at high temperatures), and (e), m. p. 147—149° (formed when the other modifications are crystallised from alcohol or ether, or by keeping). Demethylation of e or I with red phosphorus and hydriodic acid (d 1.7) at 100—110° furnishes 5-*p*-hydroxybenzyl-3-methylhydantoin-1- $\alpha$ -phenylacetic acid, m. p. 206—207.5 (ethyl ester, m. p. 125—127°), hydrolysed by barium hydroxide to *tyrosine-N- $\alpha$ -phenylacetic acid*, m. p. 223—225° (decomp.) [copper salt, blue (+3.33 H<sub>2</sub>O), green (anhydrous), m. p. 215° (decomp.)]. H. BURTON.

**Isomerism of unsaturated acids obtained in the synthesis of 5-*p*-hydroxybenzyl-3-methylhydantoin-1- $\alpha$ -phenylacetic acid.** D. A. HAHN and E. DYER (J. Amer. Chem. Soc., 1930, 52, 2505—2512).—Hydrolysis of *ethyl 5-anisylidene-3-methylhydantoin-1- $\alpha$ -phenylacetate*, m. p. 119—120.5° (preceding abstract), affords two forms, m. p. 203—204° (I) [potassium salt, m. p. 208—210° (decomp.)], and m. p. 227—229° [potassium salt, m. p. 212° (decomp.)], of the corresponding acid. The latter is also obtained from I by treatment with hydrogen chloride in acetic acid. Hydrolysis of *ethyl 5-anisylidene-3-methylhydantoin-1- $\alpha$ -phenylacetate*, m. p. 100.5—101.5° (loc. cit.), gives I and an isomeride, m. p. 58—62° [sodium (+H<sub>2</sub>O), m. p. 128—132° (decomp.), and potassium (+2H<sub>2</sub>O) salts, m. p. 192—194° (decomp.)], which when heated or kept for some time passes into another form, m. p. 178.5—180.5°. The last-named modification is converted into I by the action of hydrogen chloride. Absorption curves for the various isomerides are given. H. BURTON.

**Dialkylbarbituric acids.** H. A. SHONLE, A. K. KELTSCH, and E. E. SWANSON (J. Amer. Chem. Soc., 1930, 52, 2440—2451).—The following new ethyl alkyl- and dialkyl-malonates are described :  $\alpha$ -ethylpropyl-, b. p. 100—102°/3 mm.,  $n_D^{20}$  1.4275; cyclopentyl-, b. p. 113.8°/4 mm.,  $n_D^{20}$  1.4434; *n*-butylallyl-, b. p. 127—131°/11—12 mm.,  $n_D^{20}$  1.4387; ethyl- $\beta$ -hydroxyethyl-, b. p. 128—131°/6 mm.,  $n_D^{20}$  1.4444; ethyl- $\alpha$ -ethylpropyl-, b. p. 110—112°/4 mm.,  $n_D^{20}$  1.4329; ethyl- $\alpha$ - $\beta$ -dimethylpropyl-, b. p. 110—116°/7 mm.,  $n_D^{20}$  1.4400; cyclopentylethyl-, b. p. 115.4—116.2°/4 mm.,

$n_D^{20}$  1.4448; ethyl- $\alpha$ -methylamyl-, b. p. 126—134°/9 mm.,  $n_D^{20}$  1.4331; ethyl- $\alpha$ -propylbutyl-, b. p. 127—133°/10 mm.,  $n_D^{20}$  1.4302;  $\beta$ -phenylethylethyl-, b. p. 173—177°/5 mm.,  $n_D^{20}$  1.4829, and ethyl-*n*-heptyl-, b. p. 143.5°/3.5 mm.,  $n_D^{20}$  1.4343. It was not found possible to introduce the ethyl group into ethyl *sec*.-butyl-, *sec*.-amyl-, or cyclopentyl-malonates or the allyl group into ethyl *sec*.-butylmalonate; the larger group can, however, be introduced into ethyl ethylmalonate. The formation of mixtures of bromides from *sec*.-alcohols by distillation with hydrobromic acid is noted (cf. Sherrill and others, A., 1929, 1419). The following substituted barbituric acids were prepared, usually from the malonates and carbamide: 5- $\alpha$ -methylbutyl-, m. p. 164—166° (all m. p. are corr.; lit. 162—163°); 5- $\alpha$ -ethylpropyl-, m. p. 165—168° (lit. 198°); 5-cyclopentyl-, m. p. 221—223°; 5-ethyl-5- $\alpha$ -ethylpropyl-, m. p. 127—129° (lit. 162°); 5-cyclopentyl-5-ethyl-, m. p. 182—183°; 5-ethyl-5- $\alpha$ -methylamyl-, m. p. 121—123°; 5- $\alpha$ -methylbutyl-5-allyl-, m. p. 86—88°; 5- $\alpha$ -ethylpropyl-5-allyl-, and 5-cyclopentyl-5-allyl-, m. p. 161—163°. 5-Ethyl-5-*sec*.-butylbarbituric acid has m. p. 164—165°; the compound described by Hsueh and Marvel (A., 1928, 529) is 5-*sec*.-butylbarbituric acid. Pharmacological data are given for 21 substituted barbituric acids. H. BURTON.

**Production of histamine from histidine by ultra-violet light and absorption spectra of these.** R. B. BOURDILLON, J. H. GADDUM, and R. G. C. JENKINS (Proc. Roy. Soc. 1930, B 106, 388—398).—Solutions of histidine in transparent fused silica vessels are sterilised and irradiated by means of a mercury-vapour lamp. The amount of histamine produced is determined by the effect on the blood pressure of an ether-anæsthetised cat as compared with that of a known histamine solution. Histamine itself is rapidly destroyed by ultra-violet light, unless filtered from the wave-lengths shorter than 280  $\mu$ , although wave-lengths shorter than 265  $\mu$  are the most effective in promoting the change. Little absorption occurs with either histidine or histamine above 240  $\mu$ .

P. G. MARSHALL.

**Attempts to find new antimalarials. V. Some piperidino- and piperazino-derivatives of quinoline.** W. O. KERMACK and J. F. SMITH (J.C.S., 1930, 1356—1361).—Condensation of 4-chloro-2-methylquinoline with piperidine at 180° affords 4-piperidino-2-methylquinoline, b. p. 207°/12 mm. (picrate, m. p. 182°; chloroaurate, m. p. 174°), whilst the 6-methoxy-derivative similarly gives 4-piperidino-6-methoxy-2-methylquinoline, b. p. 220°/12 mm. (picrate, m. p. 191°; chloroaurate, m. p. 156°). Condensation with an excess of piperazine hexahydrate similarly affords 4-piperazino- + H<sub>2</sub>O, m. p. 60°, and anhydrous, m. p. 103° (4'-acetyl derivative + H<sub>2</sub>O, m. p. 70°, and anhydrous, m. p. 122°), and 4-piperazino-6-methoxy- + H<sub>2</sub>O, m. p. 55°, and anhydrous, m. p. 113° (4'-acetyl derivative + H<sub>2</sub>O, m. p. 86°, and anhydrous, m. p. 154°), 2-methylquinoline, together with small quantities of 1:4-di-2'-methyl-, m. p. 314°, and 1:4-di-6'-methoxy-2'-methyl-, m. p. 286°, 4'-quinoylpiperazine, these by-products being obtained in larger yield when relatively less piperazine is used in the condensation.

J. W. BAKER.

**Auto-oxidation of complex metallic compounds of indigotin.** H. MACHEMER (Ber., 1930, 63, [B], 1341—1347; cf. A., 1928, 306).—The yellow, crystalline product of the auto-oxidation of metallic derivatives of indigotin in pyridine is identified as anhydro- $\alpha$ -isatinanthranilide,  $\text{CO}-\text{C}_6\text{H}_4-\text{N}-\text{CO}-\text{C}_6\text{H}_4-\text{N}-\text{CO}$ , m. p. 178° (cf. Friedländer and Roschdestwensky, A., 1916, i, 80). Reaction appears to proceed with intermediate formation of isatin and not of dehydroindigotin. Unsymmetrical indigoid dyes which cannot pass through the dehydroindigotin stage all undergo oxidative decomposition and can readily be degraded by air in anhydrous pyridine in the presence of chromous acetate. With compounds such as ethyl indigotin-malonate or indigotinphenylacetate which cannot be decomposed into isatin, the reaction with pyrophoric copper leads only to complex formation. Attempts to dehydrogenate indigotin in the absence of oxygen and presence of spongy palladium and benzoquinone as hydrogen acceptor were unsuccessful. Auto-oxidation of isatin or bromoisatin in presence of bone charcoal affords the yellow dye (see above) or its dibromo-derivative. Indigotin is auto-oxidised in presence of manganese linoleate. Copper-bronze and pyridine behave towards methylene-blue in the same manner as sulphuric acid and dichromate, silver oxide, or alkali hydroxide and air; methylene-violet and methylene-azure are separated from the solution and identified spectroscopically. H. WREN.

**Heterocyclic compounds derived from 9-amino-10-hydroxyphenanthrene.** S. C. DE and T. N. GHOSH (J. Indian Chem. Soc., 1930, 7, 357—360).—9-Amino-10-hydroxyphenanthrene hydrochloride is converted by an excess of boiling formic acid into phenanthroxazole,  $\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{C}_6\text{H}_4-\text{C}(\text{N})=\text{CH}$ , m. p. above 300°, and by glacial acetic acid into methylphenanthroxazole, m. p. above 300°. With benzamidine hydrochloride at 190—200° it affords phenylphenanthriminazole,  $\text{C}_6\text{H}_4-\text{C}(\text{NH})-\text{C}_6\text{H}_4-\text{C}(\text{N})=\text{CPh}$ , m. p. above 300°, and with *o*-phenylenediamine and zinc chloride at 175—180° it gives phenanthraphenazine, m. p. 217°. With *o*-tolylenediamine and naphthylene-1:2-diamine, phenanthratolazine, m. p. above 212°, and naphthaphenanthrazine, m. p. above 273°, are produced. 9-Amino-10-hydroxyphenanthrene hydrochloride is converted by benzaldehyde and hydrogen chloride into phenyldihydrophenanthroxazole,  $\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{C}_6\text{H}_4-\text{C}(\text{NH})=\text{CHPh}$ , m. p. above 300°. Phenanthroxazine, m. p. above 300°, is prepared by heating 9-amino-10-hydroxyphenanthrene hydrochloride in a sealed tube at 230—240°; phenanthrazine, m. p. above 300°, is obtained from the hydrochloride and alcoholic ammonia at 150—160°. H. WREN.

**Formation of ketones from diarylmethyl peroxides by the action of sulphuric acid.** H. ASPELUND (Ber., 1930, 63, [B], 1352—1353).—Phenylfurodiazyl diphenylmethyl peroxide, moistened with glacial acetic acid, is converted by concentrated sulphuric acid into phenyl phenylfurodiazyl ketone,  $\text{N}(\text{CPh})=\text{O}$ , m. p. 139° (semicarbazone, m. p. 198°; oxime,  $\text{N}(\text{CBz})=\text{O}$ ).

m. p. 197—198°, also derived from the peroxide,  $[\text{CPhCl}_2\text{N}:\text{N}:\text{CCl}_2\text{CPh}_2\text{O}]_2$ . It is converted by amalgamated zinc and hydrochloric acid into mandelic and benzoic acids. Similarly, phenylthiodiazyl-diphenylmethyl peroxide affords *phenyl phenylthio-diazyl ketone*,  $\text{N}:\text{CPh} > \text{S}$ , m. p. 129° [oxime, m. p. 238° (decomp.)]. *Methylfurodiazyl-diphenylmethyl peroxide* yields *phenyl methylfurodiazyl ketone*, m. p. 115—116° (*semicarbazone*), reductively hydrolysed to mandelic and acetic acids. H. WREN.

**Synthesis of thiazan derivatives.** Reactivity of various alkyl bromides with diphenylthiocarbamide. F. G. MOORE and F. B. DAINS (Univ. Kansas Sci. Bull., 1929, 18, 633—643).—The following were prepared from arylamines, epichlorohydrin, and arylthiocarbimides: 2-phenylimino-3-p-bromophenyl-, m. p. 177° (*hydrochloride*, m. p. 191°); 2-p-tolylimino-3-β-naphthyl-, m. p. 152°; 2-p-tolylimino-3-phenyl-, m. p. 139°; 2-o-tolylimino-3-o-tolyl-, m. p. 139—140°; 5-hydroxy-1:3-thiazan; and from the disubstituted thiocarbamides and epichlorohydrin: 2-phenylimino-3-phenyl-, m. p. 175°; 2-p-tolylimino-3-p-tolyl-, m. p. 142—142.5°, and 2-m-xylylimino-3-m-xyl-, m. p. 146°, 5-hydroxy-1:3-thiazan.

#### CHEMICAL ABSTRACTS.

**Constitution of anserine.** W. LINNEWEH and F. LINNEWEH (Z. physiol. Chem., 1930, 189, 80—84).—Anserine and carnosine were hydrolysed by means of 20% sulphuric acid for 6—8 hrs. Anserine gave 66% of pure *l*-methylhistidine, m. p. 248—249°,  $[\alpha]_D^{25} -25.8^\circ$ ; the *nitrate*, m. p. 216°, and the *picrolonate* were prepared. β-Alanine was also isolated as the free amino-acid. Carnosine yielded *l*-histidine,  $[\alpha]_D^{25} -37.4^\circ$ . Thus anserine and carnosine differ only by a methyl group attached to the nitrogen of the glyoxaline ring. J. H. BIRKINSHAW.

**Reduction of nicotine and derivatives of hexa- and octa-hydronicotines.** W. WINDUS and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 2543—2546).—Reduction of nicotine with sodium and alcohol gives a mixture of 5 parts of hexahydronicotine and 1 part of octahydronicotine (3-β-methylaminobutyl-piperidine), separable by fractionation of the benzoyl derivatives. Catalytic reduction (Adams) of nicotine hydrochloride furnishes a mixture of 1 part of the hexa- and 3 parts of the octa-hydro-derivatives. Attempts to prepare piperidine derivatives with unsaturated side-chains by the exhaustive methylation of *acetyl*, b. p. 140—150°/1 mm.,  $d_4^{20} 1.034$ ,  $n_D^{20} 1.5010$ ,  $[\alpha]_D^{25} -4.07^\circ$  in alcohol, and *benzoyl-hexahydronicotine*, b. p. 195—198°/0.8—1 mm.,  $d_4^{20} 1.072$ ,  $n_D^{20} 1.5549$ ,  $[\alpha]_D^{25} -11.39^\circ$  in alcohol [*methiodide*, m. p. 99—103° (decomp.) after softening at about 85°], were unsuccessful. The *diacetyl*, b. p. 210—213°/1 mm.,  $d_4^{20} 1.041$ ,  $n_D^{20} 1.5033$ , and impure *dibenzoyl*, b. p. 280—300°/1.5 mm.,  $d_4^{20} 1.106$ ,  $n_D^{20} 1.5710$ , derivatives of octahydronicotine are optically inactive. H. BURTON.

**Bases from angostura bark.** Quinoline, 2-methylquinoline, 2-*n*-amylquinoline, and 2-keto-1-methyl-1:2-dihydroquinoline. E. SPÄTH and J. PXL (Monatsh., 1930, 55, 352—357).—The low-boiling fraction (100—190°/14 mm.) of the liquid bases isolated from angostura bark (A., 1929, 1319) is

separated into (a) b. p. 100—145°/14 mm., and (b) b. p. 145—190°/14 mm. Partial distillation of (a) with steam affords a volatile portion from which (by fractionation) quinoline [*trinitro-m-tolyl-oxide*, m. p. (vac.) 224—225° after slight previous sintering] and 2-methylquinoline [*trinitro-m-tolyl-oxide*, m. p. (vac.) 221—222° (decomp.)] are isolated. Extraction of (b) and the residue from (a) with boiling water gives 2-keto-1-methyl-1:2-dihydroquinoline (*picrate*, m. p. 129—130°). The residue from this is heated with fuming hydrochloric acid at 175°, whereby 4-methoxy-2-*n*-amylquinoline is removed as the ether-insoluble 4-hydroxy-derivative. Prolonged treatment of the residual bases, b. p. 130—170°/14 mm., with ethereal methyl iodide at 100° affords a methiodide, which on dry distillation in a vacuum gives crude 2-*n*-amylquinoline (*picrate*, m. p. 125—126°). H. BURTON.

**Optical rotation and configuration of certain bases of the type of laudanose.** W. LIETHE (Ber., 1930, 63, [B], 1498—1503; cf. A., 1929, 647, 1079, 1461).—1-Benzyl-3:4-dihydroisoquinoline is reduced by tin and hydrochloric acid or sodium and alcohol to 1-benzyl-1:2:3:4-tetrahydroisoquinoline, b. p. 207°/20 mm. (*hydrochloride*, m. p. 173°), which is resolved by successive treatment with *d*- and *l*-tartaric acid in water, thus giving 1-1-benzyl-1:2:3:4-tetrahydroisoquinoline,  $d^{25} 1.085$ ,  $[\alpha]_D^{25} -9.0^\circ$  in cyclohexane,  $-9.0^\circ$  in benzene,  $-6.1^\circ$  in ethyl alcohol,  $-6.6^\circ$  in *N*-hydrochloric acid (*hydrogen d-tartrate*, m. p. 181—182°), and *d*-1-benzyl-1:2:3:4-tetrahydroisoquinoline,  $[\alpha]_D^{25} +8.5^\circ$  in benzene (*hydrogen l-tartrate*, m. p. 181°). *r*-2-Methyl-1-benzyl-1:2:3:4-tetrahydroisoquinoline (*picrate*, m. p. 168—169°) is similarly resolved into its optical antipodes. 1-2-Methyl-1-benzyl-1:2:3:4-tetrahydroisoquinoline,  $d^{25} 1.049$ ,  $[\alpha]_D^{25} -29.4^\circ$  (among other values) [*hydrogen d-tartrate*, m. p. 157—158°; *methiodide monohydrate*, m. p. about 89°, anhydrous, m. p. 186°,  $[\alpha]_D^{25} +11.2^\circ$  in methyl alcohol], and *d*-2-methyl-1-benzyl-1:2:3:4-tetrahydroisoquinoline,  $[\alpha]_D^{25} +29.0^\circ$  (*methiodide monohydrate* and anhydrous, m. p. 89° and 186°, respectively), are described. The influence of solvent on the sign and magnitude of the optical rotation of the synthetic methyl base and of natural laudanose indicates that the last-named substance belongs to the *laevo*-series. Laudanidine and codamine have the *dextro*-configuration. H. WREN.

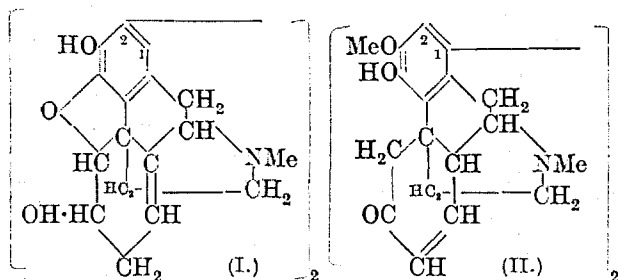
**Sinomenine and disinomenine.** XVI. *iso*-Bromosinomenine (or bromosinomenine). K. GOTO and T. NAMBO (Bull. Chem. Soc. Japan, 1930, 5, 165—169).—Although *isobromosinomenine* is always formed in small quantities (2—20%) along with bromosinomenine when sinomenine hydrochloride is brominated with 1 mol. of bromine in acetic acid at 15°, the yield is increased to 40% when 2 mols. of bromine are employed. It is now found that *isobromosinomenine* is formed by the oxidising action of an intermediate sinomenine perbromide ( $?\text{C}_{19}\text{H}_{22}\text{O}_4\text{NBr}_2$ ,  $\text{HBr}$ ,  $\text{Br}_2$ ) on sinomenine, 2 atoms of hydrogen being removed, and hence the name *bromo-sinomenine*, m. p. 217° [*hydrochloride*, m. p. 231° (decomp.)], solubility in water 2.96%; *hydrobromide*, m. p. 229°, solubility in water 0.84%; *oxime*, m. p. 162° (*hydrochloride*, m. p. above 280°, softens at 236°);

*methiodide*, m. p. 211—212°, is suggested to replace *isobromosinomenine*. This is converted by heating with 2*N*-hydrochloric acid at 100° into *bromosinomenine ketone* (*isobromosinomeninone*), m. p. 198°,  $[\alpha]_D^{25} + 119.89^\circ$  [*dioxime*, m. p. 173.5° (decomp.); *hydrochloride*, m. p. 212°; *methiodide*, m. p. 195° (decomp.)]. When sinomenine hydrochloride is left for some weeks with 2 mols. of bromine in acetic acid, 40% of bromosinomeninone is obtained, the hydrobromic acid formed hydrolysing the enolic methoxyl group. Under similar conditions in the presence of either hydrobromic acid or acetyl chloride, sinomenine is converted into sinomenine hydrate [*methiodide*, m. p. 192—195° (decomp.), not decomp. 264° as previously given (this vol., 353)]. J. W. BAKER.

**Constitution of  $\psi$ -morphine and dithebainone.** K. GOTO and Z. KITASATO (Annalen, 1930, 481, 81—90).—The proof that disinomenine is formed by the coupling through the 1 : 1'-positions of two molecules of sinomenine and may be obtained from the latter by controlled oxidation (A., 1929, 944) has led to the examination of other bimolecular alkaloids of similar nature.

Basic  $\psi$ -morphine methiodide (Polstorff, A., 1880, 408) is converted by the acetolysis method of Fischer and Gerichten (A., 1886, 563) into *bis*-2 : 2'-(3 : 4-*diacetylmorphol*), m. p. 255°, yielding on hydrolysis followed by methylation *bis*-2 : 2'-(3 : 4-*dimethylmorphol*), m. p. 222°;  $\psi$ -morphine is formulated therefore as a 2 : 2'-dimorphine (I).

Oxidation of thebainone (Pschorr, A., 1905, i, 920) by silver nitrate or potassium ferricyanide gives a mixture of  $\alpha$ -*dithebainone*, m. p. 308—310°,  $[\alpha]_D^{25} - 532.6^\circ$  (*acetyl derivative*, m. p. 272—273°,  $[\alpha]_D^{25} - 321.4^\circ$ ), reduced catalytically to *tetrahydro- $\alpha$ -dithebainone*, decomp. above 300°,  $[\alpha]_D^{25} - 390.6^\circ$ ; and  $\beta$ -*dithebainone*, m. p. 235—237°,  $[\alpha]_D^{25} - 327.91^\circ$  (*tetrahydro-derivative*, m. p. 266°,  $[\alpha]_D^{25} - 223.9^\circ$ ).  $\alpha$ -*Dithebainone dimethiodide*, m. p. 274° (decomp.), is converted by the acetolysis method into *bis*-1 : 1'-(4-*acetyl-3-methylmorphol*), m. p. 237°, the same product being also obtained from the  $\beta$ -dimethiodide, m. p. 274°. Dithebainone is formulated as II, the relation between the  $\alpha$ - and  $\beta$ -varieties remaining uncertain.



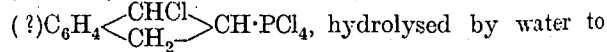
R. CHILD.

**Alkaloids of ergot.** I. S. SMITH and G. M. THOMAS (J.C.S., 1930, 1390—1395).—Pure crystalline specimens of ergotoxine + 21% benzene of crystallisation,  $[\alpha]_D^{25} - 179^\circ$ , and solvent-free, m. p. indefinite 190—200° [softens at 180° (corr.); in bath at 170°],  $[\alpha]_D^{25} - 226^\circ$ , ergotinine, m. p. 239° (corr.; decomp.; in bath at 200°),  $[\alpha]_D^{25} + 513^\circ$ , ergotamine, m. p. 213—

214° (corr., in bath at 205°),  $[\alpha]_D^{25} - 181^\circ$ , and ergotaminine, m. p. 252° (corr., in bath at 240°),  $[\alpha]_D^{25} + 450^\circ$  (all specific rotations in chloroform), have been prepared and have been shown to be definite and distinct substances. The first two are readily obtained from official ergot of rye and it is immaterial whether the alkaloid is isolated by the special process of Spiro and Stoll (A., 1922, i, 47) or by the simpler method of Kraft (A., 1906, i, 979), the average yield of crude mixed alkaloids being 0.1—0.15%. Ergotamine and ergotaminine (separated by methyl alcohol, in which the former is more readily soluble) were isolated only from specimens of non-pharmacopoeial ergot growing on tall fescue (*Festuca*) and, contrary to the statement of Spiro and Stoll (*loc. cit.*), are readily isolated by Kraft's method. J. W. BAKER.

**Modes of reaction of phosphorus pentachloride.** I. E. BERGMANN and A. BONDI (Ber., 1930, 63, [B], 1158—1173).—Evidence of the unique position of one of the chlorine atoms of phosphorus pentachloride is found in its addition to indene, styrene,  $\alpha$ -methylstyrene, *as*-diphenylethylene, and  $\alpha$ -benzylstilbene in cold benzene to products which suffer hydrolysis accompanied by intramolecular separation of the fifth chlorine atom as hydrogen chloride when treated with water. At a much higher temperature certain indones add two chlorine atoms when treated with phosphorus pentachloride, thus decisively indicating the fission,  $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ . The surprising immunity of the carbonyl group from attack is connected with other abnormalities in its reactions. The different modes of fission of the phosphorus pentachloride are ascribed to the widely-differing experimental conditions.

Indene and phosphorus pentachloride in benzene give a crystalline additive compound



*indenyl-2-phosphinic acid*,  $\text{C}_8\text{H}_4 \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C} \cdot \text{PO}_3\text{H}_2$ , m. p. 184° (slight decomp.); the possibility that the compound is indenyl-3-phosphinic acid is not excluded. It is monobasic towards methyl-orange, dibasic towards phenolphthalein. The *silver hydrogen, lead, mercurous, thallous, copper, mercuric, cadmium, nickel, ferric, ferrous, aluminium, barium, and calcium* salts are described. The acid is stable towards bromine, but the presence of the ethylenic linking is established by its hydrogenation in boiling propyl alcohol in presence of palladised barium sulphate to *hydrindyl-2-phosphinic acid*, m. p. 196° (*silver salt*). A reactive methylene group is present, since the acid affords 1-*benzylideneindenyl-2-phosphinic acid*, m. p. 188—189° (slight decomp.) (*silver, lead, and ferric salts*), 1-*anisylideneindenyl-2-phosphinic acid*, m. p. 192° (slight decomp.), and 1-*piperonylideneindenyl-2-phosphinic acid*, m. p. 194° (slight decomp.). Styrene and phosphorus pentachloride in a similar manner afford *styryl- $\beta$ -phosphinic acid*,  $\text{CHPh} \cdot \text{CH} \cdot \text{PO}_3\text{H}_2$ , m. p. 146°; indications of the formation of *cis-trans*-isomerides are obtained. The *silver, lead, mercurous, thallous, ferrous, ferric, copper, nickel, barium, and calcium* salts are described. The acid is hydrogenated to *phenylethylphosphinic acid*, m. p. 137—138°.



$\alpha$ -Methylstyrene is transformed by the successive action of phosphorus pentachloride and water into a mixture of unchanged material, a substance, b. p. 158—160°/14 mm. (possibly the unsaturated dimeride of  $\alpha$ -methylstyrene), and  $\alpha$ -methylstyryl- $\beta$ -phosphinic acid, m. p. 95° (silver, lead, mercurous, copper, ferrous, ferric, nickel, barium, and calcium salts); the corresponding hydrogenated acid could not be caused to crystallise. Oxidation of the acid by chromic acid in glacial acetic acid affords acetophenone.  $\beta\beta$ -Diphenylvinylphosphinic acid, m. p. 167°, is derived from  $\alpha\delta$ -diphenylethylene; the silver, lead, mercury, copper, nickel, ferrous, ferric, barium, and calcium salts are described. The acid is hydrogenated to  $\beta\beta$ -diphenylethyl- $\alpha$ -phosphinic acid, m. p. 213°, and oxidised to benzophenone.  $\alpha$ -Benzylstilbene and phosphorus pentachloride afford 2:3-diphenylindene accompanied by benzoyl chloride formed by auto-oxidation of the compound  $\text{CH}_2\text{Ph}\cdot\text{CClPh}\cdot\text{CHPh}\cdot\text{PCl}_4$ .

3-Phenyl-2-methylindone and phosphorus pentachloride at 165° afford 2:3-dichloro-3-phenyl-2-methylhydrindone, m. p. 110—111°, re-converted into the initial material by copper powder in boiling benzene. 2:3:4:5-Tetraphenylcyclopentadienone at 170° similarly yields 2:3(or 2:5)-dichloro-2:3:4:5-tetraphenylcyclopentenone, m. p. 188°, from which the dienone is regenerated by treatment with copper powder. H. WREN.

#### Reduction of dihydrophenarsazine derivatives.

G. RAZUBAIEV and A. BENEDIKTOV (J. Russ. Phys. Chem. Soc., 1930, 62, 549—554).—10-Chloro-5:10-dihydrophenarsazine is quantitatively reduced by the action of zinc dust and acetic acid in an inert atmosphere to 5:10-dihydrophenarsazine hydrochloride; the corresponding oxide is produced by the action of water. This oxide is converted into 5:10-dihydrophenarsazine acetate, m. p. 221—222°, by atmospheric oxygen, and into 10-iodo-5:10-dihydrophenarsazine, m. p. 217—220°, by the action of iodine. Chlorine and bromine convert 10-methyl-5:10-dihydrophenarsazine into the perchloride, m. p. 172° (decomp.), and the perbromide, respectively, m. p. 120—121°; the latter, on heating under reduced pressure, gives methyl bromide and 10-bromo-5:10-dihydrophenarsazine, m. p. 210—213°. R. TRUSZKOWSKI.

Mercurated azo-dyes derived from benzidine and *o*-tolidine. E. McMAHON and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 2528—2531).—Treatment of benzidine with mercuric acetate in acetic acid solution affords an unstable *acetoxymercuri*-derivative (+3AcOH), m. p. 144—146° (decomp.). *Acetoxymercuri-o-tolidine* (+2AcOH), m. p. 120° (decomp.), is obtained similarly. Tetrazotisation of these derivatives with butyl nitrite and hydrochloric acid in alcohol and subsequent coupling with *H*-acid or 7-amino- $\alpha$ -naphthol-3-sulphonic acid (benzidine derivative only) affords azo-dyes, which lose mercury very readily. H. BURTON.

Benzyl and phenylethyl compounds of lead. E. KRAUSE and O. SCHLÖTTIG (Ber., 1930, 63, [B], 1381—1387).—Many of the benzyl compounds of quadrivalent lead are coloured and very sensitive to air. This unusual behaviour appears to be due to the immediate neighbourhood of the phenyl group, since

the corresponding phenylethyl compounds are completely normal.

Lead chloride is converted by ethereal magnesium benzyl chloride followed by moderated bromination of the residual product into lead tribenzyl bromide, incipient decomp. about 130° according to the rate of heating. It may also be prepared from lead bromide and magnesium benzyl bromide with after-treatment of the product with 2% hydrobromic acid. *Tin tribenzyl fluoride*, m. p. 242°, and the corresponding hydroxide are incidentally described. *Lead triphenyl benzyl*, m. p. 93° after softening, incipient decomp. about 190°, is derived from lead triphenyl bromide and magnesium benzyl chloride; with bromine it affords *lead diphenyl benzyl bromide*, m. p. 143° (decomp.) after softening and darkening at 133—134°. *Lead diphenyl dibenzyl*, softening at 135° after darkening at about 127°, is prepared from lead diphenyl dibromide and excess of magnesium benzyl chloride. Successive treatment of lead chloride with magnesium phenylethyl bromide and bromine gives *lead triphenylethyl bromide*, m. p. 91—92° after slight softening, converted by magnesium phenylethyl bromide into the colourless lead tetraphenylethyl which could not be freed completely from  $\alpha\delta$ -diphenylbutane. *Lead triphenyl phenylethyl*, m. p. 116—117°, incipient decomp. about 180°, and *lead diphenyl phenylethyl bromide*, m. p. about 119° (decomp.) after softening at about 110°, are described. H. WREN.

#### Heterocyclic systems containing selenium.

III. *cycloSelenopropane*. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1930, 1497—1502).—Interaction of trimethylene dibromide and sodium selenide in alcohol at the ordinary temperature in an atmosphere of hydrogen affords only a small yield of *cycloselenopropane*, b. p. 118—119°/779 mm.,  $n_D^{25}$  1.5612,  $d_4^{25}$  1.525, the main product being a hexamolecular polymeride, m. p. 38—40°, converted by warm 2*N*-nitric acid into its nitrate, which with hydrochloric acid gives the chloride, both of which are unstable, whilst hot concentrated nitric acid converts the polymeride into oxalic acid and *trimethylenediselenious acid dinitrate*,  $\text{CH}_2(\text{CH}_2\cdot\text{SeO}_2\text{H}\cdot\text{HNO}_3)_2$ , decomp. 112°. This is also obtained by oxidation of *cyclo*trimethylene diselenide, m. p. 59° (Hagelberg, A., 1890, 949, gives m. p. 54.5°), or trimethylene diselenodicyanate, m. p. 53° (Hagelberg, *loc. cit.* gives 51°), and is converted by sodium acetate and potassium iodide into *trimethylene diseleno-di-iodide*, m. p. 124°, also obtained by the action of iodine on a chloroform solution of *cyclo*trimethylene diselenide. When the polymeride is gently heated it decomposes without elimination of selenium into propylene and the more stable *cyclo*trimethylene diselenide, this reaction suggesting that partial depolymerisation occurs initially with the intermediate formation of *cyclo*hexamethylene 1:5-diselenide. Iodine in alcohol converts *cycloselenopropane* into the monomeric *di-iodide*, m. p. 98° (converted by silver oxide into a neutral solution of the dihydroxide which decomposes forming a solid, m. p. 73—74°), together with a polymerised *di-iodide*, m. p. 87°, whilst with alcoholic mercuric chloride the *mercurichloride*,  $\text{C}_3\text{H}_6\text{Se}\cdot\text{HgCl}_2$ , decomp. 105° (shrinks at 80°), is obtained. J. W. BAKER.

**Constitution of some organic derivatives of thallium.** N. V. SIDGWICK and L. E. SUTTON (J.C.S., 1930, 1461—1473).—The mol. wt. of thallous ethoxide (solubility in ethyl alcohol 9.108% at 25°), methoxide, decomp. above 120° (solubility in methyl alcohol and benzene, 1.703 and 3.16%, respectively, at 25°), cyclohexoxide, decomp. above 110°, benzyl-oxide, m. p. 74—78° (microcrystallographic examination by T. V. BARKER and SPILLER), phenoxide, m. p. 233—235° (Christie and Menzies, A., 1926, 55, give 231—235°), *m*-tolyl-oxide, m. p. 196° (lit. 187°), *o*-, m. p. 164° (lit. 160°), and *m*-, m. p. 148° (lit. 146—148°), -methoxyphenoxide, salicylaldehyde, m. p. 197° (decomp.) (lit. 186°), and *o*-vanillin, m. p. 142° (decomp.), have been determined by the cryoscopic method in benzene, and by the ebullioscopic method in benzene, ethyl and methyl alcohols, specially designed apparatus, necessitated by the instability of some of these derivatives, being employed. All were prepared by interaction between the ethoxide and the appropriate hydroxy-compound. Both the aliphatic and aromatic alkoxides behave as salts in water, but in benzene they are highly associated, fourfold association being complete when the actual concentrations are only about 0.05*N* in the case of the aliphatic compounds and the *o*- and *m*-methoxyphenoxides, whilst the phenoxide and *o*-vanillin derivative are associated about three times even at 0.01—0.02*N* concentrations. Two alternative chelate structures are suggested for the stable fourfold polymeride, one cubic and the other an 8-membered chelate ring. Ethyl thalloacetate is completely polymerised to its dimeride in 0.125*N* solution and two possible structures are suggested, one of which resembles one of those proposed for the quadrimolecular complex. The bearing of these results on the parachors of thallium compounds is discussed. J. W. BAKER.

**Acid and alkaline hydrolysis of albumin.** I. S. YAITSCHNIKOV (J. Russ. Phys. Chem. Soc., 1930, 62, 693—702).—Protein, peptone, ammonia, amino-, and amido-group nitrogen, as well as that of organic bases, are determined in the hydrolysates of ovalbumin after treatment during 1, 4, and 9 hrs. at 37° and 100° with *N*- and 0.2*N*-sulphuric acid or -sodium hydroxide solutions, and the results obtained are analysed graphically. R. TRUSZKOWSKI.

**Thermal disaggregation of gelatin. (Röntgenographic study of its degradation.)** O. GERNGROSS, O. G. TRIANGI, and P. KOEPPE (Ber., 1930, 63, [B], 1603—1614).—Electro-osmotically purified gelatin containing 0.13% of ash is heated in Jena glass vessels in 25% solution of exactly isoelectric reaction for 24, 72, 75, and 336 hrs. at 100° and 48 hrs. at 121°. Possible peptide degradation is examined by measurement of increase of the free amino-groups according to Van Slyke, by alkalimetric determination of free carboxyl groups according to Willstätter and Waldschmidt-Leitz, and by the formaldehyde number. Physical changes are followed by measurements of the viscosity of the solutions and observations on the gelatinising power of the heated sols and mutarotation. Even after 75 hrs. at 100°, there is no sign of a chemical valency degradation by rupture of peptide linkings, whereas the gelatinising power is completely destroyed,

the viscosity reduced to 18.8%, and the mutarotation to 28.4% of the initial value of the intact gelatin. The protracted heating at 121° or exposure for 336 hrs. at 100° causes distinct, true hydrolysis. In slightly acid solution ( $p_H$  1.8) much more pronounced peptide degradation is observed after 8 hrs. at 100°. On the basis of determinations of mol. wt. and X-ray diagrams, the following picture of the structure and thermolysis of gelatin is drawn. Intact gelatin gels consist of extended structures which arise from extra-molecular union of the gelatin particles. In aqueous solution of concentration lower than 0.5% at 20° these individual particles, according to the previous history of the preparations, have a mean mol. wt. of 50,000—90,000 if the reaction is isoelectric. The particles undergo an almost completely reversible distribution into molecules of mean mol. wt. of a few thousands when the solutions are heated for a short period at 100°, but, even under these conditions, an irreversible change which reduces the mol. wt. of the intact material is also obvious. Protracted ebullition causes the formation of individual molecules (mean wt. 4500) which do not recombine to aggregates when cooled; the power of forming gels or viscous, adhesive solutions is lost. It is assumed that the molecules of the intact gelatin are not united to the structures of mol. wt. 90,000 by main valency forces, but this is not established with certainty. Re-aggregation of the thermolysed particles is observed to a certain degree if the solutions are evaporated to dryness and the residue is dissolved in water.

H. WREN.

**Critical solution temperature of the system methyl alcohol-cyclohexane as a means of detecting and determining water in methyl alcohol.** D. C. JONES and S. AMSTELL (J.C.S., 1930, 1316—1323).—The mutual solubility curve of pure cyclohexane-methyl alcohol, and those obtained in the presence of 0.331, 0.8, 1.114, 2.031, and 3.9% of added water, are determined and described. The effect of added water in raising the critical solution temperature of mixtures of this type is considerable and may be used as the basis of a method for the determination of the water content of methyl alcohol. In the method described a mixture containing 75% by weight of cyclohexane is chosen, the limit of sensitivity being  $\pm 0.002\%$  if the temperature be read to 0.02°. Benzene (1%) lowers the critical solution temperature by 1.21°, and acetone (1%) by 0.67°. In purifying the methyl alcohol used, it was discovered that careful fractional distillation gave as anhydrous a product as dehydration over quicklime followed by distillation.

H. A. PIGGOTT.

**Detection of glycerol.** M. T. SERANTES (Rev. Cent. Est. Farm. Bioquim., 1929, 18, 221—223; Chem. Zentr., 1930, i, 560—561).—Denigès' and Sanchez' procedures are modified by the use of barium dioxide, instead of lead or manganese dioxide, as oxidising agent. A. A. ELDRIDGE.

**Determination of pentoses and pentosans by different methods.** D. D. DESHPANDE (J. Indian Inst. Sci., 1930, 13A, 110—112).—The most satisfactory method is distillation of the material with 12% hydrochloric acid, and determination of the furfur-

aldehyde so formed by absorption of bromine (Powell and Whittaker, A., 1924, ii, 354). T. H. MORTON.

**Indicator for titration of aromatic hydroxy-acids and their substitution products or esters.** I. KAPLAN (Ber., 1930, 63, [B], 1589—1590).—*p*-Hydroxybenzoic acid can be titrated as a monobasic acid in the presence of an indicator with a lower  $p_H$  value than phenolphthalein (bromocresol-purple is suitable), but the entry of a negative substituent into the molecule so enhances the acidity of the phenolic group that the method becomes invalid. Such substituted hydroxybenzoic acids behave as dibasic acids in the presence of Nile-blue. A method is thus indicated for determining the hydroxyl in esters of hydroxybenzoic acids and their derivatives.

H. WREN.

**Reactions of adrenaline.** L. EKKERT (Pharm. Zentr., 1930, 71, 417).—The green colour produced by ferric chloride changes to red after a few minutes without the usual addition of alkali; 10% sodium nitrite solution produces a red colour darkening to blood-red after 1—2 min. Colour reactions with some alkaloids and concentrated sulphuric acid are described.

R. CHILD.

**Specific colour reactions of adrenaline and tyrosine.** B. KISCH (Biochem. Z., 1930, 220, 358—369).—To test for adrenaline, to 4.5 c.c. of the neutral solution 0.5 c.c. of 0.02*N*-hydrochloric acid and 0.2 c.c. of sodium or potassium nitrite solution are

added and the liquid is heated at 100° for 10 min. A pink to ruby-red colour indicates adrenaline. One part in two million parts can be detected. When 1 c.c. of 0.02*N*-sodium hydroxide is added to the liquid the colour does not change, nor does it change when the alkaline solution is re-acidified with 1 c.c. of 0.02*N*-hydrochloric acid. In testing for tyrosine, to 4.5 c.c. of the solution 0.5 c.c. of 0.04 or 0.02*N*-hydrochloric acid and 0.2 c.c. of sodium nitrite solution are added and the liquid is first heated for 5—10 min. at 100°, then shaken with 0.5 c.c. of amyl alcohol. A violet colour can be detected in the alcohol when not less than one part of tyrosine in 40,000 parts is present.

W. MCCARTNEY.

**Reactions of novocaine.** L. EKKERT (Pharm. Zentr., 1930, 71, 402—403).—Modifications of the diazotisation test for novocaine are described. Novocaine salts, treated with calcium hypochlorite, or "chloramine-T" and dilute hydrochloric acid, and subsequently with phenol and ammonia, give after 10 min. a green solution which yields a red ethereal extract.

H. E. F. NOTTON.

**Analysis of neutral-red and of the pyronines.** W. C. HOLMES and A. R. PETERSON (Stain Tech., 1930, 5, 91—96).—Neutral-red and pyronines cannot be determined by reduction with titanous chloride. The most satisfactory method is to determine spectrophotometrically the extinction coefficients of suitable solutions of the dyes.

H. W. DUDLEY.

## Biochemistry.

**Regulation of oxygen consumption in animals with inconstant alveolar gaseous tension.** H. J. JORDAN (Arch. Néerland. Physiol., 1930, 15, 198—212).—A discussion of the regulation of oxygen uptake in animals in which regular pulmonary respiration is not essential (such as certain diving birds, amphibians, molluscs, and insects), so that the tension of the alveolar oxygen may not be even approximately constant.

W. O. KERMACK.

**Gas and electrolyte equilibria in blood. XVI. Evolution of carbon dioxide from blood and buffer solutions.** D. D. VAN SLYKE and J. A. HAWKINS (J. Biol. Chem., 1930, 87, 265—279).—Carbon dioxide is evolved twelve times as rapidly from laked whole blood as from blood-serum or phosphate solution of equivalent carbon dioxide content and buffer value when the respective solutions are exposed to a vacuum. Addition of erythrocytes to a phosphate solution in amount sufficient to bring the haemoglobin concentration to 1/20 of that in whole blood brings about the same acceleration in the evolution of carbon dioxide. Since the whole of the carbon dioxide in blood can be accounted for by the hydrogen carbonate and the physically dissolved carbon dioxide the hypothesis of combination of carbon dioxide with haemoglobin (cf. Henriques, A., 1928, 1389) is rejected; the increased rate of evolution of carbon dioxide from blood is ascribed to the catalytic effect of haemoglobin on the reaction  $\text{HCO}_3' + \text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3$ .

C. R. HARRINGTON.

**Blood as a physico-chemical system. IX. Carbon dioxide dissociation curves of oxygenated human blood.** L. J. HENDERSON, A. V. BOCK, D. B. DILL, and H. T. EDWARDS (J. Biol. Chem., 1930, 87, 181—196).—The accuracy of the equation of Peters and others (A., 1924, i, 439) relating the carbon dioxide dissociation curves of oxygenated human blood to the oxygen capacity of the blood is confirmed except for especially high or low values of the total carbon dioxide of the blood at a pressure of 40 mm. carbon dioxide ( $T_{40}$ ). A graphic expression of the carbon dioxide dissociation as a function of  $T_{40}$  and of oxygen capacity is given, with the aid of which it is possible to construct the carbon dioxide dissociation curve of a sample of blood from determinations of the carbon dioxide content at any given tension of carbon dioxide, and of the oxygen capacity.

C. R. HARRINGTON.

**Respiration of red blood-corpuscles activated by substances stimulating respiration.** L. MICHAELIS and K. SALOMON (Naturwiss., 1930, 18, 566).—The respiration of red blood-corpuscles is stimulated by methylene-blue and by extracts of certain organs, the following being arranged in order of decreasing activity: liver, kidney, spleen, testicle, and lymph gland. Extracts of muscle, brain, or blood-serum are only slightly or often not at all active. The activity of these extracts is not depressed by the presence of carbon monoxide.

W. O. KERMACK.

**Combustion of carbohydrate [catalysed] by methaemoglobin. (Mechanism of catalysis by**

**methylene-blue.**) O. WARBURG, F. KUBOWITZ, and W. CHRISTIAN (*Biochem. Z.*, 1930, **221**, 494—497).—One third of the oxygen consumed in the presence of methylene-blue (cf. Barron and Harrop, *A.*, 1928, 1268) by erythrocytes from the rabbit is used to convert dextrose into pyruvic acid. It is supposed that the function of the methylene-blue is to cause the production of methæmoglobin, the iron in which catalyses the oxidation of the sugar, and this view is confirmed by the facts that amyl nitrite, which also causes production of methæmoglobin, likewise accelerates the oxidation of dextrose in red blood-cells and that carbon monoxide restricts the respiration of the cells in the presence of methylene-blue under conditions in which the production of methæmoglobin by the action of the dye is also restricted.

W. MCCARTNEY.

**Chemical properties of blood-pigments and related substances.** A. STHEEMAN (*Chem. Weekblad*, 1930, **27**, 170—174).—The general chemical and optical properties of hæmoglobin and its derivatives are described and the variations exhibited by various types of blood are discussed. H. F. GILLBE.

**Permeability [of blood-corpuscles to acids and bases].** II. W. SPRANGER (*Biochem. Z.*, 1930, **221**, 315—327; cf. this vol., 629).—The resistance of red blood-corpuscles to permeation by organic and inorganic acids is raised by treatment with cholesterol or cholesteryl ester and lowered by treatment with lecithin, the magnitude of the increase being greater in isotonic solutions of neutral salts with bivalent cations than in those of neutral salts with univalent cations but the same anion. This difference in magnitude arises because the action of the cations interferes with that of the colloids. Anions also are not without effect. Univalent and bivalent cations when present together have an antagonistic effect on the action of cholesterol. Antagonism between cations is observed in the case of lecithin also and the magnitude of the increase in permeability caused by it varies according to the salt present in solution, but is not affected by the valency of the cation. The resistance of corpuscles to permeation by ammonia is temporarily raised by treatment with cholesterol or cholesteryl ester and greatly lowered by treatment with lecithin, there being no interference between the action of the ions and that of the colloid in either case. With both acids and bases the effect produced by cholesterol or its ester can be altered or counter-balanced by that produced by lecithin. In blood-serum the effects produced by cholesterol and lecithin are the same as those produced in salt solutions.

W. MCCARTNEY.

**Application of Van Slyke and Palmer's method for the titration of organic acids in liquids containing proteins.** II. **Direct titration of organic acids in blood.** E. E. MARTINSON and E. A. VLADIMIROVA (*Biochem. Z.*, 1930, **221**, 349—358; cf. this vol., 239).—To 5 c.c. of defibrinated blood 20—25 c.c. of water are added; after hæmolysis is complete 5 c.c. of 50% trichloroacetic acid solution are added, the solution is made up to 50 c.c. with water and filtered. Then 0.75 g. of calcium hydroxide is stirred in and after 15 min. the mixture is again filtered,

15 c.c. of the filtrate being collected in a colorimeter tube and made neutral to phenolphthalein (0.2 c.c. of 1% alcoholic solution) with 0.2*N*- and 0.05*N*-hydrochloric acid. Exactly 1 c.c. of 0.05*N*-hydrochloric acid and 3.57 c.c. of dinitrophenol solution are now successively run in and the liquid is titrated with 0.05*N*-hydrochloric acid until its colour matches that of a standard solution of dinitrophenol (13.3 c.c. of a ten times diluted aqueous dinitrophenol solution made up to 100 c.c. with 0.1*N*-sodium carbonate solution). In the calculation of results allowance must be made for the presence of trichloroacetic acid and of creatinine, creatine, and amino-acids. The maximum error of the method does not exceed 10%. The amounts of organic acids in the blood of diseased persons vary greatly both with the nature of the disease and, even in the same patient, with the stage reached. Trichloroacetic acid must be added to the blood immediately after it is drawn.

W. MCCARTNEY.

**Acid-soluble phosphorus of the blood. I. Elementary composition of filtrates of deproteinised blood and fractionation of the compounds containing phosphorus. II. Participation of compounds containing phosphorus in the reducing power of the blood.** J. ROCHE (*Bull. Soc. Chim. biol.*, 1930, **12**, 636—656).—Determinations have been made of the carbon, nitrogen, and phosphorus contents of the whole blood of the pig, and of certain fractions and deproteinised filtrates and of the precipitate from the latter by barium hydroxide. This precipitate was fractionated according to its solubility in water at various hydrogen-ion concentrations and the fractions were purified by precipitation as lead salt and by phosphotungstic acid. Evidence has been obtained of the existence of a compound containing 1 atom of nitrogen and 1 atom of phosphorus to 6—8 atoms of carbon. There appear to be traces of pyrophosphate but no phosphagen in the blood. The non-fermentable reducing substances present in the blood and other body-fluids appear to be related to the contents of the deproteinised filtrates in acid-soluble phosphorus. Adenylic acid is probably of importance in this respect.

W. O. KERMACK.

**Micro-determination of the chlorides of blood.** V. V. PRAVDITSCH-NEMINSKI and Z. E. BABITSCH (*Russian J. Physiol.*, 1930, **13**, 93—101).—Since Bang's method of extracting and determining chlorides in blood results in considerable losses of chloride, the following procedure, which dispenses with the use of absorbent paper, is recommended: 0.05—0.1 c.c. of blood is blown into 5 c.c. of 92% alcohol contained in a centrifuge tube, the coagulated fibrin being either ground for 7 min. or stirred for 3 min. The tube is then centrifuged for 5 min. until the liquid becomes clear. After transference of this liquid to a beaker, the residue is mixed and centrifuged with 3 c.c. of alcohol, the clear liquid being added to the first portion. The whole is titrated, in presence of 2 drops of 7% potassium chromate solution, with 0.01*N*-silver solution. A blank titration with the alcohol alone is made, the difference between the two volumes (c.c.) of silver solution required multiplied by

0.585 giving the mg. of sodium chloride in the blood taken. T. H. POPE.

**Colorimetric determination of guanidine bases in blood.** J. J. PFIFFNER and V. C. MYERS (J. Biol. Chem., 1930, 87, 345—355).—Blood is freed from protein with tungstic acid and the filtrate is made alkaline with sodium hydroxide and treated with charcoal. The charcoal is extracted with alcoholic hydrochloric acid and the extract is evaporated. The residue is autoclaved in dilute hydrochloric acid solution, again evaporated, dissolved in water, and treated with alkaline ferrieyanide, the colour being compared with that produced by a standard solution of methylguanidine when similarly treated. This modification of the method of Weber (A., 1928, 1048) excludes interference by creatine, which is converted into creatinine during the autoclaving; the average recovery of methylguanidine added to blood is 75.5%. The average methylguanidine content of normal blood is 0.23%, and that of the blood of patients with high blood-pressure 0.33%. C. R. HARINGTON.

**Micro-determination of creatinine and creatine in blood.** E. KOPLOWITZ (Biochem. Z., 1930, 221, 264—269).—Methods previously described (A., 1929, 1326) have been improved. They are not influenced by the presence of blood-sugar. W. MCCARTNEY.

**Distribution of uric acid in blood-plasma and corpuscles, and influence of acid and alkaline diets thereon.** A. V. KOSSIAKOVA (Russian J. Physiol., 1930, 13, 145—150).—The distribution of uric acid in the blood is not uniform, the plasma always containing more than the corpuscles, even when the character of the diet is varied. When blood is kept, the content of uric acid or of substances giving Benedict's reaction (A., 1922, ii, 405) falls considerably in the corpuscles, but remains almost constant in the plasma. A colour standard for use in conjunction with Benedict's method is suggested. T. H. POPE.

**Concentration of urea in normal human blood with special reference to the question of blood-corpuscles containing urea.** K. HAYASHI (Japan. Med. World, 1929, 9, 253—266).—Blood-corpuscles contain urea, and their membranes are permeable to urea. Urease is not osmotic for the corpuscle membrane. For the determination of blood-urea fully hemolysed blood must be used.

#### CHEMICAL ABSTRACTS.

**Nitrogenous substances in zinc filtrates of human blood.** M. SOMOGYI (J. Biol. Chem., 1930, 87, 339—344).—Protein-free filtrates of normal human blood prepared by treatment of the blood with zinc sulphate and sodium hydroxide (this vol., 801) contain 11—21 mg. of nitrogen per 100 c.c. The carbamide concentration is the same in these filtrates as in those prepared with tungstic acid, whilst the creatinine concentration is lower and uric acid is absent. C. R. HARINGTON.

**Determination of blood-sugar (Baudouin, Ionescu-Matiu, and Hagedorn).** A. IONESCU-MATIU and M. VITNER (Bull. Soc. Chim. biol., 1930, 12, 626—635).—The three methods give identical results if the same precipitant is used to remove proteins, but different results are obtained with different

precipitants. As usually carried out the method of Ionescu-Matiu, in which trichloroacetic acid is used, determines the total reducing sugars of the blood, whereas those of Baudouin and Hagedorn, in which mercuric nitrate and zinc hydroxide respectively are employed, determine only the free dextrose.

W. O. KERMACK.

**Fluctuations of capillary blood-sugar in normal young women during a 24-hr. period.** M. J. DIONNE and J. J. ARENSTAM (J. Biol. Chem., 1930, 87, 393—397).—Figures are given for the blood-sugar of seven normal young women at hourly intervals throughout the 24 hrs. During complete rest in bed the values fell between 86 and 104 mg. per 100 c.c., the average figure being 94; determinations were made by the method of Folin and Malmros (A., 1929, 1096).

C. R. HARINGTON.

**Lipin-free blood-serum. Apparatus for extraction at low temperatures.** I. GREENWALD and I. LEVY (J. Biol. Chem., 1930, 87, 281—287).—On a small scale, blood-serum was poured into excess of methyl alcohol at  $-50^{\circ}$ , and the precipitate extracted in a special apparatus with successive quantities of methyl alcohol and anhydrous ether; the residual, almost lipin-free, material was completely soluble in water to give a solution which retained the original protective antibodies of the serum. On a larger scale, blood-serum was more readily freed from lipins by continuous extraction with amyl alcohol, precautions being taken to chill the extracting liquid prior to contact with the serum. C. R. HARINGTON.

**Tyrosinase in crustacean blood.** K. G. PINKEY (J. Exp. Biol., 1930, 7, 19—37).—The blackening of shed crustacean blood is due to tyrosinase, which is liberated by cytolysis. The action of the tyrosinase is inhibited by sodium cyanide in low concentration, indicating the presence of a metallic group in the enzyme molecule, and depressed by hydrogen sulphide, copper sulphate, ferric chloride, sodium fluoride, sodium pyrophosphate, and alcohols.

#### CHEMICAL ABSTRACTS.

**Combined peroxidase-Wright's stain for blood films.** A. T. BRICE, jun. (Stain Tech., 1930, 5, 101—102).—The oxidase reagent is prepared by dissolving 0.3 g. of benzidine in 100 c.c. of 95% alcohol and adding 1 c.c. of a saturated aqueous solution of sodium nitroprusside. Thin, air-dried films are flooded with this reagent for 1—1½ min. An approximately equal amount of 1 in 200 hydrogen peroxide solution is then allowed to act for 3 min., the slides are washed and air-dried, and Wright's stain is applied in the usual manner. A very clear picture of the differential characteristics of the blood-cells results. H. W. DUDLEY.

**Glutathione in Teleostei.** II. G. CANNICCI (Atti R. Accad. Lincei, 1930, [vi], 11, 601—606; cf. this vol., 945).—The proportions of glutathione found in the livers of various fishes, in mg. per 100 g. of tissue, calculated on the tripeptide formula for glutathione, are: *Box salpa*, Linn., 45.17—81.43 (mean 56.35); *Cyprinus carpio*, Linn., 30.24—54.95 (44.71) [normal feeding], 26.98—50.43 (39.19) [fasting]; *Salmo gairdneri*, Rich., 46.63—76.37 (66.60). The amounts in the muscle of these fishes are very small. T. H. POPE.

The question of the existence of glutathione in the skin: criticism of the modified method of Perlzweig and Delrue. H. C. CHANG and S. M. LING (Chinese J. Physiol., 1930, 4, 131—140).—Trichloroacetic acid extracts of skin of rat, rabbit, and dog absorb a definite amount of iodine by the method of Perlzweig and Delrue (A., 1928, 84), although giving no nitroprusside reaction. Extracts of liver after keeping for several days so that the thiol groups have been oxidised give no nitroprusside reaction, although they still absorb a small quantity of iodine. It is suggested that in these cases the iodine is not reacting with reduced glutathione, but with some other substance, e.g., unsaturated fatty acids. This is supported by the fact that trichloroacetic acid extracts of subcutaneous fat apparently containing no thiol group also absorb a definite quantity of iodine.

W. O. KERMACK.

Denaturation of proteins. X. Osmotic pressure of denatured egg-albumin and methaemoglobin in concentrated urea solutions. T. C. HUANG and H. WU (Chinese J. Physiol., 1930, 4, 221—229).—The mol. wt. of proteins not readily soluble in water has been determined in carbamide solutions (40% by weight). The mol. wt. thus found of egg-albumin denatured by urea or by alcohol is the same as that of natural egg-albumin in aqueous solution (34,000), whilst the mol. wt. of acid albumin is greater and that of alkali albumin is less. The mol. wt. in urea solutions of methaemoglobin denatured by urea is the same as that of oxyhaemoglobin in aqueous solutions.

W. O. KERMACK.

Cause of ammoniacal odour of flesh of the shark. O. MARTIN (Z. Fleisch Milch-Hyg., 1929, 40, 48—49; Chem. Zentr., 1930, i, 992).—The ammonia arises from urea (up to 2.5% of the flesh), the origin of which is not pathological; it serves to maintain the internal osmotic pressure against that of the water.

A. A. ELDRIDGE.

Distribution of nitrogen in the muscles of various species of animals. I. R. KAPELLER-ADLER and J. KRAEL (Biochem. Z., 1930, 221, 437—460).—Muscle extracts were prepared by repeated extraction of minced muscle with boiling 96% alcohol and subsequent removal of proteins by precipitation with alcohol and of phosphatides by extraction with ether. By hydrolysis of the extracts with 30% sodium hydroxide solution ammonia, methylamine, and trimethylamine are produced. In the muscle of the ox, rabbit, dog, and carp the total amounts of nitrogen and of these bases are of the same order, but the amounts in cod muscle and in earthworms are of a different order from those in the muscle of the other animals. Since the methylamine and trimethylamine obtained by hydrolysis must be derived almost entirely from methylguanidine and from carnitine (in the case of the mammals) or betaine (in the case of the fish), respectively, the amounts of methylguanidine, carnitine, and betaine originally present can be deduced. Ox muscle contains more carnitine than does the muscle of the other mammals. The ammonia formed during hydrolysis may be derived from various substances. By reduction with zinc dust in alkaline medium the trimethylamine

oxide content of cod muscle can be determined, and it can be shown that this oxide occurs also in the muscle of the ox and dog. The muscle of cod is distinguished from that of the other animals investigated by the comparatively large amounts of free bases which it contains.

W. MCCARTNEY.

Existence, origin, and significance of the so-called lutein colloid. A. ALBANESE (Arch. Ist. Biochim. Ital., 1930, 2, 269—280).—Discussion of previous work, together with new experimental results, indicate that the ruby-red test is not specific for the lutein colloidal substance, that the presence of this colloid is not sufficient for the diagnosis of a gravid lutein body, and that the so-called colloid encountered in either the menstrual or gravid lutein body is merely a metamorphic blood derivative, which is accompanied by involutive, atrophic phenomena of the lutein body itself.

T. H. POPE.

Histological evidences of the organic content and reactions of marsupial enamel. Note on human enamel. E. SPRAWSON (Proc. Roy. Soc., 1930, B, 106, 376—387).—Enamel becomes more highly calcified with age and cracks in it are ultimately closed by calcium salts conveyed by way of the dentine. A similar mechanism applies to human enamel.

P. G. MARSHALL.

Fatty acids of the phosphatides in the tissues of homeotherms. E. F. TERROINE, C. HATTERER, and P. ROEHRIG (Bull. Soc. Chim. biol., 1930, 12, 657—673).—The iodine value of the total fatty acids of the phosphatides from a particular tissue of a warm-blooded animal varies only slightly from individual to individual and does not depend on the species, but is characteristic of the tissue employed. In the cases of liver and lungs, the iodine values of the fatty acids of the total phosphatides agree exactly with that of the "unvarying fraction" (cf. A., 1927, 371), but the iodine value of the fatty acids of the "unvarying fraction" of the muscle is higher than that of the total phosphatides from that tissue.

W. O. KERMACK.

Fatty acids of the phosphatides of poikilotherms, higher plants, and micro-organisms. E. F. TERROINE, C. HATTERER, and P. ROEHRIG (Bull. Soc. Chim. biol., 1930, 12, 682—702).—The tissues of cold-blooded differ from those of warm-blooded animals in not exhibiting the same constancy in respect of the iodine value of the fatty acids of the phosphatides from a particular tissue independently of the species from which the tissue is derived. The iodine value of the fatty acids of the phosphatides is not necessarily higher than that of the fatty acids of the neutral fat in cold-blooded animals, the seeds of plants, and in bacteria, although it is so in the tissues of the warm-blooded animals. In the case of micro-organisms (*A. niger* and *B. phlei*) grown at various temperatures, the iodine value of the fatty acids of the phosphatides is the higher the lower is the temperature of growth. This behaviour is analogous to that of the fatty acids of the neutral fats of micro-organisms (cf. A., 1927, 791).

W. O. KERMACK.

Composition of fat of silver-black fox. H. A. SCHUETTE and R. W. THOMAS (Trans. Wisconsin



Acad. Sci., 1930, 25, 113—116).—The coarse-grained fat from the silver-black fox reared in captivity resembles that of the wild fox, although the effects of the artificial environmental conditions are evidenced in the characteristics, e.g., low m. p. The fat had  $d_{20}^{25}$  0.9122,  $n_D^{20}$  1.4581, m. p. 32.6°, titer test 36.17°, iodine value (Wijs) 70.46, saponification value 197.1, soluble acids 0.54%, insoluble acids 93.72%, Reichert-Meissl value 0.44, Polenske value 0.34, saturated fatty acids 32.92% (corr.), unsaturated fatty acids 55.99% (corr.), unsaponifiable matter 0.41%. The fat consists principally of the glycerides of palmitic, stearic, (? myristic), oleic, and linoleic (? trace of linolenic) acids. E. LEWKOWITSCH.

**Neutral fat of liver and other tissues of the ox.** W. R. BLOOR and R. H. SNIDER (J. Biol. Chem., 1930, 87, 399—413).—Figures are given for the total amount of acetone-soluble lipin in the liver, heart, lung, and kidney of the ox, and for the iodine value of the fatty acids obtained by hydrolysis of this fat. All tissues, but especially the liver, showed marked variations in the glyceride content, and hence in the phospholipin: glyceride ratio (the phospholipin remaining constant for each tissue). The hepatic glycerides were definitely more unsaturated than those of the other organs; it was impossible to decide whether this was due to desaturation by the liver or to selection by this organ of the more unsaturated acids from the blood. C. R. HARRINGTON.

**Unsaturated acids in fish oil. I. Oil of *Labeo Rohita*.** J. K. CHOWDHURY and P. B. SARKAR (J. Indian Chem. Soc., 1930, 7, 309—319).—The stomach-oil of *Labeo Rohita* ("ruhu") has  $d_{20}^{25}$  0.9230,  $n_D^{20}$  1.4622, saponification value 191.4, acid value 1.116, Hehner value 91.1, Reichert-Meissl value 0.668, iodine value (Wijs) 61.65—130.6 (according to the size of the fish), and contains glycerol 10.2% and unsaponifiable matter 0.34%. The unsaturated acids are separated from the total acids (obtained from the oil with iodine value 130.6) by Tortelli and Ruggeri's method, and brominated in ethereal solution at  $-10^\circ$ . The ether-insoluble bromides formed are separated by fractionation with various solvents into *tetrasapentenoic acid decabromide*,  $C_{24}H_{38}O_2Br_{10}$ , blackens at  $242^\circ$ , linolenic acid hexabromide, m. p.  $171^\circ$ , and *hexadecatrienoic acid hexabromide*, m. p.  $158^\circ$ . Linolenic acid hexabromide is also isolated from the ether-soluble bromides.

Oxidation of the liquid fatty acids from the oil with 0.75% potassium permanganate solution affords a mixture of *dihydroxyasellinic acid*,  $C_{17}H_{34}O_4$ , m. p. 116—116.5° (cf. Fahrion, Chem. Reviews, 1926, 3, 425), and *dihydroxystearic acid*.

The approximate composition of the unsaturated acid fraction is: *tetrasapentenoic* (1.34), *linolenic* (7.86), *hexadecatrienoic* (6.13), *oleic*, *asellinic*, and other acids (84%). H. BURTON.

**Determination of fat. II. Determination of neutral fat in animal substances. III. Extraction apparatus.** S. R. ZINZADZE (Biochem. Z., 1930, 220, 177—184, 185—191).—The author's method (A., 1926, 1283) is somewhat modified and the new apparatus described. The material is autoclaved

in the presence of 2—3% hydrochloric acid for 1 hr. at  $180$ — $190^\circ$ , the hydrolysis tube being then placed in an extractor and extracted for 1 hr. A new condenser for automatic recovery of solvent is described. P. W. CLUTTERBUCK.

**Enzymes of silkworms. I. M. MORI** (Bull. Chem. Soc. Japan, 1930, 5, 159—163).—Extraction of the middle intestine of silkworms (after previous extraction with acetone and ether) with water, glycerol solution, or a buffer solution ( $p_H$  9.26) and precipitation of the extract with acetone or alcohol affords an amylase which is further purified by adsorption methods. The velocity of hydrolysis of soluble starch by this enzyme reaches a maximum at  $60^\circ$  and  $p_H$  9.4—11 (no hydrolysis at  $80^\circ$ ). Cathaphoresis measurements show that the amylase is positively charged in alkaline, and negatively charged in acid solution, the isoelectric point being about  $p_H$  5.7. J. W. BAKER.

**Yeast in the Death Watch beetle.** R. C. FISHER and E. A. PARKIN (Nature, 1930, 125, 892).—Pure cultures of yeasts from *Anobium* and *Xestobium* have been isolated. L. S. THEOBALD.

**Micro-incineration of diatoms without carapace.** E. BACHRACH and (MME.) PILLET (Compt. rend., 1930, 190, 1442—1443).—No silica was detected in the hyaline body of the diatom *Navicula* without carapace. The ash contained calcium. C. C. N. VASS.

**Distribution of electrolytes in serum and cerebrospinal fluid. I. Calcium and magnesium.** Z. STARY, A. KRÁL, and R. WINTERNITZ. II. Potassium and sodium. A. KRÁL, Z. STARY, and R. WINTERNITZ (Z. ges. exp. Med., 1929, 66, 671—691, 691—701; Chem. Zentr., 1930, i, 403).—I. The cerebrospinal fluid and the blood-serum contain, respectively, calcium 4.5—6, 10—11; magnesium 2.5—4.9, 1.5—3.5 mg. per 100 c.c. On dialysis of the serum against the fluid the values for the former increase and those for the latter diminish. In tubercular meningitis, but not in other pathological conditions of the central nervous system, the magnesium content of the cerebrospinal fluid is increased.

II. The sodium contents of human blood-serum and cerebrospinal fluid are, respectively, 324 and 295 mg. per 100 c.c., the values for potassium being 21.7 and 11.7 mg. per 100 c.c. On dialysis the potassium content becomes equalised between the serum and the fluid. A. A. ELDRIDGE.

**Citric acid content of cerebrospinal fluid.** B. BENNI (Biochem. Z., 1930, 221, 270—272).—Normal human cerebrospinal fluid contains 0.000045 g. of citric acid per c.c., but the amount of this in the fluid of diseased persons may differ from the normal value and there may be different average values for different diseases. W. MCCARTNEY.

**Secretion of the small intestine. I. Secretion in physiological and febrile conditions.** M. MATSUBARA (Proc. Imp. Acad. Tokyo, 6, 23—25).—Dogs in which the temperature was raised by administration of tetrahydro- $\beta$ -naphthylamine or by keeping the external temperature high produced an intestinal

secretion small in quantity and deficient in enzyme as compared with normal juice. The small rise in temperature resulting from injection of a vaccine did not result in significant alteration in the juice.

W. O. KERMACK.

**Bile and biliary duct.** IV. L. LÖHNER (Pflüger's Archiv, 1929, 223, 436—449; Chem. Zentr., 1930, i, 988).—The degree of activity of biliary amylase is very variable; it may reach values of significance in the physiology of digestion. Unheated, fresh aqueous suspensions of starch are not attacked, but denatured starch products are sometimes attacked almost instantaneously.

A. A. ELDRIDGE.

**Determination of carbon in urine.** C. G. L. WOLF (Biochem. Z., 1930, 221, 488).—The apparatus described by Voit (this vol., 239) is practically identical with that recommended by Wolf 20 years ago (A., 1912, ii, 581).

W. MCCARTNEY.

**Detection of acetone and acetoacetic acid in urine.** I. C. OTTO. II. P. HORKHEIMER (Pharm. Ztg., 1930, 75, 730—731).—I. Aminoacetophenone, methylene-blue, and ferric chloride can be used in the detection of acetoacetic acid, whilst the iodoform and salicylaldehyde tests respond only to acetone. 2:4-Dinitrophenylhydrazine in alcoholic hydrochloric acid solution is used to detect both acetone and acetoacetic acid.

II. A criticism of Otto's work.

P. G. MARSHALL.

**Production and cure of nutritional anæmia in suckling pigs.** T. S. HAMILTON, G. E. HUNT, H. H. MITCHELL, and W. E. CARROLL (J. Agric. Res., 1930, 40, 927—938).—The hæmoglobin content of newly-born pigs decreases rapidly if the piglings are housed indoors, but is restored by living in the open air or by the daily administration of 25 mg. of iron as ferric citrate and 5 mg. of copper as sulphate. Administration of these salts to the sow in the later period of gestation and during lactation was without effect on the piglings. Copper sulphate used alone was ineffective and ferric citrate alone was of doubtful value.

A. G. POLLARD.

**Anæmia of young pigs.** E. B. HART, C. A. ELVEHJEM, H. STEENBOCK, A. R. KEMMERER, G. BOHSTEDT, and J. M. FARGO (J. Nutrition, 1930, 2, 277—294).—Administration of iron and copper to the sow did not delay the development of anæmia in piglings. The synthesis of hæmoglobin was stimulated by iron or by iron supplemented with copper. Addition of ferric chloride, free from copper, to a cow's milk diet prevented the development of anæmia. Exposure of pigs to ultra-violet light or sunlight did not stimulate the synthesis of hæmoglobin.

CHEMICAL ABSTRACTS.

**Occurrence of xanthine calculi in New Zealand sheep.** T. H. EASTERFIELD and J. A. BRUCE (New Zealand J. Sci. Tech., 1930, 11, 357—361).—Calculi found in the kidneys of certain sheep consist of xanthine. The probable cause is a deficiency of minerals in the pasturage.

C. W. GIBBY.

**Blood-lactic acid in pathological conditions.** E. M. GELSTEIN and M. I. FRANKSTEIN (Z. klin. Med., 1929, 3, 563—581; Chem. Zentr., 1930, i,

848—849).—In disease of the heart and in cancer the blood-lactic acid frequently rises. The increase of the lactic acid in peripheral blood after administration of sugar is greater in cancer than normally.

A. A. ELDRIDGE.

**Biliary colouring matter and its derivatives in blood, urine, and fæces in liver disease.** A. ADLER and B. ZU JEDDELOH (Deut. Arch. klin. Med., 1929, 164, 282—297; Chem. Zentr., 1930, i, 849).—Slight disturbance of the liver leads first to an increase of faecal urobilin, and greater disturbance to urobilinuria; yet greater disturbance leads to bilirubinæmia, followed by bilirubinuria and a fall in faecal and urinary urobilin.

A. A. ELDRIDGE.

**Distribution of residual nitrogen in the blood-serum of diseased persons.** A. A. CHRISTOMANOS (Biochem. Z., 1930, 221, 473—483).—From determinations of residual nitrogen and of the various fractions into which it can be divided as well as of the nitrogen which cannot be allocated to any such fraction and of sulphur in various combined forms in serum from diseased persons the following conclusions are reached. The ratios of amino-nitrogen to urea-nitrogen and of ammonia to urea-nitrogen are lower when the liver is slightly diseased than when it is seriously diseased. When the liver is in a toxic condition the amounts of creatinine and purines are very much increased. The amount of unallocated nitrogen is highest in diseases where the liver is affected, less in diabetes, and much less in other diseases. The amount of sulphur not present in the form of sulphate or of aromatic sulphur compounds is also greatly increased in diseases where the liver is affected and in uræmia, and this amount can be related to the amount of unallocated nitrogen. Administration of insulin has very little or no effect on the residual nitrogen content of serum.

W. MCCARTNEY.

**Diffusible calcium and the proteins of the blood-serum in jaundice.** L. GUNTHER and D. M. GREENBERG (Arch. Int. Med., 1930, 45, 983—1003).—The diffusible blood-calcium in jaundice is slightly higher, whilst the non-diffusible fraction is appreciably lower than the normal. The fall in the latter case is accompanied by a drop in the serum-albumin. A calcium deficiency is not indicated by the figures for the diffusible (i.e., physiologically available) blood-calcium. The hypotheses of the alteration of calcium diffusibility by detoxification of bile-pigments or by disturbances in the protein balance are not upheld.

F. O. HOWITT.

**Carotenosis of bovine livers associated with parenchymatous degeneration.** J. S. BUCKLEY, E. C. JOSS, G. T. CREECH, and J. F. COUCH (J. Agric. Res., 1930, 40, 991—1005).—The presence of excessive amounts of carotene in affected bovine livers is associated with the presence of a toxic substance, probably derived from some plant indigenous to the region where the cattle were raised, not yet identified. The destructive changes brought about by this toxic substance can be induced in the livers of rats fed on affected cattle livers, but excess of carotene is not developed in the rat livers.

E. HOLMES.

**Blood-lactic acid in myasthenia.** J. FRIESZ and E. MOROS (Deut. Arch. klin. Med., 1929, 164, 356—

360; Chem. Zentr., 1930, i, 849).—After exercise, but not in rest, the value is higher than in normal subjects; the blood-inorganic phosphorus and sugar are not noticeably affected by exercise.

A. A. ELDRIDGE.

**Influence of thyroxine on the blood-iodine in myxoedema.** B. EISLER and A. SCHITTENHELM (Z. ges. exp. Med., 1929, 68, 487—492; Chem. Zentr., 1930, i, 702).—In myxoedema the blood-iodine is considerably reduced (4.4—7.2 instead of 10—13  $\gamma$  per 100 c.c., the value being increased (*e.g.*, to 21  $\gamma$ ) by oral administration of thyroxine. In normal conditions the blood-iodine is not affected by thyroxine.

A. A. ELDRIDGE.

**Blood-lactic acid in nephritis.** O. JERVELL (Acta med. Scand., 1929, 72, 262—273; Chem. Zentr., 1930, i, 848).—Normal values for blood-lactic acid, determined by titration with potassium dichromate, are 20—30 mg. per 100 c.c.; in chronic nephritis a high value is often observed.

A. A. ELDRIDGE.

**Metabolism and treatment of osteomalacia. Its relation to rickets.** S. L. GARGILL, D. R. GILLIGAN, and H. L. BLUMGART (Arch. Int. Med., 1930, 45, 879—907).—In a case of advanced adult osteomalacia a negative calcium balance persisted even with excessive calcium feeding, a condition which could not be remedied by addition of 50 c.c. of cod-liver oil to the diet. No endocrine abnormality was detected. Improvement followed dosage with very large amounts of vitamin-A and -D and still more by ultra-violet light irradiation. The storage of calcium and phosphorus was further increased by ingestion of large amounts of calcium lactate and disodium phosphate. Osteomalacia is a form of adult rickets.

F. O. HOWITT.

**Zinc-porphyrinuria.** E. DERRIEN and P. CRISTOL (Arch. Soc. Sci. Méd. Montpellier, 1930, 11, 244).—A case of acute porphyrinuria in which zinc (as zinc-porphyrin) was excreted at the rate of 1 mg. per day rising to 6 mg. at the crisis is described. The possibility of zinc therapy in such cases as a parallel to that of iron in anæmia is suggested.

F. O. HOWITT.

**Psychosis and blood-lipins. Quantitative changes of total cholesterol and total fatty acids in blood.** I. S. STENBERG (Acta med. Scand., 1929, 71, 558—597; Chem. Zentr., 1930, i, 402—403).—The values are higher during periods of mania.

A. A. ELDRIDGE.

**Sodium and chlorine content of organs in uræmia.** L. BLUM and P. GRABAR (Compt. rend. Soc. Biol., 1930, 101, 717—718; Chem. Zentr., 1930, i, 543).—Variable results indicate that the term "uræmia" includes different conditions and functional changes.

A. A. ELDRIDGE.

**Blood-enzymes in uræmia.** O. KLEIN and W. NONNENBRUCH (Z. ges. exp. Med., 1929, 68, 222—231; Chem. Zentr., 1930, i, 988).—In uræmia there is a disturbance of lipolytic, glycolytic, and diastatic activity in the blood. The cause is discussed.

A. A. ELDRIDGE.

**Non-protein nitrogen of blood and organs and the alkaline reserve of the blood in experimental**

**uræmia.** M. K. DALMATOV (Zhur. exp. Biol., 1929, 11, 8—16).—The rise in non-protein-nitrogen of blood and cerebrospinal fluid in experimental uræmia in dogs is relatively, but not always absolutely, greater than that of the non-protein-nitrogen of organs. In the brain the increase follows that in the blood; that in the liver and kidney may precede or follow it. In potassium dichromate uræmia only the tissue-non-protein-nitrogen may be increased. The alkaline reserve of the blood is diminished.

CHEMICAL ABSTRACTS.

**Lipins in xanthoma.** H. C. ECKSTEIN and U. J. WILE (J. Biol. Chem., 1930, 87, 311—317).—The lipins of a xanthomatous tumour contained 48.8% of cholesterol and 8.1% of phospholipins, *i.e.*, 200 times as much of both of these constituents as is contained in normal subcutaneous fat; the xanthomatous fat was also relatively rich in unsaturated fatty acids. The fat of the tissue adherent to the tumour was slightly richer in cholesterol and phospholipin than normal subcutaneous fat, but approximated closely to the latter in composition. The characteristic nature of the xanthomatous fat is associated with the special activity of the tissue rather than with the nature of the blood-lipins.

C. R. HARRINGTON.

**Calcium in the sera of rabbits under certain experimental pathological conditions.** P. C. KIANG (Chinese J. Physiol., 1930, 4, 159—174).—The serum-calcium of rabbits affected by a number of diseases has been determined. It was below normal in cases of ear mange, dysentery, cedema manifested in the form of hydrothorax or ascites produced by the injection of concentrated Lugol's solution, nephritis produced by mercuric chloride, and in conditions associated with extensive pus formation. The serum-calcium was unchanged or slightly raised in staphylococcus infection unaccompanied by pus formation or continuous discharge and in nephritis caused by uranium nitrate.

W. O. KERMACK.

**Relative importance of hydrogen-ion concentration, temperature, dissolved oxygen, and carbon dioxide tension on habitat selection by brook trout.** C. W. CREASER (Ecology, 1930, 11, 246—262).

**Inhibition of respiration by hydrocyanic acid.** H. L. ALT (Biochem. Z., 1930, 221, 498—501).—The respiration of animal cells (from kidneys, liver, and spleen) investigated by the method of Warburg is completely inhibited by sufficient concentrations of hydrocyanic acid. The procedure of Dixon and Elliott (A., 1929, 1197) and also their conclusions are rejected.

W. MCCARTNEY.

**Sulphur-containing amino-acid. IX. Relation between thiol content of muscle-protein and oxygen consumption.** Y. OKUDA and K. KATAI (J. Agric. Chem. Soc. Japan, 1929, 5, 645—652).—Muscle-protein and cystine or oxidised glutathione in a buffer solution of  $p_H$  about 7.6 consume only a trace of oxygen, but when the two substances are combined the oxygen consumption is notable and the protein no longer gives the nitroprusside reaction. Proteins lacking the thiol group do not give the reaction. Mueller's amino-acid containing sulphur does not

interfere in Okuda's method for determining cystine and cysteine, and does not consume oxygen.

#### CHEMICAL ABSTRACTS.

**Muscular contraction.** IV. Changes in phosphorus, nitrogen, and fat produced by tetanus toxin. H. A. DAVENPORT, H. K. DAVENPORT, and S. W. RANSON (*J. Biol. Chem.*, 1930, 87, 295—298).—Muscular contraction in rabbits induced by tetanus toxin was accompanied by decrease in protein-nitrogen, total phosphorus, and phosphocreatine. Other fractions of the phosphorus and the fat were irregularly affected. C. R. HARRINGTON.

**Nitrogen metabolism in the musculature of animals deprived of carbohydrates.** E. BLÄTTLER (*Biochem. Z.*, 1930, 221, 359—374).—There is no significant difference in the ratio of residual to total nitrogen in the musculature between normal rats and those so fed that their musculatures are almost free from carbohydrates, but the ratio in the case of rats exercising until almost fatigued is smaller for those lacking carbohydrates than for normal animals. It is possible that intense muscular activity favours the conversion of nitrogen compounds of low mol. wt. in the carbohydrate-free muscles into nitrogen compounds of high mol. wt. W. MCCARTNEY.

**Nuclein metabolism.** XXIII. Effect of muscular activity on endogenous uric acid excretion. M. JENKE, R. LASER, and R. LINDE (*Z. physiol. Chem.*, 1930, 189, 162—164; cf. this vol., 1065).—Strenuous muscular effort (a 40-kilometre march) produced no increase over the resting values in the nitrogen and uric acid excreted. There was a considerable increase in creatinine.

J. H. BIRKINSHAW.

**Effect of lecithin and cholesterol on protein metabolism.** V. PIOVANO (*Rass. Clin. Terap. Sci. Aff.*, 1929, 28, 218—222; *Chem. Zentr.*, 1930, i, 1001).—Injection of lecithin (2.5 g.) into animals causes an increase in the excretion of creatinine and a decrease in that of urea; when cholesterol (2 g.) and lecithin (2.5 g.) are used together, the reverse is the case.

A. A. ELDRIDGE.

**Swine type studies.** III. Energy and protein requirements of growing swine and the utilisation of food energy in growth. H. H. MITCHELL and T. S. HAMILTON (*Illinois Agric. Exp. Sta. Bull.*, 1929, No. 323, 493—600).—Analyses of carcasses showed only inappreciable differences between types. No type differences were detected in the utilisation of food. The dry matter and fat of the carcass increased, whilst the protein and ash decreased, with age. The protoplasmic composition characteristic of maturity consists of water 75—76, protein 20—21, ash 4%. The results for female and for castrated male animals were similar.

#### CHEMICAL ABSTRACTS.

**Effects of a hyperprotein and hyperpurine diet (pancreas) on the rat.** P. RONDINI (*Arch. Ist. Biochim. Ital.*, 1930, 2, 243—268).—On a diet of pancreas, either alone or mixed with flour, rats lose weight, especially in the former case, whilst the kidney weight increases both absolutely and relatively. Other effects of such diet include: slight tendency to leucocytosis; diffuse phenomena of swelling in the

parenchymal organs; more marked vital colorability with trypan-blue; an acidotic condition; increased thermal reactivity compared with that caused by subcutaneous injection of peptone or suspension of uric acid; increased disposition to inflammation.

T. H. POPE.

**Influence of the biological value of albumin on nitrogen metabolism.** III. A. B. VOLOVİK (*Zhur. exp. Biol. Med.*, 1929, 11, 82—90).—Comparative experiments in scarlet fever with liver- and vegetable-protein are recorded.

#### CHEMICAL ABSTRACTS.

**Nitrogen metabolism on a diet without milk.** A. B. VOLOVİK (*Zhur. exp. Biol. Med.*, 1929, 11, 91—98).—Destruction of protein in scarlet fever was made good by means of a diet free from milk but containing large quantities of carbohydrate and moderate amounts of protein of high biological value.

#### CHEMICAL ABSTRACTS.

**Paired-feeding method in nutrition experiments and its application to the problem of cystine deficiencies in food proteins.** H. H. MITCHELL and J. R. BEADLES (*J. Nutrition*, 1930, 2, 225—243).—The proteins of white bread and lean beef are not deficient in cystine. The proteins of navy beans, potatoes, milk, and garden peas are deficient in supplying the growth requirements of the rat. The addition of cystine to the garden pea ration did not modify the completeness of digestion of the nitrogen compounds contained in it. The method is satisfactory.

#### CHEMICAL ABSTRACTS.

**Fate of di-iodotyrosine in the animal organism.** G. L. FOSTER and A. B. GUTMAN (*J. Biol. Chem.*, 1930, 87, 289—294).—After oral administration of large amounts of di-iodotyrosine to rabbits, 60% was recovered unchanged from the urine; 10% of the iodine was present as iodide, and 18% as partly racemised d-3 : 5-di-iodophenyl-lactic acid, m. p. 158—159°. The remaining 12% of the iodine could not be traced.

C. R. HARRINGTON.

**Physiology of pyrimidines.** II. Metabolism of uridine and cytidine. O. H. EMERSON and L. R. CERECEDO (*J. Biol. Chem.*, 1930, 87, 453—462).—After oral administration of small amounts to dogs both uridine and cytidine were oxidised to carbamide, the behaviour of cytidine being thus markedly different from that of cytosine (A., 1928, 200). Administration of larger amounts of cytidine caused an excretion of more residual nitrogen than can be accounted for by that administered; a stimulation of metabolic processes was thus indicated. The carbon:nitrogen ratio of the urine, which under normal conditions had the practically constant value of 0.65, was increased after administration of the nucleosides.

C. R. HARRINGTON.

**Nutritive value of cereal breakfast foods.** III. Rate of digestion and absorption as determined by experiments on rats. H. A. MATTILL and H. G. SMITH (*J. Nutrition*, 1930, 2, 217—224).—Physical consistency, rather than the presence of roughage, determines the time during which the food remains in the stomach.

#### CHEMICAL ABSTRACTS.

**Relative nutritive value of carbohydrates and related compounds.** T. ARIYAMA and K. TAKA-

HASHI (J. Agric. Chem. Soc. Japan, 1929, 5, 674—688).—In experiments on rats, maltose, laevulose, dextrose, starch and dextrin gave the best results; in the next group were galactose, mannose, arabinose, xylose, lactose, sucrose, inulin, and glycogen. Agar-agar, dihydroxyacetone, and  $\alpha$ -methylglucoside are inert. Glucosamine and ethylene glycol (1.25 g.) are toxic. Of the alcohols, ethyl alcohol is most nutritive, followed by glycerol; mannitol is inferior. The urine contained reducing substances after administration of lactose, galactose, mannose,  $\alpha$ -methylglucoside, glucosamine, arabinose, xylose, and dihydroxyacetone.

#### CHEMICAL ABSTRACTS.

**Carbohydrate metabolism of the normal newborn infant.** I. H. M. GREENWALD and S. PENNELL (Amer. J. Dis. Children, 1930, 39, 281—287).—The blood-sugar (fasting), 0.060—0.100% (average 0.076%), is independent of the body-weight.

#### CHEMICAL ABSTRACTS.

**Effect of a yeast concentrate, parenterally and enterally administered, on carbohydrate metabolism.** A. BICKEL and I. A. COLLAZO (Biochem. Z., 1930, 221, 295—303).—A sugar- and protein-free yeast concentrate, administered to fasting rabbits, reduces the sugar content of the blood by 30—40%. Similarly administered along with dextrose to feeding rabbits it produces in 3 hrs. an increase of 450—550% in the liver-glycogen and one of 500—850% in the muscle-glycogen.

W. MCCARTNEY.

**Light and carbohydrate metabolism.** A. GIGON (Strahlenther., 1929, 34, 592—597; Chem. Zentr., 1930, i, 1001).—After administration of dextrose the blood is less, and after that of insulin more, transparent to infra-red rays. The transparency in pathological conditions was determined.

A. A. ELDRIDGE.

**Fat metabolism. I. Rate of digestion of fats as determined by chylomicrons of the blood.** E. H. MACARTHUR (J. Biol. Chem., 1930, 87, 299—306).—A variety of fats, alone or admixed with cellophan or bran, was administered to white rats and to normal young women after a fasting period of 12—15 hrs.; the rates of absorption were determined from the number of chylomicrons (microscopic fat particles) present in the blood at definite intervals. Butter or cod-liver oil alone is absorbed much more rapidly than butter admixed with bran.

C. R. HARRINGTON.

**Are the fatty acids of the phosphatides of homeotherms independent of the nature of the food?** E. F. TERROINE and C. HATTEMER (Bull. Soc. Chim. biol., 1930, 12, 674—681).—The iodine values of the total fatty acids of the phosphatides of the liver or muscle of the rabbit or of the pigeon are the same in normal animals, whether fasting or on a diet exclusively of carbohydrate or of fats of high iodine value.

W. O. KERMACK.

**Effect of iron on metabolism.** R. SANDERS (Arch. exp. Path. Pharm., 1930, 151, 1—11).—During the administration of ferrous chloride by mouth to dogs, no definite variation in the weight of nitrogen balance, or gas metabolism, of the animals was observed.

W. O. KERMACK.

**Ferric citrate as an ingredient of mineral mixtures in paired-feeding experiments with growing swine.** W. E. CARROLL, H. H. MITCHELL, and G. E. HUNT (J. Agric. Res., 1930, 40, 921—926).—Feeding of ferric citrate (3 g. daily) to young pigs did not affect their rate of growth. The blood of treated pigs had higher iron contents and red cell counts, but the results were without physiological significance.

A. G. POLLARD.

**Effect of addition of iron to an adequate diet.** M. T. POTTER and M. M. KRAMER (Trans. Kansas Acad. Sci., 1929, 32, 31—33).—Ferric chloride increases the haemoglobin content of the blood of the young rat.

#### CHEMICAL ABSTRACTS.

**Behaviour of ferrous salts in the digestive tract.** M. MESSINI (Ar. Int. Pharm. Ther., 1929, 35, 206—217; Chem. Zentr., 1930, i, 1001).—Ferrous salts, administered orally, are resorbed, ferrous phosphate being found in the wall of the intestinal canal.

A. A. ELDRIDGE.

**Late results of intravenous injection of colloidal iron.** D. F. CAPPELL (J. Path. Bact., 1930, 33, 175—196).—A compound, probably with plasma-proteins, which can pass through capillary walls is formed.

#### CHEMICAL ABSTRACTS.

**Deposition of calcium in the skin.** R. MASUDA (Mitt. allg. Path. Anat. Tohoku, 1930, 6, 103—152).—Daily administration of calcium lactate (3 g. by the mouth) or chloride (2 c.c. of a 5% solution, intravenously) causes only a transitory increase in the serum-calcium. In animals so treated, but not normally, the skin and muscles in the vicinity of the effects of a blow contain markedly more calcium (chiefly as phosphate) than uninjured areas. Intragluteal injections of lead acetate, basic bismuth nitrate, copper sulphate, or mercuric chloride sometimes produced calcium deposits in the kidney, liver, and muscles at the site of injection. No relation between calcium deposition and free fatty acids or lipins was found.

#### CHEMICAL ABSTRACTS.

**Distribution of arsenic in the organism after intravenous injection.** A. MANTEGAZZA (Biochem. Terap. sperim., 1929, 16, 153—159; Chem. Zentr., 1930, i, 1001).—With rabbits (after death in 0.5—1 hr.) the muscle contained 16.66—19.74, the liver 9.18—10.19, kidneys 1.83—3.12, and all other organs less than 1% of the quantity of arsenic injected.

A. A. ELDRIDGE.

**Influence of drugs on the transmission of arsenic into aqueous humor.** A. C. KRAUSE, A. M. YUDKIN, M. A. STEVENS, W. W. BUNNEL, and D. T. HUGHSON (J. Pharm. Exp. Ther., 1930, 39, 153—163).—No arsenic was detected in the aqueous humor of dogs 2 hrs. after the intravenous injection of various arsenicals. After repeated paracentesis of the anterior chamber, arsenic was present.

The instillation of pilocarpine into the conjunctival sac caused arsenic to appear in the aqueous humor after the injection of salvarsan, sulpharsphenamine, and tryparsamide. Eserine, after injection of neo-salvarsan and sulpharsphenamine, and arecoline after injection of sulpharsphenamine, gave similar results. The amounts of arsenic present in the aqueous humor after pilocarpine treatment were not proportional

to the respective arsenic contents of the different arsenicals. Treatment with hypertonic saline, atropine, and adrenaline did not cause the penetration of arsenic into the anterior chamber.

Instillation of adrenaline, eserine, and pilocarpine caused an increase in the protein in the aqueous humor, ethylmorphine caused a variable increase, whilst atropine and ephedrine caused no increase.

G. F. MARRIAN.

Investigation of the water economy of the skin by means of the weal test. II. Influence of local cutaneous application of compounds and active substances derived from the blood on the absorption of intracutaneous saline weals. D. ADLERSBERG and A. PERUTZ (Arch. exp. Path. Pharm., 1930, 151, 129—145).—Xylene hastens the absorption of saline weals; ethyl chloride retards it. Amyl nitrite, theophylline, and pituitrin all accelerate the absorption, although the effect of the first two can be counteracted by pituitrin. P. G. MARSHALL.

Toxicology of "benzene." N. V. LAZAREV (Arch. Hyg., 1929, 102, 227—239; Chem. Zentr., 1930, i, 553).—Experiments on mice indicate that in acute poisoning the toxic effect depends chiefly on the percentage ratio between paraffins, cycloparaffins, and aromatic hydrocarbons. For a small content of benzene and its homologues the toxicity (for the same b. p.) is increased with increasing content of cycloparaffins. The "one-phase" toxicity increases with rise of b. p., whilst the "two-phase" toxicity decreases. The density affords some indication of the relative toxicity of samples, especially if the percentage of aromatic hydrocarbons is low and in equal b. p. limits of the naphtha fractions to be compared. The toxicity of "benzene" was not markedly altered by purification. "Benzene" obtained by Bergius' process is similar to natural "benzene" in toxicity.

A. A. ELDRIDGE.

Comparison of the premedication values of barbituric acid derivatives in their relation to nitrous oxide anaesthesia. M. F. STORMONT, I. LAMPE, and O. W. BARLOW (J. Pharm. Exp. Ther., 1930, 39, 165—175).—Experiments showing the effect on nitrous oxide-oxygen anaesthesia in adult albino rats, of previous administration of "dial," isopropylallylbarbituric acid, "neonal," "luminal," "amytal," and "barbital" are described. The first three of these, which have the higher therapeutic coefficient (narcotic dose/lethal dose) when administered alone, are effective in prolonging the duration of anaesthesia with a 85 : 15 mixture of nitrous oxide and oxygen, previously induced with a 95 : 5 mixture, from about 2—5 min. to more than 30 min., in doses of 30% of the M.L.D. They are also effective in similar doses in lowering the effective concentration of nitrous oxide for the induction of the anaesthesia from a 95 : 5 to a 85 : 15 mixture.

The last-named three substances, which have a lower therapeutic coefficient, require to be administered in doses of 37.5—45% of the M.L.D. to produce these effects.

G. F. MARRIAN.

Blood-sugar curve in "pernocton" anaesthesia. I. N. DIMITRIJEVIĆ (Arch. exp. Path. Pharm., 1930, 151, 91—99).—Administration of "pernocton"

(sodium *sec.*-butylbromoallylbarbiturate) to rabbits usually results in a small increase in the blood-sugar concentration. The effect of the simultaneous administration of adrenaline, insulin, or ergotamine tartrate has also been studied. W. O. KERMAK.

Duration of action of drugs. I. Analgesics and hypnotics. II. Mydriatic actions of adrenaline and atropine. T. KOPPANYI and A. LIEBERSON (J. Pharm. Exp. Ther., 1930, 39, 177—185, 187—199).—I. The average minimum fatal dose of the analgesics antipyrine and amidopyrine were determined for cats by oral and intravenous administration, and of the hypnotics barbital and amytal by intravenous administration. The amounts of these substances required to produce death when administered at short intervals in fractions of the M.L.D. were also determined. The difference between this figure and the M.L.D. was considered to represent the amount of the substance eliminated during the experiment.

The amounts of the drugs eliminated over 24 hrs. were calculated to be: antipyrine, orally 115% of the M.L.D., intravenously 550%; amidopyrine, orally 120% of the M.L.D., intravenously 300%; barbital and amytal intravenously, 5 and 45—50% of the M.L.D. respectively.

II. The duration and intensity of mydriasis in cats induced by intravenous, intra-arterial, and intra-ocular injection of adrenaline and atropine (not intra-arterially) in graded doses were studied. From a comparison of the amounts required to produce a given effect by the different methods of administration, the fraction of the dose responsible for the mydriatic effect was roughly calculated. The circulation time was found by noting the interval between the induction of mydriasis in the left and right eyes after injection of adrenaline into the left common carotid artery.

Paraldehyde anaesthesia causes an increased susceptibility to adrenaline mydriasis.

G. F. MARRIAN.

Cocaine glycogenolysis and influence of atropine on the glycogen mobilisation by cocaine. R. ISHII, S. SAKATA, and T. TANIUCHI (Folia Pharmacol. Japon., 1929, 9, No. 1, 9).—Experiments with toad-liver show that cocaine augments glycogen mobilisation, whilst atropine is without action. The alkaloids are antagonistic in the carbohydrate metabolism of the liver.

CHEMICAL ABSTRACTS.

Pharmacology of tropine. Relationship between its secondary alcoholic group and its cardiovascular action. R. HAZARD (J. Pharm. Chim., 1930, [viii], 11, 513—522).—Tropine has a vasodilator action similar to that of atropine, whilst  $\psi$ -tropine has a vasoconstrictor action similar to that of nicotine. If the tertiary amino-group is oxidised to *N*-oxytropine, both isomerides lose all physiological action. Nortropine has no action, but nor- $\psi$ -tropine has a vasoconstrictor action similar to that of  $\psi$ -tropine itself. Tripinone has properties resembling those of  $\psi$ -tropine, tropinoneoxime is inactive, whilst the semicarbazone greatly augments the activity of the ketone, at the same time rendering it more constant.

B. W. TOWN.



**Action of substances of the pilocarpine group (pilocarpine, arecoline, physostigmine) on the gas content of the blood.** A. M. PREOBRASCHENSKI (Russian J. Physiol., 1930, 13, 19—32).—Experiments on dogs show that all substances of the pilocarpine group diminish greatly the oxygen content of venous blood and leave unchanged or increase slightly that of arterial blood; decrease of the latter is, however, caused by large doses of physostigmine. If the decrease of the amount of oxygen in venous, with normal content in arterial, blood is the result of increased oxygen absorption by the tissues, and diminution of the oxygen content of arterial blood the result of insufficient arterialisation of the blood in the lungs, the increased consumption of oxygen must be a characteristic common to all substances of the group. The arterialisation of the blood in the lungs thus compensates for the oxygen consumed, except that, in most of the cases in which physostigmine and all in which toxic doses of the other substances were administered, the oxygen content of the arterial blood falls.

T. H. POPE.

**Dependence of the sugar curves of the blood on acid and alkaline diets with subcutaneous injection of pilocarpine.** E. T. MINKER-BOGDANOVA (Russian J. Physiol., 1930, 13, 151—156).—An acid or an alkaline diet influences the sugar of the blood but little, the sugar content and its maximum and minimum values being approximately the same in the two cases. With either diet, subcutaneous injection of pilocarpine produces neither a definite increase nor a definite lowering of the sugar content of the blood, but the divergences from the mean value are more marked than those of most of the control experiments.

T. H. POPE.

**Effect of curare on the carbohydrate metabolism and on the urinary secretion; protective action of the liver.** A. PARTOS (Pflüger's Archiv, 1929, 223, 40—46; Chem. Zentr., 1930, i, 705).—Injection of curare into rabbits causes hyperglycæmia. The urinary solids are diminished.

A. A. ELDRIDGE.

**Fixation of cocaine hydrochloride on nerve fibres.** J. RÉGNIER and G. VALETTE (Compt. rend., 1930, 190, 1453—1454).—The adsorption of cocaine hydrochloride on animal charcoal or on strips of the pneumogastric nerve of the ox conforms to the normal adsorption curve of Freundlich and is complete within 2 hrs.

C. C. N. VASS.

**Detoxification of nicotine by ultra-violet rays.** A. J. PACINI and H. MCGUIGAN (J. Pharm. Exp. Ther., 1930, 39, 241—244).—Aqueous solutions of nicotine were exposed to ultra-violet light from a mercury-vapour lamp. Injection of such solutions into the lymph sac of frogs failed to produce the typical symptoms of nicotine poisoning, whilst intravenous injection into a dog showed that the vasopressor action and the stimulating action on respiration were also lost. Simultaneously with the loss of toxicity, the solutions turned yellow and lost their basicity, finally becoming acid.

It is calculated that each nicotine molecule requires roughly  $1.9 \times 10^{-16}$  g.-cal. of radiant energy to effect the change.

G. F. MARRIAN.

**Relation between composition and uric acid excretive action of various cinchophen derivatives.** I, II. T. KAKU and I. YAMAGUCHI (Folia Pharmacol. Japon., 1929, 8, No. 4, 289, 307).—Esters of cinchophen and the erycon groups have in general a weak action; hydroxylated phenyl radicals and acetylated derivatives react strongly. Cinchophen derivatives with a methyl group in position 8 in the quinoline nucleus react strongly, in position 6 weakly, and in position 7 not at all; two groups (6- and 8-) retard the excretion. A methoxyl group in the phenyl nucleus increases the excretion, whilst a hydroxyl or acetyl group in that nucleus has no effect. The action of cinchophen esters and erycon esters is very weak in comparison with that of cinchophen and erycon.

CHEMICAL ABSTRACTS.

**Relationship between chemical composition and uric acid-excreting effect of cinchophen.** T. KAKU (Folia Pharmacol. Japon., 1929, 9, No. 1, 13).—Cinchophen becomes inactive on decarboxylation; reduction of the pyridine or benzene nucleus weakens the effect. Disintegration of the pyridine nucleus decreases, and of the benzene nucleus increases, the excretory action.

CHEMICAL ABSTRACTS.

**Heart tonics. II. Application of biometric methods to digitalis standardisation.** W. NYIRI and L. DUBOIS (J. Pharm. Exp. Ther., 1930, 39, 99—109).

**Evaluation of digitalis by pigeon-emesis and other methods.** J. H. BURN (J. Pharm. Exp. Ther., 1930, 39, 221—239).

**Toxicity of *Bikukulla formosa* (Western Bleeding-heart).** O. F. BLACK, W. W. EGGLESTON, and J. W. KELLY (J. Agric. Res., 1930, 40, 917—920).—The alcoholic extract of tops of *B. formosa* (also known as *Dicentra*) contained an alkaloid which in doses of 2.5—5.0 mg. injected subcutaneously proved fatal to mice by producing respiratory paralysis.

A. G. POLLARD.

**Toxin of the water snake (*Tropidonotus natrix*).** II. Pharmacological action of the blood, saliva, and secretion of the anal glands and of organ extracts. Comparison with the blood and secretion of the poison glands of the common European viper. O. GESSNER (Arch. exp. Path. Pharm., 1930, 151, 22—32).—Pharmacological investigation of the toxins of the water snake and of the common European viper indicates that the principles acting on the heart are in both cases apparently of a saponin-like nature.

W. O. KERMACK.

**Saponins; pharmacology of jegosaponin, an active component of *Styrax japonicus*.** T. KONDO (Keijo J. Med., 1930, 1, 71—90).—Jegosaponin, m. p. 246°, is more lethal than Merck's saponin to fish and other cold-blooded animals, but to warm-blooded animals both are about equally toxic. Jegosaponin hæmolyses red blood-corpuscles. When the corpuscles of various species of animals are used the resistances do not follow the Rywosch series. Jegosaponin forms a non-hæmolytic additive compound, m. p. 297°, with cholesterol.

W. O. KERMACK.

**Absorption, distribution, elimination, and photodynamic action of "rivanol."** O. SCHAUMANN (Arch. exp. Path. Pharm., 1930, 151, 197—218).—"Rivanol" can be determined by means of the fluorescence of its solutions in 50% acetic acid under the influence of ultra-violet light. Intravenously injected rivanol is excreted in the bile and urine. Red blood-corpuscles retain rivanol to some extent. The appearance of traces of rivanol in the foetus and the amniotic fluid follows excessive doses. In man only minimal amounts of rivanol appear in the urine following oral administration, if the liver function is normal. The toxicity to warm-blooded animals is not raised by exposure to ultra-violet light.

P. G. MARSHALL.

**Relationships between constitution and odour.** A. ANGELI (Atti R. Accad. Lincei, 1930, [vi], 11, 535—541).—The cyclic polymethylene carbonyl compounds described by Ruzicka (cf. A., 1928, 642; 1929, 67, 315) have odours similar to those of the artificial musks (aromatic nitro-compounds) and of ketones such as ionone, but do not contain methyl groups. The view is advanced that the presence of a large number of methylene groups in the molecules of the former compounds may result in deformations of the ring leading to the production of lateral nodes composed of several such groups and able to act as methyl groups. Evidence in support of this suggestion is discussed.

T. H. PORE.

**Peptone shock.** III. Substance which causes the so-called peptone blood. IV, V. Alcohol-soluble (blood-depressive) substances in peptone. T. YOKOTA (Sei-i-kwai Med. J., 1929, 48, No. 10, 39—53, No. 11, 67—72).—Since peptone contains albumose the coagulability of the blood is inhibited and the pressure falls. When ordinary peptone is injected the blood-sugar rises; this falls with return to normal coagulability. The blood-calcium is unaffected. The depressor substance in peptone is believed to be choline.

CHEMICAL ABSTRACTS.

**Excitant substance in the central nervous system.** L. HABERLANDT (Pflüger's Archiv, 1929, 223, 171—179; Chem. Zentr., 1930, i, 703).—The excitant action of emulsions of the cerebrum or mid-brain when injected into frogs is due to a substance which is soluble in water, but not in alcohol or ether; it is dialysable, and is decomposed when heated.

A. A. ELDRIDGE.

**Dilatometric studies in enzyme action.** M. SREENIVASAYA and B. N. SASTRI (J. Indian Inst. Sci., 1930, 13A, 57—62).—See A., 1929, 1488.

**Enzymic action in oxido-reduction systems and its relation to non-enzymic catalysis in aqueous solutions.** F. TÖDT and R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1930, 80, 81—92).—From the fact that numerous cases of autoxidation have been found to involve the catalytic action of iron, the formation of hydrogen peroxide, and the co-operation of "active" surfaces, it is concluded that the action of iron consists in the discharging of two hydrogen ions, an atom of adsorbed or reduced iron passing into solution as ferrous iron at the same time. It is known that in the corrosion of iron the dissolution of

the metal as ferrous ions is accompanied by formation of hydrogen peroxide, by combination of the displaced hydrogen with dissolved oxygen. The authors consider that ferrous ions adsorbed on an active surface become quasi-metallic iron, owing to neutralisation of their charges by the negative surface charges of the adsorbent; in this condition the iron is unstable and tends to redissolve, with further peroxide formation. This hypothesis accounts for many hitherto conflicting observations regarding enzymic oxido-reduction and purely chemical autoxidation. From this point of view the specific action of enzymes appears as specific adsorptive properties of surfaces.

J. H. LANE.

**Mode of action of the dehydrases. I. Dehydrase of peas and its so-called co-enzyme.** A. FODOR and L. FRANKENTHAL (Fermentforsch., 1930, 11, 469—489).—A dehydrase was prepared from peas by precipitating an aqueous potassium phosphate extract of the meal with acetone and further purification with kaolin. The activity was studied by the Thunberg technique. Potassium formate up to 0.2M increased the rate of decolorisation of methylene-blue, whereas lactate and pyruvate had an inhibitory action; these effects were less marked with a strong enzyme preparation (no kaolin purification). Acetaldehyde also has an inhibiting action. In some cases an aqueous potassium phosphate extract of pea meal was used after dialysis. The activity was greatly reduced, but was restored by addition of boiled pea juice. The restoration was slight with boiled yeast juice and detected only after addition of formate. The co-enzyme of yeast, unlike that of peas, is not adsorbed by kaolin. With germinated pea extracts, phosphate mixture accelerated only in presence of boiled juice. Boiled yeast juice now stimulated strongly even without formate.

J. H. BIRKINSHAW.

**Degradation of fructosediphosphoric, glycerophosphoric, and propionic acids in muscle.** A. HAHN and W. HAARMANN (Z. Biol., 1930, 90, 231—236).—Pyruvic acid is produced from these acids by a dehydrogenase present in muscle pulp, and is isolated as the phenylhydrazone. This action takes place even when the lactic acid enzyme has been removed by washing. Lævulose is also converted into pyruvic acid in the presence of a hydrogen acceptor such as methylene-blue. In the case of propionic acid, acrylic and lactic acids are postulated as intermediate products in the formation of pyruvic acid.

P. G. MARSHALL.

**Influence of salts on the activity of malt catalase.** IV. M. O. CHARMANDARIAN and A. B. TIUTIUNNIKOVA (Biochem. Z., 1930, 221, 273—283; cf. A., 1929, 471, 722).—Inorganic salts influence the activity of the catalase gradually. In some circumstances they may inhibit, in others they may stimulate the activity and these effects are independent of the hydrogen-ion concentration. There is a reciprocal inhibitory effect in the case of ferric ions and the catalase when the concentration of the ions is low and that of the catalase is high. The action of salts may be related to a change in the charge on the colloid and to an increase in the degree of its dispersion.

W. MCCARTNEY.

The complex between enzyme and products of hydrolysis in the inversion of sugar. H. COLIN and A. CHAUDUN (Compt. rend., 1930, 190, 1415—1417).—Whilst dextrose and, to a greater extent, levulose decrease the initial velocity of the inversion of sucrose they do not reduce the amount of hydrolysis effected by the invertase by uniting with the enzyme. Methyl and ethyl alcohols and glycerol act like dilute alkalis in diminishing the initial rate of hydrolysis but increasing the amount of sugar inverted.

C. C. N. VASS.

Separation of  $\alpha$ -glucosidase and  $\beta$ -*h*-fructosidase in yeast autolysates. R. WEIDENHAGEN (Z. Ver. deut. Zucker-Ind., 1930, 80, 155—165).—The separation of maltase from invertase described by Willstätter and Bamann (A., 1926, 433) is according to the author a separation of  $\alpha$ -glucosidase from  $\beta$ -*h*-fructosidase, the former enzyme being capable of hydrolysing both maltose and sucrose (A., 1928, 1157, 1281). From extracts of autolysed bottom-fermentation yeast containing about 3 times as much fructosidase as glucosidase, the author obtained the latter free from the former by adsorption on polyaluminium hydroxide *B* (cf. B., 1923, 181 A), which under certain conditions adsorbed 80% of the glucosidase and only 4% of the fructosidase present. Before elution of the glucosidase the fructosidase was removed from the adsorbent by pre-elution with monopotassium phosphate solution. Finally a solution of glucosidase was obtained having 77% of the activity of the original yeast extract.

J. H. LANE.

Influence of neutral salts on the activity of malt amylase. H. C. SHERMAN, M. L. CALDWELL, and M. CLEVELAND (J. Amer. Chem. Soc., 1930, 52, 2436—2440).—Sodium chloride has no appreciable effect in concentrations of 0.01—0.1M on the activity of malt amylase in acetate buffers at  $p_H$  4.3—5.1 (cf. this vol., 813). The activity of the enzyme is, however, increased at  $p_H$  4.0—4.3 with lower concentrations, and at  $p_H$  5.1—6.2 with higher concentrations of the chloride. Potassium chloride shows a similar behaviour; its influence is slightly greater. The effect of sodium sulphate is similar in type, but at  $p_H$  4.0 and 5.5 it is less favourable than the above chlorides. Sodium nitrate is not so efficient as the chlorides.

H. BURTON.

Neutral salt action. I. Diastase. D. NARAYANAMURTI (J. Indian Inst. Sci., 1930, 13A, 63—68).—The effect of sodium chloride on the rate of hydrolysis of electrolyte-free amylose by cholam diastase was studied. The salt had the greatest effect when it was added to the enzyme before the addition of the starch. Salt concentrations of 0.000166N and above retarded the hydrolysis. A concentration of 0.0000166N caused a slight acceleration. It is suggested that at the low salt concentration the charge on the enzyme is reduced, thereby increasing the adsorption of the electrically neutral amylose at its surface. With higher concentrations the charge is neutralised and reversed, leading to decreased adsorption of the substrate and consequently to a slower rate of hydrolysis. 0.0000166N-Sodium chloride had no effect in mixtures buffered to the optimum  $p_H$ . On the acid side of the optimum an

4A

acceleration was observed, on the alkaline side an inhibition.

The hydrolysability of different starches by diastase depended on their ash content, those with a low ash content being the more readily hydrolysed. The degree of hydrolysis of amylopectin varied with the method of preparation.

G. F. MARRIAN.

Action on methyl- and phenyl-glyoxal of the enzymes of green leaves. Lime-tree leaves. C. PI-SUÑER BAYO (Anal. Fis. Quim., 1930, 28, 371—379).—By the action of enzymes extracted from fresh green lime-tree leaves on methylglyoxal inactive lactic acid is formed, but with phenylglyoxal *l*-mandelic acid is obtained in about 80% yield; higher yields cannot be obtained on account of the presence in the leaf extract of substances which retard crystallisation. Addition of co-enzyme does not appreciably influence the reaction.

H. F. GILLBE.

Stereochemical specificity of the esterases. R. AMMON (Fermentforsch., 1930, 11, 459—468).—The stereochemical specificity of the esterases is dependent on the combined effect of the dissociation and hydrolysis constants of the enzyme-ester complex formed as intermediate product.

J. H. BIRKINSHAW.

Asymmetric esterification and hydrolysis caused by the esterases of the pancreas and liver of the pig. P. RONA, R. AMMON, and M. WERNER (Biochem. Z., 1930, 221, 381—391; cf. this vol., 373).—When powdered pig pancreas acts on mixtures of *n*-butyric acid and isoamyl alcohol, isoamyl alcohol and water, or isobutyl alcohol, esterification takes place. The powdered pancreas produces *l*-sec.-butyl *n*-butyrate more rapidly than the *d*-compound from mixtures of *dl*-sec.-butyl alcohol and the acid, and, correspondingly the *l*-component of *dl*-sec.-butyl *n*-butyrate is more rapidly hydrolysed by the powdered pancreas (or, much better, by powdered pig liver) than is the *d*-component. *dl*-sec.-Butyl *n*-butyrate, prepared from its components by the action of hydrogen chloride, has b. p. 149—150.5°, *d* 0.862.

W. MCCARTNEY.

Nuclein metabolism. XXII. Enzymic fission of thymus-nucleic acid with liver-nucleotidase. Thyminnucleoside. S. J. THANNHAUSER and M. ANGERMANN (Z. physiol. Chem., 1930, 189, 174—176; cf. this vol., 249).—Crystals obtained from an oily fraction of the products of enzymic fission of thymus-nucleic acid proved to be thyminnucleoside, m. p. 185°,  $[\alpha]_D^{25} + 37.5^\circ$ .

J. H. BIRKINSHAW.

Nature of proteases. IV. Does the  $p_H$  optimum in the process of protein digestion depend on the activity of the enzyme preparations? J. A. SMORODINCEV, A. N. ADOVA, and O. N. BARMINA (Z. physiol. Chem., 1930, 189, 107—111; cf. A., 1929, 1198).—The optimum  $p_H$  for digestion of egg-albumin by both a strong and a weak pepsin preparation was 1.10—1.20.

J. H. BIRKINSHAW.

Nature of proteases. V. Relations between activity of enzymes and surface tension of their solutions. J. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1930, 189, 165—173).—Active preparations of pepsin depress the surface tension of

water more strongly and have a smaller conductivity than weak preparations. Addition of hydrochloric acid to constant  $p_H$  depresses the surface tension. At constant  $p_H$  a rise of temperature from 18° to 38° lessened the surface tension of weak and increased that of strong preparations. With decreasing activity the electrical conductivity decreases. The surface tension and conductivity of caseinogen and gelatin solutions during digestion were compared.

J. H. BIRKINSHAW.

**Action of N-alkali, erepsin, and trypsin-kinase on compounds of polypeptide nature containing  $\beta$ -alanine.** E. ABDERHALDEN, T. RYNDIN, and E. SCHWAB (Fermentforsch., 1930, 11, 515—528).—The following substrates (polypeptides and their precursors) were prepared:  $\beta$ -alanylglycylglycine, m. p. 199—200°, from  $\beta$ -chloropropionylglycylglycine, m. p. 165°; dl-leucyl- $\beta$ -alanylglycylglycine, m. p. 134° (decomp., froths at 95°), from dl- $\alpha$ -bromoisohexoyl- $\beta$ -alanylglycylglycine, m. p. 161°; dl-leucyl-dl-leucyl- $\beta$ -alanylglycylglycine, froths at 124°, m. p. 135° (decomp.), from dl- $\alpha$ -bromoisohexoyl-dl-leucyl- $\beta$ -alanylglycylglycine, m. p. 192°;  $\beta$ -alanyl-l-tyrosine, m. p. 193°, from ethyl  $\beta$ -iodopropionyl-l-tyrosinate, m. p. 115°, or corresponding chloro-ester; dl-leucyl- $\beta$ -alanyl-l-tyrosine, m. p. 200° (decomp.), from dl- $\alpha$ -bromoisohexoyl- $\beta$ -alanyl-l-tyrosine, m. p. 170°;  $\beta$ -alanyl-dl-leucine, m. p. 245—246°, from  $\beta$ -chloropropionyl-dl-leucine, m. p. 105°; dl-leucyl- $\beta$ -alanyl-dl-leucine, m. p. about 183° (decomp.), from dl- $\alpha$ -bromoisohexoyl- $\beta$ -alanyl-dl-leucine, m. p. about 134° (decomp.); glycyl-dl-leucyl- $\beta$ -alanyl-dl-leucine from chloroacetyl-dl-leucyl- $\beta$ -alanyl-dl-leucine. All the halogenoacyl substances were hydrolysed by sodium hydroxide but not the two polypeptides  $\beta$ -alanyl-l-tyrosine and  $\beta$ -alanylglycylglycine. Erepsin did not hydrolyse the halogenoacyl substances or any polypeptides in which  $\beta$ -alanine has a free amino-group; with substances containing the  $\beta$ -alanine linking, but at neither end of the chain, slight fission was observed. With trypsin-kinase,  $\beta$ -alanylglycylglycine, dl- $\alpha$ -bromoisohexoyl- $\beta$ -alanylglycylglycine, dl-leucyl- $\beta$ -alanylglycylglycine,  $\beta$ -chloropropionyl-dl-leucine, dl-leucyl- $\beta$ -alanyl-dl-leucine, and possibly dl- $\alpha$ -bromoisohexoyl- $\beta$ -alanyl-dl-leucine were not attacked; the remainder were hydrolysed. For hydrolysis by erepsin the free amino-group, and for trypsin-kinase the carboxyl group, must not be carried by the "unnatural" component.

J. H. BIRKINSHAW.

**Significance of the amino- or of the carboxyl group in polypeptides for the action of definite enzyme complexes.** E. ABDERHALDEN and F. SCHWEITZER (Fermentforsch., 1930, 11, 529—538).—Derivatives of dl-leucylglycyl-dl-leucine with protected amino- and carboxyl groups, viz., N-methyl-dl-leucylglycyl-dl-leucyldecarboxyglycine, m. p. 127—128° (uncorr.), dl-leucylglycyl-dl-leucyldecarboxyglycine, m. p. 92—93°, were not attacked by trypsin-kinase, but the latter was hydrolysed by erepsin. The N-methyl compound was not hydrolysed by yeast maceration juice. Both compounds were hydrolysed by N-alkali hydroxide at 37°.

J. H. BIRKINSHAW.

**Action of N-alkali, erepsin, and trypsin-kinase on isomeric polypeptides containing**

**d-alanine, d- $\alpha$ -aminobutyric acid, and l-leucine.** E. ABDERHALDEN and M. SAITO (Fermentforsch., 1930, 11, 539—556).—As starting materials for the preparation of the di- and tri-peptides there were used l- $\alpha$ -bromopropionic acid,  $[\alpha]_D^{20}$  -36.5°, l-alanine,  $[\alpha]_D^{20}$  -12.50°, d- $\alpha$ -bromopropionic acid,  $[\alpha]_D^{20}$  +33.2°, formyl-d-leucine,  $[\alpha]_D^{20}$  +18.14°, d- $\alpha$ -bromoisohexonic acid,  $[\alpha]_D^{20}$  +53.75°, l- $\alpha$ -aminobutyric acid,  $[\alpha]_D^{20}$  -8.9° (d-component, +8.5°), d- $\alpha$ -bromobutyric acid,  $[\alpha]_D^{20}$  +27.5° (chloride,  $[\alpha]_D^{20}$  +27.50°). The polypeptides prepared with their precursors were l-leucyl-d- $\alpha$ -aminobutyric acid, yellow at 228°, decomp. at 245°,  $[\alpha]_D^{20}$  +25.0°, from d- $\alpha$ -bromoisohexoyl-d- $\alpha$ -aminobutyric acid, m. p. 121°,  $[\alpha]_D^{20}$  +33.8°; l-leucyl-d-alanine,  $[\alpha]_D^{20}$  +19.5°, from the corresponding bromo-compound; d- $\alpha$ -aminobutyryl-l-leucine, m. p. 238° (decomp.),  $[\alpha]_D^{20}$  -5.0°, from d- $\alpha$ -bromobutyryl-l-leucine, m. p. 121°,  $[\alpha]_D^{20}$  +4.7°; d- $\alpha$ -aminobutyryl-d-alanine, m. p. 245° (260° previously given),  $[\alpha]_D^{20}$  +7.0°, from the bromo-compound, m. p. 142°,  $[\alpha]_D^{20}$  +16.18°; d-alanyl-d- $\alpha$ -aminobutyric acid, m. p. 226° (decomp.),  $[\alpha]_D^{20}$  -6.8°, from d- $\alpha$ -bromopropionyl-d- $\alpha$ -aminobutyric acid, m. p. 132°,  $[\alpha]_D^{20}$  +8.8°; d-alanyl-l-leucyl-d- $\alpha$ -aminobutyric acid, m. p. 248°,  $[\alpha]_D^{20}$  -39.3°, from d- $\alpha$ -bromopropionyl-d- $\alpha$ -aminobutyric acid, m. p. 125°,  $[\alpha]_D^{20}$  -33.5°; d- $\alpha$ -aminobutyryl-l-leucyl-d-alanine, m. p. 231°,  $[\alpha]_D^{20}$  -38.4°, from d- $\alpha$ -bromobutyryl-l-leucyl-d-alanine, m. p. 136°,  $[\alpha]_D^{20}$  -23.9°; d-alanyl-d- $\alpha$ -aminobutyryl-l-leucine, m. p. 192°,  $[\alpha]_D^{20}$  -35.7°, from d- $\alpha$ -bromopropionyl-d- $\alpha$ -aminobutyryl-l-leucine, m. p. 108°,  $[\alpha]_D^{20}$  -25.2°; l-leucyl-d- $\alpha$ -aminobutyryl-d-alanine, m. p. 205°,  $[\alpha]_D^{20}$  -4.2°, from d- $\alpha$ -bromoisohexoyl-d- $\alpha$ -aminobutyryl-d-alanine; l-leucyl-d-alanyl-d- $\alpha$ -aminobutyric acid, m. p. 206°,  $[\alpha]_D^{20}$  +7.4°, from d- $\alpha$ -bromoisohexoyl-d-alanyl-d- $\alpha$ -aminobutyric acid, m. p. 106°.

Of the five dipeptides d-alanyl-d- $\alpha$ -aminobutyric acid was most readily hydrolysed. d- $\alpha$ -Aminobutyryl-l-leucine was practically unattacked. Erepsin attacked the first-named dipeptide and d- $\alpha$ -aminobutyryl-d-alanine most strongly; d-alanyl-d- $\alpha$ -aminobutyric acid was practically unchanged. Trypsin-kinase hydrolysed none of the five. The slight alkalinity of the reaction ( $p_H$  7.8) for erepsin action does not account for hydrolysis by erepsin, since the actions of alkali hydroxide and erepsin are not parallel. As regards the tripeptides N-alkali hydroxide most readily hydrolyses those in which d- $\alpha$ -aminobutyric acid carries the carboxyl group. Erepsin hydrolysed d- $\alpha$ -aminobutyryl-l-leucine-d-alanine completely, but only one  $\cdot\text{CO}\cdot\text{NH}\cdot$  linking in d-alanyl-l-leucyl-d- $\alpha$ -aminobutyric acid and l-leucyl-d-alanyl-d- $\alpha$ -aminobutyric acid. Trypsin-kinase hydrolysed d- $\alpha$ -aminobutyryl-l-leucyl-d-alanine most readily. Trypsin-kinase hydrolysed none of the bromo-compounds of the dipeptides, but all the halogenoacyl derivatives of the tripeptides.

J. H. BIRKINSHAW.

**Proteolytic enzyme in ficin, the anthelmintic principle of leche de ligueron.** B. H. ROBBINS (J. Biol. Chem., 1930, 87, 251—257). Leche de ligueron (the sap of *Ficus laurifolia*) was centrifuged and the clear solution was precipitated by addition of 3 vols. of acetone, the precipitate was redissolved, again precipitated, and dried; it had the elementary

composition of a protein. This substance contains an enzyme capable of attacking *Ascaris*; the enzyme is also able to hydrolyse caseinogen and coagulate egg-albumin. It is irreversibly destroyed by heating at 75° in aqueous solution for 5 min., or by keeping at  $p_H$  2.3 for 1½ hrs.; it is active over the range  $p_H$  4—8.5.

C. R. HARRINGTON.

**Enzymic fission of glutathione.** I. W. GRASSMANN, H. DYCKERHOFF, and H. EIBELER (Z. physiol. Chem., 1930, 189, 112—120).—Glutathione is not hydrolysed by pepsin, pancreatic proteinase, papain, or the dipeptidase and amino-polypeptidase from yeast and intestine. It is readily attacked by pancreatic carboxy-polypeptidase, which, however, hydrolyses only one peptide linking, yielding the total glycine in the free state and a peptide residue recovered in 80% yield. This shows that the glycine is at the end of the chain and that the carboxyl group is free. Since Hopkins (A., 1929, 1491) obtained glycylcystine anhydride by boiling glutathione with water the glycine is probably attached to cysteine. Two formulæ are possible for glutamylcysteinyl-glycine according as to which carboxyl group of glutamic acid is linked up; that in which the amino-group is in the  $\alpha$ -position to the free carboxyl group is preferred.

J. H. BIRKINSHAW.

**Fermentation by yeast with altered permeability of the cell membranes.** K. MEYER (Biochem. Z., 1930, 221, 418—424).—The respiration of yeast which had been suspended in phosphate solution and shaken with olive oil or oleic acid was restricted, whilst its fermenting power was increased in proportion. When oil was added to a suspension in phosphate solution of acetone-dried yeast which no longer respired, the originally very weak fermenting power was increased tenfold. It is concluded that the rate of diffusion through the oil-covered cell membrane is sufficient to allow fermentation to proceed. Both sugar and co-enzyme can pass through the oil-covered membrane and there is no reason for supposing that sugar changes into a lipid-soluble form before diffusing.

W. MCCARTNEY.

**Factors determining ergosterol content of yeast.** I. Species. C. E. BILLS, O. N. MASSENGALE, and P. S. PRICKETT (J. Biol. Chem., 1930, 87, 259—264).—The ergosterol content of 29 yeasts varied from 0.2 to 2.0% of the dried material. Variations were observed not only between different species, but between different strains of the same species. A high content of ergosterol was associated with rapid growth, but the reverse was not necessarily the case. On the whole, species is a more important determining factor for the ergosterol content than cultural condition.

C. R. HARRINGTON.

**Enzymes of cap-fungi.** N. N. IVANOV, E. V. DODONOVA, and V. J. TSCHASTUCHIN (Fermentforsch., 1930, 11, 433—458).—Aqueous extracts of the crushed tissue of the mushroom (*Psalliota campestris*) contain maltase, glycogenase, amylase, proteolytic enzymes, and catalase. These enzymes are unequally distributed, the stem and cap showing the highest and the hymenium comparatively low enzyme content. Most enzyme is present when the

fruiting bodies are fully developed and sporing. Invertase, inulinase, and urease are absent. Other fungi, *Lepiota procera* and *Coprinus radiatus*, were grown in pure culture on synthetic liquid media, and the latter were examined for enzymes. Peptone and amino-acids are utilised extremely slowly; this is related to the weak development of some enzymes and the absence of others (invertase, inulinase, and urease). Amylase was most strongly developed in a starch medium; maltase was present only in small amount. The limited distribution of the higher fungi is correlated with their weak enzymic activity.

J. H. BIRKINSHAW.

**Toxicology of the higher fungi.** I. *Lactarius torminosus*. H. STEIDLE (Arch. exp. Path. Pharm., 1930, 151, 232—252).—Although certain strains of this fungus are non-toxic to protozoa and cold-blooded animals in general, the frog is particularly susceptible. Subcutaneous injection of an extract of the dried fungus gives rise to hyperæmia and fatty degeneration of the liver. Oral administration of extracts to warm-blooded animals produces symptoms of poisoning such as fatty degeneration. Parenteral administration in rabbits reduces both the number and hæmoglobin content of the corpuscles. Choline and traces of muscarine are probably present in the fungoid extracts, which act like convulsive poisons.

P. G. MARSHALL.

**Acid formation, respiration, oxidase reaction, and dehydrogenating power of some *Aspergillus* species.** H. TAMIYA and T. HIDA (Acta Phytochim., 1929, 4, 343—361).—When grown under conditions favourable to the formation of acids, gluconic acid was produced by *A. aureus*, *Avamori*, *candidus*, *clavatus*, *flavus*, *flavus* var., *fumigatus*, *giganteus*, *gymnosardæ*, *melleus*, *niger*, *ochraceus*, *Onikii*, *oryzæ*, *varians*, and *Wentii*, but not by *A. ostianus* and *soya*; kojic and citric acids were less common, whilst oxalic acid was found only in cultures of *A. flavus* and *varians*. Respiration and cellular oxidation were studied. Thunberg's citricodehydrogenase was not observed. No relation was found between the rate of respiration, acid formation, action of indophenolase, anabolic quotient, and methylene-blue reaction.

CHEMICAL ABSTRACTS.

**Enzymes and salt ions.** I. Invertase of *Penicillium* lacking potassium. G. VON DOBY and Z. I. KERTÉSZ (Z. physiol. Chem., 1930, 189, 177—192).—*Penicillium glaucum*, Link, was cultivated on a medium consisting of sucrose and inorganic salts. The maximum dry weight of mycelium was attained on 20% sugar; in absence of potassium the yield was considerably depressed. The invertase of the mould does not diffuse into the medium at acid reaction; it was obtained and the amount present, as shown by the reaction constant, determined using an aqueous suspension of the crushed mycelium. The  $p_H$  optimum of the enzyme under all conditions was 4.5. In absence of potassium the effect of the nutrient sugar concentration on the quantity of invertase secreted was the opposite of that observed with a complete medium. By omitting the potassium a considerable increase in invertase was attained. Salts did not activate the invertase of *Penicillium*,

contrary to that of sugar-beet (cf. A., 1927, 79). The autolysis optimum was at  $p_{\text{H}}$  5.

J. H. BIRKINSHAW.

**Soluble enzymes secreted by *Hymenomyces*. Degradation of lignin.** L. LUTZ (Compt. rend., 1930, 190, 1455—1457).—The jellyfication of the lignin of the beech by *Coriolus versicolor* proceeds in a similar manner to that in the formation of insoluble gums. The gum consists mainly of xylan with traces of galactan, mannan, and l  vulan. Further hydrolysis yields soluble gums and sugars which form the source of carbon for the growth of the fungus. Simultaneously the fungus ferments the sugars, producing alcohol.

C. C. N. VASS.

**Sterilising wood blocks to be used in the culture of wood-inhabiting fungi.** C. W. FRITZ (Phytopath., 1930, 20, 449—450).—Wood blocks may be sterilised by exposure to fumes of glacial acetic acid for 6 hrs., the blocks being turned after 3 hrs. Absorbed acid is removed by transferring the blocks to large sterile vessels in which most of the acid may be evaporated, and finally washing in sterile water.

A. G. POLLARD.

**Influence of gaseous nitrogen on the organic catalysis of nitrogen fixation by *Azotobacter*.** D. BURK (J. Physical Chem., 1930, 34, 1174—1194).—The chemical mechanism of nitrogen fixation by *Azotobacter* at the ordinary temperature and pressure has been investigated. At 0.2 atm. of oxygen, nitrogen is fixed at an appreciable rate only above 0.05 atm. and tends to reach a maximum at 5—10 atm. Between 0.05 and 5 atm. the rate of fixation is practically directly proportional to the pressure of nitrogen. In the presence of humic acid or at 0.05 atm. of oxygen, the proportionality begins at zero pressure of nitrogen. Humic acid increases the rate and efficiency of nitrogen fixation and decreases the limiting available nitrogen pressure to below 0.05 atm., but it is not directly concerned in the chemical mechanism of fixation. Nitrogen fixation has been established by measuring decreases of gaseous nitrogen as well as by increases of fixed nitrogen. The failure of legume bacteria to fix nitrogen in the absence of a host plant has been confirmed at various pressures from 0 to 1 atm. of nitrogen, hydrogen, or oxygen.

L. S. THEOBALD.

**Influence of gaseous oxygen on the organic catalysis of nitrogen fixation by *Azotobacter*.** D. BURK (J. Physical Chem., 1930, 34, 1195—1209).—The oxygen pressure functions controlling *Azotobacter* (cf. preceding abstract) with respect to respiration, growth, efficiency of growth,  $p_{\text{H}}$ , and humic acid obtain in both free and fixed nitrogen, and give no indication of the chemical mechanism of nitrogen fixation. The mechanism of respiration is discussed.

L. S. THEOBALD.

**Influence of unsaturated fatty acids on the virulence of tubercle bacilli.** G. PLATONOV (Amer. Rev. Tuberc., 1930, 21, 362—369).—Fats of the unsaturated type act bacteriolytically, retard the growth of tubercle bacilli, and lower their virulence.

CHEMICAL ABSTRACTS.

**Use of precipitated diphtheria toxin in the preparation of anti-diphtheria serum.** P. S  DAL-

LIAN and (MME.) CLAVEL (Compt. rend., 1930, 190, 1525—1526).—The precipitate obtained when diphtheria toxin is adjusted to  $p_{\text{H}}$  4.7 (cf. A., 1928, 1286; 1929, 220) is dissolved in a neutral peptone broth (Martin), and then injected (in increasing amounts during 3 months) into horses. The serum obtained is of the same value (as an antigen) as that resulting from injection of the original toxin.

H. BURTON.

**Factors influencing survival of bacteria in water and in saline solutions.** E. N. BALLANTYNE (J. Bact., 1930, 19, 303—320).—The effect of sodium chloride solutions on the survival of certain pathogenic organisms is examined. Low temperature, a minimum of nutrients, and a minimum of sodium chloride favoured survival but not growth of the organisms.

A. G. POLLARD.

**Oligodynamic action of metals and metallic salts on bacteria at various oxygen pressures.** P. HOFMANN (Zentr. Bakt. Par., 1929, 114, 216—227; Chem. Zentr., 1930, i, 846).—Colloidal silver, gold, or copper has a more intense oligodynamic action the higher is the oxygen content; metallic salts exhibit unchanged oligodynamic action in absence of oxygen. The oligodynamic action is an effect of the metallic ion.

A. A. ELDRIDGE.

**Bactericidal action of chlorine.** C. A. SAGASTUME and A. A. SOLARI (Rev. fac. cienc. quim. La Plata, 1929, 6, I, 37—51).—In experiments designed to test the radiation hypothesis of the bactericidal action of hypochlorites inconsistent results were obtained.

CHEMICAL ABSTRACTS.

**Preservation of fruit juice with formic acid.** A. HANAK (Biochem. Z., 1930, 221, 467—472).—Non-motile bacilli which are unaffected by intense ultra-violet irradiation have been found to grow on raspberry juice which contained 0.27% of formic acid in addition to other free acids. The presence of air favours if it is not essential to the growth of the organisms, which can be stained with carbolfuchsin and may belong to several species or exist in several forms. As a result of the growth of the bacilli the formic acid content of the juice decreases or disappears.

W. MCCARTNEY.

**Fungicidal action of sulphur. I. Alleged r  le of pentathionic acid.** F. WILCOXON and S. E. A. MCCALLAN (Phytopath., 1930, 20, 391—417).—The toxicity of pentathionic and sulphuric acids and of hydrogen sulphide towards several pathogenic fungi is examined. Pentathionic and sulphuric acids exhibit identical toxicity, which is apparently due to hydrogen-ion concentration. Hydrogen sulphide has 200 times the toxicity of these acids. Neutral pentathionates are non-toxic to *Sclerotinia americana*, but become toxic when decomposed by sodium carbonate with the formation of colloidal sulphur. Water extracts of sulphur contain pentathionic acid, but are non-toxic. The toxicity of a 300-mesh sample of sulphur is unaltered by removal of adhering pentathionic acid with alkali. Pentathionic acid is not an important factor in the toxicity of sulphur.

A. G. POLLARD.

**Comparative experiments on the influence of *l*- and *dl*-adrenaline and adrenalone on the blood**



[sugar] picture of rabbits. S. ANAN (*Folia Pharmacol. Japon.*, 1929, 8, No. 3, 1—7).—*dl*-Adrenaline is half as potent as *l*-adrenaline; adrenalone is 0.01 as potent.

CHEMICAL ABSTRACTS.

Influence of the blood-calcium on the pressor action of adrenaline. H. MACHII (*Folia Pharmacol. Japon.*, 1929, 8, No. 3, 184).—Rise in blood-calcium diminishes the action of adrenaline.

CHEMICAL ABSTRACTS.

Action of calcium and potassium ions in sugar metabolism through adrenaline. R. ISHII and S. SAKATA (*Folia Pharmacol. Japon.*, 1929, 8, No. 4, 276).—Experiments on toad liver show that potassium ions enhance, whereas calcium ions depress, adrenaline glycogenic action.

CHEMICAL ABSTRACTS.

Antagonistic action of choline against adrenaline glycogen mobilisation. J. TANAKA (*Folia Pharmacol. Japon.*, 1929, 8, No. 4, 282).—Choline, when injected into rabbits, raises the blood-sugar but reduces adrenaline hyperglycæmia.

CHEMICAL ABSTRACTS.

Influence of choline on glycogen mobilisation in the toad liver through adrenaline. T. KIYOHARA and Y. TANIUCHI (*Folia Pharmacol. Japon.*, 1929, 8, No. 4, 314).—Choline depresses glycogen mobilisation; choline and adrenaline are antagonistic in their action on carbohydrate metabolism.

CHEMICAL ABSTRACTS.

Synergism between adrenaline and cocaine by the sugar mobilisation from the toad liver. R. ISHII and S. SAKATA (*Folia Pharmacol. Japon.*, 1929, 8, No. 3, 179).

CHEMICAL ABSTRACTS.

Antagonistic action of atropine against the adrenaline sugar mobilisation in the liver. Y. TANIUCHI and T. KIYOHARA (*Folia Pharmacol. Japon.*, 1929, 8, No. 3, 214).—The sugar mobilisation in perfused toad liver is decreased by atropine.

CHEMICAL ABSTRACTS.

Circulatory hormone. IV. Detection of a circulatory hormone in the pancreas. H. KRAUT, E. K. FREY, and E. WERLE (*Z. physiol. Chem.*, 1930, 189, 97—106; cf. A., 1928, 1057).—Extracts of the pancreas of the ox, pig, sheep, horse, dog, and man were compared as to their content of circulatory hormone by injection of acetic acid or ammoniacal extracts into dogs. The extract of pig's pancreas gave the most active product (1 unit in 1.5 mg.); human pancreas contained 1 unit per 20—40 mg., and horse pancreas only 1 unit per 130—150 mg. of the dried preparation. The activity of these extracts is destroyed by a substance present in blood and is restored by acid. Preparations from urine retain their activity over long periods, but pancreas and blood preparations are rapidly inactivated. Otherwise all preparations behave similarly. The activity is destroyed by boiling. The name "callicrein" is proposed for the new hormone.

J. H. BIRKINSHAW.

Heart hormone ("eutonon") from the liver. H. SALOMON and G. ZUELZER (*Z. ges. exp. Med.*, 1929, 66, 291—324; *Chem. Zentr.*, 1930, i, 543).—A clinical report.

A. A. ELDRIDGE.

Biochemistry and pharmacodynamics of the thyroid gland. H. SIMONNET (*Bull. Soc. Chim. biol.*, 1930, 12, 579—614).—A lecture.

Influence of insulin on a united synthetic process in the animal organism. R. ISHII, H. MATSUSHIMA, and Y. TANIUCHI (*Folia Pharmacol. Japon.*, 1929, 9, No. 1, 1).—Injection of insulin into rabbits increases resistance to poisoning by phenol (injected together with sugar), especially in presence of lævulose.

CHEMICAL ABSTRACTS.

Effect of insulin. I. M. OGAWA (*Folia Pharmacol. Japon.*, 1929, 8, No. 3, 157).—The smallest active dose of insulin is (with rabbits) almost independent of the method of injection, but the rate of fall of the blood-sugar (except with large doses) is not.

CHEMICAL ABSTRACTS.

Effect of insulin. II, III. M. OGAWA (*Folia Pharmacol. Japon.*, 1929, 8, No. 4, 254; 9, No. 1, 38).—The effect on the blood-sugar of various methods of administration of insulin was studied.

CHEMICAL ABSTRACTS.

Regulation of secretion of insulin. G. JORNS (*Klin. Woch.*, 1929, 8, 2319—2322; *Chem. Zentr.*, 1930, i, 848).

Action of compounds of insulin with bile acids on subcutaneous administration. R. STEPHAN (*Deut. med. Woch.*, 1930, 56, 88—91; *Chem. Zentr.*, 1930, i, 995).—Oral administration of the additive compound of insulin with sodium deoxycholate causes a hypoglycæmia less marked, but of longer duration, than for subcutaneous injection. The compound appears to become stored in the body. The differences in behaviour are attributed to differing chemical structures of the active substances.

A. A. ELDRIDGE.

Mechanism of formation of "duodenal secretin." J. P. RASENKOV (*Pflüger's Archiv*, 1929, 223, 156—162; *Chem. Zentr.*, 1930, i, 699).—It is postulated that by the decomposition of protein by gastric juice substances are formed from which the intestinal mucous membrane produces substances having the properties of duodenal secretin.

A. A. ELDRIDGE.

Female sexual hormone, menoformon. E. BORCHARDT, E. DINGEMANSE, S. E. DE JONGH, and E. LAQUEUR (*Z. ges. exp. Med.*, 1929, 68, 86—105; *Chem. Zentr.*, 1930, i, 700).—A study of anti-masculine effect in rats.

A. A. ELDRIDGE.

Effect of folliculin on the blood-sugar of ovariectomised dogs. F. RATHERY, R. KURILSKY, and GIBERT (*Compt. rend. Soc. Biol.*, 1929, 99, 667—669; *Chem. Zentr.*, 1930, i, 400).—Ovariectomy causes only small changes in the blood-sugar curve, but folliculin hyperglycæmia is thereby rendered scarcely more marked than in castrated animals; it is followed by hypoglycæmia. Ovariectomy appears to affect the mechanism of the regulation of blood-sugar.

A. A. ELDRIDGE.

Preparation of crystalline ovarian follicular hormone: theelin. C. D. VELER, S. THAYER, and E. A. DOISY (*J. Biol. Chem.*, 1930, 87, 357—371).—Urine of pregnant women is siphoned from the natural sediment, made acid to Congo-red, and extracted

continuously in a special apparatus with butyl alcohol; the extract is evaporated in a vacuum and the residue is leached with hot benzene. The latter is removed by distillation, the residue dissolved in butyl alcohol, and the solution is largely diluted with light petroleum and extracted with dilute sodium hydroxide; the alkaline solution is extracted with ether, the extract is evaporated and steam-distilled until free from volatile compounds, and the residue is leached with hot dilute sodium hydroxide. Extraction with ether and removal of the solvent is repeated, the residue being this time leached with cold dilute sodium hydroxide; the alkaline solution is again extracted with ether, and the residual oil left on evaporation of the latter is crystallised from 25% alcohol, and then from butyl alcohol. The crystalline hormone so obtained, now designated theelin, has m. p. 243° (cf. Butenandt, this vol., 118). C. R. HARRINGTON.

**Sexual hormone of the anterior pituitary lobe.** M. REISS and F. HAUROWITZ (Z. ges. exp. Med., 1929, 68, 371—378; Chem. Zentr., 1930, i, 701).—The crude (urinary) hormone solution is treated with an excess of 3% uranyl acetate solution, the precipitate centrifuged, shaken with an excess of 2% ammonium phosphate solution, shaken, and again centrifuged. Most of the hormone is in the eluate. The hormone is absorbed by alumina gel. The solution is not precipitated by ammonium sulphate; the hormone is readily dialysed and is nearly related to the peptones. The gland extract (corresponding fully with the urinary hormone) lost its activity at the ordinary temperature in 14 days.

A. A. ELDRIDGE.

**Corpus luteum and sexual hormone.** L. FRAENKEL and E. FELS (Z. ges. exp. Med., 1929, 68, 172—184; Chem. Zentr., 1930, i, 699).—Corpus luteum contains a hormone which is not identical with the oestrus hormone.

A. A. ELDRIDGE.

**Male sexual hormone (androkinin) in urine.** S. LOEWE, H. E. VOSS, F. ROTHSCHILD, and E. BORCHARDT (Biochem. Z., 1930, 221, 461—466).—Both male (androkinin) and female (thelykinin) sexual hormones occur in male urine and this can be so treated that they are found in separate fractions. The procedure of Funk and others (Proc. Soc. Exp. Biol. Med., 1929, 26, 569) is unsatisfactory and their results cannot be confirmed.

W. MCCARTNEY.

**Vitamin-A content of yellow and white-capped yellow dent maize.** W. C. RUSSELL (J. Nutrition, 1930, 2, 265—269).—The former variety contains much more vitamin-A than the latter.

CHEMICAL ABSTRACTS.

**Quantitative comparison of the vitamin-A of yellow maize and the grain sorghums hegari and yellow milo.** M. C. SMITH (J. Agric. Res., 1930, 40, 1147—1153).—Rats given less than 3 g. of hegari daily in addition to an otherwise A-free diet showed loss of weight, and all which received less than 5 g. had a survival period of less than 56 days. Yellow maize is 20 times as rich in A as hegari and 10 times as rich as yellow milo.

P. G. MARSHALL.

**Comparative nutritive value of yellow maize and the grain sorghums hegari and yellow milo.**

M. C. SMITH (J. Agric. Res., 1930, 40, 1129—1145).—The chief chemical difference between yellow maize and the sorghum grains is that the former contains more fat and less protein than the latter, which have a lower coefficient of digestibility. Yellow maize is superior to hegari in vitamin-A content. Like yellow maize, the sorghum grains are deficient in both protein and mineral salts, but when these are added in suitable quantity to the hegari diet, growth and function are optimal.

P. G. MARSHALL.

**Effect of inadequate rations on the composition of the blood and of the bone of chicks.** A. G. HOGAN, C. L. SHREWSBURY, and H. L. KEMPSTER (Missouri Agric. Exp. Sta. Res. Bull., 1929, No. 124, 17 pp.).—Analyses of the blood and bone of chicks receiving rations deficient in vitamin-A gave normal values; deficiency in vitamin-B raised the blood-sugar, whilst that in vitamin-D lowered the ash and inorganic phosphorus content of the bones. Synthetic diets raised the blood-sugar.

CHEMICAL ABSTRACTS.

**Carotene and animal growth.** M. JAVILLIER (Bull. Soc. Chim. biol., 1930, 12, 554—578).—A lecture.

**Chemical detection of vitamins; existence of a specific growth-vitamin.** E. REMY (Arch. Pharm., 1930, 268, 299—308).—A review.

H. E. F. NOTTON.

**Dextrose tolerance in deficiency of vitamin-B<sub>1</sub>.** S. LEPKOVSKY, C. WOOD, and H. M. EVANS (J. Biol. Chem., 1930, 87, 239—250).—Rats on a diet deficient in vitamin-B<sub>1</sub> show no alteration in their tolerance for dextrose until the onset of beriberi is imminent, when the tolerance becomes lowered.

C. R. HARRINGTON.

**Beef extract as a source of vitamin-B<sub>2</sub>.** R. HOAGLAND and G. G. SNIDER (J. Agric. Res., 1930, 40, 977—990).—Experiments on albino rats indicated that four of five commercial beef extracts, at an intake level of 7.5% of moisture-free material, furnished sufficient vitamin-B<sub>2</sub> for good to excellent growth. The actual daily intake averaged approx. 0.80 g. for males and 0.65 g. for females. Fair and excellent growth was induced by 20% and 25% intakes of dried lean beef respectively, the actual daily intake in the second case being 2.7 g. for males and 2.2 g. for females. It is concluded that, as judged by their content of vitamin-B<sub>2</sub>, 1 lb. of beef extract is equivalent to 11 lb. of fresh lean beef.

E. HOLMES.

**Occurrence of the antirachitic vitamin in fish-liver oils.** E. POULSON (Strahlenther., 1929, 34, 648—649; Chem. Zentr., 1930, i, 997).—Different values for vitamin-A and -D content, especially the latter, are recorded for the same species. Cartilaginous fish contain very little, but the amount is increased by irradiation.

A. A. ELDRIDGE.

**Action of vitamin-D.** A. HOTTINGER (Strahlenther., 1929, 34, 639—645; Chem. Zentr., 1930, i, 997—998).—The activity of vitamin-D is not based on an action on the digestive organs.

A. A. ELDRIDGE.

**Photoactivation of ergosterol to vitamin-D.** F. HOLTZ (Strahlenther., 1929, 34, 637—638; Chem.

Zentr., 1930, i, 998).—A study of the effect of different conditions of irradiation. A. A. ELDRIDGE.

**Treatment of rickets with irradiated ergosterol.** H. KREITMAIR (Strahlenther., 1929, 34, 636; Chem. Zentr., 1930, i, 998).—Bone calcification is unsuitable for use in standardising vitamin-D preparations. A. A. ELDRIDGE.

**X-Ray standardisation of vitamin-D preparations.** J. VAN NIEKERK and J. W. R. EVERSE (Strahlenther., 1929, 34, 646—647; Chem. Zentr., 1930, i, 1000).—The effect on the bones of the paws of animals is recorded by means of X-rays.

A. A. ELDRIDGE.

**Ergosterol and antirachitic vitamin.** M. COMEL (Arch. Ist. Biochim. Ital., 1930, 2, 281—306).—When administered in excessive doses, irradiated ergosterol maintains its efficacy as a calcium-fixing and antirachitic remedy, but gives rise to the toxic phenomena. The toxicity is displayed mainly by precipitation of lime in the viscera and by a characteristic atrophy of their cellular elements, and is probably due to the ergosterol itself rather than to admixed substances. This toxicity throws doubt on the identity of irradiated ergosterol with the lime-fixing vitamin, but the irradiated ergosterol may represent the active constituent of the vitamin, the latter being formed by union of the ergosterol with a protective lipid. T. H. POPE.

**Action of irradiated ergosterol in the chicken.** I. Effect on calcium and inorganic phosphorus of the blood-serum. II. Prevention of leg weakness. O. N. MASSENGALE and M. NUSSMEIER (J. Biol. Chem., 1930, 87, 415—422, 423—426).—I. The birds were fed on diets lacking vitamin-D and containing varying amounts of calcium and phosphorus, and the effect of administration of irradiated ergosterol was observed. With diets rich in calcium and poor in phosphorus, the low serum-phosphate and the high serum-calcium both tended to increase when irradiated ergosterol was administered, although the change in phosphate was not marked in extreme cases. With diets adequate in calcium and phosphorus, irradiated ergosterol caused a rise in the calcium of the blood only after some weeks, whilst with diets low in both calcium and phosphorus it restored the blood-calcium to the normal value but did not affect the phosphate.

II. Irradiated ergosterol was much less effective than cod-liver oil in preventing leg weakness in chickens on a rachitic diet. C. R. HARRINGTON.

**Calcification of the lung of the healthy or tuberculous rabbit by large doses of irradiated ergosterol.** H. SIMONNET and G. TANRET (Compt. rend., 1930, 190, 1526—1529; cf. this vol., 506, 822).—Administration of large amounts of irradiated ergosterol to healthy rabbits causes an increase in the calcium content of the lung from 0.1—0.15 to 0.42—2.06%. The aorta, in the thoracic and abdominal regions, also shows a large increase in calcium content. With tuberculous animals, the calcium content of the lung increases from 0.16—0.67 to 1.19—9.68%; the aorta is also calcified to varying extents.

H. BURTON.

**Determinations of calcium and phosphate in animals poisoned by "vitasterol."** W. HEUBNER (Strahlenther., 1929, 34, 634—635; Chem. Zentr., 1930, i, 1000).—The important organs contained 10—100 times as much calcium as usual. Irradiated ergosterol exercises no particular effect on the total excretion. Within certain limits of dose the increase in phosphate appears to be parallel with the amount of ergosterol administered. A. A. ELDRIDGE.

**Spectroscopic demonstration of a concomitant of cholesterol from the calcified aorta.** I. H. PAGE and W. MENSCHICK (Naturwiss., 1930, 18, 585—586).—The cholesterol separated from aorta calcified as the result of the administration of irradiated ergosterol shows two absorption bands with intensity maxima at 238  $\mu$  and 320  $\mu$  and with intensities in the ratio of 200:1. The compound responsible for these bands may be cholestenone (absorption maxima at 243  $\mu$  and 312  $\mu$ ; cf. Windaus, Nachr. Ges. Wiss., Math.-physik. Kl., 1930, 36). W. O. KERMACK.

**Vitamins. XVII. Ossifying potency of raw and evaporated milks.** H. E. HONEYWELL, R. A. DUTCHER, and C. D. DAHLE (J. Nutrition, 1930, 2, 251—256).—The ossifying potency of raw milks is the greater. The prepared milks were not rich in vitamin-D, to which the calcifying properties are attributed. The ash of evaporated milks, when fed to rats, showed less ossifying power than the corresponding milks.

CHEMICAL ABSTRACTS.

**Effect of various treatments on the carbon dioxide and oxygen in dormant potato tubers.** O. SMITH (Hilgardia, 1929, 4, 273—306).—Moist tubers, whether treated with ethylene chlorohydrin or not, are more permeable than dry tubers to carbon dioxide and oxygen; all tubers become less permeable with increase in the period between harvesting and extraction of gas. CHEMICAL ABSTRACTS.

**Iron-ion concentration in relation to growth and other biological processes.** E. F. HOPKINS (Bot. Gaz., 1930, 89, 209—240).—Growth of *Chlorella* sp. in culture solutions containing ferric chloride and alkali citrates indicates that iron is physiologically active only in the ionic condition, irrespectively of the total amount of soluble iron present. A study is made of the ferric-ion concentration of ferric chloride-citrate mixtures and an explanatory theory of complex ion formation presented. A. G. POLLARD.

**Chemical conditions in maturation, dormancy, and germination of seeds of *Gymnocladus dioica*.** G. J. RALEIGH (Bot. Gaz., 1930, 89, 273—294).—In *G. dioica*, the imperviousness of the seed coat is associated with the presence of insoluble pectic substances. In the cotyledons during germination and in the immature stages the starch content is high, but falls to a minimum at maturity, when the oil content reaches its maximum. Non-reducing sugar is an important storage form in the seed. Reducing sugars are absent from the mature seed but appear in small quantities in the immature and germinating stages. A. G. POLLARD.

**Acetylmethylcarbinol and butylene  $\beta$ -glycol in the higher plants during germination.** M. LEMOIGNE and P. MONGUILLON (Compt. rend., 1930,

190, 1457—1459).—Acetylmethylcarbinol and butylene  $\beta$ -glycol are present in germinating cereals. The former has been determined as nickel dimethylglyoxime (cf. Lemoigne, A., 1920, ii, 198); the treatment does not oxidise the glycol, which is then converted into the carbinol by treatment with an excess of bromine at 100°.

C. C. N. VASS.

**Autolysis in seeds.** I. A. W. BARTON (Trans. Kansas Acad. Sci., 1929, 32, 34—36).—So-called autolytic changes do not occur in sterile seeds.

CHEMICAL ABSTRACTS.

**Sugars and sugar derivatives in brown algae.** H. COLIN and P. RICARD (Compt. rend., 1930, 190, 1514—1516; cf. Kylin, A., 1913, i, 435; 1915, i, 931; 1918, i, 476).—Determinations have been made of the amounts of mannitol, laminarin, and algin (cf. A., 1929, 856) in 15 species of brown algae. None of the species contains a determinable amount of reducing sugar, but all except *Asperococcus bullosus* contain mannitol (0.3—5.8% of fresh material). Laminarin (1.2—19.4%) is found in *Laminaria flexicaulis* and *saccharina*, *Fucus serratus*, and *Ascophyllum nodosum*, whilst algin (0.9—5.2%) occurs in all the algae except *Himantalia lorea*, *Bifurcaria tuberculata*, and *Dictyota dichotoma*.

H. BURTON.

**Variations in the oxygen content of the hydrostatic vesicles of various brown algae.** S. COLLA (Atti R. Accad. Lincei, 1930, [vi], 11, 614—618).—With *Fucus serratus*, L., oxygen accumulates in the vesicles during exposure to light, and is consumed or eliminated in the dark. The formation of oxygen thus appears to be a photosynthetic effect.

T. H. PORE.

**Effect of certain hypoglycæmic drugs on the growth of the seedlings of *Lupinus albus*.** J. C. KRANTZ, jun. (J. Amer. Pharm. Assoc., 1930, 19, 458—461).—Commercial insulin and Abel's crystalline insulin exert an inhibiting action on the growth of *Lupinus albus* seedlings, but there is no quantitative relationship between the retardation in growth and the concentration of insulin in units. Synthalin and neosynthalin are very toxic to the seedlings. Myrtilin is practically non-toxic in small doses (cf. Ellis and Eyster, B., 1924, 882).

E. H. SHARPLES.

**Hourly variations of the carbohydrate content of leaves and petioles.** H. F. CLEMENTS (Bot. Gaz., 1930, 89, 241—272).—The carbohydrate metabolism of the potato, soya bean, and sunflower was examined. Environmental conditions affect the rate of formation and translocation of carbohydrates in these plants. The simple sugars (hexoses and pentoses) are the first formed. Sucrose is not a by-product of vacuolating protoplasm, but probably is a temporary storage product in the leaf. The hemicellulose content varies frequently, and to a considerable extent, in leaves growing under favourable conditions and serves as a temporary reserve. In unfavourable growing conditions (e.g., deficient moisture or warmth), the hemicellulose content is high and does not vary appreciably. Plants of high hemicellulose content are resistant to drought.

A. G. POLLARD.

**Alkaloids and carbon dioxide assimilation. Biogenesis of morphine.** H. EMDE (Naturwiss.,

1930, 18, 539—542).—On the basis of the formula advanced by Gulland and Robinson (A., 1926, 83) for the structure of morphine a scheme is indicated for the biogenesis of the alkaloid from carbohydrate in which the precursor is assumed to be a compound containing a carboxyl group, which is eliminated in the final stages of the synthesis. The scheme also offers an explanation of the relationship of meconic acid to morphine.

W. O. KERMACK.

**Colorimetric determination of lactic acid.** G. V. DERVIZ (Zhur. Exp. Biol. Med., 1929, 12, 147—150).—In Mendel and Goldscheider's method the concentrated sulphuric acid is distilled in a vacuum and then diluted to 90 vol.-%. The veratrole is dissolved in 95% acetic acid free from aldehyde.

CHEMICAL ABSTRACTS.

**Biochemical gravimetric methods. I. Determination of protein fractions of body-fluids.** L. JENDRASSIK and K. KRIGL (Biochem. Z., 1930, 220, 19—26).—The total protein, albumin, and globulin contents of body-fluids are most conveniently determined by the gravimetric method, filtration and washing being carried out on a suction filter, the filter and precipitate being weighed on the torsion balance. The method is suitable for clinical purposes.

P. W. CLUTTERBUCK.

**Astringency. I. Method of measuring astringency.** E. R. THEIS (J. Amer. Pharm. Assoc., 1930, 19, 326—327).—A dilatometer is used for measuring astringency; a well-hydrated tissue (skin) is placed in the bottle together with the astringent liquid and a net expansion of the system occurs which is measured in the capillary tube. The astringent action of various materials is described (cf. B., 1929, 405).

E. H. SHARPLES.

**Determination of small quantities of mercury in organic fluids and tissues.** D. BROWN, F. KAYSER, and J. SFIRAS (Bull. Soc. Chim. biol., 1930, 12, 504—509).—After destruction of the organic matter the mercury is precipitated as the sulphide, barium sulphate is added, and the mixture centrifuged in order to carry down the mercuric sulphide with it. The precipitate is treated with sodium hypobromite and formaldehyde, thus liberating metallic mercury. After removal of the hypobromite and formaldehyde by washing, a definite quantity of potassium iodide in dilute sulphuric acid is added, followed by a solution of mercuric iodide and sodium iodide and the iodine liberated is titrated by means of sodium thiosulphate.

W. O. KERMACK.

**Methods for investigating small quantities of mercury in organic mixtures.** G. VITTE (Bull. Soc. Chim. biol., 1930, 12, 510—523).—After destruction of the organic matter the mercury is brought into solution in nitric acid. A copper wire is added on which the mercury is deposited. After washing with alcohol and ether the wire is placed on a piece of folded cigarette paper; this is then enclosed in paper containing ammoniacal silver nitrate, the whole pressed for a suitable period up to 1 hr., and the stains on the silver nitrate paper are examined. Methods for the treatment of body-fluids and tissues are given.

W. O. KERMACK.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

SEPTEMBER, 1930.

### General, Physical, and Inorganic Chemistry.

**Contours of hydrogen lines in stellar spectra.** C. T. ELVEY (*Astrophys. J.*, 1930, 71, 191—208).—The contours of the hydrogen lines  $H_\beta$  and  $H_\gamma$  have been determined for 64 stars. The effective numbers of atoms producing the absorption lines have been determined and do not agree with Milne's application of the theory of thermal ionisation in its present form.

L. S. THEOBALD.

**Intensity ratios of Balmer to Paschen lines.** L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1930, 62, 636—639).—The ratios of the intensities of the lines  $H_\beta$  to  $P_\alpha$ ,  $H_\gamma$  to  $P_\beta$ ,  $H_\delta$  to  $P_\gamma$  determined for a discharge tube operating within the pressure range 0.001—0.1 mm., and within the current range 100—300 milliamp., are 2:6, 2:5, and 2:1, respectively. There are two theoretically possible values for these ratios, one corresponding with a temperature distribution of the upper excited energy levels and another corresponding with upper excited states of  $P$  energy levels only. The second is expected if electron collision excites atoms in the same way as radiation absorption (cf. A., 1929, 4). The experimental values agree with neither of the theoretical values. This discrepancy is discussed.

A. B. D. CASSIE.

**Significance of the continuous hydrogen molecule spectrum.** W. FINKELNBURG (*Z. Physik*, 1930, 62, 624—635).—Winans and Stueckelberg's (A., 1929, 118) suggested origin of the continuous hydrogen spectrum requires modification to accord with recent results. The dispersion of excitation voltages (Lau and Reichenheim, this vol., 267) shows this spectrum excited by electrons having energy of voltage 12.6—13.9. The lower voltage exceeds the excitation potential of the  $2^3\Sigma$  term, and suggests that transitions giving the continuous spectrum take place only from third and higher vibrational levels of the  $2^3\Sigma$  term. This also accounts for changes in intensity of the continuous spectrum with changes in pressure. An upper limit to the excitation potential agrees with Franck and Jordan's observation that electron collisions cause transitions between singlet and triplet levels only if the energy of the electrons lies within a small voltage range.

A. B. D. CASSIE.

**Intensity of Balmer lines as function of conditions of excitation.** L. S. ORNSTEIN and H. LINDEMAN (*Z. Physik*, 1930, 63, 8—19).—The intensities of the Balmer lines from a Wood discharge tube were measured for various current strengths and pressures. The intensity of the  $H_\alpha$  and  $H_\beta$  lines at 0.018 mm. pressure was found to be approximately

proportional to the square of the current strength, but somewhat less than this with the strongest currents. This could be explained by the electron stream first dissociating the hydrogen molecule into atoms, and then exciting these atoms, both effects being taken as approximately proportional to the current strength. The decrease at high current densities is explained by self-absorption. The ratio of the intensity of the lines  $H_\alpha$  and  $H_\beta$  was found to decrease with increase in the current strength, whereas the ratio of the intensity of the other lines was practically constant. The intensities of the  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ , and  $H_\delta$  lines were all found to increase with the pressure. Instead of the intensity being proportional to the pressure, actually it was much less. This is explained as due to variation in the velocity of the electrons due to variation in their mean free path with pressure. At higher pressures the higher lines were shown to become weaker compared with the lower lines. Only a small portion of the emission is due to recombination of ions and electrons, the major part being due to excited atoms. Owing to the space-charge in the tube, and the incomplete knowledge of the electron velocity, it was not possible to test directly Elsasser's quantum-mechanical treatment of the excitation of hydrogen by electron collisions. The intensity ratios found were used to show that the electron excitation could not be described by means of an "effective temperature," as put forward by Carst and Ladenburg (A., 1928, 573). H. A. JAHN.

**Spectrum of  $H_2$ : bands ending on  $2p^{11}\Pi$ .** (MISS) M. L. CHALK (*Proc. Roy. Soc.*, 1930, A, 128, 579—587).—An extension of Richardson's work (this vol., 387) on the new system of bands arising in par-hydrogen levels with principal quantum numbers 3 and 4 and ending on the  $2p^{11}\Pi$  or  $C$  level of Dicke and Hopfield. Some apparent anomalies in the rotation structure of the  $2p^{11}\Pi$  levels for the vibrational states corresponding with  $v''=1, 2$ , and 3 are investigated. The bands for  $3^1B \rightarrow 2p^{11}\Pi$  transitions, which were not found in the original analysis, have now been identified both for the  $0' \rightarrow 0''$  and  $1' \rightarrow 1''$  vibration transitions. A complete redetermination of the  $2' \rightarrow 2''$  bands has been carried out, and a number of new lines have been introduced in place of those previously listed.

L. L. BIRCUMSHAW.

**Continuous spectrum of the hydrogen molecule.** D. CHALONGE (*Compt. rend.*, 1930, 191, 128—130).—From previous work (cf. A., 1929, 616; this vol., 509) the following deductions are made. (i) At

all pressures from 0.03 to 100 mm. of mercury the lines of the singlet systems with base level  $2p^1\Sigma$  have intensities which, although varying absolutely according to the means of excitation, are relatively constant. (ii) As pressure decreases the general intensity of the triplet system  $3p^3\Pi-2s^2\Sigma$  ( $\alpha$  or Fulcher bands) is almost constant down to 0.5 mm., but thereafter diminishes rapidly, at the same time showing variations in the relative intensity of the different bands of the system. The system  $4p^3\Pi-2s^3\Sigma$  ( $\beta$  bands) shows similar variations. (iii) The intensity of the continuous spectrum decreases with pressure, becoming very small at 0.03 mm., but the relative decrease for different wave-lengths between 2400 and 4400 Å. varies, becoming less for greater wave-lengths. It is suggested in explanation that at higher pressures, excitation being small, the proportion of molecules brought to the  $2s^3\Sigma$  level is greatest, this level being nearest the base level  $1s^1\Sigma$ . As pressure decreases so does this relative preponderance. The changes noted as regards the continuous spectrum agree with the theory of Winans and Stueckelberg (cf. A., 1929, 118).

C. A. SILBERRAD.

**Some bands of the carbon molecule.** G. H. DIEKE and W. LOCHTE-HOLTGREVEN (Z. Physik, 1930, 62, 767—794).—A formerly undiscovered band system of the  $C_2$  molecule has been photographed and analysed under high dispersion. The bands belong to the transition  $1\pi \rightarrow 1\pi$ . This is the first observed example for normal  $1\pi \rightarrow 1\pi$  bands. The structure is in every detail that expected by theory. The bands show considerable similarity to the Swan bands, so that it is probable that the new bands are the corresponding singlet bands to the Swan bands.

A. J. MEE.

**New band system probably due to a molecule CP.** G. HERZBERG (Nature, 1930, 126, 131—132).—An extended band system between 4000 and 2900 Å. has been obtained from a discharge in a mixture of argon and phosphorus vapour. The new bands are probably due to CP, the carbon arising from tap grease and sealing wax. A provisional vibrational analysis yields the formula  $\nu = 29103.6 + [832.4(v' + \frac{1}{2}) - 5.44(v' + \frac{1}{2})^2] - [1239.0(v'' + \frac{1}{2}) - 6.75(v'' + \frac{1}{2})^2]$  as representing most of the bands. L. S. THEOBALD.

**Corona discharge in nitrogen.** L. G. H. HUXLEY (Phil. Mag., 1930, [vii], 10, 185—191).—Using the apparatus previously described (cf. A., 1928, 567), the corona discharge in nitrogen was investigated spectroscopically by means of a high-frequency discharge through the gas. Measurements were made of the potentials between the electrodes required to start discharges and to maintain currents through the gas over a range of pressures. Results are plotted showing the potentials required to start a discharge as a function of the gas pressure, and show that a discharge occurs more easily with the inner electrode at a negative than at a positive potential. Both curves have well-defined minima, and results are in agreement with Townsend's theory. The velocities of the positive ions in the direction of the electric force were calculated from the potentials required to maintain various currents through the gas.

N. M. BLYTH.

**Separation of spark and arc lines of oxygen and nitrogen in the far ultra-violet.** K. WIEN (Ann. Physik, 1930, [v], 5, 553—560).—Using W. Wien's method, the lines 1492, 1243, 1200, 1168, 1134, 963, and 951 Å. were classified as arc lines of nitrogen, and the lines 1085 and 915 Å. as spark lines. Arc lines for oxygen were found at 1305 and 990 Å., and a spark line for carbon at 1334 Å. The 1640 Å. line for helium II was not obtained. A. J. MEE.

**Arc spectrum of nitrogen.** E. EKEFORS (Z. Physik, 1930, 63, 437—443).—A quartz gas discharge tube containing nitrogen much diluted with helium was used as the source of light and the measurements were carried out by means of a vacuum spectrograph. A few new terms and a displacement of 32 frequency units of the whole doublet system were established. The measurements also indicate splitting of the B-term of about 7 units. W. GOOD.

**High-frequency discharges.** B. D. CHATTERJEE (Z. Physik, 1930, 62, 712—718).—The general character of luminosity accompanying discharges in nitrogen, oxygen, and air is described. Magnetic and electrical excitation was employed, and an additional direct-current discharge was maintained in the gas; for the excitation damped wave-trains of unspecified amplitude were employed at frequencies corresponding with wave-lengths of 2085, 670, and 80 m.

R. W. LUNT.

**Zeeman effect in the OH bands.** G. M. ALMY (Physical Rev., 1930, [ii], 35, 1495—1512; cf. this vol., 264).—The Zeeman effect in the  $2\Sigma \rightarrow 2\Pi$  OH bands in the near ultra-violet was photographed at field strengths from 5000 to 34,000 gauss, using a discharge in water vapour as the source up to 22,000 gauss, and at high fields the Back box are operating in water vapour. The structure of the bands is reviewed; new data are given for the satellite lines, from which the p-type doubling in the  $2\Sigma$  states for which  $v=0$ , and 1, is found to be  $0.216(K + \frac{1}{2})$  (cf. Van Vleck, A., 1929, 623). Wave-number data on the previously unobserved  ${}^oP_{21}$  branch are given. The Zeeman patterns in OH are calculated by the application of Hill's theory of the Zeeman effect in doublet bands (cf. this vol., 265), and are in satisfactory agreement with experiment. The exact treatment of a  $2\Sigma$  molecular state is given and discussed.

N. M. BLYTH.

**Spectrum of ionised fluorine (F II).** H. DRING (Proc. Roy. Soc., 1930, A, 128, 600—624).—The spectrum of singly-ionised fluorine, obtained by passing powerful discharges through silicon tetrafluoride in vacuum tubes, has been investigated from the infra-red to the Schumann region. 409 lines have been obtained, of which 173 have been classified as term-combinations. The analysis is discussed in relation to theoretical considerations. The spectrum would be expected to be based on the ground configuration of the  $F^{++}$  ion, viz., an electron structure  $1s^2 2s^2 2p^3$ , corresponding with a stable  $4S$  state and metastable states  $2P$ ,  $2D$ . Terms based on each of these three states are recognised, as well as a triplet and a singlet term apparently arising from other electron configurations. The existence of quintuplet, triplet, and singlet terms is established, but



no intercombinations have been found between them. The numerical values of the terms are tabulated and compared with those of the similar O I spectrum. An ionisation potential of 34.6 volts has been deduced for  $F^+$ , in good agreement with Turner's value of 34.5 volts calculated from other considerations (cf. A., 1929, 113).  
L. L. BIRCUMSHAW.

**Spectrum of inert gases in their second stage of ionisation.** S. C. DEB and A. K. DUTT (Nature, 1930, 126, 13).—Data for argon and xenon are discussed.  
L. S. THEOBALD.

**Ultimate rays of the alkali and alkaline-earth elements.** DESLANDRES (Compt. rend., 1930, 191, 169–173).—Since the generally accepted ultimate rays of the elements previously studied (A., 1924, ii, 577) are multiples of  $d_1$  (1062.5) and are obtained by moderate or feeble excitation of the vapour of the element, the data for the 22 elements of at. wt. 1–200 have been studied, excluding the high-frequency lines of the ultra-violet region, the emission of which requires considerable energy. With the exception of strontium (and of silver and gold among the related elements of higher at. wt.) the lines which are probably most intense are approximately multiples of  $d_1$ . In the cases of potassium, hydrogen, cadmium, and neutral calcium these are in the infra-red, whilst for mercury the resonance line is the ultimate and most intense ray.  
J. GRANT.

**Intensity of quadrupole radiation in the alkali metals and the occurrence of forbidden lines.** A. F. STEVENSON (Proc. Roy. Soc., 1930, A, 128, 591–599).—Mathematical. The absorption intensities of the "forbidden" line  $1S-3D$  for the alkali metals, lithium, sodium, potassium, and rubidium are calculated on the supposition that this line is due to "quadrupole" radiation, using Hartree's method of self-consistent fields (A., 1928, 216) to obtain values of the radial wave-functions. The calculated intensities are found to agree fairly well with the available experimental values. It is considered that quadrupole radiation may not be an adequate explanation for the occurrence of forbidden emission lines.

L. L. BIRCUMSHAW.

**Vibrational quantum analysis of the blue-green bands of magnesium oxide.** P. N. GHOSH, P. C. MAHANTI, and B. C. MUKHERJEE (Physical Rev., 1930, [iii], 35, 1491–1494).—The blue-green magnesium oxide bands in the region  $\lambda$  5210–4700 were photographed from the flash of a mixture of magnesium metal and nitrate, thus avoiding the continuous radiation of the glowing oxide. Wave-lengths, frequencies, and vibrational quantum numbers are tabulated, and an equation is given for the band heads. The vibration frequencies for infinitesimal amplitude are 716 and 751  $\text{cm}^{-1}$  for the upper and lower states, respectively; the calculated heat of dissociation is approximately 5.8 volts.

N. M. BLIGH.

**Phosphorus in stellar spectra.** O. STRUVE (Astrophys. J., 1930, 71, 150–152).—Several absorption lines in the spectrum of  $\delta\gamma$  Pegasi have been identified with the strongest lines of P III.

L. S. THEOBALD.

**Absorption of luminous radiations by liquid sulphur.** P. MONDAIN-MONVAL, R. JOB, and P. GALET (Bull. Soc. chim., 1930, [iv], 47, 545–556).—Liquid sulphur ( $120^\circ$ ) absorbs violet and blue radiation, but the absorption limit progresses slowly towards the red end of the spectrum as the temperature of the sulphur rises to  $160^\circ$ , at which point green rays ( $550-565 \mu\mu$ ) are absorbed, although a general absorption over the whole visible spectrum occurs (change from liquid sulphur to viscous sulphur); above this temperature the progression of the absorption limit is 2–3 times as rapid, whilst a second absorption limit approaches from the red end of the spectrum as well. The phenomena observed by Smith and co-workers (A., 1905, ii, 580) on chilling viscous sulphur are confirmed. A photo-electric potassium cell adapted for measuring luminosity in spectrographic work is described.

S. K. TWEEDY.

**Zeeman effect in the red CaH bands.** W. W. WATSON and W. BENDER (Physical Rev., 1930, [ii], 35, 1513–1523).—Using an intermittent direct-current arc in a modified Back chamber and a calcium electrode in hydrogen, the Zeeman effect in the red  $\lambda$  7000  $^2\Pi \rightarrow ^2\Sigma$  and  $\lambda$  6389  $^2\Sigma \rightarrow ^2\Sigma$  CaH bands was investigated. Data are tabulated and discussed, and, for the former bands, compared with the predictions of Hill's theory (cf. this vol., 265); for the latter bands broad and prominent Zeeman patterns occur for  $K' > 8$ , similar to those found in a  $^2\Pi$  state. Data are given for the satellite series in the  $^2\Pi \rightarrow ^2\Sigma$  bands (cf. Mulliken, A., 1928, 1166), and the size of the  $\Lambda$ -type doubling is determined. N. M. BLIGH.

**Band systems associated with selenium.** T. E. NEVIN (Nature, 1930, 126, 13).—The heads in the spectrum of selenium can be arranged into three systems for which formulæ are given; one system appears to be due to a  $^3\Sigma \rightarrow ^3\Sigma$  transition.

L. S. THEOBALD.

**Hyperfine structure of the arc spectrum and the nuclear rotation of indium.** D. A. JACKSON (Proc. Roy. Soc., 1930, A, 128, 508–522).—The arc spectrum of indium has been investigated with the object of finding whether any of its lines possess hyperfine structure, resulting from a quantised nuclear spin and a corresponding magnetic moment of the nucleus. The lines observed were the two resonance lines  $2^2P_{1/2} - 2^2S_{1/2}$  and  $2^2P_{3/2} - 2^2S_{1/2}$ , and the first three lines of the diffuse series,  $2^2P_{3/2} - 3^2D_{3/2}$ ,  $2^2P_{3/2} - 3^2D_{5/2}$ , and  $2^2P_{1/2} - 3^2D_{3/2}$ . It is concluded that the structure of the energy levels can be quantitatively explained by ascribing one quantum of rotation to the nucleus, and that the value of the magnetic moment of the indium nucleus is about 5/1840 of that of a spinning electron. The comparison of the fine structure of the  $2^2P_{1/2}$  and  $2^2P_{3/2}$  levels gives an accurate quantitative proof of Fermi's wave-mechanical calculation of the interaction of electron and nuclear spins.

L. L. BIRCUMSHAW.

**First spark spectrum of antimony.** D. G. DHAVALE (Nature, 1930, 126, 97).—Analysis of the first spark spectrum of antimony from  $\lambda$  8500 to  $\lambda$  3000 shows its origin to be the transitions  $P_1 \leftarrow P_2$ ,  $P_2 \leftarrow P_3$ , and  $P_2 \leftarrow Q_1$ . The lines  $^3(P_2D_3)$ ,  $^3(P_2P_2)$ ,

and  $^3(P_2S_1)$  of the  $P_2 \leftarrow P_2$  transition are 12,863, 16,714, and 19,310, respectively; the difference  $^3P_1 - ^3P_2$  is 0.4814. L. S. THEOBALD.

**Resonance and quenching of the third principal series line of caesium.** C. BOECKNER (Bur. Stand. J. Res., 1930, 5, 13—18).—A helium discharge was used to study the resonance radiation from the third principal series line of caesium, which coincides with a strong helium line 3888 Å. Caesium arc lines were also observed in the fluorescence radiation; they have their origin in lower levels populated by radiation transitions from the initial level ( $4P_{1/2}$ ). It was found that collisions between helium and caesium atoms in the  $4P_{1/2}$  state transfer the latter to states differing by less than several hundredths of a volt from the initial state. C. J. SMITHELLS.

**Regularities in the spectra of lutecium.** W. F. MEGGERS and B. F. SCRIBNER (Bur. Stand. J. Res., 1930, 5, 73—81).—The lines in the arc and spark spectra of lutecium have been divided into three classes, due to neutral atoms (Lu I), singly-ionised atoms (Lu II), and doubly-ionised atoms (Lu III). Regularities have been found in each of these spectra. The structures of lutecium spectra resemble those of yttrium more closely than those of lanthanum or scandium. C. J. SMITHELLS.

**Ultra-violet radiation from the sun and heated tungsten.** W. E. FORSYTHE and F. CHRISTISON (J. Opt. Soc. Amer., 1930, 20, 396—410).—Theoretical. The relation between the wave-length of ultra-violet radiation, its therapeutic value, and the erythema or reddening effect on the skin is discussed. Calculated values of the energy in various parts of the spectrum radiated by the sun and by tungsten are tabulated (cf. Holladay, A., 1929, 116). The energy of different wave-lengths reaching the earth's surface from the sun was calculated from the spectral distribution of energy and the transmission of the atmosphere; about 0.22% of the energy of the sun between wave-lengths 2900 and 3250 Å. reaches the earth. Curves are given of the solar energy reaching the earth at different seasons and times of the day. The relative erythema produced by a black body and by tungsten at different temperatures is calculated and plotted. The ultra-violet energy below 3100 Å. from a 500-watt tungsten lamp is approximately that from the sun. N. M. BLIGH.

**Arc spectrum of radium emanation.** E. RASMUSSEN (Z. Physik, 1930, 62, 494—507).—The spectrum due to radium emanation was photographed and measured. Addition of varying quantities of helium, neon, and argon helped the separation of spark from arc lines. 115 Arc lines were measured, and 110 classified into 6  $p$ -term sequences, 6  $d$ -term sequences, three  $x$ -terms, and 4  $s$ -terms. Resonance lines were also photographed; from them the ground term is shown as  $p_0$ , and the ionisation potential 10.689 volts. A. B. D. CASSIE.

**Spectrum of radium emanation.** H. H. NIELSEN (Naturwiss., 1930, 18, 620—622).—Hartree's method (A., 1928, 216, 933) of estimating spectral terms has been applied to unpublished data obtained spectroscopically by Rasmussen. The poten-

tials corresponding with electronic distances from the nucleus from 0 to  $\infty$  are tabulated. In determining the ionisation potentials the wave equation for a  $p$  electron with principal quantum number  $n=6$  is numerically integrated for distances  $r=0$  and  $r=\infty$  and a mean value of  $r$  is obtained. The orientation of the outer electrons to the atomic nucleus is discussed. Calculations of the quantum defect,  $q_0$ , gave a value of 0.513, whilst the value extrapolated from Rasmussen's results was 0.50. The electronic configuration of the different states of the valency electrons and the corresponding empirical and theoretical values in volts for the spectral terms of radium emanation are tabulated. As a test of the accuracy of this method similar calculations have been made for the two states of the hydrogen atom, and results show less than 0.03% difference between the "eigen" values calculated by analytical and numerical methods. W. R. ANGUS.

**Ultra-violet transmission band of metallic silver, as affected by temperature.** (LORD) RAYLEIGH (Proc. Roy. Soc., 1930, A, 128, 131—133).—A rise of temperature causes a definite shift of the transmission maximum to the red; the breadth of the band does not appear to be affected.

L. L. BIRCUMSHAW.  
**Physical interpretation of perturbations in band spectra.** E. HULTHÉN (Nature, 1930, 126, 56—57).—Theoretical. L. S. THEOBALD.

**Theory of the Stark effect in intense fields.** C. LANCZOS (Z. Physik, 1930, 62, 518—544).—Theoretical. The wave equation for the Stark effect was investigated by a direct asymptotic method; the usual perturbation method fails for intense fields. The cloud of electric charge surrounding a nucleus is distended towards the positive plate. This disturbance of the distribution of electric density accounts for the disappearance of spectral lines emitted in a strong electric field. A. B. D. CASSIE.

**Occurrence of the neon spark lines in the negative glow.** M. J. DRUYVESTEYN (Z. Physik, 1930, 62, 764—766).—The neon spark lines suddenly occur in the negative glow as soon as the cathode drop is larger than the excitation potential of the lines. They are caused by electrons coming from the cathode which have lost little energy in the cathode fall, and simultaneously excite and ionise neon atoms. A. J. MEE.

**Method of obtaining a visible spectrum of waves of radio frequency.** J. C. McLENNAN and A. C. BURTON (Nature, 1930, 126, 130).

L. S. THEOBALD.  
**Elementary theory of the Zeeman effect.** J. ZAHRADNÍČEK (Z. Physik, 1930, 62, 694—695).—The Lorentz equations for the motion of a bound electron in a magnetic field are best solved by the usual transformation of two real equations into one imaginary equation. A. B. D. CASSIE.

**[Relation between gas pressure and translational energy of the gas molecule.]** W. ANDERSON (Z. Physik, 1930, 62, 719—720).—Polemical against Schaposhnikov (this vol., 404).

A. B. D. CASSIE.

**Statistical calculation of the spectrum of an ionised atom.** E. SEGRÈ (Atti R. Accad. Lincei, 1930, [vi], 11, 670—673).—A method of calculating the energy levels, the doublet separation, and the Rydberg correction by a statistical method based solely on the atomic number and the degree of ionisation of an ionised atom is described. The calculated values are in satisfactory agreement with experiment. F. G. TRYHORN.

**Fine structure of spectral lines in relation to selective absorption.** B. VENKATESACHAR (Mysore Univ. J., 1930, 4, 1—40).—A lecture summarising recent work. W. E. DOWNEY.

**Plasmoidal discharges in gases.** S. P. MCCALLUM (Nature, 1930, 126, 169).—The discharge named plasmoid by Wood (this vol., 653) appears to be the same type of discharge as that previously described by the author (A., 1928, 342).

L. S. THEOBALD.  
**Doppler effect in relation to atoms.** D. S. KOTHARI (Indian J. Physics, 1930, 4, 575—584).—The increase in the kinetic energy of an enclosed volume of gas, due to the rise in temperature on adiabatic compression, is interpreted as a consequence of the increased frequency caused by the Doppler effect taking place at the reflexion of the atoms from the walls of the containing vessel. An expression is obtained in terms of De Broglie's wave theory of matter and is analogous to that obtained for the Doppler effect for light quanta, the wave velocity being substituted for the velocity of light. The Compton effect is also studied from the same point of view. An expression for Wien's displacement law for atoms is derived and confirmed by application of Fermi-Dirac statistics. W. R. ANGUS.

**Mechanism of the arc light. III. Arc discharge at low pressures.** R. SEELIGER and H. WULFHEKEL (Physikal. Z., 1930, 31, 691—695).—Apparatus for investigating the conditions of working of an arc at low pressures is described. The change occurring in a glow discharge with decreasing pressure, and the capacity of a cathodic substance of supporting an arc at low pressures, are connected with the thermal conductivity of the cathodic substance. If the thermal conductivity is great no arc can be established, and conversely. The position of the hot patch appears to depend on some property of the surface. The support of an arc at low pressures is also dependent on the vapour pressure of the cathodic substance. The results are not in agreement with those of Ratner and Newman. An experiment on the theory of the Stolt arc is also described. A. J. MEE.

**Arrangement for measuring small light intensities.** B. RAJEWSKY (Z. Physik, 1930, 63, 576).—By the introduction of an appropriate photo-electrically sensitive surface in a Geiger counter waves in the visible and ultra-violet ranges of frequencies could be measured. W. GOOD.

**Mechanism of spark discharge.** L. B. LOEB (J. Franklin Inst., 1930, 210, 15—30; cf. A., 1929, 1334).—Theoretical. Difficulties, for fields of the order of 30,000 volts per cm., in the Townsend theory of spark discharge at atmospheric pressure between

parallel electrodes led to the view that space charges are formed which produce fields near the cathode high enough to cause rapidly moving electrons to generate the necessary ionisation. This, and the analogous theory of von Hippel and Franck (cf. Z. Physik, 1929, 57, 696), are considered critically with reference to quantitative data on ionisation by positive ions; values of  $\alpha$ , the ionising efficiency of electrons, required by values of  $\beta$ , the number of ions per cm. path produced by positive ions, to permit the Townsend mechanism; electron velocities at high fields; calculations of the values of  $\alpha$  to give high gradients in  $10^{-8}$  sec., the experimental minimum spark lag; and the theoretical evaluation of  $\alpha$  (cf. also Rogowski, this vol., 513). N. M. BLIGH.

**Perturbations in molecules and the theory of predissociation and diffuse spectra. II.** O. K. RICE (Physical Rev., 1930, [ii], 35, 1551—1558; cf. A., 1929, 734).—Mathematical. The method previously developed (cf. this vol., 1087) is applied to the case of predissociation. The discrete states, and spectral lines involving these states, are broadened; the shape of the broadened lines is found, and a complete analogy is shown with the results for radioactive decay. N. M. BLIGH.

**Operational wave equation and the Zeeman effect.** G. TEMPLE (Proc. Roy. Soc., 1930, A, 128, 487—507).—The theory of the Zeeman effect has been developed from the operational wave equation given in a previous paper (this vol., 837). Since the changes in the energy levels produced by a magnetic field depend on the magnetic moment of the atom, and this is dependent on the distribution of currents in the atom, it is necessary to obtain the appropriate mathematical expression for these quantities in terms of the wave operators. The microscopical properties of the atom (its charge and current density at any point) are determined by tensors with components of the form  $(T\psi, \phi)$ , its macroscopic properties (electric and magnetic moments) by the matrix elements of some operator  $T$ . The general principles available for the calculation of these expressions are investigated, and the special matrix elements required in the theory of the Zeeman effect determined. The resolution of optical doublets in a uniform magnetic field is also considered. L. L. BIRCUMSHAW.

**Excitation of soft X-rays from single-crystal surfaces and from polycrystalline surfaces of graphite and aluminium.** O. W. RICHARDSON and (Miss) U. ANDREWES (Proc. Roy. Soc., 1930, A, 128, 1—15).—A comparison of experiments on the soft X-ray excitation from natural graphite and from spectroscopically pure carbon, over the range 50—310 volts, indicates that the simpler is the crystal structure of the surface the fewer are the number of critical potentials likely to be found. There are evidently a large number of critical potentials which have little or nothing to do with the Bohr levels, and the possible origin of these discontinuities is discussed. The values obtained can be arranged according to a regular numerical scheme, showing the same type of relationship as that of the frequencies of the lines in a set of bands. It is obvious that a metal is a structure which has parts capable of vibrating under electronic

excitation and the voltage differences found are of the right order of magnitude for such effects. Measurements have also been made over the range 0—150 volts with polycrystalline and single-crystal aluminium targets, 15 breaks being observed in the former case and 11 in the latter. The values given by the crystal fall into two groups with an arithmetical structure similar to that given by the graphite data.

L. L. BIRCUMSHAW.

**Excitation of soft X-rays from some polycrystalline metal surfaces.** O. W. RICHARDSON and S. R. RAO (Proc. Roy. Soc., 1930, A, 128, 16—36).—In continuation of the work of Richardson and Chalkin (A., 1928, 692; 1929, 15), using similar experimental methods, a determination has been made of the discontinuities in the  $i_p/i_c$ -exciting voltage curves for nickel, cobalt, copper, and tungsten. The results confirm the work of previous investigators, as regards the reality of the inflexions, but their number is found to be very much greater than had hitherto been supposed. Thus in the case of cobalt, although in the region from 210 to 335 volts the values are in good agreement with those given by Thomas (A., 1925, ii, 336), between 343.8 and 700 volts 35 new inflexions are noted, and above 700 volts the agreement is poor. With nickel, 38 inflexions are obtained in the range 300—565 volts. With copper, good agreement is found with the values of Compton and Thomas (A., 1926, 1186) in the range 100—250 volts and also above 800 volts; all the inflexions above 800 volts approximate closely to the hard X-ray values calculated from the data of Thoräus (A., 1926, 329). The number of inflexions found for tungsten in the range 0—540 volts is comparable with that for copper and the iron group. Experiments with an impure copper target indicate that it is unlikely that any considerable proportion of the discontinuities observed can be attributed to the presence of small amounts of impurities. Curves are drawn showing the variation of  $i_p/i_c$  with  $i_c$  (for nickel and tungsten targets) and with the inclination of the target. There is a slight tendency, particularly at high voltages and low thermionic currents, for  $i_p/i_c$  to increase as  $i_c$  diminishes. Experiments with a cobalt target indicate that the intensities of the inflexions are highly dependent on the previous heat treatment of the target, and it is considered that this may explain the divergence between the results of different investigators. Curves showing the relation between  $i_p/i_c$  and the applied potential are given for copper over the range 30—1050 volts and for tungsten over the range 30—600 volts, determinations being made at intervals of 20—50 volts. From these it appears that when most of the inflexions are smoothed out by choosing larger intervals, the values coinciding with the X-ray term values still remain.

L. L. BIRCUMSHAW.

**Excitation of soft X-rays from a single crystal face of nickel.** O. W. RICHARDSON and S. R. RAO (Proc. Roy. Soc., 1930, A, 128, 37—41).—Determinations have been made of the discontinuities in the  $i_p/i_c$ -applied potential curves for a single crystal of nickel (face 100) over the range 45—300 volts. All the inflexions found with the crystal are close to the values given by Thomas (A., 1925, ii, 336), but a

number of his strong inflexions are absent from the curves given by the crystal. The inflexions are to be regarded as properties of the crystal faces, those given by the polycrystalline material representing a mixture of effects characteristic of the different faces present. Throughout the range below 400 volts, the intensity of the soft X-radiation from the crystal is greater than that from the polycrystalline material, and the curve shows a saturating tendency at higher potentials.

L. L. BIRCUMSHAW.

**Spectroscopy of ultra-soft X-rays.** M. STEGBAHN and T. MAGNUSSON (Z. Physik, 1930, 62, 435—456).—Methods hitherto used in the spectroscopy of ultra-soft X-rays, of wave-length range 10—100 Å., are summarised. A new spectroscope is described, in which the grating surface is only 1—3 mm. wide, and so acts as the second spectrometer slit. The ruling machine, which gave good gratings with as many as 1800 lines per mm., is also described.

A. B. D. CASSIE.

**Influence of chemical state on critical X-ray absorption frequencies.** H. R. ROBINSON and C. L. YOUNG (Phil. Mag., 1930, [vii], 10, 71—75).—The method of magnetic spectroscopy of the photo-electrons ejected from an element and its compounds was used to investigate the slight displacement of X-ray spectral lines by changes in the state of chemical combination of an atom. The critical absorption frequencies of the atomic and the displaced level were measured with high dispersion for the *K* level of chromium in the metallic state and as hydroxide, using copper  $K\alpha_1$  as primary radiation. The displacement was in the sense of, but somewhat less than, that found by X-ray spectroscopy, the mean value being  $0.5 \pm 0.15$  Rydberg unit.

N. M. BLIGH.

***K*-Absorption spectra of nickel, copper, and zinc.** A. E. LINDH (Z. Physik, 1930, 63, 106—113).—The fine structure on the short wave-length side of the *K*-absorption edge in the X-ray absorption spectra of nickel and copper have been quantitatively investigated and the wave-lengths of the absorption edges and fine structure lines tabulated. It was found that the spectra of layers sufficiently thin (less than  $10 \mu$ ) to give the fine structure had a double absorption edge, of which the component  $K_1$ , of longer wave-length, had the same wave-length as the single edge obtained in the absence of a fine structure. The component  $K_2$  of shorter wave-length was found to have the same wave-length as the absorption edge occurring in the spectra of compounds of the respective metal. A fine structure was obtained with cuprous sulphate and with cupric chloride, the wave-length of the first fine structure line being identical for the two compounds, but not agreeing with that of the free metal. Preliminary experiments only have been made with zinc owing to the small dispersion of the spectrograph, but these show a definite although small difference between the wave-length of the absorption edge for zinc in the free state and in its compounds. H. A. JAHN.

**Bluish-grey hot radiation from the Lilienfeld X-ray tube.** F. ROTHER and W. M. COHN (Physikal. Z., 1930, 31, 687—691).—The visible hot radiation of

the Lilienfeld X-ray tube has been re-investigated. Spectrographic observations indicate that the radiation possesses a continuous spectrum. This had an intensity maximum at wave-length 450 m $\mu$ , and extends in the ultra-violet to 225 m $\mu$ , at least. By the use of quartz and glass apparatus the conditions for the production can be studied. It was found that the radiation proceeded from the anticathode if potential was applied between the filament and the perforated cathode, and not between the perforated cathode and the anticathode. The continuous spectrum is probably due to the interaction of electrons and ions. The use of this continuous spectrum for investigations in the blue and ultra-violet is suggested.

A. J. MEE.

**Molybdenum L-series wave-lengths by ruled gratings.** J. M. CORK (Physical Rev., 1930, [ii], 35, 1456—1462).—Using plane ruled gratings having 30,000 and 14,400 lines per inch, and distances up to 1 m. in a vacuum between the photographic plate and grating, about 160 photographs were taken of the molybdenum L series lines. The wave-lengths for  $L\alpha_1$  and  $L\beta_1$  were 5.4116 and 5.1832 Å., respectively, being somewhat longer than the wave-lengths obtained by using gypsum or calcite crystals. The possibility of the variation being due to anomalous variation of the refractive index of the crystal is discussed.

N. M. BLIGH.

**Possible effects of nuclear spin on X-ray terms.** G. BREIT (Physical Rev., 1930, [ii], 35, 1447—1451).—Theoretical. Using Dirac's equation for a single electron it is shown that magnetic moments of nuclei are likely to cause small measurable separations of X-ray terms. For K terms of the heavier elements the effect is relatively greater, and should require a lower resolving power for its detection.

N. M. BLIGH.

**Independence of X-ray absorption on temperature.** J. A. BEARDEN (Physical Rev., 1930, [ii], 35, 1463—1468).—In order to investigate a reported change in the atomic absorption coefficient of X-rays with a change in the temperature of the absorbing screen (cf. Read, A., 1926, 551; 1927, 83), measurements were made on thick screens of aluminium, copper, iron, nickel, silver, and lead, using heterogeneous X-rays with voltages from 30 to 80 kilovolts, and also the monochromatic X-ray lines  $K\alpha_{1,2}$  of silver and copper. No temperature effect was found. The anomalous results reported by Read, and for  $\gamma$ -rays by Bastings (cf. A., 1929, 371), are attributed to an error in the determinations of the linear absorption coefficient.

N. M. BLIGH.

**Effect of an electric field on the X-ray diffraction pattern of a liquid.** R. L. McFARLAN (Physical Rev., 1930, [ii], 35, 1469—1475; cf. Stewart, A., 1927, 1015).—Replacing the crystal of a Bragg spectrometer with a cell containing the liquid, an investigation was made of the effect produced on the X-ray liquid diffraction pattern by an electric field designed to give the Kerr effect for benzene and nitrobenzene. The latter showed an increase in peak intensity, on applying the field, and a large Kerr effect; the former showed no observable effect, and only a slight Kerr effect. This effect cannot be due

to molecular orientation alone, but is attributed to an increase in the regularity of the spatial distribution of molecular scattering centres.

N. M. BLIGH.

**Resolving power of calcite for X-rays and the natural widths of the molybdenum  $K\alpha$  doublet.** S. K. ALLISON and J. H. WILLIAMS (Physical Rev., 1930, [ii], 35, 1476—1490; cf. this vol., 390).—The half widths at half maximum of the rocking curves in parallel positions of the double X-ray spectrometer have been observed for the first five orders of reflexion of molybdenum  $K\alpha_1$  from calcite. The calculated half widths for a single crystal are compared with the theoretical results of Darwin (cf. Phil. Mag., 1914, [vi], 27, 325, 675) and Ewald (Physikal. Z., 1925, 26, 29), and are of the same order of magnitude but slightly larger. The rocking curve widths in 8 anti-parallel positions for molybdenum  $K\alpha_1$  at 50 kilovolts were observed; the half width at half maximum was 0.147 Å., corresponding with an energy width of 3.6 volts, showing no variation with voltage. For molybdenum  $K\alpha_2$  the corresponding values were 0.161 Å. and 3.9 volts, respectively. The observed values are 2.5 times as great as the width to be expected from a classical electronic oscillator damped by its electromagnetic radiation. The computed life of the excited K state of molybdenum is  $1.8 \times 10^{-16}$  sec. No evidence of fine structure of molybdenum  $K\alpha_1$  or  $\alpha_2$  was found.

N. M. BLIGH.

**Measurements on the Langmuir dark space.** A. GÜNTHER-SCHULZE (Z. Physik, 1930, 62, 619—623).—The Langmuir dark space which surrounds an electrode maintained at a negative potential, with respect to a region in which a discharge is maintained, is due to the relative inefficiency of positive ions in producing new ions of collision and is accompanied by a positive space charge. The dimensions of this dark space may be calculated, provided certain conditions are fulfilled, by the simple form of the space charge equation. Experiments have been carried out in hydrogen, helium, neon, and argon in which the above-mentioned conditions are approximately fulfilled; a fairly satisfactory agreement exists between the observed and calculated dimensions of the dark space.

R. W. LUNT.

**Photo-ionisation of caesium by line absorption.** F. L. MOHLER and C. BECKNER (Bur. Stand. J. Res., 1930, 5, 51—71).—Ionisation of caesium by line absorption was investigated by the space-charge method, and the relative sensitivity in the region of line absorption, as compared with the region of continuous absorption beyond the limit, was measured. Ionisation of caesium vapour by light on the red side of the limit is the result of line absorption in lines of width about 0.01 Å. below 0.01 mm. pressure. The subsequent ionisation is independent of temperature, but depends on vapour pressure in a manner suggesting that collision with a normal caesium atom must occur during the life of the excited state.

C. J. SMITHELLS.

**Possible explanation of the selective photo-electric effect.** R. H. FOWLER (Proc. Roy. Soc., 1930, A, 128, 123—130).—Theoretical. The known facts about the normal and selective photo-electric effects are briefly reviewed. The essential condition

for selective emission appears to be entirely a surface one, and the theory is developed that the observed selectivity should be referred to  $D(W)$ , the transmission coefficient through the surface potential field for an electron incident from within with energy  $W$  in its motion normal to the surface. It is shown that  $D(W)$  can, in fact, have the required selective properties for the type of potential barrier which might be expected to occur for surfaces of the kind known to exhibit the selective effect. L. L. BIRCUMSHAW.

**Photo-electric intensity measurements in the mercury spectrum.** L. S. ORNSTEIN and J. F. CUSTERS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 473—487).—A potassium on silver photo-electric cell has been used to measure photometrically the relative intensities of certain mercury lines and their variation with current density and with pressure. The intensities of the lines 4047, 4358, and 5461 Å. vary in an exactly similar way with changing external conditions, showing that they arise from the same initial energy level, whilst that of the singlet line at 4916 Å. arising from the  $2^1P_1-3^1S_0$  change varies in a completely different manner. The variations of the intensities of the components of the triplet system and of the singlet line are shown in graphical form. J. W. SMITH.

**Moseley diagram of the ionisation voltages of the light atoms and ions.** W. BRAUNBEK (Z. Physik, 1930, 63, 20—29).—The square root of the ionisation voltages for the elements and ions of the first three short periods (to potassium) are plotted against the atomic number of the element as abscissa, and it is shown that each isoelectronic series (e.g., Li, Be<sup>+</sup>, B<sup>++</sup>, C<sup>+++</sup> . . .) gives points lying on a straight line, the gradient of these lines being constant in each period. The only point deviating appreciably is that corresponding with Cl<sup>+</sup> and for this ion the ionisation voltage of 22.2 volts is predicted instead of the provisionally accepted value of 18.32 volts. It is shown that this means that a linear relation exists between the screening number  $s$  and the nuclear charge  $Z$  in an isoelectronic series, although in the first period (hydrogen and helium) the screening number is independent of the nuclear charge. It is shown that  $s$  decreases with increase in the nuclear charge in an isoelectronic series, contrasted with the X-ray terms, in which  $s$  increases with increase in  $Z$ . A slight concavity in the lines of the Moseley diagram points to a decrease of  $s$  with  $Z$  which is not exactly linear, the concavity being greatest in the second period and not observable in the first period. On this basis values for the ionisation potential of the ions Li<sup>+</sup>, Be<sup>++</sup>, B<sup>++</sup>, C<sup>+++</sup> are extrapolated from the known value of  $s$  for helium, assuming complete linearity. These values agree to within 1% with the values calculated by Hylleraas (this vol., 267) by means of wave mechanics, which agree very exactly with the unpublished measurements of Edlén (*ibid.*). The equation of Hylleraas is shown to predict a slight decrease of  $s$  with increase in the nuclear charge in the above-mentioned series. H. A. JAHN.

**Activation and ionisation produced by rotating fields of high frequency.** W. LÜDKE (Z. Elektrochem., 1930, 36, 298—300).—The application of

rotating electric and magnetic fields for the production of ionisation and activation in gases is discussed. It is thought that it will be possible to determine the state of ionisation and of activation by a suitable choice of field strength and frequency.

R. W. LUNT.

**Photo-electric method of integrating sunlight.** J. A. C. TEEGAN and G. R. RENDALL (Indian J. Physics, 1930, 4, 585—589).—Sunlight was integrated over short periods of time by means of a potassium photo-electric cell enclosed in a metal casing and exposed horizontally. The current from the cell was amplified by a valve and the anode current passed through a galvanometer in series with a copper voltmeter, and the amount of copper removed from the solution was determined by Hahn and Leimbach's method (A., 1922, ii, 870). A comparison is made between the results and those obtained by Atkins and Poole (A., 1929, 659) using a sodium cell.

W. R. ANGUS.

**Application of generalised statistics to thermal ionisation.** K. C. KAR and A. GANGULI (Z. Physik, 1930, 62, 510—517).—The Langmuir adsorption formula, previously obtained by means of the Gibbs statistics (Kar and Ganguli, this vol., 151), is now derived by use of the generalised statistics of Kar and Mazumdar (Z. Physik, 1929, 55, 546). Treating thermal ionisation as a special case of adsorption equilibrium, the Saha equation for thermal ionisation is obtained. The electron emission from metals in degenerate and in non-degenerate systems is treated in the same way, and in both cases the formula obtained contains the term  $T^2$ , in agreement with the formula of Dushman and Roy and of Houston (A., 1928, 467), but in disagreement with that of Richardson and of Sommerfeld (*ibid.*), which contains  $T^{\frac{1}{2}}$ . H. A. JAHN.

**Geiger tube electron counter.** L. F. CURTISS (Bur. Stand. J. Res., 1930, 5, 115—123).—It is shown that the sensitive surface of the Geiger tube counter is not on the wire electrode, but on the inner surface of the tube. This result explains why the operation of the counter is only slightly affected by the condition of the surface of the wire electrode. An explanation of the operation of the counter is offered.

C. J. SMITHELLS.

**Total secondary electron emission from polycrystalline nickel.** S. R. RAO (Proc. Roy. Soc., 1930, A, 128, 41—56).—Using an improved form of the method described by Krefft (A., 1928, 341), the inflexions in the total secondary electron curve for a polycrystalline nickel target have been determined over the range 0—540 volts. Six peaks were found below 30 volts, and 25 discontinuities in the range from 30 to 540 volts. There is good agreement with the 11 values obtained by Petry (A., 1925, ii, 1017), and, moreover, almost every inflexion in the secondary electron emission curve coincides with a soft X-ray discontinuity, although the number of these is much greater (cf. Richardson, Proc. Roy. Soc., 1928, A, 119, 531). The effect of heating and of bombarding the target in an atmosphere of hydrogen for some hours has also been investigated (cf. this vol., 1078). The results are discussed. L. L. BIRCUMSHAW.



**Total secondary electron emission from a single crystal face of nickel.** S. R. RAO (Proc. Roy. Soc., 1930, A, 128, 57—62).—Experiments have been carried out on the total secondary electron emission from the 100 face of a single crystal of nickel. The fact that in the range 1—30 volts only two peaks are found supports the view that the peaks with a polycrystalline target are due to reflexion or diffraction of electrons from the crystal faces of different orientations on the surface. There is a close coincidence between the soft X-ray inflexions from the 100 face of the crystal and the secondary electron discontinuities from the same face. A resemblance may be traced even in the intensities. It appears that at those potentials at which there is an intense scattering of electrons according to the Davisson and Germer effect, there is a corresponding increased intensity of soft X-radiation. A comparison of the total secondary electron curve in the range from 30 to 550 volts with the corresponding curve for the polycrystalline target (cf. preceding abstract) shows that whereas at potentials below 60 volts the two curves are almost coincident, at higher potentials there is a great difference in the absolute values, although the general shapes of the curves are similar.

L. L. BIRCUMSHAW.

**Emission of secondary electrons and the excitation of soft X-rays.** O. W. RICHARDSON (Proc. Roy. Soc., 1930, A, 128, 63—74).—Theoretical. The experimental data given by various investigators are discussed, and a mechanism of the origin of secondary electrons and soft X-rays is suggested by means of which the established facts can be harmonised. The existence in crystals generally of "structure" electrons is postulated; these are not free and have no counterpart in the structure of the constituent atoms. When an electron reaches a crystal face it is either diffracted by the crystal grating or it reacts with one of the structure electrons by raising its energy from the normal to some excited state. To do this, it must lose at least as much energy as is equivalent to the level difference between the ground state and the next higher state. The true secondary electrons (low energy group) and the soft X-rays are generated largely by the normal return of the excited structure electrons to lower states and ultimately to the ground state, without the intervention of other electrons. The agreement of the soft X-ray with the secondary electron breaks is accounted for, since both are excitation potentials of the structure electrons, and the theory also accounts for the band-like structure of the discontinuities found experimentally for carbon, aluminium, and nickel. The nature of the levels occupied by the structure electrons is discussed.

L. L. BIRCUMSHAW.

#### Magnetic spectroscopy of X-ray electrons.

H. R. ROBINSON and C. L. YOUNG (Proc. Roy. Soc., 1930, A, 128, 92—114).—An extension of previous work (cf. A., 1923, ii, 818; 1925, ii, 728; 1927, 3).—Results are recorded for targets of uranium oxide, bismuth oxide, lead, gold, cerium oxide, silver, molybdenum, copper, zirconium oxide, strontium oxide, and arsenic oxide, the primary X-radiation being silver  $K$ + "white" radiation, i.e., practically

unfiltered radiation from a gas-filled tube with a silver anticathode. The measurements of both the secondary and the fluorescence lines have been appreciably extended, and the improved technique has brought out a great deal of new detail in the corpuscular spectra. A graphical representation is given of the relative intensities of the secondary cathode-ray groups, and the results are discussed, particularly with reference to the variation with  $\nu_0$ , the primary X-ray frequency, of the individual lines within a given group. The effect previously observed—that lines corresponding with levels of smaller azimuthal quantum number  $k_1$ , which are relatively weak when the primary radiation is just hard enough to excite all members of a group, become relatively more intense with increasing  $\nu_0$ —has now been established over the range 600—1600 $\nu/R$ .

L. L. BIRCUMSHAW.

**Electron diffraction by "forbidden" planes.** G. P. THOMSON (Nature, 1930, 126, 56).—The extra reflexions attributed by previous investigators to electrons selectively reflected by crystal planes which would not give a corresponding Bragg reflexion with X-rays may be due to Kikuchi lines.

L. S. THEOBALD.

**Interaction of free electrons and radiation according to Dirac's theory of electrons and quantum-electrodynamics.** I. TAMM (Z. Physik, 1930, 62, 545—568).—Mathematical. The Klein-Nishina formula is deduced. Transitions between negative energy levels are essential to the scattering formula. A simple method for calculation of the wave function of a free electron is given.

A. B. D. CASSIE.

**Behaviour of electrons amongst the molecules  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HCl}$ .** V. A. BAILEY and W. E. DUNCANSON (Phil. Mag., 1930, [vii], 10, 145—160).—Using a new method previously described (cf. this vol., 657), the statistical behaviour of electrons amongst molecules to which they may become attached was investigated for conditions where ionisation by collision is absent and the negative ions are permanent. From measurements of  $K$ , the mean energy of electron agitation,  $\alpha$ , the probability of attachment per unit distance,  $W$ , the mean electron drift velocity, and  $Z$ , the electric intensity, values are calculated for  $u$ , the velocity of agitation of an electron,  $L$ , its mean free path at 1 mm. gas pressure,  $\lambda$ , its fractional energy loss at a collision, and  $h$ , the probability of attachment at a collision for gaseous ammonia, water vapour, and hydrogen chloride at pressure  $p$ . Results are tabulated, and graphs are given for  $K$  and  $\alpha/p$  as functions of  $Z/p$ , and for  $L$ ,  $\lambda$ , and  $h$  as functions of  $\mu$ . The results indicate that  $\lambda$  bears some relation to the light-absorbing power of the molecule, and that  $h$  for a given kind of molecule varies considerably with the energy of the electron, generally increasing with its penetration into the molecule.

N. M. BLYTH.

**"Eigen"-energy of an electron on the quantum theory of scattering.** I. WALLER (Z. Physik, 1930, 62, 673—676).—Mathematical. The difficulty of an infinite eigen-energy of a free electron in an electromagnetic field is discussed using Dirac's relativity and non-relativity dynamics.

A. B. D. CASSIE.

**Electron emission by collision of positive ions at low gas pressures.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1930, **62**, 600—606).—The efficiency of positive ions for the liberation of electrons has been examined at a copper surface acting as a subsidiary electrode adjacent to a low-voltage arc in argon, neon, and helium, the pressure ranges being 0.0017—0.0036, 0.0126—0.0156, and 0.019—0.026 mm., respectively. The efficiency is of the same order in all these gases and increases from about 10 to 30% as the potential of the subsidiary electrode is increased sevenfold.

R. W. LUNT.

**Single collisions of electrons in nitrogen.** E. RUDBERG (*Nature*, 1930, **126**, 165—166).—The energy losses suffered by electrons of homogeneous speed in passing through nitrogen at a pressure excluding multiple collisions have been measured. The distribution curves obtained show a strong, sharp peak, due to electrons retaining the whole of their energy, with several small maxima close to it on the side of lower velocities in addition to a continuous distribution. The significance of the energy losses is discussed. No evidence of excitation processes belonging to the *K*-level of nitrogen was obtained.

L. S. THEOBALD.

**Simple method for investigating structure of various substances by means of electron waves.** F. KIRCHNER (*Naturwiss.*, 1930, **31**, 707).—To obtain films of suitable thickness ( $10^{-5}$  to  $10^{-7}$  cm.) the substance to be examined is scattered, if in sufficiently fine powder, or deposited from vapour, solution, or suspension, on a thin film of celluloid or collodion. The method has been applied to potassium, sodium, and mercuric chlorides, sodium iodide, gold, lead, and camphor.

C. A. SILBERRAD.

**Electrons in metals, and the rôle of Bragg's conditions of selective reflexion.** L. BRILLOUIN (*Compt. rend.*, 1930, **191**, 198—200).—An equation expressing Bragg's conditions is deduced by Schrödinger's method from the consideration of a cubic lattice in which the electric potential is a triply-periodic function of the co-ordinates, and across which free electrons move forming a Broglie wave. The conditions of formation of waves showing this type of "anomaly of degeneration" are discussed.

J. GRANT.

**Motion of electrons in carbon monoxide.** H. B. WAHLIN (*Physical Rev.*, 1930, [ii], **35**, 1568—1571; cf. *A.*, 1926, 653).—With the data previously obtained, the Compton theory of electron mobilities is shown to be valid for high pressures and low fields, assuming that the energy loss of the electrons on impact with the molecules is greater than that due to momentum transfer. The calculated mean free path in carbon monoxide when the electrons are in thermal equilibrium with the gas is 0.069 cm. at 1 mm. pressure.

N. M. BLIGH.

**Camera for electron diffraction.** G. P. THOMSON and C. G. FRASER (*Proc. Roy. Soc.*, 1930, **A**, **128**, 641—648).—Full details are given of an apparatus for the study of the diffraction patterns formed by the reflexion of cathode rays from crystalline surfaces. The method of detection is photographic, and the energy of the electrons is much greater than in the

case of the apparatus devised by Davisson and Germer (*i.e.*, about 6000—30,000 instead of only 300 volts). No elaborate vacuum technique is necessary.

L. L. BIRCUMSHAW.

**Analysis of surface layers by electron diffraction.** G. P. THOMSON (*Proc. Roy. Soc.*, 1930, **A**, **128**, 649—661).—Experiments have been made to demonstrate the possibilities of the "electron camera" (cf. preceding abstract), using a number of targets composed either of a polycrystalline mass or of a single crystal. The surfaces of many solids give diffraction patterns with electrons, and owing to the slight penetrating power of the electron the method affords a means of investigating surface layers, comparable with that provided by *X*-rays in the case of matter in bulk. The following surfaces showed measurable diffraction rings corresponding with a polycrystalline structure, the nature of which, so far as it could be determined from the rings, is given in parentheses: gold spluttered on quartz (gold); the same, bombarded from a filament coated with barium oxide (gold and barium oxide); the same after severe bombardment from a tungsten filament (quartz); platinum-black deposited on zinc or aluminium (platinum); platinum-black on copper (a cubic structure, probably an alloy of platinum and copper); platinised asbestos and the same asbestos unplatinised (a complex structure, unidentified); copper heated in air (either cuprous oxide, or a complicated structure which is not cuprous or cupric oxide, according to the method of heating); copper dipped in sulphide, selenide, and telluride solutions (analogous compounds, not cuprous sulphide, selenide, or telluride); rusted iron (ferric oxide); polished iron, dipped in concentrated nitric acid, washed, and dried (ferric oxide). Single crystals of calcite, galena, and rock-salt gave diffraction patterns of spots. No patterns were obtained with polished or etched metals, or with electro-deposited gold or copper. The conditions which determine whether or not a surface will give a diffraction pattern are discussed. The actual surface must be crystalline, and it appears to be a general rule that a polished surface which has recently been attacked chemically gives some kind of rings. In general, the clearness of the rings tends to diminish with the age of the specimen, perhaps indicating that larger crystal units are formed. The fact that no refractive index effect has been observed is strong evidence for supposing that, for example, the gold deposited by sputtering is in the form of small irregular lumps, through which the electrons pass, rather than crystals with extended flat surfaces.

L. L. BIRCUMSHAW.

**Excitation of light by low-voltage positive rays.** E. T. S. APPLEYARD (*Proc. Roy. Soc.*, 1930, **A**, **128**, 330—344).—Tate's experiments (*A.*, 1925, ii, 1106) have been repeated, using a glowing tungsten spiral spread with a sodium or potassium source instead of a platinum strip coated with sodium phosphate, and his results are confirmed. Experiments are described with a sharply-defined beam of sodium ions projected into mercury vapour, and from a consideration of the light emitted by the sodium atoms in the beam it is concluded that the greater part of the sodium light is

emitted by recapture of an electron from a mercury atom into some excited state of the sodium atom. An approximate efficiency-voltage curve for the line groups  $\lambda$  (4357, 4347) and  $\lambda$  (3650, 3655, 3663) of mercury is obtained and compared with the efficiency-voltage curve for electrons. It is shown that, in general, the Elsässer formula (Z. Physik, 1927, 45, 152) accounts for the differences observed between electron and positive ion impact. L. L. BIRCUMSHAW.

**Collision between positive ions and atoms.** F. M. PENNING and C. F. VEENEMANS (Z. Physik, 1930, 62, 746—763).—The loss of energy when positive potassium ions of 200 volts velocity pass through argon is compared with that for the passage of positive argon ions. The amount of energy lost by the potassium ions is considerably less than that lost by the argon, a result that would not be expected on the basis of the kinetic theory of gases. The cause of this difference of loss is sought in a charging of the argon ion. Experiments with a mixture of argon and neon (10:90) led to the same conclusion. The charge cross-section of argon ions of energy 200 volts in argon is 0.8 of the value calculated from the kinetic theory. Using higher energies (750 volts), the same difference in behaviour was found between potassium and argon ions in argon. It is not possible to reach any quantitative conclusions from the latter observations, as the curves deviate considerably, the deviations being ascribed to ionisation due to the positive ions. Some conclusions in connexion with the theory of breakdown of gases are recorded.

A. J. MEE.

**"Carrier" of the hydrogen striæ.** L. EBELER and E. HIEDEMANN (Ann. Physik, 1930, [v], 5, 625—643).—It was found that in atomic hydrogen at high concentration no striæ are formed. The striæ formed by excitation of hydrogen by an oscillatory current of frequency  $50\text{--}1.5 \times 10^6$  were investigated spectroscopically. The blue striæ are associated with strong relative intensity of the continuum, the red with that of the Fulcher spectrum. They are therefore due to the hydrogen molecule. The dependence of the spectral intensity distribution on frequency and damping was found, and the effect of oscillatory discharges of very high frequency on the reflexion of electrons was specially investigated. Although it is evident that the striæ are due to the hydrogen molecule, it is not yet certain in which state the molecule is. A. J. MEE.

**Length of coherence of light emitted from canal rays.** H. STRAUB (Ann. Physik, 1930, [v], 5, 644—656).—The apparatus used corresponded in the main with that of Rupp. A photographic method was used to measure the coherence length of the emitted light, the underlying principle being that of interference. The coherence length of light emitted from inhomogeneous canal rays is essentially smaller than that of the glow, amounting at the most to 2 mm. An abnormal increase for the hydrogen lines was not found. The interference of light from mercury canal rays was also investigated. A. J. MEE.

**Ionisation and range of hydrogen canal rays in air and hydrogen.** C. GERTHSEN (Ann. Physik, 1930, [v], 5, 657—669).—The hydrogen canal rays

used had velocities within the range 20—60 kilovolts. The relationship between ionisation current and the pressure was first found for five velocities. The curves show a critical saturation pressure. The penetration law for canal rays was then found. If  $R$  is the range and  $v$  the velocity,  $R = av^{1.5}$ ,  $a$  being a constant. The law is thus quite different from that for  $\alpha$ - and  $\beta$ -rays, for which the exponent is greater than 2. The ionising power was determined as a function of the velocity. A. J. MEE.

**Absorption of canal rays by solid bodies.** K. P. JAKOVLEV (Z. Physik, 1930, 63, 114—128).—The absorption by thin films (from 0.3 to  $1\mu$ ) of glass, mica, aluminium, and platinum of positive hydrogen and neon rays is measured by means of two compensated thermo-elements. The one element is exposed to the direct action of the rays, whilst the other is exposed to rays that have passed through the films in question, and in this way the effect of the unavoidable variation with time of the intensity of the canal rays can be eliminated. The velocity of the rays was directly determined by the deflexion in an electric field. It was found that the absorption coefficient for positive hydrogen rays decreased with increase of the velocity of the rays. Increase in absorption was found in the order glass, mica, aluminium, platinum, and the neon rays were considerably more strongly absorbed than the hydrogen rays. The absorption coefficient was found to increase with the thickness of the absorbing layer, this deviation from the exponential law being greater for the neon rays. H. A. JAHN.

**Ionisation of inert gases by slow alkali ions.** O. BEECK (Naturwiss., 1930, 18, 719).—A systematic study has been made of the ionisation of helium, neon, and argon by alkali ions. An inert gas atom is most easily ionised by the alkali ion which has the same number of external electrons as the inert gas, e.g., neon by sodium ions and argon by potassium ions. The ionisation of helium by potassium, rubidium, or caesium ions is so slight as to lie within the limits of experimental error. The ionisation produced in helium by lithium ions is greater than the measurable ionisation produced by sodium ions. Further work on krypton and xenon is in progress.

W. R. ANGUS.

**Reactions of excited mercury atoms with hydrogen and with water, with special reference to the effective cross-sections of the reactions and the rotations of the mercurous hydride molecules produced.** H. BEUTLER and E. RABINOVITSCH (Z. physikal. Chem., 1930, B, 8, 403—426).—Largely theoretical. The relationships previously deduced (this vol., 975) between the effective cross-section, the heat effect, and molecular rotation in elementary processes have been applied to the above reactions. It is suggested that in the reaction between excited mercury atoms and hydrogen the primary process is the formation of mercurous hydride by mercury atoms in the  $2^3P_0$  state,  $\text{Hg}(2^3P_0) + \text{H}_2 = \text{HgH} + \text{H} + 0.62$  volt, the mechanism proposed by Gaviola and Wood (A., 1929, 239) being shown to be unacceptable. In this process the effective cross-section is about eight times the gas-kinetic value, and the hydride molecules formed have about 20 quanta of

rotation. A similar primary process is postulated for the reaction with water:  $\text{Hg } (2^3P_0) + \text{H}_2\text{O} = \text{HgH} + \text{OH} - 0.1 \text{ volt}$ . Here, however, the hydride molecules have only about 4 rotational quanta and the effective cross-section is about 0.0003 of the gas-kinetic figure. Compared with the yield of these reactions, that of the reactions with  $2^3P_1$  atoms is only small. In bringing about the transition from  $2^3P_1$  to  $2^3P_0$  at the ordinary temperature nitrogen has about 5 times and water about 100 times the gas-kinetic cross-section, whilst the hydrogen molecule has no effect. R. CUTHILL.

**Effective cross-section of the free atomic nucleus.** W. WESSEL (Ann. Physik, 1930, [v], 5, 611—624).—Mathematical. The probability of the formation of ions and atoms by the collision of electrons and atomic nuclei characterised by a certain cross-section of the atomic nucleus was calculated. The general formula obtained enables the effective cross-section for very high velocities (greater than 50 volts) to be calculated exactly. A. J. MEE.

**Measurements of the effective cross-sections of reactive gas molecules by means of slow electrons.** H. L. BRÖSE and E. J. SAAYMAN (Ann. Physik, 1930, [v], 5, 797—852).—Published data are collated and critically discussed and several new measurements have been made in order to confirm and complete the available results. The limitations of the Townsend diffusion method for measuring the velocity of agitation and the drift velocity of electrons in gases are indicated. Townsend's definition of the length of the mean free path of the electrons is discussed and may be calculated from the formula  $L = (8Wp\sqrt{k/Z}) \times 10^{-9}$  (where  $L$  is the mean free path of electrons at 1 mm. pressure and  $W$  the drift velocity in the direction of an electric field of strength  $Z$ ). The following gases were examined by an apparatus which is fully described: hydrogen, oxygen, carbon monoxide, pentane, nitrogen, ethylene, carbon dioxide, and nitrous oxide, and the values of the effective cross-section are compared with those obtained by other investigators using the diffusion method. The agreement is good and both methods are trustworthy. An outline of the mathematical theory is appended. W. R. ANGUS.

**Exchange of energy between gas, solid, and adsorbed layer in a vacuum. I. Method of detecting variations in the thermal efficiency of molecular collisions. II. Effect of a deposited unimolecular layer on the efficiency of molecular collisions.** M. C. JOHNSON (Proc. Roy. Soc., 1930, A, 128, 432—444, 444—451).—I. A method is described for tracing small changes in the thermal efficiency of encounters between gas molecules and a solid surface. This efficiency determines the rate at which conductive equilibrium is re-established between the filament and walls of a Pirani gauge chamber when the pressure is varied over the range  $10^{-1}$  to  $10^{-4}$  mm., the medium of thermal exchange being hydrogen. A differential method is found to be the most suitable; i.e., the desired variations in reaching thermal equilibrium are observed superposed in a constant difference between the rates at which pressure equilibrium is attained by two wire-gas-wall systems

in parallel. If two Pirani gauges are balanced in a resistance bridge and evacuated simultaneously through long capillaries, the disturbance of balance, due to unequal rates of gas flow and to the finite time for reaching thermal equilibrium, passes through a maximum at a characteristic time  $t$  (max.). This has a lower limiting value of 120 sec., dependent on the dimensions of the apparatus, and above this its value varies with the thermal efficiency of the gas-solid collisions. It is found that the progressive change of  $t$  (max.) from 10 to 6 min., consequent on outgassing, corresponds with a 17% increase in the "accommodation coefficient"  $\alpha$  for hydrogen at the glass surface as the latter is purified.

II. The above method is extended to determine the change in  $\alpha$  for the hydrogen molecule when a unimolecular layer of hydrogen has been deposited on the glass. It has previously been shown (A., 1929, 639) that the adsorption of hydrogen on a baked glass surface in a vacuum can be made to take place so as to have a definite saturation density and to be independent of the presence of metals. The method of depositing and measuring a unimolecular layer in the present apparatus is described. If Knudsen's value  $\alpha = 0.26$  be taken as representing the state of ordinary untreated glass (Ann. Physik, 1911, 34, 593), and it rises to  $\alpha = 0.305 \pm 0.005$  when the initial layers, mainly of water vapour, are removed, the present experiments indicate that it decreases slightly, to  $\alpha = 0.295 \pm 0.005$ , when the surface is covered by a layer of hydrogen atoms. The variation of  $\alpha$  deduced from variations in  $t$  (max.) is in agreement with the hypothesis that in these cases elastic collision is the principal mechanism of energy exchange, and that not only the hydrogen atoms, but also the water molecules form unimolecular attachments to the solid lattice.

L. L. BIRCHSHAW.

**At. wt. of vanadium.** A. F. SCOTT and C. R. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 2638—2648).—Modifications in the preparation of vanadyl trichloride are described. From determinations of the ratio  $\text{VOCl}_3 : 3\text{Ag}$ ,  $0.535527 \pm 4 \times 10^{-6}$ , the at. wt. of vanadium is found to be 50.947.

J. G. A. GRIFFITHS.

**Nitrogen isotope of mass 15.** G. HERZBERG (Z. physikal. Chem., 1930, B, 9, 43—48).—The presence of the new nitrogen isotope of mass 15, discovered by Naudé by a study of the isotope effect in the nitric oxide bands, has been confirmed by an investigation of the second positive group of nitrogen. The isotopic displacement measured was somewhat smaller than that expected by theory, which points to a different packing effect for the two isotopes. The intensity ratio is about 1:800. A nitrogen isotope of mass 16, in agreement with theory, was not found.

A. J. MEE.

**Isotope effect in neon lines.** E. THOMAS and E. J. EVANS (Phil. Mag., 1930, [vii], 10, 128—134; cf. Nagaoka, A., 1929, 964).—The faint and bright interference fringes of neon were photographed, and intensity distributions across the fringes measured, and are illustrated by curves for the lines  $\lambda$  6717, 6164, 6030, and 5882. The separations of the faint components from the bright lines were calculated for about 20 lines in the visible region, and are tabulated

with the wave-lengths of the lines. Slight deviations from Nagaoka's values were found. N. M. BLIGH.

**Triatomic hydrogen.** J. L. BINDER, E. A. FILBY, and A. C. GRUBB (*Nature*, 1930, **126**, 11—12).—The results of Smallwood and Urey (A., 1928, 493) have been confirmed. No appreciable activation of hydrogen was observed under their conditions, but in the presence of a trace of oxygen activation takes place in agreement with the findings of Wendt and Landauer (A., 1922, ii, 369). Poisoning of the walls of the discharge tube with stearic acid, omitting the oxygen from the stream of pure hydrogen, gives positive results for activation. Wood's theory that water vapour poisons the walls of the tube and prevents reversion to molecular hydrogen is supported.

L. S. THEOBALD.

**Scattering of  $\alpha$ -particles in helium.** J. CHADWICK (*Proc. Roy. Soc.*, 1930, **A**, **128**, 114—122).—It has been pointed out by Mott (this vol., 269) that in the case of the collision of two identical particles the scattering laws given by the wave-mechanics will be very different from those of the classical theory. With the object of testing this, observations have been made, by means of Rutherford and Chadwick's annular ring method (A., 1927, 1003), of scattering in helium with  $\alpha$ -particles of four different ranges, 2.94, 2.04, 1.4, and 1.2 cm. The experimental results approach the value of twice the classical scattering as the energy of the incident  $\alpha$ -particle decreases, i.e., the results approach more and more closely to the quantum theory scattering. The discrepancy from classical scattering cannot be ascribed to a divergence from coulomb forces and must be attributed to a failure of the classical theory itself. Mott's calculation and the assumption on which it is based, that it is impossible to distinguish one helium nucleus from another of the same velocity, are thus verified by experiment, and it is proved that the field of force of the helium nucleus is perfectly spherical. The observations also indicate that as the distance between the colliding  $\alpha$ -particle and nucleus is decreased, the observed scattering rises slightly above that calculated from the quantum theory, then falls, and finally rises rapidly again. The initial rise and fall may be due to a true change in the law of force between the particles, but the asymmetry shown at small distances of collision can be due only to a distortion of the structure of the particles.

L. L. BIRCUMSHAW.

**Artificial disintegration by  $\alpha$ -particles.** J. CHADWICK and G. GAMOW (*Nature*, 1930, **126**, 54—55).—Mainly theoretical. With incident  $\alpha$ -particles of energy of approximately  $5 \times 10^6$  volts, the process of ejection of a proton from the nucleus without capture of the  $\alpha$ -particle is more frequent than the process of ejection with capture of the  $\alpha$ -particle.

L. S. THEOBALD.

**Transformation of paraffin under the influence of radioactive substances.** C. PAWLOWSKI (*J. Chim. phys.*, 1930, **27**, 266—276).—Microscopical and X-ray studies of layers  $40 \mu$  thick of paraffin wax, produced by dropping small pieces of wax into warm water and depositing the resulting film on glass, show that the anisotropic needle-shaped crystals of the

saturated hydrocarbons are normally distributed at random. Exposure to  $\alpha$ -particles from polonium produces the effect of irreversible fusion (super-saturation) with the formation of numerous small crystals in the mass of paraffin. After prolonged action, however, larger crystals separate accompanied by a decrease in viscosity of the liquid constituents. The radioactive energy generated per min. is approximately equivalent to that required to melt the layer of paraffin by direct heat, although it was actually found that "fusion" by the former method is complete only after 2 weeks. The phenomenon cannot be accounted for completely either by direct rupture of the molecules or by the ionising influence of the  $\alpha$ -particles, but there is evidence of oxidation of the paraffin due indirectly to the latter effect.

J. GRANT.

**Absorption method of investigating  $\beta$ -particles of high energy: the maximum energy of the primary  $\beta$ -particles of mesothorium-2.** N. FEATHER (*Physical Rev.*, 1930, [ii], **35**, 1559—1567).—Using Chalmers' method (cf. A., 1929, 1124) the maximum effective range mass,  $R$ , of the primary  $\beta$ -particles of radium-C and -E, and mesothorium-2 was determined with paper and aluminium. The constants in the formula  $R = aE + b$  are found to be  $a = 0.511$  and  $b = -0.091$ , where  $E$  is the maximum energy of the particles in million electron volts. For mesothorium-2 (cf. Yovanovitch, A., 1927, 915),  $R = 0.955 \pm 0.015$  g. per cm.<sup>2</sup> and  $E = 2.05 \pm 0.03$ . Reasons are given for the preference of the above empirical relation over the data of Madgwick (cf. A., 1927, 1120) in the interpretation of absorption measurements.

N. M. BLIGH.

**Passage of slow  $\beta$ -particles through matter. Production of branches.** E. J. WILLIAMS (*Proc. Roy. Soc.*, 1930, **A**, **128**, 459—468).—An investigation of the number of branches produced by  $\beta$ -particles with energy of about 20,000 volts in nitrogen and oxygen has been made. The experimental results support the quantum theory formula. A study of the energy relations in branch collisions indicates that, within the limits of experimental error, a  $\beta$ -particle loses an amount of energy in a branch collision equal to that acquired by the branch electron.

L. L. BIRCUMSHAW.

**Absorption of hard monochromatic  $\gamma$ -radiation.** G. T. P. TARRANT (*Proc. Roy. Soc.*, 1930, **A**, **128**, 345—359).—With the object of testing the accuracy of the various scattering theories that have been proposed, measurements have been made of the absorption of 15 elements for a practically homogeneous  $\alpha$ -radiation of very high frequency. For this purpose, hard thorium-C''  $\gamma$ -rays ( $2.649 \times 10^6$  volts) were used, the hard rays being isolated from the softer components by filtering through a suitable thickness (about 3 cm.) of lead. After applying a correction of 1% for scattering and about 3% for the soft component not eliminated by the lead filter, a mean value of  $124.6 \times 10^{-27}$  is obtained for the absorption coefficient of a number of the elements tested. This is in excellent agreement with the value calculated from the Klein and Nishina formula (A., 1929, 373), which is thus shown to be much more accurate than any hitherto proposed. In some of the elements, however,

the absorption showed a marked irregularity, which cannot be ascribed to a normal photo-electric effect, since it varies irregularly with the atomic number; there is evidently an additional absorbing mechanism in these elements, which may perhaps be due to an interaction of the high-frequency  $\gamma$ -rays with the nuclei of the elements. L. L. BIRCUMSHAW.

**Absorption coefficient of hard  $\gamma$ -rays.** C. Y. CHAO (Proc. Nat. Acad. Sci., 1930, 16, 431—433).—In order to ascertain more accurately the relation between the frequency of hard radiation and the absorption coefficient, determinations of the absorption coefficients of several elements have been made. Thorium-C'', which emits a narrow beam of  $\gamma$ -rays of wave-length approximately 4.7 X, was used and the soft rays cut off by lead filters. Two methods of measuring the ionic current were employed: (1) Millikan's cosmic-ray electroscope at a distance of 2 metres from the source, and (2) an ionisation chamber and a Hoffmann vacuum electrometer placed 1 metre from the source. The results from these two methods are in good agreement. The absorption coefficient,  $\mu$ , has been determined for different thicknesses of lead. The variation in the value of  $\mu$  with atomic number is shown by results from water, aluminium, copper, zinc, and tin, after the  $\gamma$ -radiation has been filtered by 6.8 cm. of lead. These results are in fair agreement with the value of  $\mu$  calculated from Klein and Nishina's formula (cf. A., 1929, 373). Theoretically  $\mu_e$  (absorption coefficient  $\div$  number of external electrons per c.c.) should have a constant value, whereas the experimental values increase with atomic number. This increase may be due to scattering by nuclear electrons, or to a photo-electric effect, or it may arise from the fact that the tightly bound electrons of atoms of high atomic number may possess greater scattering power than loosely-bound electrons. W. R. ANGUS.

**Nuclear  $\gamma$ -radiation of light elements.** W. BOTHE and H. BECKER (Naturwiss., 1929, 18, 705).—The side of a silver plate on which a preparation of polonium had been deposited was covered with the substance under examination, and the intensity of the  $\gamma$ -radiation produced by the  $\alpha$ -particles from the polonium measured by means of a sensitive point-counter (cf. A., 1929, 227). The following results for the intensity ( $\times 10^6$ ) were obtained: lithium  $4.7 \pm 0.4$ , lithium carbonate  $1.0 \pm 0.3$ , beryllium  $34.0 \pm 0.7$ , boron (about 90%)  $4.2 \pm 0.3$ , graphite  $0.15 \pm 0.2$ , paracyanogen  $0.2 \pm 0.24$ , magnesium  $1.0 \pm 0.2$ , aluminium  $1.3 \pm 0.2$ , silver  $0.03 \pm 0.27$ , nitrogen and oxygen (deduced from paracyanogen and lithium carbonate, respectively) 0. Interposition of a sheet of lead 1 cm. thick reduced the boron and beryllium radiation by 44 and 20%, respectively, and filtered radium-B+C radiation of equal strength by 52%. The radiation is so hard that there is no doubt that it proceeds from the nucleus of the atom struck. C. A. SILBERRAD.

**Possible effect of radiation of short wave-length on atomic nuclei.** G. I. POKROVSKI (Z. Physik, 1930, 63, 561—573).—The irradiation of elements of atomic number greater than about 30 (zinc) with X- and  $\gamma$ -rays revealed phenomena (scintillation etc.) the origin of which must be sought

in the nucleus. A comparison of the brightness of the scintillations with those produced by radioactive substances permitted the conclusion that the energy liberated must be of the order of  $10^{-6}$  to  $10^{-5}$  erg and the particles are probably  $\alpha$ -particles. Evidence of intermediate states in the nucleus was found. A few theoretical considerations of the possibility of transformation of these elements is discussed.

W. GOOD.

**Scattering of hard  $\gamma$ -rays.** I. L. H. GRAY (Proc. Roy. Soc., 1930, A, 128, 361—375).—Since the absorption coefficient of the hard thorium-C''  $\gamma$ -rays in a number of light elements has been found to be in good agreement with the theoretical Klein-Nishina values (A., 1929, 373), whilst in other elements the experimental value exceeds the theoretical, the conclusion has been reached that a new absorption mechanism, associated with the nuclei of the elements, is operative in the abnormal cases (cf. Tarrant, this vol., 1085). With the object of testing this conclusion, a comparison of the scattering power of aluminium, sulphur, and lead for hard radium-C  $\gamma$ -rays has been carried out. No very accurate results could be obtained with lead owing to the magnitude of the reabsorption corrections. The aluminium-sulphur comparison, however, is considered to be trustworthy to 0.5%, and the experimental results indicate that the scattering per extra-nuclear electron is the same for the two elements within the limits of experimental error, as judged by measurements of the radiation scattered between  $16^\circ$  and  $90^\circ$ . This is in marked contrast with Tarrant's thorium-C''  $\gamma$ -ray absorption measurements (*loc. cit.*). It is concluded that no measurable proportion of the energy absorbed in the new way is re-emitted in the forward direction between  $16^\circ$  and  $90^\circ$ , or that the new mechanism is almost inoperative in aluminium in the case of quanta of energy  $1.5 \times 10^6$  e-volts, and becomes of considerable magnitude only as the quantum energy approaches that of the hard thorium-C'' line ( $2.65 \times 10^6$  e-volts).

L. L. BIRCUMSHAW.

**Determination of the period of radium-C'; experiments with thorium-C'.** F. JOLIOT (Compt. rend., 1930, 191, 132—134; cf. Barton, A., 1927, 86; Jacobsen, A., 1928, 104).—The period of radium-C' has been determined by a slight modification of Jacobsen's method as  $(3 \pm 1.5) \times 10^{-6}$  sec. Although the results showed considerable divergence, it is clear that there was no trace of a maximum in the (number of  $\alpha$ -particles)/(distance from source) curve. The existence of such a maximum in Jacobsen's experiment is attributed to variation in the observed effect of the reflexion of the recoil atoms according to the relative positions of source and of observation tube. A similar experiment with thorium-C' shows its period to be much less than  $10^{-6}$  sec. There was no evidence to support Jacobsen's suggestion of an interval between the emission of the nuclear electron and of the quantum  $\gamma$ . C. A. SILBERRAD.

**New discrete range groups of H-particles from aluminium.** H. POSE (Naturwiss., 1930, 18, 666—667).—Disintegration of aluminium foil ( $30 \mu$  thick) by  $\alpha$ -particles showed that three distinct range groups of H-particles existed (cf. A., 1929, 971). The



primary energy necessary for the production of the H-particles in the individual groups has been measured. Further work has been done on the intermediate (47 cm.) range group. For the production of this group it is necessary to employ  $\alpha$ -particles having a range of 2.23–2.60 cm.; these particles may be either fast or slow. The experimental data indicate a resonance phenomenon in agreement with theoretical deductions.

W. R. ANGUS.

**Nuclear classification of atoms in relation to their possible genesis and their radioactive disintegration.** G. FOURNIER (J. Phys. Radium, 1930, [vii], 1, 194–205).—An attempt is made to connect the relationship between atomic number and atomic weight with the prime numbers.

C. W. GIBBY.

**Quantum mechanical theory of radioactivity and the dissociation by rotation of diatomic molecules.** O. K. RICE (Physical Rev., 1930, [ii], 35, 1538–1550).—Mathematical. The potential energy curves occurring in the theory of radioactive decay (cf. Gurney, A., 1929, 374; Gamow, *ibid.*, 7), and in the theory of dissociation of a diatomic molecule by the acquisition of rotational energy (cf. Oldenberg, *ibid.*, 1368) are investigated.

N. M. BLIGH.

**Cathode sputtering at very low gas pressures.** A. GÜNTHER-SCHULZE and K. MEYER (Z. Physik, 1930, 62, 607–618).—The sputtering of silver and copper cathodes in helium, neon, argon, hydrogen, and nitrogen has been investigated at pressures so low (generally less than 0.01 mm., in the apparatus described) that the sputtering is not dependent on the gas pressure. The sputtering electrode, changes in the weight of which were noted by observing the motion of a spiral spring by which it was supported, was placed near to a low-voltage arc consuming 3–5 amp. at 50 volts; it was maintained at a potential of from 300 to 1200 volts negative with respect to the anode of the arc. The amount of sputtered metal increases with the potential applied to the cathode, and the amount per unit ion current reaching the cathode increases in the order hydrogen, neon, nitrogen, argon, at any given cathode potential. No sputtering was observed in helium up to the highest potential applied, 800 volts.

The efficiency of the sputtering calculated as the ratio of heat of vaporisation of the metal sputtered to the energy delivered by the ion current ranges from 0.3% in hydrogen to 1.3% in argon.

Data have also been compiled relating to the amount of gas adsorbed per g. of metal sputtered under various conditions of gas pressure and sputtering electrode potential; the values obtained are in the neighbourhood of 0.4 mg. in argon, 1.0 mg. in neon, 0.7 mg. in hydrogen, and 1–6 mg. in nitrogen.

R. W. LUNT.

**Composition of active nitrogen. Identification of its constituents and determination of the conditions under which it is formed.** Z. BAY and W. STEINER (Z. physikal. Chem., 1930, B, 9, 93–127).—The presence of the fourth positive group of the nitrogen band spectrum in the spectrum of active nitrogen when subjected to the auxiliary discharge in the apparatus previously described (A., 1929, 733,

1359) does not, as Kaplan has supposed (*ibid.*, 375), constitute a proof of the presence of metastable molecules. A satisfactory test has, however, been devised by utilising the partial excitation of the luminescence spectrum of mercury by the active gas. This effect appears to be due both to the action of nitrogen atoms,  $N + N + Hg \rightarrow N_2 + Hg'$  and to the action of metastable molecules in the A state,  $N_2^{3.0V} + Hg \rightarrow N_2 + Hg'$ . Addition of 15% of hydrogen practically suppresses the after-glow, and the luminescence spectrum now terminates at 7.7 volts. corresponding, it would seem, with the second reaction only. The effect of the hydrogen is due both to its combining with nitrogen atoms and to its reducing the velocity of the electrons in the exciting discharge. As a result of the reduction of the electron velocity there is a tendency for the nitrogen molecules to emit the positive groups of bands and pass into the metastable state rather than break up into atoms, and under these conditions it seems possible that the metastable molecules may exist for some time after being drawn off from the vicinity of the discharge (the mean life being estimated as 0.1 sec.), and may far outnumber the atoms. The relationship of the electrical conditions of excitation to the proportion of atoms to metastable molecules in the active gas has also been studied.

R. CUTHILL.

**Dirac's equation.** A. PROCA (J. Phys. Radium, 1930, [vii], 1, 235–248).—Mathematical.

**Three-dimensional periodic orbits [of an electron] in the field of a non-neutral dipole.** L. PAGE (Phil. Mag., 1930, [vii], 10, 314–323).—Mathematical.

**Mutual influence of the chromophoric groups of a molecule on their [ultra-violet] absorption bands.** R. LUCAS (Compt. rend., 1930, 190, 1497–1499).—It is assumed that the influence of chromophores is associated with oscillators analogous to those considered in the classical theories of dispersion and absorption, by virtue of which the absorbing electron can create a varying electric field. It is then shown mathematically that, for the simple case of two identical chromophores separated by 2.5 Å., the single absorption band may be substituted by two bands displaced towards the red and ultra-violet, respectively, by an amount which is of the same order as that found by experiment for the saturated organic mono- and di-basic acids.

J. GRANT.

**Structure of absorption-resonators of organic chromophores. IV. Determination of number and geometrical arrangement of electrons in a common resonator.** D. RĂDULESCU, V. ALEXA, and F. BĂRBULESCU. **V. Factors causing a loss in sharpness of the characteristic absorption bands of a common resonator.** D. RĂDULESCU and A. GEORGESCU. **VI. Chromophoric characteristics of the nitro-group and the structure of its resonator.** **VII. Polarity of the nitro-group in organic compounds and the existence of *m*-quinonoids.** D. RĂDULESCU and V. ALEXA (Z. physikal. Chem., 1930, B, 8, 365–369, 370–381, 382–394, 395–402; cf. A., 1929, 1213).—IV. The structure of the naphthacene common resonator previously proposed has been confirmed by an investigation of the optical

properties of crocetin (cf. Karrer and Salomon, A., 1928, 869), the molecule of which is practically equivalent to the naphthacene molecule opened out into a straight chain.

V. The position of the characteristic absorption bands of a given substance is influenced by changes in substituent groups, *e.g.*, as a result of ionisation or solvation. In solution, therefore, the effective polarity of such a group may simultaneously exhibit several gradations, each giving a characteristic spectrum. The sharpness of the bands is reduced if one portion of the molecule, *e.g.*, a benzene ring, is capable of oscillation in respect of the other, so that if substituents are introduced the sharpness is affected. As would be anticipated, the effect of substitution in the *o*-position to the chromophore is greater than that of *p*-substitution. Judging by its effect on the absorption spectra of aromatic compounds, the negative polarity of the methyl group exceeds that of the chlorine atom.

VI. From an investigation of the absorption spectra of derivatives of 1:4-dihydroxyphthalazine it is concluded that the colour of nitro-compounds cannot be accounted for by salt formation by the nitro-group. The theory is therefore advanced that the nitro-group can exist in at least two electromeric forms. One of these, in which the nitrogen atom has a negative polarity, exhibits pronounced absorption into the visible part of the spectrum, whereas the other, in which the nitrogen has a positive polarity, absorbs only in the ultra-violet. Experimental evidence in favour of this theory is produced.

VII. The above theory of the electromerism of the nitro-group in conjunction with the theory of induced polarity in the benzene ring gives a satisfactory explanation of the chemical and optical properties of 2:4:6-trinitrobenzene and its derivatives.

R. CUTHILL.

**Structure and activation of the carbonyl chloride molecule.** I. Introduction. Predissociation of molecules. II. Raman spectrum of carbonyl chloride. III. Ultra-violet absorption spectrum of carbonyl chloride vapour. V. HENRI and O. R. HOWELL (Proc. Roy. Soc., 1930, A, 128, 178—189, 190—191, 192—214).—I. From a study of the ultra-violet absorption spectra of carbonyl chloride and thiocarbonyl chloride it is concluded that these molecules have a structure similar to that of formaldehyde, but possessing greater moments of inertia. The absorption spectrum obtained with polyatomic molecules having large moments of inertia is a pure vibration spectrum with a series of states of electronic activation, and its investigation involves an analysis of this vibration spectrum. The vibration periods of the atoms in the normal molecule obtained from the infra-red vibration spectra can also be obtained from the Raman spectra, and the study of the ultra-violet absorption spectrum should always be accompanied by a study of the latter. For a number of substances the vibration bands become diffuse at a certain wave-length and increase in breadth as they approach the ultra-violet. This broadening of the vibration bands and disappearance of the quantisation of molecular rotation are accompanied by certain changes in the molecule, and under the influence of light and heat the molecule changes into another state

intermediate between the normal and the dissociated molecule (predissociation). Reasons are given for these changes in the spectrum, and experimental studies of the photochemical decomposition of benzaldehyde and acetaldehyde demonstrate the agreement between the wave-length at which the spectrum begins to become diffuse and the energy of dissociation of the molecule. Similar good agreement is found for sulphur vapour. The special interest of carbonyl chloride, due to the fact that the molecule contains a carbonyl group, and the possibility of determining the isotope effect of  $\text{Cl}^{35}\text{Cl}^{35}$ ,  $\text{Cl}^{35}\text{Cl}^{37}$ , and  $\text{Cl}^{37}\text{Cl}^{37}$ , are discussed.

II. Experimental details are given of the manipulation of the carbonyl chloride and the method of obtaining the Raman spectrum. The latter is described. There are three vibration frequencies corresponding with wave-lengths 17.6, 22.5, and 34.4  $\mu$ .

III. The experimental arrangements are described. The source of ultra-violet light was a high-frequency spark between copper or aluminium electrodes under water, and exposures were made with pressures of gas varying from 0.1 to 680 mm. of mercury. The absorption spectrum of carbonyl chloride is composed of about 270 bands distributed at regular intervals between 3050 and 2380 Å.; the absorption becomes increasingly great towards the region of shorter wave-length. The spectrum consists of a large number of intense doublets and sometimes triplets, many fainter lines being irregularly distributed between the doublets. The separation of the doublets in the region of 2900 Å. is about 0.8—1.0 Å., and increases towards the ultra-violet. They are attributed to the isotopes  $\text{COCl}^{35}\text{Cl}^{37}$  and  $\text{COCl}^{35}\text{Cl}^{35}$ , the latter giving the more intense band on the ultra-violet side. The separation of the doublets is less than that for the chlorine molecules  $\text{Cl}^{35}\text{Cl}^{37}$  and  $\text{Cl}^{35}\text{Cl}^{35}$ . The vibration frequencies of the normal molecule are  $\alpha_0=582$  and  $\beta_0=302\text{ cm}^{-1}$ , and those for the activated molecule  $\alpha^1=422$  and  $\beta^1=254\text{ cm}^{-1}$ . The ultra-violet frequencies  $\alpha_0$  and  $\beta_0$  probably correspond with the Raman frequencies 567 and 290  $\text{cm}^{-1}$ . Since the frequency  $\alpha_0$  is similar to that found for the atoms in the chlorine molecule, it is considered that  $\alpha_0$  corresponds with the vibration of the chlorine atoms and  $\beta_0$  with that of the carbonyl group. The molecule of carbonyl chloride is more deformable than that of formaldehyde, but less than that of chlorine or acetaldehyde. The region of "predissociation" begins between 2750 and 2700 Å., this change in the character of the spectrum coinciding with a diminution in the frequency  $\alpha'$ , which falls from 422 to 416 and then to 412  $\text{cm}^{-1}$ , indicating that at this stage the chlorine atoms are mutually repelled. The mechanism of the photochemical dissociation of carbonyl chloride is discussed. The initial process is represented by the primary reaction  $\text{COCl}_2 \rightarrow \text{CO}^* + \text{Cl} + \text{Cl}$ , the carbon monoxide being in an unstable active state corresponding with an energy 22,000 g.-cal. This represents an electronic distribution analogous to that of a carbon atom in the 5S state.

L. L. BIRCHUMSHAW.

**Characteristic absorption of ultra-violet radiation by certain purines.** E. R. HOLIDAY (Biochem. J., 1930, 24, 619—625).—The ultra-violet absorption spectra of uric acid, guanine, adenine,

hypoxanthine, caffeine, and theobromine have been determined. They all follow Beer's law. The effect of hydrogen-ion concentration on the absorption spectra has been also measured. Uric acid and guanine have two bands in acid solution, the remaining compounds only one. The extinction coefficient is unaffected in all cases by change of hydrogen-ion concentration. The combination of a purine in the form of a nucleoside or nucleotide does not alter the absorption. Ergothioneine shows selective absorption very similar to that of purines and the molecular extinction coefficient is of the same order. It is completely transparent, however, to rays of short wave-length as far as 1900 Å.

S. S. ZILVA.

**Transmission spectrum of mercurochrome.** E. H. HARVEY (Amer. J. Pharm., 1930, 102, 397—402).—An aqueous solution of mercurochrome has a strong absorption band between 400 and 550 mμ, with a maximum at 500 mμ. Transmission of ultra-violet light decreases with decreasing wave-length until it is zero at 300 mμ. Irradiation with ultra-violet light has no effect on the absorption. R. K. CALLOW.

**Absorption and luminescence of benzene and benzene derivatives at -259°.** A. KRONENBERGER (Z. Physik, 1930, 63, 494—532).—The absorption spectra of benzene, chlorobenzene, and *m*-xylene at the temperature of liquid hydrogen were analysed and compared with the absorption spectra of the corresponding vapours and in some cases also with the spectra of other states of aggregation. The source of light was a large water-cooled Geissler tube containing hydrogen. The luminescence examined was excited by continuous ultra-violet and also with mercury-lamp radiation (Hg-line λ 2537).

W. GOOD.

**Ultra-violet emission bands of hydrogen chloride.** M. KULP (Naturwiss., 1930, 18, 719).—An analysis of the band system between 3000 and 4000 Å., using great dispersion, shows that the bands arise from a  ${}^2\Sigma \rightarrow {}^2\Pi$  transition. The spectrum is that of  $\text{HCl}^+$ . The bands arrange themselves in pairs the long-wave components of which belong to a  ${}^2\Sigma \rightarrow {}^2\Pi_{-1}$  and the short-wave components to a  ${}^2\Sigma \rightarrow {}^2\Pi_{+1}$  transition. The lower term is also an inverted  $\Pi$  term. Each doublet component has six branches; the three stronger correspond with  ${}^2\Sigma_{-1} \rightarrow {}^2\Pi_{-1}$  or  ${}^2\Sigma_{+1} \rightarrow {}^2\Pi_{+1}$ , and the three weaker with  ${}^2\Sigma_{-1} \rightarrow {}^2\Pi_{+1}$  or  ${}^2\Sigma_{+1} \rightarrow {}^2\Pi_{-1}$ . Approximate values of the constants for these states have been calculated. For the  ${}^2\Pi$  state,  $I = 2.8 \times 10^{-40}$  g./cm.<sup>2</sup> and  $r = 1.32 \times 10^{-8}$  cm., whilst for the  ${}^2\Sigma$  state the corresponding values are  $I = 3.81 \times 10^{-40}$  g./cm.<sup>2</sup> and  $r = 1.54 \times 10^{-8}$  cm.

W. R. ANGUS.

**Band spectra of  $\text{OsO}_4$  in gaseous state and in solution.** (Miss) S. KATO (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 13, 248—253).—Gaseous osmium tetroxide and 0.001 *M*-aqueous solutions have been investigated from 3200 to 2400 Å. and two groups of oscillation absorption bands have been identified. In the first group the intensity maxima appear at 2960 and 2947 Å. in the gas and at 2983 and 2970 Å. in the solution, giving a frequency difference of 149 cm.<sup>-1</sup>, whilst the maxima of the second group appear at 2475 and 2460 Å. for the gas and at 2515

and 2500 Å. for the solution, giving a frequency difference of 246 cm.<sup>-1</sup>. The intensity of absorption in the first group is greater in the long-wave maxima, whilst in the second group the short-wave maxima are more intense. The shift of maxima towards the red in the spectra of the solutions is attributed to hydration. The effect of hydration is shown to be a linear function of the frequency for both sets of bands.

W. R. ANGUS.

**Transparency of gypsum and mica in the ultra-violet.** W. HAUSMANN and O. KRUMPEL (Strahlenther., 1930, 35, 387—390; Chem. Zentr., 1930, i, 1746).—Gypsum is highly transparent for ultra-violet rays, which are largely absorbed by mica.

A. A. ELDRIDGE.

**Interpretation of a type of diffuse band spectra.** H. KUHN (Z. Physik, 1930, 63, 458—476).—The source of a type of diffuse band spectra which does not result from predissociation is discussed theoretically. The method is based on the application of the Franck and Condon principle to the case of flat potential curves.

W. GOOD.

**Division of light between two absorbing substances in the same medium.** K. WEBER (Archiv Hemiju, 1930, 4, 113—136).—The division of light between two absorbing substances in the same medium has been investigated by studying the influence on the fluorescence of solutions of foreign substances which also absorb light. The absorption constants of æsculin, quinine sulphate, sodium naphthoxide, amyl nitrite, and potassium chromate have been determined for the wave-length 366 mμ.

C. W. GIBBY.

**Infra-red investigations of molecular structure.** V. Simplest kind of polyatomic molecule. C. P. SNOW (Proc. Roy. Soc., 1930, A, 128, 294—316).

—By means of the apparatus previously described (Snow and Taylor, A., 1929, 865) an investigation has been made of the vibration-rotation band spectrum of nitrous oxide. Seven vibration bands are found between 2 and 7 μ, the heads being at the wave-numbers 2223, 2569, 2466, 2800, 3487, 3361, and 4404. The form and fine structure of all the bands show a close similarity, and the values of  $I$  from the doublet separation are the same within the limits of error. These data, and the fact that the fine structure, although not completely established, appears to give a value of  $I$  which is half of that from the separation of the doublets, suggest a symmetrical straight line, NON, for the form of the molecule. This form is consistent with the Raman spectrum of nitrous oxide, which has been shown to consist of one line separated from the exciting line by an interval of 1281 cm.<sup>-1</sup> (Dickinson, Dillon, and Rasetti, A., 1929, 1215); confirmation is also obtained from the value of the dielectric constant and from one of two recent determinations of the specific heat of the gas. The molecular constants are given. The vibration bands are arranged into a scheme based on the three fundamental frequencies. Carbon dioxide, nitrous oxide, and carbon disulphide are compared, and it is shown that all the evidence points to their possessing a symmetrical linear structure. An attempt is made to connect the values of the

vibration frequencies of a diatomic group with the electronic binding of the group; the group is shown to have frequencies comparable with those of the corresponding diatomic molecule.

L. L. BIRCUMSHAW.

**Infra-red absorption spectrum of sulphur dioxide.** C. R. BAILEY, A. B. D. CASSIE, and W. R. ANGUS (*Nature*, 1930, 126, 59).—Bands have been found at 2498, 2321, 1871 (weak), 1355, 1152, and 606  $\text{cm}^{-1}$ ; that at 1355  $\text{cm}^{-1}$  is the strongest and appears to be complex in structure. The fundamental frequencies are probably  $\nu_1=1355$ ,  $\nu_2=1152$ , and  $\nu_3=606$   $\text{cm}^{-1}$ .

L. S. THEOBALD.

**Infra-red spectrum of sodium nitrate.** C. SCHAEFER and C. BORMUTH (*Z. Physik*, 1930, 62, 508—509).—The infra-red absorption spectrum of sodium nitrate was determined from 2 to 10  $\mu$ . The nitrate group has a spectrum similar to the carbonate group, with active fundamental modes of vibration at 7.17  $\mu$ , 14.44  $\mu$ , 12.04  $\mu$ , and an inactive mode at 9.30  $\mu$ . The bands are arranged as combination bands of these fundamental frequencies.

A. B. D. CASSIE.

**Comparative absorptions of aqueous solutions of active and racemic tartaric acids.** G. BRUHAT and J. TERRIEN (*Compt. rend.*, 1930, 191, 125—127; cf. Cotton, this vol., 193; Gheorgiu, *ibid.*, 132).—The absorption for ultra-violet light of *d*-, *l*-, and *r*-tartaric acids has been determined. Freshly made solutions were used, that of the *r*-acid being prepared by mixing solutions of the two active acids, thereby avoiding the change in absorption noted in solutions that have been in contact with glass (cf. Stewart, J.C.S., 1907, 91, 1537). The absorption of the *l*-acid in general exceeded that of the *d*-acid, but to a very varying amount; that of the *r*-acid deviates from the arithmetic mean of the absorptions of the two active acids by amounts varying from -9 to +10%, the average of the results showing practically identical absorption. It is concluded that no molecules of the racemic acid exist in solution (cf. Darmon, A., 1914, ii, 787). C. A. SILBERRAD.

**Absorption of ultra-violet light by the alkyl iodides.** G. EMSCHWILLER (*Compt. rend.*, 1930, 191, 208—210).—The absorption constants (*k*) of methyl, ethyl, propyl, butyl, *iso*-, *sec*-, and *tert*-butyl, *iso*-propyl, and methylene iodides and of iodobenzene have been measured photographically at 20° for thicknesses of liquid of 2—16 mm. The relation  $\log k = a - b\lambda$  is established for the liquid state, where  $\lambda$  is the wave-length and *a* and *b* are positive constants dependent on the nature of the substance, and may be used to obtain values of *k* by extrapolation over a wide range of radiations. In the gaseous state absorption increases exponentially with decrease in  $\lambda$ , but attains a maximum (at 2570 Å. for methyl, ethyl, propyl, and butyl iodides) and then a minimum value. For all the iodides the wave-length corresponding with a particular value of *k* is increased by about 12 Å. for a rise in temperature of 10° between 20° and 110°, but the point of maximum absorption is not appreciably altered.

J. GRANT.

**Infra-red absorption of some organic liquids under high resolution.** R. B. BARNES (*Physical*

*Rev.*, 1930, [ii], 35, 1524—1532; cf. A., 1929, 1127).—Using an echelette grating spectrometer of high resolving power and radiation from a Nernst filament the infra-red absorption spectrum was measured from 3.1 to 3.6  $\mu$  for benzene, toluene, *o*-, *m*-, and *p*-xylene, ethyl-, butyl-, monochloro-, and monobromo-benzene, for the purpose of comparison with the Raman effect for these compounds (cf. Wood, A., 1929, 741). Wave-lengths are tabulated, and absorption curves given. The bands in the region investigated, due to the CH vibration, and previously examined under low dispersion, have been resolved into many components. The 3.25  $\mu$  benzene band was resolved into three equally strong components at 3.231, 3.253, and 3.291  $\mu$ . The shifts of these bands, caused by the various substitutions, did not exceed 0.01  $\mu$ .

N. M. BLIGH.

**Raman spectra of some aldehydes and of mesitylene.** S. VENKATESWARAN and S. BHAGAVANTAM (*Proc. Roy. Soc.*, 1930, A, 128, 252—262).—The results of a study of the Raman spectra of acetaldehyde, paraldehyde, benzaldehyde, anisaldehyde, salicylaldehyde, hexaldehyde, undecaldehyde, and lauric aldehyde, and of mesitylene, are reported and discussed. The line corresponding with a shift of 1700  $\text{cm}^{-1}$  appears in the spectra of all the aldehydes studied with the exception of paraldehyde, and is evidently due to the carbonyl group common to all of them. A comparison of the results obtained with benzene and a large number of derivatives shows that the Raman line corresponding with  $\Delta\nu$  993, which is strong in benzene, becomes weaker in mono-substituted derivatives, and still more feeble in di-substituted. There is a small increase in this frequency on substitution amounting to about 10 wave-numbers, and, furthermore, practically every substituted compound gives a new Raman line at about  $\Delta\nu$  1030. The fact that, contrary to expectation, the line  $\Delta\nu$  993 appears very strongly in the tri-substituted derivative, mesitylene, points to a close similarity between benzene and mesitylene, evidently connected with the symmetrical ring structure common to both. Mecke's theory of unsymmetrical loading is not supported by the fact that the line  $\Delta\nu$  1030 appears in both mesitylene and cyclohexane. The characteristic frequencies,  $\nu$ , of the C=O and C=C linkings are calculated from Dadiou and Kohlrausch's formula (cf. A., 1929, 976)  $\nu = K\sqrt{A/\mu}$ , where *A* is the thermal dissociation constant,  $1/\mu = 1/m_1 + 1/m_2$ , *m*<sub>1</sub> and *m*<sub>2</sub> being the masses of the two atoms, and *K* is a constant. The calculated and experimental values are in good agreement.

L. L. BIRCUMSHAW.

**Physical methods in the chemical laboratory. XII. Raman effect as an aid in investigating constitution.** G. KORNFIELD (*Z. angew. Chem.*, 1930, 43, 393—396).—The usefulness of Raman spectra in the investigation of chemical constitution is discussed generally (cf. Dadiou and Kohlrausch, this vol., 663).

S. K. TWEEDY.

**Raman effect of nitric acid in solution.** L. A. WOODWARD (*Nature*, 1930, 126, 58).—Rao's results (A., 1929, 1361) are, in the main, supported, but are criticised in certain respects. L. S. THEOBALD.

**Raman bands of water.** W. GERLACH (Physikal. Z., 1930, 31, 695—698).—The structure of the blue Raman band for water is investigated, and all the photographs show that the line is not simple, but at least double. The effect of the dissolution of salts in the water on the structure of the blue band was found. Chlorides of lithium, sodium, potassium, calcium, cadmium, and zinc, and nitrates of sodium and lithium were used. Salts cause a typical change in the structure of the band. Without strictly monochromatic excitation the accurate structure of the water bands cannot be obtained with certainty. Raman experiments at higher temperatures require a parallel investigation of the absorption of water at corresponding temperatures. A. J. MEE.

**Raman bands of water.** E. H. L. MEYER (Physikal. Z., 1930, 31, 699—700).—Photographs of the Raman line for water at 4696 Å. are given. The effect of the addition of electrolytes is noted and the results obtained are the same as those of Gerlach (cf. preceding abstract). There are undoubtedly two maxima in the photometric curves. A. J. MEE.

**Raman effect in paramagnetic crystals.** P. KRISHNAMURTI (Nature, 1930, 126, 169).—The Raman spectra for crystals of magnesium or zinc sulphate show a strong line with a frequency shift of about 980  $\text{cm}^{-1}$ , which is characteristic of the  $\text{SO}_4^{2-}$  ion. With ferrous sulphate, however, the line does not appear with the crystals and is only feeble in aqueous solution. In other paramagnetic sulphates, such as those of copper and manganese, the line is again weak. L. S. THEOBALD.

**Chemical constitution and Raman effect.** LESPIEAU and BOURGUEL (Compt. rend., 1930, 190, 1504—1506).—A Raman line of about 1620  $\text{cm}^{-1}$  is characteristic of the ethylenic linking, and may vary slightly around this value according to the positions of the linking and of the neighbouring groups. In the case of benzene compounds a Raman line (about 1600) characteristic of the cyclic double linking is always obtained, and in the presence of an acyclic side-chain with a double linking another line occurs (1630—1660). Phenyltrimethylene (this vol., 900) was shown to give only one Raman ray, namely, 1605, characteristic of the benzene nucleus, and therefore contained no side-chain double linking. J. GRANT.

**Raman effect and constitution of the molecule.** I. S. TRUMPY (Z. Physik, 1930, 62, 806—823).—The Raman spectra of some structurally isomeric alcohols were found. Both the normal and secondary alcohols have a strong Raman line of frequency 1448  $\text{cm}^{-1}$ . This frequency has been ascribed by Dadiou and Kohlrausch to the type of combination  $\cdot\text{CH}_2\cdot$ . This assumption is in agreement with the present determinations, the frequency being stronger in the normal than in the secondary alcohols. The frequencies ascribed by Dadiou and Kohlrausch to the grouping  $\text{CH}_3\cdot\text{C}$ , viz., 2865 and 2929  $\text{cm}^{-1}$ , were observed to be present with a certain amount of irregularity in similar alcohols. For butyl alcohol the latter frequency is, however, split into two, 2903 and 2932  $\text{cm}^{-1}$ . In isobutyl alcohol the frequency 2929 is missing, but the other frequency,

2865, is especially strong. With *tert.*-butyl alcohol with three groups of the type  $\text{CH}_3\cdot\text{C}$  a frequency of 2915 is found to be especially strong, whilst the frequency 2865 is either missing entirely or is very weak. The frequency of 2967  $\text{cm}^{-1}$  ascribed by Dadiou and Kohlrausch to a grouping of the type  $\text{X}\cdot\text{CH}_2\cdot\text{X}$  has been observed for similar alcohols. *iso*Propyl alcohol, however, has this characteristic Raman frequency, although, according to its structural formula, it contains no groups of this type. The same is true of *tert.*-butyl alcohol. It is also shown that a characteristic frequency can be ascribed to the hydroxyl group in conjunction with the neighbouring  $\text{CH}_2$  group. The value calculated for this frequency from the simple theory is in good agreement with the observed values. *iso*Butyl alcohol gives the same value as *n*-butyl alcohol, thus showing its primary nature; these alcohols also show very similar chemical properties. The relationship is quite different for the secondary alcohols which have no  $\cdot\text{CH}_2\cdot\text{OH}$  grouping. The Raman frequencies of secondary compounds lead to the conclusion that the hydroxyl group in these compounds, and especially in *isopropyl* alcohol, is less strongly bound than in primary compounds. These facts are in accordance with the chemical properties of the compounds. A. J. MEE.

**Raman effect. VII. Raman spectra of organic substances.** A. DADIEU and K. W. F. KOHLRAUSCH (Monatsh., 1930, 55, 379—402).—To explain Raman spectra, many of which are very complicated, the spectra due to a number of comparatively simple molecules have been investigated. Organic substances were used containing the radicals Me, Et, Ac, and Ph, combined with Me, Ph, OH,  $\text{NH}_2$ ,  $\text{NO}_2$ , CHO,  $\text{CO}_2\text{H}$ , CN, Cl, Br, I. The inner oscillations of the compounds (if present) were already known from previous work. In the amines (methylamine, ethylamine, and benzylamine were used) the N·H frequency was found to be 3310 and 3360  $\text{cm}^{-1}$ . The methyl halides show a strong group frequency which is displaced towards the blue. In methyl chloride it is least strong. The C·O frequency is increased greatly in acetyl chloride and bromide, and is doubled in pyruvic acid. Benzoic acid dissolved in benzene gives the normal acid value of 1648. In alcoholic solution it gives the higher value, 1689, whilst in ether it gives the highest value, 1716, which, however, is the normal value for esters. The thiocyanates show two frequencies in solution, the higher, 2070  $\text{cm}^{-1}$ , being due to the C·N oscillation, whilst the second is due to the oscillation of the group S·CN. A. J. MEE.

**Raman effect of the cyanide radical.** A. PETRIKALN and J. HOCHBERG (Z. physikal. Chem., 1930, B, 8, 440—444).—The Raman effect has been investigated with phenylthiocarbimide, methyl thiocyanate, liquid cyanogen, mercuric cyanide in methyl-alcoholic solution, and silver argenticyanide and potassium thiocyanate in aqueous solution. The results show that the carbon and nitrogen of the cyanide radical are combined most firmly in cyanogen. R. CUTHILL.

**Raman effect, fluorescence, and colour of of diamonds.** S. BHAGAVANTAM (Nature, 1930,

126, 168).—The infra-red wave-number for 7 diamond was found to be  $1331.5 \pm 0.5 \text{ cm}^{-1}$  (cf. Ramaswamy, this vol., 662; Robertson and Fox, *ibid.*, 662). A continuous spectrum with a fairly well defined edge at  $4240 \text{ \AA}$ . accompanies the Raman lines; it is preceded by two bands of which the first at  $4152\text{--}4162 \text{ \AA}$ . is the more intense. The intensity of the bands and of the continuous spectrum varies with the colour of the diamond, being marked with pale blue diamonds and feeble with those which are white. The Raman lines are difficult to observe with the blue diamonds. L. S. THEOBALD.

**Molecular scattering of light from certain organic liquids.** N. B. REYNOLDS and J. W. WILLIAMS (J. Franklin Inst., 1930, 210, 41–54).—With the view of discovering in the molecular scattering of light a method by which atomic linkings in molecules may be recognised, the Raman spectrum was photographed for benzene, nitrobenzene, toluene, *o*-, *m*-, and *p*-nitrotoluene, carbon tetrachloride, aniline, and *o*-chlorophenol, using mercury arc and helium arc excitation. Results for 48 lines of carbon tetrachloride are tabulated (cf. Pringsheim, A., 1928, 1307; Dadiou, A., 1929, 976), and data and deductions for toluene are summarised; the wave-number differences for the substances investigated are shown graphically, and a molecular energy diagram for toluene is given and discussed. N. M. BLIGH.

**Scattering of light by dielectrics of small particle size.** G. F. A. SRUTZ (J. Franklin Inst., 1930, 210, 67–85).—The diffusion of light by a dielectric material, zinc oxide, was investigated in the range of particle sizes where, with increasing particle size, Rayleigh scattering rapidly diminishes and reflexion and refraction effects increase in importance. The turbidity maximum for zinc oxide dispersed in water, determined for three wave-lengths of light, occurs at  $0.25 \mu$  for the wave-length  $5500 \text{ \AA}$ ., and at smaller particle sizes for shorter wave-lengths; the particle size of maximum turbidity was found to be proportional to the wave-length of the light in the range  $4800\text{--}6300 \text{ \AA}$ . An apparatus for determining the angular distribution of the light scattered by a suspension of fine particles is described. The total observed intensity has not the same distribution as calculated by Blumer (cf. Z. Physik, 1926, 38, 304); the observed depolarisation is in fair agreement with theory (cf. Lange, A., 1928, 360).

N. M. BLIGH.

**Influence of the wave-length of exciting rays on the fluorescence spectrum of aetioporphyrin. Structure of this spectrum from the infra-red to the ultra-violet.** J. AHARONT and C. DHÉRE (Compt. rend., 1930, 190, 1499–1501).—The fluorescence spectra of aetioporphyrin in pyridine solution (A., 1926, 885) produced by radiation from 8 sources covering the range  $330\text{--}546 \mu$  are almost identical as regards number, position, and intensity of the emission bands. At least 15 emission bands exist, viz.,  $\lambda$  769, 756, 734.5, 706.5, 688.3, 672, 651.5, 636, 622.1 (principal band), 610, 595.3, 579.5, 565.8, 555.5, and  $539.5 \mu$ . J. GRANT.

**Sensitivity of the luminescence of some magnesium aryl halides.** H. GILMAN, R. E.

FOTHERGILL, and J. McGLUMPHY (Rec. trav. chim., 1930, 49, 726–728).—A general and extensive luminescence is obtained when nitrobenzene or *o*-nitrotoluene is distilled into magnesium *p*-chlorophenyl bromide under conditions such that the distillate reaches the Grignard reagent without contact with atmospheric oxygen. Under similar conditions substances which do not react with the organomagnesium halides (ether, benzene, chlorobenzene, and bromobenzene) give no luminescence. These substances, however, give a localised luminescence if the drops of the distillate traverse 1–2 cm. of air before falling into the magnesium *p*-chlorophenyl bromide. It is suggested that this local luminescence is due to atmospheric oxygen adsorbed or entrapped in the drops of distillate. F. G. TRYHORN.

**Effect on the fluorescence of solutions of amino-acids of their photo-oxidation products.** C. WIEGAND (Pflüger's Archiv, 1929, 223, 378–394; Chem. Zentr., 1930, i, 1435–1436).—Diketopiperazine and Curtius' biuret base,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}[\text{NH}\cdot\text{CH}_2\cdot\text{CO}]_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , fluoresce more strongly than glycine; the enol form of the former does not, however, do so. For an exciting wave-length of  $3660 \text{ \AA}$ ., glyoxylic acid, non-fluorescent, somewhat reduces the fluorescence, but does not affect the absorption, of glycine. Formaldehyde, of which an aqueous solution fluoresces in the ultra-violet, increases that of glycine but does not affect the absorption. Aqueous formic acid, non-fluorescent, has no effect. Pyruvic acid, non-fluorescent, diminishes that of alanine and increases the absorption; acetaldehyde diminishes the fluorescence without affecting the absorption, whilst acetic acid has little effect. *iso*Valeraldehyde, non-fluorescent, diminishes the fluorescence but does not affect the absorption of leucine; *isovaleric* acid has no effect.  $\alpha$ -Ketoglutaric acid, fluorescent, increases the fluorescence of aqueous glutamic acid but does not affect its absorption; irradiation increases the fluorescence of glutamic acid. *p*-Hydroxyphenylpyruvic acid, non-fluorescent, does not affect the fluorescence or absorption of tyrosine, the fluorescence of which is increased by irradiation. A. A. ELDRIDGE.

**Phosphorescence of solutions of eosin in glycerol. Influence of iodides.** (MLLE.) S. Boudin (J. Chim. phys., 1930, 27, 285–290).—Eosin ( $0.5 \times 10^{-4}\%$ ) dissolved in anhydrous glycerol shows (1) a fluorescence due to the reversible absorption of energy by the molecules, which consequently pass into a (first) active state; (2) a phosphorescence, in which the molecules pass from the first to a second (metastable) active state, from which they have to return to the normal state by way of the first active state. The intensity of phosphorescence is  $1/400$  of that of the fluorescence, but its duration ( $1.1 \times 10^{-3} \text{ sec.}$ ) is more than 300,000 times as great; i.e., there are 800 times the number of active molecules in the former as in the latter case. Potassium iodide ( $0.06\%$ ) halves the mean duration of the phosphorescence owing probably to the more complete diffusion resulting from the longer duration of the metastable active state. Increase in concentration of eosin ( $0.3\text{--}1.0 \times 10^{-4}$ ) decreases the duration of emission. J. GRANT.



**Optical dissociation of diatomic molecules in gases and vapours.** I. II. III. G. H. VISSER (Chem. Weekblad, 1930, 27, 237—241, 380—384, 390—393).—A survey of recent work.

H. F. GILLBE.

**Distribution of potential and of charge in a diatomic molecule.** L. GOLDSTEIN (Compt. rend., 1930, 190, 1502—1504).—A mathematical generalisation of the statistical method of Fermi and Thomas (A., 1928, 456) applied to diatomic molecules on the assumption of the spherical symmetry of the atom. Approximate formulæ for the distribution of the potential and charge on the nuclear axis are obtained, and it is shown that the electrons in the internal layers of an atom play only a negligible rôle in the formation of the atom. The formulæ are more accurate for heavier molecules, and an exact statistical solution of the equations is obtained if the electrons of the molecule are considered as a single gaseous system.

J. GRANT.

**Photo-electric studies on metal and oxide electrodes in distilled water and dilute solutions.** B. LÁNYI and E. THEISZ (Magyar Chem. Fol., 1929, 35, 129—139, 145—151; Chem. Zentr., 1930, i, 1436—1437).—Experiments with silver, copper, silver oxide, and cupric oxide electrodes in a vacuum or in an atmosphere of hydrogen, nitrogen, or oxygen are described. With pure, compact metals (cathode-sputtered electrodes) the photo-electric sensitivity is 0.1—1 millivolt, with other metallic electrodes of the order of 10 millivolts, and with oxide-coated electrodes 20—200 millivolts, independently of the electrolyte or atmosphere. The change of potential is confined to the illuminated electrode and its immediate neighbourhood, where the process is chemical and irreversible, becoming reversed, however, on exclusion of light.

A. A. ELDRIDGE.

**Physical methods in chemical laboratories.** XIII. **Electrical moment of molecules.** O. WERNER (Z. angew. Chem., 1930, 43, 663—669).—A review of recent work.

A. R. POWELL.

**Attempt to determine nuclear moments.** W. H. RODEBUSH and W. A. NICHOLS, jun. (J. Amer. Chem. Soc., 1930, 52, 3024—3025).—The Stern-Gerlach experiment has been performed with the vapours of iodine and hydrogen iodide, but diffuseness of the image prevented detection of any deflexion.

J. G. A. GRIFFITHS.

**Temperature coefficient of dielectric constant of water.** E. LANGE and A. L. ROBINSON (J. Amer. Chem. Soc., 1930, 52, 2811—2813).—The factor  $1 + TdD/DdT$  ( $D$ =dielectric constant; Lange and Meixner, A., 1929, 1389) used in calculating integral heats of dilution is very sensitive to changes of  $dD/dT$ , which should be known to  $\pm 0.5\%$ . The more probable values of  $dD/dT$  for water lie between  $-0.368$  and  $-0.393$  at  $12.5^\circ$ ,  $-0.337$  and  $-0.362$  at  $25^\circ$ , and  $-0.296$  and  $-0.341$  at  $40^\circ$  (cf. Drude, A., 1897, ii, 438; Drake and others, and Wyman, this vol., 666).

J. G. A. GRIFFITHS.

**Dielectric polarisation of liquids.** IX. **Electric moments of alkyl halides and halogenated methanes.** C. P. SMYTH and H. E. ROGERS (J.

Amer. Chem. Soc., 1930, 52, 2227—2240).—Densities and dielectric constants of heptane solutions of butyl chloride, bromide, and iodide, and heptyl bromide at temperatures in the range  $-90^\circ$  to  $90^\circ$ , and of benzene solutions of methylene bromide and iodide, bromoform, and iodoform in the range  $10$ — $70^\circ$  have been determined. The corresponding electric moments are 1.88, 1.81, 1.59, 1.83, 1.39, 1.08, 0.99, and  $0.8 \times 10^{-18}$  e.s.u., respectively. The polarisations show that the butyl group exerts a pronounced screening effect on intermolecular action, as do the halogen atoms in methylene bromide and bromoform. The electric moments of alkyl halides are independent of the number of carbon atoms when this is greater than two. Consideration of the distortion of the tetrahedral structure in di- and tri-halogenated methane, due to the repulsive forces between the halogen atoms, leads to calculated electric moments in good agreement with those observed.

J. G. A. GRIFFITHS.

**Electrical properties of molecules.** II. A. H. W. ATEN (Chem. Weekblad, 1930, 27, 235—236).—The changes of the dipole moment produced by the substitution of organic radicals for hydrogen in compounds such as water, ammonia, and hydrogen chloride are described, and "group moments" are given for various substituents.

H. F. GILLBE.

**Variation of the electrical moments of "flexible" molecules with temperature.** O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1930, B, 8, 357—364).—It has not been possible to confirm Werner's observation that the dipole moment of the molecule of quinol diethyl ether varies with temperature (A., 1929, 1217), nor has any variation in the dipole moments of the dimethyl ether and certain other non-rigid molecules between  $20^\circ$  and  $60^\circ$  been detected.

R. CUTHILL.

**Electrical moments of the stereoisomeric stilbene dichlorides.** A. WEISSBERGER and R. SÄNGEWALD (Z. physikal. Chem., 1930, B, 9, 133—140).—From measurements of the refractivities and dielectric constants of the two stilbene dichlorides in benzene solution it is calculated that the dipole moment of the  $\alpha$ -compound has the value  $1.27 \times 10^{-18}$ , whereas for the  $\beta$ -compound the value is  $2.75 \times 10^{-18}$  e.s.u. Since neither compound is associated in solution, this difference is interpreted as meaning that the two halves of the molecule are not able to rotate freely about the central linking. The dipole moment of benzyl chloride is  $1.87 \times 10^{-18}$ .

R. CUTHILL.

**Molecular volume, viscosity, and temperature relationships.** W. HERZ (Z. Elektrochem., 1930, 36, 454—455).—It is found that if  $L = (M \cdot d)^{1/3}$ , where  $M$  is the mol. wt. and  $d$  the density of a non-associated liquid,  $L \times \eta^{1/3}$  is approximately a common constant nearly independent of temperature; also  $L/T^{1/6}$  is approximately constant. These relations hold for ether, ethyl acetate, benzene, carbon tetrachloride, chlorobenzene, methyl acetate, and fluorobenzene.

H. I. DOWNES.

**Refractive indices of some organic vapours.** E. BERL and L. RANIS (Z. Elektrochem., 1930, 36,

453—454).—The refractive indices of hexane, di-, tri-, and per-chloroethylene, tetra- and penta-chloroethane vapours were determined experimentally by an interferometric method, and also calculated from the Lorenz-Lorentz relation; fair agreement is shown.  
H. I. DOWNES.

**Dispersion of some organic liquids in the ultra-violet.** P. GUILLERY (Physikal. Z., 1930, 31, 701—710).—The refractive indices of a number of organic liquids were determined in the ultra-violet by a method depending on total reflexion. The liquids used were alcohol, glycerol, and acetone. The wavelengths of the light used were as low as 265  $\mu$ , and the determinations were carried out at different temperatures between 0° and 100° and the b. p. of the liquid. For these liquids the constants for Ketteler's dispersion formula were found, enabling the refractive index to be calculated with great accuracy. The Lorenz-Lorentz law holds over a wide range, especially for glycerol. The temperature coefficient was also found.  
A. J. MEE.

**Anomalous dispersion and adsorption of electric waves.** S. MIZUSHIMA (Bull. Chem. Soc. Japan, 1930, 5, 163—164).—Debye's formula,  $\epsilon = \epsilon_0 + \omega^2 \epsilon_\infty [(\epsilon_0 + 2)/(\epsilon_\infty + 2)]^2 (4\pi\eta\alpha^3/KT)^2 / \{1 + \omega^2 [(\epsilon_0 + 2)/(\epsilon_\infty + 2)]^2 (4\pi\eta\alpha^3/KT)^2\}$ , where  $\epsilon$  is the dielectric constant measured for the frequency  $\omega/2\pi$ ,  $\epsilon_0$  and  $\epsilon_\infty$  are the static and optical dielectric constants, respectively,  $\eta$  is the viscosity,  $\alpha$  the molecular radius,  $K$  Boltzmann's constant, and  $T$  the absolute temperature, yields reasonable values for  $\epsilon$  and  $\eta$  for methyl, ethyl, propyl, butyl, and amyl alcohols; for glycerol the results are not satisfactory, and if this substance be regarded as a colloiddally dispersed system the discrepancy may be due to differences between the effective viscosity responsible for retardation of the molecular rotation and the bulk viscosity of the liquid.  
H. F. GILLBE.

**Effect of concentration on the values of the dispersion and rotation constants for solutions of camphor in ethyl alcohol.** G. OWEN (Trans. Faraday Soc., 1930, 26, 423—427).—Values are tabulated for the constants in the three-constant Drude equation calculated from measurements of the rotatory power of alcoholic solutions of camphor of concentrations from 5.978 to 50.493 g. per 100 g. of solution.  
F. G. TRYHORN.

**Polarimetry as a means of investigating solutions of strong electrolytes.** (Mrs.) J. LIQUIER-MILWARD (Trans. Faraday Soc., 1930, 26, 390—397).—Measurements have been made of the effect on the rotatory power of neutral *l*-asparagine of the presence of a number of salts in concentrations varying from 0.03*M* up to saturation. The results show that the nature and in particular the size of each ion play an important part even in very dilute solutions. The theory of Debye and Hückel is applied to calculate the mean ionic radii of the salts employed, and values are obtained which agree satisfactorily with those afforded by electrometric measurements. It is pointed out that the polarimetric method has the advantage of rendering possible the study of

electrolyte solutions without disturbing the pre-existing fields.  
F. G. TRYHORN.

**Salt effect and rotatory power.** E. DARMOIS (Trans. Faraday Soc., 1930, 26, 384—390).—An account is given of previously published work on the effect of neutral salts on the rotatory power of salts and esters of tartaric and malic acids, and on complexes of these acids with molybdic acid. The dehydration and the deformation of the tartrate ions serve, at least partly, to account for the properties of tartaric acid in solutions of neutral salts, but the behaviour of the esters is not susceptible to this explanation, and must be attributed to the existence of two or more modifications of the compound. Brief mention is made of unpublished work on the sensitivity of the mutarotation of the alkaline molybdo-tartaric complexes to the presence of neutral salts.  
F. G. TRYHORN.

**Absorption and rotatory dispersion of solutions of tartaric acid.** G. BRUHAT (Trans. Faraday Soc., 1930, 26, 400—411).—Preliminary results are given of measurements of the absorption of aqueous solutions of *d*-tartaric acid throughout the ultra-violet region. Absorption is perceptible from the end of the visible region and increases continuously as the wave-length decreases, but begins to increase rapidly only at about 2600—2500 Å. It was found qualitatively that the maximum absorption in dilute solution is near 2225 Å. and corresponds with a density four or five times that observed in the region of 2400 Å. Neutral sodium and potassium tartrates possess similar molecular absorptions in the region of 2400 Å., but in each case the absorption is lower than that of the free acid. Near 3000 Å. the sodium salt absorbs twice as much as the potassium salt, which, in turn, is 2.5 times as absorbent as the free acid. The application of the Ketteler-Helmholtz formulae show that the absorption of tartaric acid solutions in the region from the visible to 2360 Å. is sufficiently well represented by the action of a single narrow band at 2330 Å. Complex dispersion formulae are suggested which have the advantage over previous ones of remaining valid in the ultra-violet region. It is further found that the variation with concentration of the absorption of tartaric acid in the ultra-violet presents no anomaly such as should exist if the chemical constitution of the molecule varied with the concentration. This confirms the deduction made from measurements of the variation of rotatory power with concentration that if there is any sort of chemical modification, whether due to polymerisation, dehydration, or dynamic isomerism, it can involve only a very small proportion of the molecules.  
F. G. TRYHORN.

**Optical superposition.** J. READ (Trans. Faraday Soc., 1930, 26, 441—541).—A review of recent work.  
F. G. TRYHORN.

**Relations between the rotatory powers of the members of homologous series.** J. KENYON (Trans. Faraday Soc., 1930, 26, 439—441).—*n*-Alkyl ethers of *d*- $\gamma$ -nonanol exhibit anomalies in contrast with the generalisations which may be laid down for other homologous series.  
F. G. TRYHORN.

**Molecular dissymmetry.** W. H. MILLS (Trans. Faraday Soc., 1930, 26, 431—438).—A summary of the different types of molecularly dissymmetric molecules. F. G. TRYHORN.

**Variations in the rotatory power of a compound.** R. LUCAS (Trans. Faraday Soc., 1930, 26, 418—422).—The influence of temperature and of solvent on the rotatory power of compounds is discussed. The effect of temperature is explained by assuming that the molecules, whilst remaining unimolecular, do not retain the same configuration and are capable of deformation. A method, based on Darbais' rule, is suggested for calculating the number of isomeric configurations present in a solution from measurements of rotatory power at two or three wave-lengths. Application of the method to the case of ethyl tartrate leads to the assumption of three active modifications. The effect of temperature on such a system results from changes in the thermal equilibria set up among the active forms in accordance with Boltzmann's law. F. G. TRYHORN.

**Rotatory dispersion of tartaric acid and its derivatives.** P. C. AUSTIN (Trans. Faraday Soc., 1930, 26, 411—417).—The origin of complex dispersion is discussed and reasons are advanced for assuming that this dispersion can be simplified only by stabilising one component of an isomeric mixture present in solutions of tartaric acid. Evidence is adduced supporting the hypothesis that, although simple dispersion may be simulated by certain derivatives of tartaric acid, the dispersion does not become really simple until some form of bridging is present in the molecule. Examples are given of types of bridging which are actual or possible. F. G. TRYHORN.

**Principle of free rotation in optically active molecules.** K. L. WOLF (Trans. Faraday Soc., 1930, 26, 315—320).—In discussing the above principle it is pointed out that in tartaric acid, so far as the orientation of its polar groups is concerned, the forces operating between these groups are from their close proximity so constituted that there exist clearly marked "troughs" of energy which cause preference to be given to one or more definite positions at the ordinary temperature at the cost of free rotation. These positions must be identical for *d*- and *l*-tartaric acids, but the positions of least potential energy for the *meso*-acid will be quite different if the rotation of the half molecules is not quite free. Measurements of the dipole moments at 22° of the esters of the tartaric acids made to test this conclusion gave identical values of  $(3.12 \pm 0.025) \times 10^{-18}$  for the *d*- and *l*-acids and the value  $(3.66 \pm 0.030) \times 10^{-18}$  for the *meso*-acid ester. Thus in one part of the esters of isomeric tartaric acids completely free rotation is absent at 22°. The conclusion is further supported by the fact that the dipole moments increase with rise of temperature. The general conclusion is that for the tartaric esters the principle of free rotation does not hold at the ordinary temperature, but that with rising temperature a limit is to be expected above which it becomes valid. F. G. TRYHORN.

**Influence of polar substituents on the optical rotatory power of organic compounds.** H. G.

RULE (Trans. Faraday Soc., 1930, 26, 321—336; cf. A., 1924, ii, 645).—A re-statement and extension in the light of recent knowledge of dipoles of the hypothesis that the rotatory power of a molecule is a function of the moments of the four groups attached to the asymmetric atom, and that the influence of a substituent on the optical rotation will therefore depend in sign and magnitude on the polarity of the substituent. F. G. TRYHORN.

**Optical rotatory power and chemical constitution.** M. BETTI (Trans. Faraday Soc., 1930, 26, 337—347).—A summary and review of the author's work since 1907. F. G. TRYHORN.

**Dependence of optical rotatory power on chemical constitution.** B. K. SINGH and B. BHADURI (Trans. Faraday Soc., 1930, 26, 347—350).—A summary of the authors' work on the effect of unsaturated conjugation on optical rotatory power. Some previously unpublished results are given illustrating the depression in the rotatory power which accompanies the reduction of azethenoid linkings in compounds containing a number of conjugated double linkings. F. G. TRYHORN.

**Methods for measuring rotatory power in the ultra-violet region.** R. DESCAMPS (Trans. Faraday Soc., 1930, 26, 357—371).—A critical and chronological review of the principles, apparatus, and technique of ultra-violet spectropolarimetry. F. G. TRYHORN.

**Calculation of dispersion equations.** T. M. LOWRY and G. OWEN (Trans. Faraday Soc., 1930, 26, 371—376).—A summary of the methods of analysis of simple and complex dispersion curves by means of two-, three-, and four-constant equations, with a table of constants relating to 33 spectral lines used in dispersion measurements. F. G. TRYHORN.

**Rotation dispersion of optically active substances.** E. KEESER (Strahlenther., 1929, 34, 574—577; Chem. Zentr., 1930, i, 1746).—The circular dichroism and optical activity of various proteins were studied; the curve of the anomalous rotation dispersion of a 5% egg-albumin solution in presence of copper sulphate is reproduced. A. A. ELDRIDGE.

**Anisotropic liquids.** C. W. OSEEN (Fortschr. Chem., Physik, physikal. Chem., 1929, B, 20, 1—87; Chem. Zentr., 1929, i, 1533—1534).—Born's theory is discussed and a new theory is advanced. This assumes that the forces which the rigid molecules exert on each other are partly those of attraction and partly those of moment of rotation which tend to gather the molecules together in definite, superimposed layers. L. S. THEOBALD.

**Variation with temperature of the specific magnetic rotatory powers of cerium nitrate and nickel chloride.** H. OLLIVIER (Compt. rend., 1930, 191, 130—132).—The magnetic rotation of a solution of cerium nitrate containing equal masses of the anhydrous salt and of water ( $d^{20}_D$  1.6337,  $d^{21}_D$  1.5822) has been determined at various temperatures from 0° to 70°. Calculating the magnetic rotation per g. of anhydrous salt ( $\gamma$ ) by the additive law (cf. A.,

1928, 573) the relation  $\gamma(t+292.1) = -17,090$  ( $t$  in  $^{\circ}\text{C}.$ ) is deduced. The temperature corresponding with the Curie point is thus  $-19.1^{\circ}$  Abs. For nickel chloride in aqueous solution  $\gamma$  decreases slightly with fall of temperature, but in methyl alcohol it increases, thus not following an analogue to the Curie law.

C. A. SILBERRAD.

**Measurement of circular dichroism in the ultra-violet.** W. KUHN and E. BRAUN (Z. physikal. Chem., 1930, B, 8, 445—454).—An apparatus for the measurement of circular dichroism for wave-lengths down to 1900 Å. is described. This depends on the change in axial ratio undergone by elliptically polarised light when passed through a medium exhibiting circular dichroism. The results obtained with ethyl  $\alpha$ -azidopropionate are reproduced. R. CUTHILL.

**Dispersion of optical rotation of amorphous systems.** G. KORTÜM (Physikal. Z., 1930, 31, 641—679).—A full summary of theoretical and experimental work. A. J. MEE.

**Complexity of phosphorus pentoxide.** I. A. SMITS and H. W. DEINUM (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 514—525; cf. Smits and Rutgers, A., 1925, ii, 268).—When pure phosphorus pentoxide is heated rapidly to  $700^{\circ}$  it still remains in the solid state, although this temperature is more than  $100^{\circ}$  above the triple point. This is analogous to the behaviour of sulphur trioxide (cf. Smits and Schoenmaker, A., 1925, ii, 267; 1926, 669, 785), but the experiment is not so dangerous. The equilibrium vapour-pressure curve of the stable form of phosphorus pentoxide has been redetermined. The triple point is at 55.5 cm. and  $580^{\circ}$ . The discrepancy between this value, that obtained previously, and that of Hoefflake and Scheffer (A., 1926, 342) is attributed to the necessity of long keeping at each temperature in order that the inner equilibrium may be fully attained. When the unstable, more volatile form is heated rapidly from  $400^{\circ}$  to  $700^{\circ}$  the vapour pressure is always greater than the equilibrium value of the stable modification for the same temperature. Removal of a fraction from the more stable form causes a lowering of the vapour pressure of the residue. The significance of these results in the light of Smits' theory of allotropy is discussed. J. W. SMITH.

**Complexity of nitrogen.** II. A. SMITS, H. GERDING, and (FRL.) W. HERTOOGH (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 526—529, and Physikal. Z., 1930, 31, 768—769).—Using an improved method of temperature control it has been confirmed that the vapour pressure of a rapidly evaporated fraction of liquid nitrogen is 0.5—1.0 mm. greater than that of the residue and remains practically constant for about 30 sec., after which it falls to the normal value (cf. this vol., 659). The observations of Justi (*ibid.*, 524) are shown to be due to the use of insufficiently pure nitrogen (cf. also *ibid.*, 721).

J. W. SMITH.

**Constitution of the polyborates.** E. WIBERG (Z. anorg. Chem., 1930, 191, 43—48).—The constitution of the polyborates may be very readily deduced by means of the theory of the valency of boron previously described (A., 1928, 936). R. CUTHILL.

**Borohydrates and boron suboxides.** E. WIBERG (Z. anorg. Chem., 1930, 191, 49—59).—The constitution of the borohydrates and boron suboxides (Travers and Ray, A., 1912, ii, 938; Rây, J.C.S., 1914, 105, 2162; 1918, 113, 803; 1922, 121, 1088; A., 1925, ii, 417) has been deduced by means of the theory of the valency of boron previously advanced (A., 1928, 936). A close relationship between the borohydrates and the boron hydrides is revealed. R. CUTHILL.

**Co-ordination. I. Ion hydrates. A correction. II. Ion ammoniates.** F. J. GARRICK (Phil. Mag., 1930, [vii], 10, 76—77, 77—80).—I. An equation previously given (cf. this vol., 276) is corrected and the calculations therefrom are re-tabulated. The co-ordination number of the ion  $\text{Rb}^{+}$  is 8, in agreement with Sidgwick's rule.

II. The electrostatic theory of co-ordination previously developed is extended to amino-compounds. The co-ordination numbers found are:  $\text{Mg}^{++}$ , 4;  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{++}$ , and  $\text{Sr}^{++}$ , 6;  $\text{Rb}^{+}$ ,  $\text{Cs}^{+}$ , and  $\text{Ba}^{++}$ , 8, in agreement with Sidgwick's rule, except  $\text{Mg}^{++}$  and  $\text{Sr}^{++}$ , which require the values 6 and 8, respectively. The stability and power of hydrate formation of amines are discussed. The theory cannot be applied to tervalent ions, since the force constants are unknown; the stable amines of  $\text{Cr}^{+++}$  and  $\text{Co}^{+++}$  can probably be explained on the electrostatic basis. A group of abnormal amines is considered, such as those of silver, copper, zinc, and nickel, which differ in the solid state and in solution, and are regarded as hydrato-ammines. N. M. BUGH.

**Magnetism and molecular structure. I. Magnetic susceptibilities of some liquid organic isomerides.** S. S. BHATNAGAR, R. N. MATHUR, and R. S. MAL (Phil. Mag., 1930, [vii], 10, 101—109; cf. A., 1928, 454, 941).—Contrary to earlier views, the magnetic properties of isomerides should differ. Using a sensitive magnetic balance method the magnetic susceptibilities were determined for *n*- and *iso*-propyl alcohol, *n*-, *iso*-, and *tert*-butyl alcohol, *o*-, *m*-, and *p*-cresol, *o*- and *m*-nitrotoluene at  $34^{\circ}$ , and for *o*- and *p*-chlorophenol at  $45^{\circ}$ . Slight differences in the values for the different isomeric forms were found. Magnetic and other molecular properties of the above substances are tabulated for comparison, and conclusions therefrom are discussed.

N. M. BUGH.

**Association and constitution.** E. C. BINGHAM and H. J. FERNWALT (Science, 1930, 71, 564—565).—Association measured by the fluidity method varies regularly in a homologous series and can be calculated by means of a formula (cf. Bingham and Darrall, this vol., 534). Predicted associations, together with the calculated and observed temperatures required to give a definite fluidity, are tabulated for the alcohols, the fatty acids, and the mercaptans.

L. S. THEOBALD.

**Molecular structure and the properties of homopolar compounds. II. Stereoisomerism and the structure of the carbon atom.** A. DIBROVA (Ukraine Chem. J., 1930, 5, 1—34).—Molecules of organic substances may possess a tetrahedral or a pyramidal structure; the former configuration is the more stable at higher temperatures,

and in cases in which a central carbon atom is combined with electronegative radicals corresponds with a higher level of molecular energy. The above hypothesis explains the existence at low temperatures of two isomerides of  $\alpha\beta$ -dibromopropionic acid, and also affords an explanation of the periodicity of the m. p. of members of homologous series. A number of cases of stereoisomerism, such as that of the tartaric acids, of the *cis-trans*-isomerism of alicyclic compounds, and of compounds possessing ethylenic linkings, are explicable on the basis of this hypothesis.

R. TRUSZKOWSKI.

**Mechanism of homopolar linking.** F. LONDON (Prob. mod. Physik, Debye-Sommerfeld Festschr., 1928, 104—113; Chem. Zentr., 1929, i, 1533).

**Stereochemistry of crystalline compounds.** P. WIGGLI (Ber., 1930, 63, [B], 1823—1838).—A theoretical paper in which the principal phenomena of crystallography are deduced from stereochemical considerations.

H. WREN.

**Chemical activity of substances in the nascent state.** A. PINKUS (Bull. Soc. chim. Belg., 1930, 39, 271—286).—A lecture.

C. W. GIBBY.

**Surface tension of liquid nitrous oxide.** E. L. QUINN and G. WERNIMONT (J. Amer. Chem. Soc., 1930, 52, 2723—2730).—The surface tension,  $\gamma$ , of liquid nitrous oxide has been determined by capillary rise at temperatures in the range  $-50^\circ$  to  $30^\circ$  and the data are reproduced with an average deviation of 2.6% by the van der Waals relation in the form  $\gamma = 72.8(1 - T/311.8)^{1.26}$ . The position of liquid nitrous oxide in the internal pressure series of Hildebrand indicates that the liquid should be a slightly better solvent than liquid carbon dioxide.

J. G. A. GRIFFITHS.

**Chemical importance of surface tension and internal friction of liquids.** L. LORENZ (Z. Elektrochem., 1930, 36, 336—346).—A summary of existing knowledge of the subject, with a full bibliography.

J. W. SMITH.

**X-Ray investigation of iron nitrides.** G. HÄGG (Z. physikal. Chem., 1930, B, 8, 455—474).—By means of the results previously obtained (this vol., 138) an equilibrium diagram for the system iron-nitrogen has been constructed and the structure of iron nitride explained.

R. CUTHILL.

**Effect of temperature and dissolved electrolytes on the monochromatic Debye-Scherrer diagram for water.** H. H. MEYER (Ann. Physik, 1930, [v], 5, 701—734).—The effect of temperature and dissolved electrolytes on the structure of water was determined by obtaining Debye-Scherrer diagrams for the different cases. The electrolytes used were lithium and sodium chlorides. Copper and molybdenum  $K\alpha$ -rays, made monochromatic by reflexion at a sodium chloride crystal, were used, because the more usual method applying filtered X-rays will not be of service in this case. The results of the photometric work are given in the form of curves as well as in tables. The Debye-Scherrer diagram for water at  $20^\circ$  shows four maxima, the identity periods calculated by Bragg's equation being 3.132, 2.12, 1.34, and 0.89 Å. When the

temperature is raised and the concentration of dissolved electrolyte is increased the position and strength of the maxima are all changed in the same sense. For 8*N*-lithium chloride solution, however, the second maximum (identity period 2.12 Å.) entirely disappears. The observed changes are in agreement with the assumption that the first maximum is due to interference at the single molecules, whereas the second is due to the interference at molecules inside the molecular complex.

A. J. MEE.

**Molecular rotation in the solid state.** S. B. HENDRICKS (Nature, 1930, 126, 167—168).—The X-ray diffraction data obtained for primary amylammonium chloride at the temperature of liquid air indicate that the carbon atoms in a  $C_5H_{11}$  group are arranged in a zig-zag manner and that the characteristics of the X-ray patterns obtained at the ordinary temperature arise partly from rotation of the  $C_5H_{11}$  groups about their chain axes (cf. A., 1929, 495).

L. S. THEOBALD.

**Liquid structure and X-ray diffraction in liquids.** K. BANERJEE (Indian J. Physics, 1930, 4, 541—556).—The work of Raman and Ramanathan (A., 1924, ii, 816), applying the Boltzmann principle to explain the diffraction effects in liquids, has been modified by taking into account the nature of the field of force surrounding the molecule. A liquid is considered as a degeneration of the crystal structure due to thermal agitation. The occurrence of certain crystal diffraction lines in the liquid and the non-appearance of others are explained. The intensity distribution of the diffracted rays and the sharpness of different rings are discussed. Special consideration is given to sodium, potassium, argon, and mercury; the calculated values of diffraction rings are in good agreement with values obtained by experimental observation on these substances in the liquid state. The intensity distribution of the diffracted rays in liquid mercury is calculated from the crystal structure and the compressibility and agrees with the experimental results of Prins.

W. R. ANGUS.

**Orientation of the molecules in naphthalene and anthracene crystals.** K. BANERJEE (Indian J. Physics, 1930, 4, 557—573).—The intensities of X-ray diffraction in naphthalene and anthracene do not conform to orientations of the molecules along any cell face. Investigations were made by a Shearer X-ray tube. The integrated intensities for reflexions from different planes and the corresponding structure factors are tabulated. Oscillation photographs about the *a* and *b* axes were taken and the integrated intensities for reflexion from the 001 face and its higher orders compared photometrically. The carbon atoms of the benzene ring in both compounds are arranged in a hexagonal ring which may be either elongated or contracted along the length of the molecule. The molecules are inclined to the cell faces, the correct position being determined by placing them first along the *bc* plane and then by successive rotation about the *b* and *c* axes. The rotations are, respectively,  $25^\circ$  and  $12^\circ$  for naphthalene and  $25^\circ$  and  $9^\circ$  for anthracene. None of the crystallographic axes lies in the plane of the molecule. The molecules are nearer to the *bc* plane than to any other cell face, a

conclusion in complete agreement with experimental results on the diamagnetic susceptibility and optical anisotropy of the compounds. W. R. ANGUS.

**Determination of polymerisation of some polymerised formaldehydes by X-ray methods.** E. OTT (Science, 1930, 71, 465—466).—The presence of inner lines in the X-ray diagrams has been confirmed (cf. A., 1929, 746). In highly polymerised substances molecules of identical length crystallise together. The following results have been obtained:  $\delta$ -polyoxymethylene is closely hexagonal with the length of the molecule equal to 45.1 Å. and 24 CH<sub>2</sub>O groups each of length 1.88 Å;  $\gamma$ -polyoxymethylene is pseudo-hexagonal, the length of the molecule is 113.4 Å. with 60 CH<sub>2</sub>O groups each 1.89 Å. in length; paraformaldehyde is pseudo-hexagonal with a molecular length of 60.6 Å. containing 32 CH<sub>2</sub>O groups each 1.89 Å. long. L. S. THEOBALD.

**X-Ray diagrams of thin celluloid films.** F. KIRCHNER (Naturwiss., 1930, 18, 706—707).—The X-ray diagram of celluloid, obtained when the celluloid has been exposed to the radiation for a short time only, indicates complete absence of any ordered arrangement of the crystallites. After a longer period of irradiation a diagram is obtained showing definite spots, similar to those obtained for mica (cf. Linnik, A., 1929, 492; Bragg, *ibid.*, 984), and indicating a definite orientation of the crystallites. It is concluded that this is due to a rearrangement of crystals of camphor under the influence of the X-rays. C. A. SILBERRAD.

**Influence of absorption on Debye-Scherrer photographs.** A. A. RUSTERHOLZ (Z. Physik, 1930, 63, 1—7).—The same expression is obtained as that of Claassen (this vol., 278) for the total absorption factor for X-rays reflected by a strongly-absorbing powder. Claassen stated that this expression could only be integrated graphically, but it is now shown that it can be rigorously integrated, and a graph of its values for varying glancing angles is given. H. A. JAHN.

**X-Ray investigation of methylcellulose.** H. MARK and G. VON SUSICH (Z. physikal. Chem., 1930, B, 9, 157—159).—X-Ray examination of methylcellulose has shown that Hess and Trogus' deduction of the values 21.3 and 25.6 Å. for two of the periods of identity of the elementary cell (A., 1929, 1222) rests on a misinterpretation of the X-ray diagram. The most probable value is  $10.3 \pm 0.2$  Å. for the period of identity along the axis of the fibre. R. CUTHILL.

**X-Ray fibre-diagrams of trimethylcellulose and cellulose triacetate.** II. K. HESS and C. TROGUS (Z. physikal. Chem., 1930, B, 9, 160—168; cf. A., 1929, 1222, and preceding abstract).—The interpretation of X-ray diagrams of cellulose esters and ethers is attended with grave difficulties, even in respect of the determination of the period of identity along the axis of the fibre, and a further complication arises from the possibility that any given fibrous preparation may be a mixture of several forms. From the position of the diatropic interferences it is inferred that the minimum value of the period of identity along the axis of the fibre of cellulose triacetate II is  $10.7 \pm 0.1$  Å. R. CUTHILL.

**Reflexion of X-rays in absorbent ideal crystals.** J. A. PRINS (Z. Physik, 1930, 63, 477—493).—Theoretical. Introduction of the influence of absorption (due to photo-effect as well as incoherent scattered radiation) into Darwin's theoretical treatment of the reflexion of X-rays in ideal crystals led to an asymmetric distribution of intensity of the spectral lines around the angle which is given by Bragg's relation corrected for refraction. In cases of strong absorption this asymmetry, although not large, nevertheless requires in precision measurements a noticeable displacement of the "centres of gravity" of the spectral lines. The absorption has also an appreciable although not large influence on the integrated reflexion. W. GOOD.

**Arrangement of the micro-crystals in compressed single-crystal plates of aluminium.** II. Y. FUKAMI (Mem. Coll. Sci. Kyoto, 1930, A, 13, 229—237).—On compression of a flat single-crystal plate of aluminium the new micro-crystals formed by the breaking up of the large crystal rotate about the (111), (110), or (112) axis until their (110) planes become nearly parallel to the flat surface. The maximum angle of rotation attains its greatest value with a reduction of 35—50% in the thickness of the specimen. With circular plates compressed to less than 30% of their original thickness the micro-crystals begin to rotate about the (110) axis, which is perpendicular to the flat surface. A. R. POWELL.

**Structure of rolled and of recrystallised sheet iron.** G. KURDJUMOV and G. SACHS (Z. Physik, 1930, 62, 592—599).—The orientation of the crystals in rolled electrolytic iron is determined from the reflexions of low order of a beam of monochromatic X-rays (Mo-K $\alpha$  rays). Photographs of the reflexions give rise to a series of characteristic concentric rings for each different crystallographic face. Owing to the orientation of the crystals these rings are more intense at certain points, and the intensity relations vary with the angle between the beam and the direction of rolling. The results are represented in the ordinary crystallographic way by stereographic projection (polar figure) of the polar sphere of the directions of reflexion. Two degrees of intensity are estimated and represented in these figures, which are drawn for the (110) and for the (200) faces. It is shown that these figures cannot be explained by one single orientation of the crystals as suggested by Konobejewski, but that three simultaneous orientations in which the (100), (112), (111) faces, respectively, are parallel to the plane of rolling, and the (011), (110), (112) directions parallel to the direction of rolling, the last orientation being weaker than the others, would explain the distribution of both degrees of intensity. The polar figures for the (200) and (110) faces of iron recrystallised between 550° and 840° were likewise obtained, and could be explained only by a similar triple orientation. A simple relation is found to exist between the orientations in the rolled and recrystallised iron, two orientations in the recrystallised metal being obtained from those of the rolled metal by rotation through an angle of about 15° in the plane of rolling, whilst the third orientation is identical in both cases, although the relative intensities of the various orientations are different in



the two cases. Samples recrystallised at temperatures above the point of transition into  $\gamma$ -iron showed a structure similar to that of the recrystallised  $\alpha$ -iron, showing that in the change from  $\alpha$ - to  $\gamma$ -iron the two modifications take up a definite relative orientation.

H. A. JAHN.

**Crystal structure of krypton.** W. H. KEESOM and H. H. MOOY (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 447—449).—Debye-Scherrer photographs have been taken with solid krypton at the b. p. of hydrogen, using Cu- $K\alpha$  radiation and unfiltered iron radiation. The lines may be interpreted as reflexions from the planes of a face-centred cubic lattice with a lattice constant of 5.59 Å. The calculated density at  $-252.5^\circ$  is 3.13. The distance between the centres of neighbouring krypton atoms is 3.95 Å. The ratio of this distance to the diameter of the molecule calculated from viscosity measurements ( $3.23$  Å.) is 1.22, the corresponding ratios for neon, argon, and xenon being 1.35, 1.29, and 1.23, respectively.

J. W. SMITH.

**Polar properties of single crystals of ice.** J. M. ADAMS (Proc. Roy. Soc., 1930, A, 128, 588—591).—Photographs are reproduced of single microscopic ice crystals, grown under controlled conditions. A short right hexagonal prism, with the height nearly equal to the diameter of the base, is a frequently occurring shape for these small crystals. A number of specimens give evidence of crystallographic polarity by the appearance of a jut at one end only of the  $C$  axis when the crystal is brought into an atmosphere favourable to evaporation. Two other types of disintegration, characterised respectively by juts at each end and in the middle of the  $C$  axis, are observed in crystals of the same external form. These two types are explained as being due to the two possible modes of twinning of a polar crystal on the basal plane. The conclusion that the  $C$  axis in ice is a polar axis is not necessarily contradictory to the conclusion reached by Barnes that the (0001) plane must be a plane of symmetry so far as the arrangement of oxygen ions in the lattice is concerned (this vol., 20). It is possible that the asymmetric location of hydrogen ions in a non-polar oxygen lattice confers the necessary polarity on the structure as a whole.

L. L. BIRUMSHAW.

**Polymorphism of sodium sulphate. IV. X-Ray analysis.** F. C. KRACEK and C. J. KSANDA (J. Physical Chem., 1930, 34, 1741—1744; cf. this vol., 231).—Three forms of sodium sulphate have been detected by the powder method.  $\text{Na}_2\text{SO}_4$ -I is stable above  $240^\circ$ ,  $\text{Na}_2\text{SO}_4$ -V, or thenardite, is stable at the ordinary temperature, and  $\text{Na}_2\text{SO}_4$ -III is metastable below  $185^\circ$ , but is inert, when dry, at the ordinary temperature. The constants of the diffraction lines of the various patterns are recorded.

L. S. THEOBALD.

**Crystalline form of zirconium dioxide in relation to its previous history.** W. M. COHN and S. TOLKSDORF (Z. physikal. Chem., 1930, B, 8, 331—356; cf. Ruff and Ebert, B., 1929, 474).—By X-ray examination the existence of three polymorphic varieties of zirconium dioxide has been demonstrated. The  $C$  form, which is monoclinic, is stable up to about

$1000^\circ$ , above which it passes into the  $B$  variety (tetragonal), the change being reversible. On prolonged heating of the former variety at  $1900^\circ$  or above, the  $A_1$  form, which is either trigonal or pseudo-hexagonal rhombic, results. From an investigation of the thermal expansion of this variety it appears that there is a transition point at about  $625^\circ$ , below which the  $A_2$  form is the stable modification. Apparently the  $C$  variety can be converted into the  $A_2$  variety by prolonged heating, this process being, however, irreversible. In samples of the oxide containing magnesium oxide the presence of a cubic lattice has been detected.

R. CUTHILL.

**Crystal structure of hydrogen iodide and its relation with that of xenon.** G. NATTA (Nature, 1930, 126, 96).—The lines obtained for hydrogen iodide at  $-170^\circ$  correspond with a face-centred cube,  $a$  6.18 Å. The cell consists of 4 mols. and  $d_{\text{calc.}}$  is 3.59. The lattice constant of hydrogen iodide is practically identical with that of xenon (this vol., 528), confirming the view that the ionic radius of  $\text{I}^-$  is very near the atomic radius of Xe.

L. S. THEOBALD.

**Structure of nepheline and analcite.** E. SCHIEBOLD (Naturwiss., 1930, 18, 705—706).—Nepheline from Parco Chigi (Starrabba, A., 1920, ii, 550) has  $a$  10.1,  $c$  8.51 Å., space-group  $C_{6v}^{22}$ ,  $8\text{NaAlSiO}_4$  in the unit cell. The structure is that of  $\alpha$ -tridymite ( $a$  0.5  $\times$  10.06,  $c$  8.02 Å., with  $16\text{SiO}_2$  in 4 unit cells). The groups  $\text{SiO}_4$  and  $\text{AlO}_4$ , as in the feldspars, form a framework linked by oxygen, in which the  $\text{Na}^+$  ions are enclosed. The symmetry of analcite is not cubic but at most tetragonal, space-group  $D_{2h}^{22}$ , with  $\text{Si}^{\text{IV}}$  and  $\text{Al}^{\text{III}}$  in two layers,  $32g$  and  $16d$ , in accordance with the ratio  $2\text{Si} : \text{Al}$ , forming with oxygen a framework as in nepheline with  $\text{Na}^+$  ions similarly distributed. The  $\text{H}_2\text{O}$  molecules have definite positions (in contradistinction to most zeolites), but are weakly attached owing to the electrically neutral framework (cf. oxygen in antimony oxide; Dehlinger, this vol., 138).

C. A. SILBERRAD.

**Crystal structure of thallos hydrogen fluoride.** O. HASSEL and H. KRINGSTAD (Z. anorg. Chem., 1930, 191, 36—42).—X-Ray examination shows the crystals of thallos hydrogen fluoride to belong to the cubic system with the probable space-grouping  $T_h^h$ , the unit cell containing 8 mols. R. CUTHILL.

**Crystal structure of bastnäsite.** I. OFTEDAL (Z. Krist., 1929, 72, 239—248; Chem. Zentr., 1930, i, 1611).—Bastnäsite,  $\text{MFCO}_3$ , where M is Ce, La, etc., has  $c$   $4.859 \pm 0.004$ ,  $a$   $7.094 \pm 0.007$  Å. (crystallographically,  $c : a = 0.67986$ ); the unit cell contains 3 mols.; probable space-group  $D_{3h}^{12}$ .

A. A. ELDRIDGE.

**Crystal habit of zinc blende.** G. KALB and L. KOCH (Zentr. Min. Geol., 1929, A, 353—357; Chem. Zentr., 1930, i, 1114).—Zinc blende is referred to the octahedral isoharmonic crystal type; two forms, respectively black and reddish-brown to reddish-yellow, are distinguished.

A. A. ELDRIDGE.

**Crystal lattice of eulytine,  $\text{Bi}_2\text{Si}_2\text{O}_{12}$ .** G. MENZLER (Zentr. Min. Geol., 1928, A, 420—421; Chem. Zentr., 1929, i, 1557).—Powder photographs show a

cubic, space-centred lattice,  $a_c$   $10.25 \pm 0.02$  Å.;  $d$   $6.32 \pm 0.21$ . Assuming a mol. wt. 1109, there are 3.7 mols. in the unit cell. L. S. THEOBALD.

**Scapolite group.** B. GOSSNER and K. BRÜCKL (Jahrb. Min., 1928, A., 58, 349—384; Chem. Zentr., 1929, i, 1559; cf. A., 1928, 693).—Nine new analyses of scapolites of different origin are considered together with the physical constants. The results of X-ray examinations are tabulated. The mineral consists of three plagioclases+one salt, and in the end member extensive replacement must be possible. The results do not decide between a space-group  $C_{4h}^2$  with  $a$  17.25 and  $c$  7.65 Å. and 4 mols. of scapolite, and  $C_{4h}^1$  with  $a$  12.21 and  $c$  7.65 Å. with 2 mols., but the former is preferred. L. S. THEOBALD.

**[Crystallography of] theelin.** C. B. SLAWSON (J. Biol. Chem., 1930, 87, 373—374; cf. this vol., 821).—Theelin forms monoclinic crystals usually rhomboid in outline with included angles  $112^\circ$  and  $68^\circ$ . They are optically negative:  $n_a$  1.520,  $n_\beta$  1.642,  $n_\gamma$  1.692 (all  $\pm 0.003$ ), and  $2V$   $50-55^\circ$ .

C. R. HARRINGTON.

**$\alpha$ - and  $\beta$ -Crystals of fatty acids.** J. THIBAUD and F. DUPRÉ LA TOUR (Compt. rend., 1930, 191, 200—202).—The lozenge-shaped  $\beta$ -crystals of stearic acid (this vol., 740) are monoclinic, with a plane of symmetry normal to the plane faces. They differ from the  $\alpha$ -crystals of palmitic acid only in that the plane of symmetry passes through the bisector of the obtuse instead of the acute angle of the faces. Both crystals are strongly refractive and X-ray measurements showed that the crystal units had rectangular bases of dimensions 9.36 and 4.95 Å. for palmitic acid ( $\alpha$ ), and 5.65 and 7.36 Å. for stearic acid ( $\beta$ ), the acute angles of the lozenge being  $55^\circ$  and  $74^\circ$ , respectively. The spacing of the crystalline strata parallel to the principal faces decreases by 10% on passing from the  $\beta$  to the  $\alpha$  form, so that the volume of the unit is practically unchanged. J. GRANT.

**Atomic separation in tetrahedral crystals.** K. F. NIESSEN (Physikal. Z., 1930, 31, 610—616).—For elements in the same horizontal row of the periodic classification the atomic distances increase slightly, in the direction diamond type  $\rightarrow$  wurtzite type, although the increases in the differences are small compared with those in ionic lattices. So far as compounds of elements of groups III and V are concerned, the increase is negligible, but, with greater horizontal distances,  $u$ , from group IV, the increase varies as  $u^2$ . The binding force is considered mathematically as the difference between the electron attraction and the repulsion of the positively-charged nuclei, and the deduced equations are applied to the theory of crystal lattices. W. R. ANGUS.

**Space-filling numbers of crystalline salts.** W. HERZ (Z. anorg. Chem., 1930, 191, 60—61).—The space-filling numbers of various crystalline salts have been calculated from refractivity data, the average value being found to be about 0.33 (cf. A., 1923, ii, 801). R. CUTHILL.

**Pleochroism and crystal structure.** K. S. KRISHNAN and A. C. DASGUPTA (Nature, 1930, 126, 12).—The absorption of polarised ultra-violet light in

crystals of sodium and potassium nitrates has been examined. The selective absorption at 3000 Å., which appears in aqueous solutions, is shown in the crystals only when the vibrations are in the plane of the  $\text{NO}_3$  ions; vibrations perpendicular to this plane are freely transmitted. Beyond 2600 Å., there is another region of strong absorption in the crystals polarised in the same direction as the 3000 Å. band. Silberstein's theory of molecular refractivity receives support.

L. S. THEOBALD.

**Gyromagnetic effect for paramagnetic substances. I. Description of method and results for dysprosium oxide.** W. SUCKSMITH (Proc. Roy. Soc., 1930, A, 128, 276—293).—Measurements by previous investigators of the gyromagnetic ratio for ferromagnetic substances have shown that the source of magnetic moment is due to the spin of the electron. Evidence from various sources indicates that in paramagnetic substances the magnetic moment arises from both spin and orbital contributions, and this is confirmed by measurements of the gyromagnetic ratio for dysprosium oxide. Assuming that the paramagnetic ion is free, the value of the gyromagnetic ratio involves the Landé splitting factor  $g$ , which is found to be  $1.28 \pm 0.07$  for the  $\text{Dy}^{+++}$  ion in dysprosium oxide. This is in good agreement with the theoretical value  $4/3$ , corresponding with the  $^6H_{15/2}$  state deduced by Hund as being the most probable for this ion.

L. L. BIRCHUMSHAW.

**Diamagnetism of ions.** P. WEISS (J. Phys. Radium, 1930, [vii], 1, 185—193).—See this vol., 277.

**Magneto-chemistry of the dia- and paramagnetic metals and alloys.** H. J. SEEMANN (Z. tech. Physik, 1929, 10, 399—408; Chem. Zentr., 1930, i, 1750—1751).—A discussion.

A. A. ELDRIDGE.

**Magnetic transitions of regular ferric oxide.** H. SACHSE and R. HAASE (Z. physikal. Chem., 1930, 148, 401—412).—Measurements of the susceptibility of ferromagnetic ferric oxide, at different temperatures, indicate that the oxide is unstable at all temperatures. The susceptibility of a 4-year-old specimen had fallen by about 60% of its initial value, indicating that, even at ordinary temperatures, slow transition takes place. The times in which the susceptibility fell to half value were determined for the same specimen at different temperatures and varied from 8 min. at  $375^\circ$  to 4800 min. at  $170^\circ$ . The rate of transition was much smaller in a freshly-prepared sample and varied from 1 hr. at  $520^\circ$  to 1995 hrs. at  $270^\circ$ . Besides the fall of susceptibility due to actual transition there is also a fall of susceptibility with rise of temperature, so that, by heating for a time which is short compared with the time of transition, an apparent reversibility may be obtained, although true reversibility is not possible. There is a maximum temperature and minimum rate of cooling beyond which the phenomenon of apparent reversibility cannot be observed, the temperature being much higher for the freshly-prepared oxide. The results indicate the connexion between lattice type and the property of ferromagnetism and are in agreement with Heisenberg's theory of ferromagnetism (A., 1928, 1300). M. S. BURR.

**Magnetic and magneto-thermal properties of ferromagnetics.** E. C. STONER (Phil. Mag., 1930, [vii], 10, 27—48; cf. A., 1929, 1371).—Theoretical. Using the quantum modification of the Weiss theory of ferromagnetism, formulæ for the variation of magnetisation with field and temperature are derived, and tabulated in a form suitable for comparison with experiment. Expressions for the change of specific heat at the Curie point are given. Heisenberg's theory of ferromagnetism and certain resulting discrepancies with experiment are discussed. The gyro-magnetic ratio and the variations of magnetisation with temperature indicate that magnetisation in ferromagnetics is due to the change of orientation of electrons, the number per atom up to the Curie point, as indicated by saturation magnetisation and change of specific heat, being the same. Magnetic moments, above and below the Curie point, are discussed.

N. M. BLYTH.

**Ferromagnetic ferric oxide as a model for the Heisenberg theory of ferromagnetism.** H. SACHSE (Z. physikal. Chem., 1930, B, 9, 83—91).—Regular ferric oxide possesses ferromagnetism and will serve as a good model for the Heisenberg theory of ferromagnetism. The relationship between ferromagnetism and lattice structure is discussed, and it is shown that this property depends on the fields of neighbouring atoms.

A. J. MEE.

**Ferromagnetic theories of Weiss and Heisenberg.** K. HONDA (Z. Physik, 1930, 63, 141—148).—Theoretical. A discussion of Langevin's theory of paramagnetism, Weiss' and Heisenberg's theories of ferromagnetism, and of the work of Fowler and Kapitza on magnetostriction and the phenomena of critical points.

J. FARQUHARSON.

**Crystallographic investigation of some mechanical properties of metals. I, II.** Y. KIDANI (J. Fac. Eng. Tokyo, 1930, 19, 1—6, 7—15).—I. The form of aluminium crystals after plastic bending has been investigated by means of Laue photographs.

II. Rotational slip occurs in the uniform bending of aluminium crystal plates.

C. W. GIBBY.

**Stretching of gold-silver crystals.** G. SACHS and J. WEERTS (Z. Physik, 1930, 62, 473—493).—Gold-silver crystals behave like those of zinc-copper (cf. Göler and Sachs, *ibid.*, 1929, 55, 581). The breaking point has a maximum value in the alloy AuAg. Stress-strain curves are given for different proportions of silver to gold. Gold with small quantities of silver has a stress-strain curve like that of silver rather than like that of gold. The alloy always has a more definite breaking point than the pure metal, and the stress-strain curve is linear up to larger strains. The slip of atomic planes is less symmetrical in the alloy. A vacuum oven for melting gold-silver crystals is described.

A. B. D. CASSIE.

**Cohesive properties of anhydrous calcium chloride crystals.** G. HEYSE (Z. Physik, 1930, 63, 138—140).—In agreement with Slawson (A., 1929, 1264) a tetragonal (or rhombic pseudo-tetragonal) structure is deduced for artificially prepared single crystals of anhydrous calcium chloride from goniometrical measurement of the planes of cleavage. The force of cohesion perpendicular to the (100) plane

was found to be 500 g./mm.<sup>2</sup>, and perpendicular to the (001) plane 2100 g./mm.<sup>2</sup>, although in the last case the crystal generally broke across an uneven surface consisting of (112) and a smaller number of (001) planes. The cubic structure of strontium chloride is shown by the perfect cleavage along the octahedral plane, and the force of cohesion across this (111) plane was found to be 1100 g. per mm.<sup>2</sup>

H. A. JAHN.

**Influence of a magnetic field on the passivity of metals.** U. SBOGCI and A. BORGIA (Gazzetta, 1930, 60, 449—468; cf. A., 1926, 1212).—Reasons are adduced for the assumption of a relationship between magnetisation and passivity and preliminary measurements have been made of the effect of a very strong magnetic field on the polarisation of anodes of iron, nickel, cobalt, and chromium in 15% sulphuric acid. The effect of magnetisation is marked in the case of iron and cobalt, but only slight for nickel. In general, the current density at which passivity occurs is increased in the magnetic field, and at the same time the anode potential may be increased somewhat above its usual value before the metal becomes passive. The effect of the magnetic field becomes negligible at higher potentials.

F. G. TRYHORN.

**Random nature of molecular motion. II.** W. JAZYNA (JACYNO) (Z. Physik, 1930, 62, 846—851).—Molecular motion is regarded as partly disordered and partly as ordered motion and the regularity and distribution coefficients are calculated for different gases. For monatomic gases the "heat" mol. wt. differs by about 0.5—1.5% from the true mol. wt.

A. J. MEE.

**Diamagnetism and sub-molecular structure.** F. W. GRAY and J. FARQUHARSON (Phil. Mag., 1930, [vii], 10, 191—216).—Theoretical. The diamagnetic susceptibility of a g.-atom is considered in relation to the expressions obtained by wave mechanics, and by Pauling from quantum mechanics (cf. A., 1927, 394). A discussion is given of the relation of diamagnetism to covalency and electrovalency linkings, and the diamagnetic changes brought about by the closer approach of the widely-separated ions of a neutral group to form a molecule, and afterwards, by an imaginary forced merging of the ionic nuclei, to form a single merger atom; the relation of the experimental molecular diamagnetism to the theoretical values for the neutral group and for the merger atom is examined. Van Vleck has developed an expression for the atomic susceptibility (cf. A., 1928, 572), the terms of which are considered with reference to Pauling's values. After the formation of a molecule all the atomic diamagnetisms are subject to a depression, which is partly due to fluctuation of angular momentum. The increment of diamagnetism when a pair of electrons is added to a given ion, the effective nucleus acting on each electron, and ionic diamagnetic susceptibilities are tabulated for a number of ions. The data and theory developed are applied to various trial structures of the diamagnetic molecules of water, ammonia, hydrogen peroxide, the halides of ammonium and potassium, the hydrochlorides of hydroxylamine, hydrazine, and methylamine, the methyl sub-

stitution derivatives of ammonium, the halogenates and perhalogenates of potassium, iodic and periodic acids, iodine pentoxide, and the change from halide to halogenate and from halogenate to perhalogenate.

N. M. BLIGH.

**Crystal structure, electrical resistance, thermo-electric force, conductivity for heat, magnetic susceptibility, hardness, and ageing phenomena of the system Au-Pt, in combination with phase-rule diagram.** C. H. JOHANSSON and J. O. LINDE (Ann. Physik, 1930, [v], 5, 762—791).—The gold-platinum system was investigated in the solid state by electrical resistance and X-ray structure methods. The results show, in agreement with the phase diagram of Doerincel, but in contradiction to that of Grigoriev, that beneath the solidus curve there is an uninterrupted mixed-crystal area. Below 1150° a second phase is present, the width in the diagram increasing with fall of temperature. The single-phase alloy supercooled to the ordinary temperature was also investigated for electrical conductivity and lattice structure, thermo-electric force per degree, magnetic susceptibility, and hardness. A supersaturated alloy, aged at low temperatures, was also used for the determination of hardness and magnetic susceptibility. The ageing phenomena were also investigated by determining electrical resistance and lattice structure. The results of this investigation lead to the assumption that at low temperatures there are homogeneous phases with a regular distribution of both types of atoms. It is also explained how the conductivity-concentration curve may be used to determine boundary concentrations between phases.

A. J. MEE.

**Change in the resistance of bismuth crystals in a magnetic field at the temperature of liquid hydrogen.** L. SCHUBNIKOV and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 418—432; cf. this vol., 675).—A crystal of bismuth which shows less residual resistance at 11.3° Abs. than those employed previously has been prepared. Qualitatively, however, the behaviour is completely analogous to that observed in the former experiments.

J. W. SMITH.

**Change in the resistance of bismuth crystals in a magnetic field at the temperature of liquid nitrogen.** L. SCHUBNIKOV and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 433—439).—The variation of the resistance of bismuth crystals at 77.40 and 64.25° Abs. with different intensities of magnetic field parallel or perpendicular to the binary axis has been investigated. The change in the ratio  $R_H/R_0$  with field strength at these temperatures is much simpler than at the temperature of liquid hydrogen. The values obtained with different crystals are in good agreement with one another but differ considerably from the results of other authors.

J. W. SMITH.

**Measurements with the aid of liquid helium. VIII. Superconductivity of niobium.** W. MEISSNER and H. FRANZ (Z. Physik, 1930, 63, 558—560).—A Dicselhorst compensation apparatus was used in the determination of the resistance of the niobium specimen. The latter became superconducting be-

tween 8.74° and 8.18° Abs. Possible error in this result due to the presence of some metallic impurities in the niobium is considered.

W. GOOD.

**Measurement of the contact potentials of some metals.** M. FORRO and E. PATAI (Z. Physik, 1930, 63, 444—457).—The method consisted in determining the parallel displacement of the characteristic curve of a three-electrode tube which results from alteration of the grid. Molybdenum, platinum, tungsten, nickel, copper, and iron were compared with sodium, which proved to be very suitable for alternate deposition and removal from the grid surface. The values of the contact *P.D.* found agree well with the energy differences corresponding with the photo-electric critical frequencies of the metals in question. Mercury was also used as a standard to determine the contact *P.D.* between molybdenum and mercury. The method was extended to measurements at high temperatures and showed independence of contact *P.D.* on temperature up to about 800°. W. GOOD.

**Existence of electronic isomerides in the solid state and in solution. Magnetic susceptibility of  $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and its variations with temperature.** S. FREED (J. Amer. Chem. Soc., 1930, 52, 2702—2712).—A modified Gouy method has been applied to the determination of the magnetic susceptibility of  $\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  at temperatures between 73.8° and 290.6° Abs. In this range, the susceptibility of the samarium ion ( $\text{Sm}^{++}$ ) changes by about 40%, and hence Curie's law is not obeyed. It is concluded that samarium ions in the solid state and in solution consist of a mixture of electronic isomerides which are in thermal equilibrium, and an electronic configuration for the isomeride stable at the lowest temperature is suggested (cf. Freed and Spedding, A., 1929, 490).

J. G. A. GRIFFITHS.

**Surface conductivity of compressed amber.** E. LEISTE (Z. Physik, 1930, 62, 646—672).—An elaborate investigation has been carried out on the surface and volume resistivity of compressed amber (amberite) cylinders on account of the growing use of this material in electrometer construction. The influence of the applied potential, state of surface, atmospheric humidity, and dust has been examined over a very wide range of conditions. When the humidity reaches 30% the volume conductivity becomes negligible in comparison with that over the surface.

R. W. LUNT.

**Magnetic susceptibility of gases. I. Pressure dependence.** F. BITTER (Physical Rev., 1930, [ii], 35, 1572—1582).—In order to investigate certain anomalies reported by Glaser (cf. this vol., 277, 278) the magnetic susceptibility was investigated by an improved method of measuring the torque exerted by a gas on a test body in a non-homogeneous field. The volume susceptibility of carbon dioxide, nitrogen, and hydrogen was found to be proportional to the pressure. Deviations from proportionality as observed by Glaser were found for these gases on introducing as impurity an amount of water vapour of the order 0.01%.

N. M. BLIGH.

**Intensive drying of liquids.** A. SMITS (J. Physical Chem., 1930, 34, 1861—1865).—A reply to

Lenher (A., 1929, 1372). The superheating of liquids is discussed, and it is claimed that the author's previous work is not invalidated by this phenomenon.

L. S. THEOBALD.

**Heat capacities of bismuth and bismuth trioxide at low temperatures.** C. T. ANDERSON (J. Amer. Chem. Soc., 1930, 52, 2720—2723).—The specific heat of bismuth and of bismuth trioxide at temperatures between 61° and 298° Abs. has been determined and the results have been fitted to Debye and Einstein functions. The corresponding entropies at 298° Abs. are 12.4 and 36.2 units, respectively. The free energy of bismuth trioxide is computed to be -118,000 g.-cal.

J. G. A. GRIFFITHS.

**Heat capacities at low temperatures of antimony, antimony trioxide, antimony tetroxide, and antimony pentoxide.** C. T. ANDERSON (J. Amer. Chem. Soc., 1930, 52, 2712—2720).—Data for temperatures between 60° and 295° Abs. are tabulated, and are fitted to Debye and Einstein functions. The corresponding entropies at 298° Abs. are 10.5, 29.4, 30.3, and 29.9 units, respectively. The heat of formation at 25° of orthorhombic antimony trioxide is -167,300 g.-cal.

J. G. A. GRIFFITHS.

**Heat capacity of silicon at low temperatures.** C. T. ANDERSON (J. Amer. Chem. Soc., 1930, 52, 2301—2304).—The specific heat of "metallic" silicon at temperatures between 61° and 296° Abs. has been determined and the entropy (in g.-cal. per 1°) at 25° is computed to be  $4.52 \pm 0.05$ .

J. G. A. GRIFFITHS.

**Heat capacities of arsenic, arsenic trioxide, and arsenic pentoxide at low temperatures.** C. T. ANDERSON (J. Amer. Chem. Soc., 1930, 52, 2296—2300).—The above have been determined at temperatures from about 57° to 296° Abs. and the corresponding entropies (in g.-cal. per 1°) at 25° are calculated (8.4, 25.6, and 25.2, respectively). The free energy of formation of arsenic pentoxide ( $\Delta F^\circ_{298}$ ) is computed to be -185,400 g.-cal. per mol.

J. G. A. GRIFFITHS.

**Determination of the ratio of the specific heats ( $C_p/C_v$ ) of helium gas at the b. p. of oxygen by means of the velocity of sound.** W. H. KEESOM and A. VAN IJTERBEEK (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 440—446).—A resonance method is described for determining the velocity of sound in gases at low temperatures, using a closed tube with variable length and constant frequency. The velocity of sound in helium at -182.90° and 76.5° c'm is 559.1 m. per second. Hence, correcting to zero pressure,  $C_p/C_v = 1.661$ .

J. W. SMITH.

**Specific heats of nitrous oxide, ammonia, and hydrogen fluoride from 10° Abs. upwards.** K. CLUSIUS, K. HILLER, and J. V. VAUGHEN (Z. physikal. Chem., 1930, B, 8, 427—439).—The specific heats of nitrous oxide, ammonia, and hydrogen fluoride have been determined from 10° to 178°, 134°, and 77° Abs., respectively. For ammonia below 20° the molecular heat,  $C_p$ , is given by the equation  $C_p = 4.73 \times 10^{-5} T^3$ , where  $T$  is the temperature. The experimental data for hydrogen fluoride suggest association even in the solid state. The  $C_p$ -temperature curve for nitrous oxide is closely similar to that for carbon dioxide, and

necessitates the assumption that the atoms composing the molecule are arranged in a straight line, probably thus: N·O·N. By the statistical method the value of the vapour-pressure constant is found to be 0.695, whereas the figure  $0.857 \pm 0.07$  is obtained thermodynamically.

R. CUTHILL.

**Exact measurement of the specific heats of solid substances at high temperatures. III. The specific heats of palladium and of tungsten.** F. M. JAEGER and E. ROSENBOHM (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 457—472; cf. A., 1928, 469, 696).—An improved method for the determination of specific heats at high temperatures is described. The specific heat of palladium has been determined at various temperatures up to its m. p. (1549.2°) and also in the liquid state just above its m. p. There is a maximum value of  $c_p$  at about 1520°, although no allotropic transformations occur below the m. p. The atomic heat  $C_v$  exceeds the value of  $3R$  g.-cal. at 148°, after which it increases with rising temperature, attaining a maximum at about 1320° and falling again to the m. p. There is no theory to account for this behaviour. The specific heat of tungsten has been measured up to 1604°. In both cases the values of the atomic heats for each 100° over the temperature ranges investigated are tabulated.

J. W. SMITH.

**Specific heat of barium nitrate from 15° to 300° Abs. Entropy of the nitrate ion.** H. M. LATIMER and J. E. AHLBERG (Z. physikal. Chem., 1930, 148, 464—470).—The specific heat of barium nitrate has been determined between 15° and 300° Abs. and thence the entropy of barium nitrate, at 298.1° Abs., calculated to be  $51.1 \pm 0.4$  g.-cal. per degree. In combination with earlier data for the entropy of the barium ion (A., 1926, 1102), this gives 35.3 g.-cal. per degree per g.-mol. for the entropy of the nitrate ion in a molar solution referred to entropy  $H^+ = 0$ . The free energy of formation of the nitrate ion, calculated from thermal data, is -26,050 g.-cal. The value obtained by Lewis and Randall from equilibrium constants is -26,500 g.-cal. The influence of hydration on the vibration energy of the nitrate ion is discussed.

M. S. BURR.

**Critique of the electrical differential method of measuring the specific heats of gases at constant volume. IV. Determinations. Standardisation with argon.** M. TRAUTZ and F. KAUFMANN (Ann. Physik, 1930, [v], 5, 581—605).—Previous determinations of the specific heats of gases at constant volume have taken air for a standard. Measurements of air against argon and the introduction of the assumption  $C_p = 3R/2$  have removed this difficulty. The values for the specific heats of air and of methane at constant volume against argon are, respectively, 4.955 and 6.57 g.-cal. (at 20°).

A. J. MEE.

**Calculation of latent heats of vaporisation of the normal paraffin hydrocarbons, using specific heat data.** J. W. SCHULTZ (Ind. Eng. Chem., 1930, 22, 785—788).—The molal entropies of vaporisation of the series methane to  $C_{19}H_{40}$  have been calculated for various pressures from 760 mm. to the critical pressures and have been used to calculate the latent

heats. Charts showing molal entropy of vaporisation as a function of mol. wt. for pressures between 760 and 18,000 mm. and molal heat of vaporisation as a function of temperature for normal hydrocarbons are reproduced.

L. S. THEOBALD.

**Vapour pressure of nickel carbonyl.** J. S. ANDERSON (J.C.S., 1930, 1653—1656).—Concordant values for the vapour pressure of nickel carbonyl can be obtained only after the removal of all adsorbed air from the apparatus. The vapour pressure can be represented by the equation  $\log p = 7.690 - 1519/T$  between  $40^\circ$  and the triple point,  $-22^\circ$ . Values of the vapour pressure of the solid at  $-25^\circ$ ,  $-30^\circ$ , and  $-35^\circ$  are given. The latent heat of vaporisation is calculated to be 6920 g.-cal. per mol. C. W. GIBBY.

**Vapour pressure and vapour density of sodium.** W. H. RODEBUSH and E. G. WALTERS (J. Amer. Chem. Soc., 1930, 52, 2654—2665).—The vapour pressure of sodium has been determined at temperatures between  $650^\circ$  and  $845^\circ$  by a static method, and the data, together with those of Rodebush and de Vries (A., 1925, ii, 1142) and Edmondson and Egerton (A., 1927, 103), are reproduced satisfactorily by the equation  $\log p(\text{mm.}) = 7.5510 - 5400.0/T$ . The vapour density has been determined at  $705.8^\circ$  and  $570.5^\circ$ , and the corresponding apparent mol. wts. are 24.1 and 25.1, the latter being in fair agreement with the spectroscopic value.

J. G. A. GRIFFITHS.

**Vapour pressure of allene as a function of temperature.** R. LIVINGSTON and G. B. HEISIG (J. Amer. Chem. Soc., 1930, 52, 2409—2410).—The vapour pressure of allene at temperatures between  $-76.0^\circ$  and  $-36.5^\circ$  is reproduced by the relation  $\log p(\text{mm.}) = -0.05223 \times 20,852/T + 7.455$ . The normal b. p.  $-35.0^\circ$  is computed.

J. G. A. GRIFFITHS.

**Vapour pressure of silicon tetrafluoride.** W. I. PATNODE and J. PAPISH (J. Physical Chem., 1930, 34, 1494—1496).—The triple point is at  $-90.2^\circ$  and 1318 mm. and the sublimation temperature at 1 atm., derived from the vapour pressure-temperature curve, is  $-95.7^\circ$ . For the solid-vapour curve  $\log p = -1346.2/T + 10.48$  and for the liquid-vapour curve  $\log p = -975.0/T + 8.453$ .

L. S. THEOBALD.

**B. p. and vapour-pressure formulæ for organic compounds.** W. HERZ (Z. anorg. Chem., 1930, 191, 62—64).—For temperatures between the b. p. and about  $100^\circ$  below, the vapour pressure,  $p$ , of many organic liquids may be satisfactorily represented by the equation  $\log p = -A/T + C$ , where  $T$  is the temperature and  $A$  and  $C$  are constants. The relationship between the value of  $A$  and the b. p. previously observed for inorganic compounds (this vol., 403) is valid here also.

R. CUTHILL.

**Saturation pressure.** W. HERZ (Z. Elektrochem., 1930, 36, 300—301; cf. A., 1928, 470).—The temperature at which the saturation pressure sinks to one half or one tenth of its critical pressure forms a constant fraction of its critical temperature, the behaviour thus being the same as in the case of the density of the saturated vapour (cf. A., 1925, ii, 494, 850). Below the critical point the density of the

saturated vapour diminishes with fall of temperature more rapidly than the saturation pressure.

J. W. SMITH.

**Density and compressibility of phosphine gas; atomic weight of phosphorus.** M. RITCHIE (Proc. Roy. Soc., 1930, A, 128, 551—579).—Determinations have been carried out, by means of the density-globe method, of the density of gaseous phosphine at pressures of 1,  $\frac{3}{4}$ ,  $\frac{1}{2}$ , and  $\frac{1}{4}$  atm., the temperature in each case being that afforded by crushed and moistened ice. The gas was prepared by the action of dilute potassium hydroxide solution on solid phosphonium iodide. Two density globes of the ordinary stopcock type were employed, each being roughly 350 c.c. in volume and 80 g. in weight, and each being provided with a counterpoising bulb of which the external volume differed from that of the corresponding globe by less than 0.2 c.c. Weighings were carried out by means of a Staudinger balance, the weights of gas involved ranging from 0.52 g. at 1 atm. to 0.13 g. at  $\frac{1}{4}$  atm. The apparatus was constructed entirely of soft glass, with the exception of the rubber joints used to attach the density globes. Full details are given of the phosphorus pentoxide tubes, the mano-barometer, the cathetometer, and the vacuumeter. In the standardisation of the density globes, Travers' method was used for the determination of the contraction in volume on evacuation ("Study of Gases," p. 120), and Germann's method for the determination of the internal volume of the globes (J. Physical Chem., 1915, 19, 463). The value obtained for the normal density is  $L_N = 1.5307$ , and the factor for compressibility between 0 and 1 atm. pressure is  $(1 + \lambda) = 1.0091$ . From this the mol. wt. of phosphine is calculated to be 34.000 and the at. wt. of phosphorus 30.977, representing a difference of 1 in 6000 from Aston's value of 30.982 (A., 1927, 914). The estimated accuracy is of the order of 1 in 10,000.

L. L. BIRCUMSHAW.

**Density of glycine.** R. C. HOUCK (J. Amer. Chem. Soc., 1930, 52, 2420).—Contrary to previous statements, glycine has  $d_4^{20} 1.575$ .

J. G. A. GRIFFITHS.

**Derivation of a general formula for the temperature dependence of the specific gravity of homogeneous liquids from experimental observation and in relation to similar problems.** E. SALZWEDEL (Ann. Physik, 1930, [v], 5, 853—886).—A mathematical equation expressing the dependence on temperature of the value of the specific gravity of homogeneous liquids has been successfully derived from data on the specific gravity of water; it is equally applicable for all data irrespective of pressure. Good results were obtained when the formula was applied to carbon tetrachloride, ethyl and methyl alcohol, and mercury. All the calculated examples show a variance with published data and an explanation of this discrepancy is offered. It has been shown that the applicability of previous equations to special cases only was due to the fact that the dependence of the value of the specific gravity on the temperature ends at the critical point; no account of this had been taken by other investigators. The shape of the vapour-pressure and vapour-density curves can be deduced from data on the temperature



dependence of the specific gravity. Experimentally it was found that the critical temperature of methyl alcohol was  $240^{\circ}$ , its critical pressure 99 atmospheres, its m. p.  $-98.2^{\circ}$ , and the specific gravity of the liquid phase at the critical temperature 0.3587 g. per c.c.

W. R. ANGUS.

**Variation with temperature of the density and mol. wt. of fused cadmium.** A. JOUNIAUX (Bull. Soc. chim., 1930, [iv], 47, 524—528).—The density of liquid cadmium was measured by means of a modified hydrostatic balance between  $325^{\circ}$  and  $767^{\circ}$ . It is a linear function of temperature, and the extrapolated values at the b. p. and m. p. are 7.54 and 8.02, respectively. The mol. wt. of cadmium is calculated for several temperatures from the Eötvös-Ramsay-Shields equation and from cryoscopic experiments on cadmium in liquid metal solutions. Cadmium is monatomic between  $250^{\circ}$  and  $900^{\circ}$ ; in any case, combination of atoms to form a molecule is only a feeble endothermic reaction. S. K. TWEEDY.

**Variation with temperature of the density and mol. wt. of fused silver.** A. JOUNIAUX (Bull. Soc. chim., 1930, [iv], 47, 528—531).—The density of silver, measured between  $970^{\circ}$  and  $1302^{\circ}$  by means of a hydrostatic balance, is given by  $d^{-1} = 0.1071 + 117 \times 10^{-7}(t - 961.5)$  (cf. Krause and Sauerwald, A., 1929, 993). From surface tension measurements on liquid silver and, more particularly, cryoscopic experiments in liquid metal solutions it is found that the silver molecule is monatomic between  $327^{\circ}$  and  $1950^{\circ}$ , in conformity with the author's rule that if a molecule is monatomic below the m. p. it is monatomic within the temperature limits studied. S. K. TWEEDY.

**Variation of the viscosity of a liquid with temperature.** E. W. MADGE (J. Physical Chem., 1930, 34, 1599—1606).—The formula  $\eta = Ae^{bT}/(\tau - b)$  holds for water, ethyl alcohol, benzene, octane, and propylene bromide, as well as for a number of other liquids.  $\tau$  is the relaxation time, and  $A$ ,  $b$ , and  $\beta$  are constants specific to a given liquid.

L. S. THEOBALD.

**Method for determining viscosity of corrosive gases and molecular diameter of nitrogen pentoxide.** H. EYRING and G. A. VAN VALKENBURGH (J. Amer. Chem. Soc., 1930, 52, 2619—2624).—The viscosity of nitrogen pentoxide vapour at  $4^{\circ}$  has been determined by a capillary-tube method. The molecular diameter is found to be  $8.53 \times 10^{-8}$  cm.

J. G. A. GRIFFITHS.

**Viscosity, heat conductivity, and diffusion in gas mixtures. VIII. Viscosity of hydrogen, helium, neon, and argon and their binary mixtures.** M. TRAUTZ and H. E. BINKELE (Ann. Physik, 1930, [v], 5, 561—580).—The viscosity coefficients of hydrogen, helium, neon, and argon were determined for different temperatures between  $20^{\circ}$  and  $250^{\circ}$ . The temperature coefficient of the viscosity was also determined. For hydrogen and helium it can be expressed by the formula  $\eta_1/\eta_2 = (T_1/T_2)^n$ , where  $n = 0.66$ , even for high temperatures. A different formula holds for neon, which forms the transition between the light and heavy gases. The equation here is  $\eta = KT^{0.5}[1/(1 + C/T)]$ . Argon obeys the Sutherland relationship. In the neighbourhood

of the critical temperature both  $n$  and  $C$  attain maximum values;  $n$  then decreases with rising temperature from a value a little above 1 to a limiting value between 0.5 and 0.6. The viscosity isotherms of the mixtures hydrogen-helium, hydrogen-neon, hydrogen-argon, helium-neon, helium-argon, and neon-argon were determined over the range  $20$ — $250^{\circ}$ . The mixture equation connecting the viscosity of a gaseous mixture with that of the two components separately is used to find the value of  $q$ , the cross-section ratio, and of  $F$ , a constant connected with the viscosities of the mixture and components by the relationship  $\eta_m^2 = F\sqrt{\eta_1\eta_2}$ . The cross-section ratio is within the error quotient for the constant for pure nitrogen. It lies between 0.45 and 1 for the six mixtures tested. A. J. MEE.

**Dielectric strengths of explosive mixtures containing carbon monoxide.** B. W. BRADFORD and G. I. FINCH (J.C.S., 1930, 1540—1546).—The dielectric strengths of "detonating gas" ( $2CO + O_2$ ) have been measured. It is found that (1) drying over phosphorus pentoxide increases the dielectric strength, (2) small additions of hydrogen reduce but do not inhibit the effect, and (3) successive small additions of steam to the dry gas first reduce and then increase the dielectric strength. The conclusion of Smithells, Whitaker, and Holmes (this vol., 428) that hydrogen is more effective than water vapour in conferring ignitability on detonating gas is criticised. H. I. DOWNES.

**Viscosity, heat conductivity, and diffusion in gas mixtures. IX. Knowledge of the concentration function of the diffusion constant of gases.** M. TRAUTZ and O. LUDWIG. X. Whole number relationships of constants and quantum numbers in viscosity of gases. M. TRAUTZ (Ann. Physik, 1930, [v], 5, 887—918, 919—928).—IX. The defects of the vaporisation method of determining the diffusion constant,  $D$ , are critically examined and the method has been modified by improved apparatus and technique as well as by quantitative calculation. Theoretically the values of  $D$  are differential, whilst integral values are obtained experimentally. From vaporisation experiments relative values of  $D$  are obtainable which are trustworthy to within 1%, but the errors in the absolute values are probably 2—3 times as great by reason of the indefiniteness of the cross-section and the height of the diffusion vessel. Results for benzene-oxygen and benzene-hydrogen mixtures were obtained at  $23^{\circ}$  with wide variations of the heights and times of diffusion and the velocity of the gas streams. The dependence of  $D$  on the relative concentration of the two gases is considered. The product of the diffusion and the square root of the mol. wt. is approximately constant for both mixtures and from this the diffusion constant of benzene is deduced as  $0.059$  cm.<sup>2</sup>/sec.

X. The invariant temperature constants of viscosity are defined and discussed, and the method of their calculation is indicated. The relative cross-section,  $q$ , is additively related to the at. wt.; for reactive gases  $q^2 = \{(n+1)/2\}\sqrt{A}$ , whereas  $q^2 = n\sqrt{A}$  for inert gases except helium, for which  $q^2 = 2n\sqrt{A}$ , where  $A$  is the at. wt. and  $n$  the principal quantum

number. The constants,  $F$ , the mean factor, and  $M\theta$ , the molecular temperature, are expressed in terms of the atomic numbers and mol. wt.; in each case a whole-number relationship exists. Numerical values of these factors are given for simple gases, gaseous mixtures, vapours, and compounds.

W. R. ANGUS.

**Systems water-acetic acid and acetic acid-acetic anhydride as a complete system water-acetic anhydride on the basis of vapour-pressure measurements.** K. P. MISCHTSCHENKO and S. J. TSCHERBOV (*Z. physikal. Chem.*, 1930, **148**, 386—393).—The authors' vapour-pressure measurements for the systems water-acetic acid and acetic acid-acetic anhydride are considered collectively from the point of view of the system water-acetic anhydride. Breaks in the curves obtained by plotting various properties such as total or partial vapour pressures or vapour densities as functions of the concentration of acetic anhydride occur at 50 mol.-%, indicating the presence of the compound acetic acid.

F. L. USHER.

**Electrical conductivity of butyric acid-water mixtures.** J. GRINDLEY and C. R. BURY (*J.C.S.*, 1930, 1665—1668).—The conductivity of various butyric acid-water mixtures at 0° and 25° shows a sharp maximum at about 12% acid concentration. The form of the solubility curve is discussed.

H. I. DOWNES.

**Dynamic azeotropism.** (Mlle.) G. SCHOUFS (*Bull. Acad. roy. Belg.*, 1930, [v], **6**, 628—645).—A mathematical investigation of the distillation of pure substances and mixtures.

E. S. HEDGES.

**Mechanism of mutual diffusion in solid bodies. Diffusion of gold in silver.** W. JOST (*Z. physikal. Chem.*, 1930, **B**, **9**, 73—82).—The velocity of diffusion of gold in silver, and its dependence on temperature and thickness of layer, have been measured. Over a range of 700° the diffusion constant can be expressed as a simple exponential function. The velocity is independent of the thickness of the layer, and obeys Fick's law. This result would be incompatible with a mechanism of mutual diffusion in which there were boundary surfaces or where specially favoured places played a part. It is inferred that mutual diffusion is a lattice phenomenon.

A. J. MEE.

**X-Ray analysis of copper-manganese alloys.** E. PERSSON (*Z. physikal. Chem.*, 1930, **B**, **9**, 25—42).—Copper-manganese alloys containing different amounts of copper have been examined. The  $\gamma$ -modification of manganese which is stable at higher temperatures can be fixed if it is alloyed with a certain amount of copper and chilled to the ordinary temperature. With increasing copper content the axial ratio of this face-centred tetragonal phase approaches unity. From the data for a series of alloys which have undergone different heat treatment it is possible to determine the boundary lines of the phases on the phase diagram for copper-manganese alloys. Outside the two copper-manganese phases the  $\alpha$ - and  $\beta$ -forms of manganese crystals were found. The solubility of copper in  $\alpha$ - and  $\beta$ -manganese cannot be found by an X-ray method. The lattice parameter of the copper phase increases with increasing manganese content at first rapidly and then, when the manganese

content is about 50 at.-%, it remains constant. The volume per atom in the two simple manganese-copper phases appears to change continuously throughout the whole system.

A. J. MEE.

**Limits of application of the electrical conductivity method in determining the constitution of alloys.** W. HUME-ROTHERY (*Metall. Wirt.*, 1929, **8**, 1243—1246; *Chem. Zentr.*, 1930, **i**, 1210).

**Ternary alloys of aluminium, silicon, and copper.** G. G. URASOV, S. A. POGODIN, and G. M. SAMORUEEV (*Min. Ssyrye Zwet. Met.*, 1929, **4**, 160—195; *Chem. Zentr.*, 1930, **i**, 1038—1039).—A study, by thermal analysis, of the aluminium triangle up to 24% Si and 40% Cu. The alloys in this domain consist of mechanical mixtures of silicon,  $\text{CuAl}_3$ , and a solid solution of silicon and copper in aluminium. The solubility of copper is increased by silicon in the interval 450—350°. The hardness of the ternary solid solutions was determined. Ageing of the alloys at the ordinary temperature diminishes with increasing content of silicon. The technical application of the results is considered.

A. A. ELDRIDGE.

**Solubility relations in gas-liquid systems. I. New apparatus for determining gas solubilities.**

**II. Solubility and rate of dissolution of oxygen in water.** J. L. R. MORGAN and H. R. PYNE (*J. Physical Chem.*, 1930, **34**, 1578—1582, 1818—1821).—I. The new apparatus involves repeated bubbling of the gas through a known volume of liquid at constant temperature and pressure. The apparatus has been checked by a determination of the solubility of carbon dioxide at 25°; the ratio of the volume of gas absorbed at 25° to the volume of liquid is 0.8265. The supersaturation feared by some investigators in the shaking method of saturation does not appear to occur.

II. The solubility of oxygen in water at 25° has been determined by means of the apparatus previously described (sec I above). The Ostwald solubility coefficient, is  $0.0310 \pm 0.0002$ , a value in agreement with those of previous investigators. The rate of dissolution of oxygen in water agrees with the equation of Adeney and Becker (*Phil. Mag.*, 1921, [vi], **42**, 81).

L. S. THEOBALD.

**Cause of periodicity generally occurring with rising mixtures of gas and liquid.** J. VERSLUYS (*Proc. K. Akad. Wetensch. Amsterdam*, 1930, **33**, 450—456).—The periodic flow observed when mixtures of gas and liquid rise in a vertical channel is attributed to the presence of foam and mist in the mixture. These dispersions, however, are never such as to prevent the phases from segregating owing to their difference in specific gravity. The difference in velocity of rise of the components is small in the foam condition, but greater in the mist, and it is to the oscillation between these two conditions that the periodic movement is attributed.

J. W. SMITH.

**Diffusion of organic substances in aqueous solutions of electrolytes.** H. FREUNDLICH and D. KRÜGER (*Z. Elektrochem.*, 1930, **36**, 305—309).—The diffusion of quinone, quinol, carbamide, and dextrose in pure water and in aqueous solutions of electrolytes has been investigated. The diffusion

of quinone in pure water follows Fick's law, the diffusion constant agreeing well with the value calculated from the mol. wt. by means of Euler's formula. On the other hand, the diffusion does not follow the law for the solutions, but the concentration in the uppermost layer attains abnormally high values. The anomaly increases with increasing electrolyte concentration, and varies with the nature of the electrolyte, being higher with oxygen-containing anions (sulphates, nitrates, and perchlorates) than it is with halides. Carbamide also shows normal diffusion in pure water, but behaves abnormally in cadmium chloride, potassium chloride, or sodium nitrate solution. Since carbamide is known to form complex compounds with these electrolytes, it is inferred that such complex formation also occurs in the case of quinone, with the production of rapidly diffusing ions containing the organic compound. Quinol shows the same behaviour as quinone, but less markedly, whereas the diffusion of dextrose in sodium nitrate solution appears to be exactly the same as in pure water.

J. W. SMITH.

**Solubilities of the soluble electrolytes. III.** The solubilities and densities of saturated solutions of the bromides and iodides of sodium and potassium between 0° and 92°. A. F. SCOTT and E. J. DURHAM (J. Physical Chem., 1930, 34, 1424—1438; cf. this vol., 537).—Data are recorded. The transition temperatures for sodium bromide and iodide are 50.2° and 68.1°, respectively. A new and simple technique for determining the densities of saturated solutions of very soluble salts is described.

L. S. THEOBALD.

**Solubility of inorganic precipitates in various aqueous solvents and the relation to modern theories of solution. I. Silver chloride.** S. POPOV and E. W. NEUMAN (J. Physical Chem., 1930, 34, 1853—1860).—The solubility of silver chloride in water and in aqueous solutions of hydrogen, sodium, potassium, and barium nitrates at 25° has been determined using the first appearance of the Tyndall beam. The solubility of silver chloride in water at 25° is  $1.278 \times 10^{-5}$  mol. per litre. The method is sensitive to  $\pm 2 \times 10^{-8}$  mol. per litre. The activity coefficients of the strong electrolytes used, calculated from the formula  $-\log f = \log (S/S_0) - \log f_0$ , are in agreement with those derived from the limiting form of the Debye-Hückel equation.

L. S. THEOBALD.

**Solubility of silver halides in methyl and ethyl alcohols; normal potentials of halogens in methyl and ethyl alcohol.** F. K. V. KOCH (J.C.S., 1930, 1551—1558).—Solubilities (determined by an electrochemical method) of silver chloride, bromide, and iodide in methyl and ethyl alcohols are given as  $3.9 \times 10^{-7}$ ,  $3.0 \times 10^{-8}$ ,  $6.2 \times 10^{-9}$  mol. per litre for methyl alcohol, and  $9.6 \times 10^{-8}$ ,  $8.7 \times 10^{-9}$ ,  $2.1 \times 10^{-10}$  for ethyl alcohol, respectively. These values do not conform to the Walden relation. Distribution coefficients of the three halogen ions in the solvent pairs methyl alcohol-water and ethyl alcohol-water are calculated, and from these the normal potentials in these solvents are deduced. The normal P.D. of the halogens and silver thus obtained agree with those calculated by a formula of Born (A., 1920, ii, 527).

From this agreement it is deduced that Brodsky's formula (A., 1926, 688) is valid for these ions and solvents, and the conditions existing in the solutions in consequence of this validity are discussed.

H. I. DOWNES.

**Solubility of lead iodate in water and in 0.1N-salt solutions.** V. K. LAMER and F. H. GOLDMAN (J. Amer. Chem. Soc., 1930, 52, 2791—2793; cf. A., 1929, 1386).—The solubility in water at 25° is  $3.61 \times 10^{-5}$  g.-mol. per litre, which is lower than previously reported. The greater solubility in 0.1N-chloride solutions as compared with solutions of sodium and potassium nitrates is attributed to the formation of complex chlorides. The principle of specific interaction holds, but the Debye-Hückel limiting law is not obeyed.

J. G. A. GRIFFITHS.

**Solubility of the octahydrates of the rare-earth sulphates.** K. S. JACKSON and G. RIENACKER (J.C.S., 1930, 1687—1691).—The solubilities of the octahydrates of the rare-earth sulphates at 20° and 40° show a minimum at europium. The connexion between this and a possible sub-grouping of the rare earths is discussed.

H. I. DOWNES.

**Solubility of neodymium sulphate in water and in aqueous sulphuric acid.** J. A. N. FRIEND (J.C.S., 1930, 1633—1642).—A modified form of saturation bottle for solubility determinations is described, the solubilities being determined by precipitating the neodymium as oxalate and igniting it to oxide. Solubility in water decreases with rise in temperature with a break above 80°, apparently due to polymorphic change. A new hydrate,  $\text{Nd}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ , is obtained at 0°, but the existence of Matignon's pentahydrate could not be substantiated. Dilute sulphuric acid tends to reduce solubility, but to increase relative solubility with rise of temperature, possibly by preventing basic salt formation.

H. I. DOWNES.

**Comparative solubilities in water of dichlorobenzenes. Method of determining the solubility of slightly soluble but very volatile substances.** A. KLEMENC and M. LOW (Rec. trav. chim., 1930, 49, 629—640).—Expressions are derived for the free energy of dissolution of isomerides on the assumption that (a) dissolution may be regarded as a reaction between solute and solvent brought about by forces acting at localised points in the molecules, (b) the solvent and solute are mutually soluble, and (c) the magnitudes of the reaction forces acting in the dissolution of isomerides are such that their temperature coefficients may be taken as equal. The equation  $K_1 = T \log m_2/m_1 + k'T$  is obtained, where  $m_1$  and  $m_2$  are the respective solubilities of two isomerides at the temperature  $T$ . The application of this expression has been tested and found to hold satisfactorily at temperatures between 20° and 60° for the isomeric dichlorobenzenes, provided the isomerides are compared in similar physical states. A method is described for the determination of the solubility of substances such as *p*-dichlorobenzene, in which a large volume of water is drawn extremely slowly at a fixed temperature through a length of the substance which is contained in a spiral tube separated by a porous glass membrane from a narrow capillary tube. The solubility is calculated from the loss of

weight of the spiral tube under conditions in which the substance is weighed under a layer of water. A marked fall in the solubility of *p*-dichlorobenzene between 30° and 35° is attributed to the formation within that range of a more stable modification.

F. G. TRYHORN.

**Solubility, specific gravity, and index of refraction of aqueous solutions of fumaric, maleic, and *i*-malic acids.** N. A. LANGE and M. H. SINKS (J. Amer. Chem. Soc., 1930, **52**, 2602—2604; cf. Weiss and Downs, A., 1923, i, 534).—Solubility data are recorded for temperatures between 5° and 80°; densities and refractive indices for 20°.

J. G. A. GRIFFITHS.

**Solubility relations of the isomeric nitrobenzoic acids.** A. R. COLLETT and C. L. LAZZELL (J. Physical Chem., 1930, **34**, 1838—1847).—The solubilities of the three nitrobenzoic acids in acetone, ether, benzene, carbon tetrachloride, and chloroform at temperatures from 25° to the m. p. of the acid have been determined by the synthetic method. Above 170°, explosions occur with the *p*-acid and ether, chloroform, or carbon tetrachloride. The solubility curve for each isomeride in any one solvent has the same general shape, and the curves for the various solvents do not intersect. The order of decreasing solvent power for each isomeride is the same, viz., acetone, ether, chloroform, benzene, and carbon tetrachloride.

L. S. THEOBALD.

**Solubilities of substituted benzoic acids in chlorinated benzene hydrocarbons.** CHAPAS (Compt. rend., 1930, **191**, 257—259).—The solubilities, expressed as the number of molecules,  $x$ , of solute in 100— $x$  molecules of solvent, have been determined of benzoic, *o*-, *m*-, and *p*-toluic, and *o*- and *m*-chlorobenzoic acids in chlorobenzene, and *o*- and *p*-chlorotoluene, at one or more of the temperatures 0°, about 15°, and about 32°. Plotted as  $1/T - \log x$  curves an almost straight line is obtained passing through the point  $x=100$ ,  $T$ =m. p. of the pure acid. The solubilities of isomerides are in the order of their m. p.

C. A. SILBERRAD.

**Ternary systems and their relationship to the solubility of pharmaceutical preparations in glycerol.** J. W. BIRZA (Pharm. Weekblad, 1930, **67**, 729—738).—Diagrams are given expressing the solubility of zinc sulphate, sodium carbonate, sodium phosphate, copper sulphate, and calcium acetate in glycerol—water mixtures. In general the solubility increases with the glycerol concentration; from solvents rich in water the salts crystallise with the same number of mols. of water of crystallisation as from water, but from solvents containing a large proportion of glycerol the solid phase contains glycerol of crystallisation.

H. F. GILLBE.

**Chemical conception of adsorption phenomena.** E. V. ALEXEEVSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 817—826).—A theoretical consideration of hypothetical active centres of charcoal, silica, and alumina in relation to their probable chemical structure.

R. TRUSZKOWSKI.

**Sorption of ammonia by charcoal.** J. SAMESHIMA (Bull. Chem. Soc. Japan, 1930, **5**, 173—180).—The velocity of sorption of ammonia by sugar charcoal

has been measured over periods extending to 6 months, several months being required for the establishment of equilibrium. The first stage of the process, completed within about 1 hr., consists of the entry of the gas into the larger interstices between the charcoal molecules, and cannot be treated quantitatively, but the second stage, during which the gas penetrates to the smaller intermolecular cavities, is governed by the resistance to the passage of a molecule of gas through a capillary of comparable size. On this assumption the equation  $x=K \log t+k$ , where  $x$  is the quantity adsorbed,  $t$  is the time, and  $K$  and  $k$  are constants, has been derived, and is in close agreement with the experimental values.

H. F. GILLBE.

**Sorption of organic vapours by activated sugar charcoal.** J. W. MCBAIN, D. N. JACKSON, A. M. BAKR, and H. G. SMITH (J. Physical Chem., 1930, **34**, 1439—1453).—The sorption of the vapours of toluene, benzene, hexane, methyl alcohol, etc. by sugar charcoal, activated in three different ways, has been investigated. The form and position of the sorption curve for a given vapour and charcoal depend to a marked extent on the freedom from other sorbed impurities, the time required for adsorption being greater when these are present. When evacuation is thorough, most of the sorption occurs at very low pressures. The usual empirical isotherm fails to represent this phenomenon, but the Langmuir formula is satisfactory.

L. S. THEOBALD.

**Sorption of organic vapours by highly evacuated, activated sugar charcoal.** J. W. MCBAIN, H. P. LUCAS, and P. F. CHAPMAN (J. Amer. Chem. Soc., 1930, **52**, 2668—2681).—The McBain-Bakr sorption balance (A., 1926, 493) has been used to determine the sorption of acetic acid, acetone, methyl alcohol, and five hydrocarbons chiefly at 120° and 205° by two air-activated and two steam-activated sugar charcoals (samples of same original material) which had been degassed at 440° over long periods. Most of the sorption occurs at pressures amounting to only a few hundredths of the saturated vapour pressure and therefore capillary condensation is not a significant factor. Steam-activated charcoal is not nearly as active as the best air-activated charcoal, which, however, does not in all cases permit saturation values to be obtained. The sorption decreases with rise of temperature. In general, the data are adequately represented only by the Langmuir formula (cf. McBain and Britton, this vol., 990).

J. G. A. GRIFFITHS.

**Activated charcoal.** N. SCHILOV (Kolloid-Z., 1930, **52**, 107—110).—The adsorption of acids and alkalis by activated charcoal and the formation of carbon dioxide in solution by exchange are discussed in the light of experiments on adsorption under different pressures of oxygen, and it is held that at low and high oxygen pressures, respectively, a primary and a secondary oxy- or hydroxy-compound are formed at the surface of the adsorbent.

E. S. HEDGES.

**Adsorption of xanthates on carbon suspensions.** W. PETERSEN (Kolloid-Z., 1930, **52**, 174—177).—Alkaline suspensions of coal dust are improved by adding to the suspensions a small amount

of potassium ethyl xanthate. The collected product contains less ash and in particular less clay and bound water than the original. This effect is not due to hydroxyl ions, but to a peptising influence of the xanthate, which is found to be strongly adsorbed by the suspension, peptising the clay particles in particular.

E. S. HEDGES.

**Sorption of vapour by chabazite.** T. BABA (Bull. Chem. Soc. Japan, 1930, 5, 190—202).—Chabazite, dehydrated by heating in a vacuum at 370°, adsorbs at 25° negligible quantities of benzene, ether, chloroform, carbon tetrachloride, acetone, and ethyl acetate, but considerable quantities of methyl alcohol, methylamine, carbon dioxide, and carbon disulphide; ethyl alcohol and ethyl-, propyl-, and butyl-amines are but slightly adsorbed. By repeated adsorption and desorption of methyl and ethyl alcohols and of methylamine the mineral becomes very fragile and ultimately disintegrates to a fine powder. The quantity of vapour adsorbed appears to be governed chiefly by the mol. vol. of the substance. The semi-empirical equation  $\log(b+x)/(a-x) = kt + h$ , where  $x$  is the quantity adsorbed at time  $t$ , and  $a$ ,  $b$ ,  $k$ , and  $h$  are constants, is valid for the adsorption of the alcohols.

H. F. GILLBE.

**Adsorption of arsenious acid by hydrous ferric oxide.** J. H. YOE (J. Amer. Chem. Soc., 1930, 52, 2785—2790).—The initial rate of adsorption of arsenious acid by hydrous ferric oxide at 25° is very rapid, and after 12 hrs. only a very small further adsorption occurs. Adsorption isotherms at 25° have been obtained with ferric oxide precipitated at 0°, 25°, 50°, 75°, and 100°. The results for the first two satisfy the equation  $X = kC^{1/n}$ , but those obtained for the oxide formed at the higher temperatures exhibit marked deviations from this equation and that of Langmuir. The higher is the temperature at which the adsorbent is formed, the lower is its adsorption capacity, and that of the oxide precipitated at 100° is further diminished by subsequent boiling.

J. G. A. GRIFFITHS.

**Nature of calcium hydroxide absorption by hydrated silica.** W. M. SHAW and W. H. MACINTYRE (Soil Sci., 1930, 29, 429—456).—The degree of hydration of amorphous silica has little effect on the rate of absorption of lime by silica. The rate of reaction varies inversely with the size of the silica particles. Above concentrations of 0.005*N* the reaction is represented by the equation  $x = 2.34C^{0.1818}$ , where  $x$  = molecular ratio CaO/SiO<sub>2</sub> in the absorption product and  $C$  = final concentration of Ca(OH)<sub>2</sub>. The formation of a series of hydrated calcium silicates varying in solubility and CaO/SiO<sub>2</sub> ratio is indicated. The "absorption product" and "solid phase reaction product" may be distinguished by the difference in the solubility of their silica contents in dilute hydrochloric acid.

A. G. POLLARD.

**Adsorption by silicic acid gel in the system *n*-butyl alcohol-benzene.** D. C. JONES and L. OUTRIDGE (J.C.S., 1930, 1574—1584).—The apparent adsorption curve is determined throughout the entire range of equilibrium concentrations and the results are discussed in the light of Williams' equation. A method is given for obtaining the true adsorption (cf.

A., 1914, ii, 111) of the gel without further experimentation and this is confirmed by vapour adsorption experiments. The results agree with the view of Ostwald and Izaguirre (A., 1922, ii, 480) that the apparent adsorption curve can be satisfactorily interpreted if the true adsorption of both components is expressed by a Freundlich isotherm, any differences between the values of the true adsorption being attributed to capillary adsorption. The concentration of the solution thus adsorbed is shown to be equal to that of the equilibrium solution. H. I. DOWNES.

**Constitution of starch iodide.** A. LOTTERMOSER and A. OTT (Kolloid-Z., 1930, 52, 138—159).—Experiments have been directed at a distinction between chemical reaction and adsorption processes in the formation of starch iodide. Measurements were made of the distribution of iodine between carbon tetrachloride and an aqueous 0.1*N*-potassium iodide solution containing starch, and potential measurements were carried out to study the adsorption of the different molecular species in the polyiodide system. The I<sub>3</sub>' ion was most strongly adsorbed by the starch. The course of adsorption was also followed by ultrafiltration of the system starch iodide-potassium iodide solution and titration of the filtrate, and the results agree with those obtained potentiometrically. Further measurements were conducted by causing the starch iodide to coagulate when formed. This can be effected by using a sufficiently concentrated solution of potassium iodide. The distribution of iodine between benzene and aqueous starch solution and also between carbon tetrachloride and aqueous starch solution was measured. Some preliminary experiments on the kinetics of the adsorption of iodine by starch were conducted. The conclusion reached from all the experiments is that the taking up of iodine by starch is in the first place an adsorption process and can be expressed by the ordinary adsorption isotherm. There is also a slower process, however, which continues after adsorption equilibrium is attained, but whether this secondary sorption is due to a dissolution process or to chemical combination has not been determined.

E. S. HEDGES.

**Distribution of non-reacting fluids in the gravitational field.** M. MUSKAT (Physical Rev., 1930, [ii], 35, 1384—1393).—Mainly mathematical. An analysis is given of the equations of Lewis and Randall for the effect of gravity in causing a variation with height in the composition of a mixture of non-reacting fluids. Binary mixtures are treated in detail, and illustrated for a mixture of two paraffins and for a dilute solution of sodium chloride in water.

N. M. BLYTH.

**Sources of error and inaccuracies in surface tension measurements by means of the drop apparatus.** I. H. JUNKER (Kolloid-Z., 1930, 52, 231—239).—Sources of error in making surface tension determinations by means of a dropping apparatus are pointed out and their magnitude is computed. Suggestions are made for obviating the errors.

E. S. HEDGES.

**Thermodynamical study of surface tension. Affinity and velocity of adsorption.** R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], 6, 598—605; cf.

this vol., 853, 861).—Mathematical. A further hypothesis having no thermodynamical basis but justified by general experience, to the effect that each portion of a system in true equilibrium constitutes in itself a system in equilibrium, is introduced. The hypothesis of localisation of equilibrium is applied to interfacial tension, adsorption, and catalysis.

E. S. HEDGES.

**Orientation of fatty acids in contact with a liquid phase.** J. J. TRILLAT and A. NOVAKOVSKI (Compt. rend., 1930, 191, 203—205).—The tangential-drop method (A., 1928, 938) applied to solid stearic, palmitic, or lauric acid shows that well-defined rays of orientation are produced parallel to the surface of the molten drop. The absence of Debye-Scherrer rings indicates that the resulting films are composed of small well-oriented crystals. With the solid acids in contact with water good orientation normal to the surface was obtained, whilst molten acids showed a confused microcrystalline structure. In the absence of dilute acetic or hydrochloric acid the effect due to water is modified by an increase in size and by irregular distribution of the crystals. Sodium hydroxide solution in concentrations greater than 10% gives rise to long chains of sodium laurate perfectly oriented normally to the drop with the sodium extremity in the aqueous layer.

J. GRANT.

**Three fundamental types of wetting. Adhesion tension as the measure of degree of wetting.** H. J. OSTERHOF and F. E. BARTEL (J. Physical Chem., 1930, 34, 1399—1411).—A more precise definition of wetting and a re-classification of existing terms are attempted. In order to designate degree of wetting correctly, three types, adhesional, spreading, and immersional wetting, must be considered. A distinction between the wettability of a solid and the wetting power of a liquid is drawn. Adhesion tension can be used to designate degree of wetting.

L. S. THEOBALD.

**Stability of unimolecular films. IV. Amines.** C. G. LYONS and E. K. RIDEAL (Proc. Roy. Soc., 1930, A, 128, 468—472; cf. A., 1929, 875).—The force-area curves of *n*-heptadecylamine and octadecylamine hydrochloride have been determined, special attention being paid to condensed and solid films. For the former compound it was found that above a certain temperature a solid film of area  $26.2 \text{ \AA}^2$  was obtained, whilst below a lower temperature the film had an area of  $20.5 \text{ \AA}^2$  per mol. The transition temperature was slightly lower on the more alkaline solutions. The latter substance gave solid condensed films of  $20.5 \text{ \AA}^2$  per mol. on alkaline and almost neutral solutions, identical with those obtained by Adam, but not the same as those given by the free base. On borate solutions ( $p_H$  8.8—9.6) the hydrochloride forms films with areas identical with those of the free base. On phosphate buffers, the amine gives a film of  $26.2 \text{ \AA}^2$  per mol. on *M*/20 and *M*/1000 solutions, the hydrochloride giving  $20.5 \text{ \AA}^2$  per mol. (cf. Adam, A., 1922, i, 424; ii, 687). All these films were found to be solid. The results are discussed and are considered to support the hypothesis of interlocking chains as a factor in the stability of solid crystalline unimolecular films.

L. L. BIRCHUMSHAW.

**Solid-solid surface phenomena.** D. BALAREV and N. LUKOVA (Kolloid-Z., 1930, 52, 222—227).—The addition of powdered zinc oxide, alumina, cadmium oxide, or calcium molybdate to powdered calcium carbonate lowers the dissociation temperature of the latter, although the addition of the powdered oxides of magnesium, silicon, zirconium, or tin has practically no influence. There is no relation between the lowering of the dissociation temperature and the chemical nature of the substance, but the phenomenon is considered to be a surface property, which, however, penetrates through several molecular layers.

E. S. HEDGES.

**Adherence of microscopic particles to a wall of the same nature. III.** A. VON BUZÁCH (Kolloid-Z., 1930, 52, 46—61; cf. this vol., 686).—The adherence of quartz particles on a surface of quartz has been studied by measuring the angle through which a horizontal plate has to be tilted in order to dislodge the particles and a method and apparatus for measuring the angle of tilt ("Abreisswinkel") are described. Using homodisperse suspensions in water and in 0.1*M*-barium chloride, the relation between angle of tilt and size of particle has been determined. When the sine of the angle is plotted against radius of particle the curve obtained for a suspension in water falls to a minimum and thereafter rises to approach a limiting value; the curve for a suspension in barium chloride solution falls continuously. The effect of the electrolyte appears to be the alteration of the thickness of the sheath surrounding the particles; in water the layer is thick and easily deformable, whilst in an electrolyte solution it is thin, dense, and not readily deformable. Electrolytes which have a coagulating influence on negatively-charged dispersed particles increase the angle of tilt to an amount which increases with the concentration of the electrolyte; electrolytes having a stabilising influence reduce the angle of tilt. The effect of electrolytes in increasing the angle of tilt is in the following order:  $\text{LiCl} < \text{NaCl} < \text{KCl} < \text{MgCl}_2 < \text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$ . For salts of aluminium and thorium, which can reverse the charge on the particles, the curve connecting the sine of the angle of tilt with the concentration of electrolyte passes through a maximum in the isoelectric region and through a minimum in the positive region. Parallel experiments on the electrokinetic potential of the particles have been carried out by the cataphoretic method and the relation between potential and adherence of the particles is discussed. In general, there is an antagonism between electrokinetic potential and adherence, but the adherence is controlled both by the electric charge and by the thickness of the layer surrounding the particle. Some preliminary experiments on the effect of adding dehydrating substances, such as ethyl alcohol and tannin, show that these raise the adherence value of the particles.

E. S. HEDGES.

**Tribo-electricity and friction. V. Surface strain and relaxation of like solids. VI. Surface strain and relaxation of unlike solids.** P. E. SHAW and R. F. HANSTOCK (Proc. Roy. Soc., 1930, A, 128, 474—480, 480—487; cf. Shaw and Jex, A., 1928, 467).—V. It has been shown that when



two identical non-conductors (ebonite, celluloid, or silk) are rubbed together, each surface becomes charged, and as rubbing continues the charges change in amount, and even in sign, in a systematic way. The effects are attributed to progressive strain on the surface, caused by pressure and friction. An attempt is made to standardise these effects by measuring the charges arising between known areas pressed together by known forces at given temperatures. Since rubbing raises the temperature locally, and since recovery from strain can be completely attained by rise of temperature, strain and partial relaxation from strain must proceed simultaneously. The relaxation temperature of high-grade annealed ebonite is about 100°. From the fact that experiments in a vacuum give results similar to those obtained in dry air, it is concluded that adsorbed air films do not play any part in the observed strain phenomena, but that the effects are entirely due to changes on the solid surfaces.

VI. Curves are given for the strain effects produced when zinc, copper, tin, cadmium, and iron rods are rubbed with annealed ebonite rods at various temperatures. Zinc and tin are initially negative, copper, cadmium, and iron positive to ebonite. Iron is peculiar in showing no tendency for the charge to reverse sign on continued rubbing. Using fully strained surfaces and raising the temperature in steps to 300°, it is found that copper begins to relax at 162° and iron at 192°, relaxation proceeding rapidly in both cases at 300°. The nature of surface strain is discussed. An effect which simulates strain, inasmuch as the tribo-electric state of a solid surface is altered by the process of rubbing it with a fabric, is shown to be due to the deposition on the surface of organic films derived from the fabric (cf. Hardy's "primary" films). L. L. BIRCHSHAW.

**Validity of the interference method for the measurement of the specific area of a copper surface.** F. J. WILKINS (J.C.S., 1930, 1304—1309).—In the application of the Constable interference method to the measurement of the specific area of the oxide films on non-activated copper surfaces the values obtained for the ratio ( $A$ ) of the specific to the apparent area are anomalous inasmuch as they are always less than unity. Moreover, this ratio is not constant, but increases by nearly 50% with a rise in the oxidation temperature from 183° to 305°. The ratio increases also with increase in the thickness of the film. Although activation of the copper surface by oxidation and reduction results in values of  $A$  greater than unity, the values are still dependent on the temperature of oxidation. These facts render the interference method untrustworthy in the application to the measurement of copper surfaces. A suggested explanation of the results is based on the occurrence in the oxide film of unchanged metal occlusions. The proportion of unchanged metal to oxide varies with the conditions and extent of oxidation. F. G. TRYHORN.

**Coloured crystalline stratifications. Study of *p*-toluidine,  $\beta$ -naphthylamine, and diphenylamine.** (MLLE.) S. BOUDIN (Compt. rend., 1930, 190, 1282—1284).—A 10% mixture of the crystalline

compound with water or with 15% alcohol is warmed in a small dish until the crystals melt and remain superfused to the extent of 20—25°. On seeding with a solid crystal the coloured stratifications observed by Marcelin (A., 1918, ii, 433) were obtained. With diphenylamine similar effects are produced by diluting an alcoholic solution with a large excess of water. J. GRANT.

**Coloured stratifications [produced] by sublimation.** A. MARCELIN and (MLLE.) S. BOUDIN (Compt. rend., 1930, 190, 1496—1497; cf. preceding abstract).—An apparatus is described for the simultaneous production and observation of crystalline tablets of (*e.g.*) *p*-toluidine, with the object of studying the coloured stratification produced by discontinuities in thickness. The objective of a horizontal microscope is inserted in a metallic chamber containing a small electrical sublimation hot-plate, and a safety-razor blade is placed so that its plane is vertical and normal to the axis of the objective. The crystals develop in the direction of the plane of the blade and appear to prolong the edge. J. GRANT.

**Adsorption and the permeability of membranes. II. Copper ferricyanide as a semi-permeable membrane.** H. B. WEISER (J. Physical Chem., 1930, 34, 1826—1837; cf. this vol., 538).—The adsorption of sucrose, and of the chloride, sulphate, and ferriyanide of potassium by copper ferricyanide, and the permeability of the copper ferricyanide membrane to these substances in aqueous solution, have been determined. Copper ferricyanide shows strong negative adsorption for sucrose from aqueous solution, and the membrane is impermeable to sucrose on account of this. The order of adsorption by the copper ferricyanide gel is potassium ferri-cyanide > sulphate > chloride. The adsorption of the ferriyanide is strong, but is not completely reversible at any concentration, and hence the salt diffuses slowly through the copper ferricyanide membrane. The rate of diffusion of the salts through the membrane is in the reverse order to that of adsorption. The presence of an adsorbed solute in a membrane retards the rate of diffusion of the solute into and through the pores, and if adsorption is sufficiently great, the membrane becomes impermeable. The adsorption of potassium ferriyanide by cadmium ferriyanide gel is of the same order of magnitude as that by copper ferricyanide, but the permeability of the former to potassium ferriyanide is greater, since the adsorption in this case is more readily reversible at low concentrations, and since the cadmium salt is less gelatinous and gives a membrane with larger pores. A porous membrane will be semi-permeable to a solute provided that it shows (i) sufficiently strong negative adsorption for the adsorbed film of pure solvent to fill the pores completely, or (ii) sufficiently strong positive adsorption to fill the pores with a network of oriented chains of adsorbed solute molecules so that no more can enter, within the range of irreversible adsorption.

L. S. THEOBALD.

**Collodion membranes. XI. Sieve effect of membranes on a polydisperse chromium hydroxide sol.** E. MANEGOLD and R. HOFMANN (Kolloid-

Z., 1930, 52, 201—214).—Two polydisperse chromium hydroxide sols are defined. Selective ultrafiltration shows that one of them contains about 25% of the chromium in a form which passes through a membrane having pores of radius  $4.7 \mu\mu$ , and the other contains about 30% in a form which passes through pores of  $4.4 \mu\mu$  radius, whilst the percentage of particles having a radius of less than  $5 \mu\mu$  is identical with the percentage of sol not precipitated by sulphuric acid. The course of the filtration curves of polydisperse sols is affected by a space hindering due to particles of certain sizes and an electrostatic hindering due to other particles. Only when the electrokinetic potential is maintained constant during the filtration can the sieve effect of the membrane be expressed quantitatively. E. S. HEDGES.

**Collodion membranes. VIII. Theory of sieve effect of ideal membranes on polydisperse dissolved particles.** E. MANEGOLD and R. HOFMANN (Kolloid-Z., 1930, 52, 19—24).—Theoretical. A further application of the principles of filtration developed in previous papers (cf. this vol., 688).

E. S. HEDGES.

**Viscosity coefficient of a liquid.** R. O. HERZOG (Z. physikal. Chem., 1930, 149, 89—96).—It is found empirically that in order to use Einstein's diffusion equation to calculate the molecular radius,  $\rho$ , of a dissolved substance from diffusivity data the term representing the molecular radius in the equation should be replaced by  $\rho V_g/V_i$ , where  $V_g$  is the specific volume of the solute and  $V_i$  that of the solvent. It appears also that  $\rho$  is approximately equal to  $(V-b)^{1/3}/2N^{1/3}$ , where  $V$  is the specific volume,  $b$  is van der Waals' coefficient, and  $N$  is Avogadro's number. If now Einstein's equation is applied to a pure liquid by employing the diffusion coefficient of the liquid into itself, calculated from the diffusion coefficient of an isomeric liquid, it assumes the form  $\eta = 2Pt/3.7\pi$ , where  $\eta$  is the viscosity,  $P$  the internal pressure, and  $t$  the mean time between two collisions of any given molecule. Values of  $\eta$  calculated by means of this equation are in good agreement with the experimental values. R. CUTHILL.

**Utilisation of diffusion coefficients for the determination of mol. wt., particularly of amphoteric hydroxides in aqueous solution.** G. JANDER and A. WINKEL (Z. physikal. Chem., 1930, 149, 97—122; cf. A., 1925, ii, 528).—From measurements of the diffusion of potassium, lithium, and barium chlorides and thallous nitrate in aqueous solution in presence of a large excess of the corresponding acid the diffusion coefficients,  $D$ , of the cations have been obtained. In order to eliminate the effect of viscosity on  $D$ , however, the value of  $Dz$ , where  $z$  is the relative viscosity of the solvent, is used for comparative purposes. At salt concentrations of 0.001—0.1N  $Dz$  does not vary much with the concentration, except in the case of lithium chloride, the diffusivity of which rises rapidly with increasing dilution, doubtless as a consequence of the presence of molecular and ionic complexes (cf. Drucker, A., 1913, ii, 1015). For a rise in temperature of  $1^\circ$   $Dz$  increases by 2.6% for all the salts. With cations with comparatively large nuclei, such as  $K^+$  and  $Ba^{++}$ ,

$Dz$  is approximately equal to 1.08/valency at  $10^\circ$ , but this relationship is not valid for ions with small nuclei. Examination of the available data for non-electrolytes and weak electrolytes shows that for all the members of a group of chemically similar substances the value of  $DM^1$ , where  $M$  is the mol. wt., is approximately the same. If, therefore, the mol. wt. of one member of the group is known, the mol. wts. of the others may be calculated from the values of  $D$ . By this method the mol. wts. of the anions of the alkali tungstates, tantalates, and molybdates in aqueous solution at various  $p_H$  have been obtained. For the molybdates a stepped curve results if the  $p_H$  is graphed against the mol. wt. of the anion, showing that at each  $p_H$  there is practically only one species of anion present, and from the curve the existence of ions with 1, 3, 6, 12, and 24 times the formula  $MoO_4$  has been deduced. Ferric perchlorate, on the other hand, gives a smooth curve, indicating that several types of anion are present simultaneously at all  $p_H$  values, and that there is a continuous transition from molecular dispersity to dispersity low enough for precipitation. These conclusions are confirmed by examination of the absorption spectra. R. CUTHILL.

**Validity of Beer's law for violet solutions of iodine.** J. GRÖH and S. PAPP (Z. physikal. Chem., 1930, 149, 153—160).—For solutions of iodine in carbon tetrachloride, carbon disulphide, or hexane, Beer's law is valid for wave-lengths between 450 and 640  $m\mu$ . In the violet and ultra-violet, however, the molecular extinction coefficient increases with increasing concentration, which is regarded as pointing to the existence of the equilibrium  $3I_2 \rightleftharpoons I_6$  in the solutions. R. CUTHILL.

**Magnetic susceptibilities of sodium chloride and bromide solutions.** M. H. TRYTTEN (Univ. Pittsburgh Bull., 1928, 25, 35—44).—Determinations by the Quincke ascension method give the values  $-0.37 \times 10^{-6}$  and  $-0.33 \times 10^{-6}$ , respectively.

CHEMICAL ABSTRACTS.

**Problems of present-day colloid chemistry. VII, VIII.** H. R. KRUYT (Chem. Weekblad, 1930, 27, 176—179, 241—244).—VII. The phenomenon of lyotropy is discussed in the light of the differences of size of similar ions due to varying degrees of hydration: the greater is the hydration of the ions, the less water is available for forming the stabilising hydration layer of the colloidal particles; the conditions obtaining thus resemble those in a solution of an organic substance the solubility of which is depressed by the addition of electrolytes. The manner in which the water molecules are oriented around the colloidal particles is also of importance.

VIII. A survey of certain outstanding problems, including adsorption, thixotropy, gelatinisation, and the relationship of emulsions to true colloidal solutions.

H. F. GILLBE.

**Preparation of colloidal solutions of nickel in dry acetone and some preliminary observations on their stability.** S. J. FOLLEY and D. C. HENRY (Mem. Manchester Phil. Soc., 1928—1929, 73, 100—110).—A description of the apparatus used for the dispersion of nickel in dry acetone by means of a high-frequency alternating current. Traces of water

reduce the stability of such sols, but traces of sulphuric or hydrochloric acid appear to act as stabilisers. *m*-Hydroxybenzoic acid and *m*-nitroaniline act as stabilisers. Other *o*- and *m*-compounds act similarly, but the corresponding *p*-compounds do not.

J. O. CUTTER.

**Preparation and some properties of tungsten and chromium hydrosols.** A. LOTTERMOSER and W. RIEDEL (Kolloid-Z., 1930, 52, 133—138).—Hydrosols of tungsten were prepared by Kužel's method and the electrical conductivity was measured. When the sols were diluted they became almost optically clear on keeping and this gradual change was found to be accompanied by an increase in electrical conductivity. The increase is due to the formation of compounds by the action of dissolved gases, and experiments in which the sol was diluted with water saturated with different gases showed that oxygen has the greatest effect in raising the conductivity, whilst hydrogen lowers the conductivity. A 0.1% sol of tungsten is completely transformed into tungstic acid on keeping for 3 months and rapidly by oxidising agents such as hydrogen peroxide and potassium permanganate. The particles of the sol are negatively charged, probably by adsorbed  $\text{WO}_4^{2-}$  ions. The hydrosol of chromium prepared by alternate treatment of the finely-powdered metal with sodium hydroxide and hydrochloric acid is polydisperse and not very concentrated. A method for the purification of the sol and removal of the coarser particles is outlined and the conductivity of the product has been measured. The conductivity increased with time in a way similar to that reported for tungsten sols, the presence of oxygen having a specially marked effect, but hydrogen did not reduce the conductivity. The particles are positively charged and the mean diameter was measured as  $140 \mu\mu$ . The essential feature of Kužel's method of preparing metallic hydrosols is probably oxidation of the surface of the particles by oxygen dissolved in the washing liquids. E. S. HEDGES.

**Titanium dioxide sols.** H. FREUNDLICH and W. KROSS (Kolloid-Z., 1930, 52, 37—46).—The literature contains little information on the properties of titanium dioxide sol and these have now been investigated with the following results. The sol is positively charged and hydrophobic, but a dilute sol becomes negatively charged when sodium hydroxide is added. The dispersion medium does not contain a detectable amount of titanium ions and none appears in the dialysate, but it is probable that such ions are adsorbed on the particles because the sol as a whole gives a positive test with the usual reagents for titanium. Extraordinarily high concentrations (up to 64%) of titanium dioxide can be obtained in the sols. Some of the more concentrated sols are thixotropic and others become so on the addition of sodium chloride or potassium sulphate. Viscosity measurements show the validity of Poiseuille's law except for the most concentrated sols. The viscosity increases with the concentration of the sol, the increase being more rapid at high concentrations; the relative viscosity of a 64% sol is 35. Thixotropic sols depart from Poiseuille's law. The surface tension of even the most concentrated sols does not differ

from that of water. Density determinations indicate a value of 4.77 for the colloidal particles of titanium dioxide, whereas the density of anatase is only 3.8—4.3. The marked increase is considered to be due to the compression of the dispersion medium at the surface of the particles. The diameter of the particles is  $60\text{--}20 \mu\mu$  and they are probably not spherical; the concentrated and thixotropic sols show a weak positive streaming double refraction.

E. S. HEDGES.

**Yellow ferric hydroxide sol.** G. SCHIKORR (Kolloid-Z., 1930, 52, 25—31).—The properties of a yellow ferric hydroxide sol have been examined. The sol was made by heating 3.5% ferric chloride solution at  $90^\circ$  for 1 hr., cooling, collecting the yellow powder which precipitates, and redispersing this in water by vigorous shaking of the mixture. The sol contains a higher percentage of chlorine than the reddish-brown sol produced by other methods, and the chlorine is also more strongly bound. Nevertheless, the particles do not consist mainly of basic ferric chloride, but of  $\text{FeO}_2\text{H}$ . The general behaviour of the sols towards electrolytes is similar to that of the ferric hydroxide sol prepared by Graham's method. With both types of sol the coagulating power of the iodate ion is greater than would be expected from its valency and this is due to the slight solubility of ferric iodate. The yellow sol sediments rapidly on coagulation and does not form a gel. After prolonged boiling of the sol with very dilute hydrochloric acid a precipitate is formed which is peptised on washing, forming a brick-red sol from which the chlorine is more readily removed. The yellow sol is chemically more reactive than Graham's ferric hydroxide sol. The precipitate formed on heating ferric chloride in water at  $90^\circ$  may also be peptised to form a sol in alcohol and the properties of this sol do not differ essentially from those of the hydrosol.

E. S. HEDGES.

**Hydrophilic sol of very low viscosity: the sol of the sodium salt of the nucleic acid of yeast.** H. G. B. DE JONG and N. F. DE VRIES (Rec. trav. chim., 1930, 49, 658—661).—The viscosity-concentration curve for sols of sodium nucleate from yeast has been determined at  $42^\circ$ . The effect of the addition of potassium chloride, calcium chloride, and luteocobalt chloride is to cause a lowering in the relative viscosity of this sol. The lowering produced by addition of electrolytes increases with the valency of the cation. The addition of alcohol in small amounts (up to 20%) raises the viscosity, but with larger amounts of alcohol a rapid fall in viscosity occurs. A comparison is made between the properties of sols of sodium thymus-nucleate and sodium yeast-nucleate.

F. G. TRYHORN.

**Dielectric constants of gold and mercury sols.** A. PIEKARA (Kolloid-Z., 1930, 52, 179—184).—A description is given of an improved method for preparing sols of mercury by condensing mercury vapour in the dispersion medium. Mercury sols in water, paraffin, and glycerol, and a gold hydrosol prepared by Bredig's method were used, the measurements of dielectric constant being carried out by a sensitive resonance method. The results do not agree with

those of Keller (*ibid.*, 1921, 29, 193), but indicate that the difference between the dielectric constants of the sols and the pure dispersion media is not greater than 0.1. E. S. HEDGES.

**Mercury as a dispersion medium. Colloid nature of iron amalgam.** M. RABINOVITSCH and P. B. ZYVOTINSKI (Kolloid-Z., 1930, 52, 31—37).—Iron amalgam was prepared by electrolysis of a solution of ferrous sulphate with a mercury cathode. Such an amalgam separates into its component phases when kept and the velocity of this separation was measured by placing the liquid amalgam in vertical tubes and at various time intervals running off the lower portion of the contents and determining at what height in the tube a test for iron was obtained. From the velocity of rise of the iron in the amalgam the radius of the iron particles was calculated by application of Stokes' law. The velocity increases considerably with rising temperature and this must be ascribed to coarsening of the particles, the decrease in viscosity of the mercury being insufficient to account for the magnitude of the effect. With increasing concentration the amalgam becomes more viscous and appears to approach the state of a gel; the eventual separation from this of mercury can be considered as a case of synecrisis. The velocity of separation of the phases is not appreciably affected by the addition of sodium amalgam or lead amalgam, but is increased by the addition of amalgam of zinc or tin. This behaviour is analogous to the influence of electrolytes on hydrosols. These observations indicate that iron amalgam must be considered as a colloid system. The system appears to be of considerable interest, because in other systems where the dispersion medium is liquid the stability is regarded as determined mainly by the electric double layer at the surface of the particles and this in turn is connected with the dielectric properties of the dispersion medium. These properties are absent when mercury is the medium. E. S. HEDGES.

**Antimony hydrogel.** A. F. GERASIMOV and I. S. MOROZOV (J. Russ. Phys. Chem. Soc., 1930, 62, 827—832).—If a solution of albumin in acetic acid is heated at 100° for 10 min., added to a mixture of antimony trichloride, acetic acid, tartaric acid, and water, and treated with hypophosphorous acid the solution darkens when heated for 15—20 min. at 100°; on cooling, an antimony gel separates on the addition of a few drops of sodium carbonate solution. When dissolved in dilute sodium hydroxide solution and evaporated to dryness by heating at 100° under reduced pressure in the absence of oxygen, a black, water-soluble powder containing 39% of antimony is obtained. Antimony hydrosols prepared by dissolution of this powder keep indefinitely in the absence of oxygen; on exposure to atmospheric oxygen they gradually become colourless as a result of oxidation. The particles of colloidal antimony are charged negatively. R. TRUSZKOWSKI.

**Mercury hydrogel.** A. F. GERASIMOV and B. M. KOZIREV (J. Russ. Phys. Chem. Soc., 1930, 62, 833—838).—When a solution of albumin in acetic acid free from hydrogen sulphide is added drop by drop to a mercuric chloride solution, a black hydrosol

which may be coagulated by the addition of sodium carbonate is formed. When the coagulate is washed, dissolved in dilute sodium hydroxide solution, and the sol evaporated to dryness, a black, water-soluble residue containing 27.6% of mercury is obtained. The hydrosol may be kept indefinitely in the absence of oxygen, and is comparatively fairly stable in its presence. The colloidal particles are charged negatively. R. TRUSZKOWSKI.

**Copper hydrogel.** A. F. GERASIMOV and G. P. MATVEEV (J. Russ. Phys. Chem. Soc., 1930, 62, 839—842).—When copper sulphate solution is added at 100° to a solution of albumin in acetic acid, free from sulphuric acid, and the mixture heated for 5—6 min. with hypophosphorous acid the solution becomes black to reflected light, and ruby-red to transmitted light. Colloidal copper is precipitated from this by addition of sodium carbonate. When the coagulate is washed, dissolved in dilute sodium hydroxide solution, and the hydrosol evaporated to dryness, a brown, water-soluble residue containing 27% of copper is obtained. R. TRUSZKOWSKI.

**Preparation of borate, tungstate, molybdate, and other jellies and study of mercurisulphosalicylic acid jellies.** S. PRAKASH and N. R. DHAR (J. Indian Chem. Soc., 1930, 7, 367—378).—Jellies of chromic tungstate, ferric tungstate, zirconium molybdate and borate, and ceric borate have been prepared by coagulating the sols obtained by dialysing mixtures of chromic chloride, ferric chloride, or ceric ammonium nitrate, and sodium tungstate, potassium molybdate, or borax. Reversible, stable, transparent jellies are obtained by dissolving freshly-precipitated mercuric oxide in sulphosalicylic acid; jellies of the sodium salt are irreversible with reference to temperature and the jelly-forming tendency is less than for the free acid. The dissolving influence of chlorine ions on these jellies is ascribed to the displacement of mercury and not to the formation of chloromercuri-derivatives (cf. Wo. Ostwald and Mertens, A., 1926, 1097). J. R. I. HEPBURN.

**Clearing of clay turbidities.** F. FOERSTER (Kolloid-Z., 1930, 52, 160—163).—The rate of settling of fine, stable suspensions of clay in water is influenced by the presence of electrolytes and particularly by alkalis. Sodium hydroxide increases the stability of the suspension, but calcium hydroxide causes relatively rapid sedimentation so long as it is present at a concentration greater than  $N/400$ . Calcium and magnesium sulphates and chlorides settle the suspensions at a concentration of only  $N/1000$ . Thus, the suspensions settle more readily in hard than in soft waters. In technical practice, the addition of milk of lime or calcium sulphate causes clay turbidities to clear completely in 12 hrs. E. S. HEDGES.

**Formation of streamers in sedimentation.** B. A. KEEN and K. R. SCHOFIELD (Nature, 1930, 126, 93—94).—An explanation is suggested for the formation of streamers when suspensions are centrifuged. L. S. THEOBALD.

**Formation of streamers in sedimentation.** C. E. MARSHALL (Nature, 1930, 126, 94).—The centrifugal method previously described (this vol.,

411) for determining particle size is not invalidated by the formation of streamers. L. S. THEOBALD.

**Brownian molecular motion.** E. SAMUEL (Ann. Physik, 1930, [v], 5, 677—700).—An attempt is made to confirm experimentally the theoretical work of Einstein and Smoluchowski on the Brownian movement. The quantitative formulation involves the well-known differential equation for diffusion, and the diffusion coefficient. First, the accuracy of the general laws of the Brownian movement is investigated, substances being chosen with suitable diffusion coefficients, and, secondly, the dependence of the diffusion coefficient on viscosity of the medium is determined in order to see whether this satisfies the theory. The first part of the problem can be solved in two ways. Either the distance traversed by ultramicros in a given time can be followed statistically, or the time taken for a given change in position to occur may be obtained. The second method is adopted. The sols used for this work were gold and silver. The time taken was that for a particle to get from the interior of a limited space to the surface. On comparison with theoretical expectations it is found that there are systematic deviations. For the investigation of the dependence of the viscosity of the medium on the diffusion coefficient, glycerol or sucrose was added to the metallic sol. There is a striking deviation between the practical and theoretical results. The diffusion coefficient decreases with increasing coefficient of viscosity much more rapidly than it should according to theory. This means that if the radius of an ultramicroscopic particle is calculated by the Einstein formula, the value is much smaller if the medium is one of large viscosity coefficient than if this coefficient is small. A direct determination of the radius of the particles by counting and estimating the concentration of metal in the solution shows that the time determined in the first part of the experimental work, using aqueous solutions, was of the right order. A discussion of the sources of error is given. A. J. MEE.

**Determination of number of particles in sols by counting in the ultramicroscope.** G. WIEGNER and E. W. RUSSELL (Kolloid-Z., 1930, 52, 1—18).—An investigation of the methods of counting colloidal particles in the ultramicroscope has been made and the errors due to different influences are computed. The methods of numbering the micrometer squares, the effect of confining counts to each particular square, and the arrangement of the ultramicroscope have received attention. A comparison is made of the results of different single observers in making the counts and the effect of two observers working in conjunction; the results of using different methods of registering the counts are also compared. A study of the influence of polydispersity of the sol on the determination of average particle size shows that a bright particle in the field may prevent the detection of many smaller particles and lead to erroneous results. E. S. HEDGES.

**Determination of number of particles in sols by counting in the ultramicroscope.** G. WIEGNER and E. W. RUSSELL (Kolloid-Z., 1930, 52, 189—201;

cf. preceding abstract).—A mathematical investigation of the errors of counting particles in the ultramicroscope.

E. S. HEDGES.

**Use of ultra-violet light in the microscopical measurement of particle size.** G. S. HASLAM and C. H. HALL (J. Franklin Inst., 1930, 42, 777—789).—Photomicrographs of zinc oxide dispersions have been taken using ultra-violet light. No advantage over ordinary blue light is found in the case of coarser particles, but with fine ones the ordinary methods give results which are too large. W. E. DOWNEY.

**Application of the photo-electric effect to the determination of the relation between number of particles, particle size, and magnitude of light dispersion.** I. N. N. ANDREEV, N. A. KUDR-JAVZEV, and T. A. STESSEL (Kolloid-Z., 1930, 52, 184—189).—Rayleigh's formula,  $I = K\pi r^2/\lambda^4$ , giving the relation between light dispersion, particle size, and wave-length suffers from the fact that the constant  $K$  cannot be evaluated because the measurement of turbidity by the colorimetric method does not give absolute values for the magnitude of light dispersion. A photo-electric method of measuring the dispersed light has been applied to turbidities of colophony and of staphylococci (particle radius 0.146—0.42  $\mu$ , and thus of the order of magnitude of wave-lengths of light) and to suspensions of certain spores having a radius of 1.85—2.04  $\mu$  (considerably greater than wave-lengths of light). From the measurements of light dispersion, of number and size of particles by counting under the ultramicroscope, and using light of known wave-length, the mean value of  $K$  is calculated to be  $3.98 \times 10^{-6}$ . The light dispersion is expressed in amperes and not in units of light. E. S. HEDGES.

**Dependence of viscosity of cellulose solutions on temperature.** E. BERL and H. UMSTÄTTER (Z. physikal. Chem., 1930, 148, 471—474).—A method for determining the viscosity of small quantities of solution is described. Viscosity measurements of solutions of cellulose acetate and cellulose nitrate in acetone have been made at temperatures between 20° and 48.5°. The fluidity varies approximately linearly with the square of the temperature. M. S. BURR.

**Flocculation of colloidal solutions.** A. BOUTARIC (Chim. et Ind., 1930, 23, 1339—1352).—A résumé of the action of electrolytes and of radiations on colloids, and the interaction of hydrophobic and hydrophilic sols. E. S. HEDGES.

**Effect of dilution on the coagulation of arsenious sulphide hydrosols in its relation to the arsenious oxide content.** J. N. MUKHERJEE and S. C. GANGULY (J. Indian Chem. Soc., 1930, 7, 465—472).—The coagulation of arsenious sulphide hydrosols with solutions of hydrogen, potassium, lithium, and barium chlorides shows that increasing concentration of arsenious oxide sensitises the sol; this is in keeping with the observed decrease in cataphoretic speed (A., 1929, 261). Dilution diminishes the speed, but stabilises the sol. This contrast can be accounted for, not on the basis of a change in the concentration of arsenious oxide, but from a consideration of the effect of dilution (cf. Mukherjee and Sen, J.C.S., 1919, 115, 461; also Kruyt and Speck, A., 1919, ii, 498).

J. R. I. HEPBURN.

**Rate of coagulation of silver hydrosol.** E. W. R. STEACIE (*J. Physical Chem.*, 1930, **34**, 1848—1852).—The rate of coagulation by sodium chloride of silver hydrosol, prepared by the reduction of silver oxide with hydrogen, has been followed ultramicroscopically. The Smoluchowski equation holds for conditions of rapid, but not for those of slow, coagulation. There is evidence that the initial particles are unequally charged. L. S. THEOBALD.

**Influence of dilution on the stability of ferric hydroxide hydrosols.** S. N. MUKHERJI (*Kolloid-Z.*, 1930, **52**, 63—66).—By measuring the cataphoretic migration velocity of the particles of a ferric hydroxide sol an attempt has been made to find a relation between dilution and stability of a sol. The results show that the influence of dilution is very complicated and that the relation cannot yet be discussed successfully. E. S. HEDGES.

**Coagulation of ferric oxide sols by gas bubbles.** H. M. STARK (*J. Amer. Chem. Soc.*, 1930, **52**, 2730—2742).—The ferric oxide sol described by Sorum (A., 1928, 703) contains particles with an average diameter of  $59\ \mu$  for which the electrokinetic potential is 64 millivolts. The colloid is coagulated by a stream of bubbles of air, nitrogen, oxygen, or hydrogen, the coagulating power of which is not widely different. The effect is not due to impurities or free electrons, since the gas does not lose its efficacy by passage through several quantities of sol. The height of the column of sol affects the weight of iron oxide coagulated only in so far as the volume of the sol varies with the height. Variation of bubble size is without effect, but with increasing rate of flow the coagulating power passes through a maximum. Carbon dioxide does not cause coagulation, since this changes the  $p_H$  of the sol from 6.4 to 4.3, and experiments with acetate buffer solutions show that the sol is unstable to air bubbles only when the  $p_H$  is greater than 4.6. The addition of electrolytes facilitates coagulation by gas bubbles and coagulation values are tabulated. The velocity of coagulation of sols in 0.02—0.1 millimolar potassium sulphate has been investigated. The Smoluchowski equation for rapid coagulation is applicable, and the logarithms of the velocity coefficients bear a linear relation to the concentration of electrolyte when this is low (cf. Schalek and Szegvari, A., 1924, ii, 115). The addition of small quantities of higher alcohols decreases the stability of the sol, and a certain concentration of alcohol corresponds with minimum stability. In view of the conclusions of McTaggart (A., 1914, ii, 762) these results show that the coagulation is not primarily due to the neutralisation of the charge on the colloid by that on the bubble. Although the sol is coagulated by any forms of mechanical agitation, this is not the chief factor in the action of the bubbles. Coagulation by bubbles is believed to occur by adsorption of the colloid which is carried to the surface of the sol, forming there, when the bubble bursts, a localised layer of liquid containing a high concentration of particles which coagulate by ordinary kinetic methods. J. G. A. GRIFFITHS.

**Chloride-free ferric oxide hydrosols and the Burton-Bishop rule.** R. C. JUDD and C. H. SORUM (*J. Amer. Chem. Soc.*, 1930, **52**, 2598—2602;

Boutaric and Perreau, A., 1927, 825).—It is found that the flocculation of chloride-free colloidal ferric oxide (Sorum, A., 1928, 703) by various electrolytes follows the Burton-Bishop rule (A., 1921, ii, 176; cf. Kruyt and van der Spek, A., 1919, ii, 498). The flocculation values are lower than previously reported and for univalent anions are increased by raising the valency of the cation. By the addition of suitable quantities of ferric chloride, the sol could be made to exhibit properties identical with those of sols prepared by other observers (*loc. cit.*). J. G. A. GRIFFITHS.

**Ageing of aqueous ferric chloride solutions.** E. LESCHE (*Kolloid-Z.*, 1930, **52**, 178—179).—Experiments on the ageing of ferric chloride solutions between the concentration  $10^{-3}$  and  $10^{-6}$  mol. per litre have been carried out by measuring the change in electrical conductivity. The formation of a precipitate during the hydrolysis does not affect the course of the ageing curve. The results suggest that the process consists of a gradual transition of the hydrolysis product from a hydrophilic to a hydrophobic colloid, the process being irreversible. The light absorption of ferric chloride solutions during ageing was also measured and the results show that the absorption is displaced in the direction of longer wave-length. E. S. HEDGES.

**Composition of the intermicellar liquid and the precipitation of colloidal solutions of uranium ferrocyanide.** N. P. CHATTERJEE (*Kolloid-Z.*, 1930, **52**, 214—219).—When colloidal uranyl ferrocyanide is precipitated by excess either of potassium ferrocyanide or of uranyl nitrate the supernatant solution gradually develops acidity when kept in contact with the precipitate and some peptisation of the precipitate occurs. It is probable that the sol owes its negative charge to the adsorption of ferrocyanide ions in the form of hydroferrocyanic acid, especially in view of the greater coagulating power of uranyl nitrate. Investigation of the precipitating action of some electrolytes showed that with the exception of sodium nitrate all the electrolytes used precipitated dilute sols more readily than the concentrated sols. Uranyl and silver ions have a greater coagulating effect than corresponds with their valency. The effect of dilution on the stabilising influence of potassium ferrocyanide was also studied, but the results are of a complicated nature. E. S. HEDGES.

**Ion-antagonism in colloid models. III. Influence of dehydrating media on the coagulation of hydrophilic sulphur sols by electrolytes and electrolyte mixtures.** W. A. DORFMAN (*Kolloid-Z.*, 1930, **52**, 66—81).—Experiments on the sensitisation of a hydrophilic sulphur sol by dehydrating organic liquids lead to the view that hydrophilic and hydrophobic colloids differ only quantitatively and not essentially in nature. Methyl and ethyl alcohols, acetone, and tannin sensitise the sulphur sol, but do not coagulate except in the presence of electrolytes, and the effect is due mainly to the dehydrating influence of these substances. The Schulze-Hardy rule and the lyotropic series of cations are maintained in the presence of the dehydrating medium. The process of coagulation consists of two stages: (a)



neutralisation of the charge on the particles and (b) salting out of the sol. E. S. HEDGES.

**Activity of ions in suspensions.** W. U. BEHRENS (Kolloid-Z., 1930, 52, 61—63).—The activity of the chlorine ion and the hydrogen ion in suspensions of some soils and of kaolin is greater than that in the centrifuged dispersion medium. This supports the theory advanced by Wiegner (this vol., 696).

E. S. HEDGES.

**Theory of the formation of periodic structures.** E. S. HEDGES (Kolloid-Z., 1930, 52, 219—222).—Experimental results are described which are at variance with Wo. Ostwald's "diffusion wave theory" of the formation of periodic structures (A., 1925, ii, 530). Examples are given of periodic structures formed through irreversible chemical reactions, by coagulation, and by salting-out, where the condition of three diffusion waves postulated by Ostwald's theory is not operative.

E. S. HEDGES.

**Formation of spirals by chemical precipitation.** R. E. LIESEGANG (Naturwiss., 1930, 18, 645—646).—The spiral structures found by Schikorr (*ibid.*, 1930, 18, 376) are simply varieties of the ordinary Liesegang rings. A photograph showing the occurrence of these spirals in silver chromate precipitated in gelatin is reproduced.

W. R. ANGUS.

**Periodic precipitation in aqueous solutions.** H. W. MORSE (J. Physical Chem., 1930, 34, 1554—1577).—A simple method for obtaining periodic precipitation by double decomposition in aqueous solution is described. Periodic precipitates have been obtained in the formation of the less soluble compounds of lead, silver, and mercury, of barium sulphate and carbonate, of cupric sulphide and chromate, manganous hydroxide and carbonate, thallous iodide and chromate, cadmium hydroxide, and caesium alum. Photomicrographs are reproduced and discussed. The precipitates are definitely crystalline, and the rings are often widely separated, but no fine structure has been observed. The specific surface of the precipitate is small. There is supersaturation of the precipitate when it appears, and the precipitation begins in the absence of solid. The rapid rate of change of concentration of the reacting substances determines the release of supersaturation in the absence of the solid phase. The resultant rapid increase in the degree of supersaturation determines the appearance of the solid phase, and the importance of other factors is negligible in comparison. The law of diffusion being assumed, periodic precipitation can be explained by the fact that solutions which are slightly supersaturated may persist for an indefinite time before release, whilst those highly supersaturated may persist for a time which is comparatively short. The rings in water follow the same rule of constancy of the ratio of separation of successive rings as do systems in gelatin.

L. S. THEOBALD.

**Silicic acid gels. IV. Effect of electrolytes on time of setting of gel-forming mixtures.** M. PRASAD and R. R. HATTIANGADI (J. Indian Chem. Soc., 1930, 7, 341—346; cf. this vol., 414).—Sodium and potassium salts of nitric, sulphuric, hydrochloric, and acetic acids accelerate the rate of setting when added

to the gel-forming mixtures—sodium silicate solution of 4% silicic acid content and ammonium acetate or acetic acid. The order of coagulating power, in acid or alkaline solution, is  $\text{KOAc} > \text{NaOAc}$ ;  $\text{KCl} > \text{NaCl}$ ;  $\text{KNO}_3 > \text{NaNO}_3$ ; and for anions  $\text{Cl} > \text{NO}_3 > \text{SO}_4$ .

J. R. I. HEPBURN.

**Influence of concentration of coagulating electrolyte, time, and temperature on the syneresis of some inorganic jellies.** S. PRAKASH and N. R. DHAR (J. Indian Chem. Soc., 1930, 7, 417—434; cf. preceding abstract).—The jellies studied were ponceaux-red, ferric arsenate, phosphate, and borate, chromium arsenate, vanadium pentoxide, zirconium hydroxide, molybdate, and borate, and manganese dioxide. Whenever a jelly is formed by the addition of electrolytes to a jelly-forming sol, the amount of subsequent syneresis increases continuously with the concentration of the added electrolyte, with rise in temperature, and—up to a limiting value—with time. The phenomenon of syneresis is explained by the authors' hydration and agglomeration hypothesis (A., 1929, 1008); the addition of a coagulating electrolyte to a jelly-forming sol diminishes the charge on the colloidal particle, and the hydration is increased until a jelly is obtained. By adding a further amount of electrolyte the same forces which bring about the hydration cause the particles to agglomerate and the structure of the jelly undergoes a shrinkage. The idea that syneresis is due to re-orientation of the particles (Arsem, A., 1926, 473) or to heterogeneity produced by intense internal packing (Usher, A., 1929, 1143) appears to be inadequate to explain the phenomenon.

J. R. I. HEPBURN.

**Syneresis.** E. N. GAPON (Ukraine Chem. J., 1930, 5, 58—61).—The expression  $X/(P_0 - P) = H$ , where  $X$  is the percentage of the disperse phase separating out,  $P_0$  that concentration of it which would not exhibit syneresis,  $P$  the given concentration of colloid, and  $H$  is the syneresis constant characteristic of the given sol, is verified for geranin and viscose sols.

R. TRUSZKOWSKI.

**Structure of jellies. II.** P. THOMAS and M. SIMI (Rev. gén. Colloid., 1930, 8, 68—81; cf. this vol., 291).—Some colloid chemical properties of sorbitol acetal, benzoylcystine, benzoyltyrosine, quinine sulphate, optoquine sulphate, lithium urate, eucupine acetate, and apiine are described, particularly their gelation in various dispersion media. When the aqueous sols of these substances are cooled they form transparent jellies which initially appear homogeneous under the ultramicroscope, but when kept or on the addition of certain organic liquids (alcohol, acetone, etc.) the jellies are transformed into masses of crystals. These are in the form of long, flexible, intertwining hairs, and when stirred or shaken the structure is destroyed. The separation of the dispersion medium offers an explanation of the general phenomenon of syneresis. The crystals may be filtered from the dispersion medium, dried, and redissolved, and when the sol is cooled the jelly is formed again. These observations support the view that jellies contain a solid phase and a similar fibrillar structure is suggested for typical jellies such as gelatin and agar. It is pointed out that gelatin and agar

jellies are rendered more fluid by repeated mechanical rupture.

E. S. HEDGES.

**Influence of  $p_H$  and concentration on surface tension of gelatin solutions.** J. M. JOHLIN (J. Biol. Chem., 1930, **87**, 319—325).—For the attainment of a condition of true equilibrium in gelatin solutions a period of about 24 hrs. is required, the period being longer in acid than in alkaline solutions. Curves are given showing the effect of  $p_H$  on the surface tension of 1% gelatin solution as determined by the sessile bubble method, both at equilibrium and at earlier stages. At equilibrium the surface tension is in general decreased by acid and increased by alkali, the previously observed minimum at the isoelectric point and maximum on the acid side being present only in those curves obtained before equilibrium is reached. A relationship between surface tension and concentration of gelatin solutions exists which is comparable to that obtaining in solutions of surface-active substances of low mol. wt.

C. R. HARRINGTON.

**Swelling of gelatin in acid and salt solutions.** II. W. VON MORACZEWSKI and S. GRZYCKI (Biochem. Z., 1930, **221**, 331—348; cf. A., 1929, 880).—In salt solutions the extent to which gelatin swells increases with the concentration of the salt, and in equally concentrated solutions of different salts that solution which has lowest density produces greatest swelling. Salts of tervalent cations cause greater swelling than do those of bivalent cations, and these again cause greater swelling than do salts of univalent cations. Possibly as a result of the formation of molecular aggregates there is, in the case of sulphates and citrates, a decrease in the swelling power at higher concentrations of the salts, for, other conditions being equal, swelling power seems to depend on molecular size. Acids are more powerful as swelling agents than are salts and in almost all cases exhibit a maximum power at a certain concentration. The swelling power of dilute acids depends on dissociation. As regards swelling power, 0.1*N*-solutions of citric, tartaric, and acetic acids form a descending series in the order given. It is supposed that swelling power is related to the space-filling capacity of the dissolved substance and hence to the extent to which it binds water.

W. MCCARTNEY.

**Work and heat of swelling.** R. FRICKE and J. LÜKE (Z. Elektrochem., 1930, **36**, 309—320).—The connexion between the vapour pressure and the composition of agar-agar, casein, and maidenhair hydrogels has been traced by a static differential method for both the dehydration and the hydration processes at 0° and at 10°. Agar-agar and casein show pronounced hysteresis, whereas maidenhair shows none and attains vapour-pressure equilibrium relatively rapidly. The values of the differential maximum work of swelling,  $A$ , are calculated from the relative vapour pressures, and those of the differential heat of swelling,  $U$ , from the temperature coefficients of the relative vapour pressures. In contradiction to the assumption made by Katz (A., 1917, ii, 245)  $U$  differs in value considerably from  $A$ . The same holds for the integrated heat of swelling  $U'$  and the integrated work of swelling  $A'$ . The change of

the heat of swelling with concentration in agar-agar and casein gels has been measured directly, yielding results in good agreement with those calculated from the vapour-pressure data.

J. W. SMITH.

**Relation to temperature of the viscosity of some protein solutions.** S. AKAGI (J. Biochem., Japan, 1930, **11**, 423—425).—Between 20° and 60° the viscosity of a 0.2% serum- or egg-albumin solution is nearly independent of the temperature.

CHEMICAL ABSTRACTS.

**Physical chemistry of proteins in non-aqueous and mixed solvents. I. State of aggregation of certain proteins in aqueous carbamide solutions.** N. F. BURK and D. M. GREENBERG (J. Biol. Chem., 1930, **87**, 197—238).—Concentrated solutions of carbamide, although less efficient ionising solvents than water, have a marked solvent capacity for proteins. The osmotic pressure of a variety of proteins in solution in 6.66*M* aqueous carbamide, buffered at the isoelectric point of the respective protein, was determined. With increase in the concentration of protein the osmotic pressure increased at a disproportionately high rate. The relation between concentration and osmotic pressure could be rendered linear by applying the equation  $C = 100C'/(100 - hC')$ ,  $C'$  being the observed concentration, and  $h$  a constant which, for caseinogen, edestin, and hæmoglobin has the value 2.80, and probably represents solvation of the proteins to the extent of 2.8 g. of solvent per g. The results lead to approximate values of 33,600, 49,500, 34,300, and 36,000 for the mol. wt. of caseinogen, edestin, hæmoglobin, and egg-albumin, respectively. The state of aggregation of hæmoglobin is thus changed in carbamide solution, since its mol. wt. in water or aqueous glycerol is twice as great. On the other hand, the aggregation of egg-albumin is not altered by the carbamide, although this protein, as well as hæmoglobin, is denatured in such solutions.

C. R. HARRINGTON.

**Complex coacervation. III. Complex coacervates in physiological media. IV. Behaviour of complex coacervates in the electric field.** H. G. B. DE JONG, W. A. L. DEKKER, and O. S. GWAN (Biochem. Z., 1930, **221**, 392—402, 403—417; cf. A., 1929, 1382; this vol., 158, 994).—III. Complex coacervates can be prepared within physiologically possible  $p_H$  limits from clupein and gelatin, ichthyocoll, crystalline egg-albumin, caseinogen, gum-arabic, thymus-nucleic acid, or yeast-nucleic acid, but when serum-albumin is the second component it undergoes rapid denaturation. It is possible to make complex coacervates either within or outside physiologically possible  $p_H$  limits when physiological concentrations of sodium chloride (or of this salt with calcium chloride) are also present. The capillary electric charges of the colloid components are factors of the greatest importance in the process of formation of complex coacervates. Complex coacervates may take part in the building up of living substance.

IV. By means of an apparatus described, the behaviour in an electric field of drops of complex coacervates has been investigated. In mixtures in which the positive component predominates the drops are positively charged; in those in which the negative

predominates they are negatively charged. In a sufficiently powerful direct or alternating electric field the drops of various coacervates exhibit in varying degree the effect described by Büchner and van Royen (this vol., 29). This effect is due to a difference in conductivity between the coacervate and the liquid with which it is in equilibrium. Under the influence of direct current of appropriate strength the drops of complex coacervates undergo reversible changes, resulting in the formation of large numbers of fine droplets. This disintegration takes place in various ways and is affected by the charge on the drops and by the viscosity of the liquids. Complex coacervates from phosphatides and proteins as well as the coacervates previously studied exhibit these effects in the electric field, but simple coacervates have not been observed to show either the Büchner or disintegration effects.

W. MCCARTNEY.

**Explanation of the irregular cataphoresis of albumin-methylene blue adsorbates by means of the hydrone theory.** A. FODOR (Kolloid-Z., 1930, 52, 81—87).—Theoretical. The anomalous cataphoresis of proteins with adsorbed methylene-blue previously described (Fodor and Mayer, A., 1926, 1091; 1928, 585) is explained by considering the state of dissociation of the water molecules in the sheath surrounding the particles.

E. S. HEDGES.

**Electrokinetic potential by the method of streaming potential.** H. LACHS and J. BICZYK (Z. physikal. Chem., 1930, 148, 441—463).—An improved method for determining streaming potentials, by which results may be reproduced with an accuracy within  $\pm 2\%$ , is described. The streaming potential of water depends, in a large measure, on the carbon dioxide content of the water. The streaming potentials of solutions of lithium, potassium, rubidium, and caesium chlorides, of concentrations  $5 \times 10^{-3}$  to  $10^{-3}$ -M in water of conductivity  $0.9 \times 10^{-6}$ , through Jena glass capillaries, have been measured and the electrokinetic potentials calculated. A maximum was found at a concentration of approximately  $3 \times 10^{-4}$ -M for all the salts investigated. The identity of the order of activity of the salts with the lyotropic series of the alkali cations has been confirmed.

M. S. BURR.

**Hydrolysis at the surface of colloidal platinum and its effect on coagulation and charge reversal phenomena.** S. W. PENNYCUICK (Z. physikal. Chem., 1930, 148, 413—433).—As previously shown (A., 1928, 1090; 1929, 643), the surface of the particles of a platinum sol contains both the strong acid hexahydroplatinic acid and an acid oxide of platinum. The sol has a strong affinity for inorganic bases. It should therefore have a hydrolytic action on salts. The presence of platinic acid will result simply in ionic exchange and the liberation of free acid in solution, the number of ionogen surface complexes remaining unchanged. The platinum oxide should bring about true hydrolysis of the salt and increase the number of ionogen surface complexes by combination of the oxide with the base set free and subsequent ionisation of the salt thus formed. This has been proved by the following observations: (1)

The initial increase in electro-kinetic potential and consequent slight peptising action due to salts of weak acids which are already hydrolysed in water. (2) The existence of a similar maximum in the electro-kinetic potential-concentration curves of neutral salts. (3) The distribution of bases at low concentrations between free acid and the platinum surface, as determined by a comparison of the titration curves of the intermicellar liquid and the platinum sol. (4) Variation in the amount of acid set free on the addition of different salts, salts of bivalent cations liberating, in general, more than salts of univalent cations. (5) Retention of base by the colloid particles as determined by back-titration of the platinum sol with acid after preliminary addition of a base. The influence of hydrolysis on coagulation is discussed, and it is shown that univalent cations at low concentration exercise a peptising action on the colloid. This action is much less marked for bivalent cations and is non-existent in the case of trivalent cations. The reversal of charge brought about by ferric and aluminium chlorides must be due to a reaction between the basic salts formed by hydrolysis and the acid oxide surface of the sol. In ferric chloride solution this salt is produced through direct hydrolysis. Aluminium chloride, on the other hand, requires the presence of a small quantity of sodium hydroxide.

M. S. BURR.

**Rational basis for the thermodynamic treatment of real gases and mixtures of real gases.** J. A. BEATTIE (Physical Rev., 1930, [ii], 36, 132—145; cf. A., 1928, 588, 1315).—Mathematical. It is shown that all the necessary relations for the treatment of real gases and mixtures of real gases at infinitely low pressures can be derived from two assumptions: that at constant temperature the energy of a pure gas approaches a function of the temperature, and that at constant temperature and composition the ratio of the equilibrium pressure of a gas in a mixture to the product of the mol. fraction of the gas in the mixture and the total pressure of the mixture approaches unity.

N. M. BLIGH.

**Gibbs-Dalton law of partial pressures.** L. J. GILESPIE (Physical Rev., 1930, [ii], 36, 121—131; cf. A., 1927, 616; this vol., 292).—Theoretical. Various formulations of Dalton's law are discussed. The Gibbs formulation is equivalent to the statement that the concentration of a gas is the same at equilibrium on either side of a membrane permeable only to itself. Application to the experimental data for ammonia and nitrogen shows that the Gibbs-Dalton law is only an approximation, and error curves are given. Other applications are outlined.

N. M. BLIGH.

**Kinetic theory of vaporisation. III. Vapour pressure of solutions.** S. C. BRADFORD (Phil. Mag., 1930, [vii], 10, 160—185; cf. A., 1925, ii, 1142).—Theoretical. Maxwell's theory of the distribution of molecular velocities has been amplified to take into account the effect of molecular attraction. The extended theory is applied to obtain expressions for the vapour pressure of a pure liquid and of a solution in terms of molecular attraction, motion, and volume only. Complete data and results are tabulated

for a number of liquids. Close agreement between the calculated and observed values indicates that the vapour pressures of liquids are dependent on these factors alone. Hence for solutions it is unnecessary to assume dissociation of salt molecules to account for the greater reductions of the vapour pressures and f.-p. depressions. Calculated and observed values tabulated for a number of salt solutions show fair agreement. It is shown that the average velocity of the molecules in a liquid cannot be the same as that in a perfect gas, since they are under the influence of strong forces. The ratio of these two velocities,  $\lambda$ , is dependent on the cohesion,  $K$ , of the liquid. Equations are given for the determination of  $K$  and  $\lambda$ .

N. M. BUGH.

**Laws of dilute solutions and of perfect solutions.** E. A. GUGGENHEIM (J. Physical Chem., 1930, **34**, 1751—1757).—Theoretical. Various formulæ are deduced and discussed.

L. S. THEOBALD.

**Dissociation theory of solution.** S. C. BRADFORD (Nature, 1930, **126**, 166—167).—The formula expressing the vapour pressure of a liquid (this vol., 1119) can be extended to solutions of non-volatile solutes and shows that the vapour pressure of salt solutions is determined by the attractions, volumes, and motions of the particles only. The fundamental assumption of the dissociation theory that the diminution of vapour pressure is proportional to the number of solute particles present is considered to be incorrect. The extra depression of the f. p. of salt solutions is determined by the increased cohesion of the liquid resulting from the presence of salt particles in it. A direct disproof of the dissociation theory is claimed. The solubilities of different substances can be accounted for and the mechanism of solution explained by a consideration of the attractions between the particles.

L. S. THEOBALD.

**Dissociation constants of quinine, cinchonine, and cinchonidine.** E. B. R. PRIDEAUX and F. T. WINFIELD (J.C.S., 1930, 1587—1595).—Results obtained in the electrometric titration of quinine, cinchonine, and cinchonidine with the quinhydrone electrode are used to calculate the dissociation constants in solutions of various concentrations. Quinine and cinchonine have almost identical constants, but cinchonidine is slightly weaker as a base in 0.002- $M$  solutions. The method is recommended for titration using end-points specified in each case.

H. I. DOWNES.

**Apparent dissociation constant of glycine ethyl ester.** O. H. EMERSON and P. L. KIRK (J. Biol. Chem., 1930, **87**, 597—600).—Glycine ethyl ester has  $K_b$   $5.37 \times 10^{-7}$ ; the difference between this and the dissociation constant of glycine accords with expectation on the hypothesis of Bjerrum (A., 1923, i, 444).

C. R. HARRINGTON.

**Spectrophotometric study of the cupripyridine ion in aqueous solution.** AUMERAS and TAMISIER (Compt. rend., 1930, **191**, 99—100).—Spectrophotometric measurements on mixed solutions of cupric and pyridine salts show the existence of the ion  $[\text{Cu}(\text{C}_5\text{H}_5\text{N})_4]^{++}$ . For the nitrate the constant  $[\text{Cu}^{++}][\text{C}_5\text{H}_5\text{N}]^4/[\text{Cu}(\text{C}_5\text{H}_5\text{N})_4]^{++} = 3.1 \times 10^{-4}$ .

C. W. GIBBY.

**Ebullioscopic determination of relative affinity in the formation of complex cadmium ammonium iodide.** F. BOURION and (Mlle.) O. HUN (Compt. rend., 1930, **191**, 97—98).—Ebullioscopic measurements show that the formation of complex salts in mixtures of potassium iodide and cadmium iodide is more extensive than for ammonium iodide and cadmium iodide.

C. W. GIBBY.

**Complex formation amongst the nitrates. II. Phenol-silver nitrate-water system.** C. R. BAILEY (J.C.S., 1930, 1534—1539).—The high solubility of silver nitrate in phenol is due to the formation of a compound  $\text{AgNO}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$  which is isolated. From the data for the ternary system at 25° it appears that silver nitrate, unlike most ionic compounds, "salts in" phenol, possibly owing to the formation of the above compound. Some new solubility values for silver nitrate in water are given.

H. I. DOWNES.

**Complex salts. III. Effect of alkyl substitution on the stability of the dimalonatocuprate ion.** H. L. RILEY (J.C.S., 1930, 1642—1652).—Determination of the effect of alkyl substitution on the tendency of the malonate ion to co-ordinate with the copper ion and form the ion  $[\text{Cu}(\text{CH}_2\text{C}_2\text{O}_4)_2]^{---}$  (cf. A., 1929, 896) shows that the co-ordinating tendency is decreased most and to an approximately equal extent by the groups Et, and  $\text{Pr}^2$ , the group  $\text{Me}_2$  having the next largest effect, and the groups Me, Et, and  $\text{Pr}^2$  causing only a slight decrease; the group  $\text{Pr}^3$  causes a relatively large increase in the co-ordinating tendency. These effects are correlated with other properties and with those of the normal salts; thus the methyl, ethyl, and  $n$ -propyl copper malonates are pale blue in colour, similar to copper malonate, the isopropyl and dimethyl compounds deep blue, and the diethyl and dipropyl compounds green.

H. I. DOWNES.

**Indicator constants. I. M. KOLTHOFF (J. Physical Chem., 1930, **34**, 1466—1483).**—Existing data are discussed. The indicator constants are a function of the ionic strength of the solution, and they also depend on the type of ion present. For each indicator should be derived a set of data which holds at different ionic strengths of various electrolytes. In practice, however, it is sufficient to give the indicator constant at ionic strengths below 0.1, and to neglect the specific ion effect. This is done for the common indicators at 20°. Methyl-orange and methyl-red are suitable for accurate  $p_H$  determinations, since their indicator constants are practically independent of an ionic strength less than 0.5.

L. S. THEOBALD.

**Dissociation constants of certain sulphone-phthalein indicators.** J. SENDROY, jun., and A. B. HASTINGS (J. Physical Chem., 1930, **34**, 1607—1608).—A reply to the criticisms of Kilpatrick and Kilpatrick (this vol., 292).

L. S. THEOBALD.

**Comparison of the buffering powers of glycine and glycyglycine.** C. FROMAGEOT and M. WATREMEZ (Compt. rend., 1930, **190**, 1459—1462).—The buffering action of glycyglycine is greater than that

of glycine, which in turn is greater than that of cycloglycylglycine. C. C. N. VASS.

**Activity coefficients of ions in dilute solution in ethyl alcohol-water mixtures.** L. A. HANSEN and J. W. WILLIAMS (J. Amer. Chem. Soc., 1930, 52, 2759—2767; cf. Williams, A., 1929, 649).—The effect of 0.001–0.01M-sodium chloride on the solubility of "croceo-tetranitro-diammino-cobaltate, croceo-sulphate, and luteo-iodate" in water and 20, 40, and 60 mol.-% ethyl alcohol-water mixtures has been determined at 25°, and the activity coefficients of these sparingly soluble salts have been deduced. The limiting law of Debye and Hückel is obeyed in sufficiently dilute solutions of the salts of the valency types 1–1 and 1–2 even when the solvents have dielectric constants as low as 34. Except in water, the salt of the 3–1 type deviates from the law, and explanations are suggested. J. G. A. GRIFFITHS.

**Thermodynamics of ionic solvation.** E. LANGE and K. P. MISCHTSCHENKO (Z. physikal. Chem., 1930, 149, 1–41).—The energy and heat effects accompanying ionic solvation have been investigated thermodynamically. In order to calculate the energy change in the solvation of a gaseous ion it is necessary to distinguish the effect of the electrical properties of the solution from that of its chemical properties. The electric potential of the solution has a component due to the existence of molecular orientation at the surface, and another due to inequality of the total positive and negative charges. The cases in which both potentials have finite values, both are zero, and one is zero, respectively, are examined. By working on these lines the heat of solvation has been related to Galvani and Volta potentials, and the relationship between surface potentials and the distribution ratio of an electrolyte between two immiscible solvents has also been examined. R. CUTHILL.

**Equilibrium constants of reactions involving hydroxyl. A correction.** D. S. VILLARS (Proc. Nat. Acad. Sci., 1930, 16, 396–397).—Two errors which occur in a previous communication (A., 1929, 1236) are corrected. One was due to an arithmetical error in the formula for the entropy of oxygen; the other was caused by omitting to take account of the nuclear degeneracy of hydrogen in the hydroxyl group. The corrected equations for the entropies of oxygen and hydroxyl and a table of the revised equilibrium constants are given. W. R. ANGUS.

**Electrometric studies of the precipitation of niobium and tantalum, and of molybdenum and tungsten.** D. D. PERCE and L. F. YNTEMA (J. Physical Chem., 1930, 34, 1822–1825).—The precipitation of niobic and tantalic acids from alkaline solutions of hexaniobates and hexatantalates, and of molybdic and tungstic acids from the corresponding potassium salts has been followed electrometrically. The  $p_H$  values at which precipitation occurs show the impossibility of separating niobium and tantalum by regulation of the acidity. Tantalic acid is more basic than niobic acid. Molybdenum and tungsten show a marked difference in the inflexion points in the titration curves, but no precipitation occurs at these points. The  $p_H$  of the

solution has to be reduced to 2 before this takes place, and a mixture of the two acids results.

L. S. THEOBALD.

**Analytical methods in phase-rule problems.** G. W. MOREY (J. Physical Chem., 1930, 34, 1745–1750).—In connexion with the graphical treatment of phase-rule problems the use of analytical methods is illustrated. L. S. THEOBALD.

**Influence of degree of dispersion of substrates on the equilibria of heterogeneous systems.** L. V. NIKITIN (J. Russ. Phys. Chem. Soc., 1930, 62, 915–924).—Dissolution and crystallisation are considered in reference to the variation of the equilibrium between solution and crystals, in so far as this depends on the dimensions of the latter. R. TRUSZKOWSKI.

**Vapour tensions of aqueous solutions of some hydrated salts.** J. PERREU (Compt. rend., 1930, 191, 254–257).—For the determination of  $i$  as required in Le Chatelier's solubility equation for hydrated salts the relation  $dp/p = i dc/c$  is used in the form  $i = (\log p_1 - \log p_2) / (\log c_1 - \log c_2)$ , where  $p_1, p_2$  are the vapour tensions, and  $c_1, c_2$  the molecular concentrations of the free water (i.e., excluding water of crystallisation) in nearly saturated solutions. This has been done for the salts  $Na_2S_2O_3 \cdot 5H_2O$ , at 20° and 27° ( $i = 1.95$  and  $1.98$ , respectively),  $Na_2SO_4 \cdot 10H_2O$ , at 30° ( $i = 1.12$ ), and  $MnCl_2 \cdot 4H_2O$ , at 20° ( $i = 2.36$ ). C. A. SILBERRAD.

**Freezing of solutions as a method of investigation in pure chemistry. III. The f.-p. curves of mixtures of optically active substances of the camphor group.** J. TIMMERMANS (Bull. Soc. chim. Belg., 1930, 39, 239–251).—Although a mixture of optical antipodes of the same substance gives rise to a racemate, or more often to a pseudo-racemate, optical antipodes of different substances generally gives a series of mixed crystals or a eutectic. C. W. GIBBY.

**Iron-nitrogen system; magnetic investigation.** E. LEHRER (Z. Elektrochem., 1930, 36, 460–473).—The iron-nitrogen alloys obtained by nitridation in hydrogen-ammonia mixtures (cf. this vol., 996) and also by thermal decomposition of  $Fe_2N$  and  $Fe_4N$  have been studied by observations on the magnetisation temperature curves (cf. *loc. cit.*), and measurement of the nitrogen content. The phase diagram obtained for the system reveals four phase boundaries in fair agreement with the work of Fry and the results of X-ray analysis. The temperatures of the two eutectoids are given as  $591 \pm 4^\circ$  and  $650 \pm 4^\circ$ , and the respective nitrogen contents as  $2.35 \pm 0.1\%$  and  $4.55 \pm 0.2\%$ . H. I. DOWNES.

**System sodium oxide-silica.** F. C. KRACEK (J. Physical Chem., 1930, 34, 1583–1598).—The work of Morey and Bowen (A., 1925, ii, 121) on the system sodium metasilicate-silica has been amplified, especially in the region rich in sodium oxide, using the method of quenching as well as heating curves. The system contains three compounds, the orthosilicate, the metasilicate, and the disilicate: the last two compounds are stable at their m. p., but the orthosilicate decomposes at  $1120^\circ \pm 0.5^\circ$  in mixtures containing less than 40.7%  $SiO_2$ , before its m. p. is

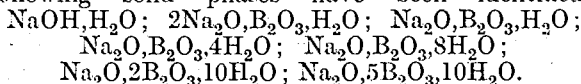
reached. The liquidus curves all indicate considerable dissociation of the liquid. The metasilicate melts at  $1089^{\circ} \pm 0.5^{\circ}$ , and the disilicate at  $874^{\circ} \pm 1^{\circ}$  (cf. Morey and Bowen, *loc. cit.*). The eutectic ortho-silicate-metasilicate is at  $1022^{\circ}$  and 43.1% of silica, whilst that of the metasilicate-disilicate lies at  $846^{\circ}$  and 62.1% of silica. The stable eutectic for quartz and the disilicate occurs at  $793^{\circ}$  and 73.9% of silica, and the metastable eutectic for tridymite and the disilicate at  $782^{\circ}$  and 74.6% of silica. Sodium disilicate shows a reversible inversion at  $678^{\circ}$ ; above  $706^{\circ}$ , it takes up excess of sodium oxide, and above  $768^{\circ}$ , excess of silica into solid solution. The equilibrium diagram of the system is reproduced.

L. S. THEOBALD.

**Influence of constitution on fusion curves of binary systems of aromatic compounds.** A. L. BERNOULLI and A. SARASIN (*Helv. Chim. Acta*, 1930, 13, 511–534).—The influence of the position of the second hydroxyl group in the benzene nucleus has been investigated for pyrocatechol, resorcinol, and quinol in the common solvent phenanthrene. With the change  $o \rightarrow m \rightarrow p$  there is a corresponding displacement of the eutectic composition, viz.,  $39 \rightarrow 13 \rightarrow 1$  mol.-% of the phenol. The fusion curve for pyrocatechol is simple, but the formation of a compound, 1 phenanthrene : 6 dihydroxybenzene, is indicated in the case of the other two phenols. This agrees with the results obtained by Kremann and Janetzky (*A.*, 1912, ii, 1151) for the same substances in naphthalene. The fusion curves of naphthalene with benzoic acid, salicylic acid, phenyl benzoate, benzoin, benzil, and benzilic acid are simple with well-defined eutectics at 32, 9, 61, 14, 41, and 4 mol.-% of the respective benzene derivative. Substitution of the hydroxyl group of benzoic acid by a more electro-negative group (as in benzoin) or addition of such a group (as in salicylic acid) causes the eutectic to occur at a smaller mol.-% of the benzene derivative, whilst substitution by or addition of electropositive groups produces the reverse effect. Benzoic acid, salicylic acid, and benzoin exist as double molecules in naphthalene solution, but the other three substances are not associated. For all the mixtures studied Raoult's law remains approximately valid up to very high temperatures.

F. L. USHER.

**Borates.** The system  $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ . U. SBORGI and L. AMELOTTI (*Gazzetta*, 1930, 60, 468–474).—The ternary isotherm for this system has been determined at  $45^{\circ}$ . At this temperature the following solid phases have been identified:



F. G. TRYHORN.

**System benzoic acid-*o*-phthalic acid-water.** H. L. WARD and S. S. COOPER (*J. Physical Chem.*, 1930, 34, 1484–1493).—The solubilities of benzoic and phthalic acids, alone and admixed, have been determined in water by the synthetic method over the range  $25^{\circ}$  to the m. p. of the acids. The critical solution temperature for benzoic acid is  $117.2^{\circ}$  with 32% of acid, and the triple point lies at  $94.6^{\circ}$ . The synthetic method is not very satisfactory in the case

of phthalic acid on account of the slowness with which equilibrium is reached. The m.-p. curve for the two acids has also been determined; the eutectic temperature lies at  $117.3^{\circ}$  with 91.3% of benzoic acid. The ternary diagram for the system benzoic acid-phthalic acid-water for temperatures above  $70^{\circ}$  is given.

L. S. THEOBALD.

**System sodium oxide-silica-zirconium dioxide.** J. D'ANS and J. LÖFFLER (*Z. anorg. Chem.*, 1930, 191, 1–35).—The f.-p. diagram for the system sodium oxide-silica and part of the diagram for the system sodium oxide-silica-zirconium dioxide have been obtained. The following compounds have been isolated: sodium pyrosilicate,  $\text{Na}_6\text{Si}_2\text{O}_7$ , m. p.  $1122^{\circ}$ ;  $\text{Na}_4\text{Zr}_2\text{Si}_3\text{O}_{12}$ , m. p.  $1540^{\circ}$ ; and  $\text{Na}_2\text{ZrSi}_2\text{O}_7$ . Sodium orthosilicate undergoes a polymorphic transformation at  $960^{\circ}$ , the  $\beta$  form being stable below this temperature and the  $\alpha$  form above. In the system sodium oxide-zirconium dioxide the only compound formed is the metazirconate, m. p. (incongruent) about  $1500^{\circ}$ .

R. CUTHILL.

**Equilibria in the system  $\text{Ca}(\text{ClO}_3)_2 + 2\text{KCl} \rightleftharpoons 2\text{KClO}_3 + \text{CaCl}_2$  at  $15^{\circ}$  and  $45^{\circ}$ .** Y. OSAKA and H. NISHIO (*Bull. Chem. Soc. Japan*, 1930, 5, 181–183).—Diagrams are given for the system  $\text{Ca}(\text{ClO}_3)_2 + 2\text{KCl}$  at  $15^{\circ}$  and  $45^{\circ}$ ; the stable pair at both temperatures is  $\text{KCl} + \text{Ca}(\text{ClO}_3)_2$ .

H. F. GILLBE.

**Exchange reactions of sparingly soluble phosphates and sulphates with permutites.** E. UNGERER (*Kolloid-Z.*, 1930, 52, 227–231).—Tertiary phosphates of lithium, barium, and strontium are transformed into soluble alkali phosphates by base exchange with potassium and ammonium permutites. With the exception of lithium and magnesium, the in-going cations fall into the lyotropic series. The dehydrating influence of the phosphate ion on the strongly hydrated ions of lithium and magnesium may account for this behaviour. In the same way, barium and calcium sulphates are transformed into soluble sulphates by base exchange with alkali permutites, the in-going cations being arranged according to the scheme:  $\text{Li} > \text{NH}_4 > \text{K} > \text{Ca} > \text{Mg}$ .

E. S. HEDGES.

**Thermodynamics and kinetics of heterogeneous equilibria.** C. SLONIM (*Z. Elektrochem.*, 1930, 36, 439–453).—The difficulties associated with the thermodynamic treatment of thermal dissociation processes such as those represented by crystal phase I  $\rightarrow$  crystal phase II + gas are the subject of analysis. X-Ray absorption measurements of such minerals as analcime, chabazite, natrolite, etc., before and after different heat treatments, and measurements of the rate of decomposition and formation of calcium carbonate lead to the supposed existence of an intermediate unstable phase, or pseudo-structure. The significance of such pseudo-structure is discussed and the thermodynamic treatment and kinetics of transition processes into which it enters are considered in some detail.

H. I. DOWSES.

**Heat of formation of mixed crystals of the series  $\text{KCl-KBr}$ .** M. M. POPOV, A. A. BUNDEL, and V. CHOLLER (*J. Russ. Phys. Chem. Soc.*, 1930, 62, 865–881).—See this vol., 703.



Transference phenomena and existence of complex ions as interpreted by their magnetochemical behaviour. S. FREED and C. KASPER (J. Amer. Chem. Soc., 1930, 52, 2632—2638).—It is to be expected that metallic ions containing unbalanced electrons, *i.e.*, paramagnetic ions, would readily form complex ions of lower magnetic susceptibility, whilst ions of the rare-gas type, *e.g.*,  $Mn^{++}$ , would not. The susceptibility of the manganous ion is unchanged by the addition of ammonium sulphate, but the migration of manganese from the anode is suppressed or reversed by suitable concentrations of the ammonium salt. On the addition of potassium cyanide, the susceptibility of the ion falls 9-fold (*cf.* this vol., 676). It is concluded that anomalous migration does not necessarily indicate the formation of complex ions (*cf.* McBain and Van Ryselberge, A., 1929, 143), and an explanation of the phenomenon is to be sought in the interionic attraction theory.

J. G. A. GRIFFITHS.

Electrical conductance of cobalt sulphate solutions. R. C. CANTELO and A. J. BERGER (J. Amer. Chem. Soc., 1930, 52, 2648—2653).—The conductance,  $\Lambda$ , of aqueous cobalt sulphate solutions (0.0001—0.5*N*) has been determined at 25°, and the results are reproduced by the equation  $\Lambda = \Lambda_0 - \Lambda^{\circ}C^{n-1}/K\Lambda_0^{n-1}$ , where  $n=1.58$  and  $\Lambda_0=134.6$  mhos. Relative viscosities have been determined and conductance-viscosity ratios are tabulated. The results satisfy the requirements of the viscosity function of Jones and Dole (A., 1929, 1385).

J. G. A. GRIFFITHS.

Electrical conductivity studies of the interaction of sulphurous acid and certain aldehydes. G. I. HOOVER, K. W. HUNTEN, and C. A. SANKEY (J. Physical Chem., 1930, 34, 1361—1368).—The specific conductances of aqueous solutions of the sulphonic acids of butaldehyde, crotonaldehyde, cinnamaldehyde, and hydrocinnamaldehyde have been determined between 18° and 155°. With the first-named,  $\kappa$  increases with a rise in temperature to a maximum at approximately 80°, and then decreases owing to hydrolysis of the acid to aldehyde and sulphur dioxide. An increase in dilution shifts the maximum to higher temperatures. The hydrolysis of the acid in aqueous solution has been measured at 45°, 65°, 75°, and 85°. Butaldehyde- and crotonaldehyde-monosulphonic acids are both strong acids of the same order of strength as hydrochloric acid. Breaks in the specific conductance curves indicate that the unsaturated monosulphonic acids of croton- and cinnam-aldehydes change rapidly, above 110°, to the corresponding saturated acids; the reaction is autocatalytic, and proceeds very slowly below 110° in dilute solution. The curves for hydrocinnamaldehydesulphonic acid have the same form as those of the butaldehyde acid, indicating that no addition of sulphurous acid takes place to the double linkings within the benzene nucleus. The specific conductance curves for dilute solutions (0.00019—0.0031*M*) of sulphurous acid between 18° and 145° indicate almost complete hydrolysis at the higher temperatures. The sulphite process for the manufacture of wood pulp is discussed in the light of the present work.

L. S. THEOBALD.

Electrochemical examination of the system aluminium bromide-potassium bromide in toluene and xylene solutions. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Russ. Phys. Chem. Soc., 1930, 62, 989—993).—The conductivity attains a maximum value of  $\kappa=4.22 \times 10^{-3}$  in a toluene solution containing 41.94% of  $AlBr_3$  and 6.54% of  $KBr$ . Aluminium and potassium bromides dissolve in moist xylene-petroleum (b. p. 122—130°) mixtures with the formation of two layers, the lower of which exhibits considerable conductivity. Using aluminium electrodes, aluminium is dissolved at the anode and deposited on the cathode, and analogous results are obtained using copper or silver anodes. The decomposition potential is 2.05 volts in toluene, 1.65 volts in *p*-xylene, and 1.53 volts for the lower layer of moist commercial xylene-petroleum mixtures.

R. TRUSZKOWSKI.

Potential of the copper electrode. F. H. GETMAN (J. Physical Chem., 1930, 34, 1454—1465).—The potential of an electrode consisting of a single crystal of metallic copper has been compared at  $25^\circ \pm 0.02$  with the potentials of a series of copper amalgam electrodes and found to be 3.5 millivolts higher. The normal potential of the single crystal is  $-0.3475$  volt, and is preferred as the standard value. The activity coefficients of solutions of copper sulphate have been calculated and are compared with the corresponding values derived from *f.p.* data. The similarity in behaviour of monocrystalline and spongy copper electrodes is discussed. The constancy and reproducibility of copper amalgam electrodes found by previous workers are confirmed as well as the results of Lewis and Lacey (A., 1914, ii, 521) obtained with electrodes of spongy copper.

L. S. THEOBALD.

Electrode potentials of iron and steel in distilled, tap, and sea water. K. HASEGAWA and S. HORI (Mem. Ryojun Coll. Eng., 1930, 2, 271—295).—Cast iron shows the highest anodic potential, and steel the next highest; below 1% C the potential decreases with decrease in the carbon content, whilst a slight decrease is also observed when the carbon content is greater than 1%. The potential of wrought iron is practically the same as that of low-carbon steel. Equilibrium is reached most rapidly in sea water and least rapidly in distilled water. Agitation lowers the potential, the diminution being decreased by exclusion of air. Oxygen in tap water lowers the potential, whilst free or combined carbon dioxide has only a slight effect. Similar observations were made on nickel and chromium steels.

CHEMICAL ABSTRACTS.

Oxidation-reduction potentials. II. Manganese dioxide. S. POPOV, J. A. RIDDICK, and W. W. BECKER (J. Amer. Chem. Soc., 1930, 52, 2624—2632).—Electrolytically prepared manganese dioxide contains lower oxides. The *E.M.F.* of the cell  $Pt|H_2, H^+|H^+ + MnO_4^- + MnO_2|Pt$  is variable owing to the instability of potassium permanganate in perchloric acid solutions. The *E.M.F.* of the cell  $Pt|H_2, H^+|H^+ + Mn^{++} + MnO_2|Pt$  reaches steady values with chemically prepared manganese dioxide containing lower oxides, but fluctuates if the pure dioxide is used. It follows that the potential of the perman-

ganate-hydrogen-manganous oxide electrode calculated from those of the manganese dioxide electrodes is not trustworthy (Brown and Tefft, A., 1926, 687; Brown and Liebhafsky, following abstract).

J. G. A. GRIFFITHS.

**Manganous-manganese dioxide and manganous-permanganate electrodes.** D. J. BROWN and H. A. LIEBHAFSKY (J. Amer. Chem. Soc., 1930, 52, 2595—2598).—From *E.M.F.* measurements with the cell  $\text{H}_2|0.05-0.3M\text{-HClO}_4, 0.001-0.3M\text{-Mn}(\text{ClO}_4)_2|\text{MnO}_2$  the oxidation potential of the reaction  $\text{MnO}_2 + 4\text{H}^+ + 2e \rightleftharpoons \text{Mn}^{++} + 2\text{H}_2\text{O}$  is found to be  $+1.236 \pm 0.002$  volts at  $25^\circ$ . Manganese dioxide prepared by thermal decomposition of manganous nitrate and dried at  $250-300^\circ$  after washing with hot nitric acid and water gives reproducible results. In conjunction with the data of Brown and Tefft (A., 1926, 687), the oxidation potential of the reaction  $\text{MnO}_2 + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{++} + 4\text{H}_2\text{O}$  is computed to be  $+1.446$  volts.

J. G. A. GRIFFITHS.

**Oxidation-reduction potentials at carbon and tungsten electrodes.** L. B. FLEXNER and E. S. G. BARRON (J. Amer. Chem. Soc., 1930, 52, 2773—2776).—The potentials at carbon and tungsten electrodes in various oxidation-reduction systems have been compared with those at platinum and gold-plated platinum electrodes. With quinhydrone at  $20^\circ$  graphite yields results identical with those given by platinum and gold, whilst tungsten does not. With the ferro-ferricyanide system at  $30^\circ$  graphite and tungsten give values 1—2 and 5—10 millivolts, respectively, below the other metals. Until indigotindisulphonate or methylene-blue at  $30^\circ$  is about 2% reduced it is necessary to wait about 30 min. for the final values at graphite electrodes, which then give the same rapidly established potentials as platinum and gold. Tungsten is less trustworthy. Hydrogen has no influence on the observed potentials.

J. G. A. GRIFFITHS.

***E.M.F.* of the hydrogen electrode in organic acids.** N. ISGARISCHEV and S. A. PLETENEV (Z. Elektrochem., 1930, 36, 457—460).—The measurement of the hydrogen electrode potential in pure acetic acid and butyric acid in the presence of (1) sodium acetate, and (2) water, is described. The *P.D.* shows an increase with increase in quantity of added substance up to a maximum limit in the case of both solutions. The significance of the phenomena is discussed.

H. I. DOWNES.

**Application of the quinhydrone electrode to the measurement of the acid reaction of unbuffered solutions.** R. J. BEST (J. Physical Chem., 1930, 34, 1815—1817).—In unbuffered dilute solutions of acids, the quinhydrone electrode can be used to measure the acid reaction of solutions of  $p_H$  1—5, but not of  $p_H$  greater than 5.

L. S. THEOBALD.

**Conception of electrical *P.D.* between two phases. II.** E. A. GUGGENHEIM (J. Physical Chem., 1930, 34, 1540—1543).—A modification of previous views (cf. A., 1929, 885).

L. S. THEOBALD.

**Diffusion potential.** V. PLETTIG (Ann. Physik, 1930, [v], 5, 735—761).—It is shown that the extended Planck's formula for diffusion potential holds for

mixtures. The single concentrations in the transition layer were calculated. For the cells  $N\text{-HCl}|0.01N\text{-KCl}$ ,  $N\text{-HCl}|0.01N\text{-LiCl}$ , and  $0.1N\text{-H}_2\text{SO}_4|0.01N\text{-Li}_2\text{SO}_4$ , the diffusion potentials were calculated according to Planck and according to Henderson, and the concentrations of single ions at different points in the transition layer were found according to both theories. The change of the total potential was found when mixtures of the above-determined concentrations were used. Boundary layers produced in different ways were investigated, and in all cases the Henderson formula was found to hold.

A. J. MEE.

**The liquid junction of dilute electrolytes.** M. PLANCK (Sitzungsber. Preuss. Akad. Wiss., 1930, 20, 9 pp.).—The *P.D.* at the junction of a solution of *N*-hydrochloric acid with a solution of 0.01*N*-potassium chloride supports the views of Henderson (A., 1907, ii, 426; 1908, ii, 655) as to the conditions obtaining at the junction of two binary electrolytes and not those of the author (A., 1928, 481; 1929, 402). These conditions are the subject of further theoretical treatment, and the possibility of utilising a chemical analysis of the two electrolyte solutions in the proximity of the junction as a further method of investigating the conditions existing there is discussed.

H. I. DOWNES.

**Electrokinetic potentials. V. Interfacial energy and the molecular structure of organic compounds. I. Electrokinetic potentials at cellulose-organic liquid interfaces.** W. M. MARTIN and R. A. GORTNER (J. Physical Chem., 1930, 34, 1509—1539).—The  $\zeta$ -potentials of cellulose-liquid interfaces have been determined by a streaming potential method. The liquids used include the commoner aliphatic alcohols, glycerol, ethylene chloride and bromide, benzene and its mono-substituted derivatives. Different diaphragms from the same samples of cellulose yield comparable results. When pure liquids are streamed through cellulose, the *E.M.F.* increases with pressure, the value for  $\zeta$  or for the ratio *E.M.F./P* increasing from zero at the point of origin and finally approaching a constant value. The  $\zeta$ -potential at a cellulose-organic liquid interface is a function of the structure of the molecules oriented there, and the relative symmetry of the molecules with respect to polar groups or double linkings determines the sign and magnitude of the potential. Addition of a  $\text{CH}_2$  group in the aliphatic alcohols alters the potential by  $\pm 36$  millivolts; the substitution of a methyl group for hydrogen to form a branched chain alters the potential by  $\pm 4$  millivolts. The data favour a helicoidal configuration for the carbon atoms in a homologous series of aliphatic alcohols. The  $\zeta$ -potential of a cellulose-benzene interface is zero, but the somewhat unsymmetrical, non-polar toluene gives a low, but measurable value for  $\zeta$ ; the highly-polar nitrobenzene gives the highest potential of all the compounds examined. In the substitution of hydrogen in the benzene molecule, the electrokinetic effect follows the order hydrogen < methyl < chlorine < bromine < amino- < nitro-group. A marked similarity between the electrokinetic potential and the Kerr electro-optical constant exists. The streaming potential

method can be used to determine the structural configuration of molecules, whilst the  $\zeta$ -potential is a criterion of the purity of a compound.

L. S. THEOBALD.

**Cells with liquid-liquid junctions. II. Thermodynamic significance and relationship to activity coefficients.** E. A. GUGGENHEIM (*J. Physical Chem.*, 1930, **34**, 1758—1766; cf. *A.*, 1929, 885).—Theoretical. An extension of previous views in which the conception of ionic activity is treated as a mathematical device. A new system of conventional ionic activity coefficients is defined.

L. S. THEOBALD.

**Cells with sodium cathodes.** G. I. COSTEANU (*Compt. rend.*, 1930, **191**, 205—207).—The *E.M.F.* of the cell  $\text{CuO}|\text{LiCl} \cdot \text{KCl}|\text{Na}$  is  $2.099 + 0.0004113(t - 380)$  volts between  $380^\circ$  and  $504^\circ$ . If lead +25% of sodium is used as cathode,  $E = 1.960$  volts ( $620^\circ$ ), and with pure lithium chloride as electrolyte in this cell  $E = 1.950$  volts at  $714^\circ$ , the temperature coefficient having nearly the same value. For the cell  $\text{CuO}|\text{CaCl}_2 \cdot \text{KCl}|\text{NaPb}$ ,  $E = 2.168 - 0.002058(t - 628)$  between  $628^\circ$  and  $750^\circ$ . The experiments were conducted in oxygen-free nitrogen. The cell reaction is given by the equation  $\text{CuO} + 2\text{Na} + 2\text{MCl} = \text{Cu} + 2\text{NaCl} + \text{M}_2\text{O}$ .

J. GRANT.

**Diffusion of hydrogen through an iron cathode.** A. H. W. ATEN and M. ZIEREN (*Rec. trav. chim.*, 1930, **49**, [iv], 641—657).—Measurements have been made of the effect of a number of poisoning agents on the rate of diffusion of hydrogen (measured directly by a gas burette), through cathodes of thin iron sheet, on the variation of potential with time and of the corresponding rate of diffusion of hydrogen. The influence of the thickness of the cathode and of the current strength was investigated using mercuric chloride, strychnine sulphate, potassium cyanide, and arsenious oxide in sodium hydroxide and dilute sulphuric acid solutions. It is suggested that the reduced rate of diffusion is the result of the retardation of the reaction  $2\text{H} \rightarrow \text{H}_2$  on the cathode surface, and that the potential becomes more negative as a result of the accumulation of uncombined hydrogen atoms. The equation  $\log D = \log A/d + m/n(\log W/B)$  is shown to hold,  $D$  being the diffusion velocity,  $d$  the thickness of the cathode,  $W$  the actual velocity of formation of molecular hydrogen, and  $B$  the velocity coefficient of the same reaction;  $A$  is the diffusion coefficient of molecular hydrogen, and  $m$  and  $n$  are experimental constants.

F. G. TRYHORN.

**Overvoltage of hydrogen.** E. BAARS and C. KAYSER (*Z. Elektrochem.*, 1930, **36**, 428—439).—The cathodic hydrogen development with very small current densities and the question of the minimum overvoltage are investigated and measurements of these quantities with improved apparatus are recorded. Results of measurements using electrodes of lead, platinum, platinised glass, gold, and copper are tabulated. It is found that the existence of overvoltage is dependent on the presence of a finite current density, and that the previously recorded and divergent minimum overvoltages at zero current are fictitious. These earlier measurements are attributed to residual current phenomena which may arise from

oxygen diffusion at the cathode, or diffusion of hydrogen into the cathode material. H. I. DOWNES.

**Hydrogen overvoltage and adsorption of ions.** P. HERASYMENKO and I. ŠLENDYK (*Z. physikal. Chem.*, 1930, **149**, 123—139).—Heyrovský's theory (*A.*, 1925, ii, 675) that the overvoltage of hydrogen at an electrode of high overvoltage is determined primarily by the rate of the reaction  $\text{H}^+ + \text{H}' = \text{H}_2$  on the electrode has been tested by measurements of the discharge voltage,  $\pi$ , of hydrogen at a dropping mercury electrode in aqueous solutions of hydrogen chloride. In very dilute solutions the overvoltage decreases with increase in the concentration, but the rate of decrease becomes less and less, and when the concentration has reached about 0.1*N* the overvoltage varies only slightly with the concentration. This behaviour is explained by supposing that at all the higher concentrations the electrode is saturated with  $\text{H}^+$  ions, and it is only in the dilute solutions that the concentration of hydrogen ions adsorbed on the electrode varies with the concentration of the solution. Addition of increasing amounts of metallic chlorides to the solution causes a progressive increase in the overvoltage, presumably because the metal ions partly displace the adsorbed hydrogen ions. In respect of this effect the various cations fall into much the same order as for the precipitation of an electro-negative colloid. When a certain concentration of salt has been attained, however,  $\pi$  reaches a steady value depending only on the hydrogen-ion concentration in the solution, and apparently corresponding with saturation of the electrode with adsorbed metal ions. In order to express this theory quantitatively, Heyrovský's theory may be combined with the Langmuir adsorption isotherm, yielding the equation  $\pi = RT/F \cdot \log\{z\omega c^2/(1 + \omega c + \omega_s c_s)\} + k$ , where  $z$  is the maximum number of adsorbing centres,  $\omega$  is a quantity characteristic of the adsorptive power of the electrode for hydrogen ions,  $c$  is the concentration of hydrogen ions in the solution,  $\omega_s$  and  $c_s$  are the corresponding quantities for the metal ion, if any,  $k$  is a constant, and  $R$ ,  $T$ , and  $F$  have their usual significance. This equation accords well with the experimental data.

R. CUTHILL.

**Theory of dissolution of metals.** M. STRAUMANNIS (*Z. physikal. Chem.*, 1930, **148**, 349—360; cf. this vol., 705).—When a zinc electrode dissolves anodically its potential decreases proportionally to the current strength. The proportionality found by Thiel and Eckell (*A.*, 1928, 376) between the current strength and the "difference effect" holds only for small currents. A quantitative expression for the "difference effect," involving the potential of the zinc plate, the overvoltage, and the resistance, is deduced from the theory of local currents, and for small currents this becomes proportional to the current strength. A method of calculating the overvoltage of local elements in a cathode is given; it leads to results which are considerably higher than those measured in the usual manner. These high values are considered to approximate more closely to the true value of the overvoltage.

F. L. USHER.

**Local current theory of corrosion and passivity.** F. TÖDT (*Z. physikal. Chem.*, 1930, **148**, 434—440).—

Theoretical. A review of the experimental data relating to corrosion of metals in feebly alkaline, neutral, or feebly acid solutions in presence of air shows that corrosion can be best explained on the assumption of the formation of an invisible film of oxide and the setting-up of local currents between this film as cathode and the free metal surface. This oxide film is to be distinguished from the visible oxide formed by corrosion. Although the film is normally porous, the pores may be closed under certain conditions and the metal then becomes passive. The periodic phenomena of passivity are discussed.

M. S. BURR.

**Isolation of the film responsible for the passivity of an iron anode in acid solution.** U. R. EVANS (*Nature*, 1930, **126**, 130—131).—Transparent films responsible for passivity have been isolated from an iron anode in dilute sulphuric acid solution as electrolyte. The films are stable chemically, and although less easy to preserve than those obtained from iron made passive with potassium chromate, can be preserved for 1 hr. in *N*-sulphuric acid. The results confirm the views of Hedges (*A.*, 1928, 600) that anodic passivity is due to a protective film.

L. S. THEOBALD.

**Function of the Wehnelt interrupter and the crystal conductor.** S. RAY (*Z. Elektrochem.*, 1930, **36**, 425—426).—A tentative explanation based on the author's views (*cf.* *A.*, 1929, 228).

H. I. DOWNES.

**Current phenomena in electrolytic and thermo-electric circuits.** S. RAY (*Z. Elektrochem.*, 1930, **36**, 425).—A galvanometer connected to two copper electrodes placed at the end of a vertical column of copper sulphate solution gives a deflexion lasting several days. The current is largely independent of changes of resistance in the circuit. A similar effect is obtained in a thermo-electric circuit of two solid elements the junction of which is exposed to the air; the effect appears to be independent of the position which the soldered connexions occupy in the room.

H. I. DOWNES.

**Passage of continuous current in acetone.** H. GARRIGUE (*Compt. rend.*, 1930, **190**, 1406—1408).—The current passing between two platinum electrodes maintained at a constant *P.D.* (80—800 volts) in purified or commercial acetone decreases continuously with time, a back-*E.M.F.* being produced, which after 24 hrs. gave a current decreasing with time over 70 hrs. Reversal of the potential (90 volts) produced a maximum on the current-time curve 1 hr. after reversal. Measurements of the distribution of potential between the electrodes indicated the formation of positive and negative columns of liquid with different properties. These diffuse together and give rise to periodic changes in current, which are eliminated if the space between the electrodes is occupied by glass-wool.

J. GRANT.

**Oxygen depolarisation current; influence of light.** L. W. HAASE (*Z. Elektrochem.*, 1930, **36**, 456—457).—The oxygen depolarisation current obtained with iron-platinum or cadmium amalgam-platinum elements in distilled or conductivity water and in potassium chloride solutions varies with the

light falling on the system. Measurements in the dark show a smaller current than those obtained in diffuse daylight, sunlight, or other light source.

H. I. DOWNES.

**Photo-voltaic effects in Grignard solutions.** I. R. T. DUFFORD (*J. Physical Chem.*, 1930, **34**, 1544—1553; *cf.* *A.*, 1927, 918).—Cells containing ethereal solutions of Grignard reagents with metals such as platinum, gold, magnesium, lead, zinc, copper, aluminium, and iron as electrodes show a photo-voltaic effect which is not due to changes in temperature. The light-sensitivity is greater for aromatic than for the corresponding aliphatic compounds, for bromides than for iodides, and probably for chlorides than for bromides. The optimum concentration for light-sensitivity is slightly higher for aromatic compounds. The initial rate of change of voltage is practically proportional to the intensity of illumination, and the light-sensitivity exists for all visible wave-lengths, with a broad maximum in the green or blue. In the dark, the voltages of these cells show marked irregularity. L. S. THEOBALD.

**Theory of third-order gas reactions.** L. S. KASSEL (*J. Physical Chem.*, 1930, **34**, 1777—1796).—A theoretical paper in which a statistical mechanical theory of termolecular gas reactions is developed. The process of triple collision in an imperfect gas is examined in detail. The negative temperature coefficient of the reaction between nitric oxide and oxygen is accounted for on the basis of clustering caused by the van der Waals forces, and the fact that the apparent efficiency of triple collisions is greatest in reactions for which the energy of activation is greatest is explained.

L. S. THEOBALD.

**Law of flame speeds.** II. Y. NAGAI.—*See B.*, 1930, 749.

**Reaction process in the formation of molecular hydrogen from its atoms.** H. SENFTLEBEN and O. RIECHEMEIER (*Naturwiss.*, 1930, **18**, 645).—The reaction process in the formation of molecular hydrogen from its atoms can be followed quantitatively by studying the thermal conductivity of a mixture of hydrogen atoms and molecules (*A.*, 1929, 982). A quantitative relation between the thermal conductivity and the number of atoms has been established. Measurements at different pressures show that if side reactions are suppressed, the reaction involves three reactants, either two atoms and a molecule or three atoms. The calculated values for the "Wirkungsquerschnitt" of the two reactions are respectively 1.3 and 20 times as great as the kinetic value.

W. R. ANGUS.

**Mechanism of combustion in the oxygen-hydrogen flame.** E. H. RISENFELD and E. WASSMUTH (*Z. physikal. Chem.*, 1930, **149**, 140—152).—In view of the results of the investigation of combustion in micro-oxygen-hydrogen flames (*cf.* *A.*, 1929, 289) it is suggested that the mechanism of combustion in the oxygen-hydrogen flame is probably represented by the following chain of reactions: (1)  $H_2 + O_2 = H_2O + O - 7 \text{ kg.-cal.}$ , (2)  $O + H_2 = OH + H + 10 \text{ kg.-cal.}$ , (3)  $H + O_2 = OH + O - 17 \text{ kg.-cal.}$ , (4)  $OH + H_2 = H_2O + H + 10 \text{ kg.-cal.}$  Of these, (2) and (4) will be accelerated by excess of hydrogen and (3)

only by excess of oxygen, which accounts for the fact that the rate of combustion of hydrogen burning in excess of oxygen is greater than that of oxygen burning in excess of hydrogen. Hydrogen peroxide must be formed by ternary molecular collisions, probably as follows:  $O + H_2 + O_2 = H_2O_2 + O + 38 \text{ kg.-cal.}$ ,  $H + O_2 + H_2 = H_2O_2 + H + 38 \text{ kg.-cal.}$ ,  $OH + H_2 + O_2 = H_2O_2 + OH + 38 \text{ kg.-cal.}$ , and  $H_2O + O + M = H_2O_2 + M$  (+45 kg.-cal.), where  $M$  represents a molecule which has taken up the energy set free. The ratio of the frequency of such collisions to that of the binary collisions leading to the formation of water will be only about 0.001, however, and von Deines has, indeed, found (Diss., Berlin, 1927) that the mol. ratio of hydrogen peroxide to water formed in a micro-oxygen-hydrogen flame is of this order, although with very small flames, *i.e.*, with very effective cooling, the value may be as high as 0.005. The absence of ozone from the products of combustion of oxygen burning in hydrogen is probably a consequence of the reactions  $O_3 + H_2 = H_2O + O_2 + 92 \text{ kg.-cal.}$ , and  $O_3 + H_2O = H_2O_2 + O_2 + 16 \text{ kg.-cal.}$  R. CUTHILL.

**Influence of nitrogen dioxide on the ignition temperature of hydrogen-oxygen mixtures.** H. J. SCHUMACHER (Nature, 1930, 126, 132—133).—Theoretical. L. S. THEOBALD.

**Propagation of combustion in hydrocarbon mixtures.** M. AUBERT and R. DUCHÈNE (Compt. rend., 1930, 191, 123—125).—The rates of propagation of explosion wave fronts at higher compression (5.9) have been determined photographically, at initial temperatures of 15° and 50°, for benzene, "auto-benzol," hexane, heptane, and "ordinary motor spirit." The increased temperature causes an increase in the rate of 50—450%. A marked difference was observed in the course of combustion of benzene and some motor spirits as compared with that of hexane, heptane, and "ordinary motor spirit." Whilst photographs of the former show the production merely of progressive darkening of the plate, with hexane etc., after a preliminary period of  $3-9 \times 10^{-3}$  sec. of very pale flame, a general inflammation with very actinic flame is demonstrated. It is suggested that this general inflammation is associated with "knocking," a suggestion supported by the fact that the addition of 4% of amylene to the "ordinary motor spirit," which very greatly reduces knocking, changes the character of the explosion flame to that of benzene. C. A. SILBERRAD.

**Ignition temperatures of gases in nitrous oxide.** H. B. DIXON and W. F. HIGGINS (Mem. Manchester Phil. Soc., 1928—1929, 73, 21—32).—The ignition temperatures of hydrogen and ethylene at normal pressures and under the same conditions are practically identical in oxygen and nitrous oxide. The ignition temperature of ether in oxygen is low, but very much higher in air, and still higher in nitrous oxide. The presence of small traces of nitrogen peroxide generally reduces ignition temperatures. Nitrogen peroxide (1 vol.) in air (140 vols.) reduces the ignition temperature of methane by 120°; 1 vol. in 200 vols. of air reduces the temperature of ignition of hydrogen by 69°, but excess of nitrogen peroxide

raises the ignition temperature. Nitric oxide at high temperatures is oxidised to the peroxide, and therefore also reduces ignition temperatures.

J. O. CUTTER.

**Experimental procedure and the kinetics of the nitrogen pentoxide decomposition at low pressures.** J. H. HIBBEN (J. Physical Chem., 1930, 34, 1387—1398).—From a discussion of the work of previous investigators it is concluded that the velocity of decomposition of nitrogen pentoxide remains unchanged at least until a pressure of a few thousandths of a mm. is reached. This suggests that the most tenable hypothesis is one of the modifications of Lindemann's theory. Determinations of the amount of oxygen removed from a system at low pressures by the condensation of nitrous oxide, nitrogen pentoxide, and nitrogen dioxide show that adsorption and occlusion of oxygen are negligible factors. An important amount of oxygen, however, may be removed at low pressures by contact with mercury. L. S. THEOBALD.

**Oxidation of phosphine.** R. H. DALTON (Proc. Roy. Soc., 1930, A, 128, 263—275).—In continuation of previous work by Hinshelwood and Dalton (A., 1929, 1243) experiments have been made on the oxidation of phosphine at higher pressures, where there exists an upper limiting pressure above which the action is negligibly slow, even in the absence of moisture, but below which the mixture explodes. The procedure was to mix known quantities of oxygen and phosphine at liquid air temperature and, after warming to the ordinary temperature, to expand until an explosion occurred. When oxygen is in large excess the mixture will not explode until expanded to very low pressures. As the proportion of phosphine is increased the pressures at explosion become rapidly greater until, in the neighbourhood of the point where oxygen and phosphine are present in equal proportion, the oxygen pressure begins to change more slowly and beyond this point becomes nearly constant. If the value of the phosphine/oxygen ratio is below about 0.1, no explosion occurs at any pressure. From the fact that the higher pressure limit is independent of the tube diameter and of the nature of its walls, but is decreased by the addition of an inert gas, it is apparent that the upper limit is subject to quite different conditions from those prevailing at the lower limit. The results are accounted for by assuming that the reaction occurs by a simple chain mechanism in which the chains are deactivated by three-body collisions in the gas. The following expression is obtained:  $[PH_3] = 4.3 \times 10^{-3} [O_2]^2 + 10 \times 10^{-3} [O_2][N_2]/(1 - 9.1 \times 10^{-3} [O_2])$ , where the bracketed expressions stand for the partial pressures of the gases, and the constants are calculated from the experimental data. If argon is the inert gas, in place of nitrogen, the coefficient of the last term of the numerator has the value  $5.3 \times 10^{-3}$ . The present results differ in several important respects from those recently published by Trautz and Gabler (*cf.* A., 1929, 887), who worked with moist gases, and the differences are attributed to the influence of water vapour. L. L. BIRCUMSHAW.

**Physical measurements with short-lived intermediate products.** H. SCHMID (Z. physikal. Chem.,

1930, 148, 321—336; cf. A., 1929, 515).—The method previously employed by the author has been applied so as to allow physical measurements to be made on a rapidly changing system. The reaction studied, in which a transient violet coloration is produced, was that between a ferric salt and an alkali thiosulphate. The reaction mixture was caused to flow at a uniform speed through a narrow cylindrical tube, at different positions in which platinum wires were sealed and used as ferric-ferrous ion electrodes. The intermediate product, which has a life of a few seconds only, has the constitution  $\text{FeS}_2\text{O}_3^+$ ;  $K = [\text{FeS}_2\text{O}_3^+]/[\text{Fe}^{+++}][\text{S}_2\text{O}_3^{--}] = 15$  at  $18^\circ$ . No indication of the formation of a similar ferrous complex was obtained.

F. L. USHER.

**Kinetics of nitrous acid. VII. Velocity and temperature.** E. ABEL, H. SCHMID, and E. RÖMER (Z. physikal. Chem., 1930, 148, 337—348; cf. A., 1928, 1194).—The temperature coefficients of the velocity coefficients ( $k_1$ ) of the decomposition of nitrous acid have been measured at six temperatures between  $0^\circ$  and  $60^\circ$  and found to vary from 6.7 to 3.2. These abnormally high values are to be expected from the reaction mechanism: (1)  $4\text{HNO}_2 = \text{N}_2\text{O}_4 + 2\text{NO} + 2\text{H}_2\text{O}$ ; (2)  $\text{N}_2\text{O}_4 + \text{H}_2\text{O} = \text{HNO}_2 + \text{HNO}_3$ ; (combining)  $3\text{HNO}_2 \xrightleftharpoons[k_2]{k_1} \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$ , where

$k_1$  is shown to be the product of a true velocity coefficient and an equilibrium constant. The temperature coefficient of  $k_2$  is normal (2.5 at  $20^\circ$ ). The connexion between velocity and temperature is expressed approximately by the equation  $\log k_{1,0} = -6250/T + 22.65$ , and more closely by an empirical power series. The velocity ( $v$ ) increases with increasing ionic concentration ( $j$ ) and the value of  $dv/dj$ , 0.078, is nearly independent of temperature.

F. L. USHER.

**Velocity of hydrolysis of ethyl formate by ammonia solution in presence of ammonium salts.** E. N. ROBERTS and (Miss) E. M. TERRY (J. Amer. Chem. Soc., 1930, 52, 2604—2611).—The rate of hydrolysis at  $25^\circ$  of 0.08*N*-ethyl formate by 0.1*N*-ammonium hydroxide is markedly accelerated by ammonium chloride or nitrate (0.04—0.4*N*). A tentative interpretation of the data is given.

J. G. A. GRIFFITHS.

**Kinetics of reduction of cystine and related dithio-acids by reversible oxidation-reduction systems.** P. W. PREISLER (J. Biol. Chem., 1930, 87, 767—784).—Cystine, dithiodilactic, dithiodihydracrylic, and dithiodiglycollic acids were reduced by mixtures of chromous and chromic chlorides and by vanadous chloride; the rates of reaction observed approximated to those of reactions of the second order. The rates of reduction were greatest with those acids in which a carboxyl or an amino-group was adjacent to the disulphide linking. The rates diminished with increase in acidity; they were different for different oxidation-reduction systems, but were not affected by changes in the potential of a given system brought about by varying the ratio of oxidant to reductant. The system  $\text{R-S-S-R-R-SH}$  is not to be regarded as reversible, since it does not conform to the definition of a reversible system (e.g., quinone  $\rightleftharpoons$  quinol) as one in which the establishment of an equilibrium

between the components can be experimentally demonstrated.  
C. R. HARRINGTON.

**Auto-oxidation of quinol.** A. SAINT-MAXEN (Compt. rend., 1930, 191, 212—214).—The rate of oxidation of quinol in aqueous-alkaline solution increases proportionally with the quantity of sodium hydroxide provided that the mol. ratio, alkali : quinol, does not exceed 0.2. Above this value the rate increases less rapidly and approaches a limit reached at the value 0.6. After passing the value 1 the rate diminishes slowly. A parallelism is noted between these data and those obtained from determinations of electrical conductivity and density of light absorption. It is suggested that the monosodium derivative of quinol is oxidised with considerable rapidity, whereas the compound itself and its disodium derivative are only very slowly attacked.

H. WREN.

**Velocity of decomposition of diazo-compounds in water.** V. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1930, 33, 231—233D).—*p*-Toluidine was diazotised and titrated with *L*-acid at various temperatures from  $0^\circ$  to  $30^\circ$ . From the values obtained the decomposition velocity coefficient at  $0^\circ$  was  $3.4 \times 10^{-6}$  and the Arrhenius temperature coefficient 12115. *o*-Toluidine was similarly treated and the decomposition velocity coefficient of *o*-diazotoluene was  $1.93 \times 10^{-4}$ . This, however, required halving, as it was found that almost all the *o*-cresol produced coupled with *o*-diazotoluene and the true value is  $0.97 \times 10^{-4}$ . These results agree approximately with those of Cain and Hantzsch.

C. IRWIN.

**Kinetics of diastatic actions.** J. B. S. HALDANE (J. Chim. phys., 1930, 27, 277—284).—The kinetics of the reactions, diastase + substrate  $\rightleftharpoons$  diastase-substrate complex  $\rightarrow$  diastase + products of reaction, are considered, and the hyperbolic relationship between the velocity of reaction and the concentration of the substrate is shown to fail at high values of the latter owing to the decrease in velocity due to dilution of the other reactants. Diastase may unite with its substrate and other substances present in such a manner as to produce catalysis, competitive or non-competitive inhibition, or in such a way as not to produce inhibition, but yet to act as a protective against heat; e.g., sucrose protects malt amylase without inhibiting it. The first two types of union are identical from the chemical point of view. It is shown that successive purifications of diastases will lead to a point when further treatment decreases the activity, the critical point probably being reached when the active portion of the diastase micelle is covered with a unimolecular layer of substrate.

J. GRANT.

**Influence of a soluble fluoride on the corrosion of iron.** A. W. CHAPMAN (J.C.S., 1930, 1546—1550).—A comparison of the corrosion produced by potassium chloride and potassium fluoride. Dilute solutions (up to 0.8*N*) of potassium fluoride corrode iron similarly to potassium chloride solutions of equivalent concentrations. 0.85*N*-Potassium fluoride solution does not attack iron, and it is suggested this abrupt change is due to the formation of a self-repairing



protective film of iron fluoride. Inhibitors (sodium carbonate or potassium chromate) are effective in lower concentrations against fluoride ion than against chloride ion attack. A special type of corrosion in which iron potassium fluoride and iron chromate were formed was exhibited in certain specific solutions containing potassium fluoride and chromate.

J. O. CUTTER.

**Kinetics of the oxidation of copper. I. Initial oxidation of copper at low temperatures.** F. J. WILKINS and E. K. RIDEAL. **II. Limiting pressure. Evidence for the lateral diffusion of adsorbed gas.** F. J. WILKINS (Proc. Roy. Soc., 1930, A, 128, 394—406, 407—417).—I. The work of Pilling and Bedworth (J. Inst. Metals, 1923, 29, 529), Dunn (A., 1926, 692), and Feitknecht (A., 1929, 517) is briefly reviewed, and the importance of the rate of diffusion of oxygen through the oxide film in determining the rate of oxidation of the metal is emphasised. The nature of this diffusion is discussed, and it is concluded that grain boundary diffusion is of predominating importance for low-temperature oxidation, whilst lattice diffusion is important for high temperatures. An experimental method is described for the study of the oxidation of copper up to a pressure of 10 mm. of oxygen and a temperature of 305°. For metal activated by repeated oxidation and reduction, oxidation may be represented by the simple equation  $\log p_0/p = kt$ , where  $p_0$  is the initial oxygen pressure,  $p$  the pressure at time  $t$ , and  $k$  a constant. It is considered that the rate of oxidation of a metal is on *a priori* grounds dependent on the rates of at least four processes: (1) the condensation of oxygen at the metal oxide-oxygen interface; (2) the evaporation of oxygen from the oxide-oxygen interface into the oxide; (3) the diffusion of oxygen through the oxide; and (4) the reaction between the metal and oxygen. The theoretical basis of the above equation is discussed. This is quite different from the parabolic law, so that the process concerned cannot be only diffusion; it is considered that the latter process is preceded by adsorption and that under these experimental conditions no adsorption equilibrium exists between the oxide-oxygen interface and the gas phase. The equation does not hold for the oxidation of active copper at high pressures or inactive copper at low pressures. From the temperature coefficient of the low-pressure oxidation the heat of activation for the diffusion of oxygen through the oxide, *i.e.*, the critical increment of energy which "Lockerstellen" on the grain boundary must possess before an oxygen molecule can diffuse, is  $9500 \pm 1000$  g.-cal.

**II.** Using the same apparatus and commercial electrolytic copper at 183°, it is found that the limiting pressure below which the oxidation of the metal ceases to follow the parabolic law is about 10 mm. This limiting pressure is the higher the more active is the copper, and it can be increased as much as thirteen times; sintering the surface decreases it. It is suggested that at the limiting pressure the grain boundaries in the surface of the cuprous oxide are just saturated with adsorbed oxygen, and it is shown theoretically on this basis, and also by assuming that the oxygen adsorbed on the cuprous oxide can diffuse

laterally, that the observed influence of activation on the limiting pressure would be expected. The parabolic law describes the oxidation of the activated metal at 183° over long periods of time if the oxygen pressure is high enough. L. L. BIRCUMSHAW.

**Rate of dissolution of magnesia ignited at various temperatures.** P. P. BUDNIKOV (Z. anorg. Chem., 1930, 191, 79—86).—Magnesium oxide prepared by igniting the pure carbonate dissolves in water most rapidly when the ignition temperature has been about 800°. With the product obtained from naturally occurring magnesite, however, the rate of dissolution becomes less and less as the temperature of ignition is raised, although the maximum solubility is attained by ignition at about 850°. Ferric oxide appears to play an important part in reducing the solubility. Addition of 1% of silica, on the other hand, increases the solubility of oxide prepared from the pure carbonate, but as the temperature of ignition rises the rate of dissolution diminishes. With 5% of silica, however, the solubility is reduced, and raising the temperature of ignition also has the same effect. R. CUTHILL.

**Kinetic measurement of a transformation reaction in solid metals [aluminium-zinc alloys].** W. FRAENKEL and E. WACHSMUTH.—See B., 1930, 717.

**Induced addition of ethylene and chlorine.** T. D. STEWART and D. M. SMITH (J. Amer. Chem. Soc., 1930, 52, 2869—2877).—The mechanism previously proposed for this reaction (A., 1929, 1420) is further elaborated. Values are given for the velocity coefficient of the specific thermal reaction, which consists in the formation of an activated modification of ethylene dichloride under the influence of a film of the liquid reaction products and the deactivation of this to ordinary ethylene dichloride. The former is the rate-determining step. In presence of oxygen this reaction occurs almost exclusively. In absence of oxygen the reaction velocity is much greater (enhanced specific reaction rate) owing to the occurrence of chain reactions involving 5—20 mols., initiated by activated ethylene dichloride or trichloroethane. Excess of ethylene or of chlorine represses the chain reactions, the latter being the more effective. The rôle of the catalyst for the thermal reaction and the mechanism of the induced reaction are discussed. H. E. F. NOTTON.

**Effect of combustion-suppressors on the limits of inflammability of carbon disulphide. Mechanism of raising of theoretical flame propagation temperature.** Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 210—216B, 216—217B).—The effects of additions of ethyl bromide, pentane, diethyl selenide, lead tetramethyl, and other compounds on the limits of inflammability of carbon disulphide were determined and recorded graphically. The first two reduce the upper limit. Others show a reduction followed by an increase ascribed to the large heat evolution from the combustion of lead tetraethyl etc. once it has commenced. The same compounds which have a much higher theoretical flame propagation temperature than carbon disulphide

when added in small proportions raise the lower limit of combustion. In larger proportions the limit falls again, the necessary temperature having been reached. These theoretical flame propagation temperatures are calculated and are found to be somewhat lower than the same temperatures calculated from the upper limits of inflammability of hydrogen mixtures. It is believed that this raising of the flame propagating temperature is due to negative catalytic action. It cannot be due to the destruction of a peroxide formed as an intermediate compound. C. IRWIN.

### Homogeneous catalysis of gaseous reactions.

**I. Decomposition of isopropyl ether under the influence of halides.** **II. Decomposition of diethyl ether catalysed by iodine.** K. CLUSIUS and C. N. HINSHELWOOD. **III. Decomposition of acetaldehyde catalysed by iodine.** C. N. HINSHELWOOD, K. CLUSIUS, and G. HADMAN (Proc. Roy. Soc., 1930, A, 128, 75—81, 82—88, 88—92).—I. The decomposition of gaseous isopropyl ether according to the equation  $(C_3H_7)_2O = CO(CH_3)_2 + C_2H_6$  is catalysed not only by iodine (cf. Glass and Hinshelwood, A., 1929, 1150), but also by various alkyl halides, and to a smaller extent by alkyl bromides. Chlorides have practically no influence and phenyl iodide is also almost inactive; hydrogen bromide, however, has a considerable action. As regards the iodides, the catalytic action appears to be inversely proportional to their own stability. The isopropyl ether catalyses their decomposition and the liberated iodine has a greater effect than any of the undecomposed iodides. The activity decreases in the order isopropyl, ethyl, methyl, phenyl iodide. The reaction whereby the hydrogen atom adjacent to the oxygen atom is transferred under the catalytic influence of iodine from one part of the ether molecule to another is a general one. The reaction is homogeneous, the rate being nearly proportional to the concentration of the catalyst and the time of half change nearly independent of the ether concentration.

**II.** The catalytic decomposition of diethyl ether under the influence of iodine occurs by two consecutive reactions:  $(C_2H_5)_2O = C_2H_6 + CH_3 \cdot CHO = C_2H_6 + CH_4 + CO$ . The aldehyde decomposes approximately ten times as fast as the ether under comparable conditions; thus the change follows an approximately unimolecular course, although consisting of consecutive reactions, and the speed of the whole reaction is principally determined by the iodine concentration. Experiments made in a bulb packed with silica beads showed that the surface reaction could not amount to more than a small percentage of the total. Thus reaction must depend on collisions between molecules of ether and of iodine. Every collision in which the kinetic energy of approach exceeds the heat of activation (35,000 g.-cal. per mol.) probably leads to decomposition. The heats of activation of this and similar reactions are considerably lower than those of the corresponding uncatalysed reactions, and the mechanism of activation is simpler.

**III.** In presence of small amounts of iodine, acetaldehyde is rapidly decomposed into carbon monoxide and methane at 400°. The reaction is unimolecular with respect to the aldehyde and its

rate is directly proportional to the concentration of the catalyst. The heat of activation, corrected for the variation in the collision number with temperature, is 32,500 g.-cal. per mol. If it is assumed that each collision between aldehyde and iodine molecules is effective when the kinetic energy of approach exceeds the energy of activation, a value is obtained for the number of molecules which should react which is 0.1 of the value actually observed. It is possible that the internal energy of the molecules is drawn on to provide some of the energy of activation, and by introducing one internal degree of freedom in addition to the translational energy the calculated and observed rates of reaction are brought into agreement.

L. L. BIRCUMSHAW.

**Influence of sodium chloride on the oxidation of iodine by potassium chlorate.** O. J. MAGIDSON and A. G. BAITSHIKOV (J. Russ. Phys. Chem. Soc., 1930, 62, 933—956).—The oxidation of iodides by potassium chlorate solution is catalysed by sodium chloride to an extent proportional to its concentration; at the same time iodine formed is partly precipitated by the sodium chloride present. A constant relation exists between free iodine remaining in solution and unoxidised iodide ions, pointing to the presence of an unstable compound. The reaction of oxidation in the presence of sodium chloride is one of the second order, indicating that chlorine acts as an oxidising agent. The reaction is best explained on the assumption that the actual oxidising agent is chloric acid, and not chlorate ion. Ferric chloride exerts a catalytic effect on the reaction even in the presence of sodium chloride. The nature of the products of oxidation depends on the relative amount of chlorate taken; thus, using 3 mols. of iodide to 1 mol. of chlorate, iodine chloride is obtained, whilst where the concentrations are as 3:5 potassium di-iodate is produced, and a mixture of these products is formed at intermediate relative concentrations. Iodate is precipitated from solution as  $KHI_2O_6 \cdot KCl$ . The above reactions afford a convenient method for the preparation of potassium di-iodate and of iodine chloride.

R. TRUSZKOWSKI.

**Oxidation of arsenite to arsenate.** Y. KATO and T. MURAKAMI (J. Soc. Chem. Ind. Japan, 1930, 33, 226—227B).—Copper oxide or cupric sulphate catalyses the oxidation of sodium arsenite provided that an excess of sodium hydroxide is present. The reaction velocity is nearly proportional to the concentration of sodium hydroxide; if less than the equivalent of the arsenious oxide is present the rate of oxidation is very slow. C. IRWIN.

**True measure of the activity of natural waters.** J. E. ORLOV (Z. anorg. Chem., 1930, 191, 87—103).—Aqueous solutions of calcium hydrogen carbonate are quite stable even when they contain no free carbonic acid, but powdered marble or powdered iron catalyses the decomposition, the rate of precipitation of carbonate in presence of marble being proportional to the square of the hydrogen carbonate concentration,  $\alpha$ . When, therefore, a water containing calcium hydrogen carbonate is brought into contact with carbonate, dissolution and deposition of carbonate occur simultaneously, the water being active or not

according as the former or the latter process predominates. The rate of dissolution is proportional to the hydrogen-ion concentration, and consequently the net rate of reaction,  $V$ , is given by the equation  $V = S\{[H^+] - Ka^2\}$ , where  $K$  and  $S$  are constants which depend on the temperature and conditions of diffusion. It is therefore suggested that the initial value of  $\{[H^+] - Ka^2\}$  is the only true measure of the activity of the water towards calcium carbonate (cf. Tillmans and Heublein, A., 1913, ii, 51). R. CUTHILL.

#### Decomposition of malic acid by sulphuric acid.

H. R. DITTMAR (J. Amer. Chem. Soc., 1930, 52, 2746—2754; cf. Whitford, A., 1925, ii, 559).—In an extension of previous work, the effect of nine inhibitors at 0.25 and 0.5M concentrations on the velocity of decomposition of malic acid by 100% sulphuric acid has been investigated at 20°, 30°, and 40°. The logarithm of the velocity coefficient of the inhibited reaction is, in most cases, not an exact linear function of the concentration of inhibitor. The temperature coefficient of the inhibited reaction generally decreases with rise of temperature, but with 0.25M-benzoic anhydride, which is the most pronounced inhibitor, an increase from 4.76 to 5.01 occurs. Most inhibitors raise the critical increment above that of the uninhibited reaction, but the increase of concentration from 0.25 to 0.5M causes at most only a small additional effect.

The solubility of malic acid in aqueous sulphuric acid at first decreases and then increases as the normality of the sulphuric acid is increased. This affords direct evidence of the formation between the acids of a molecular compound through which the reaction may proceed. An inhibitor may act by forming additive compounds with either of the acids. J. G. A. GRIFFITHS.

**Mechanism of, and the constitutional factors controlling, the hydrolysis of carboxylic esters.**  
 III. Calculation of molecular dimensions from hydrolytic stability maxima. C. K. INGOLD (J.C.S., 1930, 1375—1386).—A generalised statistical treatment is given of the velocity of hydrolysis of an ester by a catalyst, in which consideration of localised polar influences in the reacting molecules and of steric factors is included. Effects of different types due to the nature of the reaction medium are also discussed. The formula  $(k_{OH}/k_H)/(k_{OH'}/k_{H'}) = \exp. (7/10^8 r)$  is derived and used to calculate the distance  $r$  between the carboxyl groups of symmetrical dicarboxylic esters from the catalytic coefficients of hydrogen and hydroxyl ions in the first and second stages of hydrolysis. An analogous formula  $p_H^{*'} - p_H^{**} = 3/10^8 r$  is given for ionogenic monocarboxylic esters and its use is illustrated by application to the hydrolysis of ethyl aminoacetate and ethylammonium acetate. The calculated values of  $r$  are all of the right order of magnitude and place homologues of the oxalic-sebacic acid series in the right order. With one exception the calculated values of  $r$  agree to 0.5 Å. with the distances calculated by Gane and Ingold from their measurements of affinity constants. The ratio  $r(\text{fumarie})/r(\text{maleic})$  has the value 1.45. The hypothesis that the inclination of valencies external to a

double linking is about 120°, combined with other probable assumptions, requires the value 1.47.

F. G. TRYHORN.

**Atomic energy and catalyst efficiency.** B. S. SRIKANTAN (Indian J. Physics, 1930, 4, 539—540).—All the elements near the peaks of the curve connecting the vibration frequency of the elements with their at. wts. are those commonly regarded as good catalysts. Hence an attempt is made to correlate catalytic activity with the energy of vibration of the atom  $4\pi^2 m \nu^2 r^2$ , where  $m$  is the at. wt.,  $\nu$  the vibration frequency, and  $r$  the amplitude of vibration of the atoms at the m. p. of the solid calculated from the at. volume. In general it is found that the elements with the higher energies of vibration are those used as catalysts, whereas those with the lower values are the feeble catalysts and poisons. J. W. SMITH.

**Change in the area and catalytic activity of metallic surfaces on passing from the solid to the liquid state.** F. P. BOWDEN and E. A. O'CONNOR (Proc. Roy. Soc., 1930, A, 128, 317—329).—Methods which have been used for the determination of the accessible area of a metallic surface are reviewed. Using an apparatus similar to that previously described (Bowden and Rideal, A., 1928, 1088) and a cathode of fusible alloy, measurements have been made of the quantity of electricity  $\Delta Q$  which must be passed across the metal/electrolyte interface in order to produce a given change in the electrode potential, and of the relation between the electrode potential and the current density. The latter gives the rate at which hydrogen is being liberated at the surface and is a measure of the catalytic activity of the surface for the reaction. In the case of the solid metal this increases with rise of temperature, decreases at the commencement of fusion, and increases with further rise of temperature on the completion of fusion. The rates of deposition of hydrogen per cm.<sup>2</sup> of accessible area under identical conditions of temperature (15°) and potential (—1.0 volt sat. cal.) for solid frozen from liquid, solid sand-papered, and solid etched with nitric acid were 9, 5, and  $17 \times 10^{-6}$  coul. per sec., respectively, whilst the corresponding accessible areas are about 1.4, 6.3, and 800—1000 times the apparent areas. Measurements with an electrode of gallium show that this metal catalyses the evolution of hydrogen rapidly, so that relatively large current densities are necessary to establish a high hydrogen overpotential. The accessible area of the liquid surface is about the same as that of mercury, whilst on solidification the area increases to about 1.7 times its apparent area. The total catalytic activity of a metal surface for a particular reaction appears to depend on three factors which can be separately measured: (1) the accessible area of the surface; (2) the configuration of the surface metal atoms; and (3) the chemical nature of the metal. L. L. BIRCUMSHAW.

**Poisoning action of water vapour at high pressure on iron synthetic ammonia catalysts.** P. H. EMMETT and S. BRUNAUER (J. Amer. Chem. Soc., 1930, 52, 2682—2693; cf. Almqvist and Black, A., 1927, 29).—The poisoning effect of 0.08—1.23 vol.-% of water vapour in 3:1 hydrogen-nitrogen

mixtures at pressures between 1 and 100 atm. on the synthesis of ammonia by iron and promoted iron catalysts has been investigated chiefly at 450°. A surface film of iron oxide is formed and the weight of oxygen retained by the catalyst is approximately proportional to  $(P_{H_2O}/P_{H_2})^{1/2}$ . The promoted catalysts take up more oxygen than do those of pure iron. The poisoning of doubly and singly promoted catalysts by water vapour is almost completely reversible and only small permanent injury results. Repeated poisoning of pure iron catalysts leads to rapid loss of activity.

Existing data are consistent with the view that ammonia is synthesised by reduction with hydrogen of superficial  $Fe_4N$  formed by interaction of nitrogen molecules with iron atoms of sufficiently high free energies at the surface. J. G. A. GRIFFITHS.

**Catalysis by sodium chloride of oxidation of carbon.** R. K. TAYLOR (J. Amer. Chem. Soc., 1930, 52, 3025—3026).—Experiments with lamp-black are described. The oxidation of sugar charcoal at 200° is accelerated by sodium chloride, but the velocity decreases as the reaction proceeds.

J. G. A. GRIFFITHS

**Catalyst not containing platinum for the production of nitric acid.** I. E. ADADUROV and P. J. WEINSCHENKER (Ukraine Chem. J., 1930, 5 [Tech.], 1—26).—The reaction of oxidation of ammonia to nitric acid is best catalysed by substances emitting radiation of the same wave-lengths as those corresponding with the energy required for the dissociation of molecular to atomic nitrogen and oxygen. This condition is fulfilled by calcium and silicon for oxygen, and by tin for nitrogen. A catalyst containing 2.7 mols. of stannic oxide, 2.7 mols. of calcium oxide, and 1 mol. of silica gives 81.5—86.2% yields of nitric acid, free from nitrous acid, by passing a 7% ammonia-air mixture through a layer of catalyst 5.5 cm. in thickness, at the rate of 6—7.5 litres per hr., at 680°. The efficiency of catalysis at various temperatures is closely connected with the intensity of radiation of the catalyst at the given temperature. The connexion between thickness of layer of catalyst and defixation of nitrogen is explained on the basis of production of ionised nitrogen. The influence of varying the rate of flow and the ammonia content of the mixture is ascribed to variations in the energy of the active centres of the catalyst, and not to variations in the thermal effect of the reaction.

R. TRUSZKOWSKI.

**Catalytic reduction of carbon monoxide at atmospheric pressure by titanium, zirconium, and cerium oxides.** S. KODAMA (J. Soc. Chem. Ind. Japan, 1930, 33, 202—203B).—Catalysts were prepared consisting of 3 parts of cobalt oxide, 1 part of copper oxide, and 15% of the weight of the former of each of the above oxides. These were allowed to act on water-gas at various temperatures and the contraction in volume and yield of liquid products were recorded. In each case reaction commenced at 180—200° and the contraction was at first similar, but divergences occurred later. Titanium oxide gave a high yield of gaseous hydrocarbons but little liquid

product. Zirconium oxide was the best of the three, but was not so good as magnesium oxide. C. IRWIN.

**Catalytic action of reduced copper at high temperature and pressure.** S. KOMATSU, K. SUGINO, and M. HAGIWARA (Proc. Imp. Acad. Tokyo, 1930, 6, 194—197).—By heating with reduced copper and hydrogen at high pressures, benzene may be reduced to cyclohexane, naphthalene to tetrahydronaphthalene and thence to *trans*-decalin, phenol to cyclohexane and a trace of diphenyl ether,  $\alpha$ -naphthol to *ac*-tetrahydronaphthol, *ar*-tetrahydronaphthol, hydrocarbons (b. p. 201—208°), and resins,  $\beta$ -naphthol to *ar*-tetrahydro- $\beta$ -naphthol, *ac*-tetrahydro- $\beta$ -naphthol, and a trace of tetrahydronaphthalene.

C. W. GIBBY.

**Oxidation of aqueous ethyl alcohol by molecular oxygen catalysed by platinum metals.** E. MÜLLER and K. SCHWABE (Kolloid-Z., 1930, 52, 163—173).—By continuous measurement of the potential of the catalysing metal, the course of the oxidation of aqueous alcohol by oxygen in the presence of finely-divided platinum, palladium, and rhodium has been followed, both in acid and in alkaline solution. The experimental results are interpreted to show that the reaction consists of a dehydrogenation of the organic compound followed by oxidation of the activated hydrogen. The mechanism suggested is the binding of the hydroxylic hydrogen atom of the alcohol to the catalyst through an electron of the metal, so that the hydrogen atom has its complement of two electrons. The active hydrogen layer thus produced is readily oxidised, the rest of the molecule leaving the surface as aldehyde.

E. S. HEDGES.

**Catalytic action of platinum.** F. THORÉN (Svensk Kem. Tidskr., 1930, 42, 134—153).—From experiments on the decomposition of hydrogen peroxide by platinum sols prepared by Kraemer and Svedberg's method it is concluded that the activity of such sols is not due to their oxygen content. Attempts to determine a constant for the affinity between hydrogen peroxide and the colloidal platinum catalyst showed that for the range of peroxide concentration in which the reaction proceeds normally no such constant could be found. Attention is directed to the marked decrease in activity when such a sol is diluted. The addition of charcoal greatly increases the velocity of the reaction, an increase of 40% being noted in one case; the effect is ascribed to the adsorption of platinum and hydrogen peroxide on the surface of the charcoal. If the sol be treated with a current of hydrogen its activity is greatly increased; the best results occur with 10 min. treatment, a more prolonged treatment causing a diminution of activity, probably due to the poisoning of the platinum by traces of impurity in the hydrogen. Similar treatment with gaseous oxygen gave variable results. Prolonged experiments lasting 1 hr. showed that the reaction is not unimolecular, but the expression  $\log x = F(t)$  can be regarded as approximating to a straight line with two breaks in it. Calculation of the three unimolecular constants,  $K_1$ ,  $K_2$ , and  $K_3$  for each portion of the reaction showed that the ratios  $K_2/K_1$  and  $K_3/K_1$  approximate to 2/3 and 1/2, and

this result is discussed theoretically. An historical account of the subject is also given.

H. F. HARWOOD.

**Action of aqueous hydrofluoric acid on silica.** W. G. PALMER (J.C.S., 1930, 1656—1664).—The mechanism of this heterogeneous action is primarily dependent on the  $\text{HF}_2$  ion, and adsorption processes on the surface of the silica, but is not determined by any surface diffusion processes. The rate of reaction is uniquely increased by the presence of a neutral salt (ammonium sulphate), but is not generally proportional to the  $\text{HF}_2$ -ion concentration. It is suggested that the hydrogen ion may be a specific catalyst.

J. O. CUTTER.

**Thermal decomposition of ethyl ether on the surface of platinum.** E. W. R. STEACIE and H. N. CAMPBELL (Proc. Roy. Soc., 1930, A, 128, 451—458).—An attempt has been made to compare the heterogeneous decomposition of gaseous ethyl ether on the surface of platinum with that of the homogeneous reaction studied by Hinshelwood (A., 1927, 212). The ether was decomposed on an electrically heated platinum wire (625—800°) stretched axially in a bulb of about 100 c.c. capacity, the progress of the reaction being followed by observing the rate of increase of pressure by means of a capillary manometer. All the observed results agree with those obtained for the homogeneous reaction, except that the pressure at which the velocity coefficient begins to diminish increases considerably with fall of temperature. Platinum has evidently no catalytic effect on the decomposition, which is to be regarded as taking place homogeneously in a thin layer of hot gas surrounding the filament (cf. Taylor, this vol., 44).

L. L. BIRCUMSHAW.

**Osmium as a dehydrogenation catalyst for decahydronaphthalene.** A. A. BALANDIN (Z. physikal. Chem., 1930, B, 9, 49—72).—The reaction velocity of the catalytic dehydrogenation of decahydronaphthalene in the presence of metallic osmium was found under differing temperature conditions, previous treatment with hydrogen, addition of the reaction product, and differing pressures. The reaction is a zero order reaction. The reaction products, naphthalene and water, under the conditions of the experiments exerted no influence on the reaction velocity. The catalyst is scarcely a suitable one for bringing about the dehydrogenation, as there are products formed by the further catalytic decomposition of the naphthalene which soon poison it. The catalytic activity can, however, be renewed by treating the osmium with hydrogen. At 270° the dehydrogenation velocity was about 4% of the rate of vaporisation over the active osmium surface; the activation energy of the dehydrogenation gives  $Q=10,000$  g.-cal. per mol. In this respect osmium resembles nickel very closely, where  $Q=9990$  g.-cal. per mol. After working with the same catalyst for some time it was found that there was a sudden change in its activity, which increased. This was due to a decrease in the poisoning. The activation energy now becomes 16,250 g.-cal. per mol., which is about the same as that found for palladium. It is assumed that the change in activity is due to a dispersion of the

atoms of the metal in the catalytically active centres. The failure of osmium to catalyse the dehydrogenation of other six-membered ring systems is probably due to the more rapid formation of inhibiting substances than is the case with decahydronaphthalene.

A. J. MEE.

**Hydrogenation with fine foam and colloidal metals.** II. E. BIESALSKI, W. VON KOWALSKI, and A. WACKER (Ber., 1930, 63, [B], 1698—1707; cf. B., 1928, 696).—The efficiency of the authors' method of hydrogenation depends on the fine division and intimate admixture of the gas by means of the porous material and foam-producing medium with the dispersing agent and its dissolved substances. Stable, strongly-foaming systems are produced by saponins, soaps, sulphated and sulphonated organic compounds, proteins, and dextrans which, frequently in 0.01% solution, yield stiff, very homogeneous foams often stable for hours. The degree of subdivision of the bubbles is at a maximum, as is the catalytic activity. Unstable, feebly foaming systems are produced by organic compounds with minimal capillary activity (sodium cinnamate and  $\beta$ -phenylpropionate) and inorganic compounds with alkaline reaction (sodium aluminate and hydrogen carbonate, ammonium carbonate, potassium silicate) which have no capillary activity. The foam is very fugitive, whereas the size of the bubbles often approaches closely to that of the stable systems, as does the catalytic activity. Maximal activity is not attained probably by reason of the lower homogeneity of the foam. The solutions, except aluminate and silicate, are permanent and do not become decomposed or cloudy in the manner of the best producers of stable foam. Simple relationships do not exist between foam-forming power, capillary activity, and viscosity. For the production of minute bubbles, a liquid of medium alkalinity appears the prime essential. The efficiency of palladium as catalyst appears to depend on its very careful production by the use of minimal amounts of hydrazine. Attempts to prepare colloidal nickel by a similar method were unsuccessful.

The transitory formation of hydrogen peroxide during the catalysed union of hydrogen and oxygen is established.

A gas-analytical method for determining hydrogen by means of excess of oxygen in presence of fine foam and palladium is described; nitrogen and methane do not interfere with it.

H. WREN.

**Oxygen-transmitting action of substances with large specific surface.** A. KUTZELNIGG (Ber., 1930, 63, [B], 1753—1758).—A solution of potassium ferrocyanide in water is shaken for 5 min. with a definite weight of the substance; the mixture is filtered, the residue washed with water, and filtrate and washings are titrated with 0.01*N*-sodium thio-sulphate after addition of potassium iodide and zinc sulphate. The materials used are carbo medicinalis, active charcoal, fuller's earth, silica gel, fibrous alumina, ferric oxide (technical, from ferric chloride and ammonia, and by ignition of iron oxalate), lead oxide, manganese dioxide, nickel oxide, chromium sesquioxide, tricobaltic tetroxide, trimanganic tetroxide, copper oxide, stannic oxide, lead chromate,

magnesium oxide, zinc oxide, barium sulphate, calcium and barium carbonates, cadmium and mercuric sulphides. The ferrocyanide is oxidised by carbon suspensions, which can be replaced by other substances with large surface development. The oxidation can be obscured by adsorption. Since the active materials are, in part, chemically indifferent and, on the other hand, the oxidative power is depressed by ignition, evacuation, and immersion in boiling solvents, it appears probable that the action is due to atmospheric oxygen adsorbed at the surface of the powder.

H. WREN.

**Use of tantalum as cathode for the electro-deposition of copper.** B. MEARS and P. R. PINE (Ind. Eng. Chem. [Anal.], 1930, 2, 298).—A solution of ammonia ( $d$  0.90) containing 10% of trichloroacetic acid is recommended for stripping electro-deposited copper from tantalum cathodes. The electrode actually improves with use, acquiring a high metallic lustre, entirely free from oxide, and showing no tendency to brittleness. The time required for stripping is less than 5 min. and the loss of tantalum for each stripping of copper is only 0.0001 g.

E. S. HEDGES.

**Acetamide and formamide as solvents for electrodeposition of metals.** L. F. YNTEMA and L. F. AUDRIETH (J. Amer. Chem. Soc., 1930, 52, 2693—2698).—The electrodeposition of zinc, cadmium, lead, tin, cobalt, and nickel from solutions of their salts in formamide at 100° has been investigated with current densities between 0.02 and 0.06 amp. per cm.<sup>2</sup> (cf. Röhler, A., 1910, ii, 684). Corresponding observations have been made with acetamide solutions of the above metals and thallium. Metals higher than zinc in the electromotive series are not deposited from these solvents.

J. G. A. GRIFFITHS.

**Electrolytic transfer of platinum metals using fused chloride electrolytes.** R. H. ATKINSON (Trans. Faraday Soc., 1930, 26, 490—496).—By using fused chloride electrolytes of suitable composition it has proved possible to transfer electrolytically platinum, rhodium, palladium, and iridium. Ready dissolution occurred with an impure ruthenium anode, but very little was deposited on the cathode. Ternary mixtures of the chlorides of lithium, sodium, and potassium (m. p. 400—500°) to which were added double chlorides of the platinum metals were unexpectedly stable during electrolysis, and in the case of the platinum electrolyte electrolysis was possible at 700°. Dissolution of the anode was regular in all cases and passivity was absent. With rhodium and palladium high current efficiencies were obtained, but with platinum, owing to the change of valency during electrolysis, anomalous values were found. Experiments with mineral platinum showed that this may be satisfactorily refined by first melting to remove iron and then refining electrolytically to remove palladium, iridium, ruthenium, and rhodium. Rhodium cannot satisfactorily be refined at 400° owing to the difficulty of separating palladium.

F. G. TRYHORN.

**Influence of small amounts of chromic acid and of chromium sulphate on the electrodeposition of nickel.** D. J. MACNAUGHTAN and R. A. F. HAMMOND

(Trans. Faraday Soc., 1930, 26, 481—490).—The deposition of nickel is profoundly affected by the presence in the electrolyte of even small amounts of chromic acid. Not only is the chromic acid detrimental to the physical nature of the deposit, but also its presence to the extent of 0.0288 g. per litre reduces the cathode efficiency to 2.5% and at higher concentrations no deposit is obtained. Similar but much less acute effects are caused by chromium sulphate. Chromic acid also increases considerably the stress in the deposit, which in consequence readily peels off from the basis metal. The great fall in efficiency cannot be explained through reduction of the chromic acid, but appears chiefly to be related to a preferential stimulation of the discharge of the hydrogen ions. The effect of the nature of the basis metal on deposition in the presence of chromic acid has been investigated, and it is found that the addendum has less effect when the basis metal is copper or amalgamated copper than when it is nickel, steel, or platinum. No lowering of anode efficiency is caused by the presence of chromic acid in nickel-plating solutions. Methods are described for the removal of chromic acid and chromium sulphate from nickel-plating solutions.

F. G. TRYHORN.

**Rare earths. XXXV. Separation of europium by electrolytic reduction.** L. F. YNTEMA (J. Amer. Chem. Soc., 1930, 52, 2782—2784).—Europium may be separated from samarium by precipitation as  $\text{EuSO}_4$  by electrolytic reduction of an aqueous sulphuric acid solution of the chlorides. The sulphate is stable at 65° and is oxidised by dilute nitric acid.

J. G. A. GRIFFITHS.

**Chemical reactions [induced] by electrodeless discharge.** N. A. YAJNIK, R. K. SHARMA, and M. C. BHATNAGAR (Z. physikal. Chem., 1930, 148, 394—399; cf. A., 1928, 972).—The effect of the silent discharge on a number of substances is to decompose them in a manner different from that due to the action of ultra-violet light or of heat. Phosphates, oxalates, and calcium carbonate are unaffected. Other typical decompositions are:  $\text{HgO}_{\text{red}} \rightarrow \text{HgO}_{\text{yel.}} \rightarrow \text{Hg} + \text{O}_2$ ;  $\text{KClO}_4 \rightarrow \text{KClO}_3 \rightarrow \text{KClO} \rightarrow \text{KCl}$ ;  $\text{KIO}_4 \rightarrow \text{KIO}_3$ ;  $\text{KI}, \text{O}_3, \text{K}_2\text{O}, \text{I}_2, \text{O}_2 \rightarrow \text{Pb}(\text{NO}_3)_2 \rightarrow \text{PbO}_2 + 2\text{NO}_2$ ;  $\text{KI} \rightarrow \text{I}_2 + \text{K}_2\text{O}$ ;  $\text{P}_{\text{red}} \rightarrow \text{P}_4\text{O}$ .

F. L. USHER.

**Chemical action of electric discharge. II. Formation and decomposition of cyanogen.** E. BRINER and J. DESHUSSES (Helv. Chim. Acta, 1930, 13, 629—650; cf. A., 1929, 1247).—It is impossible to obtain appreciable quantities of cyanogen either from its elements or from mixtures of carbon monoxide with nitrogen or nitric oxide by the use of the electric furnace (1150—1237°), arc, or various forms of electric discharge, despite the use of an especially sensitive method for detecting the gas at great dilution. The velocity of decomposition of gaseous cyanogen has been measured at temperatures between 1000° and 1250° and found to be insufficient to explain its absence under the conditions used for the synthesis, and the lack of reaction is not due to inactivity of the solid carbon. The equilibrium concentrations of cyanogen calculated thermodynamically are considerable, and other endothermic compounds such as ozone, with a smaller equilibrium concentration and a higher



velocity of decomposition, are detectable in relatively large quantities. It is considered that the processes used are incapable of exciting the carbon and nitrogen to the state of activity necessary for their interaction, or of forming the active intermediate groups. Thermal equilibria are not the determining factors. At constant temperature the amounts of cyanogen decomposed are proportional to the time, whence it is inferred that this is a surface reaction.

F. L. USHER.

**Chemical action of electric discharge. III. True efficiency of ozone production in the silent discharge and its improvement.** E. BRINER and B. SUSZ (Helv. Chim. Acta, 1930, 13, 678—695).—The conditions influencing the production of ozone in the silent discharge have been studied. The power used in the ozoniser was measured both calorimetrically and electrically. The true efficiency of ozone production is considerably higher than that calculated from measurements of voltage and current, since the latter is out of step with the applied voltage in ozonisers of the type used,  $\cos \phi$  varying from 0.1 to 0.3. Under favourable conditions a yield of 246 g. of ozone per kilowatt-hr. has been obtained, corresponding with 20% transformation of electrical into chemical energy. The efficiency increases with increasing rate of delivery of oxygen within certain limits, and with lowering of temperature. At the temperature of liquid air there is an optimum pressure in the neighbourhood of 200 mm. F. L. USHER.

**Chemical changes under a strong electric field.** T. AONO (Bull. Chem. Soc. Japan, 1930, 5, 169—173).—A method whereby the influence of a powerful electric field on the reaction between a gas and dielectric liquid may be studied involves the use of several layers of liquids, having different dielectric constants, placed between the electrodes. The reduction by hydrogen of nitrobenzene, benzaldehyde, and a number of oils, the ozonisation by oxygen of oleic acid and olive oil, the chlorination of acetic acid, and the combination of nitrogen and hydrogen in presence of oleic acid to form ammonia have been thus investigated. The hydrogenation of oils by this method is not markedly catalysed by powdered iron, copper, or aluminium at temperatures up to 100°, but reduced nickel at 100—120° appears to have some influence. It is uncertain whether the main cause of the chemical activation produced is the electric force or the ultra-violet radiation emitted by the bubbles of gas in the reaction tube. Some curious phenomena relating to the orientation of the metallic powders used in the catalysis experiments are described.

H. F. GILLBE.

**Thermal and photochemical decomposition of ozone.** E. H. RIESENFELD and E. WASSMUTH (Z. physikal. Chem., 1930, B, 8, 314—325).—From an examination of the experimental data relating to the thermal decomposition of ozone it appears most likely that the bimolecular reaction at high concentrations is a chain reaction, the most probable scheme being  $O_3^* + O_3 = 3O_2^*$ ,  $O_2^* + O_3 = O_3^* + O_2$ , where \* denotes an activated molecule. The accelerating action of indifferent gases must then be ascribed to their transferring internal energy from the products of reaction

to undecomposed molecules, which are activated in consequence. A similar chain mechanism for the photochemical decomposition at high ozone concentrations is proposed, but here indifferent gases take up energy from the products of reaction, without, however, being able to activate undecomposed molecules, so that in this case the effect is a retardation.

R. CUTHILL.

**Effect of iodine chloride on photosynthesis of hydrochloric acid.** G. K. ROLLEFSON and F. E. LINDQUIST (J. Amer. Chem. Soc., 1930, 52, 2793—2798).—The rate of photosynthesis of hydrogen chloride in a mixture of hydrogen, chlorine, and iodine monochloride by light of wave-lengths greater than 4050 Å. is inversely proportional to the iodine chloride pressure. In light of wave-length greater than 4300 Å., no reaction occurs either in the presence or in the absence of chlorine molecules. It is concluded that the optical dissociation of iodine chloride yields atoms in the normal state (cf. Gibson and Rice, A., 1929, 375) and that the formation of hydrochloric acid requires atoms in the  $^2P_1$  state (cf. A., 1929, 522).

J. G. A. GRIFFITHS.

**Quantum efficiency for the photo-chlorination of methane.** A. COHEN and H. CORDES (Z. physikal. Chem., 1930, B, 9, 1—24).—The photo-chlorination of methane is shown to be a chain reaction of a special type in which the quantum efficiency decreases with the period of exposure to the light. For damp mixtures of methane and chlorine the quantum efficiency for light of wave-length 4358 Å. at the commencement of the exposure is of the order of  $10^4$  mols./ $h\nu$ . The effect of impurities in the gaseous mixture on the quantum efficiency is very marked. The admixture of foreign gases causes an induction period. The chlorinations of methyl and methylene chlorides are very similar reactions. They are photochemical, and in the dark there is no marked reaction. The quantum efficiency for these reactions is of the same order as that for the chlorination of methane, and follows a similar course with the duration of exposure. The chlorination of chloroform is also a photochemical reaction, there being no definite reaction in the dark. The quantum efficiency for light of wave-length 4358 Å. is, however, constant to within the experimental error throughout the whole time of exposure, and is equal to  $10^3$  mols./ $h\nu$ . The photo-chlorination of methane was also investigated in the ultra-violet, and was found to proceed in the same way as for visible light. Over the range of wave-lengths 2536—2654 Å. the quantum efficiency was of the same order as for visible light, and decreased with the time of exposure. The investigation of the products of the reaction when a mixture of chlorine and methane was exposed to monochromatic light showed that methyl chloride, methylene chloride, chloroform, and carbon tetrachloride were simultaneously formed. Under the conditions used no chloroethane was formed. An intensively dried mixture of chlorine and methane when exposed to light also undergoes reaction, but the quantum efficiency is much less than for a moist mixture.

A. J. MEE.

**X-Ray photochemical reaction between potassium oxalate and mercuric chloride.** W. E.

ROSEVEARE (J. Amer. Chem. Soc., 1930, 52, 2612—2619; cf. A., 1929, 888).—The kinetics of the reaction  $2\text{HgCl}_2 + \text{C}_2\text{O}_4^{2-} = \text{Hg}_2\text{Cl}_2 + 2\text{Cl}^- + 2\text{CO}_2$  caused by X-rays has been investigated at 25° and 35° in aqueous solution. The reaction is of the first order with respect to mercuric chloride concentration, the retarding effect of chloride ions being due to their effect on the concentration of this salt. The influence of oxalate ions is in agreement with the view that the reaction involves the decomposition of the complex  $\text{HgCl}_2\text{C}_2\text{O}_4^{2-}$ . The temperature coefficient is approximately 1.52. On the assumption that all of the incident energy leads to ionisation it is computed that  $6 \times 10^5$  molecules react per ion pair. The inhibiting effects of oxygen or ferric chloride are best explained by Bäckström's theory of the breaking of reaction chains, and a mechanism is suggested.

J. G. A. GRIFFITHS.

Speck concentration or centripetal theory of light sensitivity. A. STEIGMANN (Z. wiss. Phot., 1903, 28, 167—168).—Polemical against Trivelli (this vol., 871). The author's theory of the mechanism of the speck concentration effect is restated in accordance with modern terminology. J. LEWKOWITSCH.

Photochemical action of intermittent and complex light. M. PADOA and N. VITA (Z. wiss. Phot., 1930, 28, 153—167).—Berthoud's criticisms (A., 1929, 1404) are refuted, the contrary results obtained by him being ascribed to the use of a filament lamp deficient in blue radiation and to the neglect of several important factors. The authors' earlier experiments (A., 1928, 378, 1102) are confirmed by a fresh study of the oxidation of hydriodic acid in white (arc) light and the component blue light. It is shown that at a certain intensity the ratio of photochemical efficiency of the blue light to that of the white light reaches a maximum greater than one. The relation of incident intensity of light to photochemical efficiency is shown to agree with Berthoud's results as regards white light, but varies with the wave-length for monochromatic light (cf. Purkayastha and Ghosh, A., 1928, 172, 256). Earlier experiments on the bromination of cinnamic acid are rejected as unsatisfactory.

J. LEWKOWITSCH.

Lattice energies and photochemical decomposition of silver halides. S. E. SHEPPARD and W. VANSELOW (Z. wiss. Phot., 1930, 28, 121—153).—See A., 1929, 408.

Action of light on silver bromide. A. C. CHATTERJI and P. S. MACMAHON (J. Indian Chem. Soc., 1930, 7, 443—449).—The photochemical darkening of silver bromide when exposed to oxygen for prolonged periods is accompanied by absorption of oxygen (69.2 g. exposed for 1 year to tropical sunlight absorbed 2 c.c. of oxygen). Disperse silver, prepared by striking an arc between silver electrodes, is also capable of oxidation when exposed to dry oxygen. It is therefore suggested that the photo-halides formed are not due to the photochemical synthesis of an oxy-compound, but are due partly at least to the direct absorption of oxygen by the disperse silver produced in the photochemical decomposition of the silver halide.

J. R. I. HEPBURN.

Photo-isomerisation of allocinnamic acid sensitised by iodine. A. BERTHOUD and C. URECH (Helv. Chim. Acta, 1930, 13, 437—444; cf. A., 1925, ii, 1083; 1926, 583).—Experiments on the kinetics of the isomeric change allocinnamic acid  $\rightarrow$  cinnamic acid support Berthoud's theory of the mechanism of the isomeric change of *cis*- and *trans*-ethylene derivatives under the influence of light and in the presence of halogens as sensitisers. The results obtained with benzene solutions may be expressed as follows,  $A$  denoting allocinnamic and  $A'$  cinnamic acid, and  $I$  the intensity of illumination:  $d[A]/dt = kI[A][I_2]$  when the absorption is feeble (red light), and  $d[A]/dt = kI[A]$  when the absorption is complete (blue light). These formulae may be derived mathematically if the reaction is assumed to take place according to the following mechanism:  $I_2 + h\nu = 2I$ ;  $A + I = AI$ ;  $AI = A'I$ ;  $A'I = A' + I$ ;  $2I = I_2$ . The second step is the union of an iodine atom with a molecule of acceptor, giving an intermediate moniodo-compound, where the double linking has given place to a single; the two carbon atoms are therefore capable of free rotation and the *cis-trans* transformation becomes possible at the moments when the iodine atom combines with and detaches itself from the acceptor.

F. L. USHER.

Chain reactions produced by light and by  $\alpha$ -radiation. H. N. ALYEA (J. Amer. Chem. Soc., 1930, 52, 2743—2745).—Every ion pair produced by  $\alpha$ -radiation in benzene saturated with chlorine leads to the formation of about 720 mols. of hexachlorobenzene. In the oxidation of sodium sulphite by oxygen, 5000 mols. (approx.) of sodium sulphate are produced per ion pair. The similarity of these results with the yields per quantum obtained photochemically shows that in these reactions  $\alpha$ -radiation gives rise to chain instead of ion cluster reactions (cf. this vol., 871).

J. G. A. GRIFFITHS.

Preparation of pure hydrogen by means of a palladium electrolytic osmoregulator. H. HULBERT (Compt. rend., 1930, 191, 134—136).—As a means of introducing pure hydrogen into an enclosure an electrolytic osmoregulator constructed of palladium, with walls 0.1 mm. thick, is attached thereto. To hydrogenate the palladium a solution of phosphoric acid is electrolysed with a current of 5—20 milliamp., the palladium being made the cathode with a platinum anode so arranged as to give a uniform field around the tube. The hydrogen is liberated when desired by gentle heat.

C. A. SILBERRAD.

Preparation of alkali metals from their compounds by reduction with zirconium. J. H. DE BOER, J. BROOS, and H. EMMENS (Z. anorg. Chem., 1930, 191, 113—121).—Small amounts of caesium, rubidium, sodium, lithium, and potassium may be prepared by heating such salts as the chromate and dichromate, or, in the case of sodium, the molybdate, with excess of zirconium in a vacuum, when the alkali metal distils over in a pure state.

R. CUTHILL.

Polysulphides of the alkali metals. I. Sodium. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1930, 1473—1497).—The methods given for the preparation of sodium polysulphides have been

repeated with the exception of those involving the use of liquid ammonia. The discrepancies reported in the literature have been investigated and explained. The thermal analysis of the system sodium monosulphide-sulphur has been repeated with the control by micro-methods. Sodium tetrasulphide (m. p.  $234.8^\circ$ ) is stable, and the di- and penta-sulphides (m. p.  $473.9^\circ$  and approx.  $270^\circ$ , respectively) are slightly dissociated at their m. p. The monosulphide, m. p.  $978^\circ$ , is stable. A saturated solid solution of sulphur in the pentasulphide occurs with 78.5% of sulphur. Tetrasodium compounds are not formed. The anhydrous di-, tri-, tetra-, and penta-sulphides may be prepared from the monosulphide in dry alcohol. The action of sulphur on aqueous-alcoholic solutions of sodium monosulphide gives polysulphide solutions from which may be crystallised  $\text{Na}_2\text{S}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_3 \cdot 8\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_4 \cdot 8\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_4 \cdot 9\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_4 \cdot 11\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_5 \cdot 6\text{H}_2\text{O}$ ; and a tetrasulphide which may be either  $\text{Na}_2\text{S}_4 \cdot 7\text{H}_2\text{O}$  or a mixture of  $\text{Na}_2\text{S}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_4 \cdot 8\text{H}_2\text{O}$ . Dehydration of the first two yields  $\text{Na}_2\text{S}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_3 \cdot \text{H}_2\text{O}$ , respectively. The tetrasulphides only may be obtained from the hydrosulphides under all conditions. F. G. TRYHORN.

**Conditions of hydration of metaphosphates.** E. V. BRITZKE and S. S. DRAGUNOV (Min. Ssyrtje Zvet. Met., 1929, 4, 387—396; Chem. Zentr., 1930, i, 1022).—Sodium hexametaphosphate,  $(\text{NaPO}_3)_6$ , is hydrolysed in aqueous solution without intermediate formation of the pyro-salt; the trimetaphosphate and Mandrell's salt (Ber., 8, 122) probably behave similarly, hydration being slow, but in presence of mineral acids pyrophosphoric acid is formed. When boiled with concentrated aqueous alkali the hexametaphosphate affords the pyro-salt, which is stable under these conditions. A. A. ELDRIDGE.

**Preparation of sodium nitride and potassium nitride.** H. WATTENBERG (Ber., 1930, 63, [B], 1667—1672).—Activated nitrogen under a few mm. pressure is very rapidly absorbed by finely divided sodium and, if the change is interrupted as soon as the first rapid action has ceased, sodium nitride is produced. Prolongation of the change leads to the formation of sodium azide. With potassium the first stage is so rapidly passed that the azide is the sole isolable product. At  $100^\circ$ , however, potassium nitride is formed in addition to the azide and becomes almost the sole product at  $200^\circ$ . Rubidium appears to resemble potassium. An intimate mixture of sodium and its azide, prepared by dissolution of the components in ammonia and subsequent removal of the solvent, passes when heated into sodium nitride, which is also obtained when the azide is cautiously heated at a temperature just below that of explosion. Potassium azide behaves similarly. The colour of sodium azide varies from orange at  $-180^\circ$  to black at  $300^\circ$ . It is very sensitive to moisture and yields ammonia and alkoxide with alcohols. It is unaffected by dry oxygen at the ordinary temperature. With ammonia it slowly forms sodamide. With liquid ammonia it appears to yield a dark blue, unstable ammoniate.

H. WREN.

**Preparation of manganese-free magnesium.** E. R. ORENT and O. S. RASK (J. Amer. Chem. Soc.,

1930, 52, 2776—2779).—Traces of manganese cannot be removed from magnesium salts by the usual methods. Complete purification is effected by the oxidation of the manganese to permanganate with potassium periodate and the subsequent electrolysis of the liquid in a cell specially designed to avoid contact between the permanganate and hydrogen from the cathode compartment where the pure magnesium hydroxide is deposited.

J. G. A. GRIFFITHS.

**Morphological and physico-chemical investigations on synthetic spinels as examples of substances not of stoichiometric composition.** F. RINNE (Jahrb. Min., 1928, 58, 43—108; Chem. Zentr., 1929, i, 1556—1557).—Various properties of artificially-prepared spinels have been investigated. In contrast to the natural products, the artificial spinels show a coarse cleavage, but only at positions already indicated by fissures. The hardness is high, but decreases with an increase in the excess of alumina. Soluble substances from the artificial material in a potassium hydrogen sulphate fusion yield first a rounded rhombohedron, which by prolonged action is converted into a tetrahexahedron. The density increases continuously for a composition corresponding with  $\text{MgAl}_2\text{O}_4$  to one with  $\text{MgAl}_2\text{O}_4 \cdot 3\text{Al}_2\text{O}_3$ . Crystals corresponding with the formula  $\text{MgO} \cdot 10\text{Al}_2\text{O}_3$  were opaque and stone-like, and contained much  $\alpha$ -corundum. The refraction of light increases with an increase in the alumina content, whilst the mean dispersion remains the same ( $n_F + n_C = 0.0118$ ). Secondary double refraction is clearly shown. The X-ray spectra of  $\gamma$ -alumina and the spinel  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  are similar. A definite change in the lattice distances has been observed in the following cases: gem spinel from Ceylon,  $a$  8.02 Å.;  $\text{MgO} \cdot 3\text{Al}_2\text{O}_3$ ,  $a$  7.96 Å.;  $\text{MgO} \cdot 4\text{Al}_2\text{O}_3$ ,  $a$  7.92 Å.; and  $\text{MgO} \cdot 5\text{Al}_2\text{O}_3$ ,  $a$  7.91 Å. The author concludes that the artificial spinels with excess of alumina consist of mixed crystals of the spinel,  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ , with  $\gamma$ -alumina.

L. S. THEOBALD.

**Magnesium mercurides.** P. T. DANILTSCHENKO (J. Russ. Phys. Chem. Soc., 1930, 62, 975—988).—The fusion diagram shows the existence of the following mercurides:  $\text{MgHg}$ , m. p.  $630^\circ$ ;  $\text{Mg}_2\text{Hg}$ , m. p.  $553^\circ$ ;  $\text{Mg}_3\text{Hg}$ , m. p.  $508^\circ$  (decomp.); and  $\text{Mg}_2\text{Hg}_5$ , m. p.  $171^\circ$  (decomp.). R. TRUSZKOWSKI.

**Gypsum.** P. P. BUDNIKOV (Bull. Acad. Sci. U.S.S.R., 1930, No. 77, 1—180).—A collection of the papers published on the above subject by the author and co-workers from 1922 to 1928.

R. TRUSZKOWSKI.

**Hydration of calcined gypsum.** W. C. HANSEN.—See B., 1930, 769.

**Preparation of pure calcium phosphate.** H. DANNEEL and K. W. FRÖHLICH (Z. Elektrochem., 1930, 36, 302—305).—Previous measurements of the solubility of calcium phosphate have led to fortuitous results, since this is dependent on the amount of water in contact with a fixed amount of tricalcium phosphate. The latter cannot be prepared pure in the presence of water, but under certain conditions, which are detailed, a product containing calcium oxide and phosphoric oxide in the ratio 3:1 can be

obtained by mixing monocalcium phosphate solution with ammonia solution. On electrolysis tricalcium phosphate is anodically decomposed, yielding di- or mono-calcium phosphate according to experimental conditions. J. W. SMITH.

**Solutions of calcium phosphates in sulphurous acid. I. Behaviour towards nitrogen of solutions of calcium phosphates in sulphurous acid.** E. THILO (Z. physikal. Chem., 1930, 148, 361—385).—When a suspension of calcium phosphate is dissolved in sulphurous acid the following equilibrium is set up:  $\text{Ca}(\text{H}_2\text{PO}_4)_2 + n\text{Ca}(\text{HSO}_3)_2 \rightleftharpoons 2\text{CaHPO}_4 + (n+1)\text{SO}_2 + (n-1)\text{CaSO}_3 + (n+1)\text{H}_2\text{O}$ , in which  $n$  depends on the ratio  $\text{CaO}/\text{P}_2\text{O}_5$  in the original suspension. By removing the sulphur dioxide with a current of nitrogen at the ordinary temperature a precipitate consisting of dicalcium phosphate and calcium sulphite is obtained. Contrary to the findings of Mebano, Dobbins, and Cameron (A., 1929, 997), the phosphoric acid is always present as the dicalcium salt, whatever be the initial ratio of acid to lime. The proportion of calcium sulphite to dicalcium phosphate depends on the ratio  $\text{CaO}/\text{P}_2\text{O}_5$  in the original suspension, as much calcium as possible being precipitated as phosphate and the remainder as normal sulphite. The composition of the precipitate is independent of the duration of the experiment, the velocity of the nitrogen stream or the concentration of the solution. The rate of evolution of sulphur dioxide decreases rapidly to a minimum, and the formation of the precipitate begins immediately before this minimum is reached. Afterwards the rate of evolution increases to a maximum and then slowly decreases, indicating that the reaction is autocatalytically accelerated by the precipitate. At first the reaction velocity is proportional to the two thirds power of the amount (and therefore to the surface) of the precipitate, but this relation ceases abruptly and the reaction then proceeds at a constant rate. Explanations of this behaviour are discussed. The velocity of the total reaction varies directly with the velocity of the stream of nitrogen. F. L. USHER.

**Synthesis of calcium aluminates and their hydration. V, VI.** S. NAGAI and R. NAITO.—See B., 1930, 770.

**Formation and composition of bleaching powder. II.** DITZ (Z. Elektrochem., 1930, 36, 287—295).—The compounds  $3\text{CaOCl}_2 \cdot \text{CaO} \cdot 4\text{H}_2\text{O}$  and  $\text{CaOCl}_2 \cdot \text{CaO} \cdot 2\text{H}_2\text{O}$ , obtained by Neumann and Haebler (this vol., 176) by the action of dry chlorine on calcium hydroxide containing 3.75—4% excess of water at the ordinary temperature and at  $-15^\circ$  to  $-20^\circ$ , respectively, are identical with the bleaching powders types II and I isolated by Ditz (A., 1901, ii, 239) under similar conditions. The dehydration data given by them also agree with the observations of Ditz.

J. W. SMITH.

**Preparation of pure mercury.** H. VON STEINWEHR and A. SCHULZE (Z. Instrumentenk., 1929, 49, 566—567; Chem. Zentr., 1930, i, 1113).—Mercury for use in physical apparatus is repeatedly shaken with dilute nitric acid, and then with water; fat is removed by means of petroleum or alcohol. The mercury is then filtered through a thin leather, previously freed

from fat with petroleum, or a Haldenwanger filter tube. It is then distilled in a current of air in a water-pump vacuum in an apparatus without taps, and preserved in evacuated glass vessels.

A. A. ELDRIDGE.

**Action of ammonia on the compound  $\text{HgCl}_2 \cdot 2\text{NH}_3$ .** M. FRANÇOIS (Bull. Soc. chim., 1930, [iv], 47, 559—565).—See this vol., 557.

**Action of mercuric chloride on solutions of cupric chloride.** H. PÉLABON and (MLLE.) DELWAULLE (Bull. Soc. chim., 1930, [iv], 47, 556—559).—Measurements of the solubility of cupric oxide and of mercuric chloride in cupric chloride solutions show that the reaction  $3\text{HgO} + 4\text{CuCl}_2 = 3\text{HgCl}_2 + 3\text{CuO} \cdot \text{CuCl}_2$  proceeds to completion. An equilibrium diagram is constructed which shows that as the amount of mercuric oxide introduced is increased the composition of the solid phase passes from the oxychloride to a mixture of oxychloride with mercuric chloride, and when the amount of cupric chloride present is insufficient the solid phase becomes a mixture of solid mercuric chloride, oxychloride, and oxide of copper, and finally the oxychloride disappears altogether. Microscopical examination of the solid phases formed supports these conclusions. S. K. TWEEDY.

**Reaction between mercurous and nitrite ions.** N. A. TANANAEV and G. I. OSTROSHINSKAJA (Ukraine Chem. J., 1930, 5, 67—69).—The reaction between sodium nitrite and mercurous salts is as follows:  $2\text{HgX} + 2\text{NaNO}_2 \longrightarrow \text{Hg} + \text{HgX}_2 + 2\text{NaNO}_3$ .

R. TRUSZKOWSKI.

**Ultramarinisation of various sodium aluminium silicates.** J. HOFFMANN (Z. angew. Chem., 1930, 43, 396—399).—Attempts to make an ultramarine by fusing nepheline with sulphur or sulphur compounds were unsuccessful (cf. Hoffmann, A., 1929, 1251). Ultramarines were produced, however, from artificially prepared sodium aluminium silicates containing incompletely reacted components, the yield being smaller the higher the synthesis temperature of the silicate used. It is considered that during the formation of ultramarine simple, and not polymerised, radicals interact, probably  $\text{NaAlSiO}_4$ , which perhaps pass over into nepheline radicals,  $(\text{NaAlSiO}_4)_3$ , ions of the sulphides present immediately occupying the gaps in the symmetrical structure and producing cubic ultramarine lattices. These simple radicals are not present in nepheline or in the completely reacted sodium aluminium silicate fusion, and these substances do not yield an ultramarine on fusion with a sulphide. Ultramarine blue, and finally ultramarine white, are obtained when hauynite is reduced with hydrogen; part of the sulphate radical present is reduced to sulphide, and this seems to be accompanied by fundamental lattice rearrangements, as a result of which particles (probably polysulphide groups) occupying the lattice gaps give rise to various colours. A similar explanation probably holds for the formation of ultramarine by heating sodalite and sodium polysulphide. S. K. TWEEDY.

**Sulphides of gallium.** W. C. JOHNSON and B. WARREN (Naturwiss., 1930, 18, 666).—The results of Brukl and Ortner (cf. this vol., 720) are confirmed.

The trisulphide was also formed by passing gaseous hydrogen sulphide over the metal at  $800^{\circ}$ , and on reduction with hydrogen at  $825^{\circ}$  GaS was obtained. This, by the action of hydrogen at  $925^{\circ}$ , gave green crystals believed to be  $\text{Ga}_2\text{S}_3$ ; further reduction gave metallic gallium. N. M. BLIGH.

**Existence of carbon-nitrogen gases other than cyanogen.** A. P. LIDOV (Arbb. physik.-chem. Wiss. Univ. Charkov, 1909; Chem. Zentr., 1930, i, 1287).—Under certain conditions, nitrogen combines with carbon to give *monocyanogen*. This gas is formed by the decomposition of dicyanogen by glowing iron, or by the burning of a Liliput lamp with carbon electrodes in an atmosphere of nitrogen. Combustion of monocyanogen with copper oxide or oxygen probably forms oxymonocyanogen or *oxan*, as well as carbon dioxide, to which gas it is similar, but lighter. The presence of such a gas has also been confirmed in the gas mixture resulting from the action of phosphorus pentoxide on carbamide, nickel cyanide, and dicyanodiamide. Oxan is best prepared by the action of silver oxide on cyanogen iodide at  $80$ – $100^{\circ}$ ; its separation from carbon dioxide has not yet been accomplished. L. S. THEOBALD.

**Azidocarbon disulphide.** IV. Preparation and properties of the new inter-halogenoid, cyanogen azidodithiocarbonate. L. F. AUDRIETH and A. W. BROWNE [with C. W. MASON] (J. Amer. Chem. Soc., 1930, 52, 2799–2805).—*Cyanogen azidodithiocarbonate*, m. p.  $80.5$ – $81^{\circ}$  (decomp.), is prepared either by interaction of mercuric cyanide with azidocarbon disulphide in acetone or, better, by interaction of cold aqueous sodium azidodithiocarbonate and ethereal cyanogen bromide. The white, crystalline compound is stable at  $0^{\circ}$ , and undergoes slow autocatalytic decomposition at the ordinary temperature into nitrogen, sulphur, thiocyanogen, and cyanogen thio-cyanate. Large quantities detonate at  $65$ – $70^{\circ}$ . The solubility in water at  $0^{\circ}$  is less than in non-aqueous solvents. The reactions with acids, alkalis, ammonia, oxidising, and reducing agents have been investigated. J. G. A. GRIFFITHS.

**Azidodithiocarbonic acid.** VI. Salts of copper, silver, gold, zinc, cadmium, mercury, thallium, lead, and bismuth. G. B. L. SMITH, P. WARTMAN, and A. W. BROWNE [with C. W. MASON] (J. Amer. Chem. Soc., 1930, 52, 2806–2810).—The above salts have been prepared by interaction of the free acid with the respective metallic ions, and their behaviour towards various reagents and solvents is tabulated. Crystallographic data are recorded. The salts of zinc, bismuth, and cadmium frequently detonate under water, and that of gold decomposes thermally at the ordinary temperature. The sensitivity to mechanical shock of the salts of the heavy metals of groups I and II of the periodic table varies inversely and the brisance of the explosion varies directly with the at. wt. The converse is true of the series mercury to bismuth. J. G. A. GRIFFITHS.

**Preparation of oxygen-free nitrogen.** H. VON WARTENBERG (Z. Elektrochem., 1930, 36, 295–297).—Oxygen can be removed from nitrogen by enclosing the gas for 1 hr. in a steel bomb at 100 atm. with metallic copper and an ammoniacal solution of

ammonium chloride. The residual oxygen content is about  $10^{-4}\%$ . J. W. SMITH.

**Nature and chemical activity of active nitrogen.** E. TIEDE and H. CHOMSE (Ber., 1930, 63, [B], 1839–1847).—The amount of active nitrogen in mixtures can be determined by bringing the gas into contact with mercury thoroughly agitated at the ordinary temperature. If shaking is omitted, the metal becomes covered with a deposit which inhibits further change. The product (the nature of which is not elucidated) is treated with 2.5% sodium hydroxide and the liberated ammonia is determined by titration. The non-luminous gas does not react with mercury. Under given conditions, the yield of active nitrogen is proportional to the duration of the experiment. The activity of the gas diminishes with increasing distance from the electrodes, the drop being greatest in the neighbourhood of the activating zone. With the non-condensed discharge, the nitrogen is chemically inert so that chemical activity is not due to metastable molecules. Since diminution of the luminosity of nitrogen by means of a subsidiary discharge is accompanied by an approximately proportional diminution of the chemical affinity towards mercury, it follows that atomic nitrogen is causative of chemical change.

The union of active nitrogen with active hydrogen has been investigated, the catalytic action of the walls of the vessel being overcome by saturating the hydrogen with water vapour. Formation of ammonia occurs only when both gases are activated. If the luminosity and hence the atomic concentration of the nitrogen is diminished by a secondary discharge, the yield of ammonia diminishes.

The most suitable phosphor for use with active nitrogen is boron nitride activated with carbon; this yields an intense, bluish-green luminescence excited only by luminous nitrogen and diminishing rapidly with decrease in atomic concentration of the gas.

H. WREN.

**Synthesis of ammonia.** L. DUPARC, P. WENGER, and C. URFER (Helv. Chim. Acta, 1930, 13, 650–666).—The results of earlier experiments in which quantitative yields of ammonia were obtained by passing a mixture ( $3\text{H}_2 + \text{N}_2$ ) over heated lithium in a fine state of division have not been confirmed. The work has been continued in the following three directions: formation of metal nitrides; their decomposition by hydrogen; and the formation of complexes permitting a continuous production of ammonia. The amount of nitrogen fixed and the lowest temperature at which fixation occurs are greatly influenced by the presence of impurities. Traces of iron in the lithium lower the temperature at which complete transformation into nitride occurs from  $450^{\circ}$  to  $300^{\circ}$ , and sodium produces a still greater lowering. Pure nitrides either do not decompose in hydrogen or yield only traces of ammonia, but with impure nitrides the yield is increased. Iron, manganese, aluminium, chromium, titanium, cobalt, nickel, and tungsten react with nitrogen and give with lithium nitride additive compounds of the type  $[\text{Li}_3\text{N}, \text{Fe}_2\text{N}]$ ,  $[\text{Li}_3\text{N}, \text{AlN}]$ . At temperatures between  $550^{\circ}$  and  $600^{\circ}$  lithium nitride absorbs hydrogen

readily, yielding a solid compound  $\text{Li}_3\text{NH}_2$ , which in turn yields ammonia. Lithium nitride mixed with powdered bismuth and heated at  $400^\circ$  in a current of hydrogen gives a quantitative yield of ammonia and an alloy of the metals. The mechanism of the catalysis of the reaction  $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$  is discussed on the basis of the new results, and the necessity for assuming the existence of a labile intermediate compound is emphasised. The platinum metals are useless for the synthesis of ammonia because their hydrides do not react with nitrogen, whilst a metal such as lithium is effective because its nitride reacts with hydrogen.

F. L. USHER.

**Sulphuryl chloride and nitrogen peroxide; nitrobenzenes and sulphuryl chloride.** M. BATTEGAY and L. DENIVELLE (Bull. Soc. chim., 1930, [iv], 47, 606—612).—Sulphuryl chloride does not react with nitrogen peroxide at the ordinary temperature, even in presence of ammonium chloride, but when these substances are heated at  $180^\circ$  in a sealed tube a complex reaction occurs, the principal products being nitrosyl chloride and nitrosulphuric anhydride,  $\text{N}_2\text{S}_2\text{O}_9$ . The same products are obtained if a metal nitrite is heated with excess of sulphuryl chloride; if the nitrite is used in excess the chlorine atoms are bound and nitrosulphuric anhydride is the sole product. The mechanism of these reactions throws light on the changes occurring in the transformation of nitrobenzenes into halogen derivatives of benzene by means of sulphuryl chloride.

S. K. TWEEDY.

**Selenium trioxide. II. Investigations in the high-frequency field.** H. RHEINBOLDT, A. HESSEL, and K. SCHWENZER (Ber., 1930, 63, [B], 1865—1867).—Selenium is converted by dry oxygen under the influence of the high-frequency discharge into a mixture of selenium dioxide and *selenium trioxide*; the latter compound constitutes 20—36% of the mixture.

H. WREN.

**Preparation of  $\text{U}_3\text{O}_8$  as a standard of radioactivity.** D. K. GORALEVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 843—864).—Uranium oxide, prepared by the ignition of uranyl nitrate in a stream of oxygen, contains traces of heavy metals, which, although too small to be detected by other than spectroscopic methods, depress the radioactivity of the oxide by about 17%. Fractional crystallisation of uranyl oxalate removes part of the impurities (chiefly thorium), but the radioactivity of the oxide obtained from the nitrate prepared from the purified salt is still 6.6% below theoretical. Satisfactory purification can be effected by precipitation with "cupferron" in acetic acid solution. The oxide obtained varies in colour from olive-green and grey to black, according to the state of subdivision of the particles.

R. TRUSZKOWSKI.

**Oxidations with fluorine. XVI. Action of fluorine on solutions of salts of tin and iron; preparation of cobaltic perchlorate electrochemically and with fluorine.** F. FICHTER and A. GOLDACH (Helv. Chim. Acta, 1930, 13, 713—719; cf. this vol., 722).—Stannous sulphate is oxidised by fluorine, giving a theoretical yield of the stannic salt. Since the reaction occurs more readily than

the oxidation of iodide ion to iodine, its use is proposed as a basis for the iodometric determination of fluorine in a gas mixture. In the oxidation of solutions of ferrous fluoride the rate of stirring is an important factor in the yield, which increases from 60% at 1000 revs. per min. to nearly 100% at 4000 revs. per min. Cobaltic perchlorate has been prepared in solution by electrolytic oxidation of the cobaltous salt at  $-10^\circ$ , and also by means of fluorine. The yield is much higher in the former method. The solutions are very unstable and the solid could not be isolated.

F. L. USHER.

**Action of oxalic acid on fluorides. I. TANAEV** (Ukraine Chem. J., 1930, 5, 87—111).—All fluorides studied can be quantitatively decomposed by evaporation in a platinum basin with oxalic acid solution, using 20 c.c. of saturated oxalic acid solution per 25 c.c. of 0.1N-fluoride; the velocity of decomposition is directly proportional to the solubility of the fluoride taken, varying from 25 min. for sodium fluoride to 3 hrs. for calcium fluoride. The above method cannot be applied to the determination of fluorine.

R. TRUSZKOWSKI.

**Acidium salts of hydrogen fluoride and hydrogen chloride.** A. HANTZSCH (Ber., 1930, 63, [B], 1789—1796).—Hydrogen fluoride forms with perchloric acid and boron fluoride solid additive products, m. p.  $56-58^\circ$  and  $56-58^\circ$ , respectively, which indirectly and on account of their analogy with the compounds from nitric and perchloric acids are formulated  $[\text{FH}_2]^+\text{ClO}_4^-$  and  $[\text{FH}_2]^+\text{BF}_4^-$ . Their salt-like nature is established, since the solution of hydrogen fluoride in sulphuric acid, like that of nitric acid in sulphuric acid, is characterised by the abnormally low mol. wt. of the acidium cation  $[\text{FH}_2]^+$ , although the monosulphate  $[\text{FH}_2]^+\text{SO}_4\text{H}$ , like the nitroacidium monosulphate, could not be isolated owing to the small acidity of sulphuric acid in comparison with perchloric acid. The mol. wts. of hydrogen fluoride (and of potassium fluoride and  $\text{KF.HCl}$ ) and of fluorosulphonic acid in sulphuric acid are so abnormally low that they can be explained only by secondary changes, mainly by the formation of the dissociated hydrofluoroacidium pyrosulphate,  $[\text{FH}_2]^+\text{S}_2\text{O}_7\text{H}$ , and hydroxonium sulphate. For this reason solutions of hydrogen fluoride in sulphuric acid do not etch glass because the halogen is present as the cation  $[\text{FH}_2]^+$ .

Hydrogen chloride in the very dilute solutions which can be prepared is, on the basis of mol. wt. determinations, a normal, binary electrolyte and therefore dissolved as the completely dissociated *hydrochloroacidium sulphate*,  $[\text{ClH}_2]^+\text{SO}_4\text{H}$ . Solid salts with the strongest acids, perchloric and pyrosulphuric, could not be isolated. The production of chlorosulphonic acid and sulphuryl chloride from pyrosulphuric acid and hydrogen chloride is probably attributable to the primary formation of the salt  $[\text{S}_2\text{O}_7][\text{H}_2\text{Cl}]_2$  and its secondary dehydration to  $\text{S}_2\text{O}_7\text{Cl}_2$ .

H. WREN.

**Decomposition of manganese nitride by hydrogen.** L. DUPARC, P. WENGER, and C. CIMERMAN (Helv. Chim. Acta, 1930, 13, 675—678).—Manganese nitride is only slightly decomposed in a current of



pure dry hydrogen at 800°, and the process is very slow. This behaviour is attributed to impurities present in the manganese used. F. L. USHER.

**Higher oxy-compounds of group VIII elements. II. Nickel compounds.** D. K. GORALEVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 897—913).—Nickel oxide yields on fusion with potassium nitrate or chlorate and potassium hydroxide a bright green compound, which gradually loses oxygen on keeping. This substance is soluble in water, yielding a green solution. When kept, or more rapidly on acidification, this solution evolves oxygen, and deposits a dark grey precipitate of nickel oxide. Its colourless alkaline-earth salts are precipitated from solution on the addition of the appropriate reagents. They are stable at the ordinary temperature, and are soluble in dilute acids with the production of colourless solutions not giving the reactions for the nickel ion unless previously boiled for some time; at the same time the solution assumes a green colour, as is also the case on addition of alkali hydroxide. Analysis of the above alkaline-earth compounds shows them to be salts of *nickelic acid*,  $H_2NiO_4$ , containing quadrivalent nickel, and derived from the unknown oxide  $NiO_3$ .

R. TRUSZKOWSKI.

**Formation of double amines in aqueous solution. I. Cyanates and hexamethylenetetramine.** R. RIFAN (Bul. Soc. Stiinte Cluj, 1929, 4, 499—511; Chem. Zentr., 1930, i, 967—968).—Potassium copper and cadmium cyanates,  $K[M(CNO)_3]$ , and the following compounds containing hexamethylenetetramine (*B*) are described:  $[AB_3(H_2O)_4][Cu(CNO)_4]$ , where  $A=Co, Ni, \text{ or } Cd$ ;  $[NiB_3(H_2O)_4][Co(CNO)_4]$ ,  $[CdB_3(H_2O)_4][Co(CNO)_4]$ , and  $[CdB_3(H_2O)_4][Ni(CNO)_4]$ . A. A. ELDRIDGE.

**Compound of univalent ruthenium.** W. MANCHOT and E. ENK (Ber., 1930, 63, [B], 1635—1638).—Ruthenium tribromide is converted by carbon monoxide at 185—188°/350 atm. into the colourless, crystalline compound,  $RuBr(CO)$ . It is slowly decomposed by water and reduces ammoniacal silver solution. It evolves carbon monoxide when heated in nitric oxide at 220°. In carbon monoxide at about 200° it decomposes into ruthenium and the substance  $RuBr_2(CO)_2$ , which is also obtained in an inert atmosphere. Platinum di- and tetra-chloride at 140° give the decarbonyl  $PtCl_2(CO)_2$ . It appears therefore that iron in the periodic system is surrounded on all three sides by elements, manganese, cobalt, and ruthenium, which exhibit univalence. H. WREN.

**Supposed dehydration of hydrated platino-cyanides on cooling.** H. TERREY (Proc. Roy. Soc., 1930, A, 128, 359—360).—The platino-cyanide to which Reynolds ascribed the formula  $Li_2Pt(CN)_5 \cdot 2H_2O$  (A., 1909, i, 559) was probably potassium lithium platino-cyanide,  $KLiPt(CN)_4 \cdot 2H_2O$ . On rapidly cooling a saturated solution of this salt from 40° to 15° the trihydrate of the potassium salt separates out. On cooling to the cryohydric point, double salt and ice separate as a film on the crystals, and the supposed change of the trihydrate to the dihydrate is simply the separation on the surface of each crystal of an overgrowth of the bright red cryohydrate. The

reverse change on heating is due to the evaporation of the solvent water and deposition of the double salt. L. L. BIRCUMSHAW.

**Atomic analysis by X-ray spectroscopy.** T. H. LABY (Trans. Faraday Soc., 1930, 26, 497—509; cf. A., 1929, S67).—A review of the principles, technique, and applications of X-ray analysis to the identification and determination of elements. F. G. TRYHORN.

**Quantitative analysis by means of secondary X-rays.** G. VON HEVESY, J. BÖHM, and A. FAESSLER (Z. Physik, 1930, 63, 74—105).—An account is given of research on the use of secondary X-rays for quantitative chemical analysis. The Coster and Druvesteyn tube for the production of strong secondary X-rays was employed, except for liquids and for substances containing tungsten, when a specially designed tube was used in which the substance investigated was separated from the high-vacuum side of the apparatus and supported on a screen kept at the potential of the cathode to diminish direct action of scattered cathode rays. The characteristic, as compared with the continuous, X-ray radiation of the anticathode was much more effective in producing the secondary radiation, so long as it was a certain amount harder than the latter. The best anticathode material is a metal the characteristic radiation of which is between about 150 and 200 X shorter in wave-length than the edge of the absorption band of the element being investigated. If such a metal cannot be used, the anticathode should be made of a metal having a characteristic radiation from 200 to 600 X shorter in wave-length than the absorption edge. Copper, and therefore other elements, could be used effectively in the form of the powdered metal or oxide rubbed into a silver anticathode. Owing to the continuous X-ray radiation from the anticathode having a different intensity distribution for different excitation voltages, a dependence on the voltage of the ratio of the intensity of two lines in the secondary spectra might be expected, but it was found that this did not take place to more than 2% for lines separated by not more than 250 X, for a variation from 20 to 40 kilovolts. With proper choice of the anticathode material an exposure of 2—3 hrs. was sufficient to enable a substance present to the extent of 1% to be determined with an accuracy of 0.01%. This time could be decreased by using the method of Eggert and Noddack of counting the number of grains developed in very weak lines, instead of the ordinary photometric comparison of stronger lines. In all cases in which the lines and the corresponding edges of the two elements being compared lie close together, the presence of a third substance does not influence the result. In other cases its influence must be corrected for, but can in many cases be neglected. A table is given of the chief comparison lines for most of the elements from sodium to uranium, the usefulness of the lines of the rare earths for comparison purposes, owing to the unlikelihood of their presence in the substance being analysed, being pointed out. A second table shows, for each pair of lines, the elements which if present in large amount are likely to influence the result (cf. preceding abstract).

H. A. JAHN.

**Modern trends in analytical chemistry.** H. H. WILLARD (Ind. Eng. Chem. [Anal.], 1930, 2, 201—232).—The application of optical, X-ray, and electrical measurements to chemical analysis and the development of microanalysis, organic reagents, and radioactive indicators are reviewed.

E. S. HEDGES.

**Electrode potentials in analytical chemistry.** S. POROV (Ind. Eng. Chem. [Anal.], 1930, 2, 230—232).—A brief survey is given of the theory of electrode potentials and the use of the hydrogen, glass, oxygen, and quinhydrone electrodes. It is emphasised that erroneous results and conclusions are often reached by overlooking the fact that the electrode reactions occurring must be completely reversible.

E. S. HEDGES.

**Source of error in polariscopic measurements.** H. K. MILLER and J. C. ANDREWS (Ind. Eng. Chem. [Anal.], 1930, 2, 283).—Measurements of optical activity are affected by slight turbidity in the solution under examination, the values obtained varying with the length of the liquid column. It is recommended to make duplicate determinations in tubes of two different lengths.

E. S. HEDGES.

**Microscopical methods in analytical chemistry.** C. W. MASON (Ind. Eng. Chem. [Anal.], 1930, 2, 203—206).—A plea for the wider use of the microscope in assisting chemical analysis.

E. S. HEDGES.

**Determination of  $p_H$  of [biological] media.** M. LEMOIGNE and R. CHAMINADE (Compt. rend. Soc. Biol., 1929, 102, 922—923; Chem. Zentr., 1930, i, 1656—1657).—When the colorimetric method is inapplicable and the electrometric method troublesome the medium may be brought into electrometric equilibrium with a phosphate mixture of colorimetrically determined  $p_H$ .

A. A. ELDRIDGE.

**General (exact) equation to the potentiometric titration curve.** B. CAVANAGH (J.C.S., 1930, 1425—1447; cf. A., 1928, 607).—A generalised treatment is given of both the equations and methods previously described, which are thus made applicable to a system involving both analytical and electrode reactions of the most general type. The characteristic forms of the curves represented by the generalised equation and of the derived curves are indicated by diagrams and some concrete examples are discussed. The more important mathematical properties of the curves are exhibited; the generalised methods of titration are deduced and their precision is formulated in terms of certain bin-exponential functions regarded as generalised hyperbolic functions. Certain methods, however, still involve only the function  $f$  tabulated in the earlier paper. Routine procedures are developed whereby accurate allowance may be made for a number of inherent experimental errors. A geometrical method suitable for the investigation of new and uncertain systems is described.

F. G. TRYHORN.

**Conductometric titration with visual determination of the end-point in boiling solutions.** G. JANDER, A. PFUNDT, and H. SCHORSTEIN (Z. angew. Chem., 1930, 43, 507—510).—By the use of the apparatus previously described (Jander and

Pfundt, "Die visuelle Leitfähigkeitstiteration," Stuttgart, 1929) it is possible to determine sulphates conductometrically by titration with barium acetate in boiling neutral solutions. For the determination of sulphate in drinking water the sample is boiled to precipitate calcium carbonate, filtered, and the boiling filtrate titrated directly with barium acetate. Conductometric titration of hot potassium ferrocyanide solution with neutral zinc chloride solution shows the reaction to take place in three stages, corresponding with the formation of  $K_6Zn[Fe(CN)_6]_2$ ,  $K_4Zn_2[Fe(CN)_6]_2$ , and  $K_2Zn_3[Fe(CN)_6]_2$ , respectively; the third end-point is much sharper than the others, which are, however, quite distinctly marked on the titration curve. The converse titration yields erratic results.

A. R. POWELL.

**Potentiometric titrations.** N. H. FURMAN (Ind. Eng. Chem. [Anal.], 1930, 2, 213—224).—Development in the methods of potentiometric titration during the past 4 years is reviewed.

E. S. HEDGES.

**Conductometric titrations.** I. M. KOLTHOFF (Ind. Eng. Chem. [Anal.], 1930, 2, 225—230).—The most important applications of conductometric titrations are summarised and it is emphasised that this method may often be used successfully in cases where the ordinary or potentiometric methods fail. The limitations are also pointed out and consideration is given to the errors in the method. It is suggested that conductometric titration should prove to be useful in water analysis, the determination of alkalinity and ash of sugars, acidity of lemonades, fruit juices, wine, beer, oils and fats, lacquer, etc., and in the determination of peptising ions in a colloidal solution.

E. S. HEDGES.

**Alkalimetric titration; indicators and titration errors.** III. C. J. VAN NIEUWENBURG (Chem. Weekblad, 1930, 27, 174—176).—The different types of  $p_H$  curve obtained in the titration of acids or alkalis of various strengths are illustrated, and the method of ascertaining the most suitable indicator for any given titration is described.

H. F. GILLBE.

**Fruit and vegetable pigments as indicators.** O. B. PRATT and H. O. SWARTOUT (Science, 1930, 71, 486—487).—Solutions of many fruit pigments act as indicators and can be used in titrating acids but not bases. The colour changes and  $p_H$  ranges are described.

L. S. THEOBALD.

**Influence of substituents on indicators.** W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1930, 34, 1797—1814).—The modern theory of indicators and the effect of substituents on their acid or basic character are reviewed.

L. S. THEOBALD.

**Redox [oxidation-reduction] indicators.** L. MICHAELIS and H. EAGLE (J. Biol. Chem., 1930, 87, 713—727).—The technique of titration of reversible oxidation-reduction systems is discussed in detail, and figures are given for the value of  $E'_0$  (potential of the dye in the half-reduced state) for the three dyes, galloxyaniline, gallophenine, and brilliant alizarin-blue (cf. Rowe, "Colour Index," Bradford, 1924), over the  $p_H$  range 5—10.

C. R. HAREINGTON.

**Indicator.** N. P. SOBYANIN and S. G. SAAKOV (J. Chem. Ind., Russia, 1929, 6, 735—736).—The colouring matter of *Althaea rosea* flowers, extracted with hot dilute alum solution, shows a sharp transition from pink (acid) to green (alkaline). CHEMICAL ABSTRACTS.

**Yellow mercuric oxide as acidimetric substance.** R. BIAZZO and C. CHINES (Annali Chim. Appl., 1930, 20, 258—261).—Inceze's method of employing yellow mercuric oxide as an alkalimetric standard (A., 1917, ii, 327) gives exact results but is costly, owing to the use of potassium iodide. Similar accuracy may be attained by replacing the iodide by sodium thiosulphate (or potassium thiocyanate or bromide). This procedure cannot, however, be applied to the determination of the titre of thiosulphate solutions. T. H. POPE.

**Determination of water by distillation with tetrachloroethane.** W. LEPPER.—See B., 1930, 709.

**Rapid determination of free hydrochloric acid in presence of ferric and aluminium chlorides.** K. KUCHELER (Chem.-Ztg., 1930, 54, 582).—The titration is carried out with standard alkali in presence of phenolphthalein, after addition of a large excess of sodium fluoride and sodium chloride. S. I. LEVY.

**Determination of perchlorate.** H. H. WILLARD and J. J. THOMPSON (Ind. Eng. Chem. [Anal.], 1930, 2, 272—273).—Details are given of a method for the determination of perchlorate which is based on the fact that if a perchlorate is heated with starch and sulphuric acid under proper conditions it is completely reduced to chlorine, which is collected in alkaline arsenite solution and determined in the usual way. Chlorate, bromate, and iodate may be determined by a similar method by treating the salts with concentrated sulphuric acid, using hydrazine sulphate as the reducing agent. With chlorate and bromate, permanganate was then added to expel the halogen from the flask, but with iodate hydrogen peroxide was used, as potassium permanganate was found to oxidise some iodine to iodic acid. E. S. HEDGES.

**Determination of iodides in presence of other halides.** S. V. GORBATSCHEV and I. A. KASATKINA (Z. anorg. Chem., 1930, 191, 104—112).—The methods for determining iodide in presence of other halides hitherto described are unsuitable for determining small amounts of iodide in presence of large amounts of chloride and bromide. The usual nitrite method may, however, be improved by substituting ferric chloride in large excess for nitrite as oxidising agent, but ferric salts actively catalyse the atmospheric oxidation of iodide. Small quantities of iodide may be determined in presence of a large excess of chloride, and in absence of bromide, by shaking the acidified solution for 20—30 min. with excess of manganese dioxide, thus liberating all the iodine and then converting it into iodine monochloride, which is then titrated in the filtrate by means of thiosulphate, using starch as indicator. Alternatively, the acidified solution may be titrated with permanganate using chloroform as indicator. Under these conditions the iodine first set free is converted into monochloride, and when this conversion is complete the colour in the chloroform vanishes. This titration may also be

carried out with solutions containing bromide, using the electrometric method, in which case the complete conversion into monochloride is shown by a rapid change in potential of the indicator electrode.

R. CUTHILL.

**Starch iodide reaction: stability and proportionality of colour produced by small amounts of iodine.** R. G. TURNER (J. Amer. Chem. Soc., 1930, 52, 2768—2773).—The iodine-starch reaction affords a colorimetric determination of 0.0005—0.005 mg. of iodine in the absence of other salts. A modification of the method of Leitch and Henderson (A., 1926, 1284) and Nichols' starch reagent (A., 1929, 1411) were employed. The colour is stable for at least 1 hr. and the intensity is proportional to the weight of iodine and is independent of temperature below 70°.

J. G. A. GRIFFITHS.

**Spectroscopic detection of fluorine.** J. PAPISH, L. E. HOAG, and W. E. SNEE (Ind. Eng. Chem. [Anal.], 1930, 2, 263—264).—The direct spectroscopic detection of fluorine is not possible, using the visible range of the spectrum, but an indirect method consists of mixing the substance under examination with a calcium salt and examining the arc spectrum of the mixture for bands of calcium fluoride. The band at 5291 Å. is most persistent and is visible when 0.01 mg. of fluorine is present in the zone of excitation, although as a rule it is difficult to detect quantities less than 0.02 mg. Substances containing minute quantities of fluorine may be examined by distilling off the fluorine as hydrogen fluoride, collecting in lime-water, and arcing the calcium fluoride produced.

E. S. HEDGES.

**Detection of small quantities of fluorine in silicate minerals and rocks.** I. P. ALIMARIN (Z. anal. Chem., 1930, 81, 8—14).—The finely ground substance (0.2—0.5 g.) is intimately mixed with 1 g. of boric anhydride and the mixture is heated in a hard glass tube arranged as for the determination of combined water by Penfield's method. The liquid which collects in the bulb contains hydrofluoboric acid if the material contains fluorine; the presence of this acid is detected by its decolorising action on the violet-red colour of a solution made by mixing 3 vols. of a 0.4% zirconium nitrate solution with 2 vols. of a 0.4% alcoholic solution of alizarin. The reagent may be used as a solution or filter-paper may be soaked in it and dried for spot tests. The test will detect 0.008 mg. of fluorine in 0.3 g. of rock, which produces a pale yellow spot within 5 min. A. R. POWELL.

**Determination of oxygen in sea-water.** M. NICLOUX (Compt. rend., 1930, 191, 259—261).—The sample (5—40 c.c.) is placed in a calibrated  $\Lambda$ -tube of suitable size and containing a glass ball to facilitate mixing. Into one leg is poured 1.2—2 vol.-% of an aqueous solution of 18 g. of potassium hydroxide and 5 g. of potassium iodide in 100 c.c., and into the other 0.8—1% of a 30% solution of manganous sulphate. The tube is closed and the contents of the two legs are mixed; 0.2—0.4 c.c. of phosphoric acid,  $d$  1.712, is then added, and the liberated iodine titrated with thiosulphate. An accuracy of 2% is obtainable with 5 c.c. of sea-water, and of 0.5% with 40 c.c. C. A. SILBERRAD.

**Determination of peroxides.** R. FLATT (Bull. Soc. Ind. Mulhouse, 1930, **96**, 375—378).—The substance is introduced into a small distillation flask fitted with a dropping funnel, the tube of which extends to the bottom and is provided with a side-tube, just below the stopcock, connecting with a source of carbon dioxide. The flask itself has a downwardly-inclined side-tube connecting with two absorption vessels in series, each filled with potassium iodide solution. Hydrochloric acid is placed in the reservoir of the dropping funnel, the air in the apparatus displaced with carbon dioxide, and the acid allowed to drop slowly on the substance while the mixture is heated with a small flame. The chlorine evolved is collected in the iodide solution and the liberated iodine titrated with thiosulphate.

A. R. POWELL.

**Sensitivity of various tests for traces of hydrogen sulphide.** E. C. TRUESDALE (Ind. Eng. Chem. [Anal.], 1930, **2**, 299—302).—The sensitivity of the reagents, alkaline lead acetate, acid lead acetate, aqueous and ammoniacal silver nitrate, sodium nitroprusside, and *p*-aminodimethylaniline, in detecting hydrogen sulphide has been investigated by passing small concentrations of hydrogen sulphide in air or hydrogen through a capillary tip against a strip of filter paper wetted with the reagent. Alkaline lead acetate proved to be the most sensitive reagent, hydrogen sulphide being detected at a concentration of 1 part in  $10^7$  parts of air. As 10 c.c. of the mixture of gases were used, this corresponds with the detection of  $1.5 \times 10^{-9}$  g. of hydrogen sulphide. Hydrogen sulphide could not be detected at greater dilutions, and the failure of the test to be cumulative is probably due to lack of satisfactory coagulation of the lead sulphide on the paper.

E. S. HEDGES.

**Mechanism of the azide-iodine test for thio-sulphate and its quantitative application.** H. BAINES.—See B., 1930, 710.

**Preservation of standard thiosulphate by means of amyl alcohol.** F. H. CAMPBELL and F. J. WATSON (Chem. Eng. Min. Rev., 1930, **22**, 340—342).—Thiosulphate solutions continue to decompose indefinitely during storage owing to the action of bacteria. The addition of 1% of amyl alcohol effectively preserves the titre of standard solution for at least 2—3 months under ordinary laboratory conditions, viz., diffused daylight and periodical opening to the air. The chief objection to the use of this alcohol is that it causes the burette and containing vessels rapidly to become greasy. Amyl alcohol also forms an effective preservative for starch solutions.

A. R. POWELL.

**Determination of thiocyanate by oxidation with sodium hypobromite.** J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1929, **67**, 221—225; Chem. Zentr., 1930, **i**, 1661).—The method depends on oxidation by bromine, in absence of ammonia, to sulphate and cyanate (cf. A., 1929, 1259).

A. A. ELDRIDGE.

**Manganometric determination of thiocyanate.** J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1929, **67**, 226—232; Chem. Zentr., 1930, **i**, 1661).—Accurate results are obtained only by the use of a permanganate solution standardised against thiocyanate under

similar conditions with respect to acidity, volume, and concentration.

A. A. ELDRIDGE.

**Volumetric determination of thiocyanate with iodine and with iodate.** H. A. PAGEL and O. C. AMES (J. Amer. Chem. Soc., 1930, **52**, 2698—2702; cf. Schwicker, A., 1929, 899).—Determinations to within 0.1% may be effected by adding 5 g. of borax and then at least 5 c.c. in excess of 0.1*N*-iodine to make the measured volume of thiocyanate solution up to 150 c.c. After 10 min., 10 c.c. of 6*N*-hydrochloric acid are added and the excess of iodine is titrated with thiosulphate. The iodine solution may be replaced by an equivalent quantity of 0.1*N*-iodate together with 2 g. of potassium iodide and 10 c.c. of *N*-hydrochloric acid.

J. G. A. GRIFFITHS.

**Determination of oxides of nitrogen (except nitrous oxide) in low concentration.** J. PICCARD, E. G. PETERSON, and C. D. BITTING (Ind. Eng. Chem. [Anal.], 1930, **2**, 294—295).—Improvements have been made in the phenoldisulphonic acid method for determining oxides of nitrogen other than nitrous oxide. A detailed procedure for determining oxides of nitrogen in dynamite fumes is given.

E. S. HEDGES.

**Identification and determination of nitrates in water.** G. BINI.—See B., 1930, 742.

**Determination of small quantities of arsenic.** F. MARTIN and J. PIEN (Bull. Soc. chim., 1930, [iv], 47, 646—654).—The Gutzeit test is employed. In the first modification, sensitive to 0.0005 mg. of arsenious oxide but adapted also for the determination of large quantities, zinc and acid are treated with dilute sulphuric or hydrochloric acid, 5 min. later the arsenic material in aqueous or acid solution is added, and, 30 min. later, more dilute acid. The hydrogen evolved is passed through alkaline hypochlorite solution and then allowed to ascend a tube in which a strip of dry filter-paper charged with silver nitrate is suspended. After an hour both sides of the strip are compared with a series of standard strips, the stains on which have been "fixed" by repeated soaking of the strips in very dilute ammonia and coating with paraffin. Very much smaller quantities of zinc, acid, and arsenic material are necessary in a further modification in which the gas evolved is passed through dry cotton wool impregnated with lead acetate contained in a wide tube, across the top of which the silver nitrate paper is placed horizontally. The standard stains in this case must be prepared on paper which has been soaked in gum tragacanth and dried prior to soaking in silver nitrate, the stain produced being "fixed" by immersion in very dilute ammonia solution. The sensitivity is the same as in the first method, but may be increased to 0.0001 mg. of arsenious oxide by inserting an inverted funnel-shaped tube over the cotton wool, so that the gas impinges upon the silver nitrate paper through an orifice of about 2 mm. diameter. Compact forms of apparatus for carrying out these methods are figured.

S. K. TWEEDY.

**Determination of arsenic, antimony, and tin.** H. BILTZ (Z. anal. Chem., 1930, **81**, 82—95).—The material is dissolved in nitric acid and the solution evaporated with sulphuric acid until copious fumes

of the latter are evolved and all the sulphur is distilled out of the flask. After cooling, a few c.c. of water are added, followed by 1.5 g. of recrystallised hydrazine sulphate, 80 c.c. of hydrochloric acid (*d* 1.19), and 1 g. of potassium bromide. A slow current of carbon dioxide is passed through the flask and the solution is distilled through a fractionating column 15–30 cm. long filled with thin broken glass until about 80 c.c. of distillate have collected in 40 min. A further quantity of 20–30 c.c. of hydrochloric acid is added and distillation is continued until 20 c.c. more have been collected; this distillate is diluted and titrated with 0.1*N*-potassium bromate after addition of 1 g. of potassium bromide and two drops of methyl-orange. If only a drop or two of bromate is required to decolorise the solution, all the arsenic is in the first distillate, which is then titrated with bromate. The fractionating column is washed twice by filling it entirely with hydrochloric acid and the washings are used in the subsequent distillation of antimony from the residual liquid in the flask. This is effected by adding 7–14 c.c. of phosphoric acid (*d* 1.7) to prevent distillation of the tin, then heating the flask until the temperature of the liquid rises to 155–165°, and slowly dropping hydrochloric acid below the surface of the liquid while a current of carbon dioxide is passed through the apparatus; no fractionating column is used. The liquid should distil at the rate of 1 drop per sec., and all the antimony should be removed in 40–50 min.; the distillate is titrated with bromate as usual. For the distillation of tin from the residual liquid the temperature is maintained at 140° and a mixture of 1 part of hydrobromic acid (*d* 1.40) and 3 parts of hydrochloric acid (*d* 1.19) is slowly run below the surface of the liquid. Distillation is continued until a few drops of the distillate cease to give a reaction with hydrogen sulphide; the temperature must be kept below 145° to prevent any bismuth from passing over. The distillate is diluted with an equal volume of water and the tin reduced with iron (*ferrum reductum*) and titrated with iodine. A. R. POWELL.

**Carob-seed gum.** Its use for the detection and determination of boric acid and borates. R. HART (Ind. Eng. Chem. [Anal.], 1930, 2, 329–331).—The physical, chemical, and colloidal properties of carob-seed gum are described. The difficulty of preparing an aqueous solution has been surmounted by wetting the dry gum with its own weight of alcohol, and then adding the paste in small quantities at a time to water, heating, and stirring after each addition until uniform. Sodium hydroxide darkens sols of the gum, at the same time making them transparent, and the viscosity is greatly reduced. Acids reduce the viscosity and on boiling appear to hydrolyse the gum to water-soluble products. The addition of borax to the gum produces a transparent, irreversible gel, which is dry, firm, and cohesive, but no longer adheres to glass or other substances. This characteristic effect provides a sensitive test for boric acid and borates and a rough means of determination. The correct experimental conditions have been worked out. Alkalis interfere with the test, particularly when the concentration of borax is small, and the solution is therefore first rendered neutral to

phenolphthalein, with the addition of glycerol to prevent hydrolysis. E. S. HEDGES.

**Colorimetric determination of silica in the presence of phosphates and iron.** L. A. THAYER (Ind. Eng. Chem. [Anal.], 1930, 2, 276–283).—The influence of the presence of phosphates and of iron on the determination of silica by the colorimetric method of Diénert and Wandenbultke has been studied. Phosphates lead to an error through the formation of ammonium phosphomolybdate, iron gives a coloured iron silicomolybdate which obscures the colour of the ammonium salt, and the simultaneous presence of phosphates and iron gives rise to the formation of an intensely coloured iron phosphomolybdate. A method has been devised for eliminating these interfering substances without loss of silica. Iron is precipitated in acetic acid solution as ferric phosphate and removed by filtration; excess of phosphate is then precipitated as calcium phosphate and filtered off. Experimental results for solutions of silica in distilled water and in sea-water are given.

E. S. HEDGES.

**Spectrographic method of determining carbon dioxide in mixtures with air.** B. DE LA ROCHE (Bull. Soc. chim., 1930, [iv], 47, 660–668).—The spark spectra of air containing various known quantities of carbon dioxide (*q*%) were examined and the variation in the density of a suitable carbon line was measured by means of a microphotometer. The suitability of various functions of this measured density for plotting against *q* so as to obtain a curve adapted for interpolation is considered. A suitable function is described, and from the curve prepared with its aid the spark spectrum of the atmosphere shows that the latter contains 0.031% of carbon dioxide.

S. K. TWEEDY.

**Determination of carbon dioxide in carbonates.** C. A. JACOBSON and J. W. HAUGHT (Ind. Eng. Chem. [Anal.], 1930, 2, 334–335).—An apparatus for the determination of carbon dioxide in carbonates is described, perchloric acid being recommended for liberating the carbon dioxide. Experimental results are given and it is claimed that more accurate results are obtained than with any other method tried.

E. S. HEDGES.

**Elementary micro-analysis, especially adapted for dissolved substances.** A. KROGH (Biochem. Z., 1930, 221, 247–263).—2–20 Mg. of material are oxidised in an atmosphere of nitrogen with copper oxide contained in a special combustion apparatus, the volume of carbon dioxide produced and of nitrogen (if any) liberated being measured. After the substance has been burnt, a known volume of oxygen is passed through the apparatus and the amount of the gas required to reoxidise the copper is determined. Special apparatus and methods for dealing with substances in true or colloidal solution alone or accompanied by inorganic material are described.

W. MCCARTNEY.

**Determination of cyanide in ferro- and ferri-cyanides.** J. GOLSE (Bull. Soc. Pharm. Bordeaux, 1929, 67, 217–221; Chem. Zentr., 1930, i, 1661).—In Rose and Finkener's method the solution of 0.5 g. of salt in 20 c.c. of water is preferably boiled

for 10 min. with 15 c.c. of *N*-sodium hydroxide and 40 c.c. of 5% mercuric chloride solution, the cyanide being titrated in an aliquot part of the filtrate (cf. A., 1929, 1259). A. A. ELDRIDGE.

**Action of oxalic acid on alkali chlorides.** N. A. TANANAIEV and N. A. LASARKEVITSCH (Z. anal. Chem., 1930, 81, 117—121).—Complete conversion of sodium or potassium chloride into the corresponding oxalate is effected by evaporating the solution to dryness on the water-bath with ten times as much oxalic acid as the weight of chloride present. When all odour of hydrochloric acid has disappeared the sides of the dish are rinsed with a little water and the evaporation is repeated as before. The dry residue is then heated gently until the excess of oxalic acid sublimes, leaving a residue of alkali oxalate. On heating this residue at a dull red heat complete conversion into carbonate is effected; if difficulty is experienced in burning off the separated carbon the mass is cooled, moistened with water, dried, and again heated to dull redness.

A. R. POWELL.

**Determination of potassium using lead-containing complexes.**  $\text{NaPbCo}(\text{NO}_2)_6$ . P. S. SERGEENKO (Ukraine Chem. J., 1930, 5 [Sci.], 113—128).—Potassium salts give a precipitate of the composition  $\text{KPbCo}(\text{NO}_2)_6$  with Tananaev's reagent, consisting of a mixture of cobaltous and lead nitrates and of sodium nitrite solution acidified with acetic acid, or of the composition  $\text{K}_2\text{PbCo}(\text{NO}_2)_6$  with Cuttica's reagent, which is the same as Tananaev's but without the addition of acetic acid. The potassium content of a solution may be determined by oxidising the nitrite ions of the complex to nitrate ions by the use of permanganate. This may be done in three ways, viz., direct titration of the precipitate, in which case 1 c.c. of 0.1*N*-permanganate is equivalent to 0.3555 mg. of potassium, or titration of the products of decomposition of the complex by boiling in aqueous or aqueous alkaline solution, when the respective equivalents of 1 c.c. of permanganate are 0.444 and 0.326 mg. of potassium. The differences found between the factors are due to changes in the valency of cobalt. An alternative method consists in titration with permanganate of cobaltous oxalate prepared from the precipitate.

R. TRUSZKOWSKI.

**Gravimetric determination of potassium as potassium sodium cobaltinitrite.** A. VASSILIEV and N. MATVEEV (Z. anal. Chem., 1930, 81, 106—114).—The neutral potassium chloride or nitrate solution (5—10 c.c.) is treated with 10 c.c. of a 25% solution of cobalt sulphate crystals and 12 c.c. of a 50% solution of sodium nitrite. After stirring, 1 c.c. of 80% acetic acid is added drop by drop and the solution is heated on the water-bath until evaporation commences. To complete the precipitation 1.5 g. of sodium chloride are stirred in and the whole is set aside over-night. The precipitate is collected in a glass filter crucible, washed with cold water, dried at 100°, and weighed as  $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ . Correct results are obtained only by strict adherence to the above details. Calcium and magnesium salts do not interfere.

A. R. POWELL.

**Detection and determination of small quantities of lithium.** E. R. CALEY (J. Amer. Chem. Soc.,

1930, 52, 2754—2758).—Lithium chloride is extracted from the mixture of alkali chlorides with amyl alcohol (1—5 c.c.) and to the solution is added 2.5 times its volume of freshly-prepared reagent (2 g. of ammonium stearate in 100 c.c. of amyl alcohol) at the ordinary temperature. Less than 0.0001 g. of lithium in 1 g. of the mixed chlorides may be detected by the turbidity which develops in 5—60 min. The lithium may be determined nephelometrically to within 0.02 mg. Other alkali metals do not interfere, but magnesium, alkaline earths, and heavy metals must be absent.

J. G. A. GRIFFITHS.

**Separation of lithium from potassium and sodium by means of dioxan.** A. SINKA (Z. anal. Chem., 1930, 80, 430—435).—The mixed chlorides are placed in a 35-c.c. glass filter crucible which is suspended just above the surface of 20 c.c. of dioxan contained in a 250-c.c. conical flask fitted with a reflux condenser, the end of which is just above the top of the crucible. The dioxan is kept gently boiling for 3—4 hrs., whereby the lithium chloride is completely extracted. The solution is evaporated for the recovery of the lithium salt, which may be dried and weighed or determined volumetrically with silver nitrate. It shows no trace of sodium or potassium by the flame test.

A. R. POWELL.

**Determination of lithium.** M. H. BROWN and J. H. REEDY (Ind. Eng. Chem. [Anal.], 1930, 2, 304—306).—Measurements of the solubility of lithium, sodium, potassium, rubidium, caesium, barium, strontium, calcium, and magnesium chlorides in acetone at 25° have been made, and the results show that lithium chloride is freely soluble, whilst the chlorides of sodium, potassium, barium, and strontium are quite insoluble. A means of separation of lithium from these four metals is therefore presented. Calcium must be absent. Rubidium, caesium, and magnesium do not interfere seriously, but their presence would necessitate the use of a correction factor. Ammonium chloride is most conveniently removed by ignition. Experimental details of this method of separation are given.

E. S. HEDGES.

**Determination of small quantities of lithium.** B. BRAUNER (Coll. Czech. Chem. Comm., 1930, 2, 442—446).—Small quantities of lithium may be determined by precipitating with sodium phosphate solution and centrifuging in a capillary tube (about 1.5 mm. bore) until the precipitate attains a constant level, which is then compared with that obtained with a known quantity of lithium. With 0.3 mg. of lithium the height of the precipitate is about 6.8 mm., the error of the determination being  $\pm 0.002$  mg. Errors caused by imperfect washing of the precipitate and by its solubility are entirely eliminated by this method.

H. F. GILLBE.

**Qualitative micro-analysis of the silver group.** A. BENEDETTI-PICHLER (Ind. Eng. Chem. [Anal.], 1930, 2, 309—311).—An improved technique for the qualitative micro-analysis of mixtures of silver, lead, and mercurous mercury is described. The method enables an analysis to be carried out with 0.01 mg. of the three chlorides. 0.001 Mg. of mercury can be detected in the presence of 0.1 mg. of silver, and 0.001



mg. of silver can be detected in the presence of 1 mg. of mercury.

E. S. HEDGES.

**Precipitation of calcium as oxalate.** M. STILLER (Chem.-Ztg., 1930, 54, 422).—In the usual method of precipitating calcium oxalate small quantities of calcium carbonate are co-precipitated, so that although correct results are obtained by ignition to oxide and weighing, low results are obtained by titration with permanganate. Complete conversion into oxalate is effected by dissolving the precipitate in hydrochloric acid, adding an excess of ammonium oxalate, and boiling while adding ammonia drop by drop until the solution is just alkaline to litmus. The coarsely crystalline precipitate settles and filters readily and is quite free from carbonate.

A. R. POWELL.

**Detection of alkaline-earth metals.** P. AGOSTINI and R. ABBATE (Annali Chim. Appl., 1930, 20, 229—232).—The following methods are rapid and trustworthy. The precipitate of alkaline-earth carbonates is dissolved in acetic acid, the barium being then precipitated as chromate and filtered off, and part of the filtrate tested for strontium by Caron and Raquet's method (A., 1907, ii, 52). The rest of the filtrate is heated with a few crystals of hydrazine hydrochloride until the chromate is completely reduced to chromium salts, then rendered alkaline with ammonia, and boiled. The chromium hydroxide is filtered off and the clear filtrate tested for calcium by boiling with saturated potassium ferrocyanide solution. If calcium is present in large proportion, a part of the carbonate precipitate (0.1 g.) is boiled with 50 c.c. of 25% ammonium sulphate solution, which converts the barium and strontium into sulphates, and the calcium into the soluble calcium ammonium sulphate. The filtered liquid is tested for calcium by means of ammonium oxalate, and the precipitate for barium and strontium by the Caron and Raquet method. The use of sodium rhodizonate (cf. Feigl, A., 1925, ii, 435) is discussed.

When phosphoric, oxalic, boric, or hydrofluoric acid is present, the analysis is facilitated if the partial precipitation of the alkaline-earth metals and magnesium in group III is rendered complete. To this end, the filtrate from group II, after being freed from hydrogen sulphide and boiled with nitric acid to oxidise ferrous salts, is treated with excess of a solution containing ammonium sulphate, phosphate, and oxalate, and then with ammonium chloride and ammonia solutions. The washed precipitate is treated with dilute hydrochloric acid, which dissolves most of the precipitate and leaves a residue, mainly of barium sulphate. After further filtration, the filtrate is treated with dilute sulphuric acid and alcohol and left for some time. The calcium and strontium sulphates thus precipitated are collected and added to the insoluble residue, the subsequent procedure then being as usual.

T. H. POPE.

**Rapid opening-up of calcium cyanamide.** W. LEPPER.—See B., 1930, 710.

**Thiodiphenylcarbazide for the detection of magnesium.** P. AGOSTINI (Annali Chim. Appl., 1930, 20, 235).—Ten c.c. of the solution to be tested are treated with 2 drops of cold, saturated alcoholic

thiodiphenylcarbazide solution and a large excess of ammonia solution. In presence of magnesium, a pink gelatinous precipitate or a pink coloration appears, 1 part of the metal in 300,000 parts of solution being thus detectable. With very small quantities of the metal, a blank test is advisable. No other metal of groups V and VI gives this reaction.

T. H. POPE.

**Detection of zinc by means of resorcinol.** K. FABICH (Verh. Geol. Bundesanst. Wien, 1929; Chem. Zentr., 1930, i, 1335).—The addition of a 10% solution of resorcinol in alcohol to a dilute solution of a zinc salt gives on shaking in the cold a yellow colour, which on heating changes to olive-green or blue, the colour depending on the concentration. Other metals, such as cadmium, nickel, cobalt, copper, and manganese, give similar colours with resorcinol.

L. S. THEOBALD.

**Specific reaction for the detection of cadmium.** F. PAVELKA and E. KOLMER (Mikrochem., 1930, 8, 277—280).—Cadmium salts in acetic acid solution yield a characteristic yellowish-white crystalline precipitate with nitrophenolarsinic acid; under the microscope the crystals appear as long narrow rectangular prisms often clustered in prickly spherical aggregates. The reaction will detect 1 part of cadmium in 200,000 parts of solution and is not affected by the presence of any metal which forms a soluble acetate.

A. R. POWELL.

**Separation of lead and antimony.** H. BILTZ (Z. anal. Chem., 1930, 81, 81).—Attention is directed to the fact that complete separation of antimony and lead sulphides by digestion with sodium sulphide is complete in one operation only if sufficient sulphur is present as polysulphide to convert the antimony entirely into thioantimonate.

A. R. POWELL.

**Electrolytic determination of thallium as thallic oxide.** A. JFLEK and J. LUKAS (Chem. Listy, 1930, 24, 223—226, 245—250).—Thallium is quantitatively deposited by the electrolysis of solutions containing less than 0.25 g. of thallium as nitrate and 1—2 g. of 40% hydrogen fluoride solution, using 0.1 amp. at 2—5 volts. After 60 min. 1 c.c. of 30% hydrogen peroxide is added to dissolve metallic thallium deposited on the cathode, and the current is passed a further 60 min.; this operation is once again repeated. The anode is then washed, dried, and weighed; the increase in weight multiplied by 0.8444 gives the thallium content of the solution. Thallium is deposited on the anode as a brilliant, reddish-coloured, strongly adherent film of the approximate composition  $Tl_2O_3 \cdot HF$ .

R. TRUSZKOWSKI.

**Qualitative micro-analysis. Detection of traces of copper by capillary separation.** F. FEIGL and H. J. KAPELITZAS (Mikrochem., 1930, 8, 239—244).—Traces of copper may be detected in the presence of large amounts of nickel by placing one drop of the acetic acid solution of the elements on a filter-paper which has been dipped into an alcoholic solution of dithio-oxamide and dried. If copper is present the middle of the drop immediately develops an olive-green to black ring; the nickel diffuses further before it reacts with the amide, so that a white

ring surrounds the copper ring and is itself surrounded by a dirty violet to violet-blue ring. The reaction will detect 0.05  $\gamma$  of copper in the presence of 20,000 times as much nickel or 2000 times as much cobalt, which forms a yellowish-brown ring outside the copper ring.

A. R. POWELL.

**Effect of the presence of other elements on some microscopical tests for the metals.** W. F. WHITMORE and F. SCHNEIDER (*Mikrochem.*, 1930, 8, 293—304).—The formation of triple nitrates with potassium and lead is a test for copper or nickel in the absence of the other, the former giving black or dark brown cubes and the latter light yellow cubes; when both elements are present the colour may vary from light yellow to black. The oxalate test for manganese, cadmium, lead, and bivalent tin is specific only when each element is present alone; when two or more are present in the test solution the crystals formed usually have a different habit from the normal, or the crystals due to one element may fail to appear. Similarly, the mercurithiocyanate test for copper, cobalt, zinc, and cadmium does not distinguish the elements from one another when in admixture, the crystal habit and colour varying considerably with the nature and relative proportions of the metals present. Iron cannot be detected by the ferrocyanide test when more than ten times as much copper is present and lead and mercury cannot be detected by the iodide test when fifty times as much mercury or lead is present in the same solution (cf. B., 1930, 616).

A. R. POWELL.

**Complete precipitation of copper as cuprous thiocyanate. I. Volumetric modification of the method of determining thiocyanates by means of sodium hypobromite.** J. GOLSE (*Bull. Soc. chim.*, 1930, [iv], 47, 655—660; cf. this vol., 1144).—A known excess of standard potassium thiocyanate solution is added to the solution of copper salt; sodium sulphite solution is then added dropwise until all the copper is precipitated as cuprous thiocyanate. Sulphur dioxide is thereupon completely removed from the solution, after which the latter is filtered. The excess of potassium thiocyanate in the filtrate is oxidised to cyanate by addition of alkaline sodium hypobromite solution; the cyanate formed is removed by means of potassium iodide, which is subsequently added in excess, and the iodine liberated is titrated with thiosulphate. A blank experiment must also be carried out. A modified procedure is given for determining very small quantities of copper.

S. K. TWEEDY.

**Drop reaction for the mercurous ion.** N. A. TANANAEV (*Ukraine Chem. J.*, 1930, 5, 63—65).—Mercurous salts in quantities of not less than 0.0002 mg. of mercurous ion in 0.002 c.c. of solution can be detected by the following method. A drop of saturated sodium nitrite solution is placed on filter paper, and a drop of the solution under examination is placed on the spot, when a black coloration due to metallic mercury appears. In the presence of coloured cations a brown coloration may appear; this, however, can be removed by washing, leaving a black spot indicative of mercurous mercury. In this case the sensitivity of the reaction is 0.001 mg. When mercurous chloride or

sulphate is present, the above reaction is given only by considerably larger quantities of the salts, whilst should they be present simultaneously with silver chloride or lead sulphate the result of this reaction is doubtful.

R. TRUSZKOWSKI.

**Method of Vanino and Treubert for the gravimetric determination of mercuric salts as mercurous chloride.** E. CATTELAINE (*J. Pharm. Chim.*, 1930, [viii], 11, 580—583).—Mercuric salts may be accurately and rapidly determined by reduction with hypophosphorous acid in presence of hydrochloric acid and hydrogen peroxide. The mercurous chloride which is precipitated is collected and weighed.

W. O. KERMAK.

**Reduction of mercury salts with formaldehyde and with hydrogen peroxide.** JEAN (*Bull. Soc. Pharm. Bordeaux*, 1929, 67, 233—239; *Chem. Zentr.*, 1930, i, 1660).—For the reduction with formaldehyde of 0.1 g. of mercury in 50 c.c., the solution must be at least 0.67*N* with respect to sodium hydroxide, and for that of 0.001 g. at least *N*. For reduction with hydrogen peroxide at least *N*-alkali is necessary.

A. A. ELDRIDGE.

**Reduction of mercury salts with stannous chloride.** JEAN (*Bull. Soc. Pharm. Bordeaux*, 1929, 67, 239—243; *Chem. Zentr.*, 1930, i, 1660).—The solution must be at least 2.5*N* with respect to hydrochloric acid. With less acid the precipitate presumably contains mercurous chloride.

A. A. ELDRIDGE.

**Determination of lanthanum by ignition of the oxalate.** H. J. BACKER and K. H. KLAASSENS (*Z. anal. Chem.*, 1930, 81, 104—106).—On ignition of precipitated lanthanum oxalate the water of crystallisation is lost completely at 250° and the weight becomes constant. Above 300° carbon monoxide and carbon dioxide are evolved and the substance becomes grey, but at 400° it becomes white again and once more constant weight is attained corresponding with conversion into the basic carbonate,  $\text{La}_2\text{CO}_5$ . At 550° this compound begins to decompose, and is completely converted into oxide just above 600°. For the determination of lanthanum the oxalate is collected in a porous glass crucible and converted into basic carbonate by heating at 450° in an electric muffle for 30 min.

A. R. POWELL.

**Analytical weighing of alumina.** W. BILTZ (*Z. angew. Chem.*, 1930, 43, 370).—Attention is directed to the necessity of heating alumina at 1200° before weighing in order to convert it completely into the denser form, corundum, which has a smaller tendency to adsorb water and gases (cf. Biltz, Lemke, and Meisel, this vol., 399).

A. R. POWELL.

**Determination of alumina in aluminium and its alloys.** S. A. POGODIN.—See B., 1930, 717.

**Electrometric titration of aluminium and magnesium ions in presence of each other.** W. D. TREADWELL [with E. BERNASCONI] (*Helv. Chim. Acta*, 1930, 13, 500—509).—Two methods for the rapid determination of aluminium and magnesium in mixtures of their chlorides are described. In the titration with sodium hydroxide solution two well-marked changes in potential occur, viz., a steep rise

corresponding with complete precipitation of aluminium hydroxide, and a more gradual rise shortly before the point at which complete precipitation of magnesium hydroxide would be expected. At the end of the titration the concentration of magnesium hydroxide in the solution may be three times the saturation value. Better results are obtained by slowly titrating the solution of the mixed chlorides (saturated with carbon dioxide and sodium chloride) with sodium fluoride. In this method use is made of the different complexes formed by the aluminium and magnesium ions with the fluoride ion. Two sharp changes in potential correspond with the complete formation of  $\text{AlF}_6'''$  and  $\text{MgF}_3'$ , respectively; the first is very pronounced and but little affected by dilution or variation in the proportion of the two ions, whilst the second becomes flat and difficult to recognise if the solution is dilute. F. L. USHER.

**Use of ammonium compounds of mercury in quantitative analysis.** B. ŠOLAJA M. KRANJČEVIĆ, and M. KOCKAR (Arhiv Hemiju, 1930, 4, 136—139).—The methods of precipitation with "fusible precipitate" previously in use for separating aluminium, phosphate, manganese, iron, and calcium have been successfully applied to the separation of aluminium and phosphate from magnesium in slightly acid solutions of the sulphates. "Infusible precipitate" has been used for the quantitative separation of iron and nickel in the presence of chlorides.

C. W. GIBBY.

**Universal gravimetric method for the separation and determination of manganese.** J. MAJDEL (Z. anal. Chem., 1930, 81, 14—26).—Under the conditions prescribed by von Knorre for the precipitation of manganese with persulphate the precipitate contains appreciable quantities of manganese of iron, zinc, calcium, etc., and is therefore unsuitable for gravimetric work. By careful regulation of the acidity of the solution, however, a precipitate of pure manganic hydroxide may be obtained provided that chlorides and nitrates are absent. The sample, containing not more than 0.15 g. of manganese, is dissolved in hydrochloric or nitric acid and the solution evaporated to dryness, the residue is moistened with 1 : 1 sulphuric acid and heated until the latter evolves copious fumes, 20—30 c.c. of water are added, the mixture is heated until soluble salts dissolve, and the solution filtered and neutralised to a faint turbidity with ammonia. After addition of 25 c.c. of 3*N*-sulphuric acid, 20—25 c.c. of 20% ammonium persulphate solution and water to a volume of 250 c.c. are added, and the solution is boiled for 15 min. The precipitate is allowed to settle, collected, washed with hot water, ignited at 940—1100° to constant weight, cooled rapidly, and weighed as  $\text{Mn}_3\text{O}_4$ . Chromium and vanadium are oxidised to chromic and vanadic acids and do not interfere, but tin, bismuth, and antimony must first be removed by means of hydrogen sulphide and titanium by hydrolysis of the sulphate solution. If a large excess of iron is present, reprecipitation of the manganese is advisable.

A. R. POWELL.

**Iodometric determination of ferrous iron.** L. SZEBELLÉDY (Z. anal. Chem., 1930, 81, 26—36).—

For the determination of ferrous iron in a solution containing organic compounds not affected by iodine, e.g., sugars, lactic acid, or oxalic acid, the solution is placed in a double-necked flask, the side-neck of which is closed with a Bunsen valve, and 4 c.c. of hydrochloric acid ( $d$  1.19) are added, followed by 5 g. of potassium hydrogen carbonate, whereby the evolved carbon dioxide displaces the air in the flask. About 5 g. of ammonium fluoride or sodium pyrophosphate and 1 g. of oxalic acid are then dropped in through the side tube and the solution is titrated at 30—40° with 0.1*N*-iodine until a permanent citron-yellow colour is obtained. The theoretical iron factor of the iodine is multiplied by 1.012 to allow for dissolved oxygen.

A. R. POWELL.

**Determination of iron with potassium dichromate.** L. SZEBELLÉDY (Z. anal. Chem., 1930, 81, 97—103).—As internal indicators in this titration may be used diphenylamine and *p*-phenetidine with phosphoric acid or ammonium fluoride as complex-forming reagents for the ferric salt formed. The minimum acidity required for accurate results is 15 c.c. of 1 : 1 hydrochloric acid or 10 c.c. of 1 : 3 sulphuric acid to 50 c.c. of ferrous salt solution. Air should be removed from the solution by addition of 1—2 g. of potassium hydrogen carbonate just prior to titration.

A. R. POWELL.

**Separation of the iron-aluminium group.** T. L. YU (Science, China, 1930, 14, 810—820).—Of the precipitate obtained with ammonia and ammonium sulphide, nickel sulphide, cobalt sulphide, and aluminium hydroxide are insoluble in 4*N*-hydrochloric acid. Aluminium is detected with alizarin, cobalt with 1-nitro- $\beta$ -naphthol, and nickel with dimethylglyoxime.

CHEMICAL ABSTRACTS.

**Reduction of silver ferri cyanide by ferrous sulphate.** G. A. BARBIERI (Atti R. Accad. Lincei, 1930, [vi], 11, 685—688).—The reducing action of the ferrous ion on the ferri cyanide ion is shown in the reaction between silver ferri cyanide and ferrous sulphate in the presence of excess of silver sulphate:  $2\text{Ag}_3\text{Fe}(\text{CN})_6 + 2\text{FeSO}_4 + \text{Ag}_2\text{SO}_4 = 2\text{Ag}_4\text{Fe}(\text{CN})_6 + \text{Fe}_2(\text{SO}_4)_3$ . The reaction is quantitative, and its application to the determination of ferri cyanides is suggested. The method suggested is to add excess of standard ferrous sulphate solution to a mixture of a soluble ferrocyanide solution with a solution of silver nitrate and to determine, after filtration, the amount of unused ferrous sulphate in the filtrate by titration with potassium permanganate. Ferrocyanides, sulphocyanides, cyanides, and chlorides do not interfere.

F. G. TRYHORN.

**[Rapid determination of various elements after precipitation by the classical methods.]** L. MOSER and L. VON ZOMBORY (Z. anal. Chem., 1930, 81, 95—97).—A criticism of the work of Dick (A., 1929, 901). Washing with ether and drying in a vacuum for 10—15 min. is shown not to remove completely the adsorbed water from nickel dimethylglyoxime, barium sulphate, silver chloride, lead sulphate, or calcium oxalate.

A. R. POWELL.

**Titration with potassium dichromate.** L. ROSENTHALER (Pharm.-Ztg., 1930, 75, 808).—The

use of an external indicator may be avoided by addition of excess of dichromate solution, and iodometric determination of the excess. In titration of iron, the action of the ferric salt on the iodide used is prevented by addition of phosphoric acid.

S. I. LEVY.

**Determination and separation of titanium with 8-hydroxyquinoline.** R. BERG and M. TETTELBAUM (Z. anal. Chem., 1930, **81**, 1—8).—Titanium is quantitatively precipitated from feebly acid or ammoniacal tartrate solutions on addition of 8-hydroxyquinoline as the orange-yellow crystalline compound,  $\text{TiO}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ , which becomes anhydrous at  $110^\circ$ . The compound is converted by concentrated hydrochloric acid into purplish-red crystals of 8-hydroxyquinoline chlorotitanate,  $(\text{C}_9\text{H}_6\text{ON})_2\text{H}_2\text{TiCl}_6$ . For the determination of titanium the chloride solution (150 c.c.) is treated with 0.5—1 g. of tartaric acid, 0.5 g. of sodium acetate, ammonia to neutrality (phenolphthalein), and 1.5—3 c.c. of glacial acetic acid, heated at  $60^\circ$ , and stirred with an excess of a 3% alcoholic solution of 8-hydroxyquinoline. After boiling for 10 min. to cause the precipitate to become coarsely crystalline, the latter is collected in a porous glass crucible, washed with hot water, dried at  $110^\circ$ , and weighed; it contains 13.61% Ti. Alternatively, the precipitate may be dissolved in hydrochloric acid (*d* 1.19) and the hydroxyquinoline content determined by titration with 0.1N-bromide-bromate solution (1 c.c. = 0.000599 g. Ti). For the separation of titanium from aluminium precipitation is effected as above after addition of 70—80 times as much malonic acid as there is aluminium present. Addition of ammonia and more of the precipitant to the filtrate from the titanium precipitates the aluminium.

A. R. POWELL.

**Zirconium. VI. Use of dispersoids in detection of traces of potassium by zirconium sulphate.** R. D. REED and J. R. WITHROW (J. Amer. Chem. Soc., 1930, **52**, 2666—2668; cf. A., 1928, 858).—The addition of 1 drop of dispersoid of the desired product hastened the detection of potassium and increased the sensitivity from 0.5 to 0.3 mg. in 2 c.c. The reagent does not completely remove potassium from solution.

J. G. A. GRIFFITHS.

**Iodometric determination of quinquevalent antimony.** L. SZEPELLÉDY (Z. anal. Chem., 1930, **81**, 36—41).—The solution is treated with 20 c.c. of hydrochloric acid (*d* 1.18) in a stoppered flask and diluted to 100 c.c. To remove dissolved oxygen 2 g. of potassium hydrogen carbonate are added in small portions to the solution and the antimonious salt is reduced to antimonous by addition of 3 g. of potassium iodide. The flask is stoppered and shaken for 3 min., 3 g. of ammonium fluoride are added, and the solution is titrated with thiosulphate until the yellow colour disappears. A second trial is subjected to the whole process except that no fluoride is added until the same volume as was used in the first titration of thiosulphate has been run in; after 3 min. 3 g. of ammonium fluoride are dissolved in the solution and the titration is continued until the liquid is colourless, which usually requires a further 0.5—1 c.c.

A. R. POWELL.

**Titration of antimonious compounds by permanganate.** J. VOŘÍŠEK (Chem. Listy, 1930, **24**, 250—251).—The following method is described for the determination of antimony in bearing metal: 0.5 g. of alloy is dissolved in 25 c.c. of hot concentrated sulphuric acid, and 150 c.c. of water, 10 c.c. of 2% potassium hydrogen sulphate solution, and 10 c.c. of concentrated hydrochloric acid are added. The solution is boiled for 5 min. to remove sulphur dioxide, cooled, and 10 c.c. of 10% manganous sulphate (tetrahydrate) are added, after which the solution is titrated with 0.1N-potassium permanganate.

R. TRUSZKOWSKI.

**Rapid determination of bismuth and copper in lead bullion by internal electrolysis.** E. M. COLLIN.—See B., 1930, 773.

**Spot tests for the detection of the precious metals.** H. HOLZER (Mikrochem., 1930, **8**, 271—276).—For the detection of gold in a solution containing platinum a drop of the liquid is placed on a filter-paper and allowed to dry; on addition of a minute drop of acid stannous chloride solution to the middle of the spot it becomes yellowish-brown and a purple ring gradually forms round the outside if gold is present. Feigl's test for silver with *p*-dimethylaminobenzylidenerhodanine (A., 1928, 1108) is interfered with by gold, platinum, and palladium, which produce coloured flocculent precipitates with the reagent. The palladium precipitate is dark violet in colour and its formation serves as a specific test for palladium.

A. R. POWELL.

**Inorganic gravimetric micro-analysis. I. Determination of minute amounts of gold in the presence of much iron, lead, and copper.** J. DONAU (Mikrochem., 1930, **8**, 257—263).—To the boiling, slightly acid solution (0.2—0.3 c.c.) of the gold is added a small piece of Japanese silk previously washed in hydrochloric acid, then in water, and dried. The gold deposits rapidly on the silk, colouring it dark purple; a second piece of silk may be added to make sure that precipitation is complete. The silk is collected on a glass micro-filter, washed with hot water, dried in a small platinum foil dish, and ignited over a small flame. Further heating causes the gold residue to alloy with the platinum, which is then weighed on the micro-balance. Iron, copper, and lead do not interfere in the test.

A. R. POWELL.

**Determination of osmic acid; applications to cytological technique.** R. PALMER (J. Roy. Microscopical Soc., 1930, **50**, 221—226).—The concentration of osmium tetroxide in solutions used in cytology may be determined as follows: 0.05 c.c. is delivered from a capillary pipette into a test-tube, 8 c.c. of water, 1 c.c. of a 5% solution of thiocarbamide, and 1 c.c. of 1:5 hydrochloric acid are added. The mixture is heated to boiling and allowed to cool for a few minutes, and the red colour compared with that of a series of standard solutions previously prepared in a similar way from solutions containing known amounts of osmium. When well stoppered and preserved away from direct sunlight, the standards keep for a considerable time. Some applications

of the method to the standardisation of waste solutions and to the more accurate control of the process of osmication are indicated. A. R. POWELL.

**Apparatus for the demonstration of the Raman effect in liquids.** N. B. REYNOLDS and F. BENFORD (Rev. Sci. Instr., 1930, 1, 413—416).—A hot-cathode helium lamp (of cylindrical shape) is used in conjunction with a nickel oxide glass filter (cf. Wood, A., 1929, 741). The lamp is surrounded by a reflector of elliptical cross-section, the cross-section of the lamp being concentric with one of the foci of the ellipse. Concentric with the other focus is placed the tube containing the liquid to be examined. A hot-cathode mercury lamp has been similarly used. W. E. DOWNEY.

**Application of a new type of triode valve to the determination of hydrogen-ion concentration with glass electrodes.** G. B. HARRISON (J.C.S., 1930, 1528—1534).—By the use of a new type of valve, the characteristic curve of which is not altered by the insertion of a high resistance in the grid circuit, and a special glass from which glass electrodes can be made of resistance of the order of 100 megohms, a small, simple, robust unit was built up; it can be used for works routine measurements with an accuracy of 0.02  $p_H$  unit. Only one circuit needs good insulation, and the apparatus possesses all the advantages of the more usual high-resistance electrometer. J. O. CUTTER.

**Simple apparatus for electrometric titrations.** W. PLÜCKER and W. KEILHOLZ (Chem.-Ztg., 1930, 54, 451—452).—The apparatus comprises an elongated Allihn tube with two fine-pored glass filter plates, the larger plate closing the wider part of the tube from the narrower and the smaller plate closing the cap at the lower end of the tube against the solution to be titrated. The comparison platinum or silver electrode is placed in the wide part of the tube together with the buffer solution and quinhydrone; the second silver or platinum electrode is placed near the narrow end of the tube. The space between the two glass plates is filled with concentrated potassium chloride solution free from air bubbles. The whole is mounted on a stand carrying the leads to a sensitive galvanometer, and a switch for closing the circuit. The apparatus is suitable for the determination of free acid in fruit preserves, chlorine in milk, etc. A. R. POWELL.

**Apparatus for obtaining constant liquid flow.** W. S. GILFOIL (Ind. Eng. Chem. [Anal.], 1930, 2, 232).—An apparatus for obtaining a constant flow of liquid consists of three beakers and glass tubing; the liquid is kept moving by siphons and an air lift and is regulated by taps. E. S. HEDGES.

**Apparatus for purifying gases.** Z. VERESS (Magyar Chem. Fol., 1929, 35, 155—157; Chem. Zentr., 1930, i, 1501).—The current of gas drives the solvent into an absorption tower, whence it returns dropwise into the original container. A. A. ELDRIDGE.

**Carbon dioxide generator for combustion analysis in the determination of nitrogen.** E. J. POTH (Ind. Eng. Chem. [Anal.], 1930, 2, 250—251).—Two types of carbon dioxide generator suitable for

the determination of nitrogen in combustion micro-analysis are described. With their help it is possible to make a nitrogen determination on a 3—6 mg. sample in 20 min. with a mean error of less than 0.1%. E. S. HEDGES.

**Apparatus for the absorption of carbon dioxide in elementary analysis.** B. BOBRANSKI and E. SUCHARDA (Chem.-Ztg., 1930, 54, 412).—The apparatus comprises a vertical tube divided into two parts, the lower for soda-lime and the upper for calcium chloride. The two compartments are separated by a constriction into which fits a ground-glass stopper which operates simultaneously with the stopper closing the entrance tube at the top of the compartment. The bottom of the lower compartment is also closed by a ground-glass stopper which connects with the exit tube for the gases. In this way when the stopcocks are closed the soda-lime cannot take up moisture from the calcium chloride. A. R. POWELL.

**Modified micro-gas burette.** J. A. CHRISTIANSEN and J. R. HUFFMAN (Z. anal. Chem., 1930, 80, 435—438).—The apparatus comprises a capillary tube, 0.3 mm. internal diameter, graduated into 150 mm. and connected at the lower end with a U-tube having a lower extension carrying a steel screw in an ebonite cap and rendered gas-tight with a mercury seal. The upper end of the capillary is bent at right angles and terminates in a U-tube, the outer limb of which is 30 mm. long and serves for admitting the gas from a small tube inverted over a mercury trough. This tube acts both as the gas container and as the absorption pipette. The burette is enclosed in a water-jacket and is filled by movement of the steel screw. A. R. POWELL.

**Gas combustion pipette.** E. W. R. STEACIE (J. Amer. Chem. Soc., 1930, 52, 2811).—The platinum heating wire passes axially through the cylindrical oil-jacketed pipette, which may be used for widely different volumes of gas. J. G. A. GRIFFITHS.

**Absorption in gas-washing bottles.** A. SIEVERTS and S. HALBERSTADT (Chem. Fabr., 1930, 201—202).—The efficiencies of six types of gas-washing bottles have been compared by measuring the amount of oxygen absorbed by chromous chloride from a nitrogen-oxygen mixture containing 7% of oxygen. The results indicate that the most efficient absorption is effected in bottles into which the gas is admitted as very fine bubbles through porous filter plates; the larger is the diameter of the plate the greater is the rate of absorption. A. R. POWELL.

**Baro-burette. II. Application to gas evolution methods of analysis.** H. S. BOOTH and N. C. JONES (Ind. Eng. Chem. [Anal.], 1930, 2, 237—240; cf. this vol., 885).—The application of the baro-burette to analytical processes involving the measurement of evolved gases is described, and it is shown that the method is both rapid and accurate so long as attention is given to the unavoidable errors. These errors and the necessary corrections are indicated. A list of determinations for which the baro-burette is suitable is given. E. S. HEDGES.

**Measurement of turbidity.** C. D. INGERSOLL and R. E. DAVIS (Ind. Eng. Chem. [Anal.], 1930, 2,

248—249).—In an apparatus for the measurement of turbidity the intensity of the Tyndall cone is measured, the cone being formed at a theoretically zero depth in order to eliminate colour interference. A beam of monochromatic light is passed across the surface of the liquid and is observed through a vertical tube having an optically flat bottom. The tube contains non-turbid potassium dichromate solution, the height of which is adjusted until the Tyndall cone is eliminated from view. The height of the solution is taken as a measure of the turbidity. The apparatus is particularly suitable for the examination of liquors in the sugar-refining industry. E. S. HEDGES.

**Rapid method of qualitative colour comparison for opaque solids.** J. J. SHANK and J. S. MARTIN (Ind. Eng. Chem. [Anal.], 1930, 2, 343—344).—A simple comparator for use with opaque solids is described. E. S. HEDGES.

**Simple spectrum comparator.** D. JACK (Proc. Roy. Soc. Edin., 1930, 50, 200—203).—Two spectrum photographs are placed side by side and viewed through a travelling microscope with two objectives, which are connected optically with the eyepiece by means of two totally reflecting prisms.

C. W. GIBBY.

**Micro-colorimeter.** G. W. CHAPMAN (Analyst, 1930, 55, 443—444).—The apparatus (designed for the colorimetric determination of iron and manganese in the ash derived from the sap of fragments of plants) consists of two tubes, 10 cm. long and 0.25 cm. internal diameter, with cover glasses fixed to their lower ends, and with glass rods sliding in the tubes to vary the depth of the liquid. These rods have their lower ends smooth, and the upper ends ground to diffuse the light passing through; rubber collars exclude any light not passing through the rods. The tubes are enclosed in a case blackened on the inside and closed by a door extending to below the tubes, which are illuminated by electric lamps or daylight. A slit in the roof enables the ends of the glass rods to appear as luminous discs in a black field. A degree of accuracy may be obtained with the apparatus not much below that given by a larger colorimeter.

D. G. HEWER.

**Applications of the photo-electric cell to chemical analysis and control.** H. M. PARTRIDGE (Ind. Eng. Chem. [Anal.], 1930, 2, 207—213).—Existing types of photo-electric cells and the methods of measurement are discussed and a large number of applications to many branches of science and industry is given. E. S. HEDGES.

**Adiabatic calorimetry. III. Measurement of temperature changes of  $10^{-3}$  to  $7 \times 10^{-7}$  with an accuracy of  $\pm 5 \times 10^{-6}$  to  $\pm 2 \times 10^{-7}$ .** E. LANGE and J. MONHEIM (Z. physikal. Chem., 1930, 149, 51—88; cf. this vol., 1013).—The construction and operation of an adiabatic differential calorimeter suitable for the measurement of very small heat effects are described. Temperature differences are determined by means of a thermopile.

R. CUTHILL.

**Apparatus for the determination of ignition temperature of powder substances.** P. W. EDWARDS and R. W. HARRISON (Ind. Eng. Chem.

[Anal.], 1930, 2, 344—345).—The authors define the ignition temperature of a solid combustible as that temperature at which the exothermic reaction predominates to the extent that the reaction becomes rapidly accelerated and the ultimate appearance of glow or flame is assured without further addition of heat from external sources. An apparatus for determining this temperature is described and the results obtained for a number of dusts are recorded. Within the range 60—1000  $\mu$  diameter the size of the dust particles does not affect the ignition temperature.

E. S. HEDGES.

**Aluminium hot plate and Dutch oven.** H. V. CHURCHILL and R. W. BRIDGES (Ind. Eng. Chem. [Anal.], 1930, 2, 335—336).—An aluminium hot plate and an aluminium Dutch oven suitable for laboratory work are described and the advantages of using aluminium for such purposes are emphasised.

E. S. HEDGES.

**Phosphoric acid for determination of m. p.** F. D. SNELL (Ind. Eng. Chem. [Anal.], 1930, 2, 287).—The use of syrupy phosphoric acid in place of sulphuric acid for m.-p. determinations by the capillary tube method is advocated. When contaminated with organic matter the acid can be clarified with a crystal of potassium nitrate.

E. S. HEDGES.

**Apparatus for m.-p. determinations.** M. SPETER (Chem.-Ztg., 1930, 54, 564).—The apparatus consists of a glass tube in the shape of a parallelogram with two sides vertical, containing sulphuric acid or other suitable fluid. Near the upper end of the upper non-vertical side is fused in a suitable-sized vertical tube, into which the thermometer and m.-p. tubes are placed so that their lower ends are well in the circulating fluid, heat being applied at the diagonally opposite point. A separate tube of suitable length, closed at the upper end, serves as a cap to cover the thermometer etc.

C. A. SILBERRAD.

**Electrically heated m.-p. apparatus.** A. MONSCH (Helv. Chim. Acta, 1930, 13, 509—511).—A modification of the Berl-Kullmann "copper block" m.-p. apparatus (A., 1927, 437) is described. Electrical heating of the block permits easy regulation of the rise of temperature and does not cause clouding of the mica window.

F. L. USHER.

**Microscope hot stage.** I. AMDUR and E. V. HJORT (Ind. Eng. Chem. [Anal.], 1930, 2, 259—260).—A microscope hot stage having a range from the ordinary temperature to 600° is described. It enables accurate m.-p. data to be obtained in investigations where the yield is so small as to make capillary m.-p. determinations impossible.

E. S. HEDGES.

**Changes of temperature in volumetric analysis.** M. G. MELLON (Ind. Eng. Chem. [Anal.], 1930, 2, 260—263).—Convenient methods of correcting volume changes due to temperature variations during volumetric analysis are suggested.

E. S. HEDGES.

**Rapid evaporation.** E. JANTZEN and H. SCHMIDT-FUSS (Biochem. Z., 1930, 221, 328—330).—Many of the assumptions and calculations of Naumann (this vol., 314) are incorrect and some of his methods are either unsatisfactory or less efficient than those of other workers.

W. MCCARTNEY.



**Polarimetry of solutions having low rotations.**

**II. H. N. NAUMANN** (Biochem. Z., 1930, **221**, 425—436).—If certain conditions are observed, light from the electric arc between pure carbon electrodes is suitable for use with a half-shade apparatus in examining solutions having low optical rotations.

W. MCCARTNEY.

**Polarimetry of solutions having low rotations.**

**III. Sources of error.** **H. N. NAUMANN** (Biochem. Z., 1930, **222**, 407—415).—Sources of error and means whereby they may be avoided or minimised in the methods and apparatus recommended by the author are discussed. In favourable circumstances the error in readings need not exceed  $\pm 0.001^\circ$  and a substance of which the rotation in a 1-dm. tube containing 0.2 c.c. is  $0.1^\circ$  can be determined with an error of about 5%.

W. MCCARTNEY.

**Electrically controlled thermostat.** **J. A. CRANSTON** (J.C.S., 1930, 1458—1460).—Details are given of a thermostat of compact design and of economical current consumption.

F. G. TRYHORN.

**Modification of Ostwald's electric thermostat-regulator.** **E. BUTTERWORTH** and **D. A. DERRETT-SMITH** (J. Sci. Instr., 1930, **7**, 233).—Change in calibration due to allowing the instrument to cool is avoided by omitting the two side tubes of the standard form, sufficiently fine adjustment being obtainable by means of the screw in the terminal head. It is advisable to distil the toluene over mercury to insure complete removal of sulphur.

C. A. SILBERRAD.

**Continuous-reading aneroid manometer for moderately low pressures.** **E. A. STEWARDSON** (J. Sci. Instr., 1930, **7**, 217—221).—The instrument consists essentially of a glass tube, about 2.5 cm. in diameter, closed by a thin sheet of glass, mica, or other suitable material, perpendicular to the centre of which is fixed a short length of very light glass rod. This moves an optical lever. Full details of construction and use are given. The arrangement is sensitive to pressure differences of the order of  $10^{-4}$  mm. of mercury.

C. A. SILBERRAD.

**Disadvantages of the quartz lamp in fluorescence analysis.** **J. PLOTNIKOV** (Chem.-Ztg., 1930, **54**, 582).—The low light intensity, fragile nature, and monochromatic emission are mentioned; only those substances fluoresce under the lamp which can absorb radiation of wave-length 366  $\mu$ .

S. I. LEVY.

**Burning wet precipitates.** **P. SORS** (Chem.-Ztg., 1930, **54**, 582).—Precipitates may be burned on the paper without drying, in porcelain crucibles, if the paper is so placed in the crucible that the relatively dry upper part is supported by the rim of the crucible, without further contact.

S. I. LEVY.

**Jena glass filtering crucibles.** **E. CATTELAİN** (Ann. Falsif., 1930, **23**, 301—302).—The use of the crucibles in analysis is described.

B. W. TOWN.

**Stable crucibles for silicate fusions.** **W. KRINGS** and **H. SALMANG** (Z. angew. Chem., 1930, **43**, 364—366).—The behaviour of crucibles of alumina, spinel, and zirconia towards fused silicates and oxides of

iron, manganese, lead, and calcium has been investigated. None of the ordinary commercial brands withstood the action of the molten substance for more than 1—2 min., but after firing again at temperatures just below the m. p. they were much more resistant. The firing was performed in a Tammann furnace or in an Auer furnace fired with a compressed gas-air mixture, alumina and spinel crucibles being heated at  $1980^\circ$  and zirconia crucibles at  $2100^\circ$ . This treatment resulted in the closing of the pores so that penetration of the molten slag into the crucible walls was prevented and very little direct action of the slag on the walls took place. A slag of the composition  $2\text{FeO} \cdot \text{SiO}_2$  after 20 min. at  $1450$ — $1500^\circ$  could be poured from an alumina crucible, leaving the latter almost unwetted.

A. R. POWELL.

**Double-capillary method of surface tension measurement.** **S. T. BOWDEN** (J. Physical Chem., 1930, **34**, 1866—1868).—Apparatus for the measurement of the surface tension of reactive and of non-reactive liquids by the double-capillary method is described.

L. S. THEOBALD.

**Rapid concentration of solutions in tubes.** **H. ROSSENBECK** (Biochem. Z., 1930, **221**, 375—380).—Solutions in centrifuge or other tubes can be automatically concentrated without loss of solute to any required volume or evaporated to dryness in an apparatus in which they are maintained at temperatures just below their b. p. while a current of dried and heated air or other gas is directed upon their surfaces.

W. MCCARTNEY.

**Use of celluloid in the laboratory.** **A. KROGH** and **E. LANGE** (Biochem. Z., 1930, **221**, 489—491).—Celluloid, particularly in tube form, although not quite impermeable to gases, can easily be worked and is suitable for the construction of apparatus.

W. MCCARTNEY.

**Construction and use of Raschig's laboratory fractionating column.** **H. M. EVANS**, **R. E. CORNISH**, **S. LEPKOVSKY**, **R. C. ARCHIBALD**, and **G. FESKOV** (Ind. Eng. Chem. [Anal.], 1930, **2**, 339—343).—Fittings for the Raschig laboratory fractionating column, which simplify the construction and operation of a small, intermittent, laboratory fractionating still, are described. A laboratory vacuum fractionating still is described, as well as a simple still which recovers waste alcohol as 95 vol.-%, the latter with practically no attention by the operator. For columns operating above  $100^\circ$  the silvered vacuum jacket is inferior in insulating power to ordinary high-grade commercial steam-pipe covering, provided that the column diameter is 2 in. or more. Results of distillations are given, including an attempted separation of isotopes, and it is suggested that a mixture of carbon tetrachloride and benzene be used as a standard for testing fractionating apparatus.

E. S. HEDGES.

**Fractionating head.** **H. MAINZ** (Chem.-Ztg., 1930, **54**, 422).—The apparatus comprises a long wide tube with a side tube at the upper end for withdrawing the distillate, the whole being enclosed in a glass air-jacket which serves to prevent temperature vari-

ations. The head is particularly useful for fractionating the carbolic oil fraction from tar distillation.

A. R. POWELL.

**Distillation apparatus.** W. SWIENTOSLAWSKI (Rocz. Chem., 1930, 10, 472—479).—A number of forms of distillation apparatus are described; they differ from those ordinarily used in that a reflux condenser is fitted, the condensed liquid being directed through a 3-way tap either to the receiver or back to the distilling flask. R. TRUSZKOWSKI.

**Apparatus for the fractional distillation of small quantities of a substance.** E. BERT and F. W. ALTHOFF (Chem. Fabr., 1930, 220—224).—The apparatus comprises a column 40 cm. long and 0.7 cm. internal diameter filled with small glass rings and opening out at its upper end into a dephlegmator with about 30 cm.<sup>2</sup> of active surface. The column is surrounded by a heating jacket through which a current of hot paraffin oil passes. The oil is continuously circulated from a reservoir through a U-shaped copper heating tube, through the jacket surrounding the column, thence upwards through a vertical copper heating tube into the dephlegmator, from which it returns to the reservoir. The U-tube is 75 cm. long and the vertical tube about 50 cm., and both are wound with resistance wires 16 m. and 8 m. long, respectively (1.67 ohms per m.). A side tube at the top of the dephlegmator is provided with a thermometer and a tube leading through a condenser into a measuring burette. The liquid to be distilled is placed in a small flask below the column and is heated by means of an electric hot plate. By suitable arrangement of the current the temperature in the various parts of the apparatus may be regulated to  $\pm 0.25^\circ$ , and it may be used up to  $280^\circ$ . Examples of its use in fractionating mixtures of ether, acetone, ethyl and methyl alcohols, and water, and of benzene and its homologues are given.

A. R. POWELL.

**Laboratory extraction apparatus made of metal.** J. OBERBACH (Chem.-Ztg., 1930, 54, 462).—The apparatus comprises a copper cylinder in which a copper wire basket is suspended from wire supports engaging with small clips at the top of the cylinder. The latter is closed by a water-cooled condenser having a conical extension passing down into the basket which holds the usual paper extraction thimble. Fresh extraction liquid may be added to the vessel through an opening in the cooler from which a pipe

runs to the apex inside the thimble. Condensation of vapours is so perfect that no loss occurs between the cooler and the cylinder although there are no screw connexions between them. A. R. POWELL.

**Continuous automatic evaporation of large quantities of liquid in small vessels.** W. SELKE (Chem. Fabr., 1930, 202—203).—The liquid is placed in an inverted stock bottle the neck of which is closed with a rubber stopper carrying two tubes leading to an evaporating basin heated over a small flame. One tube passes from the top of the bottle just to the surface of the liquid in the dish and the other from just above the top of the stopper to well below the liquid surface in the dish. As the liquid evaporates, air enters the bottle through the first tube and more liquid passes into the dish through the second tube until the bottom of the first tube is covered.

A. R. POWELL.

**Inorganic lubricants. II. Phosphoric acid mixtures.** W. A. BOUGHTON (J. Amer. Chem. Soc., 1930, 52, 2813—2814).—The preparation of two almost non-hygroscopic lubricants of low water vapour pressure and little tendency to freeze is described. 100 C.c. of water containing 10 g. of metaphosphoric acid and 2 g. of boric acid are evaporated to 25 c.c., 1 c.c. of 85% orthophosphoric acid is added, and the liquid is boiled until the temperature reaches  $122^\circ$ . The other lubricant is obtained by boiling 10 g. of sodium metaphosphate and 2 g. of borax in 50 c.c. of water until the temperature reaches  $106^\circ$ .

J. G. A. GRIFFITHS.

**Vapour-pressure plotting paper.** D. S. DAVIS (Ind. Eng. Chem. [Anal.], 1930, 2, 306).—For vapour-pressure curves the use of a special form of paper is recommended. The ordinate scale is logarithmic and is intended for pressure, whilst the abscissa scale is non-uniform and constructed so that  $x = f(1/T)$ , but graduated directly in degrees C. E. S. HEDGES.

**Recommended specifications for analytical reagent chemicals.** G. P. BAXTER and others (Ind. Eng. Chem. [Anal.], 1930, 2, 351—354).—Specifications for reagents to be used in accurate analytical work are given for calcium carbonate, calcium carbonate low in alkalis, calcium chloride, cupric oxide (wire form), cuprous chloride, lead acetate, magnesium sulphate, sodium metal, and zinc sulphate.

E. S. HEDGES.

## Geochemistry.

**Effect of ozone on the temperature of the upper atmosphere. II.** E. H. GOWAN (Proc. Roy. Soc., 1930, A, 128, 531—550; cf. A., 1928, 1209).—The method previously described for calculating the radiative equilibrium temperature of the upper regions of the atmosphere, taking into account the variation of absorption with wave-length, has been modified by the introduction of some simplifications, and the diffuseness of radiation from terrestrial sources is taken into account. Preliminary estimates of the temperature variations in the upper stratosphere show

that even small changes, e.g., of  $10\text{--}30^\circ$ , would produce appreciable changes in the heights of the upper layers from day to night, and it is considered probable that mixing of the constituents is general far above 11 km. Independent evidence is cited in favour of circulation and mixing. The layers of the stratosphere will consequently radiate less, and since the absorption of ozone remains the same, their temperatures should be much higher. It is shown that a certain amount of convection is possible without much disturbance of the condition of strict radiative equilibrium.

and a table is given showing the approximate allowable velocities at various heights if the temperatures are to remain within  $1^\circ$  of their equilibrium values. The effects of various changes in the assumptions regarding the distribution of water vapour and ozone and the zenith angle of the sun are considered and illustrated by means of curves. The question of the maximum temperature attainable in the upper stratosphere is examined. From observational evidence and various calculations it is concluded that a probable distribution of ozone and water vapour can maintain a temperature of more than  $500^\circ$  Abs. from 60 km. upwards, and that the temperature gradient from 30 to 60 km. is approximately the reverse of its value from the ground to the tropopause. Sound, wave, and meteor phenomena can be satisfactorily explained by these high temperatures in the upper atmosphere.

L. L. BIRCUMSHAW.

**Colloid-chemical theory of origin of salt lakes.** S. A. SCHTSCHUKAREV and T. A. TOLMATSCHEVA (J. Russ. Phys. Chem. Soc., 1930, 62, 777—816).—Apart from purely chemical reactions two other factors also exert an influence on the nature of the water and of the deposits found in salt lakes. These factors are the biochemical reduction of sulphates, and adsorption of dissolved substances by suspended particles of soil. The disappearance of magnesium sulphate from solution leads chiefly to enhancement of the magnesium chloride content of the solution and the mud of such lakes. Increase in the calcium chloride content takes place partly as a result of the preferential adsorption on clay of magnesium and sodium ions. The above theory is illustrated by a study of certain Russian salt lakes.

R. TRUSZKOWSKI.

**Carbonates in the sediments of the Lake of Geneva.** J. ROMBEUX (Arch. Sci. Phys. Nat., 1930, 12, 202—216).—The sediments are classified as sand, coarse mud, fine homogeneous mud, fine stratified mud, whitish calcareous mud, and micaceous mud. Their distribution is described in detail.

C. W. GIBBY.

**Uranium in mineral waters.** Ratio to uranium. H. DE CARVALHO (Compt. rend., 1930, 191, 95—97).—The uranium content of water from Caria, Portugal, determined colorimetrically, is of the order of  $10^{-6}$  g. per litre. The ratio of radium to uranium is not constant.

C. W. GIBBY.

**Oil-field waters of Alberta and Saskatchewan.** W. P. CAMPBELL (Trans. Canad. Inst. Min. Met., 1929, 32, 316—332).—A discussion of the water problem in oil borings. A high chloride content generally indicates deep water; absence of chlorides and presence of sulphates and hydrogen carbonates indicate surface water.

C. W. GIBBY.

**Iron ores near Kerch, Crimea.** S. V. KONSTANTOV (Trans. I All-Russian Sci. Tech. Min. Cong. (1926), 1928, 6, 41—50).—A mixed sample contained Fe 32—38, FeO 7, SiO<sub>2</sub> 6—8, Al<sub>2</sub>O<sub>3</sub> 4—7, CaO 10—18, MgO 1.5, P 0.6—0.8%. Eltigen ore contains 3—5.4% Mn.

CHEMICAL ABSTRACTS.

**Formulae of risörite and fergusonite.** F. MACRATSKHI (Z. Krist., 1929, 72, 291—300; Chem.

Zentr., 1930, i, 1611).—Both minerals are referred to the formula  $XZ(O,OH)_4$ , where Z is chiefly Al, Ti, Nb, and Ta, and X is Ca, Yb- and Ce-earths, Fe, Th, and U. In the former more titanium, substituting niobium and tantalum, is present.

A. A. ELDRIDGE.

**Water content and degree of compactness of argillaceous rocks.** W. PETRASCHKE and B. WILSER (Berg. Hüttenm. Jahrb., 1926, 74, 57—65; Chem. Zentr., 1929, i, 1559).—The water content, other than that evolved at a red heat, diminishes with increasing metamorphosis.

A. A. ELDRIDGE.

**Basis for computing the age of a radioactive mineral from the lead content.** A. F. KOVARIK (Amer. J. Sci., 1930, [v], 20, 81—100).—The data necessary for the calculation of the age of minerals from radioactive studies are discussed. A formula is developed assuming that the radium and actinium are branch series from uranium-II, ending in isotopes of lead of the same at. wt. (206), and that ordinary lead is present in calculable quantity.

C. W. GIBBY.

**Quartz.** R. WEIL (Compt. rend., 1930, 191, 270—272).—Specimens of quartz from many localities have been examined for traces of mimetic or pseudo-paramorphic structure. Sections cut accurately perpendicular to the ternary axis were optically studied, and etched figures, and curved outlines due to corrosion compared. As a result two types have been recognised: "L" occurring at La Gardette, Binnenthal, and elsewhere, and generally corresponding with Haüy's "basoic" type; and "S" at the St. Gothard and generally in the Alps. An account of the optical examination of thin sections of "L" type, with the rectilinear areas up to 1 mm. wide, parallel to the prism faces, and showing slight double refraction thereby demonstrated, is given.

C. A. SILBERRAD.

**Antimonite of Media-Izlake in Slavonia.** L. MARIÓ (Arhiv Hemiju, 1930, 4, 142—145).—Analyses are given.

C. W. GIBBY.

**Recrystallisation of xenoliths at Cornucopia, Oregon.** G. E. GOODSPEED (Amer. J. Sci., 1930, [v], 20, 145—150).—A detailed description of Mesozoic intrusions into Triassic geosynclinal schists and greenstones is given. The influence of recrystallisation in assimilation at the boundary is discussed.

C. W. GIBBY.

**Valley of Ten Thousand Smokes.** I. Fumarolic incrustations and their bearing on ore deposition. II. Acid gases contributed to the sea during volcanic activity. E. G. ZIES (Carnegie Inst. Washington Geophys. Lab. Paper, 1929, No. 693, 79 pp.).—In the Katmai region fumarolic ferric and ferrosferic oxides were formed from iron transported as halide in the vapour phase. Ammonium chloride present in the gases assists the transportation of zinc chloride; other metals are similarly transported by the presence of halogen acids in the fumarolic gases. The formation of an ore body of economic value is not anticipated.

CHEMICAL ABSTRACTS.

**Cambrian "blue" clay.** P. A. ZEMYATCHENSKI (Trans. Ceram. Res. Inst., Moscow, 1929, No. 23, 32 pp.).—The Cambrian blue clay near Leningrad does

not contain hydrated aluminium silicates. The exceptional fusibility depends on the high dispersion and the mineralogical character of the particles.

#### CHEMICAL ABSTRACTS.

**Helium content of some Japanese minerals.** II. J. SASAKI (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 13, 244—245).—The apparatus previously described (A., 1927, 225) was used to determine the amount of helium in samples of naegite, ilmenite, sphene, rutile, apatite, tourmaline, axinite, and a conglomerate of samarskite and columbite. The conglomerate contained 4%  $U_3O_8$  and 0.036%  $ThO_2$  and the geological age of the specimen was found to be 100 million years. A table is given showing the amounts of helium in the specimens and the locality from which they were procured.

W. R. ANGUS.

**Salt and gypsum in Alberta.** J. A. ALLAN (Trans. Canad. Inst. Min. Met., 1929, 32, 232—254).—An account of the distribution of salt and gypsum in Alberta. They are mostly of Devonian or Silurian age. Interbedding of salt, anhydrite, and dolomite in the McMurray deposits shows that they have been deposited at the edge of sea of varying concentration. The anhydrite is of primary origin, but much of the gypsum, occurring as selenite, is secondary.

C. W. GIBBY.

**Origin of Copper Mountain (British Columbia) ores.** V. DOLMAGE (Trans. Canad. Inst. Min. Met., 1930, 32, 151—162).—An analysis is given of the ore, which consists of basaltic and andesitic breccia very little altered by mineralisation. Possible modes of origin of the ore are discussed: it was probably formed before the magma had solidified to any great extent.

C. W. GIBBY.

**British barytes.** (Miss) J. M. SWEET (Min. Mag., 1930, 22, 257—270).—A map of the north of England shows a central area of fluorite localities surrounded by a fringe of barytes localities, the latter following the outcrop of the Whin Sill. A map of central Derbyshire shows the fluorite localities fringing the barytes localities along the outcrop of the toadstones. Inclusions of foreign material show the variation in form of the barytes crystals during their stages of growth, and measurement of the width of the coloured zones gives the relative rates of growth on the different faces of the crystal. The lines and figures of growth on the various faces are also noted. Some honey-yellow crystals of barytes from Mowbray mine, Frizington, Cumberland, quickly change to green and afterwards to sky-blue on exposure to bright sunlight.

L. J. SPENCER.

**Mineralogical and chemical changes induced by progressive metamorphism in the Green Bed group of the Scottish Dalradian.** F. C. PHILLIPS (Min. Mag., 1930, 22, 239—256).—Analyses of the schists belonging to the "Green Bed" series of various grades of metamorphism show that, apart from the amount of silica, they are isochemical. In the chlorite zone, with the lowest grade of metamorphism, the typical rock is a chlorite-albite-epidote-schist. This passes into a biotite zone, then a garnet zone, and finally into a kyanite zone. In the last, the

highest grade of metamorphism, the ferromagnesian mineral is hornblende, and the felspar is oligoclase or andesine. Analyses are given of the green biotite and the garnet separated from these rocks.

L. J. SPENCER.

**Aluminium silicate from Allchar, S. Serbia.** F. TUCAN (Bull. Soc. Franç. Min., 1929, 52, 42—47; Chem. Zentr., 1930, i, 1114).—The product, having a composition corresponding with the formula  $Al_2O_3 \cdot 3SiO_2 \cdot 7H_2O$  has  $d^{22}_D$  1.9818; when heated it evolves water (completely at 650°) having an acid reaction. The dehydration curve (using calcium chloride, sulphuric acid, or phosphorus pentoxide) is continuous.

A. A. ELDRIDGE.

**Differentiation in the Dartmoor granite.** A. BRAMMALL (Nature, 1930, 126, 132).—Graded and significant variations in the chemical composition of granites from East Dartmoor are discussed.

L. S. THEOBALD.

**Hypersthenisation and its explanation.** D. GUIMARÃES (Ann. Acad. Brasil. Sci., 1930, 2, 1—11).—The formation of hypersthene from diopside by way of clino-enstatite is discussed from the crystallographic point of view, and a general theory is put forward to account for the chemical transformations which have occurred in silicate minerals. It is supposed that at high temperatures and pressures the small amount of water present acts as an electrolyte, and interaction of silicates, or of silicates and silica and the transformation of one mineral into another, is possible in directions controlled by the hydrogen concentration.

R. K. CALLOW.

**Mineralogical characters of oolitic iron minerals of djebel el Ank, S. Tunisia.** M. SOLIGNAC (Compt. rend., 1930, 191, 107—109).—The ferruginous substance is stilpnosiderite, a colloidal form of limonite. The phosphorous or arsenical minerals occur in pellicles round the oolites. Analyses are given.

C. W. GIBBY.

**Origin of coal and oil.** E. TERRES and W. STECK.—See B., 1930, 747.

**Oxidation of meteorites; formation of "meteorodes."** H. H. NININGER (Trans. Kansas Acad. Sci., 1929, 32, 63—67).

#### CHEMICAL ABSTRACTS.

**New meteoric iron from Piedade do Bagre, Minas Geraes, Brazil.** L. J. SPENCER [with H. H. HEX] (Min. Mag., 1930, 22, 271—282).—This mass, found in 1922 and weighing 59 kg., is of special interest in showing on one corner a well-marked octahedral fracture, and on a polished and etched section taken from this portion of the mass a complex system of very distinct Neumann lines. Neumann lines are twin-lamellæ produced by gliding on planes of the icositetrahedron (211); it is believed that these, as well as the octahedral fracture, were developed by the shock of impact when the meteorite fell with its corner on hard rock. Analysis of the iron gave: Fe 92.03, Ni 7.48, Co 0.39, Cu 0.0097, S 0.22, P trace,  $SiO_2$  0.01, Pt trace, total 100.14;  $d^{25}_D$  7.69. The Fe:Ni ratio, 12.3, agrees with the grouping as a medium octahedrite.

L. J. SPENCER.

**Composition and structure of meteorites.** G. P. MERRILL (Bull. U.S. Nat. Museum, 1930, No. 149, 62 pp.).—The minerals peculiar to meteorites, and those common to meteorites and the earth, are

listed, the former being also described. The elements occurring in meteorites are also mentioned, and a type classification of meteorites is given.

CHEMICAL ABSTRACTS.

## Organic Chemistry.

**Walden inversion.** J. KENYON and H. PHILLIPS (Trans. Faraday Soc., 1930, 26, 451—458).—The conclusions reached by a survey of development in this subject during the last decade are that if, during a displacement reaction, the asymmetric radical separates as a positively-charged ion, the optical activity of the product results from the occurrence of a Walden inversion, and that if the optically active radical separates as a negatively-charged ion, an optically active product results without the occurrence of an inversion.

F. G. TRYHORN.

**Synthesis of methane from carbon monoxide and water vapour.** P. PASCAL and E. ROTOLFSEN (Compt. rend., 1930, 191, 186—187).—When passed over a nickel catalyst, carbon monoxide and an excess of water vapour yield methane ( $4\text{CO} + 2\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + \text{CH}_4$ ) in appreciable amount at  $250^\circ$  and quantitatively at  $275^\circ$ . At higher temperature this reaction is gradually replaced by the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , which occurs appreciably at  $300^\circ$  and completely suppresses the production of methane below  $750^\circ$ .

H. WREN.

**Formation of peroxides during direct oxidation of hydrocarbons by air.** II. P. MONDAIN-MONVAL and B. QUANQUIN (Compt. rend., 1930, 191, 299—301).—Oxidation of hydrocarbons (pentane, hexane, octane, petrol) by air at  $300^\circ$  or, preferably, at a somewhat lower temperature gives, in addition to gaseous products, an oily liquid with marked oxidising properties which evolves hydrogen and gives sodium formate and methyl alcohol when treated with sodium hydroxide. When heated at about  $200^\circ$  it suffers exothermic change with production of a blue luminescence and white fumes, and formation of notable amount of aldehydes, particularly formaldehyde. The oil appears therefore to be a mixture of peroxides, containing methyl and ethyl hydrogen peroxide.

H. WREN.

**Vegetable dyes.** XXI. **Conversion of crocetin into crocetane.** P. KARRER and T. GOLDE. XXII. **Esters of xanthophyll.** P. KARRER and S. ISHIZAWA (Helv. Chim. Acta, 1930, 13, 707—709, 709—713).—XXI. Tetradecahydro- $\gamma$ -crocetin is reduced by sodium and alcohol to  $80\mu$ -trimethylhexadecane- $\alpha$ -diol, b. p.  $180$ — $181^\circ/0.1$  mm., which with hydrogen bromide in acetic acid at  $150^\circ$  yields the corresponding dibromide, reduced in the crude state by zinc-copper couple in 60% acetic acid. The product,  $80\mu$ -trimethylhexadecane (crocetane), b. p.  $135^\circ/0.5$  mm.,  $d_4^{25} 0.8027$ ,  $n_D^{25} 1.44937$ , is purified by successive treatment with concentrated sulphuric acid, water, and concentrated alkali, and is then quite colourless.

XXII. The esters of xanthophyll, unlike xanthophyll itself, are extracted from their methyl-alcoholic

solution by light petroleum. Consequently, Willstätter and Stoll's method ("Untersuchungen über die Assimilation der Kohlensäure," 1918, p. 19 *et seq.*) for the determination of carotene, depending on the separation of xanthophyll from carotene by mixtures of alcohol and light petroleum, can give accurate results only in the absence of esters of xanthophyll, or after the hydrolysis of these. Comparison of the absorption spectra of xanthophyll with those of its dibenzoate and of lutein distearate shows that in the last two the bands are shifted very slightly towards the red end of the spectrum. Perhydroxanthophyll gives an oily diacetate by the action of acetic anhydride and sodium acetate, and both perhydroxanthophyll and perhydrozeaxanthin are shown by Zerevitinov's method to contain two hydroxyl groups. Xanthophyll dibenzoate, m. p. about  $165^\circ$ , di-*p*-nitrobenzoate, m. p.  $210^\circ$ , and distearate, m. p.  $87^\circ$ , and lutein distearate, m. p.  $85^\circ$ , are readily prepared by the action of the acid chloride in pyridine; xanthophyll diacetate, m. p.  $170^\circ$ , is similarly obtained using acetic anhydride. The sparing solubility of its di-*p*-nitrobenzoate in organic solvents is of use for the characterisation of xanthophyll.

H. A. PIGGOTT.

**Comparison of McIlhiney's and Rosenmund's methods for determining unsaturated linkings in olefinic hydrocarbons.** P. AGOSTINI and R. ABBATE (Annali Chim. Appl., 1930, 20, 232—234; cf. B., 1929, 768).—*n*-Decylene and *n*-dodecylene give no hydrogen bromide when tested by McIlhiney's method, the total bromine used by this method and by Rosenmund's method approaching the theoretical additive quantity. McIlhiney's procedure gives hydrogen bromide when applied to triisobutylene and diamylene, with which Rosenmund's method gives bromine values exceeding the theoretical values. Hence, both methods yield substitution products in these cases, although with the McIlhiney method the amount of bromine added does not reach the theoretical value even after 48 hrs.

T. H. POPE.

**Transformation of ethylene into liquid and solid hydrocarbons.** A. MAILHE and RENAUDIE (Compt. rend., 1930, 191, 265—267).—When ethylene is passed over silica gel at about  $700^\circ$  under ordinary pressure, a mixture of unchanged ethylene, methane and its homologues, liquid paraffinic, ethylenic, and aromatic hydrocarbons, and heavy oil is produced. The heavy oil contains naphthalene and probably anthracene. Carbon is deposited on the catalyst.

H. BURTON.

**Replacement of positive hydrogen by halogen.** I. F. STRAUS, L. KOLLEK, and W. HEYN (Ber., 1930, 63, [B], 1868—1885).—The replacement of positive hydrogen (hydrogen replaceable by metals) is readily effected by halogen in the presence of an excess of

alkali hydroxide. Hypiodite, hypobromite, and hypochlorite react in order of decreasing rapidity. The action of acetylene on potassium hypochlorite solution containing an excess of potassium hydroxide in an atmosphere of nitrogen gives *dichloroacetylene*, m. p.  $-66^{\circ}$  to  $-64.2^{\circ}$ , b. p.  $32-33^{\circ}/748$  mm., which explodes violently when moderately heated or brought into contact with air, is stable towards light, and is converted by chlorine in carbon tetrachloride into hexachloroethane, m. p.  $187^{\circ}$ , and by bromine water into  $\alpha\beta$ -dichloro- $\alpha\beta\beta$ -tetrabromoethane, m. p.  $209-210^{\circ}$  after darkening at  $200^{\circ}$ . *Dibromoacetylene*, m. p.  $-25^{\circ}$  to  $-23^{\circ}$ , prepared similarly, is converted by cautious treatment with bromine or iodine into tetrabromoethylene, m. p.  $55-57^{\circ}$ , and  $\alpha\beta$ -dibromo- $\alpha\beta$ -di-iodoethylene, m. p.  $83^{\circ}$ . Potassium propiolate and hypochlorite give *chloropropiolic acid*,  $\text{CCl:C}\cdot\text{CO}_2\text{H}$ , m. p.  $69-70^{\circ}$ , completely stable when isolated but rapidly passing in alkaline solution into malonic acid. It is transformed by boiling, aqueous barium hydroxide into chloroacetylene and barium malonate. With concentrated hydrochloric acid it yields  $\beta\beta$ -dichloroacrylic acid, m. p.  $76-77^{\circ}$ . *Bromopropiolic acid*, m. p.  $84-86^{\circ}$ , is converted by bromine into  $\alpha\beta\beta$ -tribromoacrylic acid, m. p.  $116-118^{\circ}$ . Phenylacetylene is transformed by potassium hypobromite solution containing a little potassium stearate into  $\alpha$ -bromo- $\beta$ -phenylacetylene, b. p.  $88-89^{\circ}/13$  mm., converted into the corresponding di-iodide, m. p.  $63-64^{\circ}$ , and by concentrated sulphuric acid into  $\omega$ -bromoacetophenone.  $\alpha$ -Bromo- $\Delta^a$ -heptinene, b. p.  $57-57.5^{\circ}/13$  mm.,  $164-165^{\circ}/748$  mm., is described. The following substances are prepared by shaking the requisite alcohol with an excess of hypobromite:  $\alpha$ -bromo- $\gamma$ -methyl- $\Delta^a$ -butinen- $\gamma$ -ol, b. p.  $68^{\circ}/15$  mm.,  $d_{25}^{25} 1.4505$ ;  $\alpha$ -bromo- $\gamma$ -methyl- $\Delta^a$ -pentinen- $\gamma$ -ol, b. p.  $76.5^{\circ}/14.5$  mm.,  $d_{25}^{25} 1.3783$ ;  $\alpha$ -bromo- $\gamma$ -ethyl- $\Delta^a$ -pentinen- $\gamma$ -ol, b. p.  $87^{\circ}/14.5$  mm., m. p.  $16-17.5^{\circ}$  (*p*-nitrobenzoate, m. p.  $75.5-76^{\circ}$ ; *p*-nitrobenzoate of bromine-free alcohol, m. p.  $54-57.5^{\circ}$ );  $\alpha$ -bromo- $\gamma\delta\delta$ -trimethyl- $\Delta^a$ -pentinen- $\gamma$ -ol, b. p.  $89^{\circ}/14.5$  mm., m. p.  $38-39^{\circ}$  (*semihydrate*, m. p.  $52-52.5^{\circ}$ ). 1- $\beta$ -Bromoethynylcyclohexanol, m. p.  $55.5-56.5^{\circ}$ , b. p.  $89-90^{\circ}/0.3-0.4$  mm., is prepared under widely varied conditions of concentration of alkali. With *p*-nitrobenzoyl chloride in chloroform and pyridine it affords the corresponding *p*-nitrobenzoate, m. p.  $90.5-91^{\circ}$ , reduced by titanium trichloride to the *p*-aminobenzoate, m. p.  $127-127.5^{\circ}$  (decomp.). [The *p*-nitrobenzoate and *p*-aminobenzoate of 1-ethynylcyclohexanol have m. p.  $66-66.5^{\circ}$  (corr.) and  $97-98.5^{\circ}$  (corr.), respectively.] 1- $\beta$ -Chloroethynylcyclohexanol, m. p.  $51.5-52^{\circ}$ , b. p.  $98^{\circ}/13$  mm., is described. *cyclo-Pentadiene*, diluted with light petroleum, is converted by hypobromite into the corresponding *hexabromocyclopentadiene*, m. p.  $86-87^{\circ}$ , b. p.  $147^{\circ}/0.25$  mm.; the corresponding *hexachloro*-compound, b. p.  $78-79^{\circ}/1$  mm., is described. 1:1:3-*Tribromoindene*, m. p.  $104.5-105^{\circ}$ , and 1:1:3-*trichloroindene*, m. p.  $76^{\circ}$ , b. p.  $134^{\circ}/18$  mm., have been prepared. H. WREN.

#### Replacement of positive hydrogen by halogen.

II. *Dihalogenodiacetylenes*. F. STRAUS, L. KOLLEK, and H. HAUPTMANN (Ber., 1930, 63, [B], 1886—

1899).—Diacetylene, preserved over mercury, is almost completely polymerised after 4 months, leaving a small amount of residual gas consisting of homogeneous diacetylene. When preserved in sealed tubes at  $0^{\circ}$  in the absence of light, the substance becomes transformed into a dark brown polymeride which explodes violently on contact with a hot wire. *Dichlorodiacetylene*, m. p.  $2-3^{\circ}$ , is prepared by the action of alkaline hypochlorite at  $0^{\circ}$  on diacetylene in an atmosphere of nitrogen in the absence of light; it is characterised by conversion into a mixture of *cis*- and *trans*- $\alpha\delta$ -dichloro- $\alpha\beta\gamma\delta$ -tetraiodo- $\Delta^{\gamma\gamma}$ -butadiene, from which a homogeneous substance, m. p.  $155-157^{\circ}$ , is isolated. *Dibromodiacetylene*, m. p.  $49-50^{\circ}$ , exploding at  $67^{\circ}$ , forms characteristic clouds when exposed to air and may ultimately explode. When this does not occur, the residue consists of a small amount of a dark brown polymeride and the gaseous product contains hydrolysable bromine and ozone. It is transformed by an excess of bromine in chloroform into  $\alpha\alpha\beta\gamma\delta\delta$ -hexabromo- $\Delta^{\gamma\gamma}$ -butadiene, m. p.  $52-54^{\circ}$ , and by an excess of iodine in ether into the two forms of  $\alpha\delta$ -dibromo- $\alpha\beta\gamma\delta$ -tetraiodo- $\Delta^{\gamma\gamma}$ -butadiene, m. p.  $160-162^{\circ}$  and  $128-130^{\circ}$ , respectively. Diiododiacetylene, m. p.  $101-102^{\circ}$ , exploding at  $102^{\circ}$ , is converted into  $\alpha\beta\gamma\delta$ -tetrabromo- $\alpha\delta$ -di-iodo- $\Delta^{\gamma\gamma}$ -butadiene, m. p.  $57-60^{\circ}$ . Diiododiacetylene, when preserved, gradually becomes black and metallic. At this stage the product has lost iodine and gained oxygen in very small amount and is highly explosive. When further preserved, the explosive property is gradually lost without change in the appearance or iodine content. The polymerisation of dibromo- and dichloro-diacetylene appears to follow a similar course. The changes suffered by diiododiacetylene when heated in benzene, ether, or glacial acetic acid are described.

Magnesium diacetylene dibromide, prepared from diacetylene and magnesium ethyl bromide in ether, is converted by carbon dioxide into diacetylenedicarboxylic acid in small yield and by acetaldehyde into  $\Delta^{\gamma\gamma}$ -octadi-*inene*- $\beta\eta$ -diol, m. p.  $108-109^{\circ}$ , by acetone into  $\beta\eta$ -dimethyl- $\Delta^{\gamma\gamma}$ -octadi-*inene*- $\beta\eta$ -diol, m. p.  $129-130^{\circ}$ , and by acetophenone into  $\beta\eta$ -diphenyl- $\Delta^{\gamma\gamma}$ -octadi-*inene*- $\beta\eta$ -diol (two forms, m. p.  $195^{\circ}$  and m. p.  $142-143^{\circ}$ , respectively).

$\alpha\beta\gamma\delta\delta$ -Hexabromo- $\Delta^a$ -butene is debrominated to vinylacetylene by zinc and alcohol, magnesium in ether, or zinc coated with copper in acetone; previous failures to recognise the course of the reaction are due to the unusual retention of the gas by the solvent.

H. WREN.

**Law of periodicity.** P. PETRENKO-KRITSCHENKO (Ber., 1930, 63, [B], 1900—1902).—See this vol., 449.

H. WREN.

**Partial abnormal reaction of  $\beta$ -substituted allyl bromides with magnesium organobromides.** C. PRÉVOST and J. DAUJAT (Bull. Soc. chim., 1930, [iv], 47, 588—594).—With Grignard reagents  $\beta$ -substituted allyl bromides give a mixture of two isomeric olefines, which usually differ by about  $10^{\circ}$  in b. p. and can be separated with a good Crismar column. The method affords a more convenient method of obtaining branched olefines from  $\alpha$ -olefinic aldehydes such as crotonaldehyde and cinnamaldehyde.



hyde. Thus with a slight excess of magnesium ethyl bromide  $\alpha$ -bromo- $\Delta^2$ -pentene, prepared from the corresponding vinylcarbinol, yields  $\gamma$ -ethyl- $\Delta^2$ -pentene, b. p.  $85^\circ$ ,  $d^{20}_4$  0.6948,  $n^{20}_D$  1.3966 (*dibromide*, b. p.  $93.5^\circ$ /15 mm.,  $d^{20}_4$  1.5251,  $n^{20}_D$  1.5006, converted by alcoholic potassium hydroxide into  $\gamma$ -ethyl- $\Delta^2$ -propinene, b. p.  $87^\circ$ ,  $d^{20}_4$  0.7272,  $n^{20}_D$  1.4023, which does not yield the characteristic acetylene precipitates in the usual way, but with silver nitrate gives a silver derivative,  $C_5H_{10}Ag$ ); the yield of the branched olefine is about three to four times that of the linear hydrocarbon. Similarly, magnesium phenyl bromide yields  $\gamma$ -phenyl- $\Delta^2$ -pentene, b. p.  $71^\circ$ /12 mm.,  $191.5^\circ$ /760 mm.,  $d^{20}_4$  0.8818,  $n^{20}_D$  1.5030, and about two to three times as much  $\alpha$ -phenyl- $\Delta^2$ -pentene, b. p.  $82^\circ$ /12 mm.,  $205^\circ$ /760 mm.,  $d^{20}_4$  0.8843,  $n^{20}_D$  1.5060, and cinnamyl bromide and magnesium ethyl bromide yield  $\gamma$ -phenyl- $\Delta^2$ -pentene, b. p.  $65.5^\circ$ /9 mm.,  $d^{17}_4$  0.8848,  $n^{17}_D$  1.5070, and about twice as much  $\alpha$ -phenyl- $\Delta^2$ -pentene, b. p.  $87.5^\circ$ /9 mm.,  $217^\circ$ /760 mm.,  $d^{17}_4$  0.8924,  $n^{17}_D$  1.5318 (*dibromide*, m. p.  $62-62.5^\circ$ ), together with some *di*-cinnamyl, m. p.  $81^\circ$ . R. BRIGHTMAN.

**4'-Iododiphenyl-4-carbimide as a reagent for alcohols.** I. Corresponding urethanes from fatty unsaturated alcohols. S. KAWAI. II. Corresponding urethanes derived from  $C_1$  to  $C_{18}$  normal, saturated primary alcohols. S. KAWAI and K. TAMURA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 13, 260-269, 270-275).—I.  $\beta$ -Anthraquinonyl-carbimide (I) and *p*-diphenylaminophenylcarbimide (II) are not suitable as general reagents for alcohols, owing to the small solubilities of the derivatives in the common organic solvents and the relatively low m. p. of the derivatives of the latter. Compound I, m. p.  $163-165.5^\circ$ , is best prepared by heating  $\beta$ -aminoanthraquinone with carbonyl chloride in toluene at  $92-102^\circ$  for 4 hrs. The following anthraquinonylurethanes are described: *allyl*, m. p.  $255-256^\circ$  (decomp.); *cetyl*, m. p.  $203-204^\circ$ ; *ethyl*, decomp.  $271-272^\circ$ ; *methyl*, decomp.  $284-285^\circ$ ; *n-octadecyl*, m. p.  $202.5-203.5^\circ$ ; and *geranyl*, m. p.  $173^\circ$ . Compound II is prepared by the reduction of mono-*p*-nitrotriphenylamine (from *p*-iodonitrobenzene, diphenylamine, anhydrous potassium carbonate, copper powder, and a little xylene at  $210-220^\circ$ ) with zinc and acetic acid, followed by treatment with carbonyl chloride in toluene solution at  $85^\circ$ . The following (*N*-diphenylamino)phenyl urethanes are described: *ethyl*, m. p.  $134-135^\circ$ ; *cetyl*, m. p.  $95.5-96.5^\circ$ ; and *oleyl*, m. p.  $78-78.5^\circ$ .

The best reagent is 4'-iododiphenyl-4-carbimide, which is prepared as follows: 4-amino-4'-iododiphenyl, m. p.  $166-167^\circ$ , converted into the *benzylidene* derivative, m. p.  $207.5-209^\circ$  (with benzaldehyde in alcoholic solution), then into 4'-iodo-4-aminodiphenyl hydrochloride, m. p.  $295^\circ$  (decomp.), with alcoholic hydrochloric acid, and finally into 4'-iododiphenyl-4-carbimide, m. p.  $100-101^\circ$ , with carbonyl chloride in toluene. The following 4'-iododiphenyl urethanes are described: *ethyl*, m. p.  $200-200.5^\circ$ , and *cetyl*, m. p.  $138-138.5^\circ$ .

II. The following 4'-iododiphenyl urethanes are prepared by heating 4'-iododiphenyl-4-carbimide and the equivalent amount of alcohol in benzene solution

for 1 hr.: *methyl*, m. p.  $191.1^\circ$ ; *propyl*, m. p.  $188.7^\circ$ ; *amyl*, m. p.  $165.3-165.5^\circ$ ; *hexyl*, m. p.  $156.1-156.3^\circ$ ; *heptyl*, m. p.  $150.1-150.9^\circ$ ; *octyl*, m. p.  $148.2-149.2^\circ$ ; *nonyl*, m. p.  $148.4-149.2^\circ$ ; *decyl*, m. p.  $147^\circ$ ; *undecyl*, m. p.  $146.3-146.5^\circ$ ; *dodecyl*, m. p.  $145.7^\circ$ ; *tridecyl*, m. p.  $144.0-144.5^\circ$ ; *tetradecyl*, m. p.  $142.2-143^\circ$ ; *pentadecyl*, m. p.  $141.3-141.5^\circ$ ; *heptadecyl*, m. p.  $138.5^\circ$ ; and *octadecyl*, m. p.  $137.2-137.5^\circ$ .

A. I. VOGEL.

**Micro-determination of hydroxyl groups.** P. M. MARRIAN and G. F. MARRIAN (Biochem. J., 1930, 24, 746-752).—A micro-method for determining the percentage of hydroxyl in the higher fatty alcohols based on the volumetric determination of the methane evolved when an alcohol reacts with Grignard's reagent is described. Results accurate to  $\pm 8\%$  are obtained when the alcohol is readily soluble in the ether of the Grignard reagent. The use of pyridine as a solvent of alcohols leads to untrustworthy results. S. S. ZILVA.

**Semi-specific determination of small quantities of saturated alcohols.** W. PONNDORF (Z. anal. Chem., 1930, 80, 401-430).—A mixture of 40 c.c. of carbon tetrachloride, 20 c.c. of the alcohol solution, 2.75 c.c. of a solution of 30 g. of sodium nitrite in 70 c.c. of water, and 5 c.c. of a 7.5% solution of hydrogen chloride is shaken for 30 sec., the carbon tetrachloride is run off into 40 c.c. of a solution containing 50 g. of sodium hydrogen carbonate and 4 g. of sodium nitrite per litre, and the mixture shaken for 15 sec. and allowed to settle for 3 min. The heavy layer is then transferred to a stoppered flask. The liquid from the first extraction is again extracted with 30 c.c., then with 25 c.c. of the tetrachloride, and treated as before. The combined extracts are treated with a 20% solution of manganese sulphate in *N*-sulphuric acid and with a measured amount of 0.1*N*-permanganate to give at least 5 c.c. in excess of that required to oxidise the nitrite, and the mixture is well shaken for 10 min. The excess of permanganate is then determined iodometrically after addition of 4 g. of potassium iodide, no starch being necessary. With slight modifications the method is also available for microchemical analysis; it is more rapid than that of Fischer and Schmidt (A., 1924, ii, 427) and requires no special apparatus. Aldehydes, ketones, carboxylic, amino-, and hydroxy-acids, esters, and sugars do not interfere, but substances with ethylenic side-chains, amines, and phenols must be absent.

A. R. POWELL.

**Catalytic dehydrogenation of isopropyl alcohol.** W. A. LOTT and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1930, 19, 570-571).—*iso*Propyl alcohol is almost quantitatively converted into acetone in presence of broken crucible graphite at  $400^\circ$ . The results of Trautz and Winkler (A., 1922, i, 909), who obtained only propylene under similar conditions, are probably explained by differences in the physical structure of the catalyst. H. E. F. NOTTON.

**Preparation of allyl alcohol by means of formic esters of glycerol.** R. DELABY and P. A. DUBOIS (Bull. Soc. chim., 1930, [iv], 47, 565-588).—Esterification of glycerol with 87.6% formic acid at  $100^\circ$

gives in 2 hrs. an equilibrium mixture from which a *monoformin*, b. p. 154—157°/10 mm.,  $d_4^{25}$  1.293,  $n_D^{25}$  1.4614, and a *diformin*, b. p. 148—149°/15 mm.,  $d_4^{25}$  1.321,  $n_D^{25}$  1.4491, have been obtained. The same equilibrium is obtained in 24 hrs. at the ordinary temperature. The action of sodium formate at 150—160° on glycerol  $\alpha$ -monochlorohydrin, b. p. 118—119.5°/17 mm. (obtained from  $\alpha\gamma$ -dichlorohydrin through epichlorohydrin in 74% yield), yields a product containing 87% of monoformin and 13% of glycerol.  $\alpha\gamma$ -Dichlorohydrin similarly yields a diformin, b. p. 144—146°/11—12 mm.,  $d_4^{25}$  1.322,  $d_4^{25}$  1.305,  $n_D^{25}$  1.4486; the presence of solvents does not improve the yield.  $\alpha\beta$ -Dibromohydrin, b. p. 103—104°/12 mm., obtained in 85% yield by brominating allyl alcohol in carbon disulphide below -5°, with sodium formate at 154—160° yields a similar diformin, b. p. 151—153°/17 mm.,  $d_4^{25}$  1.321,  $n_D^{25}$  1.4503.

When heated in an evacuated sealed tube the monoformin obtained by esterification yields mainly allyl alcohol with some allyl formate, carbon monoxide and dioxide. The decomposition temperature, 286°, giving a maximum yield (57%) of allyl alcohol corresponds with the minimum formation of carbon monoxide. Although in the case of the monoformin obtained from  $\alpha$ -chlorohydrin the maximum formation of allyl alcohol also occurs at the temperature (301°) giving a minimum formation of carbon monoxide, the pyrolysis results indicate that the two products are essentially different. Decomposition commences at 150° in a vacuum and at 200° under atmospheric pressure with scission into carbon monoxide and glycerol. Only 4% of the theoretical yield of allyl alcohol is obtained, a violent evolution of gas occurring at 220°. This result is partly due to the presence of glycerol in the formin, since a mixture of 84% of the monoformin obtained by esterification and 16% of glycerol yielded only 22% of allyl alcohol, although the decomposition was less violent. Pyrolysis of the diformin at 202—248° gives a little allyl alcohol, but about four times as much allyl formate, the main reaction thus being  $C_3H_5(OH)(CHO)_2 \rightarrow CO_2 + H_2O + CH_2:CH:CH_2 \cdot O \cdot CO \cdot H$ . Some free formic acid and glycerol result from hydrolysis of the formate by the water formed. Quantitative investigation of the gases produced by pyrolysis in a vacuum and under atmospheric pressure indicate that the diformin obtained by esterification is intermediate in composition between the diformins obtained from  $\alpha\gamma$ -dichlorohydrin and  $\alpha\beta$ -dibromohydrin.

The following process gives a yield of 70—75% of allyl alcohol on the glycerol used: 300 g. of 96% formic acid are added to 184 g. of glycerol (dehydrated at 150—160°) and the mixture is heated for 2 hrs. at 65°/110—120 mm. and then distilled at 40 mm. during 1 hr., and finally to 110°. 200 Grams of 96% formic acid are then added and after 15 min. at 63°/80 mm. the mixture is allowed to distil to 135°/35 mm. during 1½ hrs. The temperature is then slowly raised to 190° and pyrolysis effected at 215—220° for 1 hr. and finally at 250°.

$\alpha\beta$ -Dichlorohydrin, b. p. 79—80.5°/18 mm., 179—181°/760 mm. (slight decomp.),  $d_4^{25}$  1.345,  $n_D^{25}$  1.4875 (benzoate, b. p. 180—183°/24 mm.,  $d_4^{25}$  1.290; p-nitrobenzoate, m. p. 37—38°), is obtained in 30% yield

by chlorination of allyl alcohol below -5°. With sodium phenoxide it yields  $\alpha\gamma$ -diphenoxypropan- $\beta$ -ol, m. p. 79°. The action of cold acetic acid on epichlorohydrin in presence of ferric chloride yielded only 25% of acetochlorohydrin, b. p. 118—120°/17 mm.; the 92% yield claimed by Knoevenagel (A., 1914, i, 163) is obtained only after 15 days at 30—40° or 2 days at 80°. With thionyl chloride this yields  $\alpha\gamma$ -dichloro- $\beta$ -acetin, b. p. 84—86°/18 mm., converted into  $\alpha\gamma$ -dichlorohydrin by alcoholysis, showing that in presence of ferric chloride the  $\beta$ -aceto- and not the  $\gamma$ -aceto-chlorohydrin is formed. R. BRIGHTMAN.

**Catalytic decomposition of divinyl [ethylene] glycol by reduced copper.** E. URION (Compt. rend., 1930, 191, 263—265).—When  $\Delta^{\alpha\epsilon}$ -hexadiene- $\gamma\delta$ -diol is decomposed with reduced copper in place of alumina (this vol., 1039), a mixture of acraldehyde, propaldehyde,  $\Delta^1$ -cyclopentene-1-aldehyde (*loc. cit.*), dipropionyl, b. p. 130°/760 mm., 32°/10 mm., m. p. about -10°,  $d_4^{25}$  0.941,  $n_D^{25}$  1.4130 [dioxime, m. p. 185°; osazone, m. p. 161°; semicarbazone, m. p. 270° (partial decomp.)], a compound,  $C_6H_8O_2$ , m. p. 104.5° (formed by dehydrogenation), and propionylethylcarbinol, b. p. 57—58°/10 mm.,  $d_4^{25}$  0.956,  $n_D^{25}$  1.4340, is produced. Dipropionyl is probably formed by the  $\alpha\gamma$ -migration of two hydrogen atoms of the glycol, yielding  $\Delta^{\beta\epsilon}$ -hexadiene- $\gamma\delta$ -diol (the dienol form of dipropionyl). Propionylethylcarbinol results from the primary addition of two hydrogen atoms across one double linking and a subsequent transformation of  $\Delta^{\alpha\epsilon}$  into  $\Delta^{\beta\epsilon}$ -hexene- $\gamma\delta$ -diol (the enolic form of the ketol). H. BURTON.

**Synthesis of styracitol.** L. ZERVAS (Ber., 1930, 63, [B], 1689—1690).—Tetra-acetyloxyglucal is converted by successive hydrogenation in glacial acetic acid in presence of spongy palladium and hydrolysis with barium hydroxide into styracitol, m. p. 157° (corr.),  $[\alpha]_D^{25}$  -49.4° in water, which is therefore a 1:5-anhydro-*d*-sorbitol. H. WREN.

**Preparation of acetals. II. Acetals of monohydric alcohols.** H. D. HINTON and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1930, 52, 2892—2896).—The authors' method (this vol., 745) has been applied to the preparation in yields of 30—54% of the theoretical of a representative series of ethylidene ethers, of which the following are new: isopropyl, b. p. 82—84°,  $d_4^{25}$  0.7855,  $n_D^{25}$  1.3790; sec.-n-butyl, b. p. 55—60°/16 mm.,  $n_D^{25}$  1.3965;  $\alpha$ -methylbutyl, b. p. 120—123°,  $d_4^{25}$  0.8128,  $n_D^{25}$  1.4069;  $\alpha\beta$ -dimethylpropyl, b. p. 142—145°,  $n_D^{25}$  1.4095;  $\alpha$ -ethylpropyl, b. p. 120—121°,  $d_4^{25}$  0.8120,  $n_D^{25}$  1.4050;  $\alpha\alpha$ -dimethylpropyl, b. p. 90—93°,  $d_4^{25}$  0.8278,  $n_D^{25}$  1.3965;  $\alpha$ -methyl- $\alpha$ -ethylpropyl, b. p. 96—99°,  $n_D^{25}$  1.3872;  $\alpha\alpha$ -diethylpropyl, b. p. 114—116°,  $n_D^{25}$  1.4135;  $\alpha$ -methyl- $\alpha$ -ethylamyl, b. p. 125—128°,  $n_D^{25}$  1.4145; tetrahydro- $\alpha$ -furfuryl, b. p. 153—155°/18 mm.,  $d_4^{25}$  1.3700,  $n_D^{25}$  1.4563; cyclohexyl, b. p. 131—134°/16 mm.,  $d_4^{25}$  0.9560,  $n_D^{25}$  1.4651; benzyl, b. p. 187—189°/16 mm.,  $d_4^{25}$  1.0455,  $n_D^{25}$  1.5397; diphenylmethyl, b. p. 201—202°/18 mm.,  $n_D^{25}$  1.5545;  $\beta$ -phenylethyl, b. p. 204—205°/16 mm.,  $d_4^{25}$  1.0180,  $n_D^{25}$  1.5302;  $\alpha$ -phenylethyl, b. p. 164—166°/17 mm.,  $n_D^{25}$  1.5365;  $\alpha$ -phenylpropyl, b. p. 185—187°/16 mm.,  $n_D^{25}$  1.5495;  $\alpha$ -phenyl- $\alpha$ -methylpropyl, b. p. 200°/14 mm.,  $n_D^{25}$  1.5801; and triphenylmethyl, b. p. 211°/18 mm., m. p. 93°.

*ethylidene ethers*. Commercial *tert.*-butyl alcohol gives an *ethylidene ether*, b. p. 78–81°,  $d_4^{25}$  0.8528,  $n_D^{25}$  1.4050, but the pure alcohol does not react. Furfuryl alcohol, tetramethyldiaminobenzhydrol, borneol, and terpineol also fail to yield acetals by this method. *Ethylidene sec.-octyl ether*, decomp. above 180°/20 mm., could not be isolated. The ease of acetal formation from tertiary alcohols increases with increasing carbon content and the b. p. of the acetal is lower than that of the parent alcohol.

H. E. F. NOTTON.

**Photochemical reactions among derivatives of *o*-nitrobenzylideneacetals.** V. **Tri-*o*-nitrobenzylidenesorbitol.** I. TANASESCU and E. MACOVSKY.—See this vol., 1039.

**Oxidation of sulphides by perbenzoic acid.**

III. **Oxidation of  $\alpha\alpha'$ - and  $\beta\beta'$ -halogeno-substituted sulphides, of  $\beta\beta'$ -dihydroxydiethyl sulphide, and unsaturated sulphides.** L. N. LEWIN (J. pr. Chem., 1930, [ii], 127, 77–91).—The oxidation with perbenzoic acid was carried out in dilute chloroform solution at –2°, the resultant benzoic acid being generally removed by dry gaseous ammonia at –15°; in the conversion of sulphides into sulphoxides 1 mol., and of sulphoxides into sulphones 0.5 mol., of oxygen is required. Thus  $\alpha\alpha'$ -dichlorodimethyl sulphide afforded  $\alpha\alpha'$ -dichlorodimethylsulphone, m. p. 70.5–72° (corr.), and the following compounds were obtained from the appropriate sulphides:  $\alpha\alpha'$ -dichlorodiethyl sulphoxide, b. p. 68–70°/1–2 mm.,  $d_4^{25}$  1.3106,  $n_D^{25}$  1.5089, and -sulphone, m. p. 78–80°;  $\beta\beta'$ -dibromodiethyl sulphoxide, m. p. 100–101.4° (corr. decomp.), and -sulphone, m. p. 111–112.5° (corr.);  $\beta\beta'$ -dihydroxydiethyl sulphoxide, m. p. 111–112° [converted by phosphorus tribromide or hydrobromic acid ( $d$  1.38) into  $\beta\beta'$ -dibromodiethyl sulphide, m. p. 30–33°], and -sulphone, m. p. 57–58° (unaffected by phosphorus tri-chloride or -bromide, and by hydrobromic acid); divinyl sulphoxide, b. p. 81°/16 mm.,  $d_4^{25}$  1.084,  $n_D^{25}$  1.5100, and -sulphone (1), b. p. 102–108°/8 mm.,  $d_4^{25}$  1.1794,  $n_D^{25}$  1.4799 [the constitution of these and other unsaturated compounds (see below) is supported by the molecular refractivities, using Strecker and Spitaler's constants (A., 1926, 1082) for sulphur, sulphonyl-, and sulphone groups, and by their non-reaction with concentrated magnesium chloride, or with ferric chloride or copper sulphate solutions, and therefore indicative of the absence of the ethylene oxide group, and also by the formation of  $\alpha\alpha'\beta\beta'$ -tetrabromodiethylsulphone, m. p. 130°, from I and bromine in carbon tetrachloride solution]; diallyl sulphoxide, b. p. 107–109°/7–8 mm.,  $d_4^{25}$  1.0261,  $n_D^{25}$  1.5115 (from allyl sulphide, b. p. 36°/16 mm., prepared by the action of potassium sulphide on allyl chloride in alcoholic solution), and -sulphone, b. p. 114°/5 mm.,  $d_4^{25}$  1.1215,  $n_D^{25}$  1.4893 (the latter yields  $\beta\beta'\gamma\gamma'$ -tetrabromodipropylsulphone, m. p. 98–100°, with bromine in carbon tetrachloride solution).

It is considered that oxonium compounds are immediately formed by the addition of perbenzoic acid to the sulphur atom and to the sulphonyl-group. The details for the preparation of perbenzoic acid from benzoyl peroxide in 75–80% yield are given.

A. I. VOGEL.

**Determination of organic acids in mixtures.**

I. **Determination of fatty acids in mixtures by partition between isopropyl ether and water.** C. H. WERKMAN (Ind. Eng. Chem. [Anal.], 1930, 2, 302–304).—Acetic, propionic, and butyric acids in mixtures are determined by measuring the distribution between isopropyl ether and water. The partition coefficients of acetic, propionic, and butyric acids at 25° between isopropyl ether and water are 0.168, 0.809, and 1.717, respectively, i.e., in the ratio 1 : 4.9 : 10.2. The range of the partition coefficients is therefore about five times the range of the distillation constants of these acids. The method is particularly applicable to the determination of volatile acids in fermentation liquids.

E. S. HEDGES.

**n-Fatty acids.** F. FRANCIS, S. H. PIPER, and T. MALKIN (Proc. Roy. Soc., 1930, A, 128, 214–252).—A number of normal fatty acids have been synthesised, that containing 17 carbon atoms from pure palmitic acid, those containing 19, 20, and 21 from stearic acid, and those containing from 23 to 26 from behenic acid obtained by the reduction of erucic acid. The m. p. of the acids from  $C_{14}$  to  $C_{26}$  and of their ethyl esters were determined. The latter when plotted against the carbon contents of the respective acids lie on a smooth curve; the differences between the m. p. of the esters and those of the acids plotted against the carbon content of the acid lie on two straight lines, one for the odd and the other for the even acids, whilst the data for the acids give two smooth curves, one for the odd and the other for the even series. The m. p. of equimolecular mixtures of acids where the acid with an even number of carbon atoms has the longer chain lie on a smooth curve when plotted against the carbon content. Those in which the odd acid has the longer chain lie on a second curve which falls below the first. The crystal spacing of the acids was determined by means of an X-ray examination, using the  $K\alpha$  line of iron and copper. The spacings of both the odd and even acids are linear when plotted against the number of carbon atoms in the chain; in certain cases two types of spacing are observed, according to whether the acid crystallises from solution (stable form at the ordinary temperature) or whether it separates from the molten state. Equimolecular mixtures were also investigated. Mixed crystals are formed with great ease and tend to assume alternately the habit of the odd and even acids, the form assumed being that of the shorter molecule. It is shown that a mixture will not as a rule give as many orders of reflexion as a pure acid, and in no case gives the two spacings and the m. p. coinciding with those of a pure acid. Details are given of the isolation and examination of a number of acids obtained by the oxidation of paraffin wax in a current of air at 100°; in every case the products were mixtures of normal fatty acids. An account is also given of the following acids isolated from natural sources: arachidic, lignoceric, cerotic, montanic, and cluynic; and of fatty acids obtained from the oxidation of the alcohols present in Chinese wax and carnauba wax. All these, when subjected to an X-ray analysis, are found to be mixtures of acids.

L. L. BIRCUMSHAW.

**Olefinic acids. II. Occurrence of spontaneous tautomeric change at temperatures near the b. p.** R. P. LINSTAD (J.C.S., 1930, 1603—1609).—Pure dry *cyclohexylideneacetic acid* and *cyclohexenylacetic acid* are interconvertible in carbon dioxide at 150° and above. An equilibrium mixture (the composition of which was apparently independent of temperature) containing about 83% of the *cyclohexenylacetic acid* was reached from either side. At above 220° the change is rapid, decarboxylation with formation of methylencyclohexane occurring simultaneously.

Similar changes have been found in cases of other olefinic acids; thus in 4 hrs. at 200° about 30% of *cyclopentylideneacetic acid* passes into its  $\beta\gamma$ -isomeride and  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -*n*-hexenoic acids are slowly isomerised at their b. p.

Dimethylacrylic and styrylacetic acids, however, which do not undergo tautomeric interconversion when treated with boiling alkali, also appear to resist the action of heat.

R. J. W. LE FÈVRE.

**Action of zinc chloride on oleic acid.** K. H. BAUER and P. PANAGOULAS (Chem. Umschau, 1930, 37, 189—193).— $\gamma$ -Stearolactone could not be detected in the products of the reaction of oleic acid and sulphuric acid, but it (24%), *isoleic acid* (62%), and *hydroxystearic acid* (14%) were obtained by heating oleic acid with zinc chloride at 180°. By acting on oleic acid in acetic acid solution with zinc chloride Saytzeff's "*isoleic acid*," m. p. 42° (for which the constitution of a  $\Delta$ -octadecenoic acid was confirmed), and a *dihydroxystearic acid*, m. p. 77—79°, were obtained. The latter could be distilled unchanged in a vacuum, but by heating at 200° at higher pressures an estolide was formed, from which the acid could be regenerated by hydrolysis.

E. LEWKOWITSCH.

**"Acid" potassium and sodium salts of normal fatty acids.** T. MALKIN (Ber., 1930, 63, [B], 1807—1811).—Experiments with lauric, myristic, palmitic, stearic, and behenic acids fail to disclose the existence of "acid" salts such as described by Ekwall and Mylius (A., 1929, 676; this vol., 65). Re-examination of the products obtained by these authors shows that they are mixtures. Rast's method is not applicable to the determination of the mol. wt. of these compounds, since the normal salt gives no depression in camphor and the depressions observed by Ekwall and Mylius are due to the acid only.

H. WREN.

**Iron soaps [complex iron compounds].** H. SALVATERRA (Z. angew. Chem., 1930, 43, 620—622).—Precipitation with ferrous sulphate of an aqueous solution of the sodium soap prepared from linseed oil, having  $d_{20}^{20}$  0.9294, acid value 2.23, saponification value 194.0, iodine value 175.0, and mean mol. wt. 276.1, gave a greyish-green ferrous soap containing 9.2% Fe. The ethereal solution rapidly oxidised in the air, changing from green to blood-red in colour; on evaporation of the ether a basic ferric soap with 8.37% Fe was obtained as a viscous mass. Extraction of this mass with 95% alcohol afforded an alcohol-soluble soap with 12.35% Fe and a residue with 2.4% Fe. Precipitation of the original sodium soap solution with ferric chloride yielded a flocculent yellowish-red substance, soluble in ether; on evapor-

ation of the ether a red, viscous mass with 6.3% Fe was obtained. After exposure to the air in thin films the basic soap with 8.37% Fe yielded a product with 7.23% Fe, partly soluble in ethyl acetate, leaving a residue with 29.8% Fe. Evaporation of the ester gave a brown substance with 4.02% Fe. The fatty acids from the soluble portion contained 70.18% C, 9.18% H, 20.64% O, and those from the insoluble portion 64.18% C, 8.41% H, 27.41% O.

A. R. POWELL.

**Hydrogenation of unsaturated lactones to deoxy-acids.** W. A. JACOBS and A. B. SCOTT (J. Biol. Chem., 1930, 87, 601—613).—When hydrogenated in alcoholic solution in presence of platinum oxide,  $\Delta^{\beta}$ -angelicalactone yielded *n*-valeric acid, whilst  $\Delta^{\alpha}$ -angelicalactone took up 1 mol. only of hydrogen to give  $\gamma$ -valerolactone, which was resistant to further hydrogenation; in this experiment a small amount of *n*-valeric acid was obtained, which is accounted for by partial isomerisation of the  $\Delta^{\alpha}$ -lactone to the  $\Delta^{\beta}$ -form.  $\alpha\alpha$ -Dimethyl- $\Delta^{\beta}$ -angelicalactone absorbed 2 mols. of hydrogen to give  $\alpha\alpha$ -dimethyl-*n*-valeric acid, whilst  $\gamma$ -methyl- $\Delta^{\alpha}$ -angelicalactone yielded  $\gamma$ -hexolactone. The lactone of  $\delta$ -hydroxy- $\Delta^{\gamma}$ -hexenoic acid afforded *n*-hexoic acid, and, contrary to the statement of Mannich and Butz (A., 1929, 442), the lactone of  $\delta$ -hydroxy- $\beta$ -phenyl- $\Delta^{\gamma}$ -hexenoic acid was readily hydrogenated to give  $\beta$ -phenyl-*n*-hexoic acid. The general rule therefore holds that those unsaturated lactones in which the doubly-linked carbon atom is involved in the lactone ring yield the corresponding deoxy-acid on hydrogenation.

C. R. HARRINGTON.

**Salts possessing o-, m-, or p-quinonoid structure. VII.** R. CIUSA and L. MUSAJO (Gazzetta, 1930, 60, 486—492; cf. A., 1924, i, 578).—Pyruvic acid *m*-nitrophenylhydrazones has m. p. 226°; o-, m-, and p-nitrophenylhydrazones of pyruvic acid by treatment with metallic carbonates in aqueous solution or suspension yield salts of the general formula  $\text{CO}_2\text{X} \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ . These may also be prepared by double decomposition of the alkali salts of the hydrazones and the appropriate metallic salt; in the case of ammonium salts, dry gaseous ammonia is passed into the alcoholic solution of the hydrazone, and the salt precipitated by addition of ether. A number of metallic salts are described (*ammonium pyruvate m*-nitrophenylhydrazone has m. p. 210—211°); all are yellow with the exception of cobalt pyruvate o-nitrophenylhydrazone and silver pyruvate p-nitrophenylhydrazone, which are red, and for these a cyclic structure is suggested.

C. W. SHOPPEE.

**Raman effect and problems of constitution.** A. DADIEU and K. W. F. KOHLRAUSCH (Ber., 1930, 63, [B], 1657—1666; cf. this vol., 840).—Comparison of the Raman spectrum of ethyl acetoacetate with those of ethyl acetate, acetone, allyl alcohol, and ethyl benzoate shows the presence of the C=O and C=C groups. Since the C=C line is very marked, although the enolic form cannot be present in great amount, the Raman spectrum must be regarded as a very sensitive indicator of the presence of the enolic variety; the presence of the alcoholic hydroxyl group is faintly shown. With liquid hydrogen cyanide the evidence of the presence of a form other than H-C≡N

is inconclusive. The Raman spectra of butadiene, piperylene, isoprene, and  $\beta\gamma$ -dimethylbutadiene are recorded. There appears to be no reason for assuming that the C:C linking in conjugated systems whether open or closed is in a state distinct from that of an ordinary double linking of the allyl type.

H. WREN.

**Derivatives of homolævulinic acid.** R. LUKÉŠ (Chem. Listy, 1930, 24, 297—300).—See A., 1929, 1165.

**Action of ultra-violet light on  $\alpha$ -keto- $\beta$ -methylbutyric acid.** C. FROMAGEOT (Compt. rend., 1930, 191, 49—51).—In neutral or alkaline aqueous solution, in the presence of air,  $\alpha$ -keto- $\beta$ -methylbutyric acid under the influence of ultra-violet light (more slowly by daylight) forms an oxygenated compound which is rapidly decomposed by acids. The oxygenated compound is not formed in the presence of the enol.

C. C. N. VASS.

**Properties of conjugated compounds. X. Variability in the mode of ester addition to butadiene esters and ketones.** E. H. FARMER and T. N. MEHTA (J.C.S., 1930, 1610—1616).—It is shown that butadiene esters can simultaneously add the components of ester addenda at both  $\alpha\beta$ - and  $\alpha\delta$ -positions in the butadiene chain. The additive product from methyl sodiomalonate and methyl sorbate has been reinvestigated; it was hydrogenated in aqueous methyl-alcoholic solution in presence of colloidal palladium; the oil, b. p. 165—170°/14 mm., thus formed was hydrolysed by alcoholic sodium hydroxide and decarboxylated by boiling with 25% hydrochloric acid. The solid product consisted of  $\beta$ -methylpimelic acid. The liquid product was dehydrated by boiling with acetic anhydride and separated by distillation into  $\beta$ -methylpimelic anhydride, decomp. above 200°/17 mm., and  $\beta$ -propylglutaric anhydride, b. p. 175°/20 mm. (the yield of the latter indicated that about 7% of the acid mixture was  $\beta$ -propylglutaric acid).

Ethyl  $\gamma$ -methylsorbate when heated with ethyl cyanoacetate in alcoholic sodium ethoxide solution for 9 hrs. at 100° yielded an additive product, which by ozonolysis in chloroform and decomposition of the ozonides furnished acetaldehyde,  $\beta$ -methyl-lævulinic acid, and the solid ketodilactone of  $\beta$ -acetylglutaric acid, m. p. 98—99°, showing that the additive product is a mixture of ethyl  $\alpha$ -cyano- $\beta\gamma$ -dimethyl- $\Delta^{\alpha}$ -pentene- $\alpha$ -dicarboxylate and ethyl  $\alpha$ -cyano- $\beta$ -isobutenylglutarate.

R. J. W. LE FÈVRE.

**Volumetric determination of tartrates.** P. H. RICHERT (Ind. Eng. Chem. [Anal.], 1930, 2, 273—274).—The following method gives slightly high results, but is sufficiently accurate for most purposes. 50 C.c. of solution containing not more than 30 mg. of tartaric acid are heated with 10 c.c. of 20% sodium hydroxide solution and 25 c.c. of 0.1N-potassium permanganate for 30 min. The solution is cooled to about 90°, 10 c.c. of 30% sulphuric acid are added, and the excess of permanganate is determined with 0.1N-potassium oxalate, adding a slight excess of the oxalate and titrating back with 0.1N-potassium permanganate. The method cannot be used in presence of other organic substances which reduce

permanganate, such as would be found in fruit juices.

E. S. HEDGES.

**isoCitric acid.** E. K. NELSON (J. Amer. Chem. Soc., 1930, 52, 2928—2933).—Repetition of Fittig's synthesis (A., 1890, 586) gave pure isocitric acid ( $\alpha$ -hydroxypropano- $\alpha\beta\gamma$ -tricarboxylic acid) (+1.5H<sub>2</sub>O), m. p. 105° after softening. It is dehydrated at 100° in a vacuum to lactoisocitric acid, m. p. 160—161°. Direct esterification of isocitric acid is accompanied by lactonisation, but barium isocitrate and alcoholic hydrogen chloride give a product, b. p. 181°/10 mm. The pure ethyl ester, obtained by the method of Wislicenus and Nassauer (A., 1895, i, 506) (*hydracide*, m. p. 199°), has the same b. p. Attempts to resolve synthetic isocitric acid, using cinchonine, cinchonidine, or brucine, were unsuccessful. Samples of ethyl isocitrate from blackberries had  $[\alpha]_D$  -9.70° to +14.75° and gave hydrazides of m. p. 170—172° to 179—180°. Recrystallisation of the last-named raised the m. p. to 196—197° and gave a product identical in optical and crystallographic properties with the synthetic hydrazide. Crystalline natural isocitric acid could not be completely freed from lactoisocitric acid, but optical examination established the identity of crystals of both with those of the synthetic products. Natural isocitric acid is a mixture of the *d*- and *l*-acids in which either may predominate, and the synthetic product is the racemic form of the same acid.

H. E. F. NOTTON.

**Spatial configuration of single valencies of allene.** C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1930, 1619—1622).—The compound isolated by Faltis and Pirsch (A., 1927, 856) from alcoholic ethyl  $\alpha$ -bromo- $\alpha\gamma$ -dicarboxyglutaconate by treatment with silver oxide followed by evaporation, and described as ethyl allenetetracarboxylate, is shown to be the compound C<sub>6</sub>H<sub>2</sub>(CO<sub>2</sub>Et)<sub>4</sub>, m. p. 86°, which on distillation (essentially the second method of preparation employed by Faltis and Pirsch) changes into ethyl 6-ethoxy- $\alpha$ -pyrone-3:5-dicarboxylate, m. p. 93°, b. p. 200—220°/11—12 mm.

R. J. W. LE FÈVRE.

**Pectin and its relation to the formation of the incrustations of cellulose. I, II.** F. EHRLICH (Cellulosechem., 1930, 11, 140—151, 161—170).—I. A summary of the chemistry of pectin.

II. The enzymic degradations and transformations of pectin, and the possible mechanism of the formation of lignin from pectin are discussed.

A new enzyme, pectolase, may be isolated from old cultures of a *Perisporiaceae* (a mould frequently found in beet pulp) in yeast water by precipitation with alcohol. The cyclic tetragalacturonic acids *a* and *c* with 5% of this preparation, at  $p_H$  4.5—6, yield in a few minutes at the ordinary temperature the open-chain tetragalacturonic acid *b*; in 2—3 days complete hydrolysis occurs with the formation of galacturonic acid, isolated as the crystalline *a*-form in a good yield. The enzyme is a component of taka-diastase, which effects complete hydrolysis in 3—4 months, is present as traces in diastase and emulsin, but is absent from maltase. The preparation of pectolase is also active in the production of soluble pectic acids from the insoluble

native pectin. It is therefore suggested that the tetragalacturonic acids, hitherto obtained only by acid hydrolysis of pectin, are intermediate products in the complete enzymic degradation of the pectin molecule.

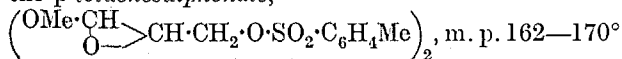
The fraction of flax hydratopectin soluble in 70% alcohol is a crude hexopentosan containing 25% of a resinous product resembling lignin. After purification by repeated precipitation by acid from an alkaline solution this substance contained no carbohydrate; its reactions suggest that furan nuclei are an integral part of its constitution. This resin, probably an intermediate in the conversion of pectin into lignin, is still in close combination with the parent substance, since prolonged extraction of flax with boiling 70% alcohol did not suffice to remove it.

T. H. MORTON.

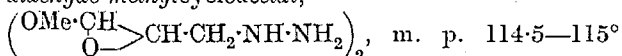
**Preparation of glyceraldehyde and glycerol.** I. S. NEUBERG (Biochem. Z., 1930, 221, 492—493).—Acraldehyde is quantitatively converted into glyceraldehyde by oxidation with chlorate activated by osmium tetroxide. The aldehyde can be reduced to glycerol with sodium or aluminium amalgam in neutral aqueous solution.

W. MCCARTNEY.

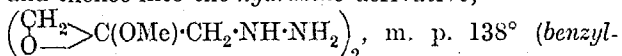
**Hydrazino-derivatives of glyceraldehyde and dihydroxyacetone.** H. O. L. FISCHER and E. BAER (Ber., 1930, 63, [B], 1741—1748).—Glyceraldehyde methylcycloacetal is converted by *p*-toluenesulphonyl chloride and pyridine in chloroform into the *p*-toluenesulphonate,



according to the mode of heating, converted by anhydrous hydrazine at  $135^\circ$  into *hydrazinoglyceraldehyde methylcycloacetal*,



(benzylidene derivative, m. p.  $108^\circ$ ). Dihydroxyacetone methylcycloacetal is similarly converted into the *p*-toluenesulphonate, m. p.  $112\text{--}113^\circ$  (decomp.), and thence into the *hydrazino*-derivative,



The *hydrazino*-derivative from glyceraldehyde is converted by concentrated hydrochloric acid at  $60^\circ$  into pyrazole, whereas that from dihydroxyacetone yields only ill-defined products.

H. WREN.

**"Acetonisation" with acetone and zinc chloride.** II. *iso*Propylideneglyceraldehyde. H. O. L. FISCHER and E. BAER (Ber., 1930, 63, [B], 1749—1753).—*iso*Propylidenedioxypropaldehyde, b. p.  $30\text{--}35^\circ/1 \text{ mm.}$ , is prepared from glyceraldehyde, acetone, and zinc chloride under very definite conditions, the exclusion of every trace of acid being necessary to avoid the formation of methylglyoxal. It is readily hydrolysed by dilute acetic acid to glyceraldehyde and is transformed by ethyl orthoformate and ammonium chloride into *isopropylidenedioxypropaldehyde* diethylacetal, b. p.  $90\text{--}95^\circ/18 \text{ mm.}$  When treated with 0.1% barium hydroxide solution at  $16^\circ$ , *isopropylidenedioxypropaldehyde* affords a pasty mass from which crystals of a *diisopropylidenehexose*, m. p.  $89\cdot5^\circ$ , are

deposited. Treatment of the non-crystalline portion with ethylene chloride affords (as a consequence of the faintly acidic nature of the solvent) an *iso*-propylidenehexose, m. p.  $160\text{--}161\cdot5^\circ$ . The free sugars have not been obtained crystalline. Since the derivatives do not give an osazone with phenylhydrazine, it is possible that their carbon chain is branched.

H. WREN.

**Bromination of acetone in organic solvents.** I. COHEN (J. Amer. Chem. Soc., 1930, 52, 2827—2835).—The bromination of acetone, alone and in carbon tetrachloride, carbon disulphide, and chloroform solutions, has been followed by titrations and conductivity measurements. The reaction is catalysed by hydrogen bromide and retarded by quinoline or water. Pyridine inhibits the reaction after an initial disturbance. The effect of increasing quantities of water on the reaction velocity coefficient is shown graphically. The dielectric constants of the solutions decrease considerably during the reaction.

H. E. F. NOTTON.

**Enolic derivatives of acetol and methylglyoxal.** H. O. L. FISCHER, E. BAER, and L. FELDMANN [with L. AHLSTRÖM] (Ber., 1930, 63, [B], 1732—1744).—*iso*Propylideneglycerol  $\alpha$ -monochlorohydrin (or the corresponding iodohydrin or *p*-toluenesulphonyl compound) is converted by powdered potassium hydroxide at  $125^\circ$  into  $\Delta^{\alpha}$ -propene- $\beta$ -diol *isopropylidene ether*, b. p.  $104\text{--}106^\circ/750 \text{ mm.}$ ,  $n_D^{20} 1\cdot4221$ . It readily decolorises potassium permanganate and adds bromine. It is reduced by hydrogen in the presence of nickel to propylene glycol, b. p.  $61\text{--}62^\circ/1\text{--}0\cdot8 \text{ mm.}$ ,  $n_D^{20} 1\cdot4319$ , oxidised by perbenzoic acid to dihydroxyacetone, and by lead tetra-acetate in benzene to  $\alpha\beta$ -diacetyl- $\beta$ -*isopropylidenepropane*- $\alpha\beta\gamma$ -tetrol,  $\begin{array}{c} \text{CMe}_2 \cdot \text{O} \\ | \\ \text{O} - \text{CH}_2 \end{array} \text{C}(\text{OAc}) \cdot \text{CH}_2 \cdot \text{OAc}$ , b. p.  $105\text{--}107^\circ/1\cdot4 \text{ mm.}$ ,  $n_D^{20} 1\cdot4327$ . Hydrolysis of the last-named compound with dilute acetic acid affords the *monoacetate* of dihydroxyacetone, b. p.  $80\text{--}82^\circ/0\cdot3\text{--}0\cdot2 \text{ mm.}$ , converted by barium carbonate suspended in water into dihydroxyacetone. The *monoacetate* is converted by acetic anhydride and pyridine into the diacetate, m. p.  $48\text{--}48\cdot5^\circ$ , and by methyl-alcoholic hydrogen chloride into dihydroxyacetone methylcycloacetal.

Methyleneglycerol  $\alpha$ -monochlorohydrin and powdered potassium hydroxide at  $110\text{--}115^\circ$  yield the *methylene ether* of  $\Delta^{\alpha}$ -propene- $\beta$ -diol, b. p.  $93\text{--}95^\circ/758 \text{ mm.}$ ,  $n_D^{20} 1\cdot4336$ . It is converted by bromine in chloroform into the corresponding *dibromide*, b. p.  $91\text{--}93^\circ/20 \text{ mm.}$ , transformed by pyridine into the quaternary *pyridinium salt*,  $\text{C}_9\text{H}_{11}\text{O}_2\text{NBr}_2$ , m. p.  $130^\circ$ . Oxidation of the *methylene ether* with lead tetra-acetate affords  $\alpha\beta$ -diacetyl- $\beta$ -*methylenepropane*- $\alpha\beta\gamma$ -tetrol, b. p.  $96\cdot5\text{--}97\cdot5^\circ/0\cdot5\text{--}0\cdot6 \text{ mm.}$ , less advantageously prepared from the *dibromide* and silver acetate. Ethylideneglycerol  $\alpha$ -monochlorohydrin (obtained from glycerol  $\alpha$ -monochlorohydrin, acetaldehyde, and 84% phosphoric acid) when boiled with powdered potassium hydroxide gives  $\Delta^{\alpha}$ -propene- $\beta$ -diol *ethylidene ether*, b. p.  $99\text{--}103^\circ/766 \text{ mm.}$ ,  $n_D^{20} 1\cdot4226$ .  $\Delta^{\alpha}$ -Propene- $\beta$ -diol *benzylidene ether* has b. p.  $106\text{--}107^\circ/16 \text{ mm.}$ ,  $n_D^{20} 1\cdot5341$ .



The *p*-toluenesulphonyl derivative of glycer-aldehyde methylcycloacetal and potassium hydroxide at 130° afford dimeric  $\beta\gamma$ -oxido- $\gamma$ -methoxy- $\Delta^a$ -propene,  $(\text{OMe} \cdot \text{CH} \cdot \text{O} \cdot \text{C} \cdot \text{CH}_2)_2$ , m. p. 55–56°, which is readily hydrolysed by 0.01*N*-sulphuric acid to methylglyoxal, but appears indifferent to emulsin. It is catalytically reduced to lactaldehyde methylcycloacetal,  $(\text{CHMe} \cdot \text{CH} \cdot \text{O} \cdot \text{Me})_2$ , m. p. 112.5°, hydrolysed by 0.1*N*-sulphuric acid to lactaldehyde (identified as the *p*-nitrophenylhydrazone, m. p. 127–128°). Lactaldehyde is converted by acetic anhydride and pyridine into the acetate, m. p. 132–134°, which with hydrogen bromide in acetic acid affords bromolactaldehyde, m. p. 76–77° or 79–81° according to the mode of heating, and thence by silver carbonate and methyl alcohol into the methylcycloacetal of lactaldehyde identical with that described above.

H. WREN.

**Constitution of nickel dimethylglyoxime.** P. PFEIFFER (Ber., 1930, 63, [B], 1811–1816).—Benzildioxime monobenzyl ether, m. p. 192°, is prepared by the action of  $\alpha$ -benzylhydroxylamine on benzilmonoxime or of hydroxylamine on  $\alpha$ -benzilmonoxime benzyl ether. Diacetyldioxime monobenzyl ether, m. p. 97–98°, is derived from  $\alpha$ -benzylhydroxylamine and oximinomethyl ethyl ketone. Neither compound yields a complex nickel salt. Similarly, complex nickel salts are not obtained from benziloxime-ethylimine,  $\text{OH} \cdot \text{N} \cdot \text{CPh} \cdot \text{CPh} \cdot \text{NEt}$ , m. p. 185–186°, prepared from  $\alpha$ -benzilmonoxime and ethylamine in alcohol and glacial acetic acid, or from diacetyloximeanil,  $\text{OH} \cdot \text{N} \cdot \text{CMe} \cdot \text{CMe} \cdot \text{NPh}$ , m. p. 118–119°, made from oximinomethyl ethyl ketone and aniline. Treatment of nickel acetate and oximinomethyl ethyl ketone with aqueous ammonia yields the complex salt,  $(\text{CMe} \cdot \text{NO} \cdot \text{CMe} \cdot \text{NH})_2 \text{Ni}$ , which closely resembles nickel dimethylglyoxime in colour, insolubility in water, solubility in organic media, and instability towards acids. Since the compounds must be closely related in structure, the hydroxyl groups of dimethylglyoxime can have no constitutional significance. From nickel acetate, ammonia, and oximinomethyl ethyl ketone the monoinmino-compound,  $\text{CMe} \cdot \text{NO} \cdot \text{CMe} \cdot \text{NH} \cdot \text{Ni} \cdot \text{NO} \cdot \text{CMe} \cdot \text{O} \cdot \text{CMe}$ , is derived, forming an important link between the internally complex salts of the  $\alpha\beta$ -diketominoxime and  $\alpha\beta$ -diketoiminoximes. Since oximinodiethyl ketone, nickel acetate, and methylamine afford the compound  $\text{CMe} \cdot \text{NO} \cdot \text{CMe} \cdot \text{NH} \cdot \text{Ni} \cdot \text{NO} \cdot \text{CMe} \cdot \text{O} \cdot \text{CMe}$ , it is not possible that hydrogen is united to oxygen instead of to nitrogen. The constitution  $(\text{CMe} \cdot \text{N}(\text{OH}) \cdot \text{CMe})_2 \text{Ni}$  is therefore rendered very probable for nickel dimethylglyoxime.

H. WREN.

**Pyrolysis of certain organic substances.** C. SANDONNINI (Annali Chim. Appl., 1930, 20, 262–270).—The pyrolysis of trioxymethylene, dextrose, sucrose, starch, cellulose, wood, and formose (obtained by treating 4% formaldehyde solution with precipitated lead hydroxide) in an autoclave at 270–300°

and at 170–190° has been studied. The percentage yields of the products obtained at 270–300° were respectively: gaseous, 26, 21, 23, 21, 18, 17, 21; carbonaceous residue and ash, 42, 41, 46, 60, 42, 53, 44; aqueous distillate, 30, 38, 30, 18, 40, 30, 33; oily substances, 2.0, —, —, 0.8, —, —, 2.0. The percentage compositions of the gas formed varied between the following limits:  $\text{CO}_2$ , 57.4–65.6;  $\text{CO}$ , 15.3–21.0;  $\text{H}_2$ , 5.0–11.0;  $\text{CH}_4$ , 3.6–11.8. Appreciably different results were obtained at 170–190° with trioxymethylene (formose), which gave 15 (19)% of gas containing 86.4 (77.2)% of  $\text{CO}_2$ . The presence of alumina, chromium oxide, or zinc oxide does not modify the reaction sensibly. The carbonaceous matter formed is non-homogeneous and apparently results partly from direct carbonisation of the original material and partly from decomposition of the primary products of the pyrolysis.

T. H. POPE.

**Determining aldose sugars by titration with iodine and alkali.** C. S. SLATER and S. F. ACREE (Ind. Eng. Chem. [Anal.], 1930, 2, 274–276).—Under specified conditions aldose sugars react quantitatively with two equivalents of iodine, forming two equivalents of hydrogen iodide and one of the aldonic acid. The aldoses may be determined by neutralising the sugar solution and adding both standard iodine and alkali in successive portions until a small excess of each is present, keeping the mixture for about 15 min., and determining the excess of alkali and iodine by the usual methods. The aldoses, dextrose, lactose, galactose, and xylose use or remove two equivalents of iodine and three of alkali, whilst xylans, galactans, levulose, and sucrose remain practically unchanged. The method has been applied to the analysis of xylose solutions made in the hydrolysis of the xylans of cottonseed-hull bran, bagasse, peanut hulls, and straw. The experimental error is about 2%.

E. S. HEDGES.

**Effect of dextrose and sucrose on the determination of levulose by Nijn's method.** F. W. ZERBAN and L. SATTler (Ind. Eng. Chem. [Anal.], 1930, 2, 307–309).—The reaction of Nijn's solution with mixtures of levulose and dextrose has been examined. With equal quantities of levulose, the reducing effect per mg. of dextrose decreases as the concentration of dextrose increases. The reducing effect per mg. of dextrose also decreases with increasing concentration of levulose present. In the analysis of raw sugars and other cane products, the reducing effect of the sucrose on Nijn's solution must be taken into consideration. 1 G. of sucrose is approximately equivalent to 1 mg. of levulose. As the percentage of sucrose in mixtures of the three sugars can readily be determined, the corresponding correction can first be applied to the weight of copper found by Nijn's method, and the resulting figure is then further corrected for the dextrose present, in order to determine the levulose.

E. S. HEDGES.

**3:6-Anhydroglucose.** I. H. OHLE and E. EULER (Ber., 1930, 63, [B], 1796–1807).—5-*p*-Toluenesulphonyl-3:6-anhydroisopropylidene-glucose is smoothly hydrolysed by 70% acetic acid at 100° to 5-*p*-toluenesulphonyl-3:6-anhydro- $\alpha$ -D-glucopyranose, m. p. 100°,  $[\alpha]_D^{25} +53.1^\circ$  in pyridine,  $+64.81^\circ$  in

chloroform,  $+56.52^\circ$  in acetone,  $[\alpha]_D^{20} +66.71^\circ$  to  $+57.89^\circ$  in alcohol, which strongly reduces Fehling's solution and colours fuchsin-sulphurous acid more slowly but more intensely than 3:6-anhydroglucose. The *p*-nitrophenylhydrazone has m. p.  $92-93^\circ$ ,  $[\alpha]_D^{20} -23.38^\circ$  in pyridine. With phenylhydrazine and a limited amount of acetic acid it affords a normal phenylosazone, m. p.  $157-158^\circ$ ,  $[\alpha]_D^{20} -177.17^\circ$  in pyridine, whereas in the presence of a large amount of acid a "semiphenylosazone,"  $C_{44}H_{44}O_{10}N_8S_2$ , m. p.  $165^\circ$ ,  $[\alpha]_D^{20} -182.01^\circ$  in pyridine,  $[\alpha]_D^{20} -141.34^\circ$  to  $-124.54^\circ$  in pyridine + 5% of water, is formed. Treatment of 5-*p*-toluenesulphonyl-3:6-anhydroglucose with pyridine and acetic anhydride at  $-10^\circ$  affords mainly 5-*p*-toluenesulphonyl-1:2-diacetyl-3:6-anhydro- $\alpha$ -D-glucosyl-1-imine, m. p.  $87^\circ$ ,  $[\alpha]_D^{20} +136.4^\circ$  in chloroform. 5-*p*-Toluenesulphonyl-1:2-dibenzoyl-3:6-anhydro- $\alpha$ -D-glucosyl-1-imine, m. p.  $128^\circ$ ,  $[\alpha]_D^{20} +135.52^\circ$  in chloroform, is obtained by means of benzoyl chloride and pyridine at  $-10^\circ$ . The diacetyl compound is converted by methyl-alcoholic ammonia at  $0^\circ$  into di-5-*p*-toluenesulphonyl-3:6-anhydro- $\alpha$ -D-glucosyl-1-imine,  $C_{56}H_{56}O_{12}N_8S_2$ , m. p.  $140^\circ$  (decomp.),  $[\alpha]_D^{20} +105.75^\circ$  in acetone, which evolves ammonia when boiled with water. With titanium tetrachloride in chloroform at  $50^\circ$  the diacetyl compound yields 5-*p*-toluenesulphonyl-2-acetyl-3:6-anhydro- $\alpha$ -D-glucosyl-1-chloride, m. p.  $105^\circ$ ,  $[\alpha]_D^{20} +194.05^\circ$  in chloroform. 5-*p*-Toluenesulphonyl-2-acetyl-3:6-anhydro- $\alpha$ -D-glucosyl-1-bromide, m. p.  $89^\circ$ ,  $[\alpha]_D^{20} +220.25^\circ$ , is obtained from 5-*p*-toluenesulphonyl-1:2-diacetyl-3:6-anhydroglucose by means of hydrogen bromide and glacial acetic acid or titanium tetrabromide or from 5-*p*-toluenesulphonylisopropylidene-3:6-anhydroglucose by the acid process (with use of magnesium ethyl bromide for the final neutralisation of the acid). The bromide is unstable. It does not yield crystalline compounds when treated with silver carbonate and methyl alcohol or moist acetone and silver carbonate. It is converted by lead tetra-acetate in boiling glacial acetic acid into 5-*p*-toluenesulphonyl-1:2-diacetyl-3:6-anhydro- $\beta$ -D-glucose, m. p.  $103^\circ$ ,  $[\alpha]_D^{20} +46.66^\circ$  in chloroform.

Isopropylidene-3:6-anhydroglucose is converted by acetic anhydride and pyridine at  $36^\circ$  into 5-acetyl-isopropylidene-3:6-anhydroglucose, m. p.  $31^\circ$ ,  $[\alpha]_D^{20} +74.78^\circ$  in chloroform, hydrolysed to 3:6-anhydro-isopropylideneglucose, m. p.  $55^\circ$ ,  $[\alpha]_D^{20} +30.5^\circ$  in chloroform. 5-Monoacetyl-3:6-anhydro-D-glucose was obtained as a colourless syrup,  $[\alpha]_D^{20} +91.18^\circ$  in chloroform. Triacetyl-3:6-anhydro-D-glucose, b. p.  $165^\circ/0.2$  mm. (bath temperature), is prepared from 3:6-anhydro-D-glucose or its monoacetate.

H. WREN.

**Effect of addition of carbonate on the oxidation of hexoses by bromine.** M. HÖNIG and W. RUZICKA (Ber., 1930, 63, [B], 1648-1649).—Oxidation of carbohydrates with bromine is advantageously effected in the presence of carbonates (calcium, barium, lead) even when hydrolysis of the oxidised product is not feared, since the immediate neutralisation of the liberated hydrogen bromide has a markedly accelerating action. The conversion of dextrose into gluconic acid (yield 63%), of *D*-galactose into *D*-galactonic acid, and of levulose into trihydroxy-

butyric (in addition to glycollic and formic) acid is described in detail.

H. WREN.

**Transformation reactions in the carbohydrate group. III. Synthetic hexosephosphates.** K. JOSEPHSON and S. PROFFE (Annalen, 1930, 481, 91-106).—Diisopropylideneglucose is converted by phosphoryl chloride in pyridine at  $-18^\circ$  to  $-20^\circ$  followed by treatment of the product with barium hydroxide into barium diisopropylideneglucose phosphate,  $C_{12}H_{19}O_9P$  Ba,  $[\alpha]_D^{20}$  yellow  $-5.2^\circ$  in 50% acetone,  $-5.1^\circ$  in water, hydrolysed to barium glucose phosphate,  $[\alpha]_D^{20}$  yellow  $+27.4^\circ$  in water. The free ester has  $[\alpha]_D^{20}$  yellow  $+38.8^\circ$  in water. After drastic hydrolysis which removes both acetone residues or milder treatment removing substantially that in the 5:6-position, addition of an excess of alkali to the resulting solution, followed later by acidification, does not lead to a change in rotation indicative of isomerisation. The ester is therefore regarded with great probability as glucopyranose 3-phosphate. It is certainly not identical with the Robison ester as judged from specific rotation or behaviour towards phenylhydrazine.

Diisopropylideneglucose 3-phosphate,  $C_{36}H_{57}O_{19}P$ ,  $[\alpha]_D^{20}$  yellow  $-45.7^\circ$  in acetone, is prepared from diisopropylideneglucose and phosphoryl chloride in pyridine. It is converted by mild hydrolysis into isopropylideneglucose phosphate,  $C_{27}H_{45}O_{19}P$ . The diisopropylidene derivative is extremely unstable in slightly acidic, neutral, or alkaline solution. In very feebly alkaline solution very marked change in specific rotation is observed, which is considered to be due to the migration of the phosphate residue from position 3 in one or all of the monoisopropylideneglucose residues.

H. WREN.

**Determination of nitrogen in osazones by Kjeldahl's method.** G. DORFMÜLLER (Z. Ver. deut. Zucker-Ind., 1930, 80, 407-412).—The ordinary Kjeldahl procedure gives low nitrogen results for osazones and phenylhydrazones, but accurate results for the osazones of disaccharides if they are previously reduced in alcoholic solution with hydrochloric acid and zinc dust or in sodium hydroxide solution with hyposulphite. Glucosazone gives high results in the first method and low results in the second, and mannosephenylhydrazone high results in the first and good results in the second method. The acid reduction is effected with 5 c.c. of 95% alcohol, 5 c.c. of hydrochloric acid (*d* 1.19), and 3 g. of zinc dust, and the alkaline reduction with 5 c.c. of alcohol, 10 c.c. of 5% sodium hydroxide, and 2.5 g. of sodium hyposulphite. After boiling for a few minutes in each case, 25 c.c. of sulphuric acid (*d* 1.84) are added slowly and the mixture is heated with 2 g. of mercury and 10 g. of potassium sulphate in the usual manner.

A. R. POWELL.

**Existence of two modifications of octa-acetylsucrose.** A. PIOTET (Helv. Chim. Acta, 1930, 13, 698-702).—Octa-acetylsucrose (variety I), m. p.  $70^\circ$ , on long keeping in moist air (but not in dry air or in a vacuum), or when kept under water, or simply by recrystallisation from water, is transformed into an isomeride (variety "II") of m. p.  $75^\circ$ , which depresses the m. p. of the ordinary form, but has the same optical rotation ( $[\alpha]_D^{20} +59.45^\circ$  in chloroform) and is

somewhat less soluble than I in organic solvents. The reverse change can be effected only by a "reacetylation" of II under the ordinary conditions for octa-acetylsucrose. These two forms do not correspond with the "A" and "B" varieties of sucrose (Pictet and Vogel, A., 1928, 1223), as both of these yield I on acetylation, convertible into II by the above methods. It is considered that II is the stable and I the labile form.

H. A. PIGGOTT.

**Variation of optical properties of octa-acetylsucrose in presence of air.** L. DUPARC and R. GALOPIN (Helv. Chim. Acta, 1930, 13, 702—707).—Determinations by Federov's method of the angle between the optical axes ( $2V$ ) of freshly prepared and older crystals of octa-acetylsucrose show that this increases steadily, when the crystals are exposed to the air, to a value  $4^\circ$  above the original. The general crystalline form, however, does not alter. At the same time the refractive index, measured along the axes of symmetry, becomes very slightly less. It seems probable that exposure to the air is the determining factor, for the change in  $2V$  is less when the crystals are kept in a sealed flask, and zero when one is immersed in sodium silicate solution (in which the goniometric measurements are made) immediately after preparation.

H. A. PIGGOTT.

**Action of mercury salts on acetohalogeno-sugars. III. Synthesis of cellobiose octa-methyl ether.** G. ZEMPLÉN (Ber., 1930, 63, [B], 1820—1823).— $\beta$ -Methylheptamethylcellobioside is hydrolysed by hydrochloric acid, and the 2:3:6-trimethylglucose is converted into a mixture of  $\alpha$ - and  $\beta$ -2:3:6-trimethylmethylglucosides. The product is treated with acetobromoglucose in benzene in presence of mercuric acetate and the resulting material, after removal of mercury, is completely methylated and fractionally distilled. The fraction of higher b. p. is shown to be a mixture of  $\alpha$ - and  $\beta$ -heptamethylmethylcellobioside by its reducing power after hydrolysis and its behaviour towards hydrogen bromide in glacial acetic acid.

H. WREN.

**Synthesis of 2-glycerol- $\alpha$ -glucoside [ $\beta\beta'$ -dihydroxyisopropylglucoside].** N. M. CARTER (Ber., 1930, 63, [B], 1684—1688).—Acetobromoglucose and  $\alpha$ -benzylideneglycerol in presence of silver carbonate and anhydrous benzene afford  $\beta$ -tetra-acetylglucosido- $\alpha$ -benzylideneglycerol, m. p.  $133^\circ$  (corr.),  $[\alpha]_D^{20} -34.2^\circ$  in chloroform, hydrolysed by methylalcoholic ammonia to d- $\beta$ -glucosido- $\alpha$ -benzylideneglycerol, m. p.  $138^\circ$ ,  $[\alpha]_D^{20} -17.7^\circ$  in alcohol. Treatment with hydrogen in presence of spongy palladium converts the last-named compound into  $\beta\beta'$ -dihydroxyisopropylglucoside, m. p.  $166^\circ$  (corr.),  $[\alpha]_D^{20} -30.1^\circ$  in water. It does not reduce Fehling's solution and is readily hydrolysed by emulsin. The corresponding hexa-acetate has m. p.  $128^\circ$ ,  $[\alpha]_D^{20} -14.9^\circ$  in chloroform,  $[\alpha]_D^{20} -15.8^\circ$  in *s*-tetrachloroethane.  $\beta$ -Tetra-acetylglucosido- $\alpha$ -benzylideneglycerol is transformed by hydrogen and spongy palladium into  $\beta$ -tetra-acetylglucosidoglycerol, m. p.  $103^\circ$  (corr.),  $[\alpha]_D^{20} -22.1^\circ$  in water,  $+3.3^\circ$  in chloroform, converted by acetic anhydride and pyridine into the hexa-acetate.

H. WREN.

**Syntheses of glucosides. V. Two new syntheses of rubiadin and syntheses of 1-*O*-methylrubiadin and of rubiadin glucoside.** E. T. JONES and A. ROBERTSON (J.C.S., 1930, 1699—1709).—Phthalic anhydride and 2:6-dichlorotoluene in presence of aluminium chloride give 2:4-dichloro-3-methylbenzophenone-2'-carboxylic acid, m. p.  $144-145^\circ$ , which is cyclised by boric and sulphuric acids to 1:3-dichloro-2-methylanthraquinone, m. p.  $172^\circ$ . This, with methylalcoholic sodium methoxide, affords 1:3-dimethoxy-2-methylanthraquinone (*O*-dimethylrubiadin), m. p.  $158^\circ$ .

2-Nitro-6-methoxytoluene, m. p.  $52^\circ$ , is converted into 6-methoxy-*o*-toluidine (acetyl derivative, m. p.  $117^\circ$ ) and this, by diazotisation, into 6-methoxy-*o*-cresol, b. p.  $164-165^\circ/20$  mm., m. p.  $47^\circ$ . Phthalic anhydride reacts with the last compound in *s*-tetrachloroethane in presence of aluminium chloride to produce 2-hydroxy-4-methoxy-3-methylbenzophenone-2'-carboxylic acid, m. p.  $161-162^\circ$ , which undergoes ring-closure as above, forming 1-hydroxy-3-methoxy-2-methylanthraquinone (3-*O*-methylrubiadin), m. p.  $186^\circ$  (acetyl derivative, m. p.  $200^\circ$ ); methylation with methyl iodide and silver oxide in acetone gives the dimethyl ether, m. p.  $158^\circ$ . 3-*O*-Methylrubiadin with boracetic and acetic anhydrides yields the diacetoborate, whilst boiling with hydrobromic and acetic acids induces demethylation and production of 1:3-dihydroxy-2-methylanthraquinone (rubiadin), m. p.  $290^\circ$  (diacetoborate prepared as in the previous case; contact with water generates 3-*O*-acetyl-rubiadin, m. p.  $191^\circ$  after sintering at  $187^\circ$ ).

3-*O*-Acetyl-rubiadin, dissolved in acetone, is methylated with methyl iodide and silver oxide at  $100^\circ$ ; the product, treated with 5% methylalcoholic alkali at the ordinary temperature, affords 3-hydroxy-1-methoxy-2-methylanthraquinone (1-*O*-methylrubiadin), m. p.  $291^\circ$ .

Rubiadin condenses with *O*-tetra-acetyl- $\alpha$ -glucosidyl bromide in acetone and 2.8% aqueous sodium hydroxide to the tetra-acetylglucoside, m. p.  $230^\circ$ , which with pyridine and acetic anhydride at  $100^\circ$  yields the natural penta-acetyl compound. The above tetra-acetylglucoside with 5% aqueous sodium hydroxide and methyl alcohol gives 1-hydroxy-3- $\beta$ -glucosidoxy-2-methylanthraquinone (rubiadin glucoside), m. p.  $270-271^\circ$ , and with silver oxide and methyl iodide in acetone forms 3-*O*-tetra-acetyl- $\beta$ -glucosidoxy-1-methoxy-2-methylanthraquinone, m. p.  $185^\circ$ .

Dry "active" silver oxide, rubiadin, *O*-tetra-acetyl- $\alpha$ -glucosidyl bromide, and quinoline furnish 1:3-*O*-octa-acetyl- $\beta$ -diglucosidoxy-2-methylanthraquinone, m. p.  $248$ .

R. J. W. LE FÈVRE.

**Colorimetric determination of starch by means of iodine.** L. PALOHEIMO (Biochem. Z., 1930, 222, 150—172).—Details of the method are given and a table summarises a series of parallel determinations by the colorimetric and the polarimetric methods on a number of starches.

P. W. CLUTTERBUCK.

**Separation and properties of two main components of potato starch.** M. E. BALDWIN (J. Amer. Chem. Soc., 1930, 52, 2907—2919).—The outer envelope ( $\alpha$ -amylose) of the grains is separated from the contents ( $\beta$ -amylose) by gelatinisation, followed by

alternate freezing and extraction with water, the process being continued until the properties of the end fractions show no further changes. The temperature of gelatinisation, the time of freezing, and the temperature of extraction necessary to effect a sharp separation of the  $\alpha$ -component are  $85^\circ$ , 10 min.,  $15^\circ$ , and of the  $\beta$ -  $63^\circ$ , 10 min.,  $55$ – $60^\circ$ .  $\alpha$ -Amylose, dispersed in water at  $120^\circ$ , has  $[\alpha]_D^{20} +220.1$ – $1.23t^\circ$ . It contains 0.076% P, gives with iodine a reddish-violet colour, free from blue, is precipitated neither by alcohol in absence of electrolytes, nor by iodine, and does not separate from solution on keeping. It forms  $84 \pm 1\%$  of the original starch, the remainder within 1% being  $\beta$ -amylose. This has  $[\alpha]_D^{20} +191.9$ – $0.13t^\circ$  ( $t=20$ – $30^\circ$  in each case), contains traces only of phosphorus, gives with iodine a blue colour, free from violet, is precipitated by alcohol and iodine, and separates to the extent of 90–95% from solution on keeping (retrogradation). This change is hastened by previous heating of the solution. The great difference in the temperature coefficients of the rotations of the two components probably accounts for the divergent values previously recorded. The original starch has  $[\alpha]_D^{20} +214.2$ – $1.00t^\circ$ , but lower values are obtained if dispersions are heated above  $130^\circ$ .

H. E. F. NOTTON.

**Starch. I. Decomposition by concentrated hydrochloric acid.** R. WEIDENHAGEN and A. WOLF (Z. Ver. deut. Zucker-Ind., 1930, 80, 265–274).—Products having the characters of Pringsheim's amylobiose and amylotriose were obtained from amylose and amylopectin, respectively, by the action of cold concentrated hydrochloric acid as described by Pringsheim and others, and it was shown that they are not definite compounds. Their iodine-absorbing powers, like their cupric-reducing powers, are quite inconsistent with Pringsheim's formulae (cf. A., 1926, 715, etc.), and repeated alcoholic precipitation showed them to be mixtures containing some dextrose and a dextrinous fraction having mol. wt. 400–420 and reducing power 9–11% of that of maltose. Products of similar character were obtained by the action of cold concentrated hydrochloric acid on glycogen and on dextrose.

J. H. LANE.

**New degradation of cellulose. II.** H. PRINGSHEIM, G. OTTO, and J. R. KATZ (Cellulose-chem., 1930, 11, 137–139; cf. A., 1928, 1226).—Partial removal of acetyl groups during the degradation of cellulose acetate ("agfa") dissolved in chloroform containing a small quantity of benzenesulphonic acid depends on the presence of a small amount of ethyl alcohol. After refluxing for 48 hrs. the acetate, now water-soluble, is hydrolysed by aqueous ammonia. The polysaccharide consists of two fractions, one insoluble (A) and the other soluble (B) in water. In presence of 0.25% of benzenesulphonic acid preparation A is the chief product, but with 1% preparation B alone is obtained. Preparation A has a lower rotation than cellulose in ammoniacal copper solution, and its acetate, obtained by treatment with acetic anhydride and pyridine, has  $[\alpha]_D^{20}$  0° in chloroform. The Debye-Scherrer diagram of preparation A is identical with that of alkali-soluble cellulose (cellulose A of Hess) and with

that of the biosan of Hess and Friese (A., 1927, 44). For preparation B  $[\alpha]_D^{20}$  in water varies from  $+46^\circ$  to  $+85^\circ$ . It is not homogeneous, since fractions of varying rotation are obtained on precipitating an aqueous solution with alcohol. Cryoscopic determinations on two samples of preparation B dissolved in water gave mol. wts. 664 and 834.

T. H. MORTON.

**Swelling and acetylation of cellulose.** A. L. BERNOULLI, M. SCHENK, and W. HAGENBUCH (Helv. Chim. Acta, 1930, 13, 534–571).—From a study of the swelling of cellulose in alkaline solutions, the acetylation of cellulose with acetic acid and anhydride, and the inter-relation of these, it is concluded that there are three successive stages in the acetylation, viz.,  $C_{24}H_{39}O_{20}Ac$ , cellulose monoacetate ( $C_6H_9O_5Ac$ ), and triacetate ( $C_6H_9O_5Ac_3$ ). In general, however, the intermediate stages are not well-defined. In the case of viscose, the affinity for substantive dyes decreases as acetylation proceeds and disappears completely at 42–44% (as AcOH). This is also the point at which complete gelatinisation in acetic anhydride, and also the complete disappearance of swelling in water, occur. The disappearance of these properties as the triacetate stage is approached points to the need of a definite number of hydroxyl groups for their existence. The swelling of viscose in sodium hydroxide solution, determined by the direct measurement of individual threads, shows maxima at alkali concentrations of 0.5N, 2.75N, and 6N, that at 2.75N being the point of maximum swelling. By titration of the alkaline liquors after immersion of the fabric, the first two maxima were shown to correspond with the compounds ( $C_6H_{10}O_5$ )<sub>4</sub>.NaOH and ( $C_6H_{10}O_5$ )<sub>3</sub>.NaOH, but no evidence of the compound corresponding with the third maximum, viz.,  $C_6H_{10}O_5$ .NaOH (known to be formed by natural cellulose in concentrated alkali), was obtained. On the other hand, evidence of the transient formation of ( $C_6H_{10}O_5$ )<sub>6</sub>.NaOH, not indicated by the swelling curve, was obtained in 0.5N-sodium hydroxide when the time of reaction was reduced. A very similar curve is given by cuprammonium silk, but the third maximum was not observed.

Comparison of methods for the determination of the acetyl content of cellulose acetate favours the alkaline hydrolysis method of Torii (B., 1922, 367) as modified by Yarsley ("Celluloseacetate," p. 29). Natural cellulose (cotton wool) does not react readily with acetic anhydride and decomposition becomes marked when heating is prolonged. Nevertheless, some triacetate is formed with acetic anhydride at  $125^\circ$ , the curve showing ill-defined points of inflexion corresponding with  $C_{24}H_{39}O_{20}Ac$  and  $C_6H_9O_5Ac$ ; at the b. p. of the anhydride these intermediate stages are much better defined, but decomposition soon occurs. The end of the reaction at the first stage when acetic acid at its b. p. is used (cf. Malm and Clark, A., 1929, 299) is confirmed, as also is their statement that pre-treatment of the cellulose with either 18% or 40% sodium hydroxide allows the reaction to proceed to the monoacetate stage. The effect of such pre-treatment when acetic anhydride is used as the acetylating agent is that the first stage disappears completely with the more dilute alkali,

and the second also when the more concentrated alkali is used.

Viscose is slowly hydrolysed by heating with glacial acetic acid, becoming brittle and easily disintegrated, but this does not seem markedly to affect either the rate or the amount of acetylation. It reacts much more rapidly than does natural cellulose with the anhydride at 100°, and gives the triacetate, passing through the usual intermediate stages. Treatment with 2% and 10% sodium hydroxide solution increases the reactivity towards acetic anhydride to approximately the same extent as do the 18% and 40% alkaline solutions in the case of cotton; thus with the former the first, and with the latter the second, intermediate stage disappears completely. The action of acetic acid at 100°, contrary to Malm and Clark, gave no maximum corresponding with the first intermediate, the reaction proceeding towards the limit of the monoacetate, this limit being unchanged by previous alkali treatment. In the presence of sufficient anhydride to combine with the water set free, esterification becomes very rapid and proceeds to the triacetate; in this case the intermediate stages are less marked, but are undoubtedly present.

The ordinary technical acetylating agents, such as mixtures of acetic acid and anhydride with zinc chloride or sulphuric acid, are unable to penetrate the viscose fibre; consequently superficial action appears to occur, and leads to the triacetate or lower esters. Further examples of the similarity of pyridine and other organic bases to sodium hydroxide in their action on cellulose are given. Technical cellulose acetate is rapidly and completely converted by acetic anhydride in pyridine solution into the triacetate. This effect is not due to the solubilising or dispersing action, since acetone is without effect.

H. A. PIGGOTT.

**Cellulose sulphuric esters.** E. GEBAUER-FÜL-NEGG and O. DINGLER (J. Amer. Chem. Soc., 1930, 52, 2849—2854).—Cellulose regenerated from its trisulphuric ester (A., 1928, 1226) by hydrolysis for 6 hrs. with 5% methyl-alcoholic hydrochloric acid shows a slightly higher rotation in cuprammonium solution than the original material, but its triacetate and trimethyl ether are identical in rotation and solubility with those from pure cellulose. Accordingly, the cellulose units in the sulphuric ester can be, at most, only slightly degraded. The direct conversion of the ester into other derivatives could not be effected.

H. E. F. NOTTON.

**Degradation products of lignin soluble in water.** II. H. FRIESE (Ber., 1930, 63, [B], 1902—1910).—Wood meal is converted almost quantitatively within a few days into products soluble in water when treated with a mixture of acetic acid and acetic anhydride (1 : 1) containing 9—10 vol.-% of sulphuric acid. The mixture is diluted with chloroform and the lignin derivatives are removed by water without admixture of sugar acetates. The product has the mean composition C 38.7, H 4, S 10—14, OMe 6—9%. It is converted by barium carbonate into a barium salt which cannot be separated into differing portions by addition of alcohol to its aqueous solution. The

free acid yields end fractions containing C 55, H 5.85, S 2.55, OMe 13.5% or C 23.76, H 4.17, S 19.98, OMe 4.5%. With increasing proportion of carbon the solubility in water disappears. Products containing more than 40% C become completely insoluble after prolonged exposure to phosphoric oxide. When similarly treated, Freudenberg's lignin is found to contain carbohydrate acetates and to yield a product soluble in water containing C 49.29, H 4.57, S 10, OMe 8.5%, which does not become insoluble in water when intensively dried. The analysis agrees with that required by a dihydroxybenzenesulphonic acid of which one hydroxyl group is etherified by a dihydroxymethoxybenzene.

Treatment of pine meal with sulphoacetic acid in acetic anhydride causes only partial hydrolysis of the polysaccharides; sulphonation of the lignin or formation of a product soluble in water does not occur. Freudenberg's lignin and sulphoacetic acid do not give a product soluble in water, but a portion of the material is transformed into a yellow syrup free from sulphur and capable of acetylation.

Polyhydric phenols and their ethers are converted into sulphonic acids by a mixture of acetic acid and anhydride containing sulphuric acid; the tendency towards sulphonation is therefore greater than that towards the production of sulphoacetic acid. Phenolic derivatives with a side-chain behave similarly. If an aldehydic group is present, the nature of the reaction is changed; thus piperonal and vanillin afford dark-coloured condensation products. Cinnamaldehyde, however, gives a sulphonic acid.

H. WREN.

**$\alpha$ - and  $\beta$ -Lignosulphonic acids.** E. HÄGGLUND (Svensk Kem. Tidskr., 1930, 42, 159—166).— $\beta$ -Lignin is not pre-existent in pine wood, but  $\beta$ -lignosulphonic acid is produced from the  $\alpha$ -acid during the treatment with sodium hydrogen sulphite at high temperatures. The lignin obtained from a sulphite pulp by extraction with an acetate buffer of  $p_H$  4.3 contained 95% of the  $\alpha$ -acid. If, however, the extraction is performed with sodium hydrogen sulphite at 135° the content of  $\alpha$ -lignosulphonic acid falls to 84%, and under similar conditions, but with the addition of 2% of dextrose, to 61%. A similar passage of the  $\alpha$ - to the  $\beta$ -acid is observed when the initial material is a pure  $\alpha$ -lignosulphonic acid salted out from the filtrate from a sulphite extraction. The rôle of dextrose in the conversion is believed to lie in the reduction of an aldehydic group of the  $\alpha$ -acid to a primary alcoholic group of the  $\beta$ -acid, itself being oxidised to gluconic acid. It is suggested that the diminution of methoxyl content in the passage from the  $\alpha$ - to the  $\beta$ -acid is due to an oxidising action of the hydrogen sulphite, since the methoxyl content of the  $\alpha$ -acid was found to fall from 9.77% to 6.14% after treatment with 2% hydrogen peroxide solution for 12 hrs. at the ordinary temperature.

T. H. MORTON.

**N-Methylcadaverine.** R. ENGER (Z. physiol. Chem., 1930, 189, 239—242).— $\alpha$ -Benzamido- $\epsilon$ -methylaminopentane hydrochloride, m. p. 153°, is obtained by treating the product from  $\epsilon$ -benzamidoamyl iodide and alcoholic methylamine at 80°, with hydrochloric acid. Hydrolysis of the hydrochloride with 20%

sulphuric acid, extraction of the benzoic acid, treatment of the solution remaining with phosphotungstic acid, and decomposition of the precipitate with barium hydroxide affords,  $\alpha$ -amino- $\epsilon$ -methylaminopentane (N-methylcadaverine), b. p. 177—178° [chloroplatinate, m. p. 228°; chloroaurate (+H<sub>2</sub>O), m. p. about 61°, m. p. (anhydrous) 121—130°]. This base is not identical with the compound described by Garcia (A., 1893, i, 538). H. BURTON.

**Preparation of alkali salts of amino-acids.** W. VOSS and R. GUTTMANN (Ber., 1930, 63, [B], 1726—1731).—The preparation of homogeneous sodium salts of *dl*-leucine, *dl*-alanine, or glycine cannot be effected by use of the calculated quantity of sodium ethoxide in ethyl alcohol; the amino-nitrogen content is invariably low and reaction is accompanied by liberation of methylamine when glycine is employed. Sodium hydrogen *d*-glutamate may be prepared in small quantity from the acid and sodium hydroxide, but the prolongation of the desiccation necessitated by the use of larger amounts results in the production of sodium pyrrolidonecarboxylate. The sodium salts of monocarboxylic and the disodium compounds of dicarboxylic amino-acids are readily prepared by treating the acids in liquid ammonia with sodium in the same solvent; the end-point is indicated by the disappearance of the blue colour. The process is not available for the preparation of sodium hydrogen dicarboxylates, of salts of semiamides or of cystine. Monocarboxylic acids are indifferent towards liquid ammonia, whereas dicarboxylic acids afford ammonium hydrogen salts (ammonium hydrogen *L*-aspartate and *d*-glutamate are described). The sodium salts of the following acids have been prepared: glycine, *dl*-alanine, *dl*-leucine, *dl*-phenylalanine, sarcosine, *L*-tyrosine,  $\beta$ -alanine,  $\gamma$ -amino-*n*-butyric acid, *d*-glutamic acid. H. WREN.

**Quinizarinsulphonic acid (rufanic acid) as precipitant.** II. W. ZIMMERMANN (Z. physiol. Chem., 1930, 189, 155—161; cf. this vol., 941).—A further series of precipitates with bases was obtained, viz., *rufanates* of sarcosine, m. p. 283—285° (decomp.); proline, m. p. 256° (froths); oxyproline, m. p. 292° (froths);  $\delta$ -aminovaleric acid, decomp. 287°; dimethylamine, m. p. 255—256°; trimethylamine oxide, m. p. 276—277° (froths); pyramine, m. p. 287—288° (froths). These salts were prepared by using a 4% solution of rufanic acid in absolute alcohol, since they are soluble in water.

J. H. BIRKINSHAW.

**Catalysis of the oxidative decomposition of glycine by oxidation products ("omega") of adrenaline.** B. KISCH and J. LIEBOWITZ (Biochem. Z., 1930, 220, 370—377).—The results of Edlbacher and Kraus (A., 1928, 1403) are confirmed, but it is shown that the decomposition of the glycine is catalysed by oxidation products ("omega") of adrenaline which are gradually converted into catalytically inactive substances. Adrenaline itself has no effect on the oxidation. The catalytic action of the adrenaline decomposition products, for which the optimum reaction is  $pH$  7.7—7.8, does not take place in the absence of oxygen. Adrenalone is much

less effective than is adrenaline for assisting the decomposition of glycine (cf. this vol., 1036).

W. MCCARTNEY.

**Deamination of cystine.** J. C. ANDREWS (J. Biol. Chem., 1930, 87, 681—690).—Further experiments confirm the outstanding effect of lead salts (A., 1929, 85) in promoting the deamination of cystine in alkaline solution at 100°. The most rapid deamination occurred in suspensions of excess of calcium hydroxide; the accelerating effect of lead salts on the deamination process was observed with suboptimal amounts of calcium hydroxide but disappeared when the optimum concentration of the latter was reached. Barium hydroxide caused less deamination than calcium hydroxide; the effect of magnesium oxide was slight and that of silver oxide negligible. Cysteine undergoes considerably less deamination than cystine under similar conditions.

C. R. HARRINGTON.

**Mechanism of cyanoacetamide and cyanoacetic ester condensations.** C. K. INGOLD (J.C.S., 1930, 184—185).—A reply to Bardhan (A., 1929, 1462). It is not justifiable to assume that carbon coupling at C<sub>a</sub> (carbonyl carbon) is the general mode of reaction between cyanoacetamide and allied substances and  $\alpha\gamma$ -dicarbonyl compounds. H. WREN.

**Mechanism of cyanoacetamide and cyanoacetic ester condensations.** J. C. BARDHAN (J.C.S., 1930, 1509—1510).—Polemical (cf. Ingold, preceding abstract). The possibility of the existence of two enolic forms of hydroxymethylencyclohexanone, one of which involves an intracyclic double linking, is pointed out.

H. A. PIGGOTT.

**$\alpha$ -Selenocyanoacrylic acid.** A. FREDGA (Svensk Kem. Tidskr., 1930, 42, 153—156).—Treatment of potassium  $\alpha\beta$ -dibromopropionate (1 mol.) with potassium selenocyanide (1 mol.) gave potassium  $\alpha$ -selenocyanoacrylate (+H<sub>2</sub>O), decomposed by sulphuric acid in ether to  $\alpha$ -selenocyanoacrylic acid, m. p. 105° (decomp.). The dissociation constant  $K_1 = 1.27 \times 10^{-2}$ ,  $\mu_0 = 369$  being assumed; slight decomposition in contact with the platinum electrodes was observed. Potassium  $\alpha$ -bromoacrylate does not react with potassium selenocyanide at the ordinary temperature.

A. I. VOGEL.

**Action of potassium hypobromite on some  $\alpha$ -trisubstituted amides.** (MILE.) M. MONTAGNE and B. CASTERAN (Compt. rend., 1930, 191, 139—141).—When treated with potassium hypobromite solution  $\alpha$ -trisubstituted amides form stable, ether-soluble carbimides which are converted quantitatively into the hydrochlorides of the primary amines on treatment with hydrochloric acid. Dimethylpropylacetamide yields  $\alpha\alpha$ -dimethylbutylcarbimide, b. p. 136—137°; ethyldibutylacetamide yields  $\epsilon$ -carbimido- $\epsilon$ -ethylnonane, which gives with aniline phenyl- $\epsilon$ -ethylnonylcarbamide, m. p. 94°;  $\gamma$ -carbimido- $\gamma$ -phenylpentane, b. p. 115°/13 mm., gives with ammonia  $\gamma$ -phenylamylcarbamide, m. p. 136°, and with aniline phenyl- $\gamma$ -phenylamylcarbamide, m. p. 197°; hydrolysis with hydrochloric acid solution furnishes  $\gamma$ -amino- $\gamma$ -phenylpentane, b. p. 108.5—109°/17 mm. (picrate, m. p. 166—167°; chloroaurate, m. p. 83°), which yields with the carbimide *s-di*- $\gamma$ -phenylamyl-



carbamide, m. p. 203°.  $\alpha$ -Phenyl- $\alpha$ -benzylpropylcarbamide, b. p. 187.5°/17 mm., with aniline furnishes N-phenyl-N'-phenylbenzylpropylcarbamide, m. p. 179°; with hydrochloric acid it gives  $\beta$ -amino- $\alpha\beta$ -diphenylbutane, b. p. 187°/18 mm. (picrate, m. p. 162—163°), which reacts with the carbimide to give s-di-( $\alpha$ -phenyl- $\alpha$ -benzylpropyl)carbamide, m. p. 179°.

C. C. N. VASS.

Arylamides of lævulic acid. R. LUKEŠ and V. PRELOG (Chem. Listy, 1930, 24, 251—253).—See A., 1929, 824.

#### Preparation of allophanic esters and amides.

Action of heat. J. BOUGAULT and J. LEBOUCC (Bull. Soc. chim., 1930, [iv], 47, 594—605, and J. Pharm. Chim., 1930, [viii], 11, 5—20).—The following allophanic esters and amides have been obtained in yields of about 70% by the action of allophanic chloride on the corresponding alcohol or amine in benzene: ethyl, m. p. 195°; benzyl, m. p. 191.5°; phenyl, m. p. 194°;  $\beta$ -phenylethyl, m. p. 197.5°; guaiacyl, m. p. 200°; and o-ethoxyphenyl, m. p. 212°; allophanates: isoamyl, m. p. 118°; benzyl, m. p. 183°; phenyl, m. p. 168°; p-chlorophenyl, m. p. 212°; o-tolyl, m. p. 180°; m-tolyl, m. p. 165°; p-tolyl, m. p. 215°;  $\alpha$ -naphthyl, m. p. 259°;  $\beta$ -naphthyl, m. p. 230°; cyclohexyl, m. p. 195°; N-methylphenyl, m. p. 168°; amides, and the phenylhydrazide, NPh-NH-CO-NH-CO-NH<sub>2</sub>, m. p. 217°. The allophanic esters decompose slightly above their m. p. either into the alcohol and cyanuric acid, or into the corresponding olefine and carbamide and carbon dioxide, the aryl esters decomposing more rapidly into the phenol and cyanuric acid. Under the same conditions the allophanic amides derived from primary or secondary amines yield cyanuric acid and the monosubstituted carbamide as the first stage, the  $\alpha$ -disubstituted carbamide being formed as a second stage by reaction between the amide and the monosubstituted carbamide. The hydrazides yield ammonia and, by cyclisation of the side-chain, the corresponding monosubstituted urazole. Thus the phenylhydrazide yields phenylurazole, m. p. 267°, but no cyanuric acid.

R. BRIGHTMAN.

Constitution of compounds with "bivalent" carbon. H. LINDEMANN and L. WIEGREBE (Ber., 1930, 63, [B], 1650—1657).—A large amount of recorded evidence leads to the formula  $C\equiv O$  as the most suitable expression for carbon monoxide, although the help of the parachor cannot be utilised in this case on account of the strong association of the liquid material. In the examination of the possibility of extending this formulation to the carbylamines, this difficulty is not encountered, since o-anisylcarbamine is not appreciably associated when liquid. Determination of the parachor value of methyl, phenyl, o- and p-tolyl, o-anisyl, b. p. 112°/16 mm., and p-anisyl, b. p. 113°/14 mm., m. p. 33°, carbylamines establishes the structure  $C\equiv NR$ .

H. WREN.

Constitution of cyanogen halides. II. Refractometric investigation of cyanogen chloride and iodide. E. V. ZAPPI (Bull. Soc. chim., 1930,

[iv], 47, 537—545).—Determinations of the molecular refraction of solutions of cyanogen chloride and iodide in water, alcohol, and chloroform confirm the evidence previously adduced (this vol., 1027) in support of a nitrile structure for the iodide and a carbylamine structure for the chloride. The values obtained for cyanogen iodide are much lower than those required for Gutmann's cyclic structure (A., 1909, i, 895) and the latter formula is rejected. The solvent has little tautomeric influence on the cyanogen halide.

R. BRIGHTMAN.

Germanium. XXXIV. Germanium trimethyl bromide. L. M. DENNIS and W. I. PATNODE (J. Amer. Chem. Soc., 1930, 52, 2779—2782).—Germanium trimethyl bromide, m. p. -25°,  $d_4^{25}$  1.544,  $n_D^{25}$  1.4705, was prepared by the interaction of hydrogen bromide and germanium tetramethyl in the presence of aluminium chloride. The vapour pressure between -25° and 120° is given by  $\log p(\text{mm.}) = 7.912 - 1956/T$ , from which the b. p. 113.7° is computed. The compound is oxidisable, yields an amine with dry ammonia, and is hydrolysed to a volatile liquid by water, but hydrogen sulphide does not precipitate germanium disulphide from the acidified solution.

J. G. A. GRIFFITHS.

Application of thallium compounds in organic chemistry. V. Thallous ethoxide and dimethylthallium ethoxide. R. C. MENZIES (J.C.S., 1930, 1571—1573).—Gentle warming of aqueous formaldehyde ( $d_4^{20}$  1.084) with thallous oxide produces thallous formate, m. p. 103—104°, in 89% yield. Treatment of crude moist thallous hydroxide, formed from the formate by hydrolysis with hot aqueous sodium hydroxide, with absolute alcohol at 20° gives thallous ethoxide in 76% yield (slightly better yields are obtained by treatment of thallous formate with a solution of sodium in absolute alcohol). This substance reacts with dimethylthallium bromide in boiling ether, producing dimethylthallium ethoxide, b. p. 110—120°/15 mm.

Thallous ethoxide is a convenient intermediate for the preparation of chelate compounds of thallium; e.g., thallium acetylacetonate is prepared in 90% yield by mixing solutions of the ethoxide and acetylacetone in dry benzene. Thallous ethoxide is as delicate a reagent for carbon disulphide and certain other sulphur compounds in benzene solution, as also is the acetylacetonate, yellowish-orange precipitates being obtained. No precipitate is obtained with thiophen.

R. J. W. LE FÈVRE.

Organo-mercuric nitrates. Method of analysis for mercury applicable to dilute solutions. I. B. JOHNS, W. D. PETERSON, and R. M. HIXON (J. Amer. Chem. Soc., 1930, 52, 2820—2822).—Mercuric methyl, m. p. 59°, ethyl, m. p. 87°, butyl, m. p. 39.5—40°, and benzyl, m. p. 90—91° (decomp.), nitrates are obtained from the mercuric alkyl halides and silver nitrate in alcohol. The last two decompose slowly when kept. The mercury in mercuric alkyl salts may be determined as sulphide after decomposition of the salt by bromine in dilute aqueous solution.

H. E. F. NOTTON.

Spectroscopic determination of decomposition products of organic compounds. Benzene in

the electrodeless discharge. W. D. HARKINS and D. M. GANS (J. Amer. Chem. Soc., 1930, 52, 2578—2580).—By maintaining anhydrous benzene vapour at about 0.1 mm. in the electrodeless discharge (1000 kilocycles per sec.) an extensive green or red glow is produced. The benzene is rapidly decomposed into the entities  $C_2$ , CH,  $C^+$ , and H, which recombine quantitatively to form a reddish-brown powder,  $(CH)_n$ , where  $n$  is much greater than 6.

J. G. A. GRIFFITHS.

**Physical constants of *p*-cymene and certain related compounds.** F. RICHTER and W. WOLFF (Ber., 1930, 63, [B], 1721—1725).—*p*-Cymene has been obtained from ajowan oil, camphor (by phosphoric oxide), and sulphite turpentine. The crude material is treated with permanganate, concentrated sulphuric acid, occasionally with bromine, and distilled over sodium until constant in properties. The isolation of a homogeneous material from ajowan oil appears impossible. The product from camphor contains toluene, after the removal of which pure *p*-cymene, m. p.  $-72.3^\circ$ , b. p.  $177.3-177.4^\circ/760$  mm.,  $d_4^{20}$  0.8570,  $n_D^{20}$  1.4904, is obtained. The material from sulphite turpentine is almost identical with it, but the indistinct m. p. indicates the presence of impurities. *m*-Cymene, obtained from *d*-fenchone and phosphoric oxide, has b. p.  $175.6-175.8^\circ/760$  mm., b. p.  $66.5^\circ/17.6$  mm., m. p. below  $-100^\circ$  to a non-crystalline glass,  $d_4^{20}$  0.8606,  $n_D^{20}$  1.4920. Dipentene from terpinol is mixed with terpinolene. A mixture of *d*-limonene, b. p.  $177.6-177.8^\circ/755$  mm.,  $64.4^\circ/15$  mm.,  $n_D^{20}$  1.473,  $[\alpha]_D^{20} +124^\circ$ , with molecular proportions of *l*-limonene, b. p.  $177.6-177.8^\circ/755$  mm.,  $64.4^\circ/15$  mm.,  $d_4^{20}$  0.8472,  $n_D^{20}$  1.4740,  $[\alpha]_D^{20} -121^\circ$ , yields dipentene, b. p.  $178^\circ/760$  mm.,  $64.4^\circ/15$  mm.,  $n_D^{20}$  1.4727, after fractional distillation. H. WREN.

**Action of sodium on organic halides in liquid ammonia.** P. M. DEAN and G. BERTHET (J. Amer. Chem. Soc., 1930, 52, 2823—2826).—The halides were treated with sufficient sodium for complete reaction. Eight among the thirteen halides examined reacted to some extent in the sense of the Würtz-Fittig synthesis. Benzyl chloride gives mainly dibenzyl, with toluene and hydrocarbons, (a) m. p.  $183-184^\circ$ , (b) b. p.  $200-240^\circ/10$  mm., and (c) b. p.  $240-270^\circ/10$  mm.  $\beta$ -Phenylethyl bromide gives mainly ethylbenzene with hydrocarbons of high b. p. and a little styrene;  $\gamma$ -phenylpropyl bromide gives propylbenzene, phenylpropylamine, hydrocarbons of high b. p., and nitrogenous products;  $\delta$ -phenylbutyl bromide gives butylbenzene, phenylbutylamine, hydrocarbons, and amines; benzylidene chloride gives mainly benzylamine with dibenzyl and a product of high b. p.; benzotrichloride gives tarry material and some dibenzyl; diphenylmethyl chloride gives *s*-tetraphenylethane and diphenylmethane; diphenylmethyle chloride gives tetraphenylethylene (yield 90% of the theoretical); *o*-xylene bromide gives *o*-xylene and a nitrogenous residue; phenyl  $\beta$ -bromoethyl ether gives phenol and  $\alpha\delta$ -diphenoxybutane; phenyl  $\gamma$ -bromopropyl ether gives phenoxypropane, phenol, and  $\alpha\delta$ -diphenoxyhexane;  $\alpha$ -chloroacetophenone gives acetophenone, a substance, m. p.  $73-74^\circ$ , and tarry matter, and  $\beta$ -chloropropiophenone gives a product of high b. p.

Benzoylchloride and liquid ammonia give a quantitative yield of benzamide. H. E. F. NOTTON.

**Decomposition of phenyl iodide dichloride.** II. E. V. ZAPPI and V. DEULOFEU (Bull. Soc. chim., 1930, [iv], 47, 612—614).—See this vol., 758.

**Substitution of one atom of nitrogen for three of chlorine in organic compounds. I. Action of ammonium chloride on benzotrichloride.** P. FIREMAN (J. Amer. Chem. Soc., 1930, 52, 2951—2954).—Ammonium chloride (1 mol.) reacts completely in 20—30 hrs. with benzotrichloride (1.6 mols.) in a sealed tube at  $210-220^\circ$ , heating being discontinued every 4—6 hrs. to permit the release of hydrogen chloride. The reaction is autocatalytic and the product is mainly benzonitrile with unchanged benzotrichloride and small quantities of cyaphenine, benzoic acid, and tetraphenylmethane. Analogous reactions are cited (cf. A., 1904, ii, 656). H. E. F. NOTTON.

**Behaviour of  $\alpha$ -bromo- $\alpha$ -nitrohydrocarbons.** II. Behaviour of  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -phenylethylene. J. LOEVENICH and H. GERBER (Ber., 1930, 63, [B], 1707—1713; cf. this vol., 572).— $\alpha$ -Bromo- and  $\alpha$ -bromo- $\alpha$ -nitro-styrene add positive groups in the same manner as the bromonitro-olefines. In consequence of the absence of the strongly negative nitro-group, the additive power of  $\alpha$ -bromostyrene is smaller than that of  $\alpha$ -bromo- $\alpha$ -nitrostyrene. The last-named compound exceeds the bromonitro-olefines in its power of adding positive groups and yields markedly more stable additive products.

$\alpha$ -Bromo- $\alpha$ -nitro- $\beta$ -phenylethylene is converted by ammonia in ether into the ammonium salt of  $\alpha$ -bromo- $\alpha$ -nitro- $\beta$ -amino- $\beta$ -phenylethane, from which the somewhat unstable free amine, m. p.  $32^\circ$  (hydrochloride), is derived.  $\alpha$ -Bromo- $\alpha$ -nitro- $\beta$ -piperidino- $\beta$ -phenylethane, m. p.  $73^\circ$  (hydrochloride; piperidinium salt, m. p.  $81^\circ$ ), is similarly prepared.  $\alpha$ -Bromo- $\alpha$ -nitro- $\beta$ -phenylethylene is transformed by aniline in ether into  $\alpha$ -nitro- $\beta$ -phenylacetylene, also obtained by use of diethylamine.

$\omega$ -Bromostyrene is converted by methyl-alcoholic sodium methoxide into phenylacetylene and styryl methyl ether, b. p.  $158^\circ/113$  mm. With ammonia in ether,  $\omega$ -bromostyrene affords  $\alpha$ -bromo- $\beta$ -amino- $\beta$ -phenylethane (hydrochloride, m. p.  $151^\circ$ ).  $\alpha$ -Bromo- $\beta$ -piperidino- $\beta$ -phenylethane (hydrochloride, m. p.  $198^\circ$ ) and  $\alpha$ -bromo- $\beta$ -anilino- $\beta$ -phenylethane, b. p.  $170^\circ/13$  mm., are described. H. WREN.

**Action of organo-magnesium compounds on sulphonyl chlorides.** R. TRUCHET (Compt. rend., 1930, 191, 296—299).—The main products of the action of magnesium ethyl bromide on benzene-sulphonyl chloride are ethyl chloride and benzene-sulphinic acid; phenyl ethyl sulphide and sulphoxide are produced in minor amount. Similar results are obtained with magnesium methyl iodide. Sulphones do not appear to be produced. The formation of sulphoxide is due to the action of the Grignard reagent on the sulphinate:  $Ar\cdot SO_2\cdot MgX + RMgX \rightarrow Ar\cdot SR(OMgX)_2 \rightarrow Ar\cdot SO\cdot R + MgO\cdot MgX_2$ . H. WREN.

Reactivity of halogens in various types of naphthalene derivatives. II. J. B. SHOESMITH and A. MACKIE (J.C.S., 1930, 1584—1586).—1-Chloro-2-methylnaphthalene with bromine vapour at 200° gives 1-chloro-2-naphthylmethyl bromide (I), m. p. 81°. 2-Hydroxy-1-naphthaldehyde, by heating with phosphorus pentachloride at 165°, followed by boiling with 100% formic acid etc., affords 2-chloro-1-naphthaldehyde, m. p. 75°, in poor yield; by reduction with 66% aqueous-alcoholic potassium hydroxide at 76°, this yields 2-chloro-1-naphthylcarbinol, m. p. 110°, from which 2-chloro-1-naphthylmethyl bromide (II), m. p. 100–5°, is prepared normally.

Reduction of 3-chloro-2-naphthoyl chloride by hydrogen in presence of palladised barium sulphate in xylene produces 3-chloro-2-naphthaldehyde, m. p. 121° (oxime, m. p. 152°; p-nitrophenylhydrazone, m. p. 263°; semicarbazone, m. p. 268°), from which 3-chloro-2-naphthylcarbinol, m. p. 111°, and 3-chloro-2-naphthylmethyl bromide (III), m. p. 97°, are obtained as above.

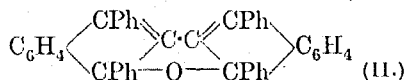
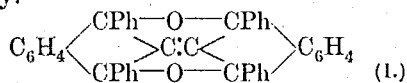
Comparative hydrolysis of bromides I, II, and III in aqueous alcohol at 25° showed values of  $k$  ( $\times 10^6$ ) of 72, 80, 70, respectively. R. J. W. LE FÈVRE.

Heteronuclear nitro- and amino-derivatives of 2-methylnaphthalene. V. VESELÝ and J. PÁČ (Coll. Czech. Chem. Comm., 1930, 2, 471—485).—2-Methylnaphthalene, dissolved in carbon tetrachloride, is condensed below  $-5^\circ$  with 1 mol. of chlorosulphonic acid. After neutralisation with barium carbonate the less soluble barium salt of 2-methylnaphthalene-8-sulphonic acid crystallises, whilst from the mother-liquor a smaller quantity of the salt of the 1-sulphonic acid is obtained. The potassium salts of these acids with 10 mols. of phosphorus pentachloride yield 2-methylnaphthalene-8-sulphonyl chloride, m. p. 96° (8-sulphonamide, m. p. 195—196°; cf. Dziewoński and Wulfsohn, A., 1929, 803), and -1-sulphonyl chloride, m. p. 83—85° (1-sulphonamide, m. p. 124°). Nitration of the 1-sulphonyl chloride below 0° with nitric acid ( $d$  1.475) furnishes a mixture of 8-nitro-, m. p. 145°, and 5-nitro-2-methylnaphthalene-1-sulphonyl chloride, m. p. 84—85°, which are reduced by sodium sulphite and sodium hydrogen carbonate at 40—60° to the corresponding sulphonic acids, from which are obtained, by treatment with 60% sulphuric acid, 8-nitro-, m. p. 36—38° (I), and 5-nitro-2-methylnaphthalene, m. p. 61—62° (II). Hydrolysis of the sulphonyl chlorides with dilute sodium hydroxide solution furnishes the sodium salts of 5-nitro- and 8-nitro-2-methylnaphthalene-1-sulphonic acid, which may be reduced by iron and acetic acid to 5-amino- and 8-amino-2-methylnaphthalene-1-sulphonic acid. Further reduction by sodium amalgam in a slightly alkaline aqueous medium affords 7-methyl- $\alpha$ -naphthylamine, m. p. 57—58° [acetyl derivative, m. p. 181—183° (III)]; benzoyl derivative, m. p. 204°; cf. Veselý and Kapp, A., 1925, i, 246, 804], and 6-methyl- $\alpha$ -naphthylamine, m. p. 90° [acetyl derivative, m. p. 160—161° (IV)], which also result from the reduction of I and II with iron and dilute hydrochloric acid. A solution of III in glacial acetic acid may be nitrated at 0° by the addition of a mixture of acetic acid and fuming nitric acid ( $d$  1.52). Recrystallisation of the product from

ethyl acetate affords 5-nitro-8-acetamido-2-methylnaphthalene, m. p. 229—230°. The second isomeride cannot be recovered from the mother-liquors by fractional crystallisation, but partial hydrolysis with alcoholic potassium hydroxide serves to convert most of the 5-nitro-compound into the amine, leaving unchanged 7-nitro-8-acetamido-2-methylnaphthalene, m. p. 219—220°. Hydrolysis of these latter with alcoholic potassium hydroxide and 60% sulphuric acid respectively yields 4-nitro-, m. p. 183°, and 2-nitro-7-methyl- $\alpha$ -naphthylamine, m. p. 185° (V). From these there are obtained by diazotisation and decomposition with boiling alcohol 5-nitro- and 7-nitro-2-methylnaphthalene, m. p. 105°, which may be reduced to 5-amino- and 7-amino-2-methylnaphthalene, m. p. 105° (acetyl derivative, m. p. 152°), by iron and dilute hydrochloric acid. Nitration of 5-nitro-2-methylnaphthalene dissolved in acetic acid with a mixture of nitric ( $d$  1.52) and sulphuric acids gives 1:5-dinitro-2-methylnaphthalene, m. p. 134° (cf. Veselý and Kapp, *loc. cit.*). Reduction of V by means of stannous chloride and alcoholic hydrochloric acid affords 7:8-diamino-2-methylnaphthalene, m. p. 80—81°, which reacts with phenanthraquinone, alcohol, and acetic acid to give 2-methylnaphthalene-7:8-phenanthrazine, m. p. 295°. The nitration of IV proceeds in a manner similar to that of III. Fractional crystallisation from ethyl acetate and alcohol affords 8-nitro-, m. p. 202°, and 6-nitro-5-acetamido-2-methylnaphthalene, m. p. 210—211°, which when hydrolysed with dilute sulphuric acid yield 4-nitro-, m. p. 167—169°, and 2-nitro-6-methyl- $\alpha$ -naphthylamine, m. p. 171°. Diazotisation and decomposition with alcohol transforms these compounds into 8-nitro- and 6-nitro-2-methylnaphthalene, m. p. 119° (VI). Nitration of 8-nitro-2-methylnaphthalene with a mixture of nitric ( $d$  1.52) and sulphuric acids affords 1:8-dinitro-2-methylnaphthalene (Veselý and Rein, A., 1927, 757), whilst reduction of the same substance with iron and hydrochloric acid yields 6-methyl- $\alpha$ -naphthylamine. If, however, the reduction is carried out with stannous chloride and hydrochloric acid, there is formed a substance, m. p. 86° (acetyl derivative, m. p. 191°), which is probably the methylnaphthylamine chlorinated in the naphthalene ring. Reduction of VI with iron and acetic acid produces the corresponding amine identical with that of Veselý and Kapp (*loc. cit.*). T. H. MORTON.

Dissociable organic oxides; transformation of rubrene into isorubrene oxide, a non-dissociable isomeride. C. DUFRAISSE and M. BADOCHÉ (Compt. rend., 1930, 191, 104—107).—Rubrene oxide undergoes a complex reaction when treated with an organo-magnesium halide to give, amongst other products, isorubrene oxide,  $C_{42}H_{28}O_2$ , m. p. 267—268, b. p. 280°/0.001 mm. ( $+C_6H_6$ , m. p. 167—168°), more readily obtained (88% yield) from the oxide by treatment with an ethereal solution of magnesium iodide. The new substance gives no trace of oxygen when heated and is exceptionally stable to heat. It does not react immediately with the Grignard reagent, and gives no methane with magnesium methyl iodide. It is inert towards the usual ketonic reagents, and the structures I and II are therefore

suggested for *isorubrene* oxide and *metarubrene*, respectively.



C. W. SHOPPEE.

**Rearrangement of *N*-chloroacetanilide.** C. D. BARNES and C. W. PORTER (J. Amer. Chem. Soc., 1930, 52, 2973—2976).—The rearrangement of *N*-chloroacetanilide in presence of constant hydrogen- and chlorine-ion concentrations at 40° has been followed in 0.05*M*-sodium acetate in glacial acetic acid saturated with sodium chloride. It is a first-order reaction. The view of Soper (A., 1927, 837) that the maximum reaction rate attainable by addition of acetanilide to the solution is a measure of the rate of liberation of chlorine from the chloroamine appears to be contradicted by the fact that acet- $\beta$ -naphthylamide produces a higher maximum rate than acetanilide. Further, addition of chlorine, which should have an effect similar to that of acetanilide, produces a quite different result. At first the reaction proceeds at the uncatalysed rate, then follows a period of rapid change during which the chlorine is used up, and afterwards the rate reverts to that of the first period. This indicates that chlorine does not act on the chloroamine, but only on its rearrangement products.

H. E. F. NOTTON.

**Rearrangement of alkylanilines. II. Course of the rearrangement in presence of metallic salts.** W. J. HICKINBOTTOM and (in part) A. C. WAINE. **III. Formation of *p*-aminoisobutylbenzene and *p*-amino-*tert*-butylbenzene from isobutylaniline.** W. J. HICKINBOTTOM and G. H. PRESTON (J.C.S., 1930, 1558—1565, 1566—1571).—II. The conversion of the alkylanilines into *p*-aminoalkylbenzenes which is known to occur on heating with anhydrous metallic halides, *e.g.*, cobalt, cadmium, or zinc chlorides or bromides, proceeds normally in a stream of nitrogen (Et, Pr<sup>1</sup>, and Pr<sup>2</sup>) or under reduced pressure (Et, Bu<sup>1</sup>). In some cases partial or complete elimination of the alkyl group occurs; thus with isopropylaniline much aniline is produced, and ethyl-*m*-4-xylidine gives only *m*-4-xylidine. Nevertheless in these cases the course of the reaction is not changed by heating in a rapid stream of nitrogen or in a sealed tube, respectively. *N*-Ethylacetanilide, in which the acetyl group is more sensitive than is the ethyl group to acid hydrolysis, when heated with cobalt chloride in nitrogen gives as principal product not ethylaniline, but *p*-acetamidoethylbenzene, together with primary amines and (probably) *p*-ethylaminoacetophenone. In no case is any appreciable internal isomerisation of the alkyl group observed. It is concluded, therefore, that the reaction occurs neither by elimination of the alkyl group as olefine followed by recombination in the *p*-position nor by formation of the amine hydrohalide and its dissociation to give alkyl halide or olefine; in fact it is not dependent on the formation of a volatile product, but is a true isomerisation. The following are described: *p*-amino-*n*-

*propylbenzene* zincichloride and cobaltobromide; *p*-toluenesulphonamido-*n*-propylbenzene, m. p. 113—114°; *p*-*n*-propyldiphenylthiocarbamide, m. p. 127—128°.

III. *iso*Butylaniline hydrobromide, when heated in a sealed tube at 220—300°, is converted into *p*-amino-*tert*-butylbenzene (*p*-toluenesulphonyl derivative, m. p. 179—180°; *p*-*tert*-butyldiphenylthiocarbamide, m. p. 156—157°) in good yield. The yield is smaller, and the product contaminated with other primary amines when the hydrochloride is used; much aniline is produced when the hydrobromide is heated with cadmium or zinc bromides. This instance of isomerisation of an alkyl group during migration from nitrogen to carbon appears to be unique in the benzene series.

When *isobutylaniline* itself is heated at 210—300° in the presence of zinc, cobalt, or cadmium halides, the sole product is *p*-aminoisobutylbenzene, b. p. 235—236°/762 mm. (uncorr.) (hydrochloride; hydrobromide; *p*-toluenesulphonyl derivative, m. p. 136—137°; *p*-isobutyldiphenylthiocarbamide, m. p. 130—131°; acetyl derivative, m. p. 127—128°), identified by conversion into isobutylchlorobenzene, oxidised to *p*-chlorobenzoic acid, and by its non-identity with the other known *p*-aminobutylbenzenes. The substance previously described as *p*-aminoisobutylbenzene (cf. Studer, Annalen, 1882, 211, 236; Lloyd, A., 1887, 721) appears to be *p*-amino-*tert*-butylbenzene (cf. Senkowski, A., 1892, 44). The production of isomeric amines by the two methods is conclusive evidence against the intermediate formation of amine hydrochloride during the isomerisation of the alkylanilines in the presence of metallic halides.

H. A. PIGGOTT.

**Composition of residual tar after distilling  $\alpha$ -naphthylamine in a vacuum.** V. A. LENKHOLO and E. A. OSTROUMOV (J. Chem. Ind., Russia, 1929, 6, 216—219).—The residue contained 6% of naphthylamine, together with 1:5-naphthylenediamine,  $\alpha$ -naphthol (0.12%),  $\beta$ -naphthol (0.20%), iron oxides, and oil.

CHEMICAL ABSTRACTS.

**Formation of  $\beta$ -naphthylamine by nitrating naphthalene and reducing.** V. A. LENKHOLO (J. Chem. Ind., Russia, 1929, 6, 805).—The  $\alpha$ -naphthylamine contains a small quantity of the  $\beta$ -isomeride.

CHEMICAL ABSTRACTS.

**Preparation of naphthionic acid.** S. LANGGUTH (Chim. et Ind., 1930, 24, 31—32).— $\alpha$ -Naphthylamine sulphate, prepared from 2 pts. of the base and 1.57 pts. of sulphuric acid, is mixed with 6.5 pts. of sodium sulphate and heated at 200—210° during 35 min. after being raised to 200° during the same length of time. The mixture is stirred and a current of carbon dioxide passed into the reaction vessel. The reaction product is freed from sodium sulphate by boiling with water (25 pts.), cooling, and filtering. The residue is dissolved in sodium carbonate solution (0.67 pt. of carbonate; 15 pts. of water), the solution made slightly acid, and then treated with diazotised benzidine to remove free naphthylamine. The colouring matter formed is filtered and the naphthionic acid (yield 70%) precipitated.

H. BURTON.

**Identification of carbonyl compounds by use of 2:4-dinitrophenylhydrazine.** C. F. H. ALLEN (J. Amer. Chem. Soc., 1930, 52, 2955—2959).—An im-

proved method of preparation is given for this hydrazine from hydrazine sulphate and chloro-2:4-dinitrobenzene. The extent of its applicability to the identification of aldehydes and ketones, especially those of the aliphatic series (cf. Brady and Elsmie, A., 1926, 394), has been determined by the preparation of a series of 2:4-dinitrophenylhydrazones, of which those of the following are new: methyl *n*-propyl ketone, m. p. 141°; methyl *n*-butyl ketone, m. p. 106°; methyl *n*-amyl ketone, m. p. 89°; methyl *n*-hexyl ketone, m. p. 58°; methyl *n*-nonyl ketone, m. p. 63°; methyl isopropyl ketone, m. p. 117°; methyl isobutyl ketone, m. p. 95°; methyl isoamyl ketone, m. p. 95°; methyl isohexyl ketone, m. p. 77°;  $\beta$ -dimethylbutan- $\gamma$ -one, m. p. 125°; pentan- $\gamma$ -one, m. p. 156°; heptan- $\delta$ -one, m. p. 75°; hexan- $\gamma$ -one, m. p. 130°;  $\beta$ -methylhexan- $\delta$ -one, m. p. 75°;  $\Delta^2$ -hexen- $\epsilon$ -one, m. p. 104°; methylheptenone, m. p. 81°;  $\psi$ -ionone, m. p. 143°; mesityl oxide, m. p. 200°; cyclopentanone, m. p. 142°; cyclohexanone, m. p. 160°; cyclohexyl methyl ketone, m. p. 140°; carvone, m. p. 189°; menthone, m. p. 145°; styryl methyl ketone, m. p. 223°; phenyl styryl ketone, m. p. 208°; benzil, m. p. 185°; acetophenone, m. p. 237°; indan-1-one, m. p. 258°; *n*-butyrolin, m. p. 99°; benzoin, m. p. 234°; *n*-valeraldehyde, m. p. 98°; *n*-octaldehyde, m. p. 106°; *n*-decaldehyde, m. p. 104°; *n*-undecaldehyde, m. p. 104°; *n*-dodecaldehyde, m. p. 106°; acraldehyde, m. p. 165°;  $\alpha$ -methyl- $\beta$ -ethylacraldehyde, m. p. 159°; citronellal, m. p. 78°; citral-I, m. p. 108—110°; citral-II, m. p. 96°;  $\alpha$ -*n*-amylcinnamaldehyde, m. p. 164°; pyruvic acid, m. p. 213°; levulic acid, m. p. 92°; ethyl mesoxalate, m. p. 128°; methyl phenylglyoxylate, m. p. 171°. The m. p. in three series of homologous 2:4-dinitrophenylhydrazones show well-marked alternations. With  $\alpha$ -hydroxyketones the reagent usually gives unsatisfactory results, owing to the occurrence of oxidation to the diketone. It failed to give solid derivatives with methyl *n*-heptyl, *n*-octyl, and *n*-decyl ketones, di-*n*-butyl ketone, commercial ionone, pure  $\alpha$ -ionone, fenchone, and pulegone. A semi-micro-modification of the Kjeldahl nitrogen determination is outlined.

H. E. F. NOTTON.

**Acyldiarylhydrazine series.** I. J. J. RITTER and F. O. RITTER (J. Amer. Chem. Soc., 1930, 52, 2815—2819).—Monoacetylation of the following unsymmetrically substituted  $\alpha\beta$ -diarylhydrazines by acetic anhydride at the ordinary temperature yields  $\alpha$ - and  $\beta$ -acetyl derivatives in approximately equal amounts:  $\alpha$ -phenyl- $\beta$ -*p*-tolylhydrazine ( $\alpha$ -, m. p. 124° and  $\beta$ -, m. p. 140—141°, -acetyl derivatives),  $\alpha$ -phenyl- $\beta$ -chlorophenylhydrazine ( $\alpha$ -, m. p. 123—124°, and  $\beta$ -, m. p. 111—112°, -acetyl derivatives), and  $\alpha$ -phenyl- $\beta$ -*p*-bromophenylhydrazine [ $\alpha$ -, m. p. 117—118° (labile isomeride, m. p. 88—89°), and  $\beta$ -, m. p. 83°, -acetyl derivatives].  $\alpha$ -Phenyl- $\beta$ -*o*-tolylhydrazine yields only an  $\alpha$ -acetyl derivative, m. p. 78°. The acetyl derivatives are identified by reduction with phenylhydrazine and isolation of the resulting amine and anilide. Phenylhydrazine is catalytically decomposed in presence of acetanilide at 160° or acet-*m*-toluidide at 185° according to the scheme  $2\text{NHPH-NH}_2 \rightarrow \text{PhH} + \text{N}_2 + \text{NH}_3 + \text{NH}_2\text{Ph}$ , and the quantitative occurrence of this reaction on further

addition of phenylhydrazine is used to ascertain when the above reductions are completed.

H. E. F. NOTTON.

**Parachor of azo-compounds.** S. A. MUMFORD and J. W. C. PHILLIPS (Ber., 1930, 63, [B], 1818—1820).—A reply to Lindemann and Groger (this vol., 595).

H. WREN.

**Colour and constitution from the standpoint of recent electronic theory.** IV. Types of anomalous nitration; chelation; complex salt formation; unusual stability of substituted aminophenols; direct acetylation of amines; inhibited hydrolysis of sulphonic acids; reaction of potassium hydroxide with benzaldehyde. H. H. HODGSON (J. Soc. Dyers and Col., 1930, 46, 183—188).—A continuation of a previous discussion (cf. this vol., 906) of the application of modern electronic conceptions to chemical reactions which are important in colour chemistry.

A. J. HALL.

**Preparation of *N*-substituted cyanoformarylamides.** DEUTS. GOLD- U. SILBER-SCHIEDEANSTALT.—See B., 1930, 706.

**Oxidation of magnesium phenyl bromide in presence of lead tetraethyl.** H. GILMAN and J. A. LEERMAKERS (Iowa State Coll. J. Sci., 1930, 4, 323).—The presence of lead tetraethyl during the oxidation of magnesium phenyl bromide in ether does not inhibit the formation of ether peroxide or increase the yield of phenol. Increased yields of phenol may be secured by the use of *p*-dichlorobenzene.

CHEMICAL ABSTRACTS.

**Oxidation of unsaturated compounds by peracetic acid.** B. A. ARBUSOV and B. M. MICHAÏLOV (J. pr. Chem., 1930, [ii], 127, 92—102).—Contrary to Böcsen's view (cf. A., 1927, 39; 1928, 734; 1929, 547) requiring the primary formation of monoacetate of the corresponding glycol in the oxidation of unsaturated compounds by peracetic acid, evidence is adduced that oxides are primary products and that mono- and di-acetates are subsequently produced by interaction of the liberated acetic acid with the oxides.

*l*-Limonene is oxidised by 1 mol. of peracetic acid in ethereal solution to limonene oxide, b. p. 74—75.5°/9.5 mm.,  $d_4^{20}$  0.932,  $[x]_D^{20}$  —65.13° (cf. Prileschaev, A., 1910, i, 86), in 63% yield, further converted by peracetic acid into limonene dioxide, b. p. 106—108°/10 mm.,  $d_4^{20}$  1.0253. Contrary to Böcsen and Elsen (A., 1929, 547), cyclohexene yields cyclohexene oxide, b. p. 129.5—130.5°,  $d_4^{20}$  0.9680, in 66—67% yield (hydrated by sulphuric acid to the *trans*-glycol, m. p. 102—103°) when treated with a 7 or 20% ethereal solution of peracetic acid, together with only traces of the monoacetate. cyclohexene oxide is unaffected by 1 equivalent of acetic acid at the ordinary temperature.

Anethole with a 1.5% ethereal solution of peracetic acid yields anethole oxide, b. p. 122.5—123.5°/10.5 mm.,  $d_4^{20}$  1.0697, in 60% yield together with a small quantity of the monoacetate; an 8% solution gave anethole glycol monoacetate, b. p. 162—163°/5 mm., m. p. 58—61° (hydrolysed to anethole glycol, m. p. 62—63°), in 60% yield, and anethole oxide in 10% yield. The latter reacts vigorously with acetic acid at the ordinary temperature, anethole glycol monoacetate and traces of the diacetate being formed.

*iso*Eugenol is rapidly (8—10 hrs.) oxidised by peracetic acid (the only isolable product was a substance, b. p. 159—160°/6 mm., probably eugenol oxide), whilst eugenol is only slowly oxidised (68% after 210 hrs.) (only impure eugenol oxide, b. p. 158.5—159.5°/5.5 mm., was isolated); these therefore behave with peracetic as with perbenzoic acid (Meerwein and others, A., 1926, 722). A. I. VOGEL.

**Bromophenols. XXXV. Chlorination of *p*-aminophenol.** M. KOHN and S. FINK (Monatsh., 1930, 56, 137—142).—The trichloro-*p*-aminophenol described by Schmitt and Andersen (A., 1882, 400) is the 2:3:6-derivative, since the trichlorophenol obtained from it (Lampert, A., 1886, 616) reacts with only 1 mol. of bromine in cold acetic acid. 2:3:6-Trichlorophenol (benzoate, m. p. 92—93°; methyl ether, b. p. 227—229°/756 mm., m. p. 45°) thus affords 2:3:6-trichloro-4-bromophenol, m. p. 80° (benzoate, m. p. 110°; methyl ether, b. p. 269—275°/742 mm., m. p. 69—70°). Bromination of the trichlorophenol in presence of iron powder gives 2:3:6-trichloro-4:5-dibromophenol, m. p. 205° (benzoate, m. p. 153°; methyl ether, b. p. 329—332°, m. p. 130°).

H. BURTON.

**Preparation of 2:4-dinitrophenol from benzene and nitric acid in presence of mercury salts as catalysts. II.** A. I. ZAKHAROV (J. Chem. Ind., Russia, 1929, 6, 698—699).—A pure product is obtained by operating at 20—30°. With a freshly-prepared solution at 25—30° in presence of 15—20% of catalyst the product contains 0.3—0.5% of picric acid, but when used solutions to which nitric acid has been added are employed, only a trace of picric acid and no 2:6-isomeride are obtained; moreover, a minimal quantity of nitrobenzene is present and the speed of nitration is doubled. The amount of catalyst used does not affect the quality or yield of the product. CHEMICAL ABSTRACTS.

**Halogenated nitrophenols.** H. VAN ERP (J. pr. Chem., 1930, [ii], 127, 20—39).—*m*-Nitrophenol gives 2-chloro-3-nitrophenol (I), m. p. 120.5° (potassium derivative, +2H<sub>2</sub>O; methyl ether, m. p. 94°; ethyl ether, m. p. 51°; acetate, m. p. 51.5°; benzoate, m. p. 94°), in 48% yield by treating a suspension in hydrochloric acid with potassium chlorate solution (cf. Henley and Turner, this vol., 907). This was also prepared from *p*-anisidine by way of the acetyl derivative, m. p. 128°, the 2:3-dinitro-compound [with nitric acid (*d* 1.42)], 2:3-dinitro-*p*-anisidine, m. p. 189° (with 20% sulphuric acid), 2:3-dinitroanisole, m. p. 102—111° (by elimination of the amino-group), 3-nitro-*o*-anisidine, m. p. 76° (by heating with alcoholic ammonia at 160° for 5 hrs.), 2-chloro-3-nitroanisole, m. p. 94°, and I (by heating with hydrochloric acid at 160° for 5 hrs.). 6-Chloro-3-nitrophenol (II), m. p. 119.5° (potassium derivative, +2.5H<sub>2</sub>O; acetate, m. p. 81.5—82°), is prepared by nitrating *o*-acetamidoanisole with nitric acid (*d* 1.42), separating the resultant 4- and 5-nitro-compounds with 20% hydrochloric acid, converting the 5-nitro-*o*-anisidine, m. p. 141°, into 5-nitro-*o*-chloroanisole, m. p. 82.5°, and subsequent hydrolysis to II by heating with excess of concentrated sulphuric acid at 100°.

4-Chloro-3-nitrophenol (III), m. p. 126.5° (potassium

derivative, +2H<sub>2</sub>O; methyl ether, m. p. 43°; acetate, m. p. 83.5°), is obtained by treatment of phenacetin with 15—25% nitric acid to give the 3-nitro-compound, m. p. 103°, and conversion successively into 2-nitro-*p*-phenetidine, m. p. 102° (with 60% sulphuric acid), 4-chloro-3-nitrophenetole, m. p. 47.5°, and III.

6-Chloro-3-nitrophenol is best prepared in quantity as follows: phenacetin on chlorination (Reverdin and Düring, A., 1899, i, 267) yields the 2-chloro-compound, m. p. 122—126°, converted by nitric acid (*d* 1.42) into 2-chloro-5-nitro-4-acetamidophenetole, m. p. 166°, then into 2-chloro-5-nitro-*p*-phenetidine, m. p. 129°, followed by elimination of the amino-group into 2-chloro-5-nitrophenetole, m. p. 64.5°, and finally into II, m. p. 119.5°.

2-Chloro-5-nitro-*p*-phenetidine has m. p. 169.5° (decomp.). A. I. VOGEL.

**Diacyl derivatives of *p*-anisidine and *p*-phenetidine.** F. REVERDIN (Helv. Chim. Acta, 1930, 13, 696—698).—The acetylation of monoacyl derivatives of *p*-anisidine and *p*-phenetidine with acetic anhydride in the presence of a little sulphuric acid was carried out at 100° over a period of  $\frac{1}{2}$ — $\frac{3}{4}$  hr. With the formyl derivatives the formyl group was eliminated and the monoacetyl derivative formed; neither chloroacetyl-*p*-phenetidine nor benzoyl-*p*-anisidine gave the expected products. The following, however, were readily obtained: benzenesulphonylacetyl-*p*-anisidine, m. p. 144°; benzenesulphonylacetyl-*p*-phenetidine, m. p. 155—156°; toluene-*p*'-sulphonylacetyl-*p*-anisidine, m. p. 149—150°; toluene-*p*'-sulphonylacetyl-*p*-phenetidine, m. p. 150°; and *o*-nitro-toluene-*p*'-sulphonylacetyl-*p*-phenetidine, m. p. 172°. These products, when nitrated in alcoholic solution, give nitro-derivatives of the arylsulphonyl compounds, the acetyl group being eliminated (cf. A., 1929, 1289).

H. A. PIGGOTT.

**Derivatives of chloroacetylated phenols and phenol-alcohols.** A. LAKNER (Magyar Chem. Fol., 1929, 35, 151—155; Chem. Zentr., 1930, i, 1464—1465).—Iodoacetyl derivatives of dihydroxy-derivatives of benzene, like chloroacetyl derivatives, are hydrolysed by ammonia. With silver nitrite halogenoacetylphenols react vigorously at 96°, affording dinitro-derivatives and silver halogenoacetate; silver cyanide behaves analogously. The following are described: chloroacetates of pyrocatechol, m. p. 56°, b. p. 185—186°/10 mm.; resorcinol, m. p. 76°, b. p. 191—192°/5 mm.; quinol, m. p. 126°; iodoacetates, m. p. 48—49°, 59—60°, 112—113°, respectively. Quinol chloroacetate forms with dimethylaniline an equimolecular compound, m. p. 152—153°, decomp. 156—157°. Phenylethyl aminoacetate has m. p. 115°; phenylpropyl aminoacetate has m. p. 105°.

A. A. ELDRIDGE.

**Some derivatives of ephedrine.** C. T. FENG and S. D. WILSON (Chinese J. Physiol., 1930, 4, 231—245).—The following compounds have been prepared from ephedrine: *N*-benzylephedrine, m. p. 49—49.5°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +11.90° in alcohol (hydrochloride, m. p. 150—150.5°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> −6.9° in water); *N*-butylephedrine, m. p. 40.3—40.7°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> −6.7° in alcohol (hydrochloride, m. p. 117—118°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> −13.9° in water). The following constants have been determined for *N*-methyl-



ephedrine, m. p. 87.0—87.5°,  $[\alpha]_D^{25}$  —29.8° in methyl alcohol, —25.8° in ethyl alcohol; hydrochloride, m. p. 189—190°,  $[\alpha]_D^{25}$  —29.8° in water.

W. O. KERMACK.

**Ionisation constants and absorption spectra of ephedrine and  $\psi$ -ephedrine.** J. ABILDGAARD and A. BAGGESGAARD-RASMUSSEN (Arch. Pharm., 1930, 268, 353—357).—See this vol., 470.

**Optical instability of tercovalent carbonium cations. Transformation of *l*-phenylmethylcarbinyl *dl*-*p*-toluenesulphinate into optically inactive *p*-tolyl- $\alpha$ -phenylethylsulphone.** J. KENYON and H. PHILLIPS (J.C.S., 1930, 1676—1685).—*l*-Phenylmethylcarbinyl *dl*-*p*-toluenesulphinate,  $[\alpha]_{5461}^{25}$  —90.8°,  $[\alpha]_{4358}^{25}$  —159° in ethyl alcohol, undistillable at 0.1 mm., is prepared by the interaction of *l*-phenylmethylcarbinol and toluene-*p*-sulphonyl chloride in presence of pyridine, and regenerates *l*-phenylmethylcarbinol on hydrolysis. It is spontaneously converted on keeping in a closed glass vessel for a few days into *dl*-*p*-tolyl- $\alpha$ -phenylethylsulphone, a little *di*-*p*-tolyl disulphoxide, and  $\alpha\alpha'$ -diphenyldiethyl ether. The *d*+*dl*-ester behaves similarly. In contrast to *d*- $\beta$ -octyl *dl*-*p*-toluenesulphinate (Phillips, A., 1926, 159), the *l*-phenylmethylcarbinyl ester is not formed by heating the alcohol with ethyl *p*-toluenesulphinate, the main product being *dl*-*p*-tolyl- $\alpha$ -phenylethylsulphone. The optical inactivity of the sulphone produced is not due to the chemical instability of the phenylmethylcarbinyl radical, for *d*-*p*-tolyl- $\alpha$ -phenylethylsulphone, m. p. 134—135°, and *d*- $\alpha$ -phenyldiethyl ether can readily be prepared from *l*- $\alpha$ -chloroethylbenzene and sodium *p*-toluenesulphinate in alcohol, optical inversion apparently occurring; the sulphone, however, is not optically pure. Partly racemised *d*- $\alpha$ -phenyldiethyl ether can also be prepared by interaction of *l*- $\alpha$ -chloroethylbenzene, ethyl alcohol, and potassium carbonate; the *l*-ether is given by *l*-phenylmethylcarbinol and ethyl bromide in ether. *l*- $\alpha\alpha'$ -Diphenyldiethyl ether is obtainable from *l*-phenylmethylcarbinol, but from *l*- $\alpha$ -chloroethylbenzene the product is the racemic form. The spontaneous production of sulphoxide from *d*- $\beta$ -octyl and ethyl *d*+*dl*-toluene-*p*-sulphinates, with loss of activity in the latter case, is recorded.

The analogy of the transformation of sulphinate into sulphone to the exchange of anions by an asymmetric carbon atom is indicated. The stable planar configuration of the carbonium cation (Lowry, 2<sup>mc</sup>. Conseil Chimie Solvay, 1925, 40) would lead to the production of an optically active sulphone, and it is concluded that the carbonium cation oscillates between two forms of opposite configuration; in the absence of the special Walden inversion mechanism, therefore, the replacement of a group attached to an asymmetric carbon atom must lead to an optically inactive or racemised product. H. A. PIGGOTT.

**Dehydration with potassium hydroxide of ethylol groups adjacent to a benzene ring. III. Dehydration of  $\alpha\alpha'$ -arylalkylethanols.** S. SABETAY (Bull. Soc. chim., 1930, [iv], 47, 614—620).—When hydratropic alcohol is dehydrated by distillation over potassium hydroxide at 170—175° the isomerisation observed in dehydration with porosite (Ramart-

Lucas, A., 1928, 170) does not occur and  $\alpha$ -methylstyrene, b. p. 159—160°/744 mm.,  $n_D^{20}$  1.535,  $d_4^{20}$  0.9065, is obtained, identical with the product obtained in 90% yield by dehydrating  $\beta$ -phenylisopropyl alcohol with acetic anhydride or, preferably, with porosite at 350—370°.  $\beta$ -Phenylisopropyl alcohol is unchanged when distilled with potassium hydroxide. Similarly,  $\beta$ -phenyl-*n*-butyl alcohol, b. p. 120—121°/12 mm., is converted by distillation over potassium hydroxide into  $\alpha$ -ethylstyrene, b. p. 177—180°/742 mm.,  $n_D^{20}$  1.5262 (liquid dibromide).  $\alpha$ -Methylstyrene is more stable than styrene. Benzylmethylcarbinol is much less readily dehydrated by potassium hydroxide, a little propenylbenzene, unsaturated hydrocarbons of low b. p., and unchanged alcohol being obtained, whilst in a partial vacuum the carbinol is partly resinified and partly unchanged. The primary alcohol is thus, abnormally, more readily dehydrated than the secondary. R. BRIGHTMAN.

**Action of ammonia and dimethylamine on ethylene, allylbenzene, and phenylcyclohexene oxides, and their homologues.** (MLLE.) J. LÉVY and J. SFIRAS (Compt. rend., 1930, 191, 261—263).—

Aralkylated ethylene oxides,  $\text{O} \begin{array}{c} \diagup \\ \text{CH}_2 \end{array} \text{CH} \cdot [\text{CH}_2]_n \cdot \text{Ph}$ ,

react with ammonia and dimethylamine in the cold, but the oxides of phenyl- and 1-phenyl-4-methylcyclohexene react only above 100°. The reactivity of these oxides varies inversely as the thermal stability (A., 1927, 662; 1928, 888).  $\gamma$ -Phenylpropylene (allylbenzene) oxide and dimethylamine afford  $\alpha$ -dimethylamino- $\gamma$ -phenylisopropyl alcohol, b. p. 140°/22 mm. (hydrochloride, m. p. 95°; benzoate hydrochloride, m. p. 155—156°), whilst with ammonia a mixture of 7% of di-( $\beta$ -hydroxy- $\gamma$ -phenylpropyl)amine (hydrochloride, m. p. 140°) and 48% of tri-( $\beta$ -hydroxy- $\gamma$ -phenylpropyl)amine (hydrochloride, m. p. 160—161°) results. Similarly, *o*-phenyl- $\Delta^a$ -butylene oxide furnishes  $\alpha$ -dimethylamino- $\delta$ -phenylbutan- $\beta$ -ol, b. p. 145°/14 mm. (hydrochloride, m. p. 60°; benzoate hydrochloride, m. p. 155°), and small amounts of mono-, di- (hydrochloride, m. p. 137—139°), and tri-( $\beta$ -hydroxy- $\delta$ -phenylbutyl)amine. The following are also described:  $\alpha$ -dimethylamino- $\epsilon$ -phenylpentan- $\beta$ -ol, b. p. 155—158°/13 mm. (hydrochloride, m. p. 75—76°; benzoate hydrochloride, m. p. 136°); tri-( $\beta$ -hydroxy- $\epsilon$ -phenylamyl)amine hydrochloride, m. p. 148°;  $\alpha$ -dimethylamino- $\zeta$ -phenylhexan- $\beta$ -ol, b. p. 171°/17 mm. (hydrochloride, m. p. 104°; methiodide, m. p. 143°; benzoate hydrochloride, m. p. 126°); tri-( $\beta$ -hydroxy- $\zeta$ -phenylhexyl)amine hydrochloride, m. p. 78°; 2-dimethylamino-1-phenylcyclohexanol, b. p. 172—173°/18 mm. (hydrochloride, m. p. 174°; methiodide, m. p. 199°; benzoate hydrochloride, m. p. 154°); 2-amino-1-phenylcyclohexanol, m. p. 105° (hydrochloride, m. p. 140°); 2-dimethylamino-1-phenyl-4-methylcyclohexanol, m. p. 103° (hydrochloride, m. p. 187°; methiodide, m. p. 205°; benzoate hydrochloride, m. p. 199°); 2-amino-1-phenyl-4-methylcyclohexanol, b. p. 185° (hydrochloride, m. p. 135°); di-(2-hydroxy-2-phenyl-5-methylcyclohexyl)amine hydrochloride, m. p. 156°. The above benzoate hydrochlorides and some of the other hydrochlorides possess local anaesthetic properties. H. BURTON.

**Configurative relationships of aromatic carb-inols.** P. A. LEVENE and P. G. STEVENS (J. Biol. Chem., 1930, **87**, 375—391).—Cinnamaldehyde with magnesium ethyl bromide yields  $\epsilon$ -phenyl- $\Delta^5$ -penten- $\gamma$ -ol (*hydrogen phthalate*, m. p. 108—109° and 160°); on resolution with cinchonidine the latter gives an *l*-isomeride, m. p. 83.5—85°,  $[\alpha]_D^{25}$   $-3.0^\circ$ , and a *d*-isomeride,  $[\alpha]_D^{25}$   $+2.4^\circ$  in alcohol, which is hydrolysed to the *l*-carbinol, b. p. 115—118°/0.2 mm.,  $[\alpha]_D^{25}$   $+2.1^\circ$  in alcohol and  $-6.9^\circ$  in ether. The preparation of this carbinol is accompanied by formation of considerable amounts of the corresponding ether,  $C_{22}H_{26}O$ ,  $[\alpha]_D^{25}$   $-71.0^\circ$  in ether, into which the carbinol also passes spontaneously when kept. The crude *d*-carbinol has  $[\alpha]_D^{25}$   $+10.4^\circ$  in ether (*phenylcarbamate*, m. p. 112.5—113°,  $[\alpha]_D^{25}$   $+117^\circ$  in alcohol). The above *d*-carbinol yields, on ozonisation and reduction of the product with sodium amalgam, *d*-*n*-butane- $\alpha\beta$ -diol, whilst with palladium and hydrogen it gives *l*- $\epsilon$ -phenyl-*n*-pentan- $\gamma$ -ol, m. p. 38—41°,  $[\alpha]_D^{25}$   $+18.8^\circ$  in ether ( $\alpha$ -*naphthylcarbamate*, m. p. 82—83°,  $[\alpha]_D^{25}$   $-8.9^\circ$  in alcohol; *phenylcarbamate*, m. p. 40—41°,  $[\alpha]_D^{25}$   $+7.9^\circ$  in alcohol), which, with hydrogen and platinum oxide, is further reduced to *l*- $\epsilon$ -cyclohexyl-*n*-pentan- $\gamma$ -ol, b. p. 103—108°/0.2 mm.,  $[\alpha]_D^{25}$   $-5.0^\circ$  in ether ( $\alpha$ -*naphthylcarbamate*, m. p. 114—115°,  $[\alpha]_D^{25}$   $+2.1^\circ$  in alcohol,  $-9.8^\circ$  in chloroform). The above-mentioned ether is reduced with hydrogen and platinum oxide to the corresponding saturated ether,  $C_{22}H_{30}O$ ,  $[\alpha]_D^{25}$   $-4.8^\circ$  in ether. *l*- $\epsilon$ -Phenyl-*n*-pentan- $\gamma$ -ol is configuratively related to *l*-lactic acid and to *l*-*n*-hexan- $\gamma$ -ol (cf. Levene and Haller, A., 1928, 394); introduction of the phenyl group has caused an enhancement of the rotation, whilst the effect of the cyclohexyl group is approximately equivalent to that of the *n*-hexyl group. *l*- $\alpha$ -Phenyl-*n*-propan- $\alpha$ -ol,  $[\alpha]_D^{25}$   $-25.68^\circ$ , is reduced with hydrogen and platinum oxide to *l*- $\alpha$ -cyclohexyl-*n*-propan- $\alpha$ -ol, b. p. 85.5—86°/9 mm.,  $\alpha_D^{25}$   $-5.86^\circ$  (by-product 60% of  $\alpha$ -cyclohexyl-*n*-propane).  $\alpha$ -Phenyl-*n*-butan- $\beta$ -ol was converted into the *l*-*hydrogen phthalate*,  $[\alpha]_D^{25}$   $-18.4^\circ$  in alcohol, hydrolysed to the *l*-carbinol,  $[\alpha]_D^{25}$   $-21.7^\circ$  in ether; the latter was reduced to *l*- $\alpha$ -cyclohexyl-*n*-butan- $\beta$ -ol, b. p. 102—103.5°/10 mm.,  $[\alpha]_D^{25}$   $-25.3^\circ$  in ether (formation of 8% of  $\alpha$ -cyclohexyl-*n*-butane). *l*- $\alpha$ -Phenyl- $\gamma$ -methyl-*n*-propan- $\alpha$ -ol,  $\alpha_D^{25}$   $-9.01^\circ$ , was reduced to *d*- $\alpha$ -cyclohexyl- $\gamma$ -methyl-*n*-propan- $\alpha$ -ol, b. p. 91—94°/9 mm.,  $\alpha_D^{25}$   $+2.75^\circ$ . In the last case alone does an optical inversion accompany reduction of the phenyl to the cyclohexyl group.

C. R. HARRINGTON.

**Aminophenyl-amino-alcohols.** E. FOURNEAU and (MLLE.) W. BRYDOWNA (Bull. Soc. chim., 1930, [iv], **47**, 626—630).—The synthesis of aromatic amino-alcohols has been attempted to obtain simpler anti-malarial compounds than plasmoquin, and to determine whether the presence of a quinoline nucleus is essential for anti-malarial activity. Nitration of  $\gamma$ -chloro- $\alpha$ -phenylisopropyl acetate with sulphuric and nitric acids at 0—15° yields a mixture of  $\gamma$ -chloro- $\alpha$ -*p*-nitrophenylisopropyl acetate, m. p. 72—73°, and a  $\gamma$ -chloro- $\alpha$ -*d*-nitrophenylisopropyl acetate, m. p. 233°. The former on hydrolysis with alcoholic sodium hydroxide is converted into  $\alpha$ -*p*-nitrophenyl- $\beta$ - $\gamma$ -propylene oxide, m. p. 126—127°, which condenses with piperidine, yielding  $\gamma$ -piperidino- $\alpha$ -*p*-nitrophenyl-

isopropyl alcohol, m. p. 87° (*hydrochloride*). The  $\gamma$ -piperidino- $\alpha$ -*p*-aminophenylisopropyl alcohol, m. p. 108°, obtained by reduction with sodium sulphide is inactive against malaria in birds, and attempts to convert this into the corresponding quinoline by the Skraup reaction eliminated the piperidine ring. Reaction with acetaldehyde and oxidation with arsenic acid yielded an amorphous product which could not be purified.

R. BRIGHTMAN.

**Action of perbenzoic acid on ergosterol and its derivatives.** S. WINDAUS and A. LÜTTRINGHAUS (Annalen, 1930, **481**, 119—131).—When titrated with perbenzoic acid, ergosterol adds 3.0 atoms of oxygen, dihydroergosterol I adds 2.6—2.7 atoms (calc. 2), and tetrahydroergosterol adds 1.0 atom. Ergotetraene A and B add only 3.0 atoms, and dehydroergosterol 3.6 atoms. The trebly unsaturated ergosterol D and F, the irradiation products of ergosterol and ergostatrienediol smoothly absorb 3.0 atoms and the doubly unsaturated dihydroergosterol II and dehydroergosteronol behave according to theoretical expectation. On the other hand, the dihydro-derivatives of irradiated ergosterols absorb 2.5—3.0 atoms of oxygen. Ergostenediol and ergostenetriol add 1.0 atom of oxygen.

$\alpha$ -Ergostenyl acetate is not converted into the corresponding oxide by rather more than 1 mol. of perbenzoic acid, but yields an apparently non-homogeneous substance converted by mineral acid into *dehydroergostenyl acetate*,  $C_{27}H_{43}OAc$ , m. p. 135—136°,  $[\alpha]_D^{25}$   $-28.5^\circ$  in chloroform, which smoothly absorbs 2.0 atoms of oxygen when titrated with perbenzoic acid. It is hydrolysed by alcoholic potassium hydroxide to *dehydroergostenol*, m. p. 141°,  $[\alpha]_D^{25}$   $-18.2^\circ$  in chloroform, which yields a precipitate with digitonin and gives a positive reaction with bromine, trichloroacetic acid, and chloral hydrate. It exhibits selective absorption. It is not hydrogenated by sodium and alcohol and does not add maleic anhydride. It is hydrogenated in presence of spongy palladium in ethyl acetate to  $\alpha$ -ergostenol, m. p. 130—131°. Ergosteryl D acetate, m. p. 171°,  $[\alpha]_D^{25}$   $+25.7^\circ$  in chloroform, is the sole isolable product of the action of 1 mol. of perbenzoic acid on dihydroergosteryl acetate. Ergosterol when treated with 1 mol. of perbenzoic acid affords, in place of the expected oxide, *ergostadienetriol monobenzoate*,  $C_{34}H_{48}O_4$ , m. p. 194°,  $[\alpha]_D^{25}$   $+48.6^\circ$  in chloroform. This is hydrolysed to *ergostadienetriol*, m. p. 241—242°,  $[\alpha]_D^{25}$   $+29.4^\circ$  in pyridine [*dibenzoate*, m. p. 225°,  $[\alpha]_D^{25}$   $+78.6^\circ$  in chloroform; *benzoate p-nitrobenzoate*, m. p. 215; *di-p-nitrobenzoate*, m. p. 213° (decomp.); *acetate benzoate*, m. p. 186—187°,  $[\alpha]_D^{25}$   $+46.5^\circ$  in chloroform; *diacetate*, m. p. 181—182°]. The one hydroxyl group of the triol (identified by the Zerevitinov method) which cannot be acylated is probably tertiary and the double linking of ergosterol which reacts first with perbenzoic acid is probably present in the group  $\cdot CH_2C<$ . Ergostadienetriol diacetate cannot be hydrogenated by means of spongy palladium in alcohol, but in acetic acid in presence of platinum sponge it yields *ergostenetriol diacetate*, m. p. 172—173°,  $[\alpha]_D^{25}$   $-9.75^\circ$  in chloroform. *Ergostenetriol*,  $2C_{27}H_{46}O_3 \cdot H_2O$ , m. p. 234°,  $[\alpha]_D^{25}$   $-4.6^\circ$  in pyridine, is oxidised by chromic acid in

acetic acid at 35° to *ergostenediol*,  $C_{27}H_{42}O_3$ , m. p. 251–252° (decomp.),  $[\alpha]_D^{25} -12.8^\circ$  in chloroform (dioxime, gradual decomp. above 205°).

H. WREN.

**Mechanism of Liebermann-Burchard reaction.**  
Application to differentiation of sterols of animal or vegetable origin. R. MEESEMAECKER and H. GRIFFON (J. Pharm. Chim., 1930, [viii], 11, 572–580).—Substitution in the Liebermann-Burchard reaction of other dehydrating agents such as potassium hydrogen sulphate, phosphorus pentoxide, calcium oxide, zinc chloride, and calcium chloride in the place of sulphuric acid results in no colour being produced when the sterol employed is cholesterol, whilst when sulphuric acid is employed acetic anhydride cannot be replaced by ethyl acetate, ethyl ether, or acetyl chloride. Similar results were obtained with phytosterol, except that a pale colour is given with acetic anhydride and potassium hydrogen sulphate, a reaction which may be used to distinguish these two sterols. Ergosterol gives colours with all the dehydrating agents except calcium chloride and calcium oxide, and when sulphuric acid is used ethyl acetate, ethyl ether, and acetyl chloride bring about the production of colour in the absence of acetic anhydride. The influence of various solvents in the place of chloroform has been investigated. When ethyl, methyl, or amyl alcohol is used the reaction is always negative. The presence of water tends to prevent the appearance of the colour. With cholesterol the addition of zinc chloride prevents the development of colour in the Liebermann-Burchard reaction, but when the colour has developed to its full intensity, addition of zinc chloride stabilises it.

W. O. KERMACK.

**So-called "ischolesterol" of wool fat.** A. WINDAUS and R. TSCHESCHE (Z. physiol. Chem., 1930, 190, 51–62).—The fractionation of the acetate of "ischolesterol" prepared from lanolin yielded the acetates of two substances which are described. *Agnosterol*,  $C_{30}H_{48}O$ , m. p. 162°,  $[\alpha]_D^{25} +70.5^\circ$ , forms *agnosteryl acetate*, m. p. 173–174°,  $[\alpha]_D^{25} +90.4^\circ$ , *bromoacetate*, m. p. 130–131°,  $[\alpha]_D^{25} +78.3^\circ$ , and *benzoate*, m. p. 203°,  $[\alpha]_D^{25} +103.8^\circ$ . Although it appears to contain three double linkings, the acetate takes up only 1 mol. of hydrogen, yielding *α-dihydroagnosterol*, m. p. 162–163°,  $[\alpha]_D^{25} +84.4^\circ$  (*α-dihydroagnosterol*, m. p. 147–148°,  $[\alpha]_D^{25} +60.9^\circ$ ), and (in presence of a trace of hydrochloric acid) *β-dihydroagnosterol*, m. p. 133°,  $[\alpha]_D^{25} +48.9^\circ$  (*β-dihydroagnosterol*, m. p. 141–142°,  $[\alpha]_D^{25} +36.4^\circ$ ). *Lanosterol*,  $C_{30}H_{50}O$ , m. p. 140–141°,  $[\alpha]_D^{25} +58.0^\circ$ , forms *lanosteryl acetate*, m. p. 113–114°,  $[\alpha]_D^{25} +56.2^\circ$  (*dibromide*, m. p. 160–162°,  $[\alpha]_D^{25} +32.3^\circ$ ), *bromoacetate*, m. p. 99–101°,  $[\alpha]_D^{25} +52.7^\circ$ , *β-iodopropionate*, m. p. 120°,  $[\alpha]_D^{25} +42.2^\circ$ , and *benzoate*, m. p. 191.5°,  $[\alpha]_D^{25} +74.5^\circ$ . Hydrogenation of the acetate yields *α-dihydrolanosteryl acetate*, m. p. 118–120°,  $[\alpha]_D^{25} +52.9^\circ$  (*α-dihydrolanosterol*, m. p. 149–150°,  $[\alpha]_D^{25} +51.9^\circ$ ).

J. H. BIRKINSHAW.

**Three isomeric cholesteryl nitrobenzoates.** H. SANDQUIST and J. GORTON (Bor., 1930, 63, [B], 1759–1760).—The substances are prepared by the gradual addition of the requisite acid chloride in chloroform to cholesterol in chloroform and pyridine.

*Cholesteryl o-nitrobenzoate*, m. p. (149.6–) 150.4–150.9°, becoming transparent at 156.2–156.9°,  $[\alpha]_D^{25} -6.0^\circ$ , *m-nitrobenzoate*, m. p. (140.3–) 140.8–141.0° becoming transparent at 174.6–175.3°,  $[\alpha]_D^{25} -11.9^\circ$ , and *p-nitrobenzoate*, m. p. (188.2–) 189.9–192.8°, becoming transparent at 261.0° (decomp.),  $[\alpha]_D^{25} -6.3^\circ$ , are described.

H. WREN.

**Chromic acid oxidation of cyclanepolyols.** S. SABETAY and J. BLEGER (Compt. rend., 1930, 191, 102–104).—Oxidation of 1:2-, 1:3-, and 1:4-cyclohexanediols with chromic anhydride in glacial acetic acid at 15° affords the corresponding cyclohexanediones. Quinitol, under conditions given in detail, yields 56% of *cyclohexane-1:4-dione*, m. p. 79°, b. p. 134°/21 mm. [disemicarbazone, m. p. 317–319°; dioxime, m. p. 218–219°; tetra-acetate, m. p. 187–188° (cf. lit.)]; the product reduces ammoniacal copper and silver nitrate solutions in the cold. The tetra-acetate, owing to the ready hydrolysability of the acetyl groups, reduces these solutions when warmed.

The oxidation of polyols by chromic acid proceeds in stages; thus by provision of chromic anhydride corresponding with 1 atom of oxygen *cyclohexane-1:4-diol* appears to yield *cyclohexan-4-ol-1-one acetate*.

C. W. SHOPPEE.

**Comparative migratory tendencies of cyclic radicals: comparison of the *p*-anisyl and *p*-tolyl groups.** A. OREKHOV and J. BROUTY (Bull. Soc. chim., 1930, [iv], 47, 621–626).—To obtain a direct comparison of the migratory tendencies of the *p*-anisyl and *p*-tolyl groups, the dehydration of *αβ-di-p-tolyl-αβ-di-p-anisylethylene glycol* has been studied. With 20% sulphuric acid a pinacolin, m. p. 81°, is obtained, shown to be *p-tolyl p-tolyldi-p-anisylmethyle ketone* by its decomposition by alcoholic potassium hydroxide into *p-toluic acid* and *p-tolyldi-p-anisylmethane*, m. p. 41–42°. Accordingly, in the dehydration of the glycol the *p*-anisyl group alone has migrated and since the affinity of the *p*-tolyl group is lower than that of the *p*-anisyl group the conclusions previously reached as to the parallelism between the affinity and migratory tendency of aromatic radicals are confirmed. *p-Tolyl p-anisyl ketone*, m. p. 89° (*oxime*, m. p. 126°), obtained in 40% yield from *p*-anisoyl chloride and toluene, is converted by reduction with zinc and acetic acid into *αβ-di-p-tolyl-αβ-di-p-anisylethylene glycol*, m. p. 130–131°, also obtained from *pp'*-dimethoxybenzil (anisil) and magnesium *p*-tolyl bromide.

R. BRIGHTMAN.

**Walther and Vlodkovski's benzoylbiuret.** A. OSTROGOVICH (Bul. Soc. Stiinte Cluj, 1929, 4, 528–537; Chem. Zentr., 1930, i, 838–839).—This compound (A., 1899, i, 590) is not formed by the action of acetic acid on benzoylcarbamide, but is a product of the action of benzoyl chloride on carbamide in presence of pyridine. Dibenzamide and benzamide are also formed.

A. A. ELDRIDGE.

**Organic compounds of quadrivalent vanadium.** A. GRIPPA (Annali Chim. Appl., 1930, 20, 244–248).—The preparation and properties of vanadyl hydroxide, benzoate, cinnamate, and succinate are described.

T. H. POPE.

**Benzoylcarbamide.** A. OSTROGOVICH (Bul. Soc. Stiinte Cluj, 1929, 4, 538–542; Chem. Zentr., 1930,

i, 839).—The carbamide and benzoyl chloride are preferably heated at 100°; benzoylcarbamide has m. p. 214—215°. A. A. ELDRIDGE.

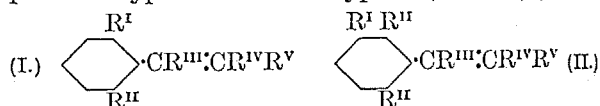
**Influence of certain substituents in the benzene ring on the catalytic hydrogenation of the cyanogroup.** H. RUPE and F. BERNSTEIN (Helv. Chim. Acta, 1930, 13, 457—473).—A comparison of the proportions of substituted benzaldehyde, benzylamine, and dibenzylamine produced by the hydrogenation in presence of nickel of *o*-, *m*-, and *p*-methyl- and -bromo-benzonitriles, and of the cyanobenzoic esters. The three toluonitriles give identical proportions, viz., 5%, 50%, and 17% (*m*-, 19%), of the theoretical calculated on the nitrile used, but *o*-toluonitrile is reduced rather more slowly than the other two. In the case of the bromobenzonitriles rather less primary base is formed, the amount of secondary base being proportionately higher; the *o*-compound is again more slowly reduced than the others and yields 17% of *o*-bromobenzaldehyde. Methyl *o*-cyanobenzoate yields mainly phthalimidine (90%) and traces of the aldehyde; the principal product from ethyl *m*- and *p*-cyanobenzoates is the *sec*-amine (40% and 44%, respectively), the primary amine being formed in correspondingly smaller amounts. The *p*-compound again gives only traces of aldehyde, but the *m*-compound gives 12%. The following are described: phenyl-*o*-methylbenzylthiocarbamide, m. p. 105°; *oo'*-dimethyl-dibenzylamine hydrochloride (nitrosoamine, m. p. 46—47°); *mm'*-dimethyl-dibenzylamine hydrochloride (hydrogen oxalate, m. p. 235°); phenyl-*p*-methylbenzylthiocarbamide, m. p. 147°; *pp'*-dimethyl-dibenzylamine (hydrochloride; nitrosoamine, m. p. 52°); phenyl-*o*-bromobenzylthiocarbamide, m. p. 175°; *oo'*-dibromodibenzylamine, m. p. 36° (hydrochloride; oxalate, m. p. 220°); *m*-bromobenzylamine, b. p. 84°/14 mm., (hydrochloride, m. p. 212°); phenylthiocarbamide derivative, m. p. 151°; *mm'*-dibromodibenzylamine, an undistillable oil (the hydrochloride, acetate, and nitrate are all sparingly soluble in cold water, and the sulphate alone is at all readily soluble in hot); *pp'*-dibromodibenzylamine nitrosoamine, m. p. 105°; ethyl *m*-cyanobenzoate, m. p. 56°, b. p. 140—141°/10 mm.; *m*-carbethoxybenzaldehydesemicarbazone, m. p. 202°; ethyl benzylamine-3-carboxylate, b. p. 150°/10 mm. (hydrochloride, m. p. 158—159°; picrate, m. p. 179°); phenylthiocarbamide derivative, m. p. 112°; ethyl dibenzylamine-3 : 3'-dicarboxylate (hydrochloride, m. p. 147°; hydrogen oxalate, m. p. 212°); ethyl benzylamine-4-carboxylate, b. p. 149—150°/10 mm. (hydrochloride; phenylthiocarbamide derivative, m. p. 117°), and ethyl dibenzylamine-4 : 4'-dicarboxylate hydrochloride (nitrate, m. p. 205°; picrate, m. p. 170°).

H. A. PIGGOTT.

**Chemical reactions induced by light.** L. VECCHIOTTI and G. ZANETTI (Gazzetta, 1930, 60, 479—486).—The action of light on mixtures of (a) nitrobenzene and naphthalene, (b) nitrobenzene and toluene, and (c) nitrobenzene and cinnamic acid, kept in an atmosphere of nitrogen, has been observed. In (a) traces of  $\beta$ -naphthol were found; in (b) small quantities of benzoic acid and *p*-aminophenol, whilst in (c) where reaction occurs to a much larger extent, benzoic acid, benzanilide, azoxybenzene, *o*-hydroxy-

azobenzene, and carbon dioxide were identified. The modes of formation of these compounds are discussed (cf. Ciamician and Silber, A., 1903, i, 39, and subsequent papers). C. W. SHOPPEE.

**Possible isomerism of analogues of resolvable diphenyl compounds.** VII. R. W. MAXWELL and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 2959—2972).—In a further search for benzene derivatives in which the substituents in the side-chain are able mechanically to prevent the free rotation of the carbon atom attached to the nucleus, as they are believed to do in the resolvable diphenyl compounds, one compound of type I and two of type II ( $R^{III}=H$ ) (cf. A.,



1928, 1234) have been prepared. Attempts to resolve these and to synthesise compounds in which  $R^{III}$  is a radical other than hydrogen were unsuccessful. Magnesium *m*-xylyl bromide and methyl sulphate in ether give  $\psi$ -cumene (50—60% yield), from which 2 : 5-dinitro-3 : 4 : 6-trimethylbenzaldehyde is obtained. This with sodium propionate and propionic anhydride gives 2 : 5-dinitro- $\alpha$  : 3 : 4 : 6-tetramethylcinnamic acid, m. p. 277—278°, which does not form a dibromide in the dark. Unsuccessful attempts were made to resolve this compound by means of its strychnine, m. p. 145—149° (corr.),  $[\alpha]_D^{25} -179^\circ$ , morphine, m. p. 178—184°,  $[\alpha]_D^{25} -60.8^\circ$ , and brucine  $[+2H_2O]$ , m. p. 129—132°,  $[\alpha]_D^{25} -18.4^\circ$  to  $-31.2^\circ$ , salts. *iso*Butyrylmesitylene (Klages, A., 1904, i, 302) is converted by nitric acid (*d* 1.52) below 15° into dinitroisobutyrylmesitylene, m. p. 137.5—138.5°, from which by standard methods nitroamino-, m. p. 98—99° (hydrochloride), nitro-, b. p. 157—158°/7 mm., and amino-, b. p. 167°/7 mm., -isobutyrylmesitylenes are obtained. The last-named is reduced by sodium and alcohol to  $\alpha$ -2 : 4 : 6-trimethyl-3-aminophenylisobutyl alcohol, m. p. 118.5—119.5°, dehydrated by 40% hydrobromic acid to amino- $\Delta^1$ -isobutenylmesitylene, b. p. 127—128°/6 mm. (d-camphorsulphonate,  $[\alpha]_D^{25} +32.0^\circ$ ; d-oxymethylcinecamphor derivative, m. p. 176—180°,  $[\alpha]_D^{25} +184.1^\circ$  to  $+200.0^\circ$ , changing when kept; acetyl derivative, m. p. 114—115°, resolidifying with m. p. 129—130°). Reduction of 3-nitro- $\alpha$ -methylcinnamic acid (Miller and Rohde, A., 1890, 1138) [ethyl ester (I), b. p. 197°/11 mm.] by iron and hydrochloric acid and bromination of the product gives 2 : 4 : 6-tribromo-3-amino- $\alpha$ -methylcinnamic acid, m. p. 208—209°. Attempts were made to resolve the strychnine, m. p. 123—127°,  $[\alpha]_D^{25} -24.0^\circ$ , brucine, m. p. 143—148°,  $[\alpha]_D^{25} -28.2^\circ$ , and quinine, m. p. 208—209°,  $[\alpha]_D^{25} -59.4^\circ$ , salts.  $\psi$ -Cumene and acetic anhydride in presence of aluminium chloride in boiling carbon disulphide give 2 : 4 : 5-trimethylacetophenone, b. p. 121—124°/5 mm., which with nitric acid (*d* 1.51) at  $-15^\circ$  gives 2 : 5-dinitro-3 : 4 : 6-trimethylacetophenone, m. p. 120—121°. Attempts to condense this with malonic acid by Knoevenagel's method were unsuccessful.  $\alpha$ -Bromophenylacetic acid and mesitylene in presence of aluminium chloride in carbon disulphide give 2 : 4 : 6-trimethyldiphenylacetic acid, m. p. 172—172.5°, the ethyl ester, b. p. 180—183°/4 mm., of which

does not react with magnesium phenyl bromide. Phenyl 2 : 4 : 6-trimethyldiphenylmethyl ketone, m. p. 111—112°, from desyl chloride (phenyl  $\alpha$ -chlorobenzyl ketone) and mesitylene, also fails to react. The ester I is converted through the dibromide, m. p. 68—69°, into  $\beta$ -bromo-3-nitro- $\alpha$ -methylcinamic acid, m. p. 131.5—132.5°, which, after reduction to the amino-derivative, failed to yield a tribromo-derivative. Reduction of the ester I with iron and hydrochloric acid and bromination of the product gives ethyl 2 : 4 : 6-tribromo-3-amino- $\alpha$ -methylcinamate, m. p. 107.5—108°, which cannot be further brominated. p-Nitrobenzamido-isobutenylmesitylene, m. p. 154—155°, yields a dibromide, which with boiling pyridine gives p-nitrobenzamido- $\alpha$ -bromoisobutenylmesitylene. Reduction of this compound did not yield a base suitable for resolution. isoButenylmesitylene, from  $\alpha$ -2 : 4 : 6-trimethylphenylisobutyl alcohol, b. p. 126°/5 mm. (cf. Klages, *loc. cit.*), gives on bromination and treatment with alcoholic potassium hydroxide  $\alpha$  : 3-dibromoisobutenylmesitylene, b. p. 140—145°/4 mm. Similar reactions with acetamido- and carbethoxyamido-isobutenylmesitylenes gave satisfactory bromo-derivatives, which could not, however, be de-acetylated without affecting the unsaturated side-chain. Amino-isobutenylmesitylenes give tarry products when brominated.

H. E. F. NOTTON.

**Activation experiments with stilbenecarboxylic acids.** P. PFEIFFER, D. J. DU PLESSIS, J. RICHARZ, and B. STALLMANN (J. pr. Chem., 1930, [ii], 127, 169—188).—Attempts to resolve certain substituted stilbenecarboxylic acids by means of the alkaloidal salts mentioned below were unsuccessful, no evidence being obtained of the non-planar configuration of ethylene compounds.

Condensation of o-nitro-p-toluenitrile with benzaldehyde to the nitrocyano-stilbene, followed by conversion into the ester with alcoholic hydrochloric acid and hydrolysis with aqueous-alcoholic sodium hydroxide, gave 2-nitrostilbene-4-carboxylic acid, m. p. 233—234° (85% yield from nitrile) (quinine, cinchonine, strychnine, and brucine salts). 2 : 3'-Dinitrostilbene-4-carboxylic acid, m. p. 249—250° (potassium salt), was prepared in 60—70% yield by heating o-nitro-p-toluenitrile and m-nitrobenzaldehyde in presence of piperidine for 1 hr. at 145°, followed by hydrolysis of the resultant 2 : 3'-dinitro-4-cyanostilbene, m. p. 255°, with alcoholic potassium hydroxide. 2-Nitro-2'-methoxystilbene-4-carboxylic acid has m. p. 232° [nitrile, m. p. 182°; ethyl ester, m. p. 93°; strychnine, m. p. 155° (decomp.), and brucine, m. p. 188—190°, salts].

p-Toluenitrile was nitrated with a mixture of equal volumes of sulphuric and nitric acids to o-nitro-p-toluic acid, m. p. 188°, the amide of which on further nitration with nitric and sulphuric acids yielded oo'-dinitro-p-toluic acid, m. p. 159° [ethyl ester (I), m. p. 75°]. I condenses with benzaldehyde in presence of piperidine at 130—140° to ethyl 2 : 6-dinitrostilbene-4-carboxylate, m. p. 125°, in 53% yield, hydrolysed by alcoholic sodium hydroxide to the acid, m. p. 235—236° (ammonium, quinine, m. p. 196°, and strychnine, m. p. 219°, salts). 2 : 6 : 3'-Trinitrostilbene-4-carboxylic acid was similarly prepared from m-nitrobenzaldehyde and I, and had m. p. 227—228° (ethyl ester, m. p. 151°;

ammonium, cinchonine, m. p. 215—217°, and brucine, m. p. 247°, salts). The following acids were likewise prepared by condensation of I and the appropriate aldehyde: 2 : 6 : 4'-trinitrostilbene-4-carboxylic acid, m. p. 228—230° (ethyl ester, m. p. 140°); 2 : 6-dinitro-2'-methoxystilbene-4-carboxylic acid, m. p. 216° (ethyl ester, m. p. 124°; strychnine and brucine, m. p. 185—188°, salts), whilst the under-mentioned acids were prepared from methyl 4 : 6-dinitrotoluate: 4 : 6-dinitrostilbene-2-carboxylic acid, m. p. 154.5° [methyl ester, m. p. 135.5°; barium, nearly +3H<sub>2</sub>O, cinchonine, m. p. 195—196°, and quinine, m. p. 186—187° (decomp.), salts]; 4 : 6-dinitro-4'-methoxystilbene-2-carboxylic acid, m. p. 174—175° (methyl ester, m. p. 142°; barium, +4H<sub>2</sub>O, quinine, m. p. 201°, and strychnine, m. p. 130—135°, salts); 4 : 6-dinitro-4'-methylstilbene-2-carboxylic acid, m. p. 170—172° (methyl ester, m. p. 165.5°; piperidine, m. p. 210°, and strychnine, +5.4H<sub>2</sub>O after drying at 100°, salts); 4'-chloro-4 : 6-dinitrostilbene-2-carboxylic acid, m. p. 205—206° (methyl ester, m. p. 160—161°; strychnine, m. p. about 140° (decomp.), and quinine, m. p. 174—176°, salts].

A. I. VOGEL.

#### Condensations of lævulic acid with aldehydes.

R. N. SEN and B. C. ROY (J. Indian Chem. Soc., 1930, 7, 401—416).— $\beta$ -Benzylidenelævulic acid, m. p. 125°, obtained in 70% yield by the action of hydrogen chloride at 0° on a mixture of lævulic acid and benzaldehyde, is converted by benzaldehyde and aqueous-alcoholic sodium hydroxide into  $\beta\delta$ -dibenzylidenelævulic acid, m. p. 146°, also prepared from the  $\delta$ -acid, benzaldehyde, and hydrogen chloride. Sodium  $\beta$ -benzylidenelævulate, benzaldehyde, and acetic anhydride at 100° afford  $\alpha\beta$ -dibenzylidenelævulic acid, m. p. 240°;  $\alpha\delta$ -dibenzylidenelævulic acid, m. p. 177°, is obtained similarly from the  $\delta$ -acid. The sodium salt of the  $\beta\delta$ -acid, benzaldehyde, and acetic anhydride afford  $\alpha\beta\delta$ -tribenzylidenelævulic acid, m. p. above 240°. Suitable lævulic acids are readily converted into cyclic compounds. Thus,  $\beta$ -p-nitrobenzylidenelævulic acid and acetic anhydride at 130—140° give 7-nitro-3-aceto- $\alpha$ -naphthol, m. p. 189°, and  $\delta$ -benzylidenelævulic acid is converted into benzo-1 : 4-diketo- $\Delta^5$ -cyclooctene,

$C_6H_4 \begin{cases} \text{CH}=\text{CH}\cdot\text{CO} \\ \text{CO}\cdot\text{CH}_2\cdot\text{CH}_2 \end{cases}$ , m. p. 196° (monophenylhydrazone; dinitro-derivative; dibenzoyl compound, m. p. 160°). Salicylaldehyde, lævulic acid, and hydrogen chloride give  $\beta$ -salicyl-lævulolactone, C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>, m. p. 151° (monophenylhydrazone, m. p. 132°; dibromo-derivative, C<sub>12</sub>H<sub>10</sub>O<sub>3</sub>Br<sub>2</sub>, m. p. 128°).

The following substituted lævulic acids are prepared by analogous methods:  $\beta$ -p-nitrobenzylidene-, m. p. 85° (phenylhydrazone, m. p. 130°; dibromo-derivative, m. p. 265°);  $\delta$ -benzylidene- $\beta$ -p-nitrobenzylidene-, m. p. 124°;  $\alpha$ -benzylidene- $\beta$ -p-nitrobenzylidene-, m. p. 260°;  $\delta$ -p-nitrobenzylidene-, m. p. 240° (phenylhydrazone, m. p. 251°; dibromo-derivative, m. p. 269°);  $\beta$ -benzylidene- $\delta$ -p-nitrobenzylidene-, m. p. 167°;  $\delta$ -m-nitrobenzylidene-, m. p. 254° (phenylhydrazone; dibromo-compound);  $\delta$ -o-nitrobenzylidene-, m. p. 169°;  $\alpha$ -o-nitrobenzylidene-, m. p. 121°;  $\delta$ -benzylidene- $\beta$ -o-nitrobenzylidene-, m. p. 157°;  $\beta$ -cinnamylidene-, m. p. 115° (dibromo-derivative; phenylhydrazone, m. p. 136°);  $\delta$ -benzylidene- $\beta$ -cinnamylidene-, m. p. 112°;  $\delta$ -cinnamylidene-, m. p. 161°;  $\beta$ -anisylidene-, m. p. 58°;  $\beta$ -

citrylidene-, m. p. 187°;  $\delta$ -vanillylidene-, m. p. 276°;  $\delta$ -salicylidene-, m. p. 166°;  $\beta$ -p-hydroxybenzylidene-, m. p. 260°;  $\delta$ -p-hydroxybenzylidene-, m. p. 109°;  $\delta$ -m-hydroxybenzylidene-, m. p. 110°;  $\delta$ -resorcyldene-, m. p. 251°.

The following naphthalene derivatives are obtained by appropriate ring-closure: 6(?8)-nitro-3-aceto- $\alpha$ -naphthol, m. p. 163°; 5-nitro-3-aceto- $\alpha$ -naphthol, m. p. 220°; 7-methoxy-3-aceto- $\alpha$ -naphthol, m. p. 164°; 7:8(?6:7)-methylenedioxy-3-aceto- $\alpha$ -naphthol, m. p. 234°; 6(?8)-hydroxy-3-aceto- $\alpha$ -naphthol, m. p. 164°; 7-hydroxy-8(?6)-methoxy-3-aceto- $\alpha$ -naphthol, m. p. 169°. 4-Hydroxy-6-acetocoumarone, m. p. 190°, is derived from furfuraldehyde, lævulic acid, and hydrogen chloride at 0–5°.

The following benzocyclooctatetraenes have been prepared: 9-nitro-1:4-dihydroxy-, m. p. 210°; 8(?10)-nitro-1:4-dihydroxy-, m. p. 296°; 1-hydroxy-3-aceto-, m. p. 230°; 1:4-dihydroxy-9-methoxy-, m. p. 78°; 1:4:9-trihydroxy-, m. p. 46°.

Cinnamylangelolactone, m. p. above 290°,  $\beta$ -resorcyllævulolactone, m. p. above 260°,  $\delta$ -salicylangelolactone, m. p. 168°,  $\beta$ -naphthyl-lævulolactone, m. p. 94° (bromo-derivative, m. p. 113°; benzylidene compound, m. p. 112°), with a substance, m. p. 223°, from 2-hydroxynaphthaldehyde, hydrogen chloride, and lævulic acid, and glucosyl-lævulolactone, m. p. 96° (tetra-acetate, m. p. 250°), are described. The lactones are all coloured compounds, those with seven-membered rings, from  $\beta$ -condensation products, being more deeply coloured than the five-membered ring compounds from  $\delta$ -condensations. H. WREN.

## 2-Naphthoylformic acid and its derivatives.

L. POPOVICI (Compt. rend., 1930, 191, 210–211).—Oxidation of  $\beta$ -naphthyl methyl ketone by potassium permanganate in alkaline solution at 53° yields 2-naphthoylformic acid, m. p. 171° (calcium, barium, magnesium, lead, and silver salts). The corresponding semicarbazone, m. p. 230°, and thiosemicarbazone, m. p. 226°, are described. Reduction of these compounds with sodium amalgam affords 2-naphthylsemicarbazidoacetic acid, m. p. 226°, and 2-naphthylthiosemicarbazidoacetic acid, m. p. 216°, respectively, which reduce Nessler's solution and are readily oxidised by iodine in alkaline solution. When warmed with dilute sodium hydroxide, the semicarbazone and thiosemicarbazone afford the triazines,  $C_{10}H_7 \cdot C \begin{smallmatrix} \diagup CO \cdot NH \\ \diagdown N \cdot NH \end{smallmatrix} \diagup CO$ , m. p. 289° (monobenzyl ether, m. p. 217°; dibenzyl ether, m. p. 179°), and  $C_{10}H_7 \cdot C \begin{smallmatrix} \diagup CO \cdot NH \\ \diagdown N \cdot NH \end{smallmatrix} \diagup CS$ , m. p. 274°.

H. WREN.

**Syntheses of arylated allene derivatives.** K. ZIEGLER and W. SAUERMILCH (Ber., 1930, 63, [B], 1851–1864).—Methenyldi-(1-phenyl-3-methylpyrazol-5-one) is converted successively into the sodium and silver compounds. The last-named salt is transformed by bromine in chloroform into a bromide,  $C_{21}H_{17}O_2N_4Br$ , m. p. 138° (decomp.), which could not be caused to lose hydrogen bromide.

Magnesium diphenylvinyl bromide and methyl benzoylformate afford methyl  $\alpha$ -hydroxy- $\alpha\alpha\gamma$ -triphenyl- $\Delta^{\beta}$ -butenoate, m. p. 128°, which could not be converted into an allenecarboxylate. When distilled in a

vacuum over aluminium phosphate, boiled with acetic anhydride (in addition to its acetyl derivative, m. p. 151°), acted on by sulphuric acid, or treated with phosphorus trichloride or thionyl chloride in presence of pyridine, it is converted into  $\gamma$ -hydroxy- $\alpha\alpha\gamma$ -triphenylcrotonolactone,  $\begin{smallmatrix} CPh \cdot CO \\ CH \cdot CPh_2 \end{smallmatrix} > O$ , m. p. 156°, also

obtained by heating  $\alpha$ -hydroxy- $\alpha\alpha\gamma$ -triphenyl- $\Delta^{\beta}$ -butenoic acid, m. p. 145° (decomp.). Since hydrogenation of the lactone in presence of palladised barium sulphate yields  $\alpha\alpha\gamma$ -triphenyl-*n*-butyric acid, it possibly exists in solution in equilibrium with traces of triphenylallenecarboxylic acid. Synthesis of the lactone is accomplished by bromination of  $\alpha\alpha\gamma$ -triphenyl- $\Delta^{\beta}$ -butenoic acid to the unstable dibromide, which immediately passes into  $\beta$ -bromo- $\gamma$ -hydroxy- $\alpha\alpha\gamma$ -triphenylbutyrolactone, m. p. 169°, transformed by sodium methoxide into the above lactone, m. p. 156°.

Ethyl  $\beta$ -phenylbutyrate is converted by magnesium phenyl bromide into  $\alpha\alpha\gamma$ -triphenylbutanol, m. p. 90–91°, which, with glacial acetic acid containing a little sulphuric acid, affords  $\alpha\alpha\gamma$ -triphenyl- $\Delta^{\alpha}$ -butene, b. p. 244°/33 mm. It is converted by addition of bromine and subsequent elimination of hydrogen bromide by heating into  $\beta$ -bromo- $\alpha\alpha\gamma$ -triphenyl- $\Delta^{\alpha}$ -butene, m. p. 107.5–108.5°, from which  $\alpha\alpha\gamma$ -triphenyl- $\Delta^{\alpha\beta}$ -butadiene ( $\alpha\alpha\gamma$ -triphenyl- $\alpha$ -methylallene), m. p. 102°, is obtained by amyl-alcoholic sodium hydroxide. The constitution of the hydrocarbon is established by reduction with sodium and alcohol to  $\alpha\alpha\gamma$ -triphenylbutane (identified by conversion into  $\alpha\alpha\gamma$ -triphenylvaleric acid) and by ozonisation to carbon dioxide, acetophenone, and benzophenone. Like tetraphenylallene, it is readily isomerised by mineral acids, but the product is not homogeneous. Protracted heating with acetic acid or acetic anhydride transforms the hydrocarbon into a hydrocarbon,  $C_{22}H_{18}$ , m. p. 163°, also obtained by the action of the acid on  $\alpha\alpha\gamma$ -trimethyl- $\Delta^{\alpha}$ -buten- $\gamma$ -ol, m. p. 61°, derived from magnesium, diphenylvinyl bromide, and acetophenone. The action of potassium phenylisopropyl on triphenylmethylallene does not consist simply in the replacement of a hydrogen atom of the methyl group by potassium.

$\alpha\alpha\gamma$ -Triphenyl- $\Delta^{\beta}$ -butene, b. p. 234°/12 mm., prepared from diphenylpropionophenone and magnesium methyl bromide, is ozonised to acetophenone. It is transformed by bromine and treatment of the product with pyridine into the compound  $CHPh_2 \cdot CH \cdot CPh \cdot CH_2 \cdot NC_5H_5 \cdot Br$ , m. p. 222°.

H. WREN.

**Configuration of molecules in space.** III. Ultra-violet absorption of the acids  $Ph \cdot [CH_2]_n \cdot CO_2H$ ,  $Ph \cdot [CH_2]_n \cdot CH(CO_2H)_2$ , and the hydrocarbons  $Ph \cdot [CH_2]_n \cdot Ph$ . (MME.) RAMART-LUCAS and J. HOCH (Compt. rend., 1930, 191, 100–102).—The ultra-violet absorption spectra of the compounds  $Ph \cdot [CH_2]_n \cdot CO_2H$  ( $n=1, 5$ , and  $6$ ),  $Ph \cdot [CH_2]_n \cdot CH(CO_2H)_2$  ( $n=0, 2$ , and  $4$ ), and  $Ph \cdot [CH_2]_n \cdot Ph$  ( $n=2, 4$ , and  $6$ ) which contain two chromophores incapable of chemical interaction, show that each chromophore influences the absorption of the other (for a physical interpretation see Lucas, this vol., 1087). In 0.1–0.01N-alcoholic solution both acids and hydrocarbons give absorption curves which are closely similar at low frequencies, and



the position of their maxima differs but little. The minima, however, diminish gradually as the number of carbon atoms separating the chromophores increases from one to four. When five carbon atoms separate the chromophores, the absorption curve becomes displaced towards the visible at low frequencies, the absorption band becoming enlarged towards the maximum, and the value of the minimum being increased.

C. W. SHOPPEE.

**Electrolytic reduction of phthalimides. I.** B. SAKURAI (Bull. Chem. Soc. Japan, 1930, 5, 184—189).—By electrolytic reduction at 20—30° of a 3% solution of phthalimide in 50% alcohol containing free hydrochloric or sulphuric acid with a current density of 2 amp./dm.<sup>2</sup>, hydroxyphthalimidine is obtained on rendering the solution alkaline and evaporating under reduced pressure. The product has m. p. 105° and is readily converted into the hydroxyphthalimidine of Reissert (A., 1913, i, 621) by dissolution in warm 6*N*-sulphuric acid and reprecipitation with alkali. Determination of the mol. wt. indicates that the electrolytic product is the normal substance, whereas Reissert's compound has the bimolecular formula. By reduction in more strongly acid solutions and at 6 amp./dm.<sup>2</sup> phthalimidine is produced. *N*-Methyl- and *N*-ethyl-phthalimides when reduced at a copper cathode yield *N*-methyl- and *N*-ethyl-hydroxyphthalimidine, m. p. 129° and 106°, respectively, but with a lead cathode the corresponding phthalimidine only is formed. Phenylhydroxyphthalimidine could not be prepared by reduction of phenylphthalimide, the phthalimidine being always formed directly. Electrolytic reduction of phthalimides in alkaline solution is impracticable, on account of rapid hydrolysis.

H. F. GILLBE.

**New isomerism of halogenohydroxybenzoyl-toluic acids. II.** 2-(5'-Chloro-2'-hydroxybenzoyl)-5(4?)-methylbenzoic acid. **III.** 2-(3'-Chloro-4'-hydroxybenzoyl)-3(or 6)-methylbenzoic acid. **IV.** 2-(4'-Chloro-2'-hydroxybenzoyl)-3(or 6)-methylbenzoic acid and 2-(2'-chloro-4'-hydroxybenzoyl)-3(or 6)-methylbenzoic acid. M. HAYASHI (J.C.S., 1930, 1513—1519, 1520—1523, 1524—1528).—I. When 4-methylphthalic anhydride is condensed with *p*-chlorophenol under the influence of aluminium chloride two chlorohydroxybenzoyltoluic acids can be separated from the product by fractional crystallisation from alcohol. They are readily interconvertible by treatment with sulphuric acid, which produces an equilibrium mixture, and are most probably 2-(5'-chloro-2'-hydroxybenzoyl)-5-methylbenzoic acid (I), m. p. 239.5—240.5°, and 2-(5'-chloro-2'-hydroxybenzoyl)-4-methylbenzoic acid (II), m. p. 227.5—228.5°, for I is produced in the greater amount (cf. A., 1927, 1187). Both acids, however, on dehydration with sulphuric acid, give the same substance, probably 8-chloro-5-hydroxy-2-methylanthraquinone, m. p. 214—215°, as I is present in the greater proportion in the sulphuric acid equilibrium mixture. This anthraquinone derivative is also produced in the initial condensation. The condensation of 4-methylphthalic anhydride with benzene gives similar, but non-interconvertible isomerides, viz., 2-benzoyl-5(or 4)-methylbenzoic acid, m. p. 150—150.5°, and

2-benzoyl-4(or 5)-methylbenzoic acid, m. p. 145—145.5°; both, when warmed with sulphuric acid, give 2-methylanthraquinone.

The following corrections to Part I (*loc. cit.*) are proposed: "β- and α-5'-chloro-2'-hydroxy-2-benzoyl-*m*-toluic acids" to 2-(5'-chloro-2'-hydroxybenzoyl)-3(or 6)- and -6(or 3)-methylbenzoic acids; "chlorohydroxymethylanthraquinone" to 8-chloro-5-hydroxy-1(or 4)-methylanthraquinone; "β- and α-5'-bromo-2'-hydroxy-2-benzoyl-*m*-toluic acids" to 2-(5'-bromo-2'-hydroxybenzoyl)-3(or 6)- and -6(or 3)-methylbenzoic acids; "bromohydroxymethylanthraquinone" to 8-bromo-5-hydroxy-1(or 4)-methylanthraquinone. 4-Methylphthalic acid was prepared by the hydrolysis of methyl 4-cyano-*m*-toluate, m. p. 60—60.5°, itself obtained from the amino-compound by the Sandmeyer reaction.

**III.** 3-Methylphthalic anhydride condenses with *o*-chlorophenol or *o*-chloroanisole to give 2-(3'-chloro-4'-hydroxybenzoyl)-3(or 6)-methylbenzoic acid, m. p. 198—199°, in 84% yield, convertible (apparently completely) by sulphuric acid into 2-(3'-chloro-4'-hydroxybenzoyl)-6(or 3)-methylbenzoic acid, m. p. 188.5—189°. Further condensation to a derivative of anthraquinone could not be effected; these orientations are derived by analogy with preceding condensations and with the interaction of *o*-chlorophenol or *o*-chloroanisole and phthalic anhydride to give 2-(3'-chloro-4'-hydroxybenzoyl)benzoic acid, m. p. 219.5—220° (methyl ether, m. p. 179—180°), unaffected by cold sulphuric acid, but converted by it at 195° into 2-chloro-3-hydroxyanthraquinone.

**IV.** Condensation of *m*-chlorophenol or *m*-chloroanisole with 3-methylphthalic anhydride gives a mixture of 2-(4'-chloro-2'-hydroxybenzoyl)-3(or 6)-methylbenzoic acid (A), m. p. 219.5—220.5°, and 2-(2'-chloro-4'-hydroxybenzoyl)-3(or 6)-methylbenzoic acid (B), m. p. 218—218.5°, converted by cold sulphuric acid into 2-(4'-chloro-2'-hydroxybenzoyl)-6(or 3)-methylbenzoic acid (A'), m. p. 177.5—178°, and 2-(2'-chloro-4'-hydroxybenzoyl)-6(or 3)-methylbenzoic acid (B'), m. p. 201—202°. The constitution of these acids is deduced from a comparison of their absorption spectra with those of the products described in the preceding parts, and from the conversion of A and A' into 6-chloro-8-hydroxy-1(or 4)-methylanthraquinone (also produced in small yield in the original condensation), m. p. 196.5—197°, by concentrated sulphuric acid at 200°, neither B nor B' giving an anthraquinone derivative under these conditions. The interaction of quinol with 3-methylphthalic anhydride under the usual conditions produces 2-(2':5'-dihydroxybenzoyl)-3(or 6)-methylbenzoic acid, m. p. 232.5—233°, not isomerised by sulphuric acid, but converted by it into 5:8-dihydroxy-1-methylanthraquinone. H. A. PIGGOTT.

**Action of phthaloyl chloride on phenyl methyl sulphide.** W. KNAPP (Monatsh., 1930, 56, 66—70).—Phthaloyl chloride reacts with phenyl methyl sulphide in presence of carbon disulphide and aluminium chloride at 30—40°, forming 4':4''-dimethylthiol-diphenylphthalide, m. p. 99—100° (cf. Chakravarti and Saha, A., 1927, 970). This is not readily demethylated, is oxidised by 30% hydrogen peroxide in acetic acid to the corresponding disulphone, m. p. 214—

216°, and reduced by sodium amalgam and alcohol to 4':4''-dimethylthioltriphenylmethane-2-carboxylic acid, m. p. 155—156°. H. BURTON.

**Odoriferous activity of the homovanillins.** J. KOETSCHET and P. KOETSCHET (Helv. Chim. Acta, 1930, **13**, 474—482).—A study of the relative strengths of odour of vanillin (I) and the four homovanillins, in which the methyl group is introduced into the  $\omega$ -position (4-hydroxy-3-ethoxybenzaldehyde; II), and into the three available nuclear positions (III, IV, and V below). By tasting an extremely dilute solution, a method claimed to be a sensitive test of odour, the following relative values were obtained: I:II:III:IV:V=1:2:0:0.4:0, III and IV having no odour of vanillin at all. The following were prepared from the appropriate alkoxycresols by the Reimer-Tiemann reaction: 4-hydroxy-5-methoxy-3-methylbenzaldehyde (III), m. p. 99° (phenylhydrazone, m. p. 125°); 4-hydroxy-5-methoxy-2-methylbenzaldehyde (IV), m. p. 174—175° (Heyden, G.P. 91,170, gives m. p. 165°) (semicarbazone, m. p. 207°; phenylhydrazone, m. p. 143—144°), together with 6-hydroxy-5-methoxy-2-methylbenzaldehyde, m. p. 61—62° (semicarbazone, decomp. without melting above 210°); and 4-hydroxy-3-methoxy-2-methylbenzaldehyde, m. p. 104.5—105.5°. An improved modification of Majima's method (A., 1916, i, 808) for the preparation of 3-methoxy-o-cresol, and the methylation of 3-nitro-o-cresol with methyl sulphate and alkali to give a 90% yield of methyl ether, are described.

H. A. PIGGOTT.

**4-Hydroxy-5-methoxyisophthalaldehyde.** J. KOETSCHET and P. KOETSCHET (Helv. Chim. Acta, 1930, **13**, 482—491).—In addition to vanillin and o-vanillin, the Reimer-Tiemann reaction on guaiacol gives 4-hydroxy-5-methoxyisophthalaldehyde, m. p. 121° (diphenylhydrazone, m. p. 188—191°; di-p-nitrophenylhydrazone, m. p. 286.5—287°; monoxime, m. p. 166.5—167°; dioxime, m. p. 185—186°; methyl ether, m. p. 123.5—124°). On nitration it yields an unidentified substance, m. p. above 300°, which does not possess aldehydic characteristics, a mononitro-derivative, either 2- or 6-nitro-4-hydroxy-5-methoxyisophthalaldehyde, m. p. 192—194° (diphenylhydrazone, m. p. 228—229°; dioxime, m. p. 196—197°), and 5-nitro-2-hydroxy-3-methoxybenzaldehyde, m. p. 136.5—137.5° (phenylhydrazone, m. p. 199.5—200.5°). The constitution of the last-named was confirmed by direct comparison with a sample prepared by the nitration of o-vanillin (cf. Davies, J.C.S., 1923, **123**, 1575).

H. A. PIGGOTT.

**Purification of some sensitive ketones.** G. A. R. KON (J.C.S., 1930, 1616—1618).—Mobile ketones of the type of cyclohexylideneacetone can be obtained pure by shaking their semicarbazones, suspended in a large volume of light petroleum, with the amount of 0.5N-sulphuric acid calculated to form semicarbazide hydrogen sulphate. In the case of isopulegone it is advisable to use one half the above proportion of acid diluted to about 0.13N. The following are described in the pure state for the first time: isopulegone, b. p. 100.5°/18 mm.,  $d_4^{25}$  0.91785,  $n_D^{25}$  1.46718;  $\Delta^1$ -cyclohexenylacetone, b. p. 80°/15 mm.,  $d_4^{25}$  0.93901,  $n_D^{25}$  1.47300; cyclohexylideneacetone, b. p. 83°/9 mm.,

$d_4^{25}$  0.94586,  $n_D^{25}$  1.49223;  $\Delta^1$ -cyclohexenylmethyl ethyl ketone, b. p. 92°/10 mm.,  $d_4^{25}$  0.93022,  $n_D^{25}$  1.47291; cyclohexylidenemethyl ethyl ketone (from both forms of the semicarbazone), b. p. 110°/20 mm.,  $d_4^{25}$  0.93622,  $n_D^{25}$  1.49118; cyclopentylideneacetone, b. p. 74—76°/14 mm.,  $d_4^{25}$  0.94282,  $n_D^{25}$  1.48541; pulegone, b. p. 109°/19 mm.,  $d_4^{25}$  0.93808,  $n_D^{25}$  1.48810.

H. A. PIGGOTT.

**Action of sulphur on ketones.** T. W. JEZERSKI (Rocz. Chem., 1930, **10**, 397—399).—Sulphur does not in an inert atmosphere substitute hydrogen atoms in the phenyl group, and does not react with the oxygen of carboxyl groups. Acetophenone, on heating with sulphur, yields diphenacyl, together with a small quantity of diphenylthiophen. With p-ethylbenzophenone the sole product is 2:5-di-(p-benzoylphenyl)-thiophen, m. p. 233—234°. Benzophenone does not react with sulphur.

R. TRUSZKOWSKI.

**Condensation of aromatic monoketones with tertiary aromatic amines under the influence of aluminium chloride.** C. COURTOT and V. OUPÉROFF (Compt. rend., 1930, **191**, 214—216).—Benzophenone is converted by dimethylaniline and aluminium chloride at 40—50° into p-dimethylaminotriphenylcarbinol, m. p. 92—93° (or the corresponding amine), whereas at 75—85° p-dimethylaminotriphenylmethane, m. p. 132°, is produced. Introduction of a dimethylamino-group into the benzophenone greatly hinders the condensation, so that, under all conditions of temperature, malachite-green is obtained only in minute amount. Condensation does not take place with Michler's ketone. Phenyl  $\alpha$ -naphthyl ketone and dimethylaniline at 40—50° afford p-dimethylaminodiphenyl- $\alpha$ -naphthylcarbinol (isolated as the compound of its hydrochloride with zinc chloride), whereas p-dimethylaminodiphenyl- $\alpha$ -naphthylmethane, m. p. 163—164°, is produced at 80—90°. Phenyl  $\beta$ -naphthyl ketone and dimethylaniline yield the corresponding carbinol (isolated as chloride or zincchloride) by a slightly exothermic reaction; reduction of the carbinol to hydrocarbon is not observed. With fluorone the change is markedly exothermic, giving pp'-tetramethyldiaminodiphenyldiphenylmethane, m. p. 161°; the intermediate carbinol could not be isolated.

H. WREN.

**Dibenzoyltetraphenylethane and its radical dissociation.** A. LÖWENBEIN and L. SCHUSTER (Annalen, 1930, **481**, 106—119).—Phenylbenzoin is converted by hydrogen chloride in glacial acetic acid containing acetic anhydride at 100—110° into benzoyldiphenylmethyl chloride, m. p. 84°. Benzoyldiphenylmethyl bromide, m. p. 99°, prepared similarly, is transformed by sodium thiocyanate in acetone into benzoyldiphenylmethyl thiocyanate, m. p. 151.5°. The bromide is rapidly converted by boiling acetone into benzoyldiphenylmethane with production of bromoacetone. A similar change is observed with ethyl acetate or acetoacetate and reaction occurs quantitatively with acetophenone. With sodium iodide in acetone, iodoacetone and benzoyldiphenylmethane are produced. Alcoholic hydrazine reduces the bromide or chloride to benzoyldiphenylmethane at the ordinary temperature. Phenylhydrazine behaves similarly and does not attack the ethanone formed.

Reduction also occurs by use of hydrazobenzene or with concentrated hydrogen bromide in glacial acetic acid. With the bromide and 2 mols. of a Grignard reagent, the intermediate production of the radical is observed and benzoyldiphenylmethane is quantitatively produced. With magnesium phenyl bromide the reaction follows the course  $\text{CPh}_2\text{Br} \cdot \text{Bz} + \text{PhMgBr} = -\text{CPh}_2\text{Bz} +$

$\text{MgBr}_2 + \text{C}_6\text{H}_5$  (diphenyl);  $-\text{CPh}_2\text{Bz} \rightarrow \text{CPh}_2\text{CPh} \cdot \text{O}^-$ ;  $\text{CPh}_2\text{CPh} \cdot \text{O}^- + \text{PhMgBr} \rightarrow \text{CPh}_2\text{CPh} \cdot \text{O} \cdot \text{MgBr} + \text{C}_6\text{H}_5$  (diphenyl). If the bromine of benzoyldiphenylmethyl bromide is replaced by the methoxy-, ethoxy-, or phenoxy-group the normal behaviour of the ketonic group towards the Grignard reagent is restored. Benzoyldiphenylmethyl bromide is most conveniently converted into *s*-dibenzoyltetraphenylethane, m. p. 148–151°, by treatment with mercury in presence of benzene. The colourless solutions of the substance become orange-red when gently warmed. The hot solution of the substance in benzene is immediately decolorised by phenylhydrazine with evolution of nitrogen and quantitative production of benzoyldiphenylmethane, which is also formed by use of magnesium phenyl bromide. With sodium in hot toluene the sodium compound of triphenylvinyl alcohol is produced, converted by hydrochloric acid into benzoyldiphenylmethane. Bromine is not decolorised by the radical. Its sensitiveness towards oxygen could not be determined, since it does not appear to yield a peroxide, although the radical colour is discharged. From boiling xylene solution benzil and benzophenone are obtained by means of oxygen.

H. WREN.

**Formation of phenols from dibromides of cyclohexenones.** A. D. PETROV (J. Russ. Phys. Chem. Soc., 1930, 62, 925–932).—Phenyl 4-methoxystyryl ketone is condensed with ethyl sodioacetate to yield 6-carbethoxy-3-phenyl-5-anisylcyclohexenone, m. p. 106–107°, from which 3-phenyl-5-anisylcyclohexenone, m. p. 98° (oxime, m. p. 173°), is prepared. *p*-Methylacetophenone is condensed with *p*-methoxybenzaldehyde to yield *p*-tolyl 4-methoxystyryl ketone, m. p. 97–98°, from which 6-carbethoxy-3-*p*-tolyl-5-anisylcyclohexenone, m. p. 156–157°, is prepared as above, and this yields on hydrolysis 3-*p*-tolyl-5-anisylcyclohexenone, m. p. 86–87° (oxime, m. p. 170°). The above homologues of cyclohexenone, as well as 5-anisyl-3-methyl- and 5-phenyl-3-methylcyclohexenone (dibromo-derivative, m. p. 69°), do not, on treatment with bromine in acetic acid according to Knoevenagel's method, yield phenolic products. Phenylacetaldehyde condenses with ethyl acetoacetate to yield ethyl phenylethylidenediacetoacetate, m. p. 136°, which gives a cyclic oxime, m. p. 172°. The above ester gives on treatment with alkali hydroxide 5-benzyl-3-methylcyclohexenone, b. p. 200–201°/20 mm., which yields the corresponding phenol (tribromide, m. p. 121–122°) on treatment according to Knoevenagel's method.

R. TRUSZKOWSKI.

**Co-ordination compounds of oximes.** O. L. BRADY and M. M. MUERS (J.C.S., 1930, 1599–1603).—*O*-Monomethyl- $\alpha$ -benzildioxime yields coloured co-ordination compounds with cobalt,  $(\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_2)_3\text{Co}$ , m. p. 165–169° (decomp.), and nickel,  $(\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_2)_2\text{Ni}$ ; apparently also compounds are

formed by interaction with copper and ferrous salts, but these are too unstable for isolation. The presence of atmospheric oxygen is necessary for formation of the cobalt derivative. The two other known *O*-monomethylbenzildioximes (this vol., 475) do not give metallic complexes. For the cobalt compound a "nitron" formula (cf. Hieber and Leutert, A., 1929, 1073) is suggested; the alternative permitted by Moisenheimer's configuration with a cobalt-oxygen linking involves a rearrangement of the oxime, whereas the nickel complex regenerates the original oxime when heated with potassium cyanide in alcoholic solution. Attempts to regenerate the oxime from the cobalt compound failed.  $\alpha$ -Benzildioxime gives a crystalline complex with cobalt,  $(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Co}$ , and a cobalt complex of indefinite composition may be obtained from  $\gamma$ -benzildioxime.

H. A. PIGGOTT.

**Oxidation of  $\alpha$ -ketols with Fehling's solution.** A. WEISSBERGER, W. SCHWARZE, and H. MAINZ (Annalen, 1930, 481, 68–80; cf. A., 1929, 1301; this vol., 475).—The oxidation of benzoin by alkaline cupric tartrate is unimolecular and the reaction velocity is proportional to the concentration of free alkali, i.e., alkali in excess of the 2 mols. concerned in forming the copper hydroxide complex (cf. Kahlenberg, A., 1896, ii, 6); the velocity is independent of the concentration of copper salt and is therefore not a measure of the direct reaction with the oxidising agent. It is suggested that the slowest phase of the complete reaction (i.e., that determining the velocity) is the transformation of the ion  $-\text{O} \cdot \text{CHPh} \cdot \text{COPh}$  into the ion of stilbenediol  $-\text{O} \cdot \text{CPh} : \text{CPh} \cdot \text{OH}$ , and this is confirmed by the small differences observed in the respective velocities of oxidation by Fehling's solution and of auto-oxidation (*loc. cit.*), where large concentration differences of the available oxidising agent obtain.

The effect of substituents follows the same rule as in the case of auto-oxidation, the rate of oxidation with Fehling's solution thus also being related to the electrolytic dissociation of the ketol.

R. CHILD.

**Anthracene derivatives.** I. E. DE B. BARNETT, N. F. GOODWAY, and J. L. WILTSHIRE (Ber., 1930, 63, [B], 1690–1697).—1 : 8-Dichloro-10-ethoxyanthrone, m. p. 177°, and 4 : 5-dichloro-10-methoxyanthrone, m. p. 136°, are readily prepared from the corresponding bromoanthrones by treatment with calcium carbonate and the requisite boiling alcohol and are transformed by acetic anhydride and pyridine into 1 : 8-dichloro-10-ethoxy-9-anthranyl acetate, m. p. 139°, and 4 : 5-dichloro-10-methoxy-9-anthranyl acetate, m. p. 178°, respectively; the co-ordinative linking between the *meso*-hydrogen atom and chlorine in positions 4 and 5 appears greatly weakened by the alkoxy-group. 4 : 5-Dichloro-10-ethoxyanthrone, m. p. 142°, and 4 : 5-dichloro-10-ethoxy-9-anthranyl acetate, m. p. 155°, are described. *Bz*-Chloro-10-nitroanthrones are readily prepared by the action of nitric acid in glacial acetic acid on the requisite anthranyl acetates and are rapidly converted by acetic anhydride and pyridine at the ordinary temperature into the nitroanthranyl acetates provided that chlorine is not present in position 4 or 5. The following compounds are described: 1-chloro-10-nitroanthrone, m. p. 157°; 1-chloro-10-nitro-9-anthr-

*anyl acetate*, m. p. 194°; 2-chloro-10-nitroanthrone, decomp. 130°; 2-chloro-10-nitro-9-anthranlyl acetate, m. p. 196°; 3-chloro-10-nitroanthrone, decomp. 153°; 3-chloro-10-nitro-9-anthranlyl acetate, m. p. 185°; 4-chloro-10-nitroanthrone, m. p. 134° (slight decomp.); 1:8-dichloro-10-nitroanthrone, m. p. 183° (decomp.); 4:5-dichloro-10-nitroanthrone, m. p. 145° (decomp.). Only Bz-chloro-10-bromoanthrones which do not contain a chlorine atom in positions 4 or 5 resemble 10-bromoanthrone in behaviour towards piperidine, whereas those with a chlorine atom in position 4 or 5 afford piperidino-compounds. In this connexion the following substances are described: 2-chloro-10-bromoanthrone, m. p. about 160° (decomp.); 2:2'-dichlorodanthraquinone, not molten below 300°; 3-chloro-10-bromoanthrone, m. p. about 160° (decomp.); 3:3'-dichlorodanthraquinone, not molten below 300°; 4-chloro-10-piperidinoanthrone, m. p. 191°, from 4-chloro-10-bromoanthrone; 1:4-dichloro-10-piperidinoanthrone, m. p. 162°; 4:5-dichloro-10-piperidinoanthrone, m. p. 189°; 1:8-dichloro-9-acetoxy-10-anthranlylpyridinium bromide, not molten below 300°; 4:5-dichloroanthronylpyridinium bromide, m. p. 192° (decomp.). 1:8-Dichloroanthrone is converted by the requisite aldehyde in boiling pyridine in presence of piperidine into the corresponding 10-benzylidene, m. p. 153°, and 10-furfurylidene, m. p. 184°, derivatives, whereas 1:5- and 4:5-dichloroanthrones are not affected by this treatment. H. WREN.

**Reaction between benzoquinone and cinnamaldehyde under the influence of light.** G. BARGELLINI and (Miss) L. MONTI (Gazzetta, 1930, 60, 474—478).—Insolation of a mixture of benzoquinone and cinnamaldehyde in varying proportions dissolved in benzene gives a good yield of *p*-hydroxyphenyl cinnamate, m. p. 172—173° (monoacetyl derivative, m. p. 121—122°), converted by treatment with ethyl iodide and alcoholic potassium hydroxide into quinol diethyl ether, m. p. 74—75°; the acetyl derivative by reduction with palladium-black and hydrogen in alcoholic solution yields *p*-acetoxyphenyl  $\beta$ -phenylpropionate, m. p. 84—86°. The reaction is comparable with that occurring between phenanthraquinone and various aldehydes, but differs from that taking place between benzoquinone and acetaldehyde, valeraldehyde, and benzaldehyde, which affords styryl methyl ketones (Klinger and others, A., 1888, 888; 1891, 900; 1898, i, 467; 1911, i, 633). C. W. SHOPPEE.

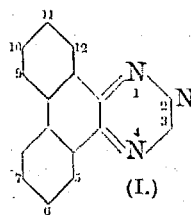
**2:5-Dichloroquinol dimethyl ether.** M. KOHN and E. GUREVITSCH (Monatsh., 1930, 56, 135—136).—Treatment of 2:5-dichloroquinol dimethyl ether with cold fuming nitric acid gives 2:5-dichloro-*p*-benzoquinone, m. p. 161—162° (cf. Kohn and Marberger, A., 1925, i, 1264), which is reduced and acetylated when heated with zinc dust and a mixture of acetic acid and anhydride, forming 2:5-dichloroquinol diacetate, m. p. 141°. H. BURTON.

**Friedel-Crafts reaction. Diphenyl series. I. Preparation of 2-4'-phenylbenzoylbenzoic acid and derivatives. II. Preparation of 2-phenylanthraquinone and derivatives.** P. H. GROGGINS (Ind. Eng. Chem., 1930, 22, 620—625, 626—630).—I. 2-4'-Phenylbenzoylbenzoic acid, m. p. 231.5° (corr.) (lit. 226°), is obtained (in yields amounting to

about 95% of the theoretical) when a mixture of diphenyl (1 mol.), phthalic anhydride (1 mol.), and anhydrous aluminium chloride (1.1 mol.) is heated at 60—65° in a horizontal rotating iron mill. The reaction mixture is agitated by means of loose iron blocks inside the mill. Similarly, 2- and 4-chlorodiphenyls afford 2-4'-2''- and 2-4'-4''-chlorophenylbenzoylbenzoic acids, m. p. 190° (corr.) and 251° (corr.), respectively. These are converted by 40% potassium hydroxide solution at 300° into 2-4'-2''- and 2-4'-4''-hydroxyphenylbenzoylbenzoic acids, m. p. 262° (corr.) and 245—246°, respectively, also prepared from 2- and 4-hydroxydiphenyls and phthalic anhydride. Treatment of the chloro-acids with ammonia at 210° in presence of cuprous chloride and copper turnings yields 2-4'-2''- and 2-4'-4''-aminophenylbenzoylbenzoic acids, m. p. 280—282° and above 300°, respectively. Oxidation of 2-4'-phenylbenzoylbenzoic acid and its chloro-derivatives with chromic oxide and 75% acetic acid affords benzophenone-2:4'-dicarboxylic acid, also prepared by oxidation of 2-*p*-toluoylbenzoic acid with alkaline potassium permanganate.

II. When 2-4'-phenylbenzoylbenzoic acid is heated with 96% sulphuric acid at 85—90° sulphonation occurs. Subsequent heating at 125° gives a 2-sulphophenylanthraquinone (sodium salt) which is not hydrolysed by alkaline hyposulphite. Similarly, 2-4'-2''-chlorophenylbenzoylbenzoic acid affords a 2-*o*-chlorosulphophenylanthraquinone (sodium salt), but the 4''-chloro-derivative furnishes 2-*p*-chlorophenylanthraquinone, m. p. 210° (corr.). 2-*o*-Chlorophenylanthraquinone, m. p. 205° (corr.), is obtained when the reaction is carried out in presence of nitrobenzene. 2-Phenylanthraquinone, m. p. 162—162.5° (corr.), is best prepared by dehydrating 2-4'-phenylbenzoylbenzoic acid with aluminium chloride in nitrobenzene at 200°. The above anthraquinones all give a red vat with alkaline sodium hyposulphite, and are oxidised by chromic oxide and acetic acid to anthraquinone-2-carboxylic acid. 2-*o*- and -*p*-Aminophenylanthraquinones, m. p. 255—256° and 220—221°, respectively, result when the corresponding chloro-derivatives are heated with ammonia at 210—220° in presence of copper, cuprous chloride, and nitrobenzene. H. BURTON.

**Hydrazides. III. Condensation of semicarbazide and thiosemicarbazide with phenanthraquinone and its derivatives and synthesis of triazines.** S. C. DE (J. Indian Chem. Soc., 1930, 7, 361—365).—Thiosemicarbazide behaves exactly like semicarbazide towards phenanthraquinone and its derivatives. Phenanthraquinone and thiosemicarbazide in acetic acid afford phenanthraquinonethiosemicarbazone, m. p. 212°, converted by protracted heating in the solvent into 3-thiolphenanthratiazine (cf. I), m. p. 198°, also obtained from phenanthraquinone monoxime and thiosemicarbazide. 2-Nitrophenanthraquinonethiosemicarbazone, m. p. 234—235°; 6-nitro-3-thiolphenanthratiazine, m. p. above 300°; 2:7-dinitrophenanthraquinonethiosemicarbazone, m. p. 253°; 6:11-dinitro-3-thiolphenanthratiazine, m. p. 220°; and 4-nitrophenanthraquinonethiosemicarbazone, m. p.



145°, are analogously prepared; 8-nitro-3-thiophenanthriazine, m. p. 230°, is derived from 4-nitro-phenanthraquinonemonoxime and thiosemicarbazide hydrochloride. Phenanthraquinonesemicarbazone is converted by protracted heating with acetic acid into 3-hydroxyphenanthriazine, m. p. 287°. Similarly, 8-nitro-3-hydroxyphenanthriazine, m. p. 286°, is prepared from 4-nitrophenanthraquinonesemicarbazone, and 6:11-dibromo-3-hydroxyphenanthriazine, m. p. 295°, from 2:7-dibromophenanthraquinonesemicarbazone, m. p. above 300°. Phenanthraquinone-phenylthiosemicarbazone, m. p. 206°, evolves hydrogen sulphide freely when heated in acetic acid, giving a green compound, m. p. above 300°. H. WREN.

**Linear pentacene series. XIX. Constitution of the disubstituted [dibromo-] derivatives of pentacene-5:7:12:14-diquinone.** G. MACHEK (Monatsh., 1930, 56, 116—134).—The dibromopentacene-5:7:12:14-diquinones previously described (this vol., 608) are most probably the 1:8- and 1:11- (more fusible) derivatives, since they differ from the 2:9- and 6:13-derivatives, the preparations of which are now described. The 2:10-dibromo-derivative has not been obtained pure. Physical data and the colorations with sulphuric acid of various substituted pentacene-5:7:12:14-diquinones are tabulated.

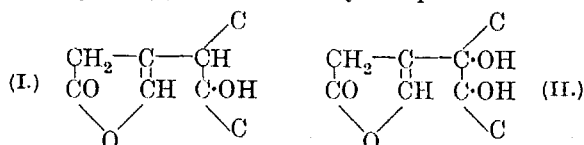
[With H. MARTIN.]—Treatment of 6:13-dihydroxy-pentacene-5:7:12:14-diquinone with phosphorus pentabromide in nitrobenzene gives the 6:13-dibromo-derivative, m. p. 400° (slight decomp.) after softening at 370°. The Friedel-Crafts reaction with pyromellitic anhydride and bromobenzene affords a product which when heated with 50 parts of sulphuric acid first at 100° and then at 150° (bath) gives 2:9-dibromopentacene-5:7:12:14-diquinone, m. p. 432° (corr.). The above reaction product is separable into (a) less fusible and (b) more fusible fractions by crystallisation from acetic acid. Neither *a* nor *b* is a pure di-*p*-bromobenzoylphthalic acid (cf. Philippi and Auslaender, A., 1921, i, 728), but *a* is probably a mixture of 2:5-di-*p*-bromobenzoylterephthalic acid and 2:5-dibenzoyl derivative, since, on heating with 20 parts of sulphuric acid at 150°, it furnishes a molecular (1:1) compound of pentacene-5:7:12:14-diquinone and its 2:9-dibromo-derivative. When either *a* or *b* is heated with 50 parts of acid the 2:9-dibromoquinone is produced.

Bromination of pentacene-5:7:12:14-diquinone in presence of a trace of iodine at 327—328° affords small amounts of impure dibromo-derivatives or two tetrabromopentacene-5:7:12:14-diquinones, m. p. 394—396° (corr.) and 318—319° (corr.), according to the amount of quinone used. H. BURTON.

**Rotenone. VI. Derric acid.** F. B. LAForge and L. E. SMITH (J. Amer. Chem. Soc., 1930, 52, 2878—2881).—Derric acid (this vol., 781) is oxidised in alkaline solution by permanganate to a dibasic acid,  $C_{11}H_{12}O_7$ , m. p. 261—263° (barium salt). In presence of magnesium sulphate traces of a second acid, (?)  $C_{10}H_{12}O_5$ , m. p. 183°, are formed. Derric acid is probably an  $\alpha$ -hydroxy- $\alpha$ -dimethoxyphenylsuccinic acid, the carboxyl groups of which are present in rotenone as ketonic and lactonic groups,

respectively. The suggestion of Butenandt (this vol., 478) that the 2H which is lost in the formation of dehydrorotenone derivatives comes from the derric acid residue is rejected in favour of the author's original theory. Dihydrodihydroxyrotenonic acid is quantitatively converted by alcoholic sulphuric acid into its ethyl ester, m. p. 98°. H. E. F. NOTTON.

**Structural correlation of gitoxigenin with digitoxigenin.** W. A. JACOBS and E. L. GUSTUS (Science, 1929, 70, 639—640).—Gitoxigenin (II) is shown to be hydroxydigitoxigenin and is related to digitoxigenin (I) as indicated by the partial formulæ



In all other respects the two substances are structurally identical. L. S. THEOBALD.

**$\gamma$ -Terpinene. III.** F. RICHTER and W. WOLFF (Ber., 1930, 63, [B], 1714—1721; cf. A., 1927, 364).— $\gamma$ -Terpinene, b. p. 183°/760 mm., 72.5°/18 mm.,  $d_4^{25}$  0.853,  $n_D^{25}$  1.4754, is readily obtained by fractional distillation under diminished pressure and in an atmosphere of nitrogen of technical "thymeno" obtained from ajowan oil. The cloudiness which develops in the material when exposed to air is due to concentrated hydrogen peroxide; the product of the change is almost exclusively *p*-cymene. Auto-oxidation is completely inhibited by traces of quinol. In presence of osmium and oxygen,  $\gamma$ -terpinene affords mainly *p*-cymene with only traces of thymoquinone. Treatment of  $\gamma$ -terpinene with hydrogen in presence of palladium-black and ether proceeds violently with absorption of only about 25% of the calculated volume of gas; the product, which is stable to perbenzoic acid, consists of menthano, menthene, and *p*-cymene. The identity of  $\gamma$ -terpinene with erithmene is established.  $\gamma$ -Terpinene is conveniently identified as the tetrabromide, m. p. 128°. The nitrosochloride of  $\gamma$ -terpinene is decomposed by sodium acetate in glacial acetic acid into azoxy- and azo-cymene and a colourless, crystalline substance, m. p. 144°, provisionally regarded as the acetyl derivative of 2-hydroxylamino-*p*-cymene,

$\text{CH} \begin{array}{c} \text{CH}=\text{CMe} \\ \text{CPr}^2-\text{CH} \end{array} > \text{C} \cdot \text{Nac} \cdot \text{OH}$ . It is converted by sulphuric acid into *p*-aminothymol, by perbenzoic acid into a green nitroso-compound, and by chromic acid into thymoquinone.

$\alpha$ -Terpinene, b. p. 173.5—174.8°/755 mm. (marked resinification),  $d_4^{25}$  0.8375,  $n_D^{25}$  1.477, is readily isolated by fractional distillation under diminished pressure of the hydrocarbon mixture obtained by the action of aniline on terpinene dihydrochloride;  $\gamma$ -terpinene and terpinolene are identified in the fractions of higher b. p. Its behaviour towards palladium and hydrogen is precisely similar to that of the  $\gamma$ -isomeride.  $\alpha$ -Phellandrene and limonene are also unstable towards palladium at the atmospheric temperature.

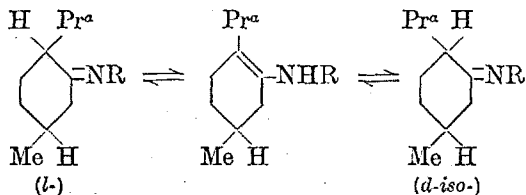
H. WREN.

**Menthones. I. Chemical and physical properties.** T. HIRAIKZUMI (Reprint Chikashige

Anniv. Vol. Kyoto, 1930, 87—110).—The values of a number of physical constants have been determined for the isomeric menthones and some of their derivatives. In conformity with the measurements of Zeitschel and Schmidt (A., 1926, 1250), they are higher for *d*-isomenthone and its derivatives than for *l*-menthone and its derivatives, consequently the Auwers-Skita rule confirms the *cis*-configuration assigned to the former by Komatsu and Kurata (A., 1925, i, 943). An attempted separation of *d*-isomenthoneoxime from an inverted *l*-menthone solution by Beckmann's method failed (cf. A., 1909, i, 245), but partial hydrolysis of the mixed oxime hydrochlorides gave the *d*-isooxime in a purity of 93% ( $[\alpha]_D +28.88^\circ$ ). The separation of *d*-isomenthone from such a mixture may also be effected by partial semicarbazone formation, the semicarbazone of the *l*-compound being formed preferentially.

*l*-Menthone, when hydrogenated in the liquid phase at  $260^\circ$  and 50 atm., gives a mixture from which *l*-menthol and *d*-neomenthol may be separated in the proportions 7:4. By a similar process *r*-menthone gives *r*-menthol and *r*-neomenthol in the ratio 2:12:1. Other methods of reduction give products in which the neomenthols predominate.

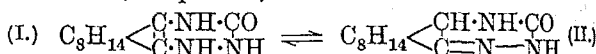
In ethereal hydrogen chloride solution *l*-menthoneoxime is transformed into *d*-isomenthoneoxime and vice versa; the latter tends to separate from the solution on account of its inferior solubility, and consequently may be completely separated from the former. Similarly, the corresponding semicarbazones form an equilibrium mixture in aqueous chloral hydrate solution, but in this case the reaction is complicated by the separation of glyoxylic acid semicarbazone, produced by hydrolysis of the chloral hydrate. Nevertheless, the semicarbazones may be hydrolysed to the optically pure ketones by potassium hydroxide in an aqueous chloral hydrate solution. These ready isomeric changes of menthone derivatives, which are not shown by the menthones themselves in similar circumstances, are explained on a tautomeric basis:



The following constants are recorded: *l*-menthone,  $d_{40}^{25} 0.8885$ ,  $n_D^{25} 1.4481$ ,  $\eta^{25} 2.330$ ; *r*-isomenthone,  $d_{40}^{25} 0.8916$ ,  $n_D^{25} 1.4496$ ,  $\eta^{25} 2.634$ ; *r*-menthone,  $d_{40}^{25} 0.8936$ ,  $n_D^{25} 1.4492$ ,  $\eta^{25} 2.493$ ; and also the rotatory dispersions, using the  $H_\alpha$ ,  $D$ ,  $H_\beta$ , and  $H_\gamma$  lines, of *l*-, *d*-iso-, and inverted *d*-menthones, their oximes, and oxime hydrochlorides. H. A. PIGGOTT.

**Cyclic nitrogen compounds derived from camphor.** H. RUPE and F. BUXTORF (Helv. Chim. Acta, 1930, 13, 444—457).—Camphorylurethane (Forster and Fierz, J.C.S., 1905, 87, 121) may be prepared by the action of ethyl chloroformate on  $\alpha$ -aminocamphor. When heated with hydrazine hydrate at  $120$ – $150^\circ$ , ring closure occurs with the formation of 5:6-camphene-2-ketotetrahydro-

1:3:5-triazine (I or II), m. p.  $314$ – $315^\circ$  (acetyl derivative, m. p.  $183^\circ$ ).



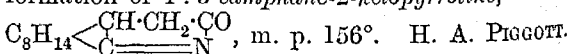
The same triazine (II) is formed when camphorylurethanehydrazone, m. p.  $143^\circ$  (phenylthiocarbamide derivative, m. p.  $208^\circ$ ), from  $\alpha$ -aminocamphorhydrazone and ethyl chloroformate, is heated above its m. p.  $\alpha$ -Formamidocamphor, when heated with hydrazine hydrate in alcohol, gives  $\alpha$ -aminocamphorylhydrazone (cf. Forster and Kunz, J.C.S., 1914, 105, 1727) (phenylthiocarbamide derivative, m. p.  $154^\circ$ ). This hydrazone is converted by formaldehyde into a substance, m. p. about  $170^\circ$ , of indefinite composition, which, on account of its ease of formation and sparing solubility in water, may be used for the detection, but not for the determination, of formaldehyde. A similar but more soluble amorphous product is produced with acetaldehyde.

$\alpha$ -Camphorylaceto-hydrazide, m. p.  $136^\circ$  (*p*-nitrobenzylidene derivative, m. p.  $143$ – $144^\circ$ ; piperonylidene derivative, m. p.  $147^\circ$ ), prepared from the corresponding ethyl ester and hydrazine hydrate, gives, when treated with nitrous acid, not the expected azide, but  $\alpha$ -camphorylacetylhydrazide, m. p.  $125^\circ$  (identified by comparison with the product of the action of ammonia on  $\alpha$ -camphorylacetyl chloride), and nitrous oxide. Acid condensing agents, e.g., zinc chloride, hydrogen chloride in ether and alcohol, or sulphuric acid, readily convert it into camphanedihydropyridazine,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}\cdot\text{CH}_2 \\ \diagdown \quad \diagup \\ \text{C}\cdot\text{N}\cdot\text{NH} \end{array} \text{CO}$ , m. p.  $216^\circ$  (nitroso-derivative, decomp.  $180^\circ$ ; methyl derivative, m. p.  $152^\circ$ ).

Ethyl camphorylideneacetate gives with hydrazine hydrate a compound containing two hydrazine residues, probably  $\omega$ -hydrazino- $\alpha$ -camphorylaceto-hydrazide,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CH}\cdot\text{CH}(\text{NH}\cdot\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \end{array}$

m. p.  $114^\circ$ , and this in the presence of acids loses water and hydrazine with the greatest ease and forms camphanepyridazine,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}\cdot\text{CH}\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{C=N-NH} \end{array}$ , m. p.  $228^\circ$

(methyl derivative, m. p.  $117^\circ$ ).  $\alpha$ -Camphorylacetylhydrazide, readily prepared by the interaction of the ethyl ester and ammonia, is dehydrated by heating with zinc chloride or phosphoric oxide with the formation of 4:5-camphene-2-ketopyrroline,



**Interaction of bromine and  $\gamma$ -diketones in hydrobromic acid solution.** I. A. TREILIEV and E. A. GOROSCHKO (Ukraine Chem. J., 1930, 5, 35—46).—Pentabromo-2:5-dimethylfuran, m. p.  $180^\circ$ , is prepared by the bromination of acetylacetone or of 2:5-dimethylfuran. Under analogous conditions iodine has no apparent action. R. TRUSZKOWSKI.

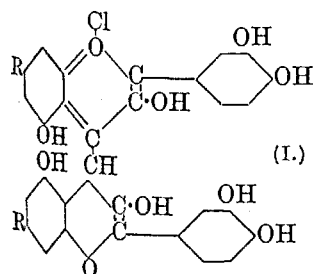
**Spirans with four aromatic radicals on the spiro-carbon atom.** R. G. CLARKSON and M. GOMBERG (J. Amer. Chem. Soc., 1930, 52, 2881—2891).—Attempts to convert *o*-phenyltriphenylcarbinol, m. p.  $87$ – $88^\circ$  (cf. Khotinsky and Patzewitch, A., 1909, i, 830), into the corresponding chloride give 9:9-diphenylfluorene. Oily *om*'m'-triphenyltriphenylcarbinol, from ethyl *o*-phenylbenzoate and magnesium



*m*-diphenyl bromide, is converted by sulphuric acid in acetic acid solution into 9:9-di-*m*-diphenylfluorene, m. p. 190—193°. Application of the same reaction to cyclic carbinols leads to the formation of spirans. Thus, 9-*o*-diphenyl-9-fluorenol, m. p. 169—170°, from fluorenone and magnesium *o*-diphenyl iodide, gives 9:9'-spirodifluorene, m. p. 198—199°. Magnesium *o*-phenoxyphenyl iodide and fluorenone give 9-*o*-phenoxyphenyl-9-fluorenol, m. p. 154°, which with acetic acid and acetyl chloride gives spiro-9-fluorene-9'-xanthen, m. p. 212—213°. This is also formed from 9-*o*-diphenyl-9-xanthenol, which is obtained as a molecular compound with xanthone, C<sub>25</sub>H<sub>18</sub>O<sub>2</sub>·C<sub>13</sub>H<sub>8</sub>O<sub>2</sub>, m. p. 130°, from magnesium *o*-diphenyl iodide and xanthone. *o*-Iodophenyl *p*-tolyl ether, m. p. 41°, b. p. 210—215°/34 mm., yields by the Grignard reaction with 2-bromofluorenone 2-bromo-9-*o*-(4-tolyl-oxyphenyl)-9-fluorenol, m. p. 175°, which is dehydrated to 2-bromo-2'-methylspiro-9-fluorene-9'-xanthen, m. p. 201°. 9-*o*-Phenoxyphenyl-9-xanthenol, m. p. 136—137°, gives 9:9'-spirodixanthen, m. p. 283—284° (corr.). *o*-Bromodiphenylmethane, b. p. 192—198°/32 mm., is converted into 9-*o*-benzylphenyl-9-fluorenol, m. p. 132—133°, and 9:10-dihydrospiro-9-anthracene-9'-fluorene, m. p. 207°. 9-*o*-Benzylphenyl-9-xanthenol, m. p. 146°; 9:10-dihydrospiro-9-anthracene-9'-xanthen, m. p. 257—259°; 9-*o*-diphenylmethylphenyl-9-fluorenol, m. p. 192°; 10-phenyl-9:10-dihydrospiro-9-anthracene-9'-fluorene, m. p. 267—268°; 9-*o*-diphenylmethylphenyl-9-xanthenol, m. p. 200—205° (decomp.); 10-phenyl-9:10-dihydrospiro-9-anthracene-9'-xanthen, m. p. 334—335° (corr.); 10:10-diphenyl-9-*o*-diphenyl-9:10-dihydro-9-anthranol, m. p. 231—234° (decomp.); 10:10-diphenyl-9:10-dihydrospiro-9-anthracene-9'-fluorene, m. p. 364°; 10:10-diphenyl-9-*o*-phenoxyphenyl-9:10-dihydro-9-anthranol, m. p. 276—278°; 10:10-diphenyl-9:10-dihydrospiro-9-anthracene-9'-xanthen, m. p. 377—380°; 9:10-di-*o*-diphenylanthraquinol, m. p. 353—355° (corr. decomp.); 9:10-dihydrodispiro-9:10-anthracene-9':9''-difluorene, m. p. 471—474° (corr.); 9:10-di-*o*-phenoxyphenylanthraquinol, m. p. 351—353° (decomp.), and 9:10-dihydrodispiro-9:10-anthracene-9':9''-dixanthen, m. p. 487—490°, are prepared by analogous methods. Attempts to convert 7:8-di-*o*-diphenyl-7-acenaphthene-8-diol, m. p. 168°, into dispiro-7:8-acenaphthene-9':9''-difluorene yielded, unexpectedly, 7:7-di-*o*-diphenylacenaphthen-8-one, m. p. 265—267°.

H. E. F. NOTTON.

**Reduction of quercetin.** T. MALKIN and M. NERENSTEIN (J. Amer. Chem. Soc., 1930, 52, 2864—2868).—The substance obtained by Wilstätter and Mallison by reducing quercetin with zinc dust and hydrochloric acid (A., 1914, i, 1080) is not cyanidin chloride, but a bimolecular product for which the name *quercetylene chloride* (I, R=OH) is proposed. This is in accordance with the reactions of other pyrones (cf. Baeyer, A., 1915, i, 290). Rhamnetin is similarly

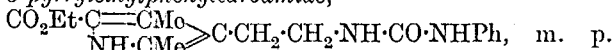


reduced to 7:7'-dimethylquercetylene chloride (I, R=OMe) (the rhamnetidin chloride of Robertson and Robinson, A., 1927, 1084). This crystallises with an excess of hydrogen chloride, which is lost on keeping. Xanthylene (Δ<sup>5:5'</sup>-dixanthyldiene) is converted by ferric chloride and hydrogen chloride or chlorine into *mono*- and *di*-ferrichlorides, m. p. above 320°, which are, however, more easily hydrolysed than the above hydroxylated derivatives.

H. E. F. NOTTON.

**Synthesis of hydropyrryl derivatives using *p*-phenylenedimagnesium dibromide.** R. LUKES and V. PRELOG (Chem. Listy, 1930, 24, 277—280).—The Grignard reagent from *p*-dibromobenzene reacts with *N*-methylsuccinimide to give only 2-hydroxy-2-*p*-bromophenyl-1-methyl-5-ketopyrrolidine, m. p. 151—153°, which on hydrolysis yields β-*p*-bromobenzoylpropionic acid, m. p. 148° (oxime, m. p. 134°). If the Grignard reagent is prepared from a mixture of *mono*- and *di*-bromobenzene the reaction product with *N*-methylsuccinimide is *p*-di-(1-methyl-2-keto-5-pyrrolinyl)benzene, m. p. 233°. R. TRUSZKOWSKI.

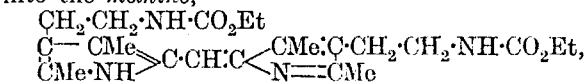
**Curtius degradation in the pyrrole series.** H. FISCHER, O. SÜS, and F. G. WEILGUNY (Annalen, 1930, 481, 159—192).—Methyl 5-carbethoxy-2:4-dimethylpyrrole-3-propionate, m. p. 104°, prepared by esterification of the corresponding acid with cold methyl-alcoholic hydrogen chloride, is converted by hydrazine hydrate in boiling ethyl alcohol into 5-carbethoxy-2:4-dimethylpyrrole-3-propionhydrazide, m. p. 211° [hydrochloride, m. p. 238° (decomp.); benzoyl compound, m. p. 163° (corr.); benzylidene derivative, m. p. 198°]. The hydrochloride is transformed by sodium nitrite into 5-carbethoxy-2:4-dimethylpyrrole-3-propionazide, m. p. 102° (decomp.), converted by aniline into 5-carbethoxy-2:4-dimethyl-3-pyrrolylethylphenylcarbamide,



The azido is reduced by zinc dust and acetic acid to 5-carbethoxy-2:4-dimethylpyrrole-3-propionamide, m. p. 199°, and converted in boiling xylene into the carbimide



m. p. 117°, from which the corresponding urethane, m. p. 128°, is obtained with boiling alcohol. Treatment of the azide with hot water affords di-5-carbethoxy-2:4-dimethyl-3-pyrrolylethylcarbamide, m. p. 260°, which could not be smoothly hydrolysed. Boiling ethyl alcohol transforms the azide into 5-carbethoxy-2:4-dimethyl-3-pyrrolylethyl-ω-urethane, m. p. 128—130°, converted by boiling, concentrated hydrochloric acid into 5-carbethoxy-2:4-dimethyl-3-β-aminoethylpyrrole, b. p. 207°/16 mm. (benzoyl compound, m. p. 157°; picrate, m. p. 121°; non-crystalline hydrochloride), which suffers loss of the carbethoxy-group when boiled with hydriodic acid (*d* 1.96) and is re-converted into the urethane by ethyl chloroformate. Hot formic acid containing a little concentrated hydrochloric acid transforms the urethane into the methine,



m. p. 177°, whereas the amine by treatment with

the same reagents at 125° affords the *methine hydrochloride*,  $C_{17}H_{29}N_4Cl_3$ .

Methyl 2:4-dimethylpyrrole-3-propionate is converted by hydrazine hydrate at 100° into 2:4-dimethylpyrrole-3-propionylhydrazide, m. p. 177°, which with benzenediazonium chloride affords the compound  $C_{15}H_{19}ON_5$ , m. p. 170°. Ethyl 3:3':5:5'-tetramethylpyrromethene-4:4'-dipropionate yields the corresponding dihydrazide,  $C_{19}H_{25}O_2N_6$ , m. p. 259°.

Ethyl 5-carbethoxy-2:4-dimethylpyrrole-3-acrylate usually suffers hydrolysis of the  $\beta$ -ester group when heated with hydrazine, but at 130° under pressure 2:4-dimethyl-3- $\beta$ -carboxyvinylpyrrole-5-carboxylhydrazide is produced, converted successively into the corresponding *azide*, m. p. 129° (decomp.), and *isoamylurethane*, m. p. 178°; the compounds are also derived from ethyl 2:4-dimethyl-3- $\beta$ -carboxyvinylpyrrole-5-carboxylate.

Ethyl 2:4-dimethyl-3-ethylpyrrole-5-carboxylate yields 2:4-dimethyl-3-ethylpyrrole-5-carboxylhydrazide, decomp. 216° [hydrochloride, m. p. 288° (decomp.)], which gives the compound  $C_{16}H_{17}ON_3$ , m. p. 204°, when heated with benzoyl chloride; the benzoyl derivative,  $C_{16}H_{15}O_2N_3$ , m. p. 233°, benzylidene compound, m. p. 213°, and acetyl derivative, m. p. 197°, are described. 2:4-Dimethyl-3-ethylpyrrole-5-carboxylazide, decomp. 126°, is converted by cryptopyrrole into the substance  $C_{17}H_{25}ON_3$ , m. p. 195°. 2:4-Dimethyl-3-ethylpyrrole and phenylcarbinide afford 2:4-dimethyl-3-ethyl-1-carbanilide, m. p. 131°. Bromine transforms the azide into 4-methyl-2-bromoethyl-3-ethylpyrrole-5-carboxylazide, m. p. 146° (decomp.), converted by warm methyl alcohol into 4-methyl-2-methoxymethyl-3-ethylpyrrole-5-carboxylazide, m. p. 95° (decomp.). According to the proportion of sulphuryl chloride in ether, the azide affords 4-methyl-2-chloromethyl-3-ethylpyrrole-5-carboxylazide, m. p. 152° (decomp.) when rapidly heated, or 4-methyl-2-dichloromethyl-3-ethylpyrrole-5-carboxylazide, m. p. 140° (decomp.); the last-named compound is converted by aqueous methyl alcohol into 2-aldehydo-4-methyl-3-ethylpyrrole-5-carboxylazide, m. p. 142° (decomp.). Treatment of the azide with boiling ethyl alcohol yields a substance,  $C_{11}H_{18}O_3N_2$ , m. p. 128°, converted by hydrazine hydrate into the compound  $C_{10}H_{17}N_5$ , m. p. 158°; with methyl alcohol the substance  $C_{10}H_{16}O_3N_2$ , m. p. 146°, is analogously produced, whereas cholesterol affords the substance  $C_{36}H_{58}O_3N_2$ , m. p. 213° (decomp.). 2:4-Dimethylpyrrole-5-carboxylhydrazide, m. p. 182° (decomp.) (hydrochloride, decomp. 261°), condenses with acetone, isatin, and ethyl acetoacetate, giving the compounds  $C_{10}H_{15}ON_3$ , m. p. 208°,  $C_{17}H_{22}O_3N_4$ , decomp. 280°,  $C_{15}H_{14}O_2N_4$ , decomp. 299°, and  $C_{13}H_{19}O_3N_3$ , m. p. 147°. The successive action of bromine in glacial acetic acid and sodium nitrite on the hydrazide yields 3-bromo-2:4-dimethylpyrrole-5-carboxylazide, m. p. 146° (decomp.). 2:4-Dimethylpyrrole-5-carboxylazide, decomp. 121°, is converted by ethyl alcohol and cholesterol, respectively, into substances  $C_9H_{14}O_3N$ , m. p. 148°, and  $C_{34}H_{54}O_3N_3$ , m. p. 208° (decomp.). With water it gives the *dipyrrolylcarbamide*, decomp. 205°; with aniline the *pyrrolylphenylcarbamide*, m. p. 167° (decomp.), and with cryptopyrrole the compound

$C_{15}H_{21}ON_3$ , m. p. 175°. 2:4-Dimethylpyrrole-5-carboxylazide and hydrocyanic acid give the imine hydrochloride, hydrolysed by water to 3-aldehydo-2:4-dimethylpyrrole-5-carboxylazide, m. p. 137° (decomp.). With boiling acetic acid the azide yields 5-acetamido-2:4-dimethylpyrrole, decomp. 188°, and with 40% sodium hydrogen sulphite and zinc dust it affords 2:4-dimethylpyrrole-5-carboxylamide, m. p. 163°. Somewhat diluted sulphuric acid converts the azide into 2:4-dimethylpyrrole. Treatment of ethyl 2:4-dimethyl-3-vinylpyrrole-5-carboxylate with hydrazine hydrate causes loss of the vinyl group and production of 2:4-dimethylpyrrole-5-carboxylhydrazide. 2:4-Dimethylpyrrole-3:5-dicarboxylhydrazide, m. p. 254° (decomp.), 4:4'-dimethyl-3:3'-diethylpyrromethane-5:5'-dicarboxylhydrazide, decomp. 238°, and 2:4-dimethylpyrrole-5-carboxylhydrazide, decomp. 210°, are described.

H. WREN.

**Dicyclic endoimines. II. 1:4-endoImino-cyclohexane.** J. VON BRAUN and K. SCHWARZ (Annalen, 1930, 481, 56—68; cf. A., 1928, 897).—The synthesis of this imine has been undertaken to remove ambiguity attaching to the structure of the dicyclic 2:6-methylenepiperidine previously described.

Quinol monoisoamyl ether, b. p. 155—158°/20 mm., m. p. 45° (benzoate, m. p. 55°), is reduced catalytically to 4-hydroxycyclohexyl isoamyl ether, b. p. 142—143°/12 mm. (probably a mixture of *cis*- and *trans*-forms). The latter is oxidised to 4-isoamylloxycyclohexanone, b. p. 125—126°/11 mm. (semicarbazone, m. p. 156—158°), the *oxime*, b. p. 160—162°/10 mm., of which is reduced by sodium and alcohol to 4-isoamylloxycyclohexylamine, b. p. 119—120°/10 mm. (hydrochloride, m. p. 208—210°; acetyl derivative, m. p. 128—129°; benzoyl derivative, m. p. 179—180°; quaternary methiodide, m. p. 237—238°); when heated with fuming hydrobromic acid at 100° this base is converted into 4-bromocyclohexylamine hydrobromide, m. p. 203—205° [picrate, m. p. 181°, depressed by the picrate of 3-bromocyclohexylamine (*loc. cit.*), new m. p. 185°]. The action of warm alkali on the latter yields a mixture of bases, the lower-boiling fraction (70%; b. p. 136—140°,  $d_4^{25}$  0.9292) of which contains tetrahydroaniline (*loc. cit.*) and the required endoimine, separated and isolated as picrates or quaternary methiodides. The quaternary methiodide,  $C_8H_{16}NI$ , from 1:4-endoimino-cyclohexane (annexed formula) has m. p. 299—300° (picrate of the secondary imine, m. p. 151—153°).

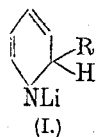
4-isoAmyloxycyclohexyl bromide, b. p. 132°/10 mm., from the alcohol (above) and phosphorus tribromide, is converted by heating with dimethylamine into 4-isoamylloxycyclohexyldimethylamine, b. p. 122—124°/10 mm. [picrate, m. p. 115—116°; methiodide (see above)], which when heated with hydrobromic acid affords 4-bromocyclohexyldimethylamine hydrobromide, m. p. 149—150° (picrate, m. p. 156°). The free base when warmed above 50° isomerises to a crystalline quaternary bromide, m. p. 295°, the corresponding iodide, m. p. 299°, being identical with that obtained as above.

3-isoAmyloxycyclohexyl bromide, b. p. 124—126°/10 mm.,

10 mm., from the corresponding alcohol (*loc. cit.*) is similarly converted into 3-isoamyloxycyclohexyldimethylamine, b. p. 124—126°/10 mm., methiodide, m. p. 234°, depressed by the corresponding 4-isoamyloxy-derivative; *hydrochloride*, m. p. 153°. The latter when heated with hydrobromic acid yields unexpectedly the crude hydrobromide of 4-bromocyclohexyldimethylamine (picrate, m. p. 156°, not depressed by sample from above preparation), the free base isomerising to the above quaternary bromide (cf. Palfray and Rothstein, this vol., 463, 768).  
R. CHILD.

**En-onium conjugation as the cause of abnormal reactions.** H. DECKER (Helv. Chim. Acta, 1930, 13, 666—675).—The explanation of the mechanism of many "abnormal" reactions, including those which take place in living organisms, is sought in the tautomerism of the conjugated ring compounds in which they occur. The compound may exist both as an onium base with nitrogen, sulphur, or oxygen bearing a positive charge and connected by a double linking to a carbon atom, and as a pseudo-base with the double linking between carbon atoms. Examples bearing out this theory are cited. F. L. USHER.

**Alkali-organic compounds. VII. Alkali metal alkyls and pyridine.** K. ZIEGLER and H. ZEISER (Ber., 1930, 63, [B], 1847—1851).—Pyridine and lithium alkyls unite to form additive compounds (I) which decompose when heated into lithium hydride and 2-alkylpyridines. 2-*n*-Butylpyridine, b. p. 191—193°, and 2-phenylpyridine, b. p. 265—267°, are thus obtained. H. WREN.



**Preparation of 2-alkyl- and 2-aryl-pyridines by the Grignard reaction.** F. W. BERGSTROM and S. H. McALLISTER (J. Amer. Chem. Soc., 1930, 52, 2845—2849).—Pyridine and its analogues react with Grignard reagents in ethyl ether at 150—160° (autoclave), the alkyl or aryl group entering the 2-position. 2-Phenylpyridine (cf. Oddo, A., 1907, i, 549, 668) (yield, 44%), 2-phenylquinoline (yield, 66%), 2-ethylpyridine (yield, 45%), and 1-ethylisoquinoline, b. p. 250° (uncorr.) (picrate, m. p. 207—210°; chloroplatinate, m. p. 199—200°; chloroaurate, m. p. 168—172°), have been prepared in this way. Experiments with nicotine, cinchonidine, 2-picoline, 2-methylquinoline, and 4:4'-dipyridyl are also described. The reaction is in accordance with the formal analogy between pyridine and the Schiff's bases.

H. E. F. NOTTON.

**Compounds of arsenious chloride and pyridine.** C. S. GIBSON, J. D. A. JOHNSON, and D. C. VINING (J.C.S., 1930, 1710—1711).—A substance,  $\text{AsCl}_3 \cdot \text{C}_5\text{H}_5\text{N}$ , m. p. 138—139°, with sintering at 120°, has been isolated. The existence of the compound  $\text{AsCl}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$  (Shirey, this vol., 787) has been confirmed.  
T. H. MORTON.

**Decomposition of products of combination of halogen-substituted esters with tertiary amines.** L. N. DJAKONOVA-SCHULTZ (J. Russ. Phys. Chem. Soc., 1930, 62, 957—974).—The products of thermal decomposition of compounds of pyridine or quinoline

with various  $\alpha$ -bromo-substituted aliphatic esters are in every case the tertiary amine, carbon dioxide, and the halide of the alcohol combined with the acid. The stability of the compounds increases with the mol. wt. of the alkyl group (Et, Me, or Pr) of the carbalkoxy-group, and with the at. wt. of the halogen atom, and is smaller for quinoline than for pyridine compounds. In the case of dibasic acids the reaction is as follows:  $\text{RBr} \cdot \text{CH}(\text{CO}_2\text{R}')_2 \longrightarrow \text{RBr} \cdot \text{CHR}' \cdot \text{CO}_2\text{R}' \longrightarrow \text{R} + \text{R}'\text{Br} + \text{CO}_2$  ( $\text{R} = \text{C}_5\text{H}_5\text{N}$  or  $\text{C}_9\text{H}_7\text{N}$ ).  
R. TRUSZKOWSKI.

**Action of hydrazine on pyridine-2:3-dicarboxylic anhydride. Formation of the corresponding cyclic hydrazide.** G. GHEORGHIU (Bull. Soc. chim., 1930, [iv], 47, 630—639).—With hydrazine hydrate in alcoholic or acetic acid solution pyridine-2:3-dicarboxylic (quinolinic) anhydride is converted into *quinolylhydrazide*, m. p. 311—312°.

$\text{C}_5\text{H}_3\text{N} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$  (potassium salt,  $\text{C}_7\text{H}_4\text{O}_2\text{N}_3\text{K}$ ; silver salt,  $\text{C}_7\text{H}_4\text{O}_2\text{N}_3\text{Ag}$ ), the structure of which is indicated by its stability to heat and its oxidation by nitric acid to pyridine-2:3-dicarboxylic acid. It is not oxidised by mercuric oxide, does not condense with benzaldehyde, and is unchanged by boiling with hydrochloric or acetic acid or with potassium hydroxide. With acetic anhydride at 150° it yields a *diacetyl* derivative,  $\text{C}_5\text{H}_3\text{N} \begin{smallmatrix} \text{C}(\text{OAc}) \cdot \text{N} \\ \text{C}(\text{OAc}) \cdot \text{N} \end{smallmatrix}$ , which is unchanged by boiling alcohol. In 0.001*N*-solution quinolylhydrazide has an absorption curve generally resembling that of phthalylhydrazide with a maximum at  $\lambda$  305 and a minimum at  $\lambda$  277, but in addition shows a second maximum and minimum at  $\lambda$  255 and 245, respectively, which are attributed to the presence of the pyridine nitrogen atom, since  $\alpha$ -aminophthalylhydrazide and  $\alpha$ -nitrophthalylhydrazide (sodium salt) also give absorption curves with maxima at  $\lambda$  350 and 295 for the amino- and 330 and 272 for the nitro-derivative and corresponding minima at 323 and 265 and 298 and 255, respectively.  
R. BRIGHTMAN.

**Salts from benzene-4-azopyridine.** A. HANTZSCH and Z. BURAWOY (Ber., 1930, 63, [B], 1775—1781).—In the monacid salts of benzeneazopyridine which cannot have a quinonoid constitution, the acid molecule is united to the more strongly basic pyridine nitrogen and not to the azo-nitrogen in accordance with the formula  $\text{NPh} \cdot \text{N} \cdot \text{C}_5\text{H}_4\text{N} \cdot \text{HX}$ . The hypothesis of Koenig that the red *p*-aminoazobenzene salts have the azoid structure  $\text{PhN}(\text{HX}) \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2$  is untenable, since in these salts the azobenzene residue is united to the hydrogen atom of the acid molecule; this can only be explained by the activity of the basic amino-group in the fixation of the anion, thus leading to the quinonoid formulation  $\text{Ph} \cdot \text{NH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 \cdot \text{X}$ . Koenig's objection to the quinonoid formulation of these salts, based on the observation that the orange-red benzeneazopyridine dissolves in concentrated acids to give violet solutions, although a quinonoid structure is impossible for its salts, is not valid, since the colour is not due to a salt of benzeneazopyridine, but to a compound of the dimeric dibenzeneazopyridine. The diacid salt of

benzeneazopyridine initially produced is orange-red and only gradually undergoes condensation with production of the violet salt. This observation disposes of the last objection to the quinonoid formulation of the deeply-coloured salts of *p*-aminoazobenzenes.

The following compounds are incidentally described: *benzeneazopyridine monohydrochloride*, m. p. 175—180° (decomp.), *methiodide*, m. p. 188°, and *methochloride*.  
H. WREN.

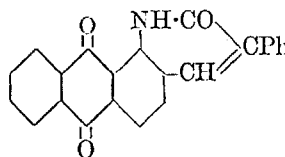
**Catalytic transference of hydrogen between organic compounds.** II. S. AKABORI and K. SATTO (Proc. Imp. Acad. Tokyo, 1930, 6, 236).—The transference of hydrogen from a saturated cyclic compound to an unsaturated substance by the catalytic influence of palladium-black (A., 1929, 1170) has been further investigated. Tetrahydrocarbazole in benzene solution is easily dehydrogenated to carbazole by safole. Hydrocoumarin yields when heated with anethole a small quantity of coumarin. Hydrohydrastinine is not reduced by safole in benzene solution, but treatment with maleic acid (2 mols.) in aqueous solution yields a dehydrohydrastinium salt, one atom of hydrogen from the acid and three atoms from the hydroisoquinoline nucleus being removed. The dehydrogenation of tetrahydroharman and tetrahydroharmine is effected by heating with an aqueous solution of maleic acid, affording harman and harmine. T. H. MORTON.

**Structure of the octahydrocarbazoles.** S. G. P. PLANT (J.C.S., 1930, 1595—1599).—2-Bromocyclohexanone is conveniently prepared by adding bromine at 50° to a mixture of cyclohexanone, water, and precipitated chalk. The sodium derivative of ethyl cyclohexanone-2-carboxylate reacts with the bromide to give *ethyl 2:2'-diketodicyclohexyl-1-carboxylate*, b. p. 190—210°/20 mm., converted by hot 10% potassium hydroxide solution into *2:2'-diketodicyclohexyl*, m. p. 70—71°, b. p. 174—177°/25 mm., and an acid,  $C_{12}H_{20}O_3$ , m. p. 41°, b. p. 203—206°/13 mm. The diketone reacts with methylamine in hot acetic acid solution to give 9-methyl-1:2:3:4:5:6:7:8-octahydrocarbazole, identical with that of Braun and Ritter (A., 1923, i, 141) obtained by the vigorous reduction of 9-methylcarbazole, but differing from the 9-methyloctahydrocarbazole of Perkin and Plant (A., 1924, i, 1104), formed by the elimination of ammonia from cyclohexylideneazine and subsequent methylation. This latter compound probably possesses the structure (9-methyl-1:2:3:6:7:8:10:13-octahydrocarbazole) assigned to it by Braun and Schörning (A., 1925, i, 1449). 9-Ethyl-1:2:3:4:5:6:7:8-octahydrocarbazole may be prepared by a process analogous to that used for the methyl derivative.

T. H. MORTON.

**Indole derivatives of the anthracene series.** P. RUGGLI and E. HENZI (Helv. Chim. Acta, 1930, 13, 409—437).—1-Aminoanthraquinone-2-aldehyde (I) [*phenylhydrazone*, m. p. 266°; *semicarbazone*, m. p. 350—360° (decomp.); *oxime*, m. p. 282° (decomp.); *azine*, m. p. 375° (cf. Cassella, G.P. 343,252)] readily gives the *acetyl* derivative (II), m. p. 237—240° (indef. and with previous sintering) [*phenylhydrazone*, m. p. 254°], with acetic anhydride in concentrated sulphuric acid, but with benzoyl chloride in nitrobenzene the *anhydrobis*-compound, m. p. 380—390° (decomp.), is

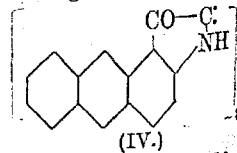
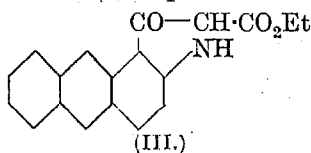
produced. The *acetyl* derivative (II) condenses with 2:4-dinitrotoluene under the influence of piperidine to give *2-acetamido-3:4-phthaloyl-2':4'-dinitrostilbene*, m. p. 268°, hydrolysable to the free *amino*-derivative,



m. p. 286—290°, and with sodium phenylacetate in acetic anhydride to give *2-hydroxy-3-phenyl-7:8-phthaloylquinoline* (annexed formula), m. p. 278° (*potassium salt*, purplish-red), also

obtainable from 1-aminoanthraquinone-2-aldehyde anil by a similar condensation. II is also produced by the acetylation of 1-aminoanthraquinone-2-aldehyde anil under the above conditions, and is fairly readily hydrolysed to I either by methyl-alcoholic potassium hydroxide or by concentrated sulphuric acid. Neither I nor its anil reacts normally with chloroacetic acid in the presence of sodium acetate: the latter gives a *substance*, m. p. 334°, capable of hydrolysis to aniline and I, and therefore regarded as the anil of the *anhydrobis*-compound. I could not be induced to react with toluene-*p*-sulphonyl chloride in pyridine, although 1-aminoanthraquinone itself readily forms a *p*-toluenesulphonyl derivative (cf. Ullmann and Fodor, A., 1911, i, 466) which with ethylene dibromide and potassium hydroxide gives a poor yield of *N*- $\beta$ -bromoethyl-*p*-toluenesulphonyl-1-aminoanthraquinone, m. p. 165°, hydrolysed by sulphuric acid to *N*- $\beta$ -bromoethyl-1-aminoanthraquinone, m. p. 157°.

1-Amino-2-methylantraquinone readily forms a *s-oxalyl* derivative, m. p. 330—335° (decomp.), but an attempt to convert this into the corresponding di-indyl derivative by Madelung's reaction (A., 1914, i, 737) failed. Neither 2-aminoanthraquinone nor its toluene-*p*-sulphonyl derivative reacts with ethyl bromomalonate at temperatures below its decomposition point, but with ethyl malonate 2-aminoanthraquinone readily forms a *malonyl* derivative, m. p. 310°. Nevertheless, 2-aminoanthracene and ethyl bromomalonate readily interact to form *ethyl  $\beta$ -aminoanthrylmalonate*, m. p. 131°, which decomposes at temperatures above 200° to give *ethyl anthra-2:1-indoxylate* (III), m. p. 203° (*potassium salt*; *acetyl* derivative, m. p. 265—270°), and a small quantity of a *substance*,  $C_{34}H_{18}O_4N_2$ , m. p. above 450°, probably the dilactam formed by elimination of alcohol from 2 mols. of III. The ester III is hydrolysed only with difficulty. Its potassium salt re-forms III when decomposed by water. On fusion with alkali at 170—180°, however, a solution from which an indigoid dye, probably the *anthrindigotin* (IV), m. p. 425—430° (decomp.), can be precipitated by air-oxidation, is produced. Anthrindigotin dissolves in



slightly fuming sulphuric acid to give the soluble sulphonic acid. The sodium salt of an anthrindigotin-sulphonic acid of indefinite composition (probably mixed with the unsulphonated compound) was obtained by hydrolysing ethyl acetyl anthrindoxylate

with 60% sulphuric acid, and oxidising the resulting solution with air. By acidification of the mother-liquors from the alkali-fusion (above), *anthrisatin*, m. p. 286° (*phenylhydrazone*, m. p. 275—277°; *quin-oxaline*, m. p. 395—400°), was isolated. Ethyl acetylthrinodoxylate is oxidised by chromic and acetic acids (poor yield) to *ethyl N-acetylthraquinoneindoxylate*, m. p. 275—290° (indef.), but oxidations of other anthracene derivatives described above gave indefinite compounds. H. A. PIGGOTT.

**Hydrogenation potential of dimethylalloxantin.** E. BILMANN and H. G. MYGIND (Bull. Soc. chim., 1930, [iv], 47, 532—537).—Pure dimethylalloxantin is prepared by dissolving methylallicuric acid (cf. Biltz and Damm, A., 1914, i, 23) and methylalloxan in boiling water saturated with carbon dioxide, rapidly cooling to 0°, and washing the crystals with alcohol and ether saturated with carbon dioxide. Biltz's method is very unsatisfactory (A., 1913, i, 166); the oxidation of theobromine by his method on one occasion led to *isocapocaffeine*.

The potential of the quinhydrone electrode against the 0.1*N*-hydrogen electrode is 0.7047 volt at 18° and 0.6995 volt at 25° (cf. Bilmann and Lund, A., 1923, ii, 605) and the hydrogenation potential of dimethylalloxantin (in 0.1*N*-sulphuric acid solution) is 0.3672 volt at 18° and 0.3648 volt at 25°. S. K. TWEEDY.

**Synthesis of antipyrine.** N. A. VALIASCHKO and V. I. BLIZNYUKOV (Ukraine Chem. J., 1930, 5, 47—57).—Antipyrine can be prepared in 70% yield by the methylation of 1-phenyl-3-methyl-5-pyrazolone with a mixture of methyl alcohol and hydrochloric acid, the best yields being obtained by using 1 part of acid to 14 parts of alcohol, at 130—150°. Heating for more than 2 hrs. does not increase the yield. The reaction is not catalysed by iron or copper. R. TRUSZKOWSKI.

**Constitution of metallic complexes of indigo colouring matters.** H. MACHEMER (J. pr. Chem., 1930, [ii], 127, 109—168).—An extensive review of previous work on metallic complexes of indigotin and related colouring matters with especial reference to their constitution.

The absorption bands, 607, 605, and 591  $\mu$ , of indigotin in pyridine, chloroform, and xylene, respectively, disappear on shaking solutions of indigotin with dry metallic acetates at the ordinary temperature, but reappear on addition of small quantities of acid or of alcohol. When indigotin is treated with copper acetate in dry xylene at 100°, or in dry pyridine solution, the copper complex is formed and 2 mols. of acetic acid are eliminated. The ferrous iron complex of indigotin is formed by reaction between ferrous acetate and indigotin in dry pyridine in a dry nitrogen atmosphere. Indigotin reacts with methyl-alcoholic sodium hydroxide at the ordinary temperature to give the compound  $C_{16}H_{10}O_2N_2 \cdot NaOH$ , which on shaking for 12 days yielded the substance  $C_{16}H_8O_2N_2 \cdot Na \cdot NaOH$ .

The following metallic complexes of ethyl indigotinmalonate are described: *copper*, *silver*, and *stannichloride*,  $C_{21}H_{13}O_4N_2 \cdot SnCl_3$  (with stannic chloride in dry xylene solution). Copper indigotinphenylacetate was obtained from indigotinphenylacetate in pyridine and alcohol, copper acetate, and concentrated

aqueous ammonia. Deoxyindigotin yields the complex  $C_{16}H_{11}ON_2 \cdot SnCl_3$  with stannic chloride in toluene. Complex salts (in parentheses) of the following dyes are described: 1-naphthalene-2-indoleindigo (*stannichloride*, *copper*, and *cobalt*); 2-naphthalene-2'-indoleindigo (*stannichloride*); 3-hydroxybenzene-2-indoleindigo (*stannichloride*); 2-thionaphthen-2-indoleindigo (*stannichloride*); 1-hydroxyanthraquinone [*copper* and *cobalt* (by interaction of a hot alcoholic solution of the dye and a concentrated solution of the metallic acetate in 10—15% aqueous ammonia); *potassium* (by heating with potassium and xylene at 150—200°)]. The anhydrophenylacetates of indigotinmalonic ester, of indigotinphenylacetate, and of 2-naphthalene-2-indoleindigo form molecular compounds with stannic chloride: no metallic complex salts can be prepared.

Indole does not react with finely-divided silver or copper in dry pyridine, but reacts readily in pyridine solution with solutions of metallic acetates in aqueous ammonia to yield metallic complexes with silver ( $C_{19}H_{15}N_2Ag$ ) and copper; a substance,  $HgOH \cdot C_{19}H_{15}N_2 \cdot 2Hg(OAc)_2$ , is formed with mercuric acetate. The *nitrate* of the indole base is produced by the addition of fuming nitric acid, sodium nitrite, or amyl nitrite to a concentrated solution in acetic acid, whilst interaction of the base in dilute formic acid solution with dilute sulphuric acid gave the corresponding sulphate. A. I. VOGEL.

**Tetrabromodimethylquinoxaline.** G. M. BENNETT and G. H. WILLIS (J.C.S., 1930, 1709—1710).—The substance, m. p. 234°, obtained by the bromination of 2:3-dimethylquinoxaline and reported as 5:6:7:8-tetrabromo-2:3-dimethylquinoxaline (Henderson, A., 1929, 580) is identical with the previously described (A., 1928, 1027) 2:3-di-( $\omega$ -dibromomethyl)quinoxaline, m. p. 228°. The bromine atoms are not easily hydrolysed, but may be removed by heating with silver acetate and acetic acid, indicating that they are situated in the side-chain. Henderson's dibromo-compound, m. p. 150°, is presumably 2:3-di-( $\omega$ -bromomethyl)quinoxaline.

T. H. MORTON.

**Benzoylbiuret and its conversion into phenyl-dihydroxytriazine.** A. OSTROGOVICH (Bul. Soc. Stiinte Cluj, 1929, 4, 521—527; Chem. Zentr., 1930, i, 538).—The anhydrous biuret and benzoyl chloride are preferably heated rapidly in a sealed tube to 130—135°, and maintained at that temperature for 4 hrs. After extraction with ether and with hot water, hot methyl alcohol extracts benzoylbiuret, m. p. (new) 223—224°. In presence of dilute potassium hydroxide solution, but not in neutral or acid medium, the substance is quantitatively converted into (monopotassium) 2-phenyl-4:6-dihydroxy-1:4:5:6-tetrahydro-1:3:5-triazine (Elzanowski's benzoguanamide). Acetylbiuret behaves similarly, but the yield is smaller. A. A. ELDRIDGE.

**Melamine.** C. E. BARNETT (J. Physical Chem., 1930, 34, 1496—1504).—Solid melamine adds on the 3 mols. of hydrogen chloride required by an amide or an imide formula, but so slowly that it is considered to change into a compound of this type under the action of hydrogen chloride. The structure of melamine is discussed. L. S. THEOBALD.

**Chlorophyll. XII. Phæoporphyrins from chlorin *e* and  $\psi$ -phyloerythrin.** H. FISCHER and O. MOLDENHAUER (Annalen, 1930, 481, 132—159).—Chlorin *e* is converted by hydrogen bromide in glacial acetic acid into a mixture of phylloporphyrin and isophæoporphyrin  $a_3$ . The last-named substance is also formed from chloroporphyrin  $e_4$  and hydrogen bromide in glacial acetic acid at 50°, whereas from chloroporphyrin  $e_3$  phylloporphyrin is exclusively produced. Phylloerythrin and  $\psi$ -phyloerythrin at 180° afford homogeneous isophæoporphyrin  $a_3$ . With chloroporphyrin  $e_5$  and  $e_4$ , a new porphyrin apparently isomeric with chloroporphyrin  $e_4$  and characterised by a methyl ester, m. p. 233° (corr.; decomp.), is formed as by-product.

Chlorin *e* is converted by methyl-alcoholic hydrogen chloride into a crystalline dimethyl ester, m. p. 207° (corr.). The partial or complete hydrolysis of the dimethyl or trimethyl (by diazomethane) ester has not been effected. With *o*-phenylenediamine, chlorin *e* gives a condensation product with the components in the ratio 2 : 1, thus probably indicating the presence of the ketonic group. With malonic acid, chlorin *e* affords phylloporphyrin in small amount; a similar result is obtained in molten succinic acid. Oxidation of chlorin *e* trimethyl ester with chromic acid in glacial acetic acid gives methylethylmaleinimide and a non-crystallisable oil containing methoxyl. Since chlorin *e* esters liberate iodine from hydrogen iodide in acetic acid at the ordinary temperature, porphyrin formation is certainly due to hydrogenation. It appears probable that chlorin *e* contains a pyridone and three pyrrole rings, with, possibly, a second ketonic group. The conversion of chlorin *e* trimethyl ester into chloroporphyrin  $e_6$  is achieved by elimination of approximately 1OMe, regarded as attached to the carboxyl group of the propionic acid residue. Chloroporphyrin  $e_6$  and chloroporphyrin  $e_4$ , which result from esters of chlorin *e*, contain two and one methoxyl groups, respectively. Consequently the compounds  $e_6$  and  $e_4$  must be regarded respectively as di- and mono-carboxylic acids. Chloroporphyrin  $e_6$  is converted by oleum into chloroporphyrin  $e_5$ , whereas the last-named substance remains unchanged. The  $e_4$  compound reacts in a different manner.

Gentle treatment of chloroporphyrin  $e_6$  with hydrogen bromide in glacial acetic acid removes the two methoxyl groups and three oxygen atoms, thus yielding  $\psi$ -phyloerythrin, isomeric and spectroscopically identical with phylloerythrin. With methyl-alcoholic hydrogen chloride it gives a crystalline methyl ester,  $C_{33}H_{36}O_3N_4$ , m. p. 263° (corr.) [copper salt,  $C_{33}H_{34}O_3N_4Cu$ , m. p. 262° (corr.)]. The esters of phylloerythrin and  $\psi$ -phyloerythrin are hydrolysed by hydrogen bromide in acetic acid to the "free acid" and give the same colorations with methyl-alcoholic potassium hydroxide. Alkaline degradation of  $\psi$ -phyloerythrin gives phyllo-, pyrro-, and rhodoporphyrin.  $\psi$ -Phylloerythrin contains a carboxyl group, whereby the function of two oxygen atoms is fixed. Since it can be converted into the dicarboxylic acid, rhodoporphyrin, a ketonic group must be present probably in a pyridone ring. An ethereal oxygen atom is excluded and the presence of an enol is not

indicated, since the ester is not methylated by diazomethane or methyl sulphate. H. WREN.

**Natural porphyrins. XXV. Conchoporphyrin and the conversion of protoporphyrin of malt into mesoporphyrin.** IX. H. FISCHER and K. JORDAN (Z. physiol. Chem., 1930, 190, 75—92; cf. A., 1929, 1466).—From the shell of a pearl muscle, *Pteria radiata* (Lamarck), there was obtained conchoporphyrin,  $C_{37}H_{38}O_{10}N_4$ , as the pentamethyl ester, m. p. 271—272°. It corresponds with a carboxylated coproporphyrin; when heated in a sealed tube with 1% hydrochloric acid one carboxyl group is removed and coproporphyrin I ester is formed. On introduction of iron it shows absorption bands at 551.1 and 520.9  $\mu$ , agreeing closely with those of the iron salt of uroporphyrin.

Porphyrin was isolated from brewer's grains and the ethyl ester was converted into mesoporphyrin by the aid of acetic and hydriodic acids. The esterified product was identical with the methyl ester of mesoporphyrin IX, affording proof that protoporphyrin is present in barley husks. It was shown spectroscopically to occur in malt culms.

J. H. BIRKINSHAW.

**Modifications of protoporphyrin and protohæmin.** A. F. RICHTER (Z. physiol. Chem., 1930, 190, 21—43).—The morphologically and optically similar porphyrins may be distinguished according to the product formed by the introduction of iron; Fischer's porphyrin gives principally  $\alpha$ -protohæmin, Hamsik's yields  $\beta$ -protohæmin. The more sensitive is the iron compound towards the reagent employed for the removal of iron, the greater is the tendency to form the  $\beta$ -modification. From Fischer's protoporphyrin pure  $\alpha$ -protoporphyrin may be obtained. An improved method of preparing  $\beta$ -protohæmin is described. In mixed crystallisation of the  $\alpha$ - and  $\beta$ -modifications of protoporphyrin and protohæmin the  $\beta$ -form of crystal is obtained. Ooporphyrin is regarded as the native form of  $\alpha$ -protoporphyrin and  $\alpha$ -metahæmin as its iron complex salt.

J. H. BIRKINSHAW.

**Carnosine "reineckate."** I. A. SMORODINCEV (Biochem. Z., 1930, 222, 425—429).—Carnosine "reineckate,"  $C_9H_{14}O_3N_4 \cdot 2C_4H_7N_6S_4Cr_4H_2O$ , melts at 205—212° with frothing, but decomposes slowly with loss of nitrogen above 50°; 0.162 g. of it is dissolved by 100 g. of water and there is a great difference between its solubilities at 50° and at 15°. Histidine "reineckate" is more soluble in water.

W. MCCARTNEY.

**Constitution of anserine.** W. LINNEWEH and F. LINNEWEH (Z. physiol. Chem., 1930, 189, 280; cf. this vol., 1049).—The laevorotation of the histidine component of carnosine follows from the synthesis of the latter by Baumann and Ingvaldsen (A., 1918, i, 454).

W. MCCARTNEY.

**Yohimbe alkaloids. VI. Two further subsidiary alkaloids of yohimbine.** G. HAHN and W. SCHUCH (Ber., 1930, 63, [B], 1638—1647; cf. this vol., 227).—Corvanthine acid, obtained from corvanthine,  $C_{21}H_{26}O_3N_2$ , by Fournéau and Fiore (A., 1912, i, 49), decomp. 242°,  $[\alpha]_D^{25}$   $-58.0^\circ$  in pyridine, appears to be converted by loss of carbon dioxide



into a variety of substances, among which yohimbol is not present. It is therefore not identical with any of the seven yohimbe alkaloids, but its precise relationship to them cannot at present be elucidated.

Examination of a technical specimen of yohimbine hydrochloride has led to the isolation of  $\alpha$ -yohimbine hydrochloride, decomp.  $286^\circ$ ,  $[\alpha]_D^{25} +55.0^\circ$ , identical with the substance described by Lillig and Kreitmayer (Merek's Ber., 1928, 20). For  $\alpha$ -yohimbine the constants, m. p.  $235^\circ$ ,  $[\alpha]_D^{25} -22.5^\circ$  in alcohol, are now recorded.  $\alpha$ -Yohimboic acid ( $+H_2O$ ),  $[\alpha]_D^{25} +49.6^\circ$  in pyridine (potassium salt), ethyl  $\alpha$ -yohimboate,  $[\alpha]_D^{25} +29.0^\circ$  in pyridine, and ethyl  $\alpha$ -yohimboate hydrochloride,  $[\alpha]_D^{25} +61.3^\circ$  in water, are described. Decarboxylation of the acid does not afford yohimbol.

Re-examination of technical samples of yohimbine shows that the isolation from them of homogeneous isoyohimbine is always possible, whereas that of yohimbine is exceedingly difficult and without certain criterion of uniformity. The following revised data for the  $\beta$ -yohimbine series are recorded:  $\beta$ -yohimbine hydrochloride,  $[\alpha]_D^{25} -104.9^\circ$  in water;  $\beta$ -yohimbine, m. p.  $215-216^\circ$ ,  $[\alpha]_D^{25} +94.8^\circ$  in pyridine;  $\beta$ -yohimboic acid, m. p.  $256^\circ$ ,  $[\alpha]_D^{25} +125.6^\circ$  in pyridine (anhydride, decomp.  $298^\circ$ ,  $[\alpha]_D^{25} +129.2^\circ$  in pyridine), decarboxylated to yohimbol. Re-esterification of  $\beta$ -yohimboic acid and conversion of the product into the hydrochloride yields a material of considerably lower specific rotation than the natural hydrochloride; the cause of this observation has not been established, but the possible presence of two alkaloids is not excluded.  $\gamma$ -Yohimbine ( $+3H_2O$ ), decomp.  $240^\circ$  after evolving water vapour at  $100^\circ$ ,  $[\alpha]_D^{25} -28.3^\circ$  in pyridine, is isolated in very small amount from the residues of the preparation of isoyohimboic acid by a process to be described later. The corresponding hydrochloride, decomp.  $312^\circ$ ,  $[\alpha]_D^{25} +37.6^\circ$  in pyridine, and  $\gamma$ -yohimboic acid ( $+H_2O$ ), decomp.  $252^\circ$ ,  $[\alpha]_D^{25} +89.5^\circ$  in pyridine (decarboxylated to yohimbol), have been prepared.

Dehydrogenation of all the isomerides, except coryanthine, with selenium gives a colourless, crystalline base, decomp.  $211^\circ$ ,  $[\alpha]_D^{25} \pm 0^\circ$  in alcohol or pyridine. The change appears to be represented by the equation  $2C_{20}H_{21}O_3N_2 \rightarrow (C_{18}H_{12}N_2)_2O + 2CO_2 + 11H_2 + H_2O + 2C$ .

H. WREN.

**Sparteine camphorsulphonate**, a derivative of camphor and sparteine soluble in water. F. MERCIER (Compt. rend., 1930, 194, 224-226).—*Sparteine camphorsulphonate*,  $C_{15}H_{26}N_2 \cdot 2C_{10}H_{15}O \cdot SO_3H$ , is prepared from a concentrated alcoholic solution of its components or by the action of barium camphorsulphonate on sparteine sulphate in boiling water.

H. WREN.

**Diphenyl series. III. Phosphorus derivatives of diphenyl.** D. E. Worrall (J. Amer. Chem. Soc., 1930, 52, 2933-2937).—Phosphorus trichloride, 4-chlorodiphenyl, powdered sodium, and a trace of antimony in benzene give *tri-p-diphenylphosphine*, m. p.  $172^\circ$ . This forms an additive product with bromine which reacts very readily with traces of water, forming *tri-p-diphenylphosphine oxide* (I), m. p.  $233-234^\circ$ . The phosphine yields with sulphur in carbon disulphide a *sulphide*, m. p.  $241-242^\circ$

with previous softening, but with phosphorus trichloride, unlike the corresponding antimony or arsenic derivatives (this vol., 486), it does not give chloroarylphosphines. It gives with methyl iodide *tri-p-diphenylmethylphosphonium iodide*, m. p.  $135-136^\circ$  (decomp.). The phosphonium base, liberated by silver oxide in warm alcohol, decomposes into diphenyl and *di-p-diphenylmethylphosphine oxide*, m. p.  $223-224^\circ$  after softening. *Tri-p-diphenylallylphosphonium bromide*, m. p.  $195-196^\circ$ , and *di-p-diphenylallylphosphine oxide* ( $+EtOH$ ), m. p.  $192-193^\circ$ , are formed similarly. *Tri-p-diphenylbenzylphosphonium bromide*, m. p.  $277^\circ$ , softening from  $269^\circ$ , gives with alcoholic potassium hydroxide toluene and the oxide I. *Tri-p-diphenylcarbethoxymethylphosphonium chloride*, m. p.  $164-165^\circ$ , also gives the oxide I at the ordinary temperature,

but at  $0^\circ$  the *betaine*,  $P(C_6H_5)_3 \cdot CH_2 \cdot CO \cdot O$ , m. p.  $109-110^\circ$  after softening, is obtained. This decomposes slowly into the oxide when kept.

H. E. F. NOTTON.

**Reaction between aminophenylarsinic acids and carbon disulphide.** J. G. EVERETT (J.C.S., 1930, 1691-1698).—The reaction between an aminophenylarsinic acid dissolved in alcohol with carbon disulphide and sodium hydroxide (A., 1929, 709) has been studied in detail. The amino-group may react to produce either a thiocarbimide or a dithiocarbamide, together with an equivalent proportion of hydrogen sulphide. This amount of hydrogen sulphide is insufficient to account for the production of the thiocarbonyl arylarsenic sulphides, which are the final products of the reaction. The additional quantity of hydrogen sulphide results from the alkaline hydrolysis of sodium ethyl xanthate or sodium metathiocarbonate, formed in the reaction mixture as intermediate products. This mechanism readily explains the formation of phenylarsenic sesquisulphide from phenylarsinic acid. If potassium ethyl xanthate is substituted for carbon disulphide a greater variation of conditions is possible. When the xanthate (1 mol.) reacts with *p*-aminophenylarsinic acid the product obtained with an excess of the former is entirely *pp'*-dithiocarbaminophenylarsenic sesquisulphide. With more than 1 mol. of the arsinic acid the yield of this substance falls with the production of increasing quantities of diphenylthiocarbamide-*pp'*-arsenic sesquisulphide, obtained in maximum quantity with 2 mols. of the acid. With the employment of 3 mols. of arsinic acid, diphenylthiocarbamide-*pp'*-diarsinic acid is the sole product. When the xanthate and 3-amino-4-hydroxyphenylarsinic acid interact, there is formed with an excess of the former 1-thiolbenzoxazolone-4-arsenic disulphide, whilst with an excess of the latter 1-thiolbenzoxazolone-4-arsinic acid preponderates. Similarly, using 3:4-diaminophenylarsinic acid, the products are 2-thiolbenziminazole-5-arsenic disulphide and -5-arsinic acid. In all cases some dearsenication occurs, arsenious acid or sulphide being present in the reaction mixture.

T. H. MORTON.

**10-Chloro-5:10-dihydrophenarsazine and its derivatives. XIII. Absorption spectra.** C. S.

GIBSON, E. S. HISCOCKS, J. D. A. JOHNSON, and J. L. JONES (J.C.S., 1930, 1622—1632).—The conclusions reached concerning the relation of visual colour and constitution of the derivatives of 10-chloro-5:10-dihydrophenarsazine (A., 1929, 945) have been confirmed and extended by measurements of extinction coefficients of the same substances in the visible and ultra-violet regions to  $\lambda$  2400 Å. The parent substance shows a weak absorption band at a frequency ( $\times 10^{-14}$ )  $\nu$  8.65, which is assigned to a transannular linking, and a double-headed band at  $\nu$  10.4. The spectra of the derivatives fall into groups according to the position of the nitro-group. 10-Chloro-4-nitro-, 10-chloro-4-nitro-2-methyl-, and 10-chloro-4-nitro-7-methyl-5:10-dihydrophenarsazine all possess absorption curves of very similar outline having a strong band at  $\nu$  6.7 and general absorption beyond  $\nu$  9. A similar curve is shown by 2-nitrodiphenylamine-6'-dichloroarsine. These compounds are assigned a chelate formula. The yellow 10-chloro-2-nitro-, and 10-chloro-2-nitro-4-methyl-5:10-dihydrophenarsazines have a very strong band at  $\nu$  7.6 and a subsidiary band at  $\nu$  8.8. The orientation of the substances obtained by the cyclisation of derivatives of 3-nitrodiphenylamine-6'-arsinic acid has been achieved by comparison of their spectra with rationally synthesised derivatives of known orientation. 10-Chloro-3-nitro-4-methyl- and 10-chloro-3-nitro-2-methyl-5:10-dihydrophenarsazine show bands of but small persistence at  $\nu$  7.5—9. Both the 3-nitro- and the 2-nitro-derivatives are formulated with the transannular linking of the parent substance. 10-Chloro-1-nitro-, 10-chloro-1-nitro-2-methyl-, and 10-chloro-1-nitro-4-methyl-5:10-dihydrophenarsazine possess a band at  $\nu$  7.5, and banded absorption to  $\nu$  13. A very similar spectrum is shown by 5-nitro-2-methyldiphenylamine-6'-dichloroarsine. Chelate formulae are suggested for the above compounds. The following substances, the constitutions of which were previously (*loc. cit.*) uncertain, have now been oriented: 10-chloro-3-nitro-1-methyl-, m. p. 245—247°; 10-chloro-1-nitro-7-methyl-, m. p. 253—255°; 10-chloro-1-nitro-, m. p. 258—259°; 10-chloro-3-nitro-2-methyl-, m. p. 225—226°, and 10-chloro-1-nitro-2-methyl-5:10-dihydrophenarsazine, m. p. 257—258°.

T. H. MORTON.

**Mercury camphorcarboxylate and derivatives.** M. PICON (Compt rend., 1930, 190, 1430—1432).—*Mercury camphorcarboxylate* is prepared by the action of yellow mercuric oxide on the free acid in the presence of a little water. On heating for 15 min. with a small amount of boiling water or benzene it loses carbon dioxide to give *mercury camphorcamphorcarboxylate*,  $(C_{10}H_{15}O)_2CO_2Hg$ ; if the heating is continued for 12 hrs. a second molecule of carbon dioxide is removed to yield *mercury dicamphor*,  $(C_{10}H_{15}O)_2Hg$ . *Basic mercury camphorcarboxylate*,  $(C_{10}H_{15}O \cdot CO_2)_2Hg \cdot HgO$ , is prepared by the action of the free acid on an excess of yellow mercuric oxide in the cold and is insoluble in all organic solvents; prolonged extraction with benzene converts it into the *basic camphorcamphorcarboxylate*,  $C_{10}H_{15}O \cdot CO_2Hg \cdot C_{10}H_{15}OHgO$ . Equimolecular aqueous solutions of sodium camphocarbonate and mercuric chloride furnish *mercury chlorocamphorcarboxylate*,  $C_{10}H_{15}O \cdot CO_2HgCl$ , which readily dissociates

in water, but only loses carbon dioxide slowly at 100° to form *mercury camphor chloride*,  $C_{10}H_{15}OHgCl$ . When heated in a vacuum these compounds decompose to mercury, camphor, and carbon dioxide.

C. C. N. VASS.

**cis- and trans-Tetrahydroselenophen-2:5-dicarboxylic acids.** A. FREDGA (J. pr. Chem., 1930, [ii], 127, 103—108).—Sodium *meso*-dibromoadipate and aqueous potassium selenide solution at 0° give *cis-tetrahydroselenophen-2:5-dicarboxylic acid* (I), m. p. 173° (*silver, lead, and copper salts*). Sodium *r*-dibromoadipate similarly yields *trans-tetrahydroselenophen-2:5-dicarboxylic acid* (II), m. p. 195° (*silver, lead, and copper salts*), resolved by brucine in aqueous solution into the *d*-acid and the *l*-acid. Both acids react with 2 equivalents of iodine on titration with iodine in sodium hydrogen carbonate solution. The primary dissociation constants in water are  $2.7 \times 10^{-4}$  and  $3.4 \times 10^{-4}$  (slight increase with decreasing concentration) for I and II, respectively,  $\nu_0=370$  being assumed.

A. I. VOGEL.

**New aromatic antimonials.** U. N. BRAHMA-CHARI and J. M. D. GUPTA (J. Asiatic Soc. Bengal, 1929, 25, 301—306).—*Sodium p- $\omega$ -sulphomethylaminophenylstibinate*,  $(SO_3Na \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot SbO_2)_2H(ONa)$ , was obtained by the interaction of formaldehyde, sodium hydrogen sulphite, and sodium *p*-aminophenylstibinate in aqueous solution; the corresponding *carbamide salt*  $(OCH_2N_2O \text{ for } ONa)$  was similarly prepared from "urea stibamine." Analogous *sulphino*-compounds were obtained when sodium formaldehydesulphoxylate was used instead of formaldehyde and hydrogen sulphite. Carbamide and the appropriate stibinic acid in aqueous solution yielded *carbamide p-acetamidophenylstibinate* and *p-hydroxyphenylstibinate*. *Sodium 2-acetamidoazobenzene-5:4'-distibinate* was obtained by coupling diazotised *p*-aminophenylstibinic acid with sodium *p*-acetamidophenylstibinate in alkaline solution. The above products are characterised by analysis only.

H. A. PIGGOTT.

**3-Acetamido-4-hydroxyphenylstibinic acid.** I. E. BALABAN (J.C.S., 1930, 1685—1687).—When *p*-amino-*o*-acetamidophenol is submitted to the Bart-Schmidt reaction for the substitution of a stibinic acid for an amino-radical, there is formed *3-acetamido-4-hydroxyphenylstibinic acid*, which is insoluble in water and the usual solvents, differing thereby from the substance of Morgan and Cook (this vol., 797) obtained by the treatment of 3-amino-4-hydroxyphenylstibinic acid with acetic anhydride. This compound has a slight trypanocidal activity against *T. equiperdum*. In a similar manner *p*-nitro-*o*-aminophenol yielded a product possibly containing *5-acetamido-2-hydroxyphenylstibinic acid*, and *3-hydroxy-1:4-benzisooxazine-6-stibinic acid* was obtained in a poor yield from the corresponding -6-amine. Attempts to prepare the *s*-carbamide of *p*-aminophenylstibinic acid were unsuccessful.

T. H. MORTON.

**Cerebrosides. XI. Partial synthesis of kersin and observations on nervone.** E. KLENK and R. HÄRLE (Z. physiol. Chem., 1930, 189, 243—253).—Treatment of galactosphingosine (psychosine) (A., 1926, 749) with lignoceryl chloride in pyridine at

the ordinary temperature affords a product which, after short boiling with dilute methyl-alcoholic sodium hydroxide to hydrolyse any *O*-acyl derivative formed, furnishes kersin, m. p. 183—185°,  $[\alpha]_D^{25}$   $-4.3^\circ$  (all rotations are in pyridine). This is reduced by hydrogen in presence of palladised barium sulphate and alcoholic acetic acid to *dihydrokersin*, m. p. 184°,  $[\alpha]_D^{25}$   $+5.26^\circ$ . Similar reduction of nervone,  $C_{48}H_{90}O_8N$ ,  $[\alpha]_D^{25}$   $-3.2$  (cf. A., 1925, i, 1346), affords *tetrahydronervone*, m. p. 185°,  $[\alpha]_D^{25}$   $+5.58^\circ$ , identical with *dihydrokersin*. Treatment of *tetrahydronervone* with 10% methyl-alcoholic hydrochloric acid gives an ester, hydrolysed to lignoceric acid. Nervone differs from kersin by virtue of the unsaturated acyl group attached to the nitrogen atom. H. BURTON.

**cycloTripeptide from caseinogen.** V. S. SADIKOV and E. A. POSCHILTZOVA (Biochem. Z., 1930, 221, 304—314).—When caseinogen is heated with 2% sulphuric acid at 180° for 12 hrs. and the product is extracted with ether a crystalline *diprol-yl-leucine*, m. p. 262—264° (decomp.), is obtained in 2% yield. Its properties indicate that it is a cyclic compound and from the yield obtained the mol. wt. 16,360 for caseinogen is calculated. W. McCARTNEY.

**Electrolytic separation of  $\alpha$ -amino-acids in protein hydrolysates.** J. A. ANDERSON (Biochem. Z., 1930, 221, 284—294).—At  $p_H$  6.0 aspartic acid can be electrolytically separated in an almost pure condition and without much loss from a mixture of the acid with glycine. A vulcanite apparatus containing five paper cells and having graphite electrodes is used. W. McCARTNEY.

**Action of *N*-alkali, erepsin, and trypsin-kinase on compounds of polypeptide nature containing  $\beta$ -alanine.** E. ABDERHALDEN, T. RYNDIN, and E. SCHWAB.—See this vol., 1066.

**Significance of the amino- or of the carboxyl group in polypeptides for the action of definite enzyme complexes.** E. ABDERHALDEN and F. SCHWEITZER.—See this vol., 1066.

**Action of *N*-alkali, erepsin, and trypsin-kinase on isomeric polypeptides containing *D*-alanine, *D*- $\alpha$ -aminobutyric acid, and *L*-leucine.** E. ABDERHALDEN and M. SAITO.—See this vol., 1066.

**Proteins. IX. Degradation of ovalbumin by hypobromite.** S. GOLDSCHMIDT, R. R. WOLFF, L. ENGEL, and E. GERISCH (Z. physiol. Chem., 1930, 189, 193—217).—From a detailed study of the action of hypobromite on ovalbumin, whereby leucine, phenylalanine, glutamic acid, arginine, and cystine are formed principally, it is inferred that the protein molecule is attacked at various points and not merely where free amino-groups occur. During the attack lysine and arginine are very rapidly destroyed, tryptophan and tyrosine are probably halogenated, and diamino-acids are broken up or destroyed slowly. From what part of the molecule the ammonia formed by the action of alkali on the various degradation products comes is not known, but it is not derived from  $\text{CO-NH}_2$  groups. The sulphur in ovalbumin is not all combined in the same way. If ovalbumin contains long polypeptide chains these are probably broken down in the manner previously suggested (A.,

1929, 937), but the expected keto-acids could not be detected. W. McCARTNEY.

**$p_H$ -Stability regions of serum-albumin and serum-globulin.** T. SVEDBERG and B. SJÖGREN (J. Amer. Chem. Soc., 1930, 52, 2855—2863; cf. A., 1929, 203).—The absorption spectra of serum-albumin and serum-globulin are unaltered by  $p_H$  changes except for a slight increase in the extinction coefficients at high alkalinity. The curve for euglobulin is similar to that of serum-globulin, but that of pseudoglobulin is markedly lower. Ultracentrifugal measurements show that the molecules of serum-albumin and serum-globulin are uniform in size in the  $p_H$  regions of 4.0—9.0 and 4.0—8.0, respectively. Outside these limits both proteins give heterogeneous solutions in which units of mol. wt. 30,000—40,000 appear to predominate, but in the case of serum-globulin this change is preceded by the formation of aggregates of high mol. wt. The changes produced in the former protein at  $p_H$  2.2 and 11.8 and in the latter at  $p_H$  11.8 are reversed by neutralisation. Pseudoglobulin and euglobulin are heterogeneous, the latter being the more degraded. They do not produce serum-globulin when mixed and are to be regarded as purely artificial products. H. E. F. NOTTON.

**Denatured proteins.** H. F. HOLDEN and M. FREEMAN (Austral. J. Exp. Biol., 1930, 7, 13—26).—Crystalline ovalbumin in ammonium sulphate solution has  $[\alpha]_{5461}$   $-37.3^\circ$  at  $p_H$  4.8; on dialysis the value falls to  $-36.5^\circ$ . The value  $-44.5^\circ$  of Hewitt (A., 1927, 583) could not be confirmed. Denatured ovalbumin is found to have values of  $[\alpha]_{5461}$  ranging from  $-58.5^\circ$  to  $-99.9^\circ$ . The variation is not due to the presence of native protein. Caseinogen has a slightly higher specific rotation in acid than in alkaline solution; it behaves similarly to denatured ovalbumin when the effect of small concentrations of salts on their solubilities is considered. In this latter respect mercuric chloride is abnormal, a saturated solution failing to precipitate denatured ovalbumin on the acid side of its isoelectric point. F. O. HOWITT.

**Hydrolysis of proteins under pressure.** K. CRONHEIM (Biochem. Z., 1930, 222, 198—203).—When ox fibrin is autoclaved for 120 min. with 3*N*-phosphoric acid at 8, 4, and 2 atm., respectively, 93, 52.5, and 22.5% of the protein is converted into non-coagulable substances, whilst with 1.5*N*-acid, the corresponding percentages are 88.4, 37.5, and 10.6.

P. W. CLUTTERBUCK.

**Separation of iodine and bromine from iodinated and brominated proteins by irradiation.** F. LIEBEN and G. EHRLICH (Biochem. Z., 1930, 222, 221—225).—Iodine and bromine can be separated as iodide and bromide from artificially halogenated caseinogen, from Merck's thyreoidin, di-iodotyrosine, and thyroxine by irradiation with the mercury lamp. The rise of temperature during irradiation (up to 62°) is not sufficient to account for the separation. The separation under the best conditions may be more or less complete, but the latter fraction of the halogen is more difficult to remove. P. W. CLUTTERBUCK.

**Structure of the polypeptide associates obtained from gelatin and gelatin-peptone by means of acetic anhydride.** VI. A. FODOR and C.

EPSTEIN (Biochem. Z., 1930, 222, 226—239).—All the fractions obtained are shown on the grounds of total analysis, acetyl determinations, titration values, mol. wts., etc. to be derived from the same complex made up of 1 proline, 2 hydroxyproline, 2 glycine, and 3 alanine groups, acetylated to different extents. The mode of union of these groups in the complex is discussed (cf. A., 1929, 1490). P. W. CLUTTERBUCK.

**Preparation and molecular size of gelatin-peptone.** M. FRANKEL and S. KUK (Biochem. Z., 1930, 222, 240—242).—Gelatin, freed from salts by electrodialysis, was digested with pepsin and hydrochloric acid, the chlorine removed with silver carbonate, and the solution evaporated in a vacuum to a brown, amorphous mass which was fractionally extracted with methyl alcohol. The mol. wt. of four fractions (by depression of f. p. of water) varied from 342 to 365.3. P. W. CLUTTERBUCK.

**Ultracentrifugal study of gelatin solutions.** K. KRISHNAMURTI and T. SVEDBERG (J. Amer. Chem. Soc., 1930, 52, 2897—2906).—The partial sp. vol. of gelatin in aqueous solution is 0.682, whereas that of other proteins is about 0.745. The difference is equivalent to the contraction which occurs when gelatin is dissolved in water (cf. Svedberg, A., 1924, i, 104). The sp. vol. is practically unaffected by temperature, concentration, and  $p_H$  changes. Its absorption curve shows a sharp decrease at 240  $\mu$ , but no maximum at 276  $\mu$ , as with other proteins. Within the  $p_H$  range 4.6—6.0, the sedimentation constant in freshly prepared 0.4% solutions corresponds with a mol. wt. of about 100,000, and is not reproducible. On keeping, the particles undergo aggregation, the more so the nearer the solution is to the isoelectric point. At and below  $p_H$  4.0 and at  $p_H$  7.5 there is practically no aggregation with time, but the apparent diffusion constants show a marked drift. Sedimentation equilibrium measurements show that at  $p_H$  4.0 particles of mol. wt. 10,000—70,000 are present, including a large proportion having a mol. wt. of about 11,000. Since no protein has been previously encountered with a mol. wt. of less than 33,000, these last may be decomposition products of the original gelatin. At  $p_H$  2.5 gelatin is completely degraded to matter which does not sediment in the strongest available centrifugal field. H. E. F. NOTTON.

**Sources of error in organic elementary analysis. VII. Influence of rubber and cork material on the hydrogen values.** J. LINDNER [with F. HERNLER] (Ber., 1930, 63, [B], 1672—1683; cf. this vol., 940).—The disadvantages of the customary uses of rubber in elementary analysis lie chiefly in its resorptive power and permeability for water. Irregularities due to the volatilisation of organic substances are of less importance in the determination of hydrogen than in that of carbon. Cork stoppers are unsuitable for elementary analysis; the absorption of water from moist air is not less than that of the more open types of caoutchouc, whilst the permeability is considerably greater. H. WREN.

**Carbon, hydrogen, and nitrogen determinations using a metal tube.** S. AVERY and D. HAYMAN (Ind. Eng. Chem. [Anal.], 1930, 2, 336—

337).—A combustion tube made of copper, having air-cooled ends and an outer jacket of nickel, is described. The tube may be used to advantage in the analysis of difficultly combustible volatile products. A nickel tube may be used satisfactorily for determining nitrogen by the Dumas method. Details are given for the determination of carbon and hydrogen in substances containing nitrogen.

E. S. HEDGES.

**Subsequent additions of acid in Carius combustions.** D. D. HARTLEY (Ind. Eng. Chem. [Anal.], 1930, 2, 328).—A simple device for adding without inconvenience a further quantity of acid to a Carius tube in which incomplete decomposition has occurred is described.

E. S. HEDGES.

**Micro-determination of arsenic in organic substances.** T. VON FELLEBERG (Mitt. Lebensm. Hyg., 1929, 20, 321—337; Chem. Zentr., 1930, i, 1239).—After combustion with hydrogen peroxide and sulphuric acid and removal of the arsenic as trichloride, the arsenic is precipitated as sulphide and titrated in alkaline solution with permanganate.

A. A. ELDRIDGE.

**Determination of organic nitro-compounds and inorganic nitrates by reduction in acid media.** J. P. LÉLHALLÉUR (Ann. Acad. Brasil Sci., 1930, 2, 31—32).—Reduction of nitro-compounds and nitrates in acid solution offers no advantages over reduction in alkaline solution; hydroxylamine is probably produced by reduction of the nitrogen peroxide present, and is then converted into nitrous oxide.

H. F. GILLBE.

**Test for lævulose (ketose) in carbohydrates.** S. TASHIRO and E. B. TIETZ (J. Biol. Chem., 1930, 87, 307—310).—A mixture of concentrated sulphuric acid with an equal volume of a freshly-prepared 0.1% solution of bile salts gives a pink or purple colour when mixed with a drop of a solution containing 0.03% or more of lævulose, free or in combination. Aldoses give the reaction, but only in concentrations of 4—10%. The test is negative with the blood-serum of normal or hyperglycæmic individuals in the fasting condition, but positive 1 hr. after ingestion of 150 g. of sucrose. It is almost always positive in urine and invariably negative in milk.

C. R. HARRINGTON.

**Determination of lactic acid.** K. J. ANSELMINO.—See this vol., 1224.

**Detection and determination of benzoic acid.** J. C. HARRAL (Analyst, 1930, 55, 445).—The sample is extracted with ether, the ether is treated with alkali, and the dried extract is nitrated, reduced with zinc, and sodium nitrite solution is added, followed by ammonia. In the presence of benzoic acid a yellow coloration results and the quantity may be determined colorimetrically. The reaction is not specific for benzoic acid in foodstuffs, but only in rare instances is a definite colour produced in its absence.

D. G. HEWER.

**Determination and separation of picric and 2:4:6-trinitrobenzoic acids.** C. KRAUZ and O. TUREK (Chem. Obzor, 1929, 4, 213—216; Chem. Zentr., 1930, i, 1781).—The method depends on the precipitation, during 24 hrs. at the ordinary tem-

perature with alcoholic silver nitrate (4 mols.), of the trinitrobenzoic acid, removal of the excess of silver with sulphuric acid, extraction of the picric acid from an aliquot part with ether, and precipitation with nitron acetate.

A. A. ELDRIDGE.

**Determination of antipyrine and pyrimidone.** S. ERIKSON (Svensk farm. Tidskr., 1930, 34, 1—7; Chem. Zentr., 1930, i, 1836).—A method for the analysis of mixtures of antipyrine and pyrimidone depends on the fact that both substances, but not the products of boiling pyrimidone with hydrogen peroxide, give sparingly soluble picrates.

A. A. ELDRIDGE.

**Improved colour standard for colorimetric determination of chlorophyll.** H. B. SPRAGUE and L. B. TROXLER (Science, 1930, 71, 666—667).—A modification of the colour standard previously described (A., 1928, 784) gives more satisfactory results. 0.9 c.c. of 0.5% aqueous solution of malachite-green and 11.2 c.c. of 0.5% aqueous solution of naphthol-yellow are diluted to 5500 c.c. with water. The colour in this standard is equivalent to that produced by 11.873 mg. of chlorophyll hydrolysed to chlorophyllins and diluted to 1000 c.c. L. S. THEOBALD.

**Formation of salts by compounds with several nitrogen atoms in sulphuric acid.** A. HANTZSCH (Ber., 1930, 63, [B], 1782—1786).—Cryoscopic determinations of mol. wt. show that compounds containing two nitrogen atoms which are not united to oxygen are present as completely dissociated disulphates; thus benzamidine, carbamides, phenylhydrazine, and ethyl hydrazinedicarboxylate are present as the salts  $CPh.NH_2(SO_4H) \cdot NH_3(SO_4H)$ ,  $CO[NR_2H(SO_4H)]_2$ ,  $Ph.NH_2(SO_4H) \cdot NH_3(SO_4H)$ , and  $[NH_2(SO_4H) \cdot CO_2Et]_2$ , respectively. Guanidino, di-

methyltriazole, and azoimide are present as trisulphates; this observation is compatible only with the cyclic structure for the last-named compound. Aminoguanidino is present as the tetrasulphate. Tetrazoles behave irregularly, since *C*-phenyltetrazole forms only a disulphate and tetrazolo a monosulphate. Aminotetrazole gives a pentasulphate. It is therefore possible by determinations of mol. wt. to establish the number of ions formed in sulphuric acid solution and thence to determine for compounds with several nitrogen atoms the number of such atoms which participate in salt formation. This is true also for certain oxygen compounds with respect to their tendency to produce oxonium sulphates. Phenols and phenolic ethers dissolve in sulphuric acid with initial production of normal oxonium sulphates  $[Ar.OH_2]SO_4H$  and  $[Ar.O.CH_3H]SO_4H$ , which rapidly yield cations of abnormally low mol. wt. This is due to subsequent passage into isomeric quinonoid or quinolide oxonium sulphates  $H_2C_6H_2.O^+H]SO_4H$  and addition of several molecules of sulphuric acid to the unsaturated ring.

H. WREN.

**Determination of alkaloids.** G. GRAZIANI.—See this vol., 1224.

**Micro-determination of proteins.** R. WINTER-NITZ and Z. STARY (Mikrochem., 1930, 8, 252—256).—A quantity of the solution containing not more than 1.5 mg. of protein is centrifuged for 15 min. with 2 c.c. of 20% trichloroacetic acid, the liquid decanted, and the precipitate washed with 4% trichloroacetic acid, and heated with a mixture of sulphuric and phosphoric acids to destroy organic matter. The mixture is diluted to 17.5 c.c., 7.5 c.c. of Nessler solution are added, and the colour developed is compared with a series of standards. A. R. POWELL.

## Biochemistry.

**Regulation of respiration. XXXIV. Carbon dioxide content of frog's brain with different oxidations.** D. A. MCGINTY (Amer. J. Physiol., 1930, 93, 528—535).—The brain-carbon dioxide increases with oxygen pressure and is decreased in the presence of cyanide. The buffering power of frog's brain is greater than that of muscle, but less than that of blood.

E. BOYLAND.

**Ability of marine fishes to remove oxygen from sea-water.** F. G. HALL (Amer. J. Physiol., 1930, 93, 417—421).—Whilst the toad fish can remove all the dissolved oxygen from sea-water, most fish can remove the oxygen only to a partial pressure of 2—16 mm. The mackerel must move forward through the water in order to obtain sufficient oxygen.

E. BOYLAND.

**Oxygen capacity of repeatedly recrystallised horse oxyhæmoglobin.** J. SZIKLAY (Biochem. Z., 1930, 223, 373—378).—The capability of the oxyhæmoglobin to combine with oxygen is not affected by repeated recrystallisation from dilute alcohol.

W. MCCARTNEY.

**Resistance of hæmoglobin to sodium hydroxide.** G. FRANCKE (Biochem. Z., 1930, 222, 482—486).—Spectroscopic examination of blood solutions of

various concentrations treated with a constant concentration of sodium hydroxide shows that there is a parallelism between the time which passes before the oxyhæmoglobin bands disappear and the hæmoglobin content.

W. MCCARTNEY.

**Green hæmin from blood hæmin.** O. WARBURG and E. NEGELEIN (Ber., 1930, 63, [B], 1816—1818).—Hæmin, from ox blood, dissolved in aqueous pyridine, is treated at 50° with a solution of hydrazine hydrochloride and sodium hydroxide in a rapid stream of oxygen. The mixture is cooled and filtered and the filtrate is extracted with ether to remove a yellow substance and then with chloroform, into which the green hæmin passes. It is stable only in the presence of pyridine. Treatment of the substance with methylalcoholic hydrogen chloride gives a green ester,  $C_{36}H_{40}O_6N_4Cl_4Fe (\pm 1C, \pm 1H)$ . Reduction of the ester with palladium and hydrogen or with cysteine gives a substance resembling tetrachloromesoporphyrin.

H. WREN.

**Preparation of crystalline methæmoglobin.** A. DÉNES (Biochem. Z., 1930, 223, 481—488).—Oxyhæmoglobin (horse) kept in suspension for several weeks at a temperature which may vary from 0° to not

much above the ordinary temperature, is converted into methæmoglobin, which can readily be recrystallised from dilute alcohol. The methæmoglobin is less soluble than that prepared by other methods, but otherwise its properties, particularly as regards absorption of light, are the same as those described by other workers. The iron content of the methæmoglobin is the same as that of oxyhæmoglobin.

W. MCCARTNEY.

**Identity of hæmatoporphyrins from various species of blood.** E. LEIKOLA (Biochem. Z., 1930, 223, 436—442).—Aqueous-alcoholic solutions of hæmatoporphyrin from the ox and the horse absorb the same amount of visible light, but similar solutions of hæmatoporphyrin from the pig absorb considerably more. With alcoholic solutions the differences in the amount of light absorbed may be greater in the case of individuals of the same species than in that of animals of different species. It is possible that hæmatoporphyrin prepared in the usual way is not a single substance and undergoes alteration during preparation.

W. MCCARTNEY.

**Determination of bilirubin in blood-serum.** L. HEILMEYER and W. KREBS (Biochem. Z., 1930, 223, 352—364).—In addition to bilirubin the alcoholic extract of serum may contain a yellow dye which cannot be diazotised and hence colorimetric determinations of bilirubin as azo-dye sometimes give unsatisfactory results. Satisfactory results can be obtained by a modification of the methods of Thannhauser and Andersen (A., 1922, ii, 671) and of Jendrassik and Cziike (A., 1928, 1392) in which the use of a simplified spectrophotometer is substituted for colorimetric comparisons.

W. MCCARTNEY.

**Determination of direct and indirect blood-bilirubin.** U. DE CASTRO (Z. ges. exp. Med., 1929, 67, 673—682; Chem. Zentr., 1930, i, 1663).—For the isolation of indirect bilirubin 1 c.c. of serum is shaken and centrifuged with 2 c.c. of chloroform and the chloroform removed by a current of air and immersion in warm water. The bilirubin is dissolved in 0.1 c.c. of chloroform and 0.9 c.c. of alcohol and determined colorimetrically with Ehrlich's reagent. Direct bilirubin is first oxidised by means of increasing quantities of Sabatini's reagent (nitrous acid). Determinations were made in jaundice and hepatic disease.

A. A. ELDRIDGE.

**Use of buffer citrate solution as a diluent and preservative for red blood-cells.** L. J. SCHULTZ (J. Lab. Clin. Med., 1929, 14, 674).

CHEMICAL ABSTRACTS.

[Apparatus for] blood chemistry determinations. W. G. GAMBLE, jun. (J. Lab. Clin. Med., 1929, 14, 684).

CHEMICAL ABSTRACTS.

**Action of blood-catalase.** G. FRANCKE (Biochem. Z., 1930, 222, 416—424).—The action of the catalase in dilute (1:1000) blood solutions is not affected by the presence of sodium chloride in concentrations up to 0.00075%, nor is this action influenced when red blood-corpuscles are washed with 1.5% sodium chloride solutions or when serum is added to the corpuscles in amounts such that the ratio of corpuscles to serum is the same as it is in blood. In solutions of washed blood-corpuscles, free from

serum, the activity of the catalase decreases considerably in 24 hrs.

W. MCCARTNEY.

**Determination of the activity of catalase in leucocytes.** K. IGLAUER (Biochem. Z., 1930, 223, 470—477).—The leucocytes in 8—10 c.c. of venous blood are isolated by a modification, in which sodium citrate is used for defibrination, of Szilard's method (Pflüger's Archiv, 1926, 211, 597) and the activity of the catalase which they contain is expressed by the number of mg. of hydrogen peroxide decomposed in 30 min. per million leucocytes. At 17° this number lies between 6 and 11 for healthy persons, but may be less in the case of diseased persons.

W. MCCARTNEY.

**Light and catalase.** H. KOEPPE (Strahlenther., 1929, 34, 598—604; Chem. Zentr., 1930, i, 1803).—Blood-catalase is regarded as storing radiant energy.

A. A. ELDRIDGE.

**Lipins of blood-plasma.** H. THEORELL (Biochem. Z., 1930, 223, 1—99).—When a cholesterol suspension is added to horse serum or plasma, part of the cholesterol passes into clear solution. Similarly, lecithin and phosphatides stirred with serum pass partly into solution. This lipin fraction in solution may be salted out by ammonium sulphate along with both the fibrinogen and the globulin fractions. The fractions precipitated by salting out and by electro dialysis contain the lipin in definite proportions, the cholesterol: lipin-phosphorus ratio decreasing from fibrinogen to globulin to albumin. The antagonistic action of cholesterol and lecithin on hæmolysis of blood-corpuscles is confirmed. Both cholesterol and lecithin have a powerful inhibitory action on the rate of sinking of corpuscles, the effect being due to adsorption of the negatively-charged lipin on the corpuscles. Plasma-cholesterol is present in a form readily extractable by ether when the  $p_H$  is 5.5—6. Ether extraction experiments show that fibrinogen and euglobulin form compounds with cholesterol which are dissociated at  $p_H$  6 and 5.5—6, respectively, the reaction being demonstrated by addition of cholesterol suspensions to be reversible. Albumin combines with cholesterol on the acid side of this  $p_H$ . Only that portion of cholesterol which is not united with fibrinogen and globulin can inhibit the sinking of corpuscles. The velocities of cataphoretic migration of fibrinogen, globulin, and albumin are as 1:1 to 8:5.

P. W. CLUTTERBUCK.

**Fat and cholesterol contents of serum from rabbits kept in air at low pressures.** W. GRIFFEL (Biochem. Z., 1930, 222, 290—300).—The increases, due to living for 4—6 days in an atmosphere at 350 mm. pressure, in the fat and cholesterol contents of serum of rabbits are much greater than the corresponding increases caused by fasting for the same periods and are related to fatty degeneration of the liver and disappearance of glycogen, which also result from living in low-pressure atmospheres.

W. MCCARTNEY.

**Photometric determination of serum-cholesterol.** E. BRILL and G. HOPF (Münch. med. Woch., 1930, 77, 142—144; Chem. Zentr., 1930, i, 1663).—The use of a step-photometer is recommended. Normal serum contains 110—250 (mean 170) mg. per 100 c.c.

A. A. ELDRIDGE.



**Determination of blood-cholesterol.** E. M. DAY and A. BOLLIGER (Austral. J. Exp. Biol., 1930, 7, 41—44).—Blood or plasma (1 c.c.) is dried on filter-papers and extracted with chloroform. 5 C.c. aliquot parts of the total extract (15 c.c.) are treated with acetic anhydride (2 c.c.) and sulphuric acid (0.1 c.c.) and the cholesterol is determined colorimetrically as in the method of Myers and Wardell (A., 1918, ii, 461). The results are in close agreement ( $\pm 5\%$ ) with those obtained by percolation methods. F. O. HOWITT.

**Citric acid content of human blood-serum.** B. BENNI, B. SCHERSTÉN, and O. ÖSTBERG (Biochem. Z., 1930, 223, 443—444).—The citric acid content of the blood-serum of 11 healthy persons ranged from 1.5 to 3.75 mg. per 100 c.c. and that of the serum of 44 diseased persons from 0.9 to 4.8 mg.

W. MCCARTNEY.

**Acetylmethylcarbinol and  $\beta\gamma$ -butylene glycol in the blood of the higher animals.** M. LEMOIGNE and P. MONGUILLON (Compt. rend., 1930, 191, 80—82).—Acetylmethylcarbinol and  $\beta\gamma$ -butylene glycol have been identified (cf. this vol., 1071) in the blood of the ox and sheep. C. C. N. VASS.

**Total sugar of blood and urine. III. Reducing action of glutathione.** M. R. EVERETT (J. Biol. Chem., 1930, 87, 761—765).—Values are given for the reducing power of glutathione in terms of dextrose as determined by four different methods. The reagents of Folin (A., 1929, 714; 1926, 648) are most affected by glutathione, but those of Benedict (cf. A., 1929, 837) and Sumner (A., 1925, i, 1491) scarcely at all. Glutathione does not account for the hydrolysable sugar (A., 1929, 89) of the blood. Glutathione, together with a part of the hydrolysable sugar, is removed from blood by the zinc hydroxide method of Somogyi (this vol., 801) for protein precipitation.

C. R. HARINGTON.

**Coloured glass standards [in blood analysis].** M. R. MATTICE (J. Lab. Clin. Med., 1929, 14, 868—875).—Methods for the determination of sugar, nitrogen, and uric acid are described.

CHEMICAL ABSTRACTS.

**Determination of uric acid in blood-serum.** L. HEILMEYER and W. KREBS (Biochem. Z., 1930, 223, 365—372).—A modification of Folin's method for the determination of uric acid (A., 1923, ii, 196) is described. The preparation of a solution for comparison is unnecessary, measurements being made with a simplified spectrophotometer. W. MCCARTNEY.

**Determination of residual nitrogen of the blood of inhabitants of the tropics.** P. J. T. VAN BERKHOUT (Med. Dienst Volksgezondheid Ned.-Indië, 1930, i, 30—43).—No difference could be detected between the residual nitrogen of the blood of 14 healthy Europeans and 21 natives, the average value being 31 mg. per 100 c.c. P. W. CLUTTERBUCK.

**Proteins. VII. Solubility of fibrinogen in concentrated salt solutions.** M. FLORKIN (J. Biol. Chem., 1930, 87, 629—649).—In the preparation of fibrinogen the maintenance of a low temperature and the avoidance of alkalinity are essential; citrated horse blood-plasma was kept at 0° for 24 hrs., filtered, brought to  $p_H$  6.0 with hydrochloric acid, and cautiously

treated with an equal volume of saturated sodium chloride solution at  $p_H$  6.0; the precipitate was collected and dissolved in 5% sodium chloride at  $p_H$  6.0, the precipitation and re-dissolution being thrice repeated. For the individual solubility determinations the fibrinogen was reprecipitated with the appropriate salt until free from sodium chloride. Values are given for the solubility at 25° of fibrinogen in concentrated solutions of sodium chloride at  $p_H$  5.8, ammonium sulphate at  $p_H$  6.0 and 6.6, and potassium phosphate at  $p_H$  6.6. The results indicate that in the equation  $\log S = \beta - Ks\mu$ , which defines the solubility of a protein in concentrated salt solutions (cf. Cohn, Physiol. Rev., 1925, 5, 359), the salting-out factor  $Ks$  is a constant for a given protein and salt independent of variations in temperature and  $p_H$ ; of the various blood-proteins in ammonium sulphate solution, fibrinogen shows the highest value for  $Ks$ . The value of  $\beta$  varies for fibrinogen from 2.81 at  $p_H$  6.6 to 2.51 at  $p_H$  6.0, indicating that the protein has an acid isoelectric point.

C. R. HARINGTON.

**Influence of hydrogen-ion concentration on the precipitation of serum-proteins by salts. III.** D. VON KLOBUSITZKY (Biochem. Z., 1930, 223, 120—129).—The author's previous work (A., 1929, 1095) on the precipitation of horse serum and electro dialysed serum-albumin and -globulin in acid and alkaline media by equimolecular solutions of sodium chloride, sodium sulphate, ammonium sulphate, and magnesium sulphate is continued. The following salt concentrations are necessary just to bring about turbidity: with acid serum  $N$ -sodium chloride or sulphate, 1.5 $N$ -ammonium sulphate, and 3 $N$ -magnesium sulphate; with normal serum 2 $N$ -sodium sulphate 3 $N$ -ammonium sulphate (3.5 $N$ -sodium chloride has no effect); with acid globulin solutions the same results are obtained with the exception of magnesium sulphate, when 2 $N$ -sulphate is required; with electro dialysed albumin solutions, 1.5 $N$ -sodium chloride,  $N$ -sodium sulphate, 2.5 $N$ -ammonium sulphate (3.5 $N$ -magnesium sulphate has no effect); with alkaline medium only ammonium and magnesium sulphates have any effect on whole serum. P. W. CLUTTERBUCK.

**Tryptophan content of sera and of fractions salted out with ammonium sulphate.** E. OHLSOHN (Skand. Arch. Physiol., 1929, 58, 77—89; Chem. Zentr., 1930, i, 1167—1168).—In experiments with horse and rabbit sera the albumin:globulin ratio varied considerably between individuals of the same species; increasing dilution diminishes the globulin fraction. Horse serum-globulin contains 4.31—5.27% (average 4.77%) of tryptophan, the albumin containing 0.87—1.22 (1.03)%. Gravid rabbit globulin contains 3.5—4.2 (3.68)%, and the albumin 0.76—0.95 (0.82)% of tryptophan. The globulin:albumin ratio  $y = (x - 0.99)/(4.45 - x)$  for concentrated, or  $(x - 1.05)/(4.88 - x)$  for dilute, solutions, where  $x$  is the percentage of tryptophan in the total protein. Methods for the determination of tryptophan are discussed. May and Rose's method was preferred.

A. A. ELDRIDGE.

**Micro-apparatus for determination of alkali reserve.** H. W. MOOK (Biochem. Z., 1930, 223, 152—160).—The apparatus employs the same

principle as, and affords as great an accuracy as, that of the Van Slyke apparatus, but it requires only a very small amount of serum (about 50 mm.<sup>3</sup>).

P. W. CLUTTERBUCK.

**Modification of the Kramer-Tisdall method for the microchemical determination of ionisable calcium in blood-plasma.** W. R. TWEEDY and F. C. KOCH (J. Lab. Clin. Med., 1929, 14, 747—750).—The calcium oxalate is washed with a saturated solution of calcium oxalate in 0.5% ammonia solution.

CHEMICAL ABSTRACTS.

**Blood of cattle and sheep in Victoria (Australia).** J. H. NORRIS (Austral. J. Exp. Biol., 1930, 7, 3—4; cf. this vol., 360).—The inorganic phosphorus, total acid-soluble phosphorus, and iron content of the blood of cattle are given.

F. O. HOWITT.

**Blood-coagulation. XXIII. Cause of inability to coagulate in peptone shock.** B. STUBER and K. LANG (Biochem. Z., 1930, 222, 313—323).—The inability to coagulate of the blood of dogs suffering from peptone shock is caused by inhibition of glycolysis in the blood. Glycolysis can be re-established and capability to coagulate restored by inspiration of carbon dioxide. Injection of peptone causes increase in the globulin fraction of the proteins of the serum. Peptone shock is not counteracted by injection of "germanin." There is no relation between the inhibition of coagulating power in peptone shock and the accompanying reduction in blood-pressure.

W. MCCARTNEY.

**Effect of reduction in atmospheric pressure on blood-coagulation and on the blood-platelets.** E. KOLOZS (Biochem. Z., 1930, 222, 301—312).—There is an increase in the rate of coagulation of the blood and of the amount of thrombocytes it contains as well as an increase in the ratio of thrombocytes to erythrocytes in rabbits and guinea-pigs as a result of keeping them for a few days at pressures of 270—390 mm. The reduction in the time of coagulation persists long after restoration to ordinary atmospheric pressure, but the normal number of thrombocytes is more rapidly re-established. Irradiation of the animals causes the number of thrombocytes to increase, but does not affect the number of erythrocytes or the time of coagulation.

W. MCCARTNEY.

**Methods in blood-coagulation experiments. Isolation of antiprothrombin from blood and tissues.** H. J. FUCHS (Biochem. Z., 1930, 222, 470—481).—Experimental details and improvements are discussed and a method for the quantitative isolation of antiprothrombin is described.

W. MCCARTNEY.

**Determination of the activity of stabilisers and of coagulants in blood.** S. S. BRIUCHONENKO and V. D. JANKOVSKI (Biochem. Z., 1930, 223, 330—340).—A description of methods.

W. MCCARTNEY.

**Blood-groups.** R. D. DE LA RIVIERE and N. KOSOVITCH (Ann. Inst. Pasteur, 1930, 45, 107—153).—A discussion of the theoretical principles underlying the determination of the blood-groups by agglutination tests, and the application of such determinations to the study of heredity and ethnology. The legal, criminal, and pathological aspects of agglutination tests are indicated. The blood-groups of animals are

similar to those found in man. Haemoglobin plays no part in agglutination.

J. H. BIRKINSHAW.

**Composition of nerve tissue. Aromatic amino-acid content of the cerebral cortex of man and other animals.** D. ZVERKALOV (Biochem. Z., 1930, 223, 145—151).—The distribution of tyrosine and tryptophan in the grey matter of various regions of the brain of man, the dog, and the ram is investigated. With man and the dog, the frontal lobes contain most amino-acids and the central zone least tryptophan, whilst with the ram no difference is found.

P. W. CLUTTERBUCK.

**Glutathione content of human placenta and denervated gastrocnemius of the toad.** J. DI L. LIRA (Compt. rend. Soc. Biol., 1929, 102, 469—470; Chem. Zentr., 1930, i, 1486).—The former contains 0.029—0.038%, the latter 0.014—0.018% (normal), 0.012—0.017% (denervated) of glutathione.

A. A. ELDRIDGE.

**Action of carbon monoxide on the metallic compounds of glutathione.** H. HARTMANN (Biochem. Z., 1930, 223, 489—493).—In an alkaline medium glutathione forms with nickel and carbon monoxide a compound in which there are 4 mols. of monoxide to 1 g.-atom of nickel, but no such compound is formed with iron, cobalt, manganese, or copper. The nickel compound does not undergo photochemical dissociation. Since cysteine forms a compound with iron and carbon monoxide but not with nickel and the oxide, the decomposition of glutathione when boiled with water can be followed and cysteine can be determined in the presence of glutathione (cf. Cremer, A., 1928, 623; 1929, 686).

W. MCCARTNEY.

**Amylase in the extracts of the salivary glands of the silk-worm larva (*Bombyx*).** S. MATSUMURA (Bull. Sericulture and Silk Ind., Japan, 1930, 2, 4—5).—Aqueous glycerol extracts of the salivary glands of the silkworm hydrolyse soluble starch to dextrin and sugar and glycogen to dextrose with optimum activity at  $p_H$  6.6—7.1. In the absence of sodium chloride the enzyme is almost inactive. Extracts made from European varieties of silkworm are less active than similar preparations from the Chinese and Japanese varieties.

W. O. KERMACK.

**Cypridina luciferin.** S. KANDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 246—247).—*Cypridina luciferin*, isolated by precipitation with ammonium sulphate or with benzene, contains respectively 3.72% and 5.91% N, together with a large amount of phosphorus, and is considered to be a lecithin-like compound.

A. I. VOGEL.

**Oxidative catalysts of insects.** P. RONA, J. A. PARFENTJEV, and H. LIPPMANN (Biochem. Z., 1930, 223, 205—212).—The ash of a number of insects was analysed and its action on the oxidation of cystine investigated. The presence of copper and iron in the ash considerably accelerates the oxidation, but after removal of these metals, the residue can still accelerate oxidation due to the presence of traces of lead and other metals.

P. W. CLUTTERBUCK.

**Iridescent colours of birds and insects.** (LORD) RAYLEIGH (Proc. Roy. Soc., 1930, A, 128, 624—641).

—Reflexion and transmission spectra of various butterfly and beetle wings have been examined. Moist gaseous chlorine does not destroy the colours of *Morpho* or of *Urania*, although the black background is bleached, nor does it decolorise the metallic beetles. The colours of all kinds of feathers are, however, rapidly destroyed. Peacock feathers undergo a progressive colour change in ultra-violet light, the colours becoming more refrangible; other feathers (*e.g.*, parrot) even when blue are slowly decolorised without change of refrangibility. It is contended that although fading under light or chlorine in certain cases favours the idea of a pigment, this view cannot be maintained. The fading must rather be attributed to the destruction of an interference structure.

L. L. BIRCUMSHAW.

**Distribution of nitrogen, phosphorus, iron, and sulphur in the myosin and myostromin of heart-muscle.** M. J. GALVIALO and C. J. KREINES (Biochem. Z., 1930, 222, 123—134).—The proteins of heart-muscle may be separated into groups, the myosin group extractable with acid buffer ( $p_H$  4.95 or 4.3) or with dilute acetic acid (0.25%), and the myostromin group extractable with alkaline buffer ( $p_H$  9.1) or with dilute sodium hydroxide (0.25%). A table summarises the percentage of nitrogen, carbon, hydrogen, phosphorus, iron, and sulphur in the two fractions. The phosphorus, iron, and sulphur contents of the myosin are much less than of the myostromin.

P. W. CLUTTERBUCK.

**Colloidal properties of the myosin and myostromin of heart-muscle.** G. E. VLADIMIROV (Biochem. Z., 1930, 222, 135—149).—Myosin and myostromin are hydrophilic and hydrophobic colloids respectively, their isoelectric points being at  $p_H$  6.0—6.3 and 5.0—5.5. They have the same specific refraction.

P. W. CLUTTERBUCK.

**Isolation of muscle-adenylic acid from kidneys.** G. EMBDEN and H. J. DEUTICKE (Z. physiol. Chem., 1930, 190, 62—66).—An adenylic acid isolated from fresh calf's kidney was identical with the muscle-adenylic acid obtained from skeletal muscle as shown by m. p. and by the liberation of 0.2 of the total nitrogen as ammonia under the action of an enzyme from rabbit muscle.

J. H. BIRKINSHAW.

**Substances in the thyroid gland containing iodine.** G. LUNDE and K. WÜLFERT (Endokrinol., 1929, 4, 321—333; Chem. Zentr., 1930, i, 1487).—The gland, after trituration with sand, was repeatedly extracted with water and the extract treated with alcohol, acetone, uranyl phosphate, ammonium sulphate, or picric acid. Of the precipitates (containing 0.19—0.26 mg. of iodine per 100 g.) that obtained with ammonium sulphate was richest in iodine.

A. A. ELDRIDGE.

**Histochemical detection of iodine.** U. HINTZELMANN (Z. wiss. Mikros., 1930, 46, 486—487; Chem. Zentr., 1930, i, 1833).—When organs are fixed in formaldehyde and thallous acetate (1%) solution, yellow crystals of thallous iodide are formed in the tissue.

A. A. ELDRIDGE.

**Presence and distribution of titanium in animals.** G. BERTRAND and (MME.) VORONCA-

SPIRT (Bull. Soc. chim., 1930, [iv], 47, 643—646).—See A., 1929, 1098.

**Protein in dental enamel.** T. ROSEBURY (J. Dental Res., 1930, 10, 187—213).—Soluble protein was not found. The substance insoluble in acid consisted chiefly of a protein closely related to neurokeratin; the average content was 0.42% of the dry (105°) enamel.

CHEMICAL ABSTRACTS.

**Best's method of staining glycogen.** K. JEFFERS (Biochem. Z., 1930, 223, 184—189).—Solutions of soluble starch and of glycogen are mixed with solutions of carmine and the amount of dye combined is determined by removing the carmine-carbohydrate complex and either determining the residual carmine colorimetrically or analysis of the complex itself. Very variable results are obtained, but the small amount of pigment uniting favours the view that the process is one of adsorption. P. W. CLUTTERBUCK.

**Micro-determination of lipins in tissues.** S. OSATO and M. HEKI (J. Biol. Chem., 1930, 87, 541—557).—The tissue is frozen and finely-ground, with the addition of small amounts of water, in a chilled mortar; the resulting powder is transferred to a flask with the aid of a mixture of 3 parts of alcohol and 1 part of ether, repeated rinsings with a mixture of equal parts of alcohol and ether being employed, and the mixture is kept some hours at the ordinary temperature, or heated to the b. p. and filtered. The filtrate contains the whole of the lipins and may be utilised for their fractional determination by standard methods.

C. R. HARRINGTON.

**Corpora lutea of mouse with special reference to fat accumulation during oestrous cycle.** R. DEANSLEY (Proc. Roy. Soc., 1930, B, 106, 578—595).—The sequence of the fat changes in the corpora lutea of ovulation, pseudo-pregnancy, pregnancy, and lactation in the mouse as indicated by staining methods is described.

C. C. N. VASS.

**Fatty oil of bull frog.** S. TASAKI and J. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1930, 33, 233—234b).—The pale yellow oil has  $d$  0.9256, acid value 0.84, iodine value 134.24,  $n_D^{20}$  1.4774, saponif. value 194.78, unsaponifiable matter 1.25%. The fatty acids separated from the oil were fractionated into liquid and solid portions, for which constants are also given.

F. R. ENNOS.

**Unsaponifiable matter in egg-yolk oil.** I. S. FRÄNKEL and H. MATHIS (Helv. Chim. Acta, 1930, 13, 492—500).—The acetone-soluble portion of the yolks of bird's eggs (free from phosphatides and protein) contains 10—12% of unsaponifiable matter other than cholesterol. When distilled in a high vacuum, this gave an unsaturated oil, b. p. 192°/0.8 mm.,  $d_{19}^{19}$  0.9556, which showed slight optical activity and had an iodine value of 142, and a small amount of a hydrocarbon,  $C_{23}H_{46}$ , m. p. 75°,  $[\alpha]_D^{25}$  —6.33° in ether. The latter gives Rosenheim's vitamin-A reaction; it also shows Carr and Price's reaction, and the typical reactions of cholesterol with chloroform, concentrated sulphuric acid, and acetic anhydride. It is not identical with cholestene, hypcholestene, or cholesterylene, which it approaches most nearly in composition and properties, and the name "yolken" is

suggested for it. An analysis of its crystal form and a comparison with that of cholesterylene is given. The main fraction, in spite of its constant b. p., appears to be a mixture. It absorbs bromine without elimination of hydrogen bromide, and forms a *tribromide*,  $C_{14}H_{25}O_2Br_3$ , m. p.  $108^\circ$ , and an oily product that does not distil in a high vacuum. The latter, freed as far as possible from solid, gives on reduction with zinc in alcohol two white, crystalline substances, separated by taking advantage of their differing solubilities in alcohol; both contain zinc. H. A. PIGGOTT.

**Cholesterol of crustacea.** A. LEULIER and A. POLICARD (Compt. rend. Soc. biol., 1930, 103, 82—83; Chem. Zentr., 1930, i, 1814).—*Carcinus maenas*, *Portunus plicatus*, and *Eriphia spirifrons* contain a substance having the same crystalline form and colour reactions as mammalian cholesterol; it has m. p.  $145\text{--}146^\circ$ ,  $\alpha -42^\circ$  (1% chloroform solution).

A. A. ELDRIDGE.

**Cholesterol of protoplasm. IV. Investigation of ox liver.** G. PFEIFFER (Biochem. Z., 1930, 222, 214—219).—Of the total cholesterol of ox liver, 31.56% is present as cholesterol, 12.2% as oxy-cholesterol, 55.46% as the oxy-ester, and 0.73% as cholesteryl ester.

P. W. CLUTTERBUCK.

**Myers-Wardell method for the determination of cholesterol.** F. KRASNOW and A. S. ROSEN (J. Lab. Clin. Med., 1929, 14, 967—979).—Modifications are proposed.

CHEMICAL ABSTRACTS.

**Silk fibroin.** R. BRILL (Naturwiss., 1930, 18, 622).—X-Ray examination shows that natural silk fibroin consists of at least two substances, one of which is crystalline. The crystals are not preformed in the glands of the silk-worm, but separate during the drying of the fluid secretion.

W. O. KERMACK.

**Salivary mucin.** J. M. INOUE (J. Dental Res., 1930, 10, 7—21).—Unstimulated normal human saliva contains  $0.25 \pm 0.06\%$  of sodium mucinate; that stimulated by mastication of paraffin contains  $0.27 \pm 0.06\%$ . The effect of other methods of stimulation is recorded. Mucin is preferably determined nephelometrically after addition of alkali and dialysis.

CHEMICAL ABSTRACTS.

**Determination of the total acidity of gastric juice.** K. INOUE (Japan. J. Gastroenterol., 1930, 2, 1—18).—The mean isoelectric point is  $p_H 6.5$ ; bromothymol-blue is used as indicator. The use of phenolphthalein involves an error of 4—24%.

CHEMICAL ABSTRACTS.

**Production of lactic acid in the stomach.** F. DELHOUGNE (Arch. exp. Path. Pharm., 1930, 152, 160—167).—Oral administration of dextrose to dogs does not normally give rise to lactic acid in the stomach. After irrigation of the stomach thrice daily with 100 c.c. of 2% silver nitrate or 60% alcohol, administration of dextrose gives rise to lactic acid with an attendant decrease in hydrochloric acid and pepsin content.

P. G. MARSHALL.

**Acidity of intestinal contents.** J. L. BOLLMAN and F. C. MANN (Proc. Staff Mayo Clinic, 1930, 5, 68—69).—Experiments on dogs, fasting and after feeding, are recorded.

CHEMICAL ABSTRACTS.

**Amylase content of the milk of various animals.** R. SCHENK (Arch. wiss. prakt. Tierheilk., 1928, 58, 375—384; Chem. Zentr., 1930, i, 1713—1714).—Human milk contains a considerable quantity of amylase; colostrum-free milk of the cow, horse, dog, cat, and guinea-pig contains only traces, whilst neither milk nor colostrum of the goat contains amylase. The markedly higher amylase content of the colostrum of the other animals, falling with the progress of lactation, indicates that the enzyme originates in the colostrum. A. A. ELDRIDGE.

**Dispersoid-chemical study of milk. II. Determination of the degree of dispersion of fat in milk.** A. SCHNECK and G. KOHLHARDT (Milch-wirt. Forsch., 1929, 9, 186—235; Chem. Zentr., 1930, i, 1716—1717).—The methods of Gutzeit and of van Dam and Sirks have been compared and their accuracy has been determined, and the effect of stall feeding observed.

A. A. ELDRIDGE.

**Salt content of human milk in some cases in which its use was not beneficial.** A. M. COURTNEY and A. BROWN (Arch. Dis. Childhood, 1930, 5, 28—35).—Milk received by infants suffering from rickets and tetany was low in calcium and magnesium and high in sodium content. Low milk-calcium is usually associated with low blood-calcium and phosphorus.

CHEMICAL ABSTRACTS.

**Protein and non-protein fractions of human milk.** A. M. COURTNEY and A. BROWN (Arch. Dis. Childhood, 1930, 5, 36—41).—The nitrogen partition is the same in both normal and abnormal samples. A large proportion of the nitrogen is present as non-protein nitrogen.

CHEMICAL ABSTRACTS.

**Souring of milk. I.** W. GRIMMER and W. PAAPE. **II.** W. GRIMMER and C. ARLART (Milch-wirt. Forsch., 1929, 9, 88—99, 100—120; Chem. Zentr., 1930, i, 1714).—Rennin coagulum and the residue of milk on porous plates differ in that the nitrogen, calcium, and phosphorus contents of the latter are the smaller. Possibly in coagulation by rennin dissolved calcium and phosphate are co-precipitated, or combination of calcium phosphate with caseinogen or casein occurs. With progressive souring the calcium content of the coagulum diminishes fairly regularly. If  $\sqrt{kS}$  is the hydrogen-ion concentration of lactic acid of acidity  $x$ ,  $c$  is a factor, and  $y$  is the hydrogen-ion concentration of the milk,  $y = cx^2\sqrt{kS}$ . The value of  $c$  was  $3.03\text{--}5.42$  (average  $4.3$ )  $\times 10^{-6}$ .

A. A. ELDRIDGE.

**Proteolysis of milk.** H. HARTWICK (Milch-wirt. Forsch., 1930, 9, 339—354; Chem. Zentr., 1930, i, 1870).—The determination of caseolytic organisms in milk is described; the determination of ammonia by distillation in a vacuum and the detection of peptone are also of value. Tryptophan was not detected. The catalase value is not always parallel with the number of proteolytes.

A. A. ELDRIDGE.

**Salamander alkaloids from the cutaneous secretion of *Salamandra maculosa*.** O. GESSNER and K. CRAEMER (Arch. exp. Path. Pharm., 1930, 152, 229—237).—The crude poison is filtered through paper pulp and the residue digested at  $100^\circ$  with water

acidified with acetic acid and filtered. The operation is repeated twice and the combined filtrates are evaporated in a vacuum at 45°. *Samandarin acetate* (I) separates on cooling and crystallises from water in needles. The remaining liquid is extracted with chloroform and the extract evaporated, when a crystalline product separates. The mother-liquors yield, on complete evaporation, an oil which is crude samandarin. Treatment of this oil with hydrochloric acid yields the crystalline *hydrochloride*. After removal of substance I, a sulphate which crystallises from water can be obtained from the filtrate. The crude oil, when purified by way of the sulphate, yields *samandarin*,  $C_{19}H_{31}O_2N$ , m. p. 187°.

P. G. MARSHALL.

**Toad poisons. II. Ch'an Su, the dried venom of the Chinese toad.** H. JENSEN and K. K. CHEN (J. Biol. Chem., 1930, **87**, 741—753; cf. A., 1929, 840).—The dried venom was extracted with 96% alcohol, and the extract was concentrated and kept over-night at 0°; cholesterol which had separated was removed by filtration and the filtrate, after further concentration, was diluted with water. The filtrate from the gummy precipitate was concentrated and extracted with chloroform. It was then acidified and extracted with ether; the latter, after drying and evaporation, yielded a residue of suberic acid and other fatty acids. The aqueous solution, after concentration and treatment with flavianic acid, gave a *flavianate*, m. p. 205°, which was converted into the corresponding *picrate*, m. p. 165° (cf. Handovsky, A., 1920, i, 495). The above-mentioned gummy precipitate was dissolved in chloroform; fractional precipitation with ether yielded *cinobufotoxin*,  $C_{43}H_{64}O_{12}N_4$ , m. p. 200° (decomp.), which on hydrolysis afforded cinobufagin, suberic acid, and arginine. The residue obtained on evaporation of the chloroform-ether mother-liquor was dissolved in alcohol, and impurities were removed by precipitation with ether; fractional precipitation of the filtrate with light petroleum yielded *cinobufagin*,  $C_{29}H_{38}O_7$ , m. p. 222—223° (*acetyl* derivative, m. p. 195—196°), which, with alcoholic potassium hydroxide, gave *cinobufaginic acid*,  $C_{27}H_{38}O_7$ , decomp. from 120° upwards. Saturation with hydrogen chloride of the ethereal mother-liquor from the isolation of cinobufagin precipitated *bufotalin chloride* (?),  $C_{24}H_{33}O_4Cl$ , m. p. 220—221° (cf. Kotake, A., 1929, 215). Cinobufotoxin and cinobufagin exhibit pharmacological properties similar to those of the digitalis glucosides.

C. R. HARRINGTON.

**Toad poisons. III. Secretion of the tropical toad, *Bufo marinus*.** H. JENSEN and K. K. CHEN (J. Biol. Chem., 1930, **87**, 755—759; cf. preceding abstract).—The fresh secretion was dried and repeatedly extracted with 96% alcohol at 50°; the extracts were evaporated to dryness, and the residue was extracted with absolute alcohol. The alcoholic solution was precipitated with ether and the process was repeated several times; the precipitate was finally crystallised from 80% alcohol, giving *marinobufotoxin*,  $C_{42}H_{62}O_{11}N_4$ , m. p. 200°, which appears to be similar in constitution to bufotoxin and cinobufotoxin (cf. preceding abstract). The ethereal mother-liquors, when concentrated and precipitated with light petroleum, yielded bufagin (cf. Abel and

Macht, A., 1912, ii, 1193), which gave a *monoacetyl* derivative, m. p. 203—204°. C. R. HARRINGTON.

**Detection of acetone in urine.** P. HORKHEIMER (Süddeut. Apoth.-Ztg., 1929, **69**, 798—799; Chem. Zentr., 1930, i, 1664).—Sodium nitroprusside is a sensitive reagent for acetoacetic acid, but it detects acetone only in quantities which scarcely ever occur in urine.

A. A. ELDRIDGE.

**Trinitrophenol as a sugar reagent.** H. SZANCER (Pharm. Zentr., 1930, **71**, 401—402).—Attempts to remove creatinine from urine, in order to render possible the application of the picric acid test for sugars (A., 1929, 1426), were unsuccessful (cf. Benedict and Osterberg, A., 1921, ii, 660).

H. E. F. NOTTON.

**Concentration of chlorides in glomerular urine from frogs.** B. FREEMAN, A. E. LIVINGSTON, and A. N. RICHARDS. **Glomerular elimination of phenol-red and indigo-carmin in frogs.** A. N. RICHARDS and A. M. WALKER. **Total molecular concentration of glomerular urine and of blood-plasma from the frog and from *Necturus*.** A. M. WALKER. **Electrical conductivity of glomerular urine from the frog and from *Necturus*.** L. E. BAYLISS and A. M. WALKER (J. Biol. Chem., 1930, **87**, 467—477, 479—498, 499—522, 523—540).—When the surviving kidneys of frogs were perfused with an oxygenated saline solution the chloride contents of the glomerular and perfusion fluids were identical; in eight out of twenty living frogs the glomerular fluid had a higher chloride content than the blood-plasma. In view of the danger of concentration of the glomerular fluid during manipulation, these results fail to confirm the suggestion of Wearn and Richards (A., 1926, 195) that the glomeruli are able to secrete chlorides.

The technique of collection of glomerular fluid from the Bowman's capsule of the kidney of the living frog is discussed. The glomerular fluid from frogs which had received subcutaneous injections of phenol-red or of indigo-carmin contained the same concentration of dye (relative to that in the blood-plasma) as did the ultrafiltrate obtained by passing the same blood-plasma through a collodion membrane.

The total molecular concentrations, determined by the method of Barger (J.C.S., 1904, **85**, 286), and the electrical conductivities (determined in a special small cell) of the glomerular fluid and the blood-plasma are identical both in the frog and in *Necturus maculosus*. All experiments thus indicate that the glomerular fluid is a simple ultra-filtrate of the blood-plasma.

C. R. HARRINGTON.

**Determination of urobilin in urine.** L. TIXIER (Bull. Sci. pharmacol., 1929, **36**, 555—556; Chem. Zentr., 1930, i, 1190).—Other colouring matters are precipitated by the addition to urine (20 c.c.) of *N*-sodium hydroxide (5 c.c.) and 10% barium chloride solution (25 c.c.) and the colour of the filtrate is compared with that of potassium dichromate solution, normal urine, the colour of the filtrate from which is similar to that of 0.004% potassium dichromate solution, being assumed to contain 0.45 mg. of urobilin per litre.

A. A. ELDRIDGE.

**Origin of hippuric acid in the urine of herbivorous animals.** P. BRIGL and A. PFÄHLER (Tierernähr., 1929, 1, 30—36; Chem. Zentr., 1930, i, 1821).—With rabbits and sheep hay as fodder produced three times as much hippuric acid as cereal straw, the greater part originating from a substance (probably a prolinin) insoluble in acetone and water but soluble in alcoholic hydrogen chloride. Folin and Flanders' method for the determination of hippuric acid was modified in that other constituents were removed by boiling with 10% sodium hydroxide solution, then treating with nitric acid and titrating the chloroform extract. A. A. ELDRIDGE.

**Rapid preparation of faecal digests for use in nitrogen and mineral analyses.** G. STEARNS (J. Lab. Clin. Med., 1929, 14, 954—957).—The digest is prepared by boiling with 10% sulphuric acid. Methods for the determination of nitrogen, calcium, phosphorus, and total fixed base are described.

## CHEMICAL ABSTRACTS.

**Influence of feeding on certain acids in the faeces in infants. III.** J. R. GERSTLEY, C. C. WANG, and A. A. WOOD (Amer. J. Dis. Children, 1930, 39, 487—492).—The acid excretion of infants fed with whole cow's milk differs from that of those fed with human milk in that no formic acid is excreted in the faeces, acetic acid predominates, propionic acid is present, less lactic acid is excreted, and the total excretion of acids is higher. The output of acid appears to be independent of the amount of lactose in the diet.

## CHEMICAL ABSTRACTS.

**Carbohydrate metabolism in acromegaly.** M. WISHNOFSKY and C. S. BYRON (J. Lab. Clin. Med., 1929, 15, 216—220).—The fact that pituitrin neutralises the effect of insulin on the concentration of blood-sugar but does not affect its action on the oxidation mechanism of dextrose may be used to determine whether the disturbance of carbohydrate metabolism is incidental to acromegaly or due to concomitant diabetes.

## CHEMICAL ABSTRACTS.

**Metabolic study of an alkaptonuric infant.** F. BRAID and E. M. HICKMANS (Arch. Dis. Childhood, 1929, 4, 389—398).—Homogentisic acid appears to be an intermediate product in the normal metabolism of protein. The ratio homogentisic acid/total nitrogen in the urine of an alkaptonuric infant was 56—60/100, increasing when egg yolk was added to the diet, and decreasing when the nitrogen retention was lowered. The output of homogentisic acid was not diminished by administration of potassium iodide. The urine contained less urea and was slightly more acid than normally. The total nitrogen absorption and retention appeared to be normal. CHEMICAL ABSTRACTS.

**Diffusible calcium of the blood-serum in allergic diseases.** D. M. GREENBERG and L. GUNTHER (Arch. Int. Med., 1930, 46, 72—74).—The total and diffusible fractions of the blood-calcium vary together within the normal limits in eczema, hay-fever, asthma, etc. F. O. HOWITT.

**Factors affecting the deposition of dental calculus.** G. H. SMITH (Austral. J. Exp. Biol., 1930, 7, 45—77).—The loss of carbon dioxide from saliva is of little importance as a cause of deposition.

The daily  $p_H$  curves for saliva follow approximately the same course and are not subjected to any alkaline tide with respect to meals. No definite  $p_H$  change could be correlated with any particular stimulus. The presence of a phosphatase, with an optimum  $p_H$  of 5.5 and contained in the desquamated epithelial cells, in saliva is confirmed. A deposition of calcium phosphate in the epithelium of the gums is produced *in vitro* by incubation of the tissue in calcium glycerophosphate solution. F. O. HOWITT.

**Body-fluids in cancerous and non-cancerous individuals.** H. C. PITTS and H. R. JOHNSON (New England J. Med., 1930, 202, 415—423).—Little difference in blood-potassium, -calcium, -sodium, and  $p_H$  was observed, although the potassium and  $p_H$  may be slightly increased in cancer. In the blister fluid in cancer the sodium and potassium contents are high, whilst the calcium content and  $p_H$  are low.

## CHEMICAL ABSTRACTS.

**Diffusible calcium and proteins of the blood-serum in malignant diseases.** L. GUNTHER and D. M. GREENBERG (Arch. Int. Med., 1930, 46, 67—71).—The inorganic phosphorus and diffusible calcium show no significant deviation from the usually accepted normal values. A rough parallelism exists between the non-diffusible calcium fraction and the protein content of the serum. F. O. HOWITT.

**Blood-cholesterol in diabetic children.** P. WHITE and H. HUNT (New England J. Med., 1930, 202, 607—616).—The blood-cholesterol is usually normal in uncomplicated diabetes. It is uninfluenced by age during childhood, but increases between 15 and 19 yrs., subsequently decreasing. Increase may be associated with over-nutrition and extreme variations from normal body-weight. CHEMICAL ABSTRACTS.

**Permeability of erythrocytes to chlorine ions in diabetes mellitus.** K. LANG (Arch. exp. Path. Pharm., 1930, 152, 168—176).—Increase in the carbon dioxide tension of the blood normally causes migration of chlorine ions from the plasma to the corpuscles. In diabetics this migration, although still occurring, is much reduced, and can be restored to normal by administration of insulin. The permeability of the membrane of the corpuscle to chlorine ions is adversely affected in diabetes, but in neither normals nor diabetics is there any migration of sugar on increasing the carbon dioxide tension. P. G. MARSHALL.

**Metabolism of diabetics. I. "Intarvin" and other fats derived from acids having an odd number of carbon atoms.** P. E. VERKADE and J. COOPS, jun. (Biochem. Z., 1930, 223, 394—403).—"Intarvin" (cf. Kahn, Proc. Soc. Exp. Biol. Med., 1922, 19, 265) contains considerable amounts of fatty acids with an even number of carbon atoms and also 17% of unsaponifiable matter (chiefly mineral oil). The preparation is unsuitable for use in the investigation of the metabolism of acids having odd numbers of carbon atoms. A suitable fat which can be made in quantity is glyceryl triundecenoate. W. MCCARTNEY.

**Behaviour of ketonic substances in blood, urine, and cerebrospinal fluid. Diabetic coma.** V. BÜLOW-HANSEN (Acta Med. Scand., 1929, 72,



399—439; Chem. Zentr., 1930, i, 1817).—Renal insufficiency leads to the accumulation of ketonic substances in the blood. Acetone is hæmolytic, precipitating the protein and arresting the peroxidase activity; insulin abolishes the latter effect. The ketone content of the cerebrospinal fluid, compared with that of the blood, rises as diabetic coma is approached; the former value is less affected by insulin than the latter. A. A. ELDRIDGE.

**Adrenals and pancreatic diabetes.** E. S. TURCATTI (Rev. soc. Argentina biol., 1929, 5, 173—187).—A study of the effect of removal of the pancreas and one or both adrenals on the blood-sugar of dogs.

CHEMICAL ABSTRACTS.

**Sugar metabolism and water regulation. II. Treatment of cardiac diabetes with insulin and dextrose.** H. TATERKA (Klin. Woch., 1929, 8, 1763—1764; Chem. Zentr., 1930, i, 1488—1489).—The action of injected insulin is retarded but more marked; dextrose causes a less rapid and less marked rise in blood-sugar. Non-cardiac diabetics with insulin oedema behave similarly. A. A. ELDRIDGE.

**Detection of necrosis of pancreatic tissue by determination of urinary diastase.** J. WOHLGE-MUTH (Klin. Woch., 1929, 8, 1253—1254; Chem. Zentr., 1930, i, 1508).—The author's method for the determination of urinary diastase in presence of a phosphate mixture of  $p_H$  7.2 is described.

A. A. ELDRIDGE.

**Arsenic in eczema and allied conditions in infants and young children.** L. S. VAN DYCK, B. THRONE, and C. N. MYERS (Arch. Pediatr., 1930, 47, 218—229).—The urine in eczema and urticaria contained arsenic (0.4—2.3 mg. per 100 g. of solids) in 55 of 105 subjects, and in 40 of these the mother's milk also contained arsenic (0.012—3.5 mg. per 100 g. of solids). The arsenic originated from food.

CHEMICAL ABSTRACTS.

**Gall-stone formation. II. Alkali, alkaline-earth, and metal content in bile. III. Effect of abnormal functioning of the vegetative nerve system on alkali and alkaline-earth metals in bile.** R. OHTA. **IV. Influence of the functions of the autonomic nervous system on gall-stone formation. V. Formation of bilirubin-calcium stones.** K. KIRITA (Japan. J. Gastroenterol., 1930, 2, 19—31, 32—40, 41—54, 55—64).—Rabbit's bile normally contains potassium, sodium, calcium, and magnesium in the ratios 6:180:6:1; injection of chlorides of these metals causes a slight rise in the concentration of the cation injected. The oxidation of bilirubin in air is a unimolecular reaction; the velocity coefficient is inversely proportional to the hydrogen-ion concentration. The oxidation is retarded by egg-albumin. CHEMICAL ABSTRACTS.

**Behaviour of free cholesterol and its ester in the blood and organs of the rabbit after artificial obstruction of the bile.** E. VON ROSZTÓCZY (Z. ges. exp. Med., 1929, 68, 690—700; Chem. Zentr., 1930, i, 1323).—The cholesterol content of all organs, and of the blood especially, is markedly increased during the first five days by artificial obstruction of the bile. The ester content falls in all organs, but increases in the blood. L. S. THEOBALD.

**Deposition of sediments and the formation of concretions in urinary ducts.** J. MEYER (Z. klin. Med., 1929, 111, 613—685; Chem. Zentr., 1930, i, 1322).—The solubility products at 37° of the substances occurring in urine, and the  $p_H$  values at which these substances are precipitated, have been determined.

L. S. THEOBALD.

**Iodine content of thyroid gland in simple and exophthalmic goitres.** P. SAINTON and H. SIMONNET (Bull. Soc. Chim. biol., 1930, 12, 773—776).—The total iodine varies between the limits 10—215 mg. (with a mean value of 95 mg.) per 100 g. of dry gland for simple goitre and 10—267 mg. (mean of 90 mg.) for exophthalmic goitre. The goitres richest in iodine are the hardest in texture, colloidal goitres having low values. F. O. HOWITT.

**Metabolism of normal and leucæmic leucocytes.** E. C. GLOVER, G. A. DALAND, and H. L. SCHMITZ (Arch. Int. Med., 1930, 46, 46—66).—No fundamental difference exists between the sugar and oxygen consumption of leucæmic and of normal leucocytes, the latter, however, having a more active metabolism. In leucæmic leucocytes the more mature are the cells the greater is the oxygen consumption and the less the glycolysis. Slight cell injury exerts a marked effect on the oxygen consumption and, to a smaller extent, on the glycolysis. Under both aerobic and anaerobic conditions the sugar consumption of normal and mature myelogenous cells resembles that of cancer tissue, whilst that of immature myelogenous and all lymphatic cells is characteristic of embryonic tissue. F. O. HOWITT.

**Liver function. Effect of addition of dextrose on bound sugar in blood of liver patients.** M. TAKUWA (Japan. Med. World, 1929, 9, 316—326).—The free sugar is normal; the bound sugar increases with progress of the disease.

CHEMICAL ABSTRACTS.

**Variations in the phosphatase activity of the blood in disease.** W. M. ROBERTS (Brit. J. Exp. Path., 1930, 11, 90—95).—Phosphatase is present in greater concentration in the plasma than in the corpuscles. The blood-phosphatase, a comparatively rapid method for the determination of which is described, is increased in osteitis deformans, active rickets, and obstructive jaundice, and to some extent in other pathological conditions.

CHEMICAL ABSTRACTS.

**Distribution of calcium in jaundiced and alcoholic dogs.** W. C. EMERSON (J. Lab. Clin. Med., 1928, 14, 122—130).—In experimentally jaundiced dogs there was a decrease in blood-, serum-, diffusible, brain-, spleen-, and subcutaneous tissue-calcium, and an increase in muscle-, bone-, heart-, thyroid-, and adrenal-calcium. In alcoholic dogs there was an increase in blood-, serum-, diffusible, thyroid-, lung-, kidney-, and bone-calcium, and a decrease in faecal, subcutaneous tissue-, heart-, gall-bladder-, and adrenal-calcium. The significance of the results is discussed.

CHEMICAL ABSTRACTS.

**Iron content of tissues in icterus.** H. HORSTERS (Arch. exp. Path. Pharm., 1930, 152, 198—209).—The iron content of fat-free skin is normally about 10.5 mg. per kg. of fresh tissue, whilst in some types

of jaundice this value may be increased by more than 100%. In cases where a positive intracutaneous blue reaction is given with potassium ferricyanide, the intensity of the colour is not related to the iron content of the skin. The kidney has an average content of about 97 mg., the spleen 404 mg., and the liver 345 mg. of iron per kg. of fresh tissue, although these values vary widely in many other pathological conditions. The iron content of the spleen and skin is lowered in obstructive jaundice. The proportion of ferric iron in tissue varies from 14 to 100% of the total.

P. G. MARSHALL.

**Lipæmia.** W. MILBRADT (Biochem. Z., 1930, 223, 278—322).—The changes which occur during lipæmia in the blood and organs of rabbits and pigeons have been studied. The condition was produced in both species by administration of fat and by bleeding. In the case of the pigeons the conditions which exist during the lipæmia which accompanies avitaminosis were also investigated.

W. MCCARTNEY.

**Blood-phosphatides in lipæmia caused by bleeding.** E. SCHMITZ and F. KOCH (Biochem. Z., 1930, 223, 257—277).—A micro-method for the determination of cephalin in blood has been devised. The acceleration of coagulation in blood from animals suffering from lipæmia caused by bleeding is due to the accumulation of cephalin in the blood. There is also an accumulation of other phosphatides at the same time.

W. MCCARTNEY.

**Potassium content of pleural discharges.** DIMITRESCU-MANTE (Compt. rend. Soc. Biol., 1929, 102, 971—972; Chem. Zentr., 1930, i, 1637).—Average values are 25—35 mg. per 100 c.c.

A. A. ELDRIDGE.

**Chemistry of tissue deposits in a case of Schüller-Christian disease.** E. EPSTEIN and K. LORENZ (Z. physiol. Chem., 1930, 190, 44—50).—The tumour-like deposits of the *dura mater* in a case of Schüller-Christian disease showed a high percentage of cholesterol (3.23% of free cholesterol and 15.35% of cholesteryl ester on the dry material). The neutral fat amounted to 14.46%. The lecithin content was normal (1.64%). The liver showed no abnormality.

J. H. BIRKINSHAW.

**Colloidal theory of silicosis.** P. HEFFERMAN (Tubercle, 1929, 11, 61—62). A discussion.

CHEMICAL ABSTRACTS.

**Blood-calcium in pulmonary tuberculosis.** V. B. DOLGOROL (Amer. Rev. Tuberculosis, 1929, 20, 931—937).—In moderately advanced pulmonary tuberculosis the serum-calcium is increased; in the far-advanced stage, only group C exhibits subnormal values.

CHEMICAL ABSTRACTS.

**Metabolism of under-nourished children.** VII. C. C. WANG, J. E. HAWKS, and M. KAUCHER (Amer. J. Dis. Children, 1928, 36, 1161—1172).—The nitrogen of a low-protein diet is utilised more efficiently than normally. The ratio of calories to urinary nitrogen varies directly with the protein intake, the nitrogen retention being directly proportional to nitrogen intake.

CHEMICAL ABSTRACTS.

**Embryonic metabolism.** V. Tyrosine, tryptophan, cystine, cysteine, and uric acid content of developing hen's eggs. H. O. CALVERY

(J. Biol. Chem., 1930, 87, 691—700).—The alcohol-insoluble residue of hen's eggs at various stages of development was hydrolysed with hydrochloric acid and analysed for the above constituents. The tyrosine decreases during development, whilst the tryptophan remains unchanged and the uric acid increases. The behaviour of the cystine is doubtful, determinations by the method of Okuda (A., 1926, 190) indicating a decrease and by that of Folin and Marenzi (A., 1929, 1093) an increase during development. The cysteine increases to the eighth day, decreases to the fifteenth day, and then increases again to the time of hatching; these fluctuations can be associated with definite periods of development and with variations in the biological activity of the tissue.

C. R. HARRINGTON.

**Rôle of calcium and potassium in the initiation of maturation in the egg [of *Barnea candida*].** A. DALCQ (Protoplasma, 1928, 4, 19—44).

CHEMICAL ABSTRACTS.

**Potassium iodide as a mineral supplement in paired feeding experiments with growing swine.** W. E. CARROLL, H. H. MITCHELL, and G. E. HUNT (J. Agric. Res., 1930, 41, 65—77).—A critical analysis of published experiments on the effect of supplemental iodides on the growth of animals not obviously suffering from hypothyroidism shows that the majority indicate no beneficial effect and that those experiments which have been interpreted in a positive way are either statistically inadequate or have been demonstrably misinterpreted. In a paired-feeding experiment involving 13 pairs of Poland-China pigs, weighing initially from 57 to 76 lb. and finally 175 lb., no evidence was obtained that the administered potassium iodide, equivalent to 1 grain of iodine daily, in any way affected the rate of growth. In 7 of the 13 pairs the control pig made the more rapid gain. The basal ration contained ground yellow maize, tankage, linseed meal, lucerne meal, and sodium chloride.

E. HOLMES.

**Influence of small quantities of potassium iodide on the assimilation of nitrogen, phosphorus, and calcium in the growing pig.** F. J. MCCLURE and H. H. MITCHELL (J. Agric. Res., 1930, 41, 79—87).—In metabolism experiments on 5 pigs, in which potassium iodide was administered for 14 days in doses of 0.248 g., and in which 14-day control periods preceded and followed this régime, there was no evidence that the utilisation of either nitrogen, calcium, or phosphorus was favourably affected. There was some indication that the retention of calcium was adversely affected. No effect of the iodine on the rate of growth of pigs was evident.

E. HOLMES.

**Geographical factors in calcium metabolism.** H. WHEELON (Endocrinol., 1929, 13, 363—366).—Results of blood-calcium determinations on inhabitants of the Puget Sound Basin, Wash., U.S.A., are recorded.

CHEMICAL ABSTRACTS.

**Magnesium as regulator of calcium metabolism.** J. BEČKA (Z. ges. exp. Med., 1929, 67, 253—259; Chem. Zentr., 1930, i, 1323—1324).—Magnesium markedly disturbs calcium metabolism. Magnesium sulphate hinders the resorption of calcium

from the intestine and even withdraws it from the body; the chloride leads to the increased secretion of calcium by the kidneys, whilst the hydroxide effects strong absorption of calcium from food, fixes calcium in the tissues, and increases its availability.

L. S. THEOBALD.

**Secretion of dextrose under the influence of phosphates and sulphates.** J. VAN DE VELDE (Compt. rend. Soc. Biol., 1929, 102, 596—599; Chem. Zentr., 1930, i, 1324).—Injection of a solution of sodium dihydrogen phosphate into a dog after that of dextrose accelerates the secretion of sugar in the urine, the blood-corpuscles giving up more sugar than the plasma. Disodium hydrogen phosphate has practically no effect on the  $p_H$  of the blood, but, as in the former case, the sugar is quickly secreted. Sodium phosphate produces such rapid secretion that the sugar content of the corpuscles falls temporarily below the normal. Sodium sulphate causes marked alkalinity, but leaves the secretion of sugar practically unchanged.

L. S. THEOBALD.

**Effect of mineral salts on endogenous nitrogen metabolism.** E. F. TERROINE and T. REICHERT (Compt. rend. Soc. Biol., 1929, 189, 1019—1020; Chem. Zentr., 1930, i, 1325).—Fully-grown rats were fed for 8 days on a diet free from protein and almost free from mineral salts, and then on the same diet to which different salts were added. Sodium chloride, dipotassium hydrogen phosphate, and calcium bring about a considerable saving in the nitrogen economy, potassium chloride and magnesium are without effect, whilst iron increases the nitrogen excretion.

L. S. THEOBALD.

**Absorption and excretion of water and salts by marine teleosts.** H. W. SMITH (Amer. J. Physiol., 1930, 93, 480—505).—Water and some salts such as sodium and potassium chlorides are absorbed in the intestines of fish, and a residue containing excess of magnesium sulphate is left. Magnesium sulphate is also excreted in the urine of fish. It is probable that fish excrete a solution hypertonic in potassium and sodium chlorides apart from kidney excretion; this possibly occurs in the gills.

E. BOYLAND.

**Absorption of water, 0.2% hydrochloric acid, gastric juice, ethyl alcohol, and various chlorides by the dog's isolated stomach.** R. O. FAITELBERG (Russ. J. Physiol., 1930, 13, 224—236).—From 22 to 31% of water introduced into the isolated small stomach of dogs is absorbed within 60 min. Addition of hydrochloric acid to 0.2% or of sodium chloride to 0.9% reduces the percentage absorption to about 17%. Natural gastric juice in some cases undergoes resorption, associated with diminution in acidity. The absolute but not the relative amount of chlorides resorbed from hypertonic solutions increases with concentration. Absorption of alcohol from 10 and 20% solutions is complete within 60 min., and amounts to 90% in the case of 40% alcoholic solutions. The velocity of absorption of chlorides and of alcohol is greatest during the 30 min. following introduction.

R. TRUSZKOWSKI.

**Variations with age in zinc content of animals: effect of a milk diet.** G. BERTRAND and Y.

BEAUZEMONT (Bull. Soc. Chim. biol., 1930, 12, 741—744).—See this vol., 953.

**Glandular metabolism. II. Carbohydrates of resting and secreting submaxillary glands.** H. E. HIMWICH and M. A. ADAMS (Amer. J. Physiol., 1930, 93, 568—573).—No carbohydrate change could be detected during secretion.

E. BOYLAND.

**Degradation of carbohydrates [in the organism].** G. ROSENFELD (Biochem. Z., 1930, 222, 457—469).—Dextrose orally administered to dogs induces deposition of glycogen and prevents formation of fat in the liver, but when given intravenously it does neither, and diabetic dogs tolerate dextrose in larger amounts when it is given intravenously than when given orally. There is also a reduction in the amount of nitrogen and of acetone substances excreted in the urine when the dextrose is administered to the dogs intravenously. These and other facts indicate that in addition to the normal process of degradation of carbohydrates in the organism there is another in which the liver is not involved. Dextrose, even when orally administered to diabetic dogs, is degraded in this other way if diastase is given at the same time.

W. MCCARTNEY.

**Gaseous exchange of the human subject. I. Ingestion of water at 37°. II. Dextrose. III. Lævulose.** T. M. CARPENTER and E. L. FOX (J. Nutrition, 1930, 2, 359—374, 375—388, 389—408).—Ingestion of less than 200 c.c. of water has little effect on carbohydrate metabolism and heat production; with larger amounts slight increases are produced. Dextrose (10 g. or more) or small quantities of lævulose cause changes in the R.Q., and increases in the carbohydrate metabolism and heat production are recorded.

CHEMICAL ABSTRACTS.

**Hydræmia in alimentary hyperglycæmia.** M. N. KALLNIKOVA (Russ. J. Physiol., 1930, 13, 193—197).—Determination of hæmoglobin and water in the blood of children, taken at various points of the hyperglycæmia-time curve at various times after ingestion of sugar, show that hydræmia is not associated with hyperglycæmia.

R. TRUSZKOWSKI.

**Cholesterolaemia in alimentary hyperglycæmia.** M. N. KALLNIKOVA and G. D. OBRAZTZOVA (Russ. J. Physiol., 1930, 13, 198—203).—In children alimentary hyperglycæmia is associated with cholesterolaemia, which attains its maximum value 15—30 min. after ingestion of sugar. No general parallelism is found between the blood-cholesterol-time curves and the dextrose-time curves.

R. TRUSZKOWSKI.

**Blood-lipase in alimentary hyperglycæmia.** E. T. MINKER-BOGDANOVA and G. D. OBRAZTZOVA (Russ. J. Physiol., 1930, 13, 204—209).—Maximum variations of the lipase-time curves of blood following the ingestion by children of large quantities of sugar coincide with the maxima of the dextrose and fat content-time curves. The types of lipase-time curves found for different individuals correspond either with the dextrose-time curves or with their mirror images.

R. TRUSZKOWSKI.

**Mobilisation of muscle-glycogen by adrenaline and its resynthesis from muscle-lactic acid in the liver.** E. GEIGER (Biochem. Z., 1930, 223, 190—

204).—Adrenaline causes a mobilisation of muscle-glycogen in frogs even after removal of the liver. Frog muscles 3–4 days after extirpation of the liver contain as much glycogen as do those of normal animals. In the isolated perfused dog's and frog's leg, the formation of sugar cannot, but of lactic acid can, be increased by adrenaline. Since adrenaline mobilises muscle-glycogen and increases lactic acid formation in the isolated muscle, whilst after removal of the muscle-glycogen depots the blood-lactic acid is not increased, it is concluded that muscle-glycogen is degraded to lactic acid under the action of adrenaline. Injection of adrenaline into frogs after removal of the liver does not cause glycosuria, but an increased urinary lactic acid. Normal wintered frogs show lactic acid in the urine, the synthesis to glycogen being incomplete when the liver is poor in glycogen. Wintered frogs after injection of adrenaline show increased urinary lactic acid.

P. W. CLUTTERBUCK.

**Action of sodium fluoride on the transformation of pyruvic acid into lactic acid [by liver].** Y. KHOUVINE, E. AUBEL, and L. CHEVILLARD (*Compt. rend.*, 1930, **191**, 162–163).—Whilst sodium fluoride diminishes the conversion of dextrose into lactic acid it exerts no action on the conversion of pyruvic acid into lactic acid, but the quantity of oxygen used is diminished and the production of carbon dioxide is somewhat increased.

C. C. N. VASS.

**Formation and degradation of phosphoric esters in muscle in the presence of fluoride, oxalate, citrate, and arsenate.** I. K. LOHMANN (*Biochem. Z.*, 1930, **222**, 324–388).—The preformed carbohydrate of muscle as well as added glycogen or starch can be converted by the action of fluoride, oxalate, or citrate into a carbohydrate diphosphoric ester which is more resistant to acid hydrolysis than is the ester of Harden and Young. If the amounts of glycogen or starch added along with inorganic phosphate are large or if the fluoride is injected into the frog, the quantity of Harden and Young's ester formed is considerable, but in aqueous muscle extracts when fluoride is present this ester is converted into the one which resists acid hydrolysis. The monophosphoric esters of Robison, Neuberg, and Embden can be converted into this resistant ester by taking up about one equivalent of phosphate from muscle extracts containing fluoride. In yeast extracts starch as well as added Harden and Young's ester can be converted into the resistant ester if fluoride is present. The hydrolysis of the hexosemonophosphoric esters of muscle is accelerated by arsenate only after they have first been converted into diphosphoric esters (chiefly Harden and Young's ester). Frog muscle is the most suitable source of the resistant ester, which has not yet been obtained pure. The alkaline-earth salts of the ester are soluble in water, and a brucine salt can be precipitated from water by acetone. The ester has little or no reducing power. It has  $[\alpha]_D$  0 to +4°. When the ester is distilled with sulphuric acid no methylglyoxal can be detected in the distillate. Determinations of mol. wt. together with other evidence indicate that the sugar component of the ester is a hexose. The rate of enzymic elimin-

ation of phosphoric acid from the ester is lower than that observed in the case of Harden and Young's ester, equimolecular amounts of lactic and phosphoric acids being formed.

W. McCARTNEY.

**Conversion of Harden and Young's hexosediphosphoric ester [into another ester of the same type]. Production of carbohydrate phosphoric esters in extract of frog muscle.** F. LIPMANN and K. LOHMANN (*Biochem. Z.*, 1930, **222**, 389–403; cf. preceding abstract).—Harden and Young's ester when added to extracts of frog muscle is partly converted into a resistant ester very similar to, or identical with, that produced by the action of fluoride. This resistant ester, which has not yet been obtained pure, has  $[\alpha]_D$  0 to –4°. During the conversion of starch and of laevulose into lactic acid in frog-muscle extract varying amounts of Embden's hexosemonophosphoric ester are formed together with Harden and Young's ester. Further confirmation of the view that the esters of Robison, Embden, and of Harden and Young are stabilised forms of an ester which is formed in intact cells during degradation of carbohydrate is thus afforded.

W. McCARTNEY.

**Formation of hexosediphosphoric acid during the preparation of expressed juice of muscles.** G. EMBDEN, H. JOST, and M. LEHNARTZ (*Z. physiol. Chem.*, 1930, **189**, 261–272).—The equimolecular amounts of lactic and phosphoric acids found by Embden, Griesbach, and Schmitz (*A.*, 1915, **i**, 344) were derived from hexosediphosphoric acid formed during the preparation of the juice by the action of the kieselguhr which is added. The hexosediphosphoric acid, which is identical with that produced during fermentation of yeast and with that obtained by Embden and Zimmermann from expressed juice of rabbit muscle (*A.*, 1925, **i**, 729), can be isolated in amounts up to 6.5 g. of brucine salt per 600 c.c. of juice provided that the muscle (from the dog) contains sufficient glycogen.

W. McCARTNEY.

**Synthesis of creatinephosphoric acid in living muscle.** O. MEYERHOF and D. NACHMANSOHN (*Biochem. Z.*, 1930, **222**, 1–20).—Anaerobic resynthesis of creatinephosphoric acid in living muscle after decomposition during tetanus is as great, expressed absolutely, in muscle poisoned with curare-like substances (trimethyloctylammonium iodide) as in the unpoisoned muscle, but is much greater expressed as a percentage of the total decomposition. Resynthesis also occurs aerobically both after previous decomposition on admission of oxygen and without previous decomposition when the muscle is placed in Ringer's solution saturated with oxygen, especially after addition of phosphate. The aerobic synthesis after previous decomposition proceeds more quickly and completely at lower temperatures and most quickly at –0.5° to –1°. The velocity of resynthesis at –0.5° varies directly with the time and is independent of the extent of previous decomposition, 0.5–0.6 mg.  $P_2O_5$  being resynthesised per g. of muscle in 40 min., the oxygen utilisation amounting to about 40 cm. per g. per hr., after deduction of the resting respiration. The molecular ratios phosphate synthesised/oxygen used and phosphate synthesised/lactic acid disappearing give values approximately

of 5. The phosphagen content of the gastrocnemius in oxygen-saturated Ringer's solution on addition of phosphate may amount to 75—85% of the initial phosphorus instead of the 65—70% of freshly-removed muscle.

P. W. CLUTTERBUCK.

**Changes of  $p_H$  during activity of muscle.** O. MEYERHOF and F. LIPMANN (J. Physiol., 1930, B, 69, Proc. xxi).—In an atmosphere of nitrogen and carbon dioxide, carbon dioxide is absorbed during the first twitches, the muscle becoming more alkaline owing to the liberation of creatine from creatinephosphoric acid.

E. BOYLAND.

**Vapour pressure of muscle.** A. V. HILL and P. S. KUPALOV (Proc. Roy. Soc., 1930, B, 106, 445—477).—The apparent increase of heat production previously reported (*ibid.*, 1928, B, 103, 138) in a muscle after stimulation in an atmosphere of nitrogen is due to the increase in osmotic pressure resulting from the production of electrolytes as the result of anaërobic stimulation. The increased osmotic pressure reduces the vapour pressure of the water and hence brings about condensation of water on the surface of the muscle, the liberated latent heat accounting for the apparent heat production by the muscle. The phenomenon disappears completely when the nitrogen is replaced by paraffin oil and may be imitated without stimulation by washing out the chamber with a more dilute solution. The change of vapour pressure resulting from anaërobic stimulation is nearly proportional to the amount of energy set free. The osmotic pressure of frog's blood is equal to that of 0.725% sodium chloride solution. The osmotic pressure of frog's resting muscles, assumed to be isotonic with blood, can be almost exactly accounted for by assuming the known soluble constituents of muscle to be dissolved in its "free" water, but the osmotic pressure of fatigued muscle cannot be accounted for by the presence of all the substances at present known. In the frog's sartorius completely fatigued (lactic acid production 0.3%) the increase of osmotic pressure is the same as would be caused by the addition of 0.35% of sodium chloride to Ringer's solution. When an acid (carbonic acid) is added artificially to muscle, the increase of osmotic pressure corresponds approximately with the anions formed. The corresponding cations are therefore apparently free before combination with the acid, so that the excessive increase of osmotic pressure during stimulation cannot be accounted for by assuming that the acids produced liberate cations. The osmotic changes occurring in muscle during activity are the cause of the swelling and may be related to the stiffness of the muscles after severe exercise.

W. O. KERMACK.

**State of water in muscle and blood and the osmotic behaviour of muscle.** A. V. HILL (Proc. Roy. Soc., 1930, B, 106, 477—505).—The thermopile method previously described (this vol., 689) for the determination of vapour pressure has been applied to the determination of the "free" and "bound" water in protein solutions, blood, and muscle, the "free" water fraction being defined as the weight of water in 1 g. of fluid or tissue which can dissolve substances added to it with a normal depression of

vapour pressure. The method in the case of a fluid is to dissolve a known amount of a suitable substance in a weighed quantity of the fluid, to measure the depression of vapour pressure, and to compare this with that caused by the addition of the same substance to an approximately isotonic salt solution. In the case of a tissue, a weighed quantity of the latter is stirred for a sufficient time with a weighed amount of a hypertonic salt solution and the change of vapour pressure measured. The "free" water of blood or centrifuged corpuscles is 98—100% of the total water and the osmotic pressure of blood is exactly accounted for by assuming all the known soluble constituents of blood to be dissolved in the "free" water. The "free" water of a concentrated solution of caseinogen in 0.1N-sodium hydroxide solution or of egg-white concentrated by evaporation is almost exactly equal to the total water. The "free" water fraction of frog's muscle, whether resting or in rigor, is not less than 0.77, the total water fraction being 0.80—0.81, so that very little of the water in muscle is bound. The contrary conclusions of Overton (Pflüger's Arch., 1902, 92, 115) based on observations of the swelling of muscle in hypotonic saline are explained on other grounds.

W. O. KERMACK.

**Does the "all or none law" hold for the metabolic activity of the single muscle twitch?** P. ROTHSCILD (Biochem. Z., 1930, 222, 21—30).—Experiments were carried out with different frog's muscles to discover whether the "all or none law" holds in respect to the anaërobic formation of lactic acid in a series of muscle twitches. Lactic acid formation with the sartorius is the same for isotonic and isometric contraction, but with the semi-membranosus and the gastrocnemius with isotonic contraction it is 20—40% less than with isometric. The difference is obtained with the same initial tension and also with both direct and indirect stimulation as in the curarised muscle. The law is valid only in special cases, the metabolism in general increasing with increasing load during contraction.

P. W. CLUTTERBUCK.

**Lipin metabolism. Rôle of the pancreatic hormone in pulmonary lipin-utilisation.** I. Lipin-utilisation *in vivo* and internal secretion of the pancreas. II. Lipin-utilisation *in vitro* and internal secretion of the pancreas. I. I. NITZESCU and G. BENETATO (Bull. Soc. Chim. biol., 1930, 12, 827—848, 849—872).—I. Lung-tissue of dogs *in vivo* diminishes the fat and cholesterol content of the blood traversing the lungs to the extent of about 10%. Pancreatotomy is followed by a disappearance of this action and sometimes by even an increase of lipins in the oxygenated blood. Depancreatized animals regain the normal condition on injection of insulin, but only for the period over which the insulin is active.

II. Lung-tissue of dogs, kept aseptically *in vitro* at 38°, diminishes in fat and cholesterol content. This is not the case for depancreatized animals, and insulin added to the tissue *in vitro*, does not in this case provoke lipin-utilisation. Lung-tissue of depancreatized and insulinised dogs, however, exhibits a greater rate of lipin-utilisation than that of normal animals. Arterial

blood *in vitro* utilises fats, whilst venous blood does so only to a slight degree. This type of fat-utilisation is due to the action of a pulmonary enzyme which is activated by a co-enzyme, insulin. F. O. HOWITT.

**Rôle of esterification in lipin metabolism.** H. SOBOTKA (Naturwiss., 1930, 18, 619—620).—A scheme is given according to which cholesterol reacts with neutral fat to form cholesteryl ester, whilst the diacylglycerol by reacting with phosphoric acid and choline forms lecithin. It is suggested that in this way the neutral fats are mobilised for transport in the form of lecithin and cholesteryl ester (cf. Channon and Collinson, A., 1929, 1189; this vol., 236), the neutral fat being again re-formed if necessary by reversal of the reaction. W. O. KERMACK.

**Transport of fats and of lipins by blood after administration of olein.** I. H. PAGE, L. PASTER-NACK, and M. L. BURT (Biochem. Z., 1930, 223, 445—456).—In the blood of men each of whom had consumed 100 g. of olive oil the total lipin content of the blood had increased, the phosphatide and fatty acid content had changed irregularly, and the cholesterol content had increased almost always within the first 3 hrs. after consumption of the oil. The degree of unsaturation of the total lipins remained unchanged, whilst that of the fatty acids and phosphatides seemed to vary inversely with the change in the contents of these. It is supposed that the fatty acids are dehydrogenated in all the tissues and not in the liver only. W. MCCARTNEY.

**Source of ergosterol in the organism.** H. BEUMER and F. HEPNER (Biochem. Z., 1930, 222, 204—210).—Administration to mice of ergosterol, ergosterol+cholesterol, and ergosterol+cholic acid did not lead to an absorption of ergosterol detectable biologically. The possibility of a slight absorption is not, however, ruled out, and small amounts of adhering ergosterol are absorbed during the absorption of cholesterol. P. W. CLUTTERBUCK.

**Influence of salts of bile acids on the processes of diffusion and absorption.** O. FÜRTH and R. SCHOLL (Biochem. Z., 1930, 222, 430—456).—The physical laws of diffusion can be applied to diffusion in gels provided that the process is not accompanied by chemical or colloidal changes. Salts of bile acids seem to make lipid-soluble substances soluble in water and greatly facilitate their diffusion in gelatin, agar-agar, filter-paper, and porous earthenware, but the diffusion of substances insoluble in lipins is not affected. One mol. of sodium cholate, deoxycholate, glycocholate, or taurocholate is able to bring about the dissolution of 1 mol. of lecithin, but for dissolution of olive oil much glycocholate is required unless lecithin, which greatly facilitates the dissolving power of bile, is present. The mucins of the bile have little or no influence on its solvent power, although an artificial mixture of bile salts, lecithin, and mucin which has a solvent power equal to that of natural bile can be prepared. The absorption of emulsion of iodolecithin in rabbits and of camphor oil in mice is increased by the action of simultaneously administered bile salts. The absorption of fats in the intestine is

considered in the light of the experimental results (cf. Moore and Rockwood, A., 1897, ii, 150).

W. MCCARTNEY.

**Clinical calorimetry. XLV. Kidney function and ketosis during prolonged meat diets.** W. S. McCLELLAN and E. F. DU BOIS. **XLVI. Metabolism of nitrogen, calcium, and phosphorus during prolonged meat diets.** W. S. McCLELLAN, V. R. RUPP, and V. TOSCANI (J. Biol. Chem., 1930, 87, 651—668, 669—680).—XLV. Two normal men lived on an exclusive meat diet for 1 year, the daily intake amounting to 100—140 g. of protein, 200—300 g. of fat, and 7—12 g. of carbohydrate. Ketonuria was present throughout, the urinary excretion of acid being 2—3 times as great as under normal conditions; no ill effects were, however, observed.

XLVI. Both the above subjects showed negative calcium balances throughout the experiment, whilst one showed a slight positive and the other a slight negative balance for phosphorus; the latter was due to the heavy excretion of phosphorus in the urine. Nitrogen equilibrium was maintained by one subject with an average daily intake of 19.9 g. of nitrogen, whilst the other showed a small negative balance with a daily intake of 18.7 g. C. R. HARRINGTON.

**Nutritive value of corned beef for rats.** H. BISCHOFF (Biochem. Z., 1930, 222, 191—197).—Feeding experiments extending over 190 days are described with young albino rats on a diet of American corned beef and salts. Growth was poor on this diet and when it was supplemented with calcium carbonate, but was good when supplemented with vitamins (cod-liver oil and yeast) or by vitamins and calcium carbonate. P. W. CLUTTERBUCK.

**Biological investigations with milk changed by the removal of fats and the addition of carbohydrates.** L. RANDOIN and R. LECOQ (Compt. rend. Soc. Biol., 1929, 102, 528—531; Chem. Zentr., 1930, i, 1322).—Pigeons were fed daily with a mixture prepared from 8 g. of agar-agar, 2 g. of filter-paper, and 90 g. of dried milk or dried milk from which fats had been removed. The animals fed on the fat-free diet died in 30—50 days. In another series, the diet consisted of 50 g. of dried milk (fat-free or normal), 40 g. of carbohydrate, and 10 g. of roughage. With the fat-free diet, the animals fed with lactose, sucrose, maltose, dextrose, and dextrin died in 15—25, 50—70, 70—100 days, 3—4 months, and not less than 5 months, respectively. With the normal milk diet, only the animals fed with lactose died (50—80 days). L. S. THEOBALD.

**Choice of a test animal for the study of the nutritive equilibrium of milks.** L. RANDOIN and R. LECOQ (Ann. Falsif., 1930, 23, 132—141).—In order to evaluate the nutritive and biological value of milks it is necessary to use more than one species as the test animal. For instance, using young rats sweetened condensed milk was shown to be of superior nutritive value to dried milk, whereas using adult pigeons the latter was shown to be the better. Pigeons fed on dried skimmed milk die in 30—100 days, according to the amount of fat removed, but will live indefinitely when fed on dried whole milk; if sucrose is added to the diet the pigeons receiving



the dried whole milk die sooner than those receiving the dried skimmed milk. This is the reverse of the results obtained using young rats as the test animal. It seems that the ratio which must exist between protein, fat, and carbohydrate for the animal to be in nutritive equilibrium differs from species to species.

A. SHORE.

**Effect of hydrogen sulphide on the respiration of insects.** J. A. PARFENTJEV and H. LIPPMANN (Biochem. Z., 1930, **223**, 431—435).—An atmosphere containing about 0.4% of hydrogen sulphide kills the cockroach *Periplaneta americana* in 15 min. In atmospheres containing hydrogen sulphide the oxygen consumption of the live insect is reduced by 38—56%, but the oxygen consumption of insects for a short period after having been killed by such atmospheres is about 77% above normal.

W. MCCARTNEY.

**Toxicity of bismuth sulphide. Behaviour of bismuth compounds in the organism.** C. G. SANTESSON (Skand. Arch. Physiol., 1929, **58**, 101—136; Chem. Zentr., 1930, i, 1173).—The slight solubility of bismuth sulphide in body fluids may give rise to toxic symptoms. Basic bismuth salicylate is more toxic.

A. A. ELDRIDGE.

**Pharmacology of ointments. V. The sulphate content and transmineralisation process in human blood after use of sulphur ointment.** C. MONCORPS and R. BOHNSTEDT (Arch. exp. Path. Pharm., 1930, **152**, 57—67).—The crystalloid sulphur content of the serum of fasting man varies between 0.4 and 1.2 mg. per 100 c.c. and the mean is 0.696 mg. In an individual, the variation on different days and for different diets does not exceed 13%, and with the same diet is within the limits of error of the determination. After 12-hourly applications of 10 g. of sulphur ointment an increase is obtained in crystalloid sulphur of 87% of the mean value of the control experiment. Under the influence of percutaneous sulphur treatment, a considerable but irregular displacement (transmineralisation) of the potassium, sodium, calcium, magnesium, and iron contents of the serum and whole blood occurs.

P. W. CLUTTERBUCK.

**Biochemistry of silicic acid. I. Influence of silicic acid on the body-weight of growing rats. II. Retention of silicic acid by rats. III. Influence of silicic acid on the elasticity of connective tissue.** M. KOCHMANN and L. MAIER (Biochem. Z., 1930, **223**, 228—230, 231—242, 243—248).—Administration of silicic acid as mineral water (silvanasprudel) and as colloidal silicic acid (siliquid) had no effect on the body-weight of growing rats, whilst administration as silistren (orthosilicic acid tetraglycol ester) retarded increase of body-weight. The silicic acid content of the older animals was less than that of the younger. Animals receiving mineral water had the same silicic acid content as the controls, whilst those receiving silistren contained more. The elasticity of the skin of white mice is increased by placing in a solution of silicic acid.

P. W. CLUTTERBUCK.

**Toxicity of arsenobenzene derivatives.** E. KAHL, W. TOMCZYŃSKI, and S. WEIL (Spraw. Prac. Państw. Inst. farm., 1924, 31 pp.; Chem. Zentr., 1930, i,

1329).—Solutions (10%) of neosalvarsan and its substitutes of the same origin kept in an open vessel give for equal intervals of time similar refraction curves, but the curves differ with differing origin of the substances.

A. A. ELDRIDGE.

**Biochemistry of pyridine derivatives. II. Tautomerism and biochemical action of arsenic acids of the pyridine series.** A. BINZ, C. RÄTH, and G. WILKE (Biochem. Z., 1930, **223**, 176—183).—The chemotherapeutic index with both subcutaneous and intravenous injection of 2-hydroxypyridine-5-arsinic acid is considerably more unfavourable for the enol than for the keto-form. On the other hand, the index for *N*-methylpyrid-2-one-5-arsinic acid is more unfavourable than for the enol form, 2-methoxypyridine-5-arsinic acid. When the methyl of the *N*-methyl group is replaced by radicals of increasing size, e.g., ethyl, *n*-propyl, and *n*-butyl, the index becomes more and more unfavourable until with the last no trypanocidal action is obtained.

P. W. CLUTTERBUCK.

**Biochemistry of pyridine derivatives. III. Comparison of pyridinearsenic acids with other arsenic compounds.** A. BINZ, C. RÄTH, and A. ROST (Biochem. Z., 1930, **223**, 249—256).—The toxic and curative doses, and the chemotherapeutic indices of the sodium salts of the 5-arsinic acids of 2-hydroxy-3-aminopyridine, 2-hydroxy-3-acetamidopyridine, 2-hydroxy-3-bromopyridine, 2-hydroxy-3-carbamylmethylaminopyridine, and 2-aminopyridine have been determined in mice and the results compared with those obtained with other arsenic compounds. The monosodium salt of 2-pyridone-5-arsinic acid is the best tolerated compound so far investigated, and the other compounds named, except the last (which is surpassed also by tryparsamide and by two other substances), follow in the order given. All the compounds except the 2-hydroxy-3-carbamylmethylamino-derivative cure *ngana*. The toxicity of quinquevalent arsenic is suppressed when it is present in the 5-position of a pyridine ring which also has an oxygen atom united to the 2-position.

W. MCCARTNEY.

**Relationship of potassium to the depressor effect of liver extract.** R. H. MAJOR and C. J. WEBER (J. Lab. Clin. Med., 1929, **15**, 229—233).—The depressor substance is not potassium dihydrogen phosphate, than which it has a far greater effect.

CHEMICAL ABSTRACTS.

**Behaviour of soaps in the animal body. I. H. PAGE and E. V. ALLEN (Arch. exp. Path. Pharm., 1930, **152**, 1—26).—Most soaps on injection into white mice proved strongly toxic, especially those of hydroxy- and unsaturated fatty acids, and brought about a series of pathological changes. With parenteral injection, the total liver-fat decreased and the iodine value increased. Soaps, when intravenously injected, lowered the blood-pressure and stimulated respiration. The amount of pigment (uranin A) passing into the cerebrospinal fluid of a rabbit was increased when the soap (diethanolamine ricinoleate) was injected together with the pigment.**

P. W. CLUTTERBUCK.

**[Pharmacological] action of organic thiocyanates.** G. TAUBMANN (Arch. exp. Path. Pharm., 1930, **150**, 257—284).—Aliphatic mono- and di-

thiocyanates of the type of ethyl thiocyanate or ethylene dithiocyanate produce convulsions in animals and sometimes have an antipyretic action. The introduction of a double linking as in allyl or crotyl thiocyanate removes the convulsive and antipyretic actions and these compounds exhibit a paralysing action. Thiocynoacetic acid has a characteristic narcotic action very similar to that of bromoacetic acid. The following compounds are described: *hexyl thiocyanate*,  $C_6H_{13} \cdot SCN$ , a yellow oil, from hexyl bromide and potassium thiocyanate, and *crotyl thiocyanate*, a colourless oil, from crotyl bromide and ammonium thiocyanate. W. O. KERMACK.

**Stimulatory and inhibitory actions of quinol and its oxidation products on the leech.** R. LABES (Arch. exp. Path. Pharm., 1930, 152, 111—128).—The leech reacts twenty times as strongly in presence of oxygen to alkaline as to acid quinol solutions, the results being analogous to those obtained with frog's nerve-muscle preparations (*ibid.*, 1929, 133, 120). Whereas with alkaline quinol solutions (1/30,000) pigmented oxidation products rapidly form and the animals are completely paralysed in 3 hrs., they show almost normal behaviour after 6 hrs. with acidified quinol solutions of the same concentration. P. W. CLUTTERBUCK.

**Effect of alteration in the vegetative system on phosphate metabolism.** K. HESSE (Z. klin. Med., 1929, 111, 729—741; Chem. Zentr., 1930, i, 1324).—The daily phosphate excretion of two patients appeared to fall under the action of "gynergen." Experiments with dogs showed that the effect of ergotamine and acetylcholine is to increase the total acid-soluble phosphate in the blood and urine; atropine and ephedrine have the opposite effect. The calcium balance is not definitely altered. L. S. THEOBALD.

**Variations of catalase curve of blood after introduction of pilocarpine on an acid or alkaline diet.** S. A. POVORINSKAYA (Russ. J. Physiol., 1930, 13, 188—192).—The curves representing the catalase content of blood at various times after subcutaneous injection of pilocarpine are of a uniform type for children receiving an alkaline but not an acidic diet; where a mixed diet is taken, the curves are of a mixed type. The catalase-time curves for children on an alkaline diet not receiving pilocarpine are not of a uniform type. The catalase curves vary irregularly for the same individual according to the day and hour at which the blood is taken. No parallelism is found between blood-catalase and hæmoglobin contents. R. TRUSZKOWSKI.

**Uzara. III. Convulsive effect of uzara derivatives on the frog.** O. GESSNER and H. SCHRÖTER (Arch. exp. Path. Pharm., 1930, 152, 238—249).—The series of substances tested includes uzaridin, anhydro-uzaridin, trianhydrouzaridin, uzarin, uzarene, and uzarenin. Sublethal doses of the glucoside, uzarene, produce no signs of cramp in *R. temporaria*. 1.0 Mg. of uzaridin produces, within 1.5 hrs., convulsions in a frog of 30 g. weight. Uzarin, in relatively small doses, produces convulsions and finally death. P. G. MARSHALL.

**Comparison of physiological action of aspidospermine and quebrachine.** M. RAYMOND-

HAMET (Compt. rend., 1930, 191, 157—159).—The hydrochlorides of these alkaloids isolated from the bark of *Aspidosperma Quebracho blanco*, contrary to reported experiments, act differently on the sympathetic or vagus nervous systems. C. C. N. VASS.

**Serum-protein in histamine shock.** L. DÉRER and P. STEFFANUTTI (Biochem. Z., 1930, 223, 408—420).—There is a decrease in the concentration of protein in serum of cats to which large doses of histamine have been administered and the colloidal osmotic pressure of the serum falls to a value much lower than that which could be attributed to the decrease in the concentration of protein. W. MCCARTNEY.

**Serum-lipase in histamine shock.** P. STEFFANUTTI (Biochem. Z., 1930, 223, 421—430).—In the serum of cats and guinea-pigs suffering from histamine shock there is a decrease in the lipase content. This decrease is usually accompanied by a relatively smaller decrease in the protein content, and it seems that, for the most part, the lipase circulates uncombined with protein (*cf.* preceding abstract). W. MCCARTNEY.

**Blood-sugar-reducing action of *Rhizoma polygonati*, a popular antidiabetic remedy.** H. LANGECKER (Biochem. Z., 1930, 222, 173—190).—Extracts of the rhizome of *Polygonatum officinale* and *P. multiflorum* administered to fasting rabbits do not affect the normal blood-sugar, or the hyperglycæmia after adrenaline, but considerably reduce alimentary hyperglycæmia. The antidiabetic substance is readily soluble in water and alcohol, is not fermentable, and can be salted out with ammonium sulphate. P. W. CLUTTERBUCK.

**Inflammation. V. Alteration of the reaction of blood and carbon dioxide-combining capacity of the plasma of rabbits under the influence of drugs inhibiting respiration and inflammation.** H. FRÖHLICH (Arch. exp. Path. Pharm., 1930, 151, 323—340).—The administration to a rabbit of 0.5 g. of urethane subcutaneously or 0.75 g. of sodium bromide by mouth per kg. body-weight results in a rise in the  $p_H$  of the blood and a rise in the carbon dioxide-combining power of the plasma. An equimolecular amount of carbamide is without these effects, but sodium chloride in equimolecular quantity raises the  $p_H$  of the blood. Forced breathing inhibits the urethane action, which, however, becomes more marked when the forced breathing is stopped. The withdrawal of 6 c.c. of blood from a rabbit three times during 24 hrs. tends to raise the carbon dioxide-combining power of the plasma of the venous blood but to lower that of the carotid blood. W. O. KERMACK.

**Detection of luminal [phenylethylbarbituric acid] in urine.** W. KOENIG and H. KLUGE (Chem.-Ztg., 1930, 54, 451).—The urine is acidified with tartaric acid and extracted with ether, the ether extract is evaporated to a syrup, water is added, and the solution boiled with animal charcoal and filtered. The filtrate is rendered alkaline with sodium hydroxide and extracted with ether, the aqueous layer is acidified with sulphuric acid, treated with sodium hydrogen carbonate until it turns litmus blue, and again extracted with ether, and finally the second aqueous layer is acidified

with sulphuric acid and extracted with ether. The three ethereal solutions are separately washed with water, filtered, and evaporated to dryness. The first solution leaves an oily residue of complex composition, the second a residue of luminal, and the third hippuric acid.

A. R. POWELL.

**Distribution of amino-acids in blood during chloroform narcosis and in anæmic animals. Relationship between the osmotic resistance of the erythrocytes and amino-acid distribution.** A. SIMON and E. ANNAU (Arch. exp. Path. Pharm., 1930, 152, 129—141).—The amino-acid content of whole blood usually increases during chloroform narcosis, the maximal difference being about 2.0 mg. In anæmia of dogs and rabbits produced by bleeding there is usually a fall in the blood-amino-nitrogen which occurs chiefly in the corpuscles. There is no obvious connexion between the osmotic resistance of the corpuscles and amino-acid distribution.

P. G. MARSHALL.

**Blood-cholesterol following repeated administrations of chloroform, paraldehyde, and urethane.** S. H. GRAY (J. Biol. Chem., 1930, 87, 591—596).—Daily administration of chloroform to rabbits causes a rise in the blood-cholesterol after 3 weeks; a similar effect was not observed after repeated administration of paraldehyde or of urethane.

C. R. HARINGTON.

**Therapeutic photochemistry.** C. BENOIT and A. HELBRONNER (Compt. rend., 1930, 191, 233—235).—Examples are cited in which the therapeutic effect of certain drugs is greatly enhanced by the simultaneous employment of ultra-violet or infra-red irradiation and the possibility of obtaining a given effect with a diminished dose of the drug is thus indicated. Correlation of the absorption spectrum of the drug with the activating radiation is suggested.

H. WREN.

**Nature of the active radiations in the phenomena of photosensitisation.** J. CUZIN (Bull. Soc. Chim. biol., 1930, 12, 745—753).—The action of light radiations of various wave-lengths in sensitising eosin, methylene-blue, and hæmatoporphyrin to retard the rate of beat of the frog heart *in situ* is studied. Hæmatoporphyrin exhibits the strongest response and is sensitised by all visible and ultra-violet radiations, the heart ceasing to beat in 1—2 hrs. Eosin has the same effect on radiation with green and ultra-violet light only. Methylene-blue is similar to eosin, except that total light is also effective. The total radiation (of the mercury-vapour lamp) is less effective than certain components, indicating an antagonistic action of certain bands.

F. O. HOWITT.

**X-Ray sensitisation. I. Mechanism of sensitisation by iodine salts.** D. L. RUBINSTEIN (Strahlenther., 1929, 34, 414—420; Chem. Zentr., 1930, i, 1489).—Experiments with infusoria show that the "sensitising" action of solutions containing iodine salts is due to chemical oxidation and the toxic action of the liberated iodine.

A. A. ELDRIDGE.

**Effect of irradiation on cobra venom and antivenin.** A. EIDINOW (Brit. J. Exp. Path., 1930, 11, 65—72).—The neurotoxin present in a solution of cobra venom in saline was destroyed only by rays of

wave-length less than 2800 Å. unless sensitised with eosin. The photodynamic action of eosin is arrested by the presence of blood and serum. Hæmolysins and cytolsins were destroyed by rays of wave-length greater than 2800 Å., but not by those of wave-length greater than 3300 Å. Antivenin, as obtained in serum, is resistant to prolonged irradiation.

CHEMICAL ABSTRACTS.

**Oxidative-reductive power of tissues. I, II.** R. FABRE and H. SIMONNET (Bull. Soc. Chim. biol., 1930, 12, 777—799, 800—814).—A more detailed account of work already noted (this vol., 949).

**Cytochrome and intracellular oxidase. D.** KEILIN (Proc. Roy. Soc., 1930, B, 106, 418—444).—Observations on the oxidation of cysteine in presence of indophenol oxidase extracted from sheep's heart-muscle and the C component of cytochrome from baker's yeast are recorded. Improved methods for the separation and purification of the oxidase and of the C component are described. The purest active preparations of the former still showed faintly the absorption bands of cytochrome, but neither this oxidase preparation nor the yeast cytochrome separately brings about the oxidation of cysteine although rapid oxidation occurs when both are present. Experiments have been made on the rate of oxygen uptake in presence of various concentrations of oxidase and of the cytochrome-C. The muscle-oxidase preparation is inactivated when heated to 70°. Very small concentrations of potassium cyanide or sodium sulphide completely or partly inhibit the synthetic oxidase-cytochrome system. It is inhibited in the dark by a high concentration of carbon monoxide, but is reactivated when exposed to light or to a higher partial pressure of oxygen. Narcotics (urethane) have little or no effect on the activity of the oxidase-cytochrome system. The muscle-oxidase preparations contain small quantities of metallic impurities, but the catalytic activity of these is inactivated by certain substances accompanying them. When, however, pyrophosphate is added along with oxidase to cysteine, the metallic catalysts, in particular copper, become active and oxidation of the cysteine proceeds. These facts support the views previously expressed (A., 1929, 470) on the rôle played by cytochrome in the metabolism of the cell.

W. O. KERMACK.

**Philothione as hydrogenase.** J. DE REY-PAILHADE (Compt. rend. Soc. Biol., 1929, 99, 1700—1702; Chem. Zentr., 1929, i, 1575).—Egg-white, diluted with an equal volume of water, was used as a source of philothione; the addition of sulphur liberates hydrogen sulphide in 30 min. The philothione formed contains the -S-S- linking characteristic of cystine. The reaction does not occur after heating with dilute acid or alkaline media; further, the precipitate formed by heating does not give hydrogen sulphide after the addition of sulphur. It is maintained that philothione is an enzyme.

L. S. THEOBALD.

**Enzymic formation of L-malic from fumaric acid.** N. ALWALL (Skand. Arch. Physiol., 1929, 55, 91—93; Chem. Zentr., 1929, i, 1581).—The results of Clutterbuck (A., 1927, 693) are confirmed. The enzymic formation of L-malic from fumaric acid proceeds

at first with a high velocity, which then gradually decreases until equilibrium is reached.

L. S. THEOBALD.

**Effect of salts and of poisons on the activity of malt catalase.** V, VI. M. O. CHARMANDARIAN and A. W. TIUTUNNIKOVA (Biochem. Z., 1930, 222, 272—283, 284—289).—V. The effect of the addition of inorganic salt solutions of varying concentrations ( $M/20$  to  $M/10^7$ ) on the activity of the catalase of unextracted malt has been studied. Both cations and anions, according to their nature and to the experimental conditions, affect the activity of the catalase. When the activity is stimulated by the sodium, ammonium, calcium, manganese, and zinc ions the influence of the first two is great and that of the others slight, whilst the magnesium ion occupies an intermediate position. The inhibitory influence of bivalent cations is greater than that of univalent cations, and increase in at. wt. is accompanied by increase in this influence. As a result of the colloidal nature of the enzyme the effect produced by the salts becomes more pronounced with time. Previous observations (this vol., 1964) concerning the effect of ferric chloride have been confirmed. The higher concentrations of disodium or dipotassium hydrogen phosphates or of sodium hydrogen carbonate greatly stimulate the activity of the catalase. At low concentrations sodium nitrate and potassium dihydrogen phosphate have high stimulating effects, and the chloride, nitrate, and sulphate ions form a descending series as regards these, sulphate being practically without effect. It is supposed that certain concentrations of a salt may increase, whilst others may decrease, the degree of dispersion of the colloidal system.

VI. Especially after acting for some time and in high dilutions, potassium arsenate, cyanide, and thiocyanate, barium chloride and nitrate, mercuric chloride, quinine hydrochloride, strychnine nitrate, and uric acid may stimulate the activity of the catalase, although their action is generally inhibitory.

W. MCCARTNEY.

**Nature of amylase.** II. D. NARAYANAMURTI (J. Indian Inst. Sci., 1930, 13A, 69—72).—Bechhold's technique of electro-ultrafiltration (A., 1925, ii, 1158) was used to remove electrolytes from diastase solutions. The solid content of the original solution was 4.8 times that of the electro-ultrafiltered solution. The curves obtained for the hydrolysis of starch by diastase before and after electro-ultrafiltration were slightly different, the latter resembling an autocatalytic curve. The components of diastase causing liquefaction and saccharification (A., 1929, 216) have been partly separated by ultrafiltration. The liquefying component is probably of a higher dispersity than the saccharifying component.

G. F. MARRIAN.

**Existence of two components in malt diastase.** O. EDFELDT, G. NORDH, and T. SWAETICHIN (Biochem. Z., 1930, 223, 478—480).—The experiments of Ohlsson (A., 1923, i, 620; 1927, 277) have been repeated and his results confirmed. Statements by Ernström ("Über Amylasen," Stockholm, 1930) are rejected.

W. MCCARTNEY.

**Emulsin.** III. B. HELFERICH and H. BREDERECK (Z. physiol. Chem., 1930, 189, 273—279; cf.

A., 1923, i, 722).—The activity of  $\beta$ -glucosidase can be increased 740-fold by ultra-filtration and a product having  $\text{Sal.f.}=11.1$  obtained in 1% yield. This material has a very low ash content, is very sensitive to ultra-violet irradiation, and exhibits the reactions of proteins. It has  $[\alpha]_D -18^\circ$  to  $-25^\circ$ .  $\beta$ -*h*-Fructosidase can be purified in the same way. W. MCCARTNEY.

**Biochemical synthesis of  $\beta$ -5-iodosalicyl-glucoside.** P. DELAUNEY (Compt. rend., 1930, 191, 57—59).—5-Iodosaligenol and dextrose dissolved in an aqueous solution of acetone hydrogen sulphite furnish when treated with emulsin *l*- $\beta$ -5-iodosalicylglucoside.

C. C. N. VASS.

**Enzymic synthesis of esters.** P. RONA and O. MÜHLBOCK (Biochem. Z., 1930, 223, 130—144).—Using the enzymes of powdered pig's pancreas and liver, ester synthesis is shown to be dependent on the constitution of the components. Branching of the carbon chain of the acid decreases the rate of synthesis, but of the alcohol the effect is not obtained to the same extent. For substituted acids, the rate does not vary so much with the substituent as with its position relative to the carboxyl group. Pancreatic esterase readily esterifies butyric acid, whereas liver esterase esterifies only the lower members.

P. W. CLUTTERBUCK.

**Metabolic changes resulting from irradiation.** VII. **Effect of light on butyrase from liver and heart.** L. PINCUSSEN and T. TAKUMA (Biochem. Z., 1930, 223, 341—346).—The lipolytic power of extracts of the livers or hearts of rabbits is greatly reduced if they are exposed to radiation from powerful incandescent electric lamps and radiation from quartz mercury-vapour lamps has a similar effect in the case of the liver extracts (cf. Pincussen and Anagnostu, A., 1922, i, 485). The heat rays may be the effective agents in the process.

W. MCCARTNEY.

**Stimulating action of bile acids on pancreatic lipase, and their haemolytic action.** K. KAZIRO and K. TSUJI (J. Biochem., Japan, 1930, 11, 333—343).—*apo*Cholic, dihydro-oxycholadienoic, and dihydroxycholic acids stimulate pancreatic lipase equally, in accord with Schoda's view that the hydroxyl group in position 7 of the bile acid molecule increases the lipolytic activity of the lipase. The action of lipase is also stimulated by the hydroxytricarboxylic acid from ursodeoxycholic acid, but not by dehydrocholic or cholanolic acid. The haemolytic effect varies with the kind of red cell.

CHEMICAL ABSTRACTS.

**Alteration of fatty acids in autolysis of the liver.** J. HEPNER and O. WAGNER (Časopis Českoslov. Lék., 1929, 9, 214—216, 236—237; Chem. Zentr., 1930, i, 1662).—A qualitative examination of the fatty acids, particularly a determination of iodine value, is necessary in addition to their determination.

A. A. ELDRIDGE.

**Change of cholesterol in autolysis of the liver.** O. WAGNER (Časopis Českoslov. Lék., 1929, 9, 209—213; Chem. Zentr., 1930, i, 1662).—Lemeland's, as well as Fex's, method is satisfactory for the determination of total cholesterol in organs. In fed, but not fasted, rabbits the total liver-cholesterol was considerably diminished by autolysis.

A. A. ELDRIDGE.

**Proteases of animal tissues. I. Determination and purification of the protease of ox spleen. II. Physico-chemical behaviour of the protease of ox spleen.** The protease of ox leucocytes. H. KLEINMANN and K. G. STERN (Biochem. Z., 1930, 222, 31—83, 84—122).—The experiments of Waldschmidt-Leitz and Deutsch (A., 1927, 794) on the proteases of spleen extracts have been repeated, for the most part confirmed, and extended. The  $p_H$ -activity curves for cathepsin (spleen protease) are investigated, using albumin, caseinogen, and gelatin as substrates with unpurified and purified extracts of spleen, the reactions being followed by Van Slyke's method and also by nephelometric methods. The  $p_H$ -activity curve, obtained by Van Slyke's method with the unpurified spleen extract, shows maxima at  $p_H$  4 and 8, the second maximum disappearing when the protease is separated from the erepsin by adsorption on kaolin and subsequent alkaline elution, the eluate containing only the protease. Spleen protease free from erepsin attacks only isoelectric protein. Using the nephelometric method, which measures only protease action, and gelatin as substrate, an optimum is obtained at  $p_H$  4—5 with the unpurified and at 2—4 with the purified extract. The enzyme attacks serum-albumin, the optimal zone with unpurified extract being from  $p_H$  2.6 to 5.6, with a faint optimum at  $p_H$  4, whilst with purified extract it lies between  $p_H$  3 and 4. Caseinogen gives different optima according to whether the reaction occurs in concentrated (Van Slyke's) or in dilute (nephelometric) solution, a single optimum at  $p_H$  5—6 being obtained in the former and two maxima at  $p_H$  3 and 5 in the latter case. Hydrogen sulphide increased the action of the enzyme both of unpurified extract and of eluate. Hydrogen cyanide activated the unpurified but not the purified extract in its reaction with gelatin and caseinogen. Leucylglycine is hydrolysed by spleen erepsin three to four times as quickly as glycylglycine, the optimum for the former being at  $p_H$  8. Protease of leucocytes shows similar behaviour to that of spleen, but erepsin is absent.

P. W. CLUTTERBUCK.

**Natural activator of catheptic enzymes.** E. WALDSCHMIDT-LEITZ, A. PURR, and A. K. BALLS (Naturwiss., 1930, 18, 644—645).—The catheptic group of proteolytic enzymes from animal organs requires for activation the presence of specific substances, e.g., hydrocyanic acid or hydrogen sulphide. Zookinase, a natural activator, is developed in the organs only after death; and is identical with glutathione. The active properties of zookinase are destroyed by oxidising agents and this is of particular significance in considering the causes of autolysis in dying cells or in malignant tumours.

W. R. ANGUS.

**Capability for activation by hydrocyanic acid of intracellular animal and vegetable proteases.** X. UTKINA-LJUBOVZOVA (Biochem. Z., 1930, 222, 404—406).—As regards its capability for activation by hydrocyanic acid, Merck's "papayotin" behaves in the same way as do all other intracellular proteases. Proteases from the liver of the guinea-pig or the frog act in the same way as do vegetable proteases. If

there is specificity it is of the process, not of the enzymes.

W. MCCARTNEY.

**Inactivation of highly-purified urease by heavy metals.** J. B. SUMNER and K. MYRBÄCK (Z. physiol. Chem., 1930, 189, 218—228).—It is not possible to decide whether the purest crystalline urease obtainable consists entirely of the enzyme, but such urease is as pure as the best invertase and is readily prepared from crude material with a 700—800-fold increase in activity. The inactivation of the urease by silver is partly reversible, and substances such as gum-arabic which combine with the metal, or even urea itself (when present in excess) which combines with the enzyme and displaces the metal, can restrict or reverse inactivation. Ordinary distilled water may contain sufficient impurities, usually heavy metal compounds, to inactivate urease. The compound of urease and silver can undergo dissociation. In very dilute solutions of urea the activity of urease is reduced even when inactivating agents are absent. More than 40,000 g. of urease can be inactivated by 1 g.-atom of silver, but the enzyme can combine with more than ten times as much silver as is required for inactivation.

W. MCCARTNEY.

**Crystalline urease. Inactivation by ultra-violet light, by sunlight with aid of a photodynamic agent, and by trypsin.** H. TAUBER (J. Biol. Chem., 1930, 87, 625—628).—A solution of crystalline urease prepared by the method of Sumner (A., 1926, 1061, 1176) was rapidly inactivated by exposure to ultra-violet radiation in presence of eosin; slower inactivation occurred on exposure to ultra-violet radiation alone or to sunlight in presence of eosin. Sunlight alone had no effect. Tryptic digestion caused slow but complete inactivation of the urease.

C. R. HARRINGTON.

**Effect of ultra-violet light on the formation and alteration of skin melanin.** G. O. E. LIGNAC (Strahlenther., 1929, 34, 605—609; Chem. Zentr., 1930, i, 1821).—Melanin can be produced after death in the epidermis by ultra-violet rays.

A. A. ELDRIDGE.

**Post-mortal production of melanin in meal-worm insects (*Tenebrio molitor*, L.).** H. SCHMALFUSS and H. BARTHMEYER (Biochem. Z., 1930, 223, 457—469).—In meal-worm insects killed immediately after hatching there are an appropriate feebly-alkaline reaction, a suitable enzyme, and sufficient water to allow its precursor to be converted into melanin, but the concentration of oxygen in the insects is not sufficient to allow darkening of colour to take place. The precursor does not belong to the dihydroxy-benzenes. Organic solvents (particularly chloroform) which extract material from the insects, so making their skeletons more permeable to oxygen, stimulate oxidation and so assist in the production of melanin, which production occurs chiefly in the hæmolymph. Exclusion of oxygen, desiccation, heating at 100°, or treatment with acids (including hydrocyanic acid) or with ammonia all restrict or prevent the production of melanin, but cooling to -22° restricts although it does not prevent the production. The insects darken also in the presence of hydrogen sulphide, but this darkening is due to the action of the gas on the ferric

iron in the insects which is brought into the ionised state and converted into sulphide.

W. MCCARTNEY.

**Nuclein metabolism. XXIV. Enzymic fission of yeast-nucleic acid with liver nucleotidase for the production of purine- and pyrimidine-carbohydrate complexes.** F. BIELSCHOVSKY (Z. physiol. Chem., 1930, 190, 15—20; cf. this vol., 1060).—In the hydrolysis of thymus-nucleic acid with liver nucleotidase the yield of purine glucosides is low owing to the fission of the latter by the enzyme. With yeast-nucleic acid only small amounts of free purines are obtained and the percentage hydrolysis is lower. From the yeast product the nucleosides guanosine, inosine, and uridine were obtained in good yield. The last two are regarded as deamination products of adenosine and cytidine.

J. H. BIRKINSHAW.

**Starch-liquefying enzyme in dried yeast autolysates. Synthetic action of the enzyme.** S. NISHIMURA (Biochem. Z., 1930, 223, 161—170).—Yeast autolysate contains an enzyme which attacks amylopectin and liquefies starch. The enzyme also can synthesise higher from lower dextrans, and can accelerate the saccharification of starch by amylase. The optimal conditions are a temperature of 20—25° and a  $p_H$  of 6.0—6.2, and complete inactivation is obtained by heating the extract for 10 min. at 55—60°.

P. W. CLUTTERBUCK.

**Semicarbazide method for the detection of pyruvic acid in alcoholic fermentation.** P. ELLASBERG (Z. physiol. Chem., 1930, 189, 254—260).—The method of Kostytshev and Soldatenkov (A., 1928, 923) has been successfully applied to the isolation of pyruvic acid from the products of fermentation of sucrose by yeast. The acid can be isolated even when acetaldehyde is also present. Statements by Klein and Fuchs (A., 1929, 1491) and their procedure are criticised.

W. MCCARTNEY.

**Growth of yeasts and similar organisms on pentoses.** D. G. ROSA, E. B. FRED, and W. H. PETERSON (Zentr. Bakt. Par., 1929, II, 79, 86—92; Chem. Zentr., 1930, i, 1484).—Only yeast-like organisms, particularly *Torula*, *Mycoderma*, *Dematium*, and *Monilia nigra*, utilise pentoses (66—98%), affording carbon dioxide and alcohol. *Endomyces* attacks only xylose.

A. A. ELDRIDGE.

**Involution cultures of yeast.** I. A. T. HENLEY (J. Inst. Brew., 1930, 36, 304—307).—A strain of *S. Pastorianus* and a top-fermentation primary yeast of the Dublin type were grown as colonies on semi-liquid nutrient media, the consistency of which allowed free growth on the upper surface and prevented the sinking of the culture into the body of the medium. Under these conditions a high percentage of mycelial cells was formed with the production of an involution culture. Wort-gelatin and wort-agar were unsuitable as media, whilst gum tragacanth required careful manipulation. The best results were obtained with a 1% Irish moss-wort which was not liquefied by the yeast. The growth forms of the involution cultures made from the two species of yeast were quite different and were characteristic of the species. C. RANKEN.

**Relation between starch production and accumulation of acid in moulds (*Penicillium*).**

T. CHRZASZCZ and D. TIUKOV (Biochem. Z., 1930, 222, 243—258; cf. A., 1929, 724).—Experiments with 22 species of *Penicillium* propagated in a medium containing 5—25% of sucrose show that species which are included in the class of acid accumulators when grown under conditions which inhibit the accumulation of acid begin to act as starch producers. The concentration of sucrose does not influence the extent of development of the mould nor is the amount of sucrose consumed during propagation related to the amount of acid produced, but up to a certain point the consumption corresponds with the starch produced. It is concluded that the production of starch is a normal process in the growth of moulds, and that when citric acid is produced it forms in some cases a reserve material, in others an intermediate stage in the decomposition of the sugar.

W. MCCARTNEY.

**Inhibition of *Phytomonas malvaceara* in culture media containing sugars.** I. M. LEWIS (J. Bact., 1930, 19, 423—433).—The failure of *P. malvaceara* to grow in media containing dextrose, maltose, galactose, or levulose and various nitrogenous compounds after sterilisation at 122° for 15 min. is traced to chemical changes produced by the high temperature of sterilisation. Inhibition of growth depends on the proportion of peptone, sugar, and phosphate present, the reaction of the solution, and the temperature and period of sterilising. It is not due to changes of reaction during sterilisation. Inhibition occurs in media which in the absence of sugars are suitable for growth of the organism. Inhibition appears to be due to conversion of the nitrogen compounds into non-assimilable forms.

A. G. POLLARD.

**Bacterial decomposition of cellulose.** C. E. SKINNER (Zentr. Bakt. Par., 1929, II, 78, 508—512; Chem. Zentr., 1930, i, 1164).—Decomposition was effected by 12-yr.-old cultures of *Bacterium liquatum*, McBeth et Scales, *B. flavigenum*, McBeth et Scales, *B. gelidum*, Skinner, and other strains.

A. A. ELDRIDGE.

**Products of the thermophilic fermentation of cellulose.** S. W. SCOTT, E. B. FRED, and W. H. PETERSON (Ind. Eng. Chem., 1930, 22, 731—735).—The thermophilic fermentation of various cellulose media by crude, enriched, and purified cultures has been studied. The end-products are acetic acid (45—65%), carbon dioxide, and smaller amounts of alcohol;  $\alpha$ -hydroxy-acids (lactic acid) and residual acids (e.g., succinic acid) account for 65—80% of the carbon of the cellulose, the balance being made up by soluble, non-volatile, non-reducing substances, which are probably polysaccharides of the type of gums or cellulose-dextrans which are precipitable by acetone. Dextrose was identified as an end-product, but the amount produced is influenced by conditions of fermentation, temperature, neutralising agent, etc. ("reducing sugar"—calculated as dextrose, although probably other reducing substances were present—in one case was equivalent to 20% of the cellulose fermented). Purification of the culture tended to increase the percentage recovery of products, to decrease the production of carbon dioxide and alcohol, to increase the production of acetic and non-volatile



acids, and to cause the production of dextrose as end-product.

E. LEWKOWITSCH.

**Lactic fermentation of certain sugars at 70°.** G. GUITTONNEAU, H. DELAVAL, and M. BEJAMBES (Compt. rend., 1930, 191, 82—84).—*Thermobacillus tarbellicus* causes a 56—70% fermentation of the sucrose in a calcium salt-peptone or amino-acid medium to give chiefly lactic acid, with a preponderance of the *d*-form, smaller amounts of acetic and valeric acids, and traces of formic acid and formaldehyde. Similar results were obtained with maltose, dextrose, laevulose, and xylose, whilst lactose, galactose, and arabinose were not attacked. C. C. N. VASS.

**Influence of fixed nitrogen on *Azotobacter*.** D. BURK and H. LINEWEAVER (J. Bact., 1930, 19, 389—414).—The growth and activity of *Azotobacter* in cultures containing varying proportions of available fixed nitrogen are examined. *Azotobacter* cease to fix free nitrogen when the available nitrogen content of culture media is 0.5 mg. per 100 c.c. The rate of growth of the organisms with increasing amounts of available nitrogen reaches a maximum corresponding with 0.5—1.0 mg. of nitrogen per 100 c.c., and falls sharply with lower concentrations and more gradually with higher concentrations of nitrogen. The ratio between rates of growth and of respiration (measured directly by oxygen consumption) increases with the rate of growth. The nitrogen content of the dry matter of the cell tissue is practically the same whether the nitrogen supplied is fixed or free. It is suggested that the fixation of free nitrogen is a function resorted to only when the supply of fixed nitrogen to the organism is deficient. The physiological functions of respiration, growth, efficiency, etc. are similar whether fixed or free nitrogen is supplied.

A. G. POLLARD.

**Influence of calcium on the evolution of cultures of the anthrax bacillus.** J. BORDET and E. RENAUX (Ann. Inst. Pasteur, 1930, 45, 1—25).—The anthrax bacillus when grown on gelatin dissociates into two forms, one giving rise to flat filamentous colonies (*A*), the other producing raised whitish colonies (*B*). The effect of cultivating these two forms on oxalated gelatin (i.e., without calcium) and on gelatin with the addition of 1% of calcium chloride was studied. Type *A* on oxalated gelatin produces a precocious sporulation, so that after 3 weeks the cultures show nothing but spores. On calcium-gelatin *A* produces filaments and large forms and finally evolves as a new filamentous non-sporing type *AA* (button type of colony). When maintained on the calcium medium the filaments become thinner. When *A* is transferred from oxalated to calcium-gelatin a certain tendency to lysis is evident and very thin elements are seen, consisting of chains of coccil forms which are gradually converted into spores.

Calcium has not such a marked effect on type *B*, but sporulation is diminished and there is a tendency for the rods to associate to form filaments.

J. H. BIRKINSHAW.

**Influence of calcium on the characteristics of microbial species.** P. BORDET (Ann. Inst. Pasteur, 1930, 45, 26—41).—The effect of calcium in a gelatin broth medium for the cultivation of certain bacteria

from the atmosphere was examined. Deprivation of calcium was found to produce considerable morphological modification in certain bacilli, transforming them into short elements, frequently coccobacilli. An oxalated medium enhances the red pigment production by *Micrococcus prodigiosus*, whilst the presence of calcium produces a pale, almost white colony. These modifications are not associated with any degradation or loss of vitality of the organism, since calcium restores the normal characters.

J. H. BIRKINSHAW.

**Colouring matter of *Bacillus prodigiosus*.** I. Formation. G. GORBACH (Zentr. Bakt. Par., 1929, II, 79, 26—50; Chem. Zentr., 1930, i, 1484).—Although optimal conditions are determinable, no regular variation of yield of colouring matter with  $p_H$  and sources of nitrogen and carbon could be observed. Addition of ammonium lactate (0.75%) and glycerol (1.5%), and  $p_H$  6.4 (beginning), 5.1 (end) are desirable.

A. A. ELDRIDGE.

**Hydrogenation of the sterols of the faeces outside the intestine.** G. BISCHOFF (Biochem. Z., 1930, 222, 211—213).—The non-bromine-binding portion of the faecal sterols is greatly increased during putrefaction.

P. W. CLUTTERBUCK.

**Composition of the active principle of tuberculin. XII. Precipitin tests and differentiation of various tuberculin and timothy-bacillus proteins.** F. B. SEIBERT (Amer. Rev. Tuberculosis, 1930, 21, 370—382).—Precipitins were produced in normal guinea-pigs and rabbits by immunising them with small doses of the proteins obtained from culture liquids of human, bovine, and avian tubercle bacilli and timothy bacillus. The proteins were distinguished by means of cross-precipitation reactions.

CHEMICAL ABSTRACTS.

***d*-Mannose and *d*-arabinose in the carbohydrate fraction of the tubercle bacillus and of tuberculin.** M. MAXIM (Biochem. Z., 1930, 223, 404—407).—*d*-Mannose and *d*-arabinose as well as an unidentified carbohydrate acid have been isolated from tubercle bacilli propagated in a synthetic medium and from tuberculin.

W. MCCARTNEY.

**Physical difference amongst bacteriophages.** F. M. BURNET (Austral. J. Exp. Biol., 1930, 7, 27—35).—There is a direct relation between the resistance of bacteriophages acting on the bacilli of the salmonella-dysentery groups to heating in phosphate solution and the height to which they will ascend in filter-paper strips when diluted with phosphate solution. The method of growing the phage has no influence on its characteristic resistance to heat. Phages grown in non-nutrient saline exhibit only slight differences from those grown in nutrient broth.

F. O. HOWITT.

**Affinity of the diphtheria bacillus towards copper.** A. LEULIER and P. SEDAILLAN (Compt. rend., 1930, 191, 231—232).—The diphtheria bacillus is not affected by small doses of copper sulphate and has the power of fixing the metal in proportion scarcely encountered with other organisms. The metal is recovered in the flocculated toxins, in which it appears to be retained by the nucleoproteins.

H. WREN.

**Effect of various salts on the stability of diphtheria toxin.** S. SCHMIDT (Compt. rend. Soc. Biol., 1930, 103, 95—98, 98—100, 104—106; Chem. Zentr., 1930, i, 1636—1637).

**Rôle of the electrolyte in the diphtheria toxin-antitoxin reaction. Coagulation of the purified toxin in presence of various salts.** S. SCHMIDT (Compt. rend. Soc. Biol., 1930, 103, 101—103, 106—108; Chem. Zentr., 1930, i, 1637).

**Purification of toxins and antitoxin.** K. LINDBERSTRÖM-LANG and S. SCHMIDT (Compt. rend. Lab. Carlsberg, 1930, 18, No. 3, 1—15).—The non-denatured proteins of diphtheria antitoxin were precipitated in the cold with alcohol or a mixture of alcohol and ether, and subsequently extracted with ether. The precipitate as shown by experiments *in vivo* contained practically the whole of the antitoxin, but the Raman precipitation reactions with the toxin were not obtained. Moreover, the precipitated protein prevented this precipitation reaction between untreated sera and the toxin. Adsorption of the antitoxin on aluminium hydroxide resulted in a considerable loss of antitoxin; the residual solution contained most of the antitoxin in a reduced state of purity.

Adsorption of diphtheria toxin with aluminium hydroxide at  $p_H$  7 followed by elution with secondary phosphate solution and determination of the toxicity, dry matter, immunisation units, and nitrogen content showed that the toxin could be obtained in a considerable degree of purity in the eluate. The toxins obtained by this method retain their antigenic powers and power of flocculation to a marked extent.

C. C. N. VASS.

**Displacement of toxin from neutralised toxin-antitoxin mixtures by "toxoid" or anatoxin.** M. HEIDELBERGER and F. E. KENDALL (Science, 1930, 71, 511—512).—Theoretical. The increase in toxicity of neutralised toxin-antitoxin mixtures to which toxoid or anatoxin has been added is explained on physico-chemical lines.

L. S. THEOBALD.

**Determination of amino-nitrogen in bacteriological media.** D. A. MACPHERSON (J. Lab. Clin. Med., 1929, 14, 860—868).—For peptone water and veal infusion broth Folin's method is preferred. In Van Slyke's method a definite amount of pure "caprylic alcohol" must be used.

CHEMICAL ABSTRACTS.

**Biological determination of dextrose.** A. LE VESCONTE, J. H. BUCHANAN, and M. LEVINE (Iowa State Coll. J. Sci., 1930, 4, 331—342).—In dextrose solutions (0.01% or over) the rate of fall of  $p_H$  caused by *Aerobacter levans* is not proportional to the concentration. Under aerobic conditions simultaneous production and destruction of acid occur, the  $p_H$  falling and then rising. The course of the curve and the location of the minimal  $p_H$  are functions of the concentration of dextrose. Under anaerobic conditions, or with concentrations below 0.01%, the total change in  $p_H$  is a function of concentration of the dextrose.

CHEMICAL ABSTRACTS.

**Rapid staining of the cilia of the Ciliata.** H. ANSELMIER (Pharm. Acta Helv., 1930, 5, 83—94).—The drop of water or hay infusion is placed directly on

the slide, 4% formaldehyde is added, and the mixture, after drying in the air, is stained by treatment for 2 min. with either fuchsin-S, Ziehl's neutral fuchsin, or Ehrlich's gentian-violet. Gram's method may also be used. For parasitic protozoa, it is necessary to fix immediately with 4% formaldehyde solution and then proceed as above.

E. H. SHARPLES.

**Lipogenic and antilipogenic action of hormones as cause of obesity and leanness.** A. LUBLIN (Klin. Woch., 1929, 8, 2276—2278; Chem. Zentr., 1930, i, 1486).—Hyperfunction of lipogenic hormones (e.g. insulin) causes obesity and of antilipogenic hormones (e.g. adrenaline, thyroxine, pituitary hormone) causes leanness. Intravenous injection of thyroxine (1 mg.) causes a transient rise in blood-sugar (e.g., 0.110—0.130 g. per 100 c.c.).

A. A. ELDRIDGE.

**Adrenaline, alkali reserve, and apnoea.** D. BENNATI, J. GAUTRELET, and E. HERZFELD (Compt. rend., 1930, 191, 71—72).—A marked, transient elevation of the alkali reserve follows immediately after injection of adrenaline into a chloralosed dog. Simultaneously the  $p_H$  shows a transitory increase. Yohimbine, which inhibits the sympathetic, suppresses this reaction. Ergotamine lowers the increase of the alkali reserve after adrenaline injection. Neither of these substances effects the alkali reserve. The increase of the alkali reserve by apnoea whether by forced breathing, excitation of the vago-sympathetic, formaldehyde, or acetylcholine, is much inferior to that caused by adrenaline. Peripheral excitation of the splanchnic of the dog causes a marked increase of the alkali reserve, which is attributed to the liberation of adrenaline with a marked increase in the combustion of carbohydrates.

C. C. N. VASS.

**Rate of oxidation of adrenaline.** M. O. P. WILTSHIRE (J. Physiol., 1930, 69, Proc., xv—xvi).—The rate of oxidation of adrenaline was measured by the effect on an isolated strip of jejunum in Ringer's solution. Tissues such as liver, kidney, brain, or muscle appear to prevent the oxidative destruction of adrenaline.

E. BOYLAND.

**Effect of amino-acids on the rate of oxidation of adrenaline.** M. O. P. WILTSHIRE (J. Physiol., 1930, 69, Proc., xxiv—xxv).—Glycine, *D*-alanine, *L*-tyrosine, and *L*-leucine decrease the rate of oxidation of adrenaline. *D*-Alanine was the most effective and glycine the least.

E. BOYLAND.

**Diuretic brain hormone.** J. OLIVET (Münch. med. Woch., 1930, 77, 58—59; Chem. Zentr., 1930, i, 1489).—Local excitation of the brain leads to the mobilisation of diuretic substances which can be isolated in the serum sufficiently to permit transference to other animals.

A. A. ELDRIDGE.

**Cardiac hormone in the tortoise.** A. DE CARVALHO (Compt. rend. Soc. Biol., 1929, 102, 535—537; Chem. Zentr., 1930, i, 1321).—Electrical irritation, and the action of pilocarpine, atropine, ephedrine, and ergotamine on the heart of a tortoise failed to make a cardiac hormone detectable.

L. S. THEOBALD.

**Action of the parathyroid hormone on phosphatase.** I. H. PAGE (Biochem. Z., 1930, 223,

222—227).—Injection of parathyroid hormone considerably reduces the activity of bone phosphatase.

P. W. CLUTTERBUCK.

**Thyroxine formation from thyronine (deiodo-thyroxine) and iodine in the animal organism.** E. ABDERHALDEN and E. WERTHEIMER (Z. ges. exp. Med., 1929, 68, 563—568; Chem. Zentr., 1930, i, 1320).—Although the simultaneous addition of thyronine and potassium iodide produces the same qualitative effect as thyroxine on the respiration of rats and guinea-pigs, it has no effect on the growth and metamorphism of tadpoles. Further, the extensive addition of thyronine and potassium iodide does not bring about the disappearance of the glycogen of muscle- and liver-tissues, neither could a synthesis of thyroxine be detected in surviving mammalian organs such as the liver, muscle, and thyroid gland. Animals with extirpated thyroid glands did not generally show the usual increased respiration after treatment with thyronine and potassium iodide.

L. S. THEOBALD.

**Crystalline insulin. IX. Adsorption of insulin on charcoal.** H. JENSEN and A. DE LAWDER (J. Biol. Chem., 1930, 87, 701—712).—A concentrated solution of commercial insulin was precipitated with pyridine; the precipitate was dissolved in 0.01N-hydrochloric acid, and the solution was shaken with charcoal; the charcoal was filtered off and extracted repeatedly with 90% phenol; the insulin was recovered from the extract by precipitation with water. The product had an activity equivalent to that of crystalline insulin; the activity was not increased by repetition of the adsorption from a solution in *M*/15-disodium hydrogen phosphate. Similar adsorption of crystalline insulin failed to increase the activity of the latter, nor was the result affected by the origin of the insulin employed. The work of Dingemanse (Arch. exp. Path. Pharm., 1928, 127, 44) could not therefore be confirmed.

C. R. HARRINGTON.

**Intravenous injection of insulin. I. Normal blood-sugar curve.** E. NORGAARD and T. E. H. THAYSEN (Acta Med. Scand., 1929, 72, 492—501; Chem. Zentr., 1930, i, 1816).—Intravenous injection of 12 international units of insulin normally results in a minimal blood-sugar value (20 mg. per 100 c.c.) being reached in 25 min.; the value increases rapidly for 10—20 min. and then more slowly for 55—110 min. In the first hour of the increase the capillary blood contains more dextrose than the venous blood.

A. A. ELDRIDGE.

**Rise of blood-pressure and some so-called hypoglycemic symptoms after injection of insulin.** A. BREMS and C. HOLTEN (Acta Med. Scand., 1929, 72, 571—588; Chem. Zentr., 1930, i, 1816—1817).

**Standardisation of corpus luteum extracts.** H. KNAUS (Arch. exp. Path. Pharm., 1930, 151, 371—380).—Uteri removed from rabbits previously treated subcutaneously or intramuscularly with an active extract of corpus luteum are not sensitive to pituitrin. The rabbit uterus exhibits this insensitivity to pituitrin, although not removed from the rabbit until two days after the last injection of the corpus luteum extract.

This is probably due to the slow absorption of the extract. The antagonistic action of these extracts to pituitrin is proposed as a basis for standardisation.

W. O. KERMACK.

**Evaluation of the female sexual hormone. I. General method and calculation of results. II. Difference between rat and mouse units with the hormone dissolved in water and oil and its mode of action.** M. KOCHMANN (Arch. exp. Path. Pharm., 1930, 152, 47—51, 52—56).—The proportion of mouse to rat units for solutions of the hormone in water is 1 : 4 and in oil is 1 : 2. The action of small concentrations of the hormone for a long time is more important than the actual size of dose. For therapeutic use, preparations in oil containing 20 mouse units per c.c. are recommended.

P. W. CLUTTERBUCK.

**Physiological rôle of carotene and allied substances.** K. KAWAKAMI and R. KIMM (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 231—243).—Carotene, prepared from carrots or from *Capsicum annuum*, possesses vitamin-A potency, the daily minimal dose for curing a white rat being 0.02—0.05 mg. Lycopene,  $\alpha$ - and  $\gamma$ -crocetin, diphenyldodecahexaene, difuryloctatetraene, and the product obtained by treating squalene dodecaboromide with alkali are inactive.

Carotene in alcoholic solution exhibits two absorption bands at 470—490  $\mu$  and 440—460  $\mu$ , but the characteristic band of "biosterol" is absent. In 10<sup>-5</sup> N-alcoholic solution the maximum absorptions for "biosterol" and carotene lie at 520  $\mu$  and 470  $\mu$ , respectively, and the presence of 1/600 part of carotene in "biosterol" can readily be detected by the characteristic absorption band. The mixture of carotene and irradiated ergosterol, although possessing the same physiological potency as "biosterol," has a different absorption spectrum, and it is considered that vitamin-A potency is exerted by different substances.

A. I. VOGEL.

**Purification of carotene and the vitamin activity of purified carotene.** M. JAVILLIER and L. EMERIQUE (Compt. rend., 1930, 191, 226—229).—Crystalline carotene, m. p. 172—173°, is submitted to five successive purifications by dissolution in carbon disulphide, slow addition of the solution to boiling methyl alcohol, removal of the carbon disulphide, and filtration of the residual liquor; all operations are performed in an atmosphere of nitrogen. The product has m. p. 184—185° and retains its vitamin activity.

H. WREN.

**Carotene and animal growth.** JAVILLIER (Bull. Soc. chim., 1930, [iv], 47, 489—508).—A lecture.

**Cow's milk as a source of vitamin-B for lactation.** B. SURE (Science, 1929, 70, 583—584).—A criticism of the work of Daniels, Jordan, and Hutton (J. Nutrition, 1929, 2, 19).

L. S. THEOBALD.

**Effect of injections of brain-phosphatides on avitaminosis-B in pigeons.** E. SCHMITZ and P. KIMMELSTIEL (Biochem. Z., 1930, 223, 323—329).—The development of avitaminosis-B in pigeons is not influenced by oral or subcutaneous administration of phosphatides from brain.

W. MCCARTNEY.

**Alimentary equilibrium and nutrition. L.** RANDOIN (Bull. Soc. Chim. biol., 1930, 12, 815—

826).—Pigeons and rats on a diet including carbohydrate and no vitamin-*B* do not survive, whilst those on a diet without carbohydrate but including vitamin-*B* survive. In the absence of vitamin-*B*, carbohydrates and fats are not equivalent. The amounts of carbohydrate and mineral salts must also be proportionate in order to maintain growth and ensure successful reproduction. For the utilisation of lactose and galactose, a certain quantity of vitamin-*B* is necessary and also a strict alimentary equilibrium.

F. O. HOWITT.

**Procedure of Jansen and Donath for isolation of vitamin-*B*<sub>1</sub>.** R. R. WILLIAMS, R. E. WATERMAN, and S. GURIN (J. Biol. Chem., 1930, 87, 559—579).—An attempt to apply the work of Jansen and Donath (A., 1926, 644; 1927, 382) to an extract of brewer's yeast led to large losses of vitamin-*B*<sub>1</sub> at all stages and failure to isolate highly active material. Repetition of the work of the above authors on rice polishings afforded general confirmation of their results, although the yield of activity in the purified fraction was much lower and crystalline material could not be obtained. The crystalline material of Jansen and Donath prevented occurrence of polyneuritis, but not loss of weight in pigeons on a diet of polished rice when given in a daily dose of 0.04 mg.; similar doses caused increase in the weight of rats on a diet lacking vitamin-*B*<sub>1</sub>. The behaviour of this crystalline substance corresponds therefore in all respects with that of the highly purified (amorphous) preparations of the authors.

C. R. HARRINGTON.

**Vitamin-*B*<sub>2</sub>.** P. A. LEVENE (Science, 1930, 71, 668).—The fraction *B*<sub>1</sub> is adsorbed on silica gel at *p*<sub>H</sub> 3, the filtrate rich in vitamin-*B*<sub>2</sub> is precipitated six times with acetone, dissolved in water, and finally precipitated with alcohol containing 1% of hydriodic acid. The material thus obtained suffices to maintain the normal growth of white rats when given in daily doses of 0.0007 g.

L. S. THEOBALD.

**Williams-Waterman vitamin-*B*<sub>3</sub>.** W. H. EDDY, S. GURIN, and J. KERESZTESY (J. Biol. Chem., 1930, 87, 729—740).—The existence in the vitamin-*B* complex of a third (growth) factor, necessary for pigeons and chicks, is confirmed (cf. Williams and Waterman, A., 1928, 1058). This factor is very labile towards heat and alkali; it is present in considerable amounts in yeast, whole grains, malt (not malt extract), beef, and ox liver, and in smaller amounts in milk, orange, tomato, potato, spinach, and cane molasses.

C. R. HARRINGTON.

**Effect of antineuritic vitamin preparations on growth of yeasts.** R. J. WILLIAMS and R. R. ROEHM (J. Biol. Chem., 1930, 87, 581—590).—The substance which can be adsorbed from yeast extracts on fuller's earth and stimulates the growth of certain yeasts is not related to bios. It can be concentrated by the procedure of Jansen and Donath (A., 1926, 644; 1927, 382). The crystalline material of the latter authors is twice as active as any fraction hitherto obtained by the present authors, but only one half as active as a preparation obtained by Williams and Waterman (cf. preceding abstract) from a fraction discarded in the final stage of the Jansen and Donath method. The yeast growth-promoting substance is therefore

regarded as a complex of which the crystalline preparation of Jansen and Donath is one constituent.

C. R. HARRINGTON.

**Vitamin-*C*. Electrical transport.** R. B. McKINNIS and C. G. KING (J. Biol. Chem., 1930, 87, 615—623).—Lemon juice at varying *p*<sub>H</sub> was submitted to electrolysis in an apparatus specially designed to protect the solution from the action of alkali, oxygen, and chlorine, and from rise of temperature. In natural lemon juice (*p*<sub>H</sub> 2.4) and in acidified lemon juice (*p*<sub>H</sub> 0.9) no electrical transport of vitamin-*C* was observed. Electrolysis of lemon juice which had been brought to *p*<sub>H</sub> 7.2 by addition of ammonia caused concentration of the vitamin in the anode chamber. The vitamin is therefore acidic in character.

C. R. HARRINGTON.

**Vitamin-*C* content of Japan green tea.** H. E. MUNSELL and C. H. MILLER (J. Home Econ., 1930, 22, 314—316).—Only traces were detected in commercial samples.

CHEMICAL ABSTRACTS.

**Action of vitamins and surface activity.** F. V. VON HAHN (Biochem. Z., 1930, 222, 259—271).—The experimental procedure of Schepilevskaja (A., 1929, 476, 960, 1203) is unsatisfactory and many of her statements and deductions are incorrect. The surface activity of cabbage juice is lowered by treatment with charcoal with concurrent reduction in the antiscorbutic action. This action is to be attributed to food having high surface activity and not to specific chemically defined substances.

W. McCARTNEY.

**Antirachitic value of cod-liver meal.** F. E. MUSSEHL, R. HILL, and C. W. ACKERSON (Poultry Sci., 1928, 7, 239—242).—Whilst cod-liver meal contains vitamin-*D*, even 5% added to an otherwise complete ration does not prevent rickets in chickens.

CHEMICAL ABSTRACTS.

**Biological activity of sterols.** Sterols of plankton. G. BELLOC, R. FABRE, and H. SIMONNET (Compt. rend., 1930, 191, 160—162).—The sterols were extracted in the absence of air first with acetone and finally with chloroform. The extract was saponified with alcoholic potassium hydroxide solution and the unsaponifiable matter crystallised from methyl alcohol. The absorption spectra, Rosenheim's and Meesemacker's colour reactions, and the biological activities of the sterols were determined. The sterols from *Porcellana* and *Calanus*, collected in summer, gave positive reactions for all the ergosterol tests, whilst that from *Cydippes*, collected in early spring, showed no absorption band for ergosterol, gave positive colour reactions, and affected a rachitic rat only after irradiation.

C. C. N. VASS.

**Antirachitic vitamin in the [liver oils of] elasmobranchs.** SIGNE SCHMIDT-NIELSEN and SIGVAL SCHMIDT-NIELSEN (Z. physiol. Chem., 1930, 189, 229—238).—The liver oils of the following fish have been examined for their content of vitamins-*A* and -*D*: *Cetorhinus maximus*, Gunnerus, *Etmopterus spinax*, Lin., *Lamna cornubica*, *Somniosus microcephalus*, *Squalus acanthias*, L., *Raja fullonica*, *Raja oxyrinchus*. Very great variations were found in the contents of vitamin-*A* and there were also large variations in the -*D* content, but no relation could be

traced between the contents of the two vitamins. Oils obtained from the boiled livers by extraction with ether usually had higher contents of the vitamins than had the oils obtained by boiling with water. It is possible that there may be a relation between the calcium and vitamin-D contents of the fish.

W. MCCARTNEY.

**Action of irradiated ergosterol on tissue phosphatase.** I. H. PAGE and D. M. RESIDE (Biochem. Z., 1930, 223, 171—175).—A sample of irradiated ergosterol did not appear to bring about metastatic calcification, which was characteristic of the previously used (probably over-irradiated) samples. The activity of the phosphatase of kidney and small intestine was considerably retarded by over-irradiated ergosterol, but was little affected by the new sample. Changes in phosphatase content occur only along with changes in phosphorus-calcium equilibrium, and this change in rabbits fed with ergosterol is due to change in the toxic factor during over-irradiation.

P. W. CLUTTERBUCK.

**Effect of massive doses of irradiated ergosterol.** J. J. KLEIN (J. Amer. Med. Assoc., 1929, 92, 621—622).—The blood-calcium of albino rats was increased by 50%, the phosphorus was unaltered, the serum-protein was diminished, and the albumin:globulin ratio was higher in comparison with values afforded by animals given cod-liver oil.

CHEMICAL ABSTRACTS.

**Ergosterol poisoning.** M. HAENDEL and J. MALET (An. fac. med. Montevideo, 1929, 14, No. 4).—Irradiated ergosterol causes in animals an increase in blood-cholesterol and a disturbance of the lipin content of organs; after deactivation by heat it has a similar, but less severe, effect. The addition of deoxycholic acid restores the activity of the heated product. The toxic action of ergosterol is regarded as being a special case of sterol poisoning.

CHEMICAL ABSTRACTS.

**Furfuraldehyde-yielding substance as fission product of protopectin during the ripening of fruits.** C. M. CONRAD (Plant Physiol., 1930, 5, 93—103).—The furfuraldehyde-yielding substance formed during the development of soluble pectin is found in decreasing amounts as the quantity of protopectin in the fruit decreases during ripening. It is probably a component part of protopectin.

CHEMICAL ABSTRACTS.

**Toxicarol. A constituent of the South American fish poison *Cracca* (*Tephrosia*) *toxicaria*.** E. P. CLARK (J. Amer. Chem. Soc., 1930, 52, 2461—2464).—Details are given for the extraction of *toxicarol*,  $C_{21}H_{15}O_4(OH)(OMe)_2$ , m. p. 219° (corr.) [benzoate, m. p. 200° (corr.)], and a substance,  $C_{21}H_{16}O_4(OMe)_2$ , m. p. 173°, from the roots of *Cracca toxicaria*. The last-named compound is also a constituent of *Derris* and *Cube* roots. Both the above substances are decidedly toxic to fish.

H. BURTON.

**Examination of stems of *Coscinium fenestratum*, Coleb.** I. M. C. T. KATTI and V. P. SHINTRE (Arch. Pharm., 1930, 268, 314—321).—The alcoholic extract of the stems contains ceryl alcohol, hentriacontane, sitosterol and its glucoside, ipuranol, fats yielding on hydrolysis mainly palmitic and stearic

acids, a saponin, dextrose, and large quantities of two *alkaloids*, m. p. 205—206° (decomp.), and m. p. 223—224° (decomp.), neither of which appears to be identical with berberine (cf. Stenhouse, J.C.S., 1867, 20, 187—188).

H. E. F. NOTTON.

**Neutral constituents of sandarac.** F. BALÁŠ and Z. PEJŠOVÁ (Coll. Czech. Chem. Comm., 1930, 2, 424—432; cf. Henry, J.C.S., 1901, 79, 1144).—Extraction of a solution of sandarac (from *Callitris quadrivalvis*) in 1% sodium hydroxide with ether affords 8% of a reddish-yellow oil which was fractionally distilled. From the fraction b. p. 152—180°/744 mm., *d*- $\alpha$ -pinene and *d*-limonene were isolated, the presence of a minute quantity of  $\beta$ -pinene being detected by oxidation to nopinic acid. The fractions b. p. 75—100°/12 mm.,  $[\alpha]_D +42.74^\circ$ , and b. p. 100—115°/12 mm.,  $[\alpha]_D +44.64^\circ$ , probably consist of a complex mixture of oxygen derivatives of terpenes (menthol odour), whilst the small fraction, b. p. 115—140°/12 mm., probably contains sesquiterpenes. The comparatively large fraction, b. p. 140—170°/12 mm., consists mainly of a dicyclic *sesquiterpene alcohol* (probably tertiary),  $C_{15}H_{26}O$  (one double linking), b. p. 145—155°/12 mm.,  $[\alpha]_D +43.10^\circ$ ,  $d_4^{25}$  0.9809,  $n_D^{25}$  1.5085, which readily loses water to give a dicyclic *sesquiterpene*,  $C_{15}H_{24}$ , b. p. 125—135°/12 mm.,  $[\alpha]_D +25.29^\circ$ ,  $d_4^{25}$  0.9115,  $n_D^{25}$  1.5030, dehydrogenated with sulphur at 180—250° to cadalene, which was identified as its picrate. From the fraction, b. p. 170—210°/12 mm., was isolated a natural tricyclic *diterpene*,  $C_{20}H_{32}$  (two double linkings), b. p. 179—182°/12 mm.,  $[\alpha]_D +11.02^\circ$ ,  $d_4^{25}$  0.9497,  $n_D^{25}$  1.5200, dehydrogenation of which affords no hydrocarbon from which a crystalline picrate could be obtained. The diterpene is, therefore, not of the retene or dimethylphenanthrene type, but resembles *tricyclocamphene* closely in physical properties. The fractions b. p. above 175°/0.5 mm. (50% of the total oil) give only amorphous products from which no crystalline derivative could be prepared.

J. W. BAKER.

**Catechins of the cutch-producing *Acacias*.** M. NIERENSTEIN (J. Indian Chem. Soc., 1930, 7, 279—285).—The heart-wood of *A. catechu*, *sundra*, and *catechoides* contains a mixture of *dl*-acacatechin (3.1—22.7%), m. p. 204—205° (acetyl derivative, m. p. 160°), *l*-acacatechin (51.7—94.3%), m. p. 230° (acetyl derivative, m. p. 151°), and *l*-isoacacatechin (2.6—32.93%), m. p. 226—228° (acetyl derivative, m. p. 171°). During the manufacture of cutch from the above *Acacias*, the greater part of the catechin is destroyed. *dl*-Catechin is not epimerised when heated under pressure (cf. Freudenberg and Purmann, A., 1924, i, 868).

H. BURTON.

**Kola tannins. I. Constituents of fresh kola nuts.** P. CASPARIS. **II. Occurrence of colacatechin in tormentilla root and oak bark.** P. CASPARIS and K. REBER (Pharm. Acta Helv., 1929, 4, 181—188, 189—192; Chem. Zentr., 1930, i, 844—845).—Caffeine was not isolated; it is present as an equimolecular compound with colacatechin. Colatin was not found. The colouring matter is an anthocyan which is soluble in methyl-alcoholic hydrochloric acid giving a scarlet solution, becoming blue on careful addition of alkali. *Caffeine-colacatechin*,  $C_{28}H_{30}O_{10}N_2$ ,

has m. p. 133—134°; colacatechin,  $C_{20}H_{20}O_8 \cdot 3H_2O$ , m. p. 170—190°, decomp. 200—205° [hepta(?)acetyl-derivative, m. p. 140°]. A substance identical with colacatechin may be obtained from the sources mentioned. A. A. ELDRIDGE.

A new amino-acid in water-melon (*Citrullus vulgaris*). M. WADA (Proc. Imp. Acad. Tokyo, 1930, 6, 15—17, and Biochem. Z., 1930, 224, 420—429).—The syrup obtained by concentrating in a vacuum the filtered pressed juice of the water-melon was dissolved in water, precipitated with basic lead acetate, and the filtrate treated with Neuberg's reagent (mercuric acetate, sodium carbonate, and alcohol). The nitrogenous material recovered from the precipitate was again precipitated with phosphotungstic acid and the filtrate contained the new amino-acid *citrulline*,  $C_6H_{13}O_3N_3$ , decomp. 202°, optically inactive, forming a violet copper salt, decomp. 257—258°. Citrulline contains two amino- and one carboxyl groups, gives reactions with ninhydrin, Ehrlich's and Schiff's reagents, and with phenol and sodium hypochlorite, but does not give the biuret, diazo-, Millon's, Jaffé's, Sakaguchi's, Folin's, Adamkiewicz's, or Mörner's reaction. The constitution  $\alpha$ -amino- $\delta$ -carbamidovaleric acid,  $NH_2 \cdot CO \cdot CH \cdot [CH_2]_3 \cdot CH(NH_2) \cdot CO_2H$ , has been confirmed by synthesis from arginine by way of ornithine, dibenzoylornithine,  $\delta$ -amino- $\alpha$ -benzamidovaleric acid, and  $\delta$ -carbamido- $\alpha$ -benzamidovaleric acid.

W. O. KERMACK.

Occurrence of *l*-norephedrine and *l*-*N*-methylephedrine in European *Ephedra* species. O. WOLFES (Arch. Pharm., 1930, 268, 327—328).—These bases have been isolated from mother-liquors obtained in the manufacture of *l*-ephedrine.

H. E. F. NOTTON.

[Origin of alkaloids.] H. EMDE (Pharm. Acta Helv., 1929, 4, 81—89; Chem. Zentr., 1930, i, 846).—The biosynthesis of alkaloids is considered to be associated with the vigour of assimilation of carbon dioxide.

A. A. ELDRIDGE.

Condition of the carotenoids containing oxygen in plants. L. ZECHMEISTER and L. VON CHOLNOKY (Z. physiol. Chem., 1930, 189, 159—161).—From the red berries of buckthorn (*Lycium halimifolium*) was obtained a pigment, physalien. Hydrolysed with cold alkali hydroxide the latter yields zeaxanthin, which is a diol, and a colourless saturated fatty acid, m. p. 62°.

J. H. BIRKINSHAW.

Magnesium and life. Magnesium as a fertiliser and as a food. M. JAVILLIER (Chim. et Ind., 1930, 23, 1067—1081, and Bull. Soc. Chim. biol., 1930, 12, 709—740).—A review. E. HOLMES.

Hydrogen-ion concentration and titratable acidity of tomatoes and their resistance to *Fusarium* wilt. C. MAY (Ohio J. Sci., 1929, 29, 260—266).—No correlation was detected.

CHEMICAL ABSTRACTS.

Relation of protocathechuic acid to disease-resistance in the onion. H. R. ANGELL, J. C.

WALKER, and K. P. LINK (Phytopath., 1930, 20, 431—438).—The greater resistance to disease of brown-skinned, as compared with white-skinned, onions is traced in part to the presence of free protocathechuic acid in the coloured skins. A. G. POLLARD.

Apparent destruction of wood by the larvæ of *Annobium* [common wood-worm]. II. R. FALCK (Cellulosechem., 1930, 11, 128—129; see this vol., 968).—Meal prepared from wood has been investigated along with the mealy product resulting from the action of *Annobium striatum*, and results of analyses are given. The insect appears to consume a quantity of cellulose represented by a difference in the content of the two meals of about 9%, and since the lignin content is not at all changed, it is held that the cellulose consumed is loosely, or not at all, combined with the lignin in the original wood. A slight consumption of hexosan component of the hemicellulose complex appears to take place. T. T. PORTS.

Chemical sectioning of plant fibres. M. A. EL KELANEY and G. O. SEARLE (Proc. Roy. Soc., 1930, B, 106, 357—363).—Flax fibres which have been tendered either by storage or chemical means develop transverse fissures when slight pressure is applied in a solution of sodium hydroxide (11%). Transverse lamellation does not take place in water or very dilute sodium hydroxide. Brief boiling in 10% sulphuric acid followed by heating for  $\frac{1}{2}$  hr. at 60—70° is the best method of tendering, as the slight charring abolishes the necessity of staining with Congo-red before mounting. The thickness of the sections, which do not swell so markedly in the alkali when 10% acid is used for tendering, is usually 10—20  $\mu$ .

P. G. MARSHALL.

Improvement of Dische and Laszlo's method for determination of lactic acid. K. J. ANSELMINO (Biochem. Z., 1930, 221, 484—487; cf. A., 1927, 985).—From curves showing the relationship between the concentration of lactic acid and thickness of layer of liquid lactic acid contents can be determined after direct colorimetric comparison. W. MCCARTNEY.

Titrimetric determination of alkaloids in biology. G. GRAZIANI (Biochem. Terap. sperim., 1929, 16, 160—166; Chem. Zentr., 1930, i, 1002).—Kasperek and Votoček's method (Bull. Soc. Chim., 1923, [iv], 33, 110) gives satisfactory results if the concentration is adequate, but the method is unsuitable in biochemical studies owing to the small concentrations involved. A. A. ELDRIDGE.

Madder as a chemical and biochemical reagent. A. BAUER (Arch. exp. Path. Pharm., 1930, 151, 172—174).—The colouring matter of madder has an affinity for calcium carbonate and may be found in the bones of young rabbits fed on the root. Feeding large quantities of madder causes the secretion of a strongly acid urine which deposits coloured crystals of uric acid. The calcium salt of the colouring matter is rose-red and the magnesium salt violet, a fact which may serve to distinguish the two elements in biological material. P. G. MARSHALL.



# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

OCTOBER, 1930.

### General, Physical, and Inorganic Chemistry.

Spectra of gases lighted with strong electrical discharges. E. O. HULBURT (Physical Rev., 1930, [ii], 36, 13—15).—Hydrogen, helium, nitrogen, and oxygen were investigated under excitation by a 15,000-volt transformer or by a 0.002- or a 1-microfarad condenser, and the resulting spectra were photographed. With increasing strength of discharge the Balmer lines of hydrogen finally disappeared, and for each gas a continuous spectrum was ultimately obtained, alike for all the gases.

N. M. BLIGH.

Excitation processes in the hollow cathode discharge. R. A. SAWYER (Physical Rev., 1930, [ii], 36, 44—50; cf. Paschen, A., 1928, 97; Takahashi, A., 1929, 1350).—Theoretical. Available spectroscopic data are examined to determine the processes occurring when the negative glow in a hollow cathode discharge in a rare gas is used for the excitation of metallic spark spectra. Only those processes occur in which the metal can be excited to some term in the spark spectrum with small gain or loss of kinetic energy. Metals of high m. p., or those which sputter poorly cathodically, enter the discharge in helium in the normal state or in a low metastable state of the atom; for metals of low b. p. appreciable numbers of metallic ions enter the reactions. The conditions which determine the results are discussed.

N. M. BLIGH.

Experimental evidence for the existence of quadrupole radiation. R. FRERICHs and J. S. CAMPBELL (Physical Rev., 1930, [ii], 36, 151—152).—The transversal Zeeman effect of the forbidden green auroral line  $\lambda$  5577 Å. was photographed, and the line was found to be resolved into four components, indicating that the line is quadrupole radiation, in agreement with the theory of Rubinowicz (cf. this vol., 653).

N. M. BLIGH.

Width of spectral lines excited by electron collision. U. MENNICKE (Z. Physik, 1930, 63, 584—589).—The effect of alteration of current density and excitation potential on the width of spectral lines excited by electron collision was investigated. For the mercury resonance line 2537 Å. the width did not change within a velocity range of the excitation potential up to 600 volts, and for current densities up to 5 amp./sq. cm. It is to be expected that other lines will behave similarly. The facts thus displayed were used in the construction of a primary light source for resonance radiation experiments.

A. J. MEE.

Spectra in the extreme ultra-violet. E. EKERFORS (Physikal. Z., 1930, 31, 737—738).—A vacuum grating spectrograph is described; the grating was ruled on glass with 1183 lines per mm. The use of glass gratings in the extreme ultra-violet is discussed. The spectra of calcium, aluminium between 75 and 160 Å., oxygen at 834 Å., and the PP' groups of C III at 1175 Å. have been experimentally determined and the results are discussed.

W. R. ANGUS.

Improved quartz spectrograph. C. LEISS (Z. Physik, 1930, 63, 287—290).—A quartz spectrograph is described in which the wave-length scale can be projected by means of an objective directly on to the plate of the spectrograph and thus photographed, thereby eliminating the present unsatisfactory method of placing the scale in direct contact with the plate before photographing it. The new method can also be applied to the quantitative observation of the fluorescence spectrum on a uranium-glass plate.

H. A. JAHN.

Influence of self-absorption on measurements of the intensities of spectral lines. R. MINKOWSKI (Z. Physik, 1930, 63, 188—197).—Theoretical. It is shown that the effect of self-absorption on the relative intensity of emission lines in gases cannot be eliminated by working at low pressures and with thin layers of the gas as is commonly supposed, since the intensity of the emission and the amount of self-absorption are related. In the case of flames and discharge tubes it is shown that the amount of self-absorption depends primarily on the width of the emission line, and the necessary relation between the strength of the line and its width for negligible effect of self-absorption is deduced. It is deduced that at the Bunsen flame temperature 5300 Å., and at the oxyhydrogen flame temperature 4400 Å., are the limits of wave-length below which the true intensity ratio cannot be obtained. The work of Füchtbauer and Wolff (this vol., 3) on the intensity ratio of the second doublet of the principal series of caesium is criticised. The difficulty of measuring the true intensity ratio with discharges at very low pressure is mentioned; the more rational way consists in measurements at higher pressures, the self-absorption being measured and corrected for.

H. A. JAHN.

Incomplete Paschen-Back effect. J. B. GREEN (Physical Rev., 1930, [ii], 36, 157—160).—Theoretical. Darwin's method for the calculation of the Zeeman effect (cf. A., 1927, 707) is applied to the marked discrepancy between the old quantum theory and

experiment for the copper  $2P^2D$  and the magnesium and beryllium  $3P^3S$  multiplets, and the calculated positions and intensities of lines are in good agreement with experiment. The distorted Zeeman patterns of  $3P^3D$  of magnesium and  $2P^2D$  of sodium are attributed to the action of the magnetic field on  $3P$  and  $2P$  separations. N. M. BLIGH.

**Interpretation of molecular spectra. V. Excited levels of molecules with two like nuclei ( $H_2$ ,  $He_2$ ,  $Li_2$ ,  $N_2^+$ ,  $N_2$ ...).** F. HUND (Z. Physik, 1930, 63, 719—751).—Diatomic molecular ground levels may be specified by the Hund-Mullikan or Lennard-Jones method, but excited levels are best determined by a combination of the two. The multiplicity of terms for small nuclear distances is determined from Mullikan's scheme, and for large nuclear distances from Lennard-Jones' scheme. Rules are given for interpolating between these limits. A first approximation to the actual terms of a diatomic molecule with like nuclei is obtained from a study of an optical electron moving in a cylindrically symmetrical field superposed on the field due to the ground state of the molecular ion. The conceptions of chemical binding and of promoted electrons fall naturally into this scheme. Electron terms deduced for  $H_2$ ,  $He_2$ ,  $Li_2$ , and  $N_2^+$  correspond with empirical values. Nitrogen molecular levels are only partly interpreted. A. B. D. CASSIE.

**Resonance ( $B-A$ ) band system of the hydrogen molecule.** H. H. HYMAN (Physical Rev., 1930, [ii], 36, 187—206).—A vacuum spectrograph is described. The hydrogen bands in the extreme ultra-violet were photographed; frequencies and intensities, and quantum assignments of lines in 68 bands, are tabulated and discussed. The ionisation potential of  $H_2$  is 15.34 volts. The value of  $B_1$  is in agreement with that calculated by Birge and Jeppesen from the Raman effect (cf. this vol., 509), but that for  $B_0$  is 0.27% lower, pointing to an irregularity in the moment of inertia of hydrogen in the  $v=0$  state of the normal electronic level. N. M. BLIGH.

**Glow discharge in hydrogen.** R. D. RUSK (Phil. Mag., 1930, [vii], 10, 244—248).—Measurements of the space potential in a hydrogen discharge tube were extended to the region behind the hot filament away from the anode. It is concluded from the results that not only the glow is due to resonance of neutral molecules and excited by radiation, as has been suggested, but also that electrons accelerated into the region concerned, by producing ionisation and excitation, are probably more responsible for the effect. W. GOOD.

**Intensities in the spectra of diatomic molecules in uncoupling of the electronic orbital impulses.** R. DE L. KRONIG and Y. FUJIOKA (Z. Physik, 1930, 63, 168—174).—Theoretical. The intensity relations in the spectra of diatomic molecules are deduced by a perturbation method for the cases where the orbital impulse of the electrons is no longer quantised along the line joining the two nuclei owing to the rapid rotation of the molecule (cf. Weizel, A., 1929, 363). The calculations are made for the special case that

arises in the theoretical treatment of the observed  $He_2$  bands (cf. following abstract). H. A. JAHN.

**Intensities in  $He_2$  bands as affected by uncoupling of the orbital impulse of the electrons.** Y. FUJIOKA (Z. Physik, 1930, 63, 175—187).—A quantitative investigation of the intensities in a series of bands belonging to the singlet and triplet systems of  $He_2$  is described, and the wave-lengths and intensities of the observed transitions are tabulated. By means of the theory of Kronig and Fujioka (see preceding abstract) the relative intensities of the  $P$ ,  $Q$ , and  $R$  branches of the different bands are calculated, and plotted against the rotational quantum number  $K$ . The curves obtained by consideration of the perturbation arising from the uncoupling of the electronic orbital impulses in the initial state are shown to be in good agreement with the experimental values. H. A. JAHN.

**Lithium-like spectra of carbon, nitrogen, and oxygen, C IV, N V, and O VI.** B. EDLÉN and A. ERICSON (Z. Physik, 1930, 64, 64—74).—The spectra of carbon, nitrogen, and oxygen have been examined in the extreme ultra-violet, using the vacuum spark method. The series of lithium-like doublets was obtained. For the fundamental term  $2^2S_{0.5}$ , for the different elements, the following values were obtained: C IV, 520, 220; N V, 789, 591; O VI, 1,114, 206. These correspond with ionisation potentials of 64.19, 97.428, and 137.482 volts, respectively. The term values for the complete series for Li I, Be II, B III, C IV, N V, and O VI are compared. A. J. MEE.

**Band spectrum of ozone in the visible and photographic infra-red.** O. R. WULF (Proc. Nat. Acad. Sci., 1930, 16, 507—511; cf. Colange, A., 1927, 808).—The absorption of ozone was photographed in a tube 33 m. long, using light from a carbon arc. Dark diffuse absorption strips extend from 6100 to 4300 Å. Assuming the strong peak at 9.7  $\mu$  found by Ladenburg and Lehmann (A., 1906, ii, 509) as a fundamental, the bands at 4.7 and 3.5  $\mu$  are first and second overtones. The dissociation of  $O_3$  into normal  $O_2$  and normal O requires 1.3 volts. A series of 10 bands in the near infra-red was found. The bands are interpreted, and the diffuseness and influence of temperature on the absorption are discussed. N. M. BLIGH.

**Red radiation of oxygen in the night sky.** L. A. SOMMER (Naturwiss., 1930, 18, 752).—It has been shown on the grounds of quantum theory that the transitions of O I,  $2p^3P_{210} \rightarrow 2p^1D_2$  and  $2p^3P_{210} \rightarrow 2p^1S_0$ , should give rise respectively to lines at approximately  $\lambda$  6380 and 2970 Å. Both lines have been found by previous investigators. Examination of the red radiation in the night sky has revealed two lines at 6300 and 6363 Å. which are due respectively to the transitions  $2p^3P_2 \rightarrow 2p^1D_2$  and  $2p^3P_1 \rightarrow 2p^1D_2$  of O I. These lines must be interpreted as the radiation of a quadrupole moment. By the detection of this first combination between singlet and triplet terms it is possible to link up the singlet system of O I energetically with the already known system of triplets and quintuplets. The interpretation of the

green auroral lines is confirmed and their excitation potential is given as 4.17 volts. The convergence position of the Runge-Lyman bands occurs at 7.05 volts and the excitation potential of the  $2p^1D_2$  term is 1.96 volts; therefore the dissociation energy of the oxygen molecule may be determined from optical data and amounts to 5.09 volts. W. R. ANGUS.

**Oxygen spectrum, O I.** F. PASCHEN (Naturwiss., 1930, 18, 752).—The use of a three-prism spectrometer has revealed lines in the O I spectrum at 6300 and 6364 Å. corresponding with the transitions  $2p^3P_2 \rightarrow 2p^1D_2$  and  $2p^3P_1 \rightarrow 2p^1D_2$ , respectively, and the corresponding wave-numbers are in complete agreement with the values calculated from the data of Frerichs in the Schumann region. A diffuse line corresponding with the transition  $2p^3P_0 \rightarrow 2p^1D_2$  has been observed at 6391 Å. These results agree with the values found by Sommer from observations of the red radiation in the night sky (preceding abstract). Certain stellar nebulae exhibit these lines also. W. R. ANGUS.

**Zeeman effect in neon.** K. MURAKAWA and T. IWAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 13, 283—291).—The Zeeman effect in neon has been examined and the  $g$  values of seven of the twelve  $s'$ ,  $s''$ ,  $d$ , and  $d'$  (Paschen's notation) terms, hitherto unknown, have been determined; 32 other terms were redetermined with satisfactory agreement with previous results. Those of  $s$  and  $p$  terms appear to be independent of the field intensity, but not those of  $d$  terms, and the  $g$  values for them have been extrapolated to zero field. A term scheme and photographs of the Zeeman effect from  $\lambda$  5080 to  $\lambda$  8377 for various intensities of field are given. The Paschen-Back effect was clear for a field of 10,000 gauss in the triplet  $p^3S-d^3P$ . C. A. SILBERRAD.

**Predissociation of the phosphorus ( $P_2$ ) molecule.** G. HERZBERG (Nature, 1930, 126, 239—240).—Certain peculiarities of the emission band spectra of the phosphorus molecule indicate a predissociation of the  $P_2$  molecule similar to that obtained with sulphur. L. S. THEOBALD.

**Intensity relation of resonance and intercombination lines of calcium.** W. BLEEKER (Z. Physik, 1930, 63, 760—761).—The intensity relation of resonance and intercombination lines was determined with the aid of filters. Reversal effects were eliminated by varying the current intensity and the salt concentration. The ratio of the intensity of the 4227 Å. resonance line to the 6573 Å. intercombination line tends towards 41:1 for infinitely small currents and concentrations. A. B. D. CASSIE.

**Resonance radiation of manganese vapour.** J. FRIDRICHSON (Z. Physik, 1930, 64, 43—47).—The fluorescence in saturated manganese vapour at 700—900° was examined, using the light of the manganese spark for excitation. The triplets  $1S-2P$  and  $1S-2P'$  of the manganese spectrum correspond with the resonance lines. With rise of temperature, and consequently less dense vapour, the triplet  $1S-2P'$  becomes much more intense, whereas at a lower temperature only the triplet  $1S-2P$  is found. The resonance lines found are in agreement with Catalan's

analysis of the manganese spectrum, and indicate that  $1S$  is the lowest state of the manganese atom.

A. J. MEE.

**Spark spectrum of cobalt, Co II.** J. H. FINDLAY (Physical Rev., 1930, [ii], 36, 5—12).—The analysis of Meggers (cf. A., 1928, 807) is extended with the aid of the Zeeman effect, and full results are tabulated. The former classification of the  $^5F$  and  $^5D^1$  terms should be interchanged except for  $^5F_5$ ; the new  $^5F^5F^0$  and  $^5F^5D^0$  multiplets show irregular intensities. The strongest lines in these multiplets are respectively  $^5F_5^5F^0_{n-1}$  and  $^5F_5^5D^0_n$ . The former  $^3D$  terms should be  $d^7s^5P$  and the  $^3P$ ,  $^3D^1$ , and  $^3F$  should be partly  $d^7p^5P^0$  and  $^5D^0$ . Additional terms  $d^7s^3F$ ,  $d^7p^3D^0$ ,  $^3F^0$ ,  $^3G^0$ ,  $^5S^0$ ,  $^5P^0$ ,  $^5D^0$ , and the lowest terms  $d^8s^3F$  have been found. The limit of the  $4s^2F_5$  series gives, with Russell's correction, an ionisation potential of 16.7 and 17.1 volts from  $3d^74s$  to  $3d^7$  and  $3d^8$  to  $3d^7$ , respectively, in agreement with Russell's prediction (cf. A., 1928, 682).

N. M. BLIGH.

**Variations in relative intensities in the resonance spectrum of selenium.** L. NATANSON (Compt. rend., 1930, 191, 294—296).—The intensities of the components of five doublets in a resonance series of  $Se_2$  molecules at 600°, excited by the mercury line 4047 Å., have been measured. With one exception attributed to strong absorption, increased pressure causes the intensity of the component of greater wave-length to increase relatively to that of lesser, similarly to, but to a smaller degree than, with sulphur (cf. Swings, this vol., 650). Other relative variations in intensities observed seem explicable only by the dependence on pressure of the probabilities of transitions between different levels of rotation as well as of vibration. Comparison of the results obtained with varying thickness of vapour indicates some analogy between the distribution of vibration states and that of velocities of thermal agitation.

C. A. SILBERRAD.

**Spark spectra of silver and palladium (Ag II and Pd II)—an extension.** H. A. BLAIR (Physical Rev., 1930, [ii], 36, 173—186; cf. Shenstone, A., 1928, 450, 930).—An unsuccessful attempt was made to excite the  $4f$  electron spectrum of Ag II in the Schüler tube with helium. New terms and about 20 new lines are tabulated. The  $4d^86s$  and  $5d$  configurations of Pd II were extended by about 40 terms, using the same method. A complete list of lines arising from the high levels is given.

N. M. BLIGH.

**Structure of the absorption bands of tellurium.** A. PRZEBORSKI (Z. Physik, 1930, 63, 280—286).—The fine structure of the absorption bands of tellurium vapour is investigated, and two series of lines in the regions 5393—5406 Å. and 5357—5368 Å. have been measured and their convergence has been determined. The moment of inertia of the tellurium molecule is thereby calculated to be  $J = 8.63 \times 10^{-38}$  g.-cm.<sup>2</sup> and the distance between the atoms as  $2.87 \times 10^{-8}$  cm., in agreement with the distance calculated from X-ray investigation of solid tellurium. This distance and the value of  $J$  differ little from the values found for the iodine molecule by Kratzer and Sudholt (A., 1925, ii, 839).

H. A. JAHN.

**Transition probabilities in the two first doublets of the principal series of caesium.** R. MINKOWSKI and W. MÜHLENBRUCH (Z. Physik, 1930, 63, 198—209).—From measurements of the magnetic rotation of the plane of polarisation near the lines the ratio of the intensities of the lines in the first doublet of the caesium principal series was found to be  $2.1 \pm 0.2$ , and in the second doublet  $4.27 \pm 0.12$ . The ratio of the total intensity of the first doublet to that of the second was  $69 \pm 10$ . The absolute values of the intensities for the first doublet were 0.32 ( $1S-2P_{1/2}$ ) and 0.66 ( $1S-2P_{3/2}$ ) and for the second doublet 0.00269 ( $1S-3P_{1/2}$ ) and 0.0115 ( $1S-3P_{3/2}$ ). The measurements were made at a series of temperatures from  $374.2^\circ$  to  $592.4^\circ$  Abs. in the saturated vapour in a vacuum. The optical results agree with the vapour-pressure measurements of Kröner and Hackspill made at higher temperatures, and from these results a value of  $l = (18,200 - 2.86T)$  g.-cal. is deduced for the heat of vaporisation of caesium within the temperature range  $455-589^\circ$  Abs.

H. A. JAHN.

**Spectrum of the tungsten mercury arc.** W. E. FORSYTHE and M. A. EASLEY (Physical Rev., 1930, [ii], 36, 150—151).—The behaviour of the absorption bands for the region  $4000-2100 \text{ \AA.}$  when the pressure of the mercury vapour is increased by external heating in a mercury arc lamp between tungsten electrodes is described. The absorption spectrum is compared with that of mercury in a separate quartz absorption cell.

N. M. BLIGH.

**Measurement of capacity for reflexion of glowing tungsten in the ultra-violet part of the spectrum.** E. SPILLER (Z. Physik, 1930, 64, 39—42).—The relative intensities of emission at different wave-lengths from a lamp with a tungsten filament heated to  $2873^\circ$  Abs. were found, using a special microphotometer. The emission departs from black body radiation. The energy distribution was measured over a wave-length range of  $400-340 \mu\mu$ . The values of the emission coefficient for wave-lengths from  $436$  to  $270 \mu\mu$  for a filament at  $2100^\circ$  Abs. are tabulated.

A. J. MEE.

**Structure of the band from 2482.07 to 2476.06 Å. in the mercury spectrum.** J. BRZOWSKA (Z. Physik, 1930, 63, 577—583).—The emission spectrum of mercury in the range  $2482-2449 \text{ \AA.}$  has been investigated with greater dispersion than before. Two new bands discovered at wave-lengths  $2449.5$  and  $2458.0 \text{ \AA.}$  form a group with previously discovered bands. The bands from  $2482.07$  to  $2476.06 \text{ \AA.}$  were fully resolved and the wave-lengths of the single lines accurately measured. The bands appear to be the null branch of a rotation band.

A. J. MEE.

**Arc spectrum of mercury Hg I.** F. PASCHEN (Ann. Physik, 1930, [v], 6, 47—49).—The arc spectrum of mercury has been examined, but no proof of the presence of a new term  $3^3P_{1,0}$ , which would be required by recent work on the subject, could be found.

A. J. MEE.

**Absorption and collision broadening of the mercury resonance line.** M. W. ZEMANSKY (Physical Rev., 1930, [ii], 36, 219—238).—The frequency distribution of the radiation from a mercury

resonance lamp, the absorption coefficient in mercury vapour of the resonance line, and ratio of emission to absorption line breadth are investigated theoretically, and results compared with experimental data. A theoretical expression is obtained for the absorption coefficient when collision broadening is superimposed on Doppler broadening, and is evaluated for different values of the frequency, Lorentz collision breadth, and Doppler breadth. From experimental values of the absorption of mercury vapour in the presence of a number of gases the Lorentz collision breadth is found as a function of the pressure of each gas, and, when plotted against pressure, gives the effective broadening radius of each molecule, which is found to be proportional to the square root of the molecular diamagnetic susceptibility. Hence, from the Langevin theory, the effective broadening area of a molecule varies as the product of the number of outer electrons and the mean square radius of all the electronic orbits.

N. M. BLIGH.

**Spectra of doubly- and trebly-ionised lead.** S. SMITH (Physical Rev., 1930, [ii], 36, 1—4; cf. A., 1929, 1119; Rao, A., 1928, 1067).—Seventeen new lines are classified in the spectrum of Pb III arising from three new singlet terms,  $6s7s^1S_0$ ,  $6s7p^1P_1$ , and  $6s7d^1D_2$ . Certain discrepancies between the classification of terms and that of Rao (cf. this vol., 390) are discussed. Classifications of lines in the spectrum of Pb IV (cf. Carroll, A., 1926, 214; Rao, this vol., 511) are discussed.

N. M. BLIGH.

**Search for the source of dielectric polarisation.** R. D. BENNETT (Physical Rev., 1930, [ii], 36, 65—70; cf. Hengstenberg, this vol., 19).—A theory of the distortion of a polar cubic lattice by electric stress is derived, and the effect of the distortion on the intensity of X-ray reflexion is calculated. Measurements of change in intensity of reflected X-rays in the 4th and 5th orders for rock salt and the 5th order for sylvine indicate that the polarisation is probably not due to motion of the ions as units.

N. M. BLIGH.

**Breadth of Compton modified line.** J. W. M. DU MOND (Physical Rev., 1930, [ii], 36, 146—147).—Previous investigations on the Compton line from molybdenum  $K\alpha_1, K\alpha_2$  scattered by beryllium (cf. A., 1929, 747) are considered in relation to the work of Ross and Clark on the shifted line in the Compton effect for antimony  $K\alpha_1, K\alpha_2$  scattered from beryllium and results in the two cases are shown to be consistent.

N. M. BLIGH.

**X-Ray spectra and chemical combination.** G. B. DEODIAR (Nature, 1930, 126, 205).—The line of wave-length  $5043 \text{ X}$  (probably the  $K\beta_3$  line) is emitted by certain sulphur compounds but not by pure sulphur. The sulphates of the alkali metals, of silver and mercury, the sulphides of sodium, potassium, strontium, barium, and cadmium give an intense  $K\beta_3$  line, but not those of copper, silver, magnesium, zinc, mercury, lead, and molybdenum. The existence of a new type of X-ray line arising from transitions within a molecule is suggested.

L. S. THEOBALD.

**Simultaneous electronic transitions in X-ray spectra.** M. WOLF (Nature, 1930, 126, 205).—A fine structure of the X-ray absorption edges of zinc

has been observed when zinc foil was used as absorbing screen (cf. Suckiehi, *ibid.*, 125, 509).

L. S. THEOBALD.

**Fine structure of the  $K$ -radiation of the lighter elements.** L. Y. FAUST (Physical Rev., 1930, [ii], 36, 161—172; cf. Bazzoni and others, A., 1929, 630).—Using an improved form of Weatherby's vacuum spectrograph (cf. A., 1929, 123) and a line grating on glass, photographs were obtained of soft  $X$ -radiations from beryllium, boron, oxygen, carbon, and tungsten. On analysis with a thermo-electric densitometer these elements were found, except for oxygen and tungsten, to contain several components, the relative intensities depending on the respective exciting energies. Densitometer curves and wave-lengths are given. Wave-lengths of the  $K\alpha$  lines are: for oxygen 23.7, boron 69.3, carbon 45.3 Å., and for beryllium the radiation covered 15 Å., with maxima at 107.2, 113.2, and 118.7 Å. The complex structure is considered to be partly a true fine structure, and partly a system of satellites due to interaction with associated dissimilar atoms.

N. M. BLIGH.

#### Absorption of $X$ -rays in gases and vapours.

**I. Gases.** J. A. CROWTHER and L. H. H. ORTON (Phil. Mag., 1930, [vii], 10, 329—342).—The absorption coefficients of monochromatic copper radiation ( $K\alpha$ ) in air, nitrogen, oxygen, carbon dioxide, ethylene, and hydrogen sulphide were measured by means of an ionisation balance method which eliminates errors due to fluctuations in intensity of the radiation and in sensitivity of the electroscope and renders slight defects in insulation of little account. The ionisation produced in the various gases was compared with that of air under the same conditions and the relative total ionisation,  $T$ , produced by the complete absorption of the radiation calculated. As a measure of the relative average energy spent in producing a pair of ions in the different gases,  $1/T$  is taken and is compared with the ionisation potential,  $P$ , the comparison revealing direct proportionality of these two magnitudes except with nitrogen, for which the product  $PT$  is greater by about 15% than the mean value for the other gases investigated.

W. GOOD.

#### Optics of reflexion of $X$ -rays in crystals. III.

**Depth of penetration, mosaic structure, line width, resolution, and blackening distribution of the spectrum.** H. SEEMANN (Ann. Physik, 1930, [v], 6, 1—46).—The measurable widening of spectral lines obtained by reflexion of  $X$ -rays from crystals depends on the type of crystal, its degree of perfection, and the depth of penetration of the rays. A very well-grown specimen of rock-salt used in the camera method for the  $W$ — $K$  lines, with a half-divergence angle of only 11", showed line widening on one side for a penetration of about 1 mm. in the first order spectrum. A still better specimen of rock-salt with still smaller divergence showed a widening of only 0.5 mm. in consequence of penetration. A calcite crystal, the camera exposure of which was excellent in sharpness, showed a line widening of about 0.1 mm. Calculation of the penetration depth for rock-salt gives to a first approximation the same value as that obtained experimentally if the rock-salt is supposed to be a regular crystallite. Errors in the use of the

different methods for obtaining spectra by the reflexion of  $X$ -rays from crystals are discussed. The camera method developed is free from these, and can be used as a criterion for the perfection of a crystal.

A. J. MER.

**Calculation of the Röntgen  $K$  terms of the lightest elements and of the rare gases from "optical" ionisation potentials.** W. BRAUNBEK (Z. Physik, 1930, 63, 154—167).—The  $K$  terms in the  $X$ -ray spectra of helium, lithium, beryllium, boron, and carbon are calculated from the ionisation potentials of the corresponding series  $\text{He}$ ,  $\text{Li}^+$ ,  $\text{Be}^{+2}$ ,  $\text{B}^{+3}$ ,  $\text{C}^{+4}$  by subtraction of the outer screening terms. The ionisation potentials are calculated from the formula of Hylleraas derived from wave mechanics, whilst the screening term, *e.g.*, for lithium, is calculated approximately from classical considerations of the change of the potential energy of the  $L$  electron due to the change in the effective nuclear charge on the removal of the  $K$  electron. This potential energy is derived from the ionisation potential of a lithium atom. For the other elements the mutual action of the  $L$  electrons has to be considered. The values obtained agree with the experimental results of Södermann (A., 1929, 366). The same method is applied to the rare gases, the mutual action of the outer electrons being calculated from the inner screening constant  $s$  of Sommerfeld derived from relativistic doublet terms;  $s$  can have two values for the  $M$  level and three for the  $N$ , and it was found that the smaller values of  $s$  gave results agreeing best with the experimental values. The difficulties of extending the same method to the calculation of  $L$  and  $M$  terms are discussed.

H. A. JAHN.

#### Measurement of reflecting power for $X$ -rays of long wave-length.

M. A. VALOUCH (J. Phys. Radium, 1930, [vii], 1, 261—270; cf. A., 1929, 1120).—The rays emitted by a special tube are reflected by a plane mirror of the substance under investigation, and the intensities of the incident and reflected rays measured by means of a specially-constructed ionisation chamber. Curves representing reflecting power as a function of the angle of incidence are thus obtained. The classical theory gives an expression of the reflecting power as a function of the limiting angle which depends on two parameters, one of which is connected with the index of refraction and the other with the coefficient of absorption. Using the  $K$  radiation of carbon, measurements in agreement with theory have been obtained with flint glass and duralumin.

L. S. THEOBALD.

**Spectroscopy of ultra-soft  $X$ -rays. I.** M. SIEGBAHN and T. MAGNUSSEN (Z. Physik, 1930, 62, 439). K. F. SCHOTZKY (*ibid.*, 63, 864).—Polomical.

A. B. D. CASSIE.

**Loss of material from the cathode of a metallic arc.** R. SEELIGER and H. WULFHEKEL (Ann. Physik, 1930, [v], 6, 87—104).—Apparatus for the determination of the amount of loss of material from a cathode of a metallic arc and its dependence on current strength, thickness of cathode, length of arc, and gas pressure is described. The metals used were silver, copper, and iron. The results are discussed with reference to the physical nature of the cathode and to energy considerations.

A. J. MEE.

**Definition of saturation.** C. SCHAEFER and H. PESE (*Physikal. Z.*, 1930, 31, 720—737).—Different theories of saturation are discussed and the origin of probable errors is considered. The work of Seitz is discussed, together with luminosity and opacity. The conception of saturation as a sensation is also dealt with.

W. R. ANGUS.

**Second ionisation potential in potassium vapour.** A. L. HUGHES and C. M. VAN ATTA (*Physical Rev.*, 1930, [ii], 36, 214—218; cf. Lawrence and Edlefsen, *A.*, 1929, 1356).—In order to find the possible presence of a peak or discontinuity in the curve for ionisation by electron impact corresponding with that in the photo-ionisation curve, the ionisation in potassium vapour was investigated by Hertz's method of neutralisation of space charge by positive ions. The ionisation curve indicated a second ionisation potential at  $0.97 \pm 0.05$  volt above the first one corresponding with the series limit, i.e., at  $4.32 + 0.97 = 5.29$  volts. For mercury vapour, the presence of Lawrence's ultra-ionisation potentials (cf. *A.*, 1927, 85) was found, together with three new ones at 10.88, 11.40, and 12.76 volts.

N. M. BLIGH.

**Method of enhancing the sensitiveness of alkali metal photo-electric cells.** A. R. OLPIN (*Physical Rev.*, 1930, [ii], 36, 251—295).—Applying the fact that photo-electric emission from potassium is increased by a non-conducting hydride surface film, the cells were sensitised by introducing on to the metal surface small amounts of various inorganic dielectrics, organic compounds, or organic dyes. The increased electron emission is mainly due to increased response to red and infra-red light. Spectral response curves, showing photo-electric current against wave-length of exciting light, are similar for all cells using the same metal as cathode, and differ from the curves for pure metal by the appearance of a new selective maximum at lower frequencies, separated from the regular maximum by the frequency of a characteristic line in the vibration-rotation spectrum of the dielectric molecules. The long-wave limit shifts by an amount agreeing with the separation of the maxima. Stopping potentials were obtained for electrons, liberated by monochromatic light, from a sodium cathode before and after treatment with sulphur vapour and air. For light of wave-length range 3500—8000 Å. the electron retarding potentials were found to vary linearly with the frequency of the light, verifying Einstein's photo-electric equation for composite surfaces, and precluding an explanation on a Raman shift basis. The slope of the straight-line graph of this relationship gives  $6.541 \times 10^{-27}$  for Planck's constant; untreated sodium gives a similar value. The apparent stopping potentials, or voltages at which the photo-electric currents become zero, are the same before and after the sulphur and air treatment. The voltage at which the current just saturates is always greater after treatment than before, and is a measure of the change in contact potential of the cathode due to the presence of the sulphur and air. The application of the Lindemann formula for the frequency of the selective photo-electric maximum is discussed. Reference is made to apparently analogous

phenomena in photo-electricity, photography, fluorescence, and absorption.

N. M. BLIGH.

**Periodic system. III. Relation between ionising potentials and ionic potentials.** G. H. CARTLEDGE (*J. Amer. Chem. Soc.*, 1930, 52, 3076—3083; cf. *A.*, 1929, 269).—From considerations of atomic models it is shown that the ratio  $\Delta_v/\phi_v$  gives a measure of the ionic polarisability;  $\phi_v$  is the ionic potential (volts) and  $\Delta_v = \phi_v - 2V$ , where  $V$  is the ionisation potential referred to the production of ions of the inert-gas type. The ionic polarisability by light or by electrons varies systematically with  $\Delta_v/\phi_v$ . This ratio for alkali ions decreases greatly in passing from lithium to caesium, corresponding with the large increase in deformability. It is computed by means of the closely linear relationships between  $\Delta_v$  and  $\phi_v$  for the alkali ions and the alkaline-earth ions that the valency electron comes within the crystal radius with ions 0.3 and 0.2 Å. larger than the caesium and barium ions, respectively.

J. G. A. GRIFFITHS.

**Measurement of slow electrons by means of a point [Geiger] counter.** J. HORNOSTEL (*Ann. Physik*, 1930, [v], 6, 991—1016).—An arrangement in which the slow electrons are accelerated in a given electric field in order to pass through the foil of the Geiger counter is described, the divergence of the electron stream being prevented by subjecting it to a longitudinal magnetic field. The sensitivity of the method is thereby increased. The electron emission from a thin layer of magnesium on celluloid and of celluloid separately is analysed by an opposing electric field, and sudden changes in the velocity-intensity curve are shown to be due to electrons arising from the Auger effect. A method of analysing the electrons with a longitudinal magnetic field and a transverse electric field is described.

H. A. JAHN.

**Electron exchange between ionised and neutral types.** H. KALLMANN and B. ROSEN (*Naturwiss.*, 1930, 18, 448—452).—The general theory of reactions between neutral and ionised molecules is discussed and experiments on the absorption of ions by gases are described. This absorption, which consists in the transference of an electron from a slowly-moving gas molecule to a relatively rapidly-moving ion, can occur only when the neutralisation energy of the ion is equal to or greater than the ionisation energy of the gas. Any ion is most strongly absorbed by the gas from which it is derived, and in addition the absorption is markedly specific. Figures are given for the relative degrees of absorption of various ions by gases. The charged nitrogen molecule is absorbed by nitrogen to a much greater extent than is the charged nitrogen atom, and doubly-charged ions such as those of argon and mercury are less strongly absorbed than ions carrying a single charge, probably because such an ion is nearly always completely discharged on collision; very rarely is only one electron exchanged between a doubly-charged ion and a neutral molecule.

H. F. GILLBE.

**Deflexion of electrons by passive iron.** I. E. RUPP and E. SCHMID (*Naturwiss.*, 1930, 18, 459—461).—The nature of the passive coating on iron has been studied by measurement of the reflexion of a



stream of electrons from the surface at different initial velocities and angles of incidence. The passive surface is characterised by sharp maxima in the reflexion/velocity curve, which indicate the presence of a lattice spacing of 3.4 Å. By heating the passive surface to 300–400° the reflexion diagram reverts to that of the non-passive metal except that there is present a maximum corresponding with ferric oxide. Experiments with oxidised surfaces indicate that the phenomenon of passivity is confined entirely to the surface layer of atoms.

H. F. GILLBE.

**Velocity loss through quantum addition of slow electrons in diluted gases.** H. LÖHNER (Ann. Physik, 1930, [v], 6, 50–86).—Lenard's opposing potential method is used following the procedure of Åkesson for the determination of critical potentials and collision sharing. Two forms of apparatus with quite different ray definitions were constructed. Both gave very similar gas curves in all the determinations which could be used to find critical potentials. The values of these for hydrogen, nitrogen, and carbon dioxide agree with those previously obtained by Åkesson. The value obtained for argon agrees with that arrived at by other electrical and optical determinations. From the heights of the steps in the curves for both apparatus, the probability of a velocity loss without simultaneous diversion was calculated. The form of the sharing function and its tendency to increase are discussed in connexion with the effective cross-section curve.

A. J. MEE.

**Electron affinity of the hydrogen atom according to wave mechanics.** E. A. HYLLEAAS (Z. Physik, 1930, 63, 291–292).—In the previous paper (this vol., 518) only Kasarnovski's early negative value for  $E_H$  was quoted; it is now pointed out that the later positive value  $E_H = 0 \pm 15$  of Kasarnovski (A., 1928, 595) is not in disagreement with the value  $E_H = 16$  kg.-cal./mol. found by the author. The result is also compared with the value  $E = 17$  kg.-cal./mol. calculated by Bethe (this vol., 132).

H. A. JAHN.

**Effect of small angle scattering on the electron absorption coefficient.** M. C. GREEN (Physical Rev., 1930, [ii], 36, 239–247).—The scattering of electrons by gas molecules was studied indirectly by measuring electron absorption coefficients in argon, helium, hydrogen, and mercury vapour at accelerating potentials from 11 to 196 volts, using an apparatus containing a Faraday cylinder of variable aperture, the radius of which varied from one hundredth to one tenth of the path length. No consistent variation of the absorption coefficient with opening was found, although relatively large variations are predicted theoretically from an inverse square law. The results obtained are in agreement with calculations based on the Sommerfeld, or uniform scattering, law.

N. M. BLIGH.

**Capture of electrons by protons.** H. MARK and K. WOLF (Naturwiss., 1930, 18, 753).—A method of determining by canal rays the effective cross-section of protons against electrons as a function of the relative energy is described; the upper limit for the effective cross-section has been calculated to be less than  $10^{-9}$  cm.<sup>2</sup> It is hoped to obtain greater accuracy

by means of photographic and ionometric methods which are being developed.

W. R. ANGUS.

**Annihilation of electrons and protons.** P. A. M. DIRAC (Proc. Camb. Phil. Soc., 1930, 26, 361–375).—Theoretical.

**Exchange phenomena in the Thomas atom.** P. A. M. DIRAC (Proc. Camb. Phil. Soc., 1930, 26, 376–385).—A theoretical justification of Thomas' atomic model is obtained. The equation deduced governing the boundary between the occupied and unoccupied phase space shows an extra term which may be considered to represent the exchange phenomena.

W. GOOD.

**Theory of extraction of electrons from metals by positive ions and metastable atoms.** H. S. W. MASSEY (Proc. Camb. Phil. Soc., 1930, 26, 386–401).—The theory is developed in the light of Sommerfeld's theory of metals and the analytical methods of wave mechanics.

W. GOOD.

**Possible electron properties.** R. D. KLEEMAN (Z. Physik, 1930, 63, 859–863).—Some properties of the electron and proton, particularly the conception of inherent (Coulomb) and exchange energy, may be described without special quantum-mechanical hypotheses.

A. B. D. CASSIE.

**Recombination of ions in argon, nitrogen, and hydrogen.** O. LURN (Physical Rev., 1930, [ii], 36, 24–34; cf. this vol., 974).—Using the method previously described (cf. Marshall, A., 1929, 1210) the coefficient of recombination for positive ions and electrons in argon, nitrogen, and hydrogen and for positive and negative ions in hydrogen was measured. Free electrons are known to exist in the first three gases. Results are shown graphically and the probable mechanism of recombination is discussed. Absolute values of the coefficient  $\times 10^6$  for air, oxygen, argon, nitrogen, and hydrogen are  $1.4 \pm 0.1$ ,  $1.5 \pm 0.1$ ,  $1.2 \pm 0.1$ ,  $1.2 \pm 0.1$ , and  $0.32 \pm 0.05$ , respectively.

N. M. BLIGH.

**Mobilities of ions in dry and moist air.** J. ZELENY (Physical Rev., 1930, [ii], 36, 35–43). Using the method previously described (cf. A., 1929, 1122) the distribution of mobilities of aged ions in dry air has been determined, and the values for moist air have been re-measured. In dry air the positive and negative ions each consist of two main groups. The absolute values of the peak mobilities of the most numerous main group in very dry air, air dried by calcium chloride, and air containing 2 mg. of water per litre were 2.45, 2.37, and 2.08 cm./sec. for negative ions, and 1.05, 1.10, and 1.36 cm./sec. for positive ions, respectively, at 76 cm. and 20°. It is suggested that aged ions in air consist of molecular clusters the structure of which is affected by the presence of water molecules. Explanations of the results obtained are discussed.

N. M. BLIGH.

**Mobility of Na<sup>+</sup> ions in hydrogen.** L. B. LOEB (Physical Rev., 1930, [ii], 36, 152–153).—In order to determine the mobilities of a type of initially ionised carrier which would with difficulty alter its charge, the mobilities of Na<sup>+</sup> ions in purified hydrogen were measured. Results indicate that the ions

within  $2 \times 10^{-5}$  sec. after liberation have a mobility a little more than double that of the normal ions.

N. M. BUGH.

**Interaction between excited and unexcited hydrogen atoms at large distances.** E. C. KEMBLE and F. F. RIEKE (Physical Rev., 1930, [ii], 36, 153—154).—The calculations of Kemble and Zener (cf. A., 1929, 623) on the energy order of different quantum states of the hydrogen molecule is extended to internuclear distances  $R=5, 6, 7, 10$  (cf. Eisen-schitz and London, this vol., 525). N. M. BUGH.

**Reflexion of hydrogen atoms from lithium fluoride.** T. H. JOHNSON (J. Franklin Inst., 1930, 210, 135—152).—The method previously described (cf. *ibid.*, 1928, 206, 301) was improved so that the lithium fluoride crystal could be used for 6 hrs. before its surface became rough. Incidence was at  $30^\circ, 45^\circ$ , and  $60^\circ$ , and the crystal at temperatures of  $300^\circ, 600^\circ$ , and  $900^\circ$  Abs. When the incident beam was in the 100 azimuth, *i.e.*, with rows of alternately dissimilar ions parallel and perpendicular to the plane of incidence, the reflex patterns showed no diffraction maxima in the plane of incidence, but indicated that the rows of similar ions form a more important grating than the rows of alternately dissimilar ions. With the beam incident at  $45^\circ$  in the 110 azimuth, *i.e.*, with rows of similar ions parallel and perpendicular to the plane of incidence, definite diffraction bands were obtained, about one tenth as many atoms entering one of these in the first order as enter the specular beam. Similar results were obtained at normal incidence. Diffuse reflexion of atoms from lithium fluoride is due to thermal agitation (cf. Estermann and Stern, this vol., 515).

C. A. SILBERRAD.

**Discrete range groups of H-particles expelled from aluminium.** I. Dependence of the number and energy of the H-particles on the primary energy. H. POSE (Z. Physik, 1930, 64, 1—21).—Disintegration experiments with aluminium show that the H-particles expelled in the forward direction fall into three groups of distinct discrete ranges. Experiments were carried out to discover whether the energy of the primary particle exerted any influence on the production of H-particles in each of these groups. Two of the groups appeared only when the primary energy reached a characteristic value, but the third was produced irrespective of the energy of the primary particles. This can be explained on the new quantum theory, the first two groups being the result of resonance effects between the de Broglie waves of the  $\alpha$ -particle and a characteristic vibration of the nucleus, and the third group being due to the simple penetration of an  $\alpha$ -particle into the nucleus.

A. J. MEE.

**Absorption in hydrogen gas of hydrogen positive rays.** A. C. LAW and G. MUTCH (Phil. Mag., 1930, [vii], 10, 297—306).—The beam of hydrogen positive rays was passed through the usual electric and magnetic fields and a portion of the resulting positive-ray parabola of known energy made to pass through a slit into the absorption chamber. A photographic method was used to determine the intensities of the homogeneous beam

at different points along its course in the chamber and from these the absorption was estimated. The latter was not found to be exponential, which seemed to indicate the existence of a range for the particles rather than removal of the particles from the beam by sudden stoppage or large angle scattering. The method of experiment, depending as it does on the preservation of a fairly constant velocity of the particles, was therefore capable of yielding only qualitative results. These are compared in a general way with the results of theory. W. GOOD.

**Effective cross-section for the recombination of electrons with hydrogen ions.** E. C. G. STUECKELBERG and P. M. MORSE (Physical Rev., 1930, [ii], 36, 16—23).—Mathematical. The computation of the cross-section for combination of electrons with a positive point charge is made in polar co-ordinates by quantum mechanics, giving the fraction of the recombination to a final state of total quantum number  $n$  arising from recombination to the sub-states of different  $l$  values. This permits a comparison of results with the experimental recombination intensities for alkali metal vapours.

N. M. BUGH.

**At. wt. tables and chemical analysis.** A. THIEL (Chem.-Ztg., 1930, 54, 617—618).—Polemical against Schoorl and Bruhns. The views of these two supporters of the use of "air" at. wts. rather than "scientific" at. wts. as applied in chemical analysis to weights made in air and not in a vacuum are considered to be mutually conflicting. S. S. WOOLF.

**Constitution of chromium.** F. W. ASTON (Nature, 1930, 126, 200).—Using chromium hexacarbonyl, three new isotopes of chromium have been discovered. The mass numbers are 50, 52, 53, and 54, and their relative abundance is 4.9, 81.6, 10.4, and 3.1%, respectively. The packing fraction of  $\text{Cr}^{52}$  is  $-10 (\pm 3 \text{ pts. in } 10,000, 0^{16}=0)$ . The at. wt. of chromium derived from this is  $52.011 \pm 0.006$ .

L. S. THEOBALD.

**Isotope effect in the spectrum of boron monoxide. Intensity measurements and structure of the  $\beta$ -bands.** A. ELLIOTT (Nature, 1930, 126, 203—204).—The intensity ratios of the  $\text{B}^{11}\text{O}$  and  $\text{B}^{10}\text{O}$  bands have been determined from measurements of the intensities of the lines in four bands in the  $\beta$ -system of boron monoxide excited by active nitrogen. The mean values of the intensity for the four bands are 3.41, 3.28, 3.34, and 4.34, respectively, and, in this case at least, do not give a true measure of the relative abundance of the isotopes. The doublet  $P$  and  $R$  branches of approximately equal strength occur in the arc  $\beta$ -bands, but only the  $R$  branch occurs in the bands excited in active nitrogen. A preliminary value of  $1.53 \text{ cm}^{-1}$  for  $B'_0$  has been obtained.

L. S. THEOBALD.

**Isotopes of nitrogen, mass 15, and oxygen, mass 18 and 17, and their abundances.** S. M. NAUDÉ (Physical Rev., 1930, [ii], 36, 333—346).—Evidence for the existence of isotopes of nitrogen and oxygen is summarised. An apparatus is described by which the absorption spectra of the nitric oxide  $\gamma$ -bands, (0,0) at  $\lambda 2269$ , (1,0) at  $\lambda 2154$ , and (2,0) at  $\lambda 2052$ , were investigated in search of isotopes and to

verify the existence of isotopes  $O^{18}$  and  $O^{17}$ . Band heads were observed in the three bands investigated corresponding with the calculated heads for the molecules  $N^{14}O^{16}$ ,  $N^{15}O^{16}$ ,  $N^{14}O^{18}$ , and  $N^{14}O^{17}$ , indicating the existence of the isotope  $N^{15}$  and verifying  $O^{18}$  and  $O^{17}$ . By comparing the pressures of nitric oxide in the absorption tube at which the  $(1,0)P_1$ ,  $N^{14}O^{16}$  head had the same intensity as the  $P_1$ ,  $N^{14}O^{18}$  head the relative abundance of  $O^{16}$  and  $O^{18}$  was found to be  $1075 \pm 110$ . From the relative intensity of the  $P_1$  and  $Q_1$ ,  $N^{14}O^{16}$  heads the relative abundance of  $N^{14}$  and  $N^{15}$  was found to be  $700 \pm 140$ . From the relative abundance of  $O^{16}$  and  $O^{18}$ , and  $O^{16}$  and  $O^{17}$  the mass of the  $O^{16}$  isotope was calculated to be  $15.9980 \pm 0.0002$ , taking the at. wt. of the isotope mixture as 16.0000. The mass of the  $N^{14}$  isotope was calculated to be  $14.0069 \pm 0.0012$ .

N. M. BLIGH.

**Isotopes and geologic time.** C. S. PIGGOT (J. Amer. Chem. Soc., 1930, 52, 3161—3164).—The calculation of geologic time from the examination of uranium minerals is discussed. The results of Aston (A., 1929, 370) show that the uncertainty due to the presence of thorium can be eliminated.

J. G. A. GRIFFITHS.

**Relation between the disintegration constant of radio-elements emitting  $\alpha$ -rays and their filiation capacity.** (MME.) P. CURIE and G. FOURNIER (Compt. rend., 1930, 191, 326—329).—Combination of Fournier's formula (A., 1929, 863), the Geiger-Nuttall law, and Wolff's equation (Physikal. Z., 1921, 22, 171, 352) leads to the relationship  $\log \lambda = 268 - 3.5U$ , where  $U$  is the filiation capacity (*loc. cit.*) and  $\lambda$  the disintegration constant of a radioelement emitting  $\alpha$ -particles in air. Experimental results give a line corresponding with  $\log \lambda = 235 - 3.0U$  between  $U = 75$  and 85, but the values for polonium, actinium- $C'$ , and uranium-1 (*cf. loc. cit.*) indicate that these limits represent maximum and minimum values of  $\log \lambda$ , respectively, beyond which  $\log \lambda$  rises with increase in  $U$  instead of falling.

J. GRANT.

**Origin of the high-range  $\alpha$ -particles of thorium-C.** E. STAHEL (Z. Physik, 1930, 63, 149—153).—The recoil rays corresponding with the  $\alpha$ -particles of abnormally high range of thorium-C have a longer range in air than the recoil rays from the other  $\alpha$ -particles, and were separated from them by a layer of air of variable pressure. The decomposition product of these abnormal particles was thus collected separately and shown not to possess the half-life period of thorium- $C'$  but to be practically inactive. Contamination of the iron foil on which the product was collected was prevented by interposition of air-tight foils of celluloid  $0.014 \mu$  thick. It was previously shown (this vol., 516) that the abnormal particles are not emitted from thorium- $C'$ , and it is hence now deduced that they arise from thorium- $C''$  and not from thorium-C. The alternative explanation that the  $\alpha$ -particles are emitted from thorium-C but give rise to an isotope of thorium- $C''$  with a different life period is discussed, and it is shown that the half-life period of this isotope could not have values between a few seconds and one day.

H. A. JAHN.

**Luminescence of zinc sulphide under the action of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays.** G. S. GESSNER (Physical Rev., 1930, [ii], 36, 207—213).—The luminescence of zinc sulphide exposed to  $\alpha$ -rays or  $\beta$ - and  $\gamma$ -rays, or  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays was investigated with a specially-designed brass capsule; the luminescent material and exciting agent were kept separate. Luminosities were measured by a Nutting polarisation photometer. The curves, plotted against time, showed first an increase in brightness, followed by a decrease, and a rise to a second maximum with a final gradual decrease. The decay of luminescence after removal of the exciting agent is not a single exponential. Results are not in agreement with the theory of radioactive luminosity given by Walsh (*cf. A.*, 1927, 807).

N. M. BLIGH.

**$\gamma$ -Rays of potassium.** F. BĚHOUNEK (Nature, 1930, 126, 243).—The radiation emitted by potassium chloride has been examined; it consists of at least two groups of  $\gamma$ -rays. The absorption coefficient for the first group is of approximately the same order as in the case of the  $\gamma$ -rays of radium, but the second group is approximately twice as penetrating. Assuming that each  $\beta$ -ray of potassium is followed by one  $\gamma$ -ray, the intensity of the  $\gamma$ -rays is much lower than corresponds with a period of  $10^{12}$  years.

L. S. THEOBALD.

**Production of radium by ionium.** (MME.) P. CURIE (J. Chim. phys., 1930, 27, 347—356).—Theoretical. A graphical method for determining the true quantity of radium present at any time is given.

C. W. GIBBY.

**Theory of atomic disintegration.** G. BECK (Z. Physik, 1930, 64, 22—33).—A mathematical investigation of two kinds of quantum process leading to agreement with the experimental work of Pose on discrete range groups of H-particles (*cf. this vol.*, 1232).

A. J. MEE.

**Atomic diameters of the rare gases.** W. H. KEESOM and H. H. MOOY (Nature, 1930, 126, 243).—A correction. Using the values of the atomic diameters 2.30, 2.87, 3.10, and 3.41 Å. calculated by Rankine for neon, argon, krypton, and xenon, respectively, the ratios of the distance of nearest neighbours in the crystal lattice to the atomic diameter become 1.39, 1.34, 1.28, and 1.28, respectively. The value for krypton is lower than would be expected.

L. S. THEOBALD.

**Lattice constants of the elements.** W. HUME-ROTHERY (Phil. Mag., 1930, [vii], 10, 217—244).—Relations are described connecting atomic or ionic radii with the corresponding atomic structures. In any one sub-group of the periodic table, provided that the co-ordination number remains constant, the interatomic distance  $d$  is given by the relation  $d/n = (1/aZ)^x$ , where  $n$  is the principal quantum number of the outermost shell of electrons remaining attached to the ions,  $Z$  is the atomic number,  $x$  is a constant which is the same for groups with the same number of electrons in the outermost shell of the atomic core or ion, and  $a$  is a second constant which in some groups may be connected with the valency. The accuracy and meaning of this law are discussed and the effect of co-ordination number and crystal

structure is considered. Other relations in the periods are found. W. GOOD.

Interaction of a hydrogen and a helium atom, and of two helium atoms. G. GENTILE (Z. Physik, 1930, 63, 795—802).—Mathematical. The energy of interaction of hydrogen and helium and of two helium atoms in their respective ground states is calculated. Second-order perturbations give forces equivalent to polarisation forces (cf. this vol., 525), and these are calculable as a second order Stark effect. A. B. D. CASSIE.

Solution of the Dirac equation without specialisation of the Dirac operators. F. SAUTER (Z. Physik, 1930, 63, 803—814).—Mathematical.

A. B. D. CASSIE.

The virial hypothesis. V. FOCK (Z. Physik, 1930, 63, 855—858).—Mathematical. A quantum-mechanical virial is deduced from the variation principle, and is shown to be valid for Dirac's equation.

A. B. D. CASSIE.

Rate at which ions lose energy in elastic collisions. A. M. CRAVATH (Physical Rev., 1930, [ii], 36, 248—250).—Mathematical. An expression is deduced for the rate of energy loss of ions (including electrons) moving through a gas, the ions and molecules being regarded as smooth elastic spheres, with no attraction at a distance, and having Maxwellian velocity distributions corresponding with their respective absolute temperatures.

N. M. BLIGH.

Electrons in metals and classification of corresponding de Broglie waves. L. BRILLOUIN (Compt. rend., 1930, 191, 292—294).—Mathematical; an extension of the results deduced previously (cf. this vol., 1082).

C. A. SILBERRAD.

Analytic atomic wave functions. C. ZENER (Physical Rev., 1930, [ii], 36, 51—56; cf. Guillemin and Zener, this vol., 649).—Mathematical. The wave functions for the normal states of atoms of elements in the first row of the periodic table are written as simple analytic expressions with several parameters, the best values of which are determined by the variation method. An approximate solution is found for all the ions, positive and negative, of these atoms.

N. M. BLIGH.

Atomic shielding constants. J. C. SLATER (Physical Rev., 1930, [ii], 36, 57—64).—Mathematical. The wave functions derived by Zener (cf. preceding abstract) are extended to all atoms in any stage of ionisation. These are applied to X-ray levels, sizes of atoms and ions, and diamagnetic susceptibility.

N. M. BLIGH.

Calculation of energy values. C. ECKART (Physical Rev., 1930, [ii], 36, 149—150).—A modification of the Ritz method of calculating characteristic numbers, as applied to the quantum dynamical problem, is described, and results of calculations for the 2P and 3D states are given.

N. M. BLIGH.

What conclusions must classical physics and chemistry draw from the principle of greatest simplicity? L. ZEHNDER (Z. Physik, 1930, 63, 706—712).—Ten postulates are given based on the principle of greatest simplicity. Classical physics

must obey these, or else be wrong in its fundamental suppositions.

A. J. MEE.

Relativistic treatment of the atom with several electrons. L. GOLDSTEIN (J. Phys. Radium, 1930, [vii], 1, 271—284).—Theoretical. A development of previous views (cf. this vol., 131).

L. S. THEOBALD.

Wave-mechanical calculation of the grating energy and grating constant of lithium hydride. E. A. HYLLEAAS (Z. Physik, 1930, 63, 771—794).—The wave-mechanical theory of grating forces in a crystal composed of ions with two orbital electrons is developed. Exchange energy is shown comparable with the Coulomb energy due to interionic forces. Calculations for lithium hydride give the grating energy as 219 kg.-cal. per mol., and the grating constant as 4.42 Å., compared with the empirical values, 217±7 and 4.10, respectively.

A. B. D. CASSIE.

Colouring of alkali halide crystals by ultra-violet light. A. SNAKULA (Z. Physik, 1930, 63, 762—770).—Absorption spectra due to foreign substance colouring of the first kind are given for crystals of lithium fluoride, rubidium bromide, and potassium iodide in the range 200—800 μμ. Absolute values of the absorption coefficient are given for rubidium chloride and bromide and for potassium bromide and iodide at the ordinary temperature, and for potassium bromide at -183°. Crystals of rubidium bromide and chloride and of potassium bromide and iodide require 1.1 to 1.6 light quanta to form one colour centre when the colouring is slight. This factor is independent of the wave-length used and of the saturated colour density.

A. B. D. CASSIE.

Colloidal nature of the colouring substance in coloured rock-salt. M. SAVOSTIANOVA (Z. Physik, 1930, 64, 262—278).—Mie's theory was applied to the system Na-NaCl, and the absorption and diffusion spectra for different particle sizes were calculated and compared with the experimental curves obtained for coloured rock-salt. The absorption spectra of the following kinds of coloured salts were determined by the spectrophotometer method: (a) natural blue salt, (b) additive (in liquid sodium) coloured salt, and (c) salt obtained from yellow salt by the action of heat and pressure under the influence of light. The experimental data agree with the assumption that the colours are due to particles of colloidal sodium. Besides the absorption maxima due to the presence of colloidal sodium, a further maximum was found for yellow salt in the infra-red, the explanation of which is not clear.

A. J. MEE.

Light absorption of alkaline-earth halides in aqueous solution. H. DIAMOND and H. FROMHERZ (Z. physikal. Chem., 1930, B, 9, 289—318).—The absorption curves of aqueous solutions of pure chlorides, bromides, and iodides of magnesium, calcium, strontium, and barium, extending into the ultra-violet as far as 200 μμ, have been measured over a wide range of concentration varying from saturation to high dilutions. The weak absorption bands found by previous workers in the neighbourhood of 250 μμ are shown to be due to traces of impurities, which are effective if present at a concentration of

only 0.001 g. per litre. With increasing concentration of solutions containing only one halogen ion a proportional displacement of chloride bands towards the ultra-violet was observed, together with a slight broadening of bromide bands, and a marked broadening of iodide bands, which, however, was not proportional to the increase in concentration. The maxima of the iodide bands are not displaced even at the highest concentrations. The iodide bands are displaced towards the ultra-violet by the addition of an excess of chloride ions, the magnitude of the effect being proportional to the chloride-ion concentration, and a similar effect is produced by an added excess of potassium fluoride or magnesium sulphate. No specific influence of the cation on the form of the absorption curve or on the degree of displacement of the iodide bands was observed, but with pure chloride solutions the ultra-violet displacement due to increase of concentration increases with the size of the cation. No evidence of the association of the ions to stoichiometric complexes was obtained.

E. S. HEDGES.

**Physical properties of the fatty acids.** E. L. LEDERER (Chem. Umschau, 1930, 37, 205—208).—The method of calculating the viscosity at any temperature of a fatty acid is described, and the necessary constants have been calculated for a number of the acids. The absorption by fatty acids in the ultra-violet is described and the equations and constants required for calculating the absorption at any specified wave-length are given. H. F. GILLBE.

**Nitric oxide  $\beta$ - and  $\gamma$ -bands.** R. SCHMID, D. VON FARKAS, and T. KÖNIG (Z. Physik, 1930, 64, 84—120).—The NO lines previously measured were classified and ordered. In this way some 3000  $\gamma$ - and 1000  $\beta$ -lines were arranged. The rotation and vibration constants were in some cases calculated afresh. The doublet splitting of the levels  $2\pi$ , was obtained as a function of rotational and vibrational states. The potential energy curve for nitric oxide was obtained, as well as Condon's parabola.

A. J. MEE.

**Nitric oxide  $\delta$ -bands.** R. SCHMID (Z. Physik, 1930, 64, 279—285).—In order to produce the  $\delta$ -bands of nitric oxide in sufficient intensity to be photographed special means of excitation must be used. With a Tesla apparatus and other devices for special excitation it was found possible to produce the bands in the afterglow in the production of active nitrogen mixed with air. The rotation analysis of the band  $\delta(0.3)$  is given, and the rotation constant of the  $\delta$ -bands for the  $2\Sigma$  initial level is calculated to be  $B_0 = 1.995 \text{ cm}^{-1}$ .

A. J. MEE.

**Extinction of fluorescence of solutions of dyes by electrolytes.** A. V. BANOV (Z. Physik, 1930, 64, 121—134).—The application of the theory of Vavilov concerning collisions of the second kind to the extinction of fluorescence in solutions of dyes by adding electrolytes does not agree fully with experimental results. This leads to the search for some other cause of extinction which is to be found in the "salting-out" effect of the electrolyte on the dye. Experimental work supports this view. Calculations of the sum of the radii of the molecule of the dye and of the ion of

the electrolyte give results in agreement with those arrived at by other methods. The extinction curves reveal a connexion between the concentration of the electrolyte,  $c$ , and the intensity ratio after and before adding the electrolyte, which can be expressed in the form  $L/L_0 = e^{-k\sqrt{c}}$ .

A. J. MEE.

**Deformation of electron shells. I. Absorption spectrum, molecular volume, and refraction of neodymium perchlorate.** P. W. SELWOOD (J. Amer. Chem. Soc., 1930, 52, 3112—3120).—The densities, refractive indices, and absorption spectra of neodymium perchlorate solutions of concentrations as high as about 7*N* have been determined. Increase of concentration is associated with an increase in molecular volume and refraction, and a small shift of the absorption bands towards the red. The results agree with deductions from the Clausius-Mosotti theory of dielectrics and with the theories of Ephraim (A., 1929, 864) and Fajans on the distortion of electron shells of ions.

J. G. A. GRIFFITHS.

**Infra-red filters of controllable transmission.** A. H. PFUND (Physical Rev., 1930, [ii], 36, 71—76).—To eliminate higher orders when using an echelette grating in the infra-red, powders such as zinc or magnesium oxides, of suitable particle size, can be used spread uniformly with appropriate thickness over a polished speculum surface. Short wave-length radiations are reflected diffusely, and long wave-lengths are mainly transmitted. Satisfactory purity of spectrum is obtained.

N. M. BLIGH.

**Effect of high pressure on the near infra-red absorption spectrum of certain liquids.** J. R. COLLINS (Physical Rev., 1930, [ii], 36, 305—310).—Since a change in polymerisation of polar liquids is expected with increase of pressure, certain absorption bands of water and of methyl and amyl alcohols were studied with the liquids under pressures up to 5000 kg. and toluene up to 8000 kg./cm.<sup>2</sup> No change was found in the positions or intensities of the bands, which, being characteristic of the molecules, indicate no change in polymerisation for the pressures used. The pressure necessary to solidify toluene at 20° was found to be between 8100 and 8300 kg./cm.<sup>2</sup>

N. M. BLIGH.

**Infra-red absorption of some organic liquids under high resolution. II.** R. B. BARNES (Physical Rev., 1930, [ii], 36, 296—304; cf. this vol., 1090).—With an improved spectrometer giving wave-lengths accurate to  $\pm 0.001 \mu$ , work previously reported on the CH vibration bands in organic liquids from 3.0 to 4.0  $\mu$  has been continued and extended. Results are given for water vapour, benzene, and toluene. The CH vibration frequency close to 3.5  $\mu$  and the strong band of water near 3.0  $\mu$  indicate that almost every liquid will have pronounced absorption over the region studied, resulting in complex bands demanding high resolving power.

N. M. BLIGH.

**Rotation oscillation spectrum of acetylene. I. Band analysis.** K. HEDFELD and R. MECKE (Z. Physik, 1930, 64, 151—161).—In order to study the configuration and form of oscillation of simple gaseous molecules the spectrum of acetylene has been investigated. The spectrum was photographed in the

range 9000—7000 Å. with large dispersion (2.6 Å./mm.). Three absorption bands were found at wave-lengths 7887, 7956, and 8620 Å., of which the first was by far the most intense. The absorption lines were measured to 0.01 Å. The spectrum was analysed. The *P* and *R* branches were very simple, no fine structure of the lines being visible within the above limit of error. There were marked intensity changes. The simple structure of the bands leads to the conclusion that the four atoms of the molecule are arranged in a straight line, so that the method of rotation of a diatomic molecule has to be dealt with. The fact that only one line [*P*(0)] is missing in the spectrum is in agreement with the usually accepted electronic structure of acetylene and shows the analogy of the acetylene molecule HC≡CH to the nitrogen molecule N≡N. The moment of inertia of the molecule in the fundamental state is  $23.509 \times 10^{-40}$ . The nuclear distance for C-H is  $1.08 \times 10^{-8}$  cm., in agreement with that arrived at for the methane molecule by a study of the Raman spectrum; the value for the C≡C distance is  $1.19 \times 10^{-8}$  cm. These figures are considerably less than those for the diamond lattice.

A. J. MEE.

**Rotation oscillation spectrum of acetylene.**  
**II. Intensity measurements.** W. H. J. CHILDS and R. MECKE (Z. Physik, 1930, 64, 162—172).—Accurate intensity measurements were made with the band at 7887 Å., this being a  $^1\Sigma-^1\Sigma$  combination. The expected intensity changes for a combination of this type were found, the *i* factors (i.e., transition probabilities) being for the *R* branch, (*J*)<sub>*i*</sub> = *J* + 1, and for the *P* branch, (*J*)<sub>*i*</sub> = *J*. Conclusions are reached concerning the nuclear spin of elements. The intensity ratio is 3 : 1. The odd *J* values must therefore have three times the weight, statistically, of the even *J* values. The nuclear spin of the hydrogen in the acetylene molecule must be 0.5, whilst that of the carbon is 0. Summing up the results previously obtained for nuclear spins, it is pointed out that elements having at. wts. divisible by 4 (equal, say, to 4*n*), have no spin. This is true for helium, carbon, and oxygen. The elements with at. wts. equal to 4*n* + 1 (hydrogen) have spins equal to 0.5. Elements with at. wts. equal to 4*n* + 2 (nitrogen) have the spin 1. Elements with at. wts. equal to 4*n* + 3 have the spin 1.5 (lithium). The elements sodium, chlorine, and iodine also have spins greater than 1. This rule should be useful in dealing with isotopic elements.

A. J. MEE.

**Rotation oscillation spectrum of acetylene.**  
**III. Characteristic frequencies of simple symmetrical molecules.** R. MECKE (Z. Physik, 1930, 64, 173—190).—The characteristic frequency of a molecule may be regarded as being made up of two parts—a valency oscillation and a deformation oscillation. A number of linear molecules are considered. Molecules of this type possess *n* - 1 valency oscillations, equal to the number of valency linkings, and *n* - 2 deformation oscillations. The symmetrical molecules of carbon dioxide, nitrous oxide, carbon disulphide, acetylene, cyanogen, and possibly also hydrogen peroxide are to be regarded as linear. The triatomic molecules possess two valency oscillations,

the size of which depends mainly on the oscillating masses, and one deformation oscillation, parallel to the axis of symmetry, but in the case of a linear arrangement of atoms, it becomes a double oscillation perpendicular to the axis of the molecule. For tetra-atomic molecules (acetylene and cyanogen) there are two C-H oscillations, one (HC)≡(CH), and two deformation oscillations perpendicular to the axis of the molecule. For ethylene there are four C-H oscillations, one (H<sub>2</sub>C)≡(CH<sub>2</sub>) oscillation, and five deformation oscillations, of which one, as a pure C≡C oscillation, is independent of the mass of other atoms, and is found in all derivatives containing the C≡C linking. The five characteristic frequencies of acetylene and the nine of ethylene are calculated.

A. J. MEE.

**Raman and resonance radiation.** P. DAS (Z. Physik, 1930, 63, 224—226).—The distinction between Raman and resonance lines is pointed out, and the origin of the resonance lines is explained on the basis of Rasetti's theory of the Raman effect. According to this theory, at least three energy levels (*E<sub>m</sub>*, *E<sub>n</sub>*, *E<sub>l</sub>*) are concerned in the effect; if the two transitions *m* → *l* and *l* → *n* occur, then a frequency change *ν<sub>ml</sub>* takes place in the scattered light. These energy changes disturb the Maxwell-Boltzmann distribution of energy for the molecules, which is restored when a certain number of molecules return first from *E<sub>n</sub>* to *E<sub>l</sub>* and then from *E<sub>l</sub>* to *E<sub>m</sub>* and thereby radiate the frequencies *ν<sub>nl</sub>* and *ν<sub>ml</sub>*. These last frequencies give rise to the resonance lines. It is shown that only monochromatic light gives resonance radiation, homogeneous light giving fluorescence.

H. A. JAHN.

**Polarisation of Raman radiation and crystal structure.** F. MATOSI (Z. Physik, 1930, 64, 34—38).—It would be expected that the Raman lines from crystals with equal internal force distribution, i.e., those with symmetrical oscillations, would be missing, whereas for crystals with unsymmetrical oscillations they should be strong. It should therefore be possible to arrive at conclusions respecting the structure of crystals by investigating the Raman radiation associated with them, and especially its polarisation. Experiments were made with calcite and sodium nitrate crystals in various positions, and from the results the structure of the CO<sub>3</sub> group was derived. To explain the results it is necessary to assume that the CO<sub>3</sub> group is isosceles in form.

A. J. MEE.

**Dispersion formula and Raman effect for the symmetrical top.** M. MUSKAT (Physical Rev., 1930, [ii], 36, 363; cf. this vol., 978).—A correction.

N. M. BLIGH.

**Polarisation of the lines in Raman spectra.** S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 59—71).—The state of polarisation of Raman lines was investigated for sulphur dioxide and trioxide, carbon disulphide, ammonia, chloroform, bromoform, the trichlorides of phosphorus, arsenic, and bismuth, and the tetrachlorides of carbon, silicon, titanium, and tin. Similarity in polarisation was shown by substances having analogous structures, the influence on the polarisation being attributed to the



geometry of the various oscillations. A high degree of polarisation is usually accompanied by high intensity. Existing explanations of the polarisation phenomena in Raman spectra are briefly reviewed.

N. M. BLIGH.

**Raman effect and molecular structure.** S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 73—95).—Theoretical. On the view that Raman lines are mainly due to transitions corresponding with fundamental vibration frequencies of molecules involved in the scattering process, an interpretation of the Raman spectra is investigated through a study of the characteristic modes of oscillation of a number of simple types of polyatomic molecules using the dynamical principles developed by Dennison (cf. A., 1926, 222). Theoretical results are correlated with existing experimental data.

N. M. BLIGH.

**Raman spectrum of diamond.** R. ROBERTSON and J. J. FOX (Nature, 1930, 126, 279).—With a diamond transparent at about  $8\mu$  and also at  $2300\text{ \AA}$ ., 17 Raman lines originating from mercury lines within the range  $4358\text{--}2378\text{ \AA}$ . have been identified. The mean value of all differences is  $1333\text{ cm}^{-1}$ , a value lower than that previously reported (this vol., 662) but agreeing with that of Ramaswamy (*ibid.*) and of Bhagavantam (this vol., 1091). With a quartz spectrograph, the faint, diffuse band found by these investigators is strong with a centre at about  $4156\text{ \AA}$ .

L. S. THEOBALD.

**Raman spectrum and infra-red absorption of sulphur.** P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 105—112).—The Raman spectrum, excited by the mercury  $5461\text{ \AA}$ . line isolated by a didymium chloride filter, was investigated for rhombic sulphur by the powder crystal method, and for a solution of sulphur in carbon disulphide. Four prominent and two faint lines were observed for the solid, one line being attributed to the  $S_{16}$  molecule; three lines found for the solution correspond with the  $S_8$  molecule. The infra-red measurements of Taylor and Rideal (cf. A., 1927, 925) can be explained by a combination of these fundamental frequencies. Pure carbon disulphide showed the principal line doubled, and a faint line broadened on the long wave-length side, analogous to the results of Dickinson and others for carbon dioxide (cf. A., 1929, 1215). The presence of sulphur in solution caused a slight shift of the principal line to shorter wave-length.

N. M. BLIGH.

**Raman effect in crystal powders of inorganic nitrates.** P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 1—12; cf. Menzies, A., 1929, 1217).—The Raman spectra of 19 inorganic nitrates in fine crystalline form were obtained, using, in some cases, a filter of didymium chloride solution to eliminate the continuous spectrum and to enhance the fainter lines. Wave-lengths and frequency shifts are tabulated. The inactive frequency of the  $\text{NO}_3$  ion appeared as a sharp line with slight variation of position. The greatest departure from its value in solution was observed for lithium, sodium, and magnesium, and for mercury, bismuth, and thorium. It is concluded that the influence of the metal ion on the inactive frequency depends mainly on the volume

occupied by the ion in the crystal lattice. A faint component indicated a polymerised molecule in the case of lithium, mercuric, and aluminium nitrates. Lines at  $7$  and  $14\mu$  correspond with infra-red frequencies.

N. M. BLIGH.

**Raman effect in some organic and inorganic substances.** N. N. PAL and P. N. SENGUPTA (Indian J. Physics, 1930, 5, 13—34).—The Raman spectra were investigated for carbamide, ethyl formate, malonate, acetoacetate, monochloroacetate, and carbonate, potassium and ammonium thiocyanates, potassium cyanide and cyanate, potassium silver cyanide, acetonitrile, aniline, phenylhydrazine, hydrazine hydrate, benzaldehyde, and formaldehyde. Full data are tabulated and results are discussed in relation to chemical structure. Raman frequencies characteristic of the CN ion were found at  $836$  and  $2080$ . The difficulty due to the darkening in air under the action of light of substances such as aniline and phenylhydrazine was overcome by distillation into the observation tube in a vacuum. A theory of the continuous spectrum accompanying the Raman lines is proposed.

N. M. BLIGH.

**Raman spectra of some elements and simple compounds.** S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 35—48).—In order to obtain correlation with known molecular structure Raman spectra were investigated, and results are tabulated for the following: liquefied chlorine, sulphur dioxide, and ammonia, diamond, phosphorus, carbon disulphide, chloroform, bromoform, phosphorus, arsenic, and bismuth trichlorides, and carbon, silicon, tin, and titanium tetrachlorides. Raman spectra of allied compounds showed a close similarity.

N. M. BLIGH.

**Raman effect in trimethylethylene.** (MISS) D. FRANKLIN and E. R. LAIRD (Physical Rev., 1930, [ii], 36, 147).—Raman lines corresponding with infra-red wave-lengths  $3.44 \pm 0.05$  and  $8.4 \pm 0.2\mu$ , and an anti-Stokes line to  $8.4\mu$  were found. A continuous scattering with a marked denser band beginning near  $4600\text{ \AA}$ . appears to be due to contamination with rubber, a similar effect being observed for carbon tetrachloride.

N. M. BLIGH.

**Raman effect in solutions of sodium nitrate of varying concentration.** (MISS) V. STERLING and E. R. LAIRD (Physical Rev., 1930, [ii], 36, 148—149; cf. Carrelli and others, A., 1929, 120).—The Raman spectrum of sodium nitrate, at 5, 10, 30%, and saturated concentrations, excited by a glass mercury arc showed a line with frequency difference  $1049 \pm 6\text{ cm}^{-1}$  excited by the mercury lines  $4358$ ,  $4077$ , and  $4046\text{ \AA}$ ., equally strongly in each case. No new lines were found. The line is attributed to the  $\text{NO}_3$  ion.

N. M. BLIGH.

**Change of wave-length of light due to elastic heat waves at scattering in liquids.** E. GROSS (Nature, 1930, 126, 201—202).—The light  $4358\text{ \AA}$ . of a mercury lamp, scattered at  $90^\circ$  by various liquids, is partly split up into radiations of nearly the same intensity, with wave-lengths symmetrically displaced relatively to the incident light, by a value dependent on the kind of liquid but not differing greatly from  $0.05\text{ \AA}$ . for all the liquids investigated. With highly scatter-

ing liquids, such as benzene and toluene, lines displaced by a multiple of this value have been observed. The nature of the observed splitting is discussed, and a close connexion with the elastic heat waves similar to those discussed by Debye (Ann. Physik, 1912, 39, 789) is considered to exist. Crystalline quartz gives a similar splitting of the frequency of scattered light. L. S. THEOBALD.

**Influence of polymerisation and molecular association on the Raman effect.** S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 49—57).—The Raman spectrum of sulphur trioxide was investigated at two temperatures. The transition from  $S_2O_6$  to  $SO_3$  molecules was shown by the disappearance or weakening of certain lines, and the corresponding brightening of other lines attributed to  $SO_3$ ; the effect is reversible. The effect of molecular association on Raman spectra is discussed with reference to data for ammonia (cf. this vol., 1237). Three broad lines of widely differing intensities are found, which become of comparable intensity at low temperatures (cf. Daure, this vol., 14); another diffuse line showing no alteration in intensity is attributed to unassociated molecules. Similar results for other polar molecules are discussed. Appreciable frequency differences for the molecules as determined in the gaseous and liquid states were found. N. M. BLIGH.

**Chemiluminescence of the antimony halides.** S. S. BHATNAGAR and K. G. MATHUR (Z. physikal. Chem., 1930, B, 9, 229—240).—The chemiluminescence of a mixture of antimony and chlorine and the effect on it of the addition of anthracene, benzene, and the sulphides of calcium and zinc have been examined. When mercury is present, spectral lines corresponding with an energy greater than the heat of formation of any of the antimony chlorides are excited, and it seems that intermediate reactions, in this case the formation of antimony oxide by moisture, are responsible. R. CUTHILL.

**Photodichroism and photoanisotropy. VII. Influence of colour of exciting light on the induced dichroism.** F. WEIGERT and J. SHIDEI (Z. physikal. Chem., 1930, B, 9, 329—355).—Previous work (A., 1929, 871, 894) has been extended and repeated with more refined methods and a further study has been made of the influence of the wavelength of the exciting light on the dichroism and also the influence of the conditions of developing and the intensity of radiation. The types of curves produced can be described in terms of three principal types in the red, green, and blue, thus providing a photochemical analogy with the three-colour mixture rule observed in the sensations of the eye. A new theory of "colour-effectiveness" is evolved. E. S. HEDGES.

**Photo-ionisation of salt vapours.** A. TERENIN (Physical Rev., 1930, [ii], 36, 147—148; cf. A., 1928, 935; Butkov, A., 1929, 1362).—The photo-ionisation of the halides of thallium was investigated using ultra-violet light of wave-length longer than 1850 Å. The ionisation and dissociation energies and stability of the neutral and ionised molecule are discussed. A decrease in photo-sensitivity from the iodide to the chloride was observed. The possibility of photo-

ionisation appears to depend on the ionisation potential of the metallic atom falling within the range of ultra-violet frequencies used. N. M. BLIGH.

**Temperature and pressure variations of the dielectric constant of some organic vapours.** O. FUCHS (Z. Physik, 1930, 63, 824—848).—The apparatus described by Stuart (A., 1928, 460) has been improved to measure the temperature coefficient of the dielectric constants of substances with higher b. p. The apparatus was directly calibrated and systematic errors were investigated, especially the error due to adsorbed layers. The temperature and pressure variations of the dielectric constant were determined for ethyl ether, ethyl chloride, and methyl chloride, and the temperature variation for  $C(OMe)_4$ . The electric moments are: ethyl ether  $1.14 \times 10^{-18}$ , ethyl chloride  $2.05 \times 10^{-18}$ , methyl chloride  $1.86 \times 10^{-18}$ , and for  $C(OMe)_4$   $< 0.3 \times 10^{-18}$ . The infra-red molecular refraction constants have been determined, and the results are discussed. A. B. D. CASSIE.

**Dielectric constants of regular crystals.** S. KYROPOULOS (Z. Physik, 1930, 63, 849—854).—The dielectric constants were determined by the Stark method for regular single crystals. These included lithium fluoride, sodium fluoride, chloride, and bromide, potassium and rubidium chlorides, bromides, and iodides, and tellurium chloride and bromide. The values of these dielectric constants sometimes deviate greatly from the values for corresponding powders. The values for the single crystals show a simple correspondence with the ion radius, and the additive rule for dielectric constants appears to apply for ions of comparable radius and of small polarisability. A. B. D. CASSIE.

**Influence of the solvent on the rotatory power of the acetals derived from mannitol.** V. ETEEL (Coll. Czech. Chem. Comm., 1930, 2, 457—470).—The specific rotatory power of solutions of triethylidene- and tribenzylidene-mannitol in a number of solvents have been measured, but there appears to be no simple relationship between the refractive index of the solvent and the rotatory power of the solution. H. F. GILLBE.

**Influence of X-rays, according to Allison, on the magnetic rotatory polarisation and on the properties of inactive liquids.** N. T. ZÉ (Compt. rend., 1930, 191, 324—325).—The experiments of Allison (A., 1929, 1220) were tested on water, carbon disulphide, and nitrobenzene, using a Coolidge X-ray tube (70 kilovolts and 6 milliamp.) and an electromagnet supplying a mean field of about 21,000 gauss, with a Cotton mercury arc as source of monochromatic light. The results recorded by Allison were not confirmed, and it is considered that if they exist their magnitude will not (under the above conditions) exceed 3 min. (cf. following abstract). J. GRANT.

[Influence of X-rays, according to Allison, on the magnetic rotatory polarisation and on the properties of inactive liquids.] A. CORTON (Compt. rend., 1930, 191, 325; cf. preceding abstract).—The rules of symmetry in physical phenomena of Curie do not forbid the supposition that X-rays may modify

the magnitude of magnetic rotation. They do not, however, allow the possibility of the creation of such a power of rotation, in a determined sense, in an inactive substance by means of X-rays.

J. GRANT.

**Dispersion of gases and vapours, and its explanation on the dispersion theory. I. Dispersion of mercury vapour in the ultra-violet.** R. LADENBURG and G. WOLFSOHN (*Z. Physik*, 1930, 63, 616—633).—A Jamin interferometer of which the parts were made of quartz was used in the investigation. The anomalous dispersion of saturated mercury vapour at known pressure and temperature was studied in the neighbourhood of the mercury resonance line 2537 Å. The oscillator strength,  $f$ , i.e., the ratio  $n/N$  of the number of dispersion electrons to the total number of molecules per c.c., was found, and its variation with vapour pressure studied in the range 0.004—200 mm. Between 0.01 and 200 mm.  $f$  is constant and equal to  $0.0255 \pm 0.0005$ . At pressures below 0.01 mm. there is a rise in the  $f$  value which has not been explained. From the determinations a curve could be drawn analogous to the ordinary vapour pressure-temperature curve, and of the form  $p=p(T)$ , where  $p/f$  represents the partial pressure of atoms in the vapour. In consequence of the constancy of  $f$  above 0.01 mm. the value of  $p(T)$  is of the same form as the corresponding function for the total vapour, differing from it only by a constant factor. The heat of vaporisation of the atoms agrees to within a few per cent. with that of the total vapour. In this way the partial pressure of the molecules in the vapour can be found with fair accuracy between the pressures 0.01 and 200 mm. The constancy of  $f$  shows that the probability of transition for the mercury atom is independent of temperature and pressure in the interval under experiment, a conclusion required by the quantum theory.

A. J. MEE.

**Dispersion of gases and vapours and its explanation on the dispersion theory. II. Dispersion of mercury vapour between 7500 and 2650 Å.** G. WOLFSOHN (*Z. Physik*, 1930, 63, 634—639; cf. preceding abstract).—The apparatus used was that mentioned in the previous work. The dispersion curve, which was obtained between the wave-lengths 7500 and 2650 Å., was of the form expected on theoretical grounds, and could be represented by a formula involving three terms. The region of anomalous dispersion predicted by Herzfeld and Wolf to exist at a wave-length of 6900 Å. could not be found.

A. J. MEE.

**Quantum theory of chemical valency.** M. BORN (*Nature*, 1930, 126, 205).—The theory of the interaction of several atoms can be treated simply and without the application of the methods of the group theory (cf. Slater, this vol., 126).

L. S. THEOBALD.

**Tautomerism and related phenomena in the light of the electronic theory of valency.** L. KOVARIKI (*Z. physikal. Chem.*, 1930, B, 9, 173—200).—A general qualitative electronic theory of intramolecular rearrangements has been developed by means of the new concept of "pole-transfer." It is postulated that when a duplet linking is severed

with the formation of ions the two electrons pass to the anion, but on neither ion does the charge necessarily remain on the atom at which the linking has broken; if there is present in the ion an atom or a group of higher electrovalency the charge is transferred to it. By means of this assumption, phenomena such as tautomerism and the quinonoid transformation may be embraced by a single theory. Since an octet may be regarded as equivalent to four duplets, this theory can be combined with that of Lewis and Langmuir and utilised to explain the Beckmann and Hoffmann transformations. The structure of inorganic unsaturated anhydrides, such as sulphur dioxide, is also discussed in the light of this theory.

R. CUTHILL.

**Theory and systematic treatment of molecular forces.** F. LONDON (*Z. Physik*, 1930, 63, 245—279).—Mathematical. A general review is made of the attractive forces between molecules from the point of view of the new quantum mechanics. The previous explanation of Keesom and Debye of van der Waals attractive forces in the inert gases as due to quadrupole moments is now untenable, since quantum mechanics shows that the atoms of these gases have a spherically symmetrical distribution of electrical charge. Non-polar diatomic molecules according to the quantum mechanics possess a quadrupole moment, but the value calculated for hydrogen is much too small to explain the van der Waals attraction. It is shown that the quantum-mechanical force of attraction between two hydrogen atoms due to the reciprocal perturbation of the electronic orbits (cf. Eisenschitz and London, this vol., 525) has a potential which varies inversely as the sixth power of the distance between the molecules, and would therefore at large distances completely outweigh the forces due to quadrupoles, the potential of which varies inversely as the eighth power of the distance. The theoretical calculation of this quantum-mechanical force, which is a second order perturbation effect, is too difficult to be made directly even for the simplest molecules, but it can be easily estimated from the polarisability calculated from the molecular refraction together with the values of the excitation and ionisation potentials. This is carried out for the inert gases and the values obtained for the van der Waals  $a$  are compared with the values deduced from critical data. It is thereby shown that the quantum-mechanical force can fully account for the attraction, so that the assumption of quadrupoles is not necessary. Similar calculations are made for a series of diatomic gases, and the new force is shown to be the cause of the major portion of the attraction. The values of the two other attractive forces present, viz., the force due to the direct action of the multipoles (Keesom effect) and the force due to polarisation (Debye effect), are estimated and curves drawn for hydrogen chloride and for hydrogen bromide showing the variation with distance of the three individual forces. The quantum-mechanical force (dispersion effect) is shown to be the most important.

H. A. JAIN.

**Structure of the carbylamines and other compounds of bivalent carbon.** D. L. НАМЫСКИ, R. C. A. NEW, N. V. SIDGWICK, and L. E. SUTTON

(J.C.S., 1930, 1876—1887).—Direct evidence of the correctness of the formula  $R-N\equiv C$  for the carbylamines was obtained from the results of measurement of the parachors and dipole moments of these substances. Chemical properties are in accordance with this structure. The co-ordinate structure,  $C\equiv O$ , for carbon monoxide is also discussed. W. GOOD.

**Parachor of co-ordinated hydrogen in ortho-substituted phenols.** N. V. SIDGWICK and N. S. BAYLISS (J.C.S., 1930, 2027—2034).—Observed values of the parachors of *o*-substituted phenols show considerable differences from those calculated. It is suggested that the anomalies are due to the formation of chelate rings and, on this basis, a decrease of 14.4 parachor units in the conversion of  $=O+H-$  into  $=O\rightarrow H-$  is deduced. No explanation can be given for the fact that the experimental values for *m*- and *p*-substituted phenols show no anomalies, which would be expected as a result of the recognised association in these compounds. W. GOOD.

**Precision measurements of the glancing angle of reflexion from calcite for silver  $K\alpha_1$  X-rays by the method of displacement.** C. D. COOKSEY and D. COOKSEY (Physical Rev., 1930, [ii], 36, 85—109).—A detailed description is given of the method and apparatus used in obtaining results previously reported (cf. this vol., 526). N. M. BLIGH.

**Spectral lines obtained by the method of convergent X-rays.** T. FUJIWARA (Mem. Coll. Sci. Kyoto, 1930, 13A, 303—306; cf. A., 1928, 1175).—A detailed study of the spectral lines produced by fine single-crystal wire is presented. C. W. GIBBY.

**Dependence of the width and intensity of Debye lines and rings on the dimensions of the X-ray source, of the preparation, and of the camera.** W. BUSSE (Z. Physik, 1930, 63, 227—244).—Mathematical. The effect of absorption by the preparation is considered and the distribution of intensity within the lines determined. An absolute maximum in the intensity of the line was always obtained by a source of such width that it gave rise to lines of double the natural width. For a given width of line, the greatest intensity was also obtained, in the case of small absorption, for such widths of the source and of the preparation that the lines were double the natural width, and these optimum widths of source and preparation were calculated. The most satisfactory source-focus consists of an elongated rectangle. H. A. JAHN.

**Method of obtaining a single crystal of aluminium of any desired crystallographic orientation.** T. SANO (Mem. Coll. Sci. Kyoto, 1930, 13A, 307—309).—An aluminium crystal of any desired orientation can be obtained by bringing another crystal into contact with molten aluminium and lowering the temperature very slowly. C. W. GIBBY.

**X-Ray investigation of the alloy AuCu.** K. OHSHIMA and G. SACHS (Z. Physik, 1930, 63, 210—223).—The change from a face-centred cubic lattice to a face-centred tetragonal lattice through heat treatment of the alloy AuCu is studied by X-ray reflexions from a rotating single crystal, and also by the method of Debye and Sherrer as improved by

Sachs and Weerts (this vol., 527) on finely crystalline samples. The quenched crystals exist in the cubic form and the change on tempering to the tetragonal is investigated, the experiments on the single crystal showing that the two lattices exist side by side during the change, but with the powder method the tetragonal phase could be detected only when evidence of the regular phase had disappeared. The lattice constants were determined by the powder method for the two phases, and the gradual change in the *a/c* ratio during the heat treatment observed by Gorsky was determined. The possible kinetics of the change are discussed. H. A. JAHN.

**Micrography of piezo-electric quartz.** P. T. KAO (Compt. rend., 1930, 191, 334—335).—Corrosion figures obtained by the action of dilute hydrofluoric acid or potassium hydroxide on the positive and negative faces (perpendicular to the electrical axis) of piezo-electric quartz crystals show in relief a crystalline structure, having the form of a parallelogram with two sides parallel to the optical axis, and a fibrous structure parallel to the same axis, respectively. Corrosion occurs more rapidly on the negative than on the positive face, and must be carefully controlled if well-defined figures are to be obtained. The faces perpendicular to the optical axis show triangles which are really the bases of microscopic pyramids. J. GRANT.

**Quartz.** R. WEIL (Compt. rend., 1930, 191, 380—382).—In crystals of the *S* type the birefringence normal to the axis corresponds with flat planes normal to three non-adjacent faces of the prism and inclined to one another at angles of  $120^\circ$ , and is always very feeble ( $10^{-4}$  to  $10^{-5}$ ). Sometimes these planes are visible to the unaided eye as fibres normal to the face of the prism. Corrosion figures produced with cold concentrated hydrofluoric acid show rectangular or lenticular orifices 3 microns long parallel to the vertical edge of the faces of the prism and in a plane normal to the  $b_1$  faces. From these, fine capillary and often rectilinear twisted canals ("hairs") extend into the interior of the crystal, and may attain lengths of 1 cm. Crystals of the *L* type show hairs perpendicular to the faces of the rhombohedron, which appear to delimit certain regions of the crystal, hairs from one domain running parallel with those of an adjacent domain. Quartz with very few planes has very few hairs, but these are then correspondingly longer. In no case do the hairs penetrate the crystal beyond what appears to be a central nuclear region. J. GRANT.

**Structure of some sodium and calcium aluminosilicates.** L. PAULING (Proc. Nat. Acad. Sci., 1930, 16, 453—459; cf. A., 1929, 748).—The structures of natrolite,  $Na_2Al_2Si_3O_{10}\cdot 2H_2O$ , the scapolites, or solid solutions of marialite,  $Na_4Al_3Si_3O_{24}Cl$ , and meionite,  $Ca_4Al_3Si_3O_{24}(SO_4CO_3)$ ; davynite,  $(Na,Ca)_4Al_2Si_3O_{12}(CO_3SO_4Cl)$ , and cancrinite are described and the nature of the frameworks is deduced and illustrated by diagrams. Natrolite is pseudotetragonal, *a* : *b* : *c* = 0.97852 : 1 : 0.35362; the unit cell, *a* 18.19, *b* 18.62, *c* 6.58 Å., contains 8 mols.; the lattice is face-centred; space-group  $C_{2h}^{12}$ . The scapolites are tetragonal, *a* : *c* = 1 : 0.43925; the unit

cell,  $a$  12.27,  $c$  7.66 Å., contains 2 mols.; the lattice is body-centred; space-group  $C_{4h}^2$ ,  $C_{4h}^2$ , or  $S_6^2$ . Davynite and cancrinite (cf. Gossner, this vol., 1100) are hexagonal, the unit cells,  $a$  12.8,  $c$  5.35 and  $a$  12.6,  $c$  5.18 Å., respectively, contain 2 mols.; space-group  $D_{6h}^1$ . Cleavages of some tetrahedral framework crystals are tabulated.

N. M. BLYTH.

**Crystal chemistry of the aluminosilicates. Relationship of the anorthite group to the nepheline group.** W. EITEL, E. HERLINGER, and G. TRÖMEL (Naturwiss., 1930, 18, 469—474).—The following lattice constants in Å. have been determined from powder diagrams:  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ ,  $a$  9.98,  $c$  8.44;  $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ ,  $a$  10.41,  $c$  8.70;  $\text{Na}_2\text{Y}_2\text{Si}_2\text{O}_8$ ,  $a$  10.79,  $c$  8.80;  $\text{CaY}_2\text{Si}_2\text{O}_8$ ,  $a$  10.79,  $c$  8.80;  $\text{K}_2\text{La}_2\text{Si}_2\text{O}_8$ ,  $a$  11.01,  $c$  8.96;  $\text{Na}_2\text{La}_2\text{Si}_2\text{O}_8$ ,  $a$  11.01,  $c$  8.96;  $\text{CaLa}_2\text{Si}_2\text{O}_8$ ,  $a$  11.01,  $c$  8.96;  $\text{Na}_2\text{Nd}_2\text{Si}_2\text{O}_8$ ,  $a$  10.89,  $c$  8.85;  $\text{K}_2\text{Nd}_2\text{Si}_2\text{O}_8$ ,  $a$  10.89,  $c$  8.85;  $\text{CaNd}_2\text{Si}_2\text{O}_8$ ,  $a$  10.89,  $c$  8.85. The X-ray diagrams of nepheline and kaliophilite are indicative of differences of structure, but rubidium nepheline possesses the rhombic structure of the second modification of kaliophilite. Nephelines and anorthites wherein the aluminium has been replaced by a rare-earth element have a structure closely resembling that of kaliophilite. Although homogeneous mixed crystals are formed between the rare-earth nephelines and the corresponding anorthites, this does not occur between the aluminium compounds and their rare-earth derivatives. The theoretical significance of the results is discussed and their geochemical aspect is indicated.

H. F. GILLBE.

**Silicate system based on crystal structure.** S. VON NÁRAY-SZABÓ (Z. physikal. Chem., 1930, B, 9, 356—377).—Existing systems of classification of silicates are discussed and the characteristic features of the silicate lattices are described. A new system, applicable to all well-crystallised compounds and based on the form of the space-lattice rather than on chemical evidence, is proposed. In this classification the silicates fall into five groups: (1) orthosilicates, (2) independent chemical groups, such as  $\text{Si}_2\text{O}_7$ , (3) unidimensional chains of silicon and oxygen atoms, (4) two-dimensional planes of silicon and oxygen atoms, (5) three-dimensional networks of silicon and oxygen atoms. Various properties of silicates, such as hardness, chemical reactivity, etc., are discussed in the light of these views.

E. S. HEDGES.

**Crystal structures of the compounds  $\text{Zn}_2\text{TiO}_4$ ,  $\text{Zn}_2\text{SnO}_4$ ,  $\text{Ni}_2\text{SiO}_4$ , and  $\text{NiTiO}_3$ .** N. W. TAYLOR (Z. physikal. Chem., 1930, B, 9, 241—264).—The compounds zinc orthotitanate, zinc orthostannate, nickel orthosilicate, and nickel motatitanate have been prepared by mixing the powdered component oxides, pressing into pastilles, and heating at or above 850°. The lattice constants, densities, and molecular volumes of these compounds have been determined and the following data are given. Zinc orthotitanate: cubic, spinel type,  $a$   $8.460 \pm 0.005$  Å.,  $d$  5.295; zinc orthostannate: cubic, spinel type,  $a$   $8.650 \pm 0.005$  Å.,  $d$  6.393; nickel orthosilicate: rhombic, olivine type,  $a$   $4.705 \pm 0.005$ ,  $b$   $10.11 \pm 0.01$ ,  $c$   $5.914 \pm 0.005$  Å.,  $d$  4.920 g./cm.<sup>3</sup>; nickel motatitanate: rhombohedral, corundum-ilmenite type,  $a$   $5.023 \pm 0.005$  Å.,  $d$  5.075. No trace of nickel metasilicate, nickel orthotitanate,

zinc motatitanate, or zinc metastannate was found. Mixtures of cupric oxide with the dioxides of silicon, titanium, and tin do not react under the conditions described.

E. S. HEDGES.

**Physico-chemical investigation of amino-acids. III.** G. TAKAHASHI and T. YAGINUMA (Proc. Imp. Acad. Tokyo, 1930, 6, 201—204).—Tables show the crystal constants of the  $\alpha$ - and  $\beta$ -forms of the methyl, ethyl, and  $n$ -propyl ester hydrochlorides of  $L$ -leucine. Diagrams are furnished.

P. W. CLUTTERBUCK.

**Crystal structure of normal paraffins.** S. H. PIPER and T. MALKIN (Nature, 1930, 126, 278).—Hexacosane and tetratriacontane show two stable forms at the ordinary temperature; one form has the normal structure described by Müller (this vol., 844), but the other spacing, about 4 Å. shorter, is different from the second form of Müller. In hexacosane, this new form occurred alone when crystallised from benzene or alcohol: a fused layer showed both spacings. In tetratriacontane, crystals from benzene gave only the new spacings, whilst melted material showed only the normal form. Pure, even-numbered hydrocarbons appear to crystallise in the new form if the chain has 26 or more carbon atoms. The two spacings for hexacosane, triacontane, and tetratriacontane are 35.0 and 31.05, 40.5, and 45.3 and 40.00 Å., respectively. The appearance of the second spacing is a criterion of purity.

L. S. THEOBALD.

**X-Ray investigation of the crystals of azobenzene.** M. PRASAD (Phil. Mag., 1930, [vii], 10, 306—313).—The rotating crystal method was used, the radiation being copper  $K\alpha$  and  $K\beta$  from a Shearer tube. The dimensions of the unit cell, which contains 4 mols., were found to be  $a$  12.65,  $b$  15.60,  $c$  15.60 Å.;  $\beta$   $114^\circ 24'$ .

W. GOOD.

**Determination of the degree of polymerisation of some modifications of polyoxymethylene by X-ray methods.** E. OTT (Z. physikal. Chem., 1930, B, 9, 378—400).—An X-ray spectrographic examination of the crystal structure of some polyoxymethylenes shows them to consist of long chains of  $\cdot\text{CH}_2\cdot\text{O}\cdot$  groups, the paraformaldehyde molecule containing 32 of these groups,  $\gamma$ -polyoxymethylene 60, and  $\delta$ -polyoxymethylene 24. The length of the unit  $\cdot\text{CH}_2\cdot\text{O}\cdot$  group is 1.88—1.89 Å. An important point established is that in crystals of highly polymerised substances all the complex molecules are of the same length. Characteristic differences in the diagrams obtained from the different polymerides were observed, and the crystals are pseudo-hexagonal.

E. S. HEDGES.

**Structure of organic liquids internally and on the surface.** J. J. TRILLAT (Z. Physik, 1930, 64, 191—213).—The sources of error in the X-ray investigation of the structure of organic liquids are discussed, and an apparatus in which they are minimised is described. A series of determinations was carried out with different fatty acids, alcohols, and triglycerides. In all cases a very intense ring of large diameter was obtained corresponding with an identity period of 4.0—4.6 Å. The internal ring varied in diameter with the number of carbon atoms, but was observed only for the first members of the

fatty acid and alcohol series. Its intensity decreased with increasing number of carbon atoms, and disappeared almost completely for molecules containing six carbon atoms, even after a long exposure. In all cases there was also a general blackening, which changed with the number of carbon atoms. The distances calculated from the usual expression,  $\lambda = 2d \sin \theta$ , for the intense ring were practically constant for all substances used, except for the first members, where there was some deviation. This distance is the cross-section of the molecule which must be regarded as linear. The general blackening is supposed to be due to molecular association. The surface structure of the same series of compounds was investigated by a drop method. In certain cases a mean orientation of the molecule perpendicular to the free surface was observed. The dimensions of the molecules can be calculated approximately, and the results agree with the assumption of a perpendicular orientation of single molecules. A. J. MEE.

**Diffraction of X-rays in liquids and different substances. Effects of filtration of the general radiation. Coefficients of absorption of liquid acids.** J. THIBAUD and J. TRILLAT (J. Phys. Radium, 1930, [vii], 1, 249—260).—When the X-ray diffraction patterns of organic substances of thickness of several mm. are measured without separating the characteristic radiation of the anticathode from the general radiation, there appears, in addition to the fundamental ring or halo, *A*, characteristic of the molecular structure of the substance, a secondary halo, *B*, which is due to selective filtration from the continuous background. With a copper anticathode and the liquid fatty acids, *B* appears when the thickness is greater than 2 mm., its intensity increasing with an increase in thickness, whilst that of *A* decreases. At a constant thickness, the breadth and diameter of *B* vary with the excitation potential; under a *P.D.* of 15 kilovolts, *B* is thin and of relatively large diameter, but at 40 kilovolts it is diffuse and smaller in diameter. *A* remains constant and is always the external halo. Data for nonoic acid are given. With an anticathode of molybdenum, *A* and *B* are intermingled. This phenomenon is general and has been observed for water, the alcohols, triglycerides, glycerol, palmitic and stearic acids, cellulose, caoutchouc, aliphatic hydrocarbons, and benzene. For the liquid fatty acids using the  $K\alpha$  radiations of molybdenum and copper, the coefficients of absorption are as follow: acetic 0.73 and 7.9, heptioic 0.65, nonoic 0.5 and 4.5, stearic (fused) 0.5 and 3.72, respectively. These coefficients are additive. Precautions should be taken in structural investigations by means of X-rays to prevent the formation of secondary haloes.

L. S. THEOBALD.

**Structure of cellulose fibres of wood.** S. PIENKOWSKI (Z. Physik, 1930, 63, 610—615).—The structure of the cellulose crystallite in woods of different nature and age was investigated by the X-ray method. This method has already shown that the crystallite of cellulose from natural fibres is partly equally oriented, and it was desired to know whether the same applies to cellulose from wood. It was found that the degree of homogeneity as regards orientation depends on the

thickness of the annual rings and the hardness of the wood. Great differences in degree of dispersion were noted for crystallites from tree parts of different thicknesses, but of the same annual layer. In agreement with the anatomical structure, exact homogeneity as regards orientation was noted for elm and ash wood in the thicker parts of the same annual ring, and for fir, pine, and poplar in the thinner parts. The drying process which takes place in the wood influences the degree of dispersion only to a small extent, making it weaker. The degree of homogeneity of the crystallites is greater the more compact is the wood, and depends apparently on the size of the cell walls parallel to the tree axis. A. J. MEE.

**Sperms as living liquid crystals.** F. RINNE (Nature, 1930, 126, 279).—A summary of the evidence supporting the view that sperms are also liquid crystals. L. S. THEOBALD.

**Theory of superconductivity of elements. II. Basic conceptions of the origin of superconduction.** Z. A. EPSTEIN (Z. Physik, 1930, 63, 640—659; cf. this vol., 986).—By an examination of thermo-kinetic theory it is possible to state what properties a superconducting element should have as distinct from ordinary conductors. Superconductors have these properties to relatively greater degree than ordinary conductors. A formula is proposed to differentiate between the two classes of the form  $D \cdot \beta \cdot v^{2/3} = \text{const.}$ , where *D* is the directional force and *v* the atomic volume. Various properties of superconductors and ordinary conductors are compared.

A. J. MEE.

**Change of resistance of gold crystals in a magnetic field at low temperatures and superconductivity.** P. KAPITZA (Physikal. Z., 1930, 31, 713—720).—The interpretation of experimental results obtained by Meissner and Scheffers (this vol., 142) for the change in resistance of gold crystals at the temperatures of liquid nitrogen, liquid hydrogen, and liquid helium is discussed in the light of the author's theoretical assumptions. By applying formulæ deduced by the author, the experimental results give values in complete agreement with theoretical assumptions. Criticism by Meissner and Scheffers of the author's hypothesis of superconductivity is answered. W. R. ANGUS.

**Change of electrical resistance of platinum on outgassing in a high vacuum and then absorbing hydrogen.** K. WEIL (Z. Physik, 1930, 64, 237—247).—A strip of platinum was activated and outgassed by intermittent heating to redness in a high vacuum. The resistance decreased during the outgassing process, and on allowing the strip again to absorb hydrogen by placing it in the gas under a pressure of 250 mm., the resistance increased. The outgassed strip diminished in resistance by 3.5%, and on re-absorption of hydrogen it gained by 1%. On further outgassing only 1% decrease was noted. The results suggest the improbability of the existence of a stable platinum-hydrogen compound, the change in resistance depending on the amount of gas absorbed.

A. J. MEE.

**Hydrogenised iron of high magnetic permeability.** P. P. CIOFFI (Nature, 1930, 126, 200—



201).—Initial and maximum permeabilities of 6000 and 130,000, respectively, have been obtained by heat treating iron in moist hydrogen between 1400° and 1500° for 12 hrs., and annealing at 880°, which removes any deleterious effects on the magnetic properties due to overstrain. The high permeability of hydrogenised iron is attributed, in part at least, to absorbed hydrogen, since a further treatment at a high temperature in a vacuum reduces the permeability to that obtained when ordinary iron is treated in a high vacuum. Magnetisation curves and the hysteresis loop are reproduced. L. S. THEOBALD.

**Principal magnetic susceptibilities of bismuth single crystals.** A. B. FOCKE (Physical Rev., 1930, [ii], 36, 319—325).—The Gouy method was used to determine the magnetic susceptibilities of bismuth single crystals grown by the method developed by Goetz (cf. this vol., 401). The specific susceptibility has a constant value  $-1.487 \times 10^{-6}$  in all directions perpendicular to the principal crystallographic axis, and a minimum value  $-1.046 \times 10^{-6}$  parallel to the axis; the mean is given as  $-1.34 \times 10^{-6}$ .

N. M. BLIGH.

**Discontinuous changes in length accompanying the Barkhausen effect in nickel.** C. W. HEAPS and A. B. BRYAN (Physical Rev., 1930, [ii], 36, 326—332).—Using a heterodyne beat method with a modified form of an apparatus previously described (cf. A., 1929, 1217), allowing displacement measurements down to  $9 \times 10^{-9}$  cm., the sudden changes in length of a nickel wire subjected to a steadily changing magnetic field were measured at the instants of each Barkhausen discontinuity of magnetisation. The lengths of the wires were 1.96 and 2 cm., and the diameters 0.01 and 0.002 cm., respectively. The largest magnetostrictive jump was  $4.7 \times 10^{-7}$  cm., and the minimum value  $3.7 \times 10^{-7}$  c.c., for the volume of the element affected. A qualitative theory is discussed (cf. A., 1929, 1369), and the change in intensity of magnetisation of the volume element is shown to lie probably between 40 and 330 units. N. M. BLIGH.

**Variation of the plasticity of rock-salt, silver bromide, and silver iodide with temperature.** F. RINNE and W. RIEZLER (Z. Physik, 1930, 63, 752—759).—The variation of plasticity with temperature was determined with a Ludwik steel cone. The radius of curvature of the depression caused by this cone increases logarithmically with the time of application of the stress, and the parameters of the equation expressing this relation are given as functions of the temperature of the specimen. Corrections are required because of deviation of the depression from spherical form. Single crystals and compressed powders of one substance give the same results.

A. B. D. CASSIE.

**Relation between the mol. wt. and the density of gold in the liquid state.** A. JOUNIAUX (Bull. Soc. chim., 1930, [iv], 47, 682—686).—Cryoscopic measurements have been made of the mol. wt. of gold dissolved in various metals between 271° and 1528°. It is unimolecular between 400° and 1550°.

C. W. GIBBY.

**Relation between the mol. wt. and density of magnesium in the liquid state.** A. JOUNIAUX

(Bull. Soc. chim., 1930, [iv], 47, 686—690).—The mol. wt. of magnesium (which at 200° is triatomic), dissolved in other metals, falls with rising temperature up to 700°, above which the molecule is monatomic.

C. W. GIBBY.

**Variation of physical constants in homologous series.** A. GOSSELIN (J. Chim. phys., 1930, 27, 357—363).—Further evidence is cited in favour of a theory already put forward (cf. A., 1929, 1130).

C. W. GIBBY.

**Theory of galvanomagnetic, thermomagnetic, and thermoelectric phenomena in metals.** N. H. FRANK (Z. Physik, 1930, 63, 596—609).—Mathematical. The four transversal galvanomagnetic and thermomagnetic effects are calculated for adiabatic systems according to Sommerfeld's theory. The connexion between these effects is discussed from a theoretical point of view. The various thermoelectric effects in homogeneous circuits are discussed, and in particular the inversion of the Thomson effect (Benedick effect). The change of resistance of a metal in a magnetic field under adiabatic conditions vanishes to both a first and a second approximation. For isothermal conditions, however, it vanishes only to a first approximation.

A. J. MEE.

**Reactions in liquid hydrogen sulphide. VIII. Specific conductance of liquid hydrogen sulphide.** S. D. SATWALEKAR, L. W. BUTLER, and J. A. WILKINSON (J. Amer. Chem. Soc., 1930, 52, 3045—3047).—The specific conductance of dry liquid hydrogen sulphide at  $-78.5^\circ$  is  $3.7 \times 10^{-11}$  ohm $^{-1}$ . The resistance is increased by the addition of small quantities of water.

J. G. A. GRIFFITHS.

**M. p. of tellurium dioxide.** A. ŠIMEK and B. STEHLÍK [with J. ŠMÍDA] (Coll. Czech. Chem. Comm., 1930, 2, 447—456).—Pure tellurium dioxide, prepared by dissolving the purified element in nitric acid, evaporating to dryness, and igniting in a gold crucible, has m. p.  $732.6^\circ$ ,  $d_4^{20}$  6.02. The fused substance readily attacks glass, porcelain, quartz, and alundum, and, more slowly, platinum, but the appearance of the dark colour observed when the dioxide has been in contact with platinum at a red heat for some time is not accompanied by a change of m. p. No indication of dimorphism is given by the heating curve between the ordinary temperature and the m. p., the crystals obtained by slow crystallisation of the fused material being optically uniaxial and exhibiting double refraction. A method is described for the extrapolation of the m. p. of substances which do not exhibit a sharp step in the heating curve.

H. F. GILLBE.

**Specific heat of mercury in the neighbourhood of the m. p.** L. G. CARPENTER and L. G. STOODLEY (Phil. Mag., 1930, [vii], 10, 249—265).—The specific heat of very carefully purified mercury was determined over the range 198—285° Abs., which includes the m. p.,  $234^\circ$ . The results were reduced and corrected to obtain  $C_p$ . The accuracy of the results is discussed. In the neighbourhood of  $210^\circ$  the  $C_p$  curve shows an increase of its positive slope and on nearing the m. p. becomes flat. At the m. p. itself the value of  $C_p$  was found to be 6.02 g.-cal., thus showing an excess over  $3R$  (5.95). Two hypotheses

are considered, viz., that the anomalous rise of  $C_v$  is due to anharmonic oscillations of atoms, and that it is due to the participation of free electrons in the thermal energy of the atomic lattice. W. GOOD.

**Rotational specific heat and rotational entropy of simple gases at moderate temperatures.** G. B. B. M. SUTHERLAND (Proc. Camb. Phil. Soc., 1930, 26, 402—418).—The formula for the rotational specific heat of a diatomic gas is examined, the formula for the rotational energy of a molecule as given by Kramers and Pauli being first modified so as to conform to the new quantum mechanics. Formulæ for the rotational entropy of simple gases at moderate temperatures are derived. W. GOOD.

**Virial law in the relativistic gas theory.** V. DANILOV (Z. Physik, 1930, 63, 692—696).—Mathematical. The relativistic generalisation of the virial law is worked out for the case of an ideal gas. A. J. MEE.

**Density of carbon dioxide.** D. LEB. COOPER and O. MAASS (Canad. J. Res., 1930, 2, 388—395).—Modifications of the Maass and Russell method for determining densities (A., 1919, ii, 47) which permit an accuracy of about 1 in 10,000 are described. The density of carbon dioxide has been determined at two temperatures and over a pressure range of 75—25 cm. The mean value obtained for the mol. wt. of carbon dioxide at zero pressure is  $44.0033 \pm 0.002$ , from which the at. wt. of carbon is found to be  $12.0033 \pm 0.002$ . H. S. GARLICK.

**Saturation vapour pressure of lithium.** A. BOGROS (Compt. rend., 1930, 191, 322—324).—The author's modification of Knudsen's method (this vol., 829; Knudsen, A., 1909, ii, 216, 385) gave the values (in bars) of 4.2, 6.3, 7.1, 10.5, 15, and 18 at 510°, 527°, 529°, 537°, 563°, and 572°, respectively, with a maximum relative error of 15%. J. GRANT.

**Vapour pressure of sodium. Low-pressure measurements with the absolute manometer.** W. H. RODEBUSH and W. F. HENRY (J. Amer. Chem. Soc., 1930, 52, 3159—3161).—A modified form of the manometer of Rodebush and Coons (A., 1927, 954) is used to determine the vapour pressure of sodium at temperatures between 263° and 397°. The results are reproduced by the equation  $\log p \text{ (mm.)} = 7.551 - 5400/T$  (cf. this vol., 1104). J. G. A. GRIFFITHS.

**Flow of viscous and plastic materials along an initially empty long narrow glass tube.** G. W. S. BLAIR (J. Rheology, 1930, 1, 424—428).—The dynamics of flow of water and of starch paste when caused to flow along an initially empty glass tube of uniform cross-section have been investigated. E. S. HEDGES.

**Fluidity of liquids. I. Relation of fluidity to temperature.** S. E. SHEPPARD and R. C. HOUCK (J. Rheology, 1930, 1, 349—371).—The expression  $\phi = Ae^{-K/T}$  is derived for the relation between fluidity and temperature and is shown to be valid for a large number of liquids over a wide range of temperature. The fluidity represents the statistical equilibrium between unoriented and oriented molecules or the degree of "patchy crystallisation." The constant  $K$  expresses the work or heat of disruption of the mole-

cular fields holding a molecule in these ordered patches, and is given approximately by the expression  $C_v \times (M\vartheta)^{2/3}$ , where  $C_v$  is the specific heat,  $M$  the mol. wt., and  $\vartheta$  the density.  $K$  is defined as the specific heat per unit molecular surface. As the f. p. is approached in the case of associated liquids the relation between the logarithm of fluidity and the reciprocal of absolute temperature may deviate from linearity, and values of molecular complexity may be obtained where it varies greatly with temperature, or in less favourable cases an approximate association factor can be calculated. Those values are in reasonable agreement with those obtained by other methods. Evidence is adduced to show that liquid water consists mainly of  $(H_2O)_6$  molecules below 30° and of  $(H_2O)_3$  from 30° to 100°. E. S. HEDGES.

**Determination of the fluidity of water as a reference standard.** E. C. BINGHAM (J. Rheology, 1930, 1, 433—438).—The Society of Rheology recommends that the capillary-tube method is at present the most satisfactory for viscosity measurements and that 20° should be the standard temperature. The formula to be used for measurements with the capillary tube is  $\eta = \pi g P R^4 l / 8 \nu (l + \Lambda) - m \rho \nu / 8 \pi t (l + \Lambda)$  and a list of 26 corrections to be applied is given. E. S. HEDGES.

**Margules' method of measuring viscosities modified to give absolute values.** H. R. LILLIE (Physical Rev., 1930, [ii], 36, 347—362; cf. B., 1929, 940, 963).—A method is described for determining absolute viscosities in a Margules rotating-cylinder type viscosimeter, without the aid of calibrating liquids of known viscosities. The viscosity of commercial castor oil was found to be 9.99 and 4.61 poises at 20° and 30°, respectively. Relative viscosities measured by this and capillary-flow methods are concordant. N. M. BLIGH.

**Chemical constitution and association.** E. C. BINGHAM and H. J. FERNWALT (J. Rheology, 1930, 1, 372—417).—The fluidities and densities of 14 mercaptans have been measured at different temperatures. The 14 curves obtained by plotting fluidity against temperature approach parallelism at high temperatures and show that fluidity decreases linearly with increase in mol. wt. and that the temperature required to give a definite fluidity to a normal compound is higher than that required for the corresponding *iso*-compound. Probably the association of normal compounds is greater than that of *iso*-compounds. Sulphur is provisionally given an atomic temperature value of 64.4. The associations of the mercaptans studied can be expressed empirically by the formula  $n = 1.141 - 0.0115N_c - 0.036N_2(SH)$ , where  $n$  is the association,  $N_c$  the number of carbon atoms, and the last term is the constitutional correction for the influence of the *iso*-position. The mean deviation is 0.6%. Further measurements of fluidity and density have been made with heptioic, lauric, and stearic acids and are compared with existing data for 7 other fatty acids. The associations of the 10 fatty acids can be represented by the linear equation  $n = 1.75 - 0.0446N_c + 0.514(H \cdot CO_2H) + 0.185(AcOH)$ , which is valid up to 17 carbon atoms, associations thereafter being considered as unity. \* Formic and acetic acids do not

fall on the linear part of the curve. The average deviation is 0.68%. Existing fluidity data for 11 members of the lower esters have been used to calculate the association and three accurate logarithmic formulæ have been found to fit the case. A more simple and useful, although less accurate, formula is the linear relation  $n = 1.315 - 0.04N_c$ , with which the average deviation is 1.14%. When the ester is symmetrical the association is a minimum. Further measurements of a similar nature have been conducted with *n*-heptyl alcohol, diphenyl, ethyleneglycol, and ethyl lactate. The fluidities of two very viscous liquids, tolyl phosphate and ethyl abietate, have been measured. Measurements conducted with the paraffin hydrocarbons show again that normal and iso-compounds fall into separate groups. The investigation shows that the substances examined contain definite associating groups and that they strongly reinforce one another. Chemical constitution may be used to predict the degree of association. Among isomeric compounds the normal compound has the higher association, but this is a special case of a general law that as radicals are moved towards the centre of the molecule the association is lowered, regardless of whether the radical is an associating group or not. In all of the homologous series of compounds examined the association decreases as the mol. wt. increases.

E. S. HEDGES.

**Turbulent internal friction in binary liquid mixtures.** R. SPRINGER and H. ROTH (Monatsh., 1930, 56, 1—15).—The method previously described (A., 1927, 1133) has been employed to measure the turbulent internal friction in 20 binary liquid mixtures; the results are compared with those obtained by other workers using the Poiseuille method. The curves obtained with the mixtures methyl, ethyl, or propyl alcohol-water, chloral-water or ethyl alcohol, aniline-phenol agree closely with the Poiseuille figures, showing a positive curve indicating complex formation. The curves for the following mixtures show pronounced additive character: carbon disulphide with ether, toluene, acetone, ethyl alcohol, ethyl acetate, or benzene; benzene-chloroform and *m*-xylene-dimethylaniline. The mixtures benzene-propyl alcohol or ethyl alcohol, nitrobenzene-diethylaniline show additive turbulence curves, but the Poiseuille curves show a negative course. The mixtures ethyl alcohol-acetone and aniline-nitrobenzene show a negative course in both curves; the system propyl alcohol-aniline shows an S-shaped turbulence curve compared with a negative Poiseuille curve.

J. R. I. HEPBURN.

**Dielectric polarisation of liquid mixtures and association.** I. N. N. PAL (Phil. Mag., 1930, [vii], 10, 265—280).—Measurements of the dielectric constants of mixtures of nitrobenzene and benzene and of nitrobenzene and chloroform of various concentrations have been made by a heterodyne beat method at different temperatures. The general features of the results are tentatively accounted for by an expression derived from Debye's dipole theory and the assumption that the number of molecules is proportional to  $e^{-\epsilon RT}$ , where  $\epsilon$  is approximately determined by the residual electric attraction between the dipoles. W. GOOD.

**F. p. of benzene-toluene, -ethyl alcohol, and -gasoline mixtures.** D. TARASENKOV (J. Appl. Chem., Russia, 1930, 3, 153—155).—The following values of wt.-% of benzene and f. p., respectively, are recorded: benzene-toluene: 100, +5.5°; 89.74, -2.1°; 78.92, -9.3°; 70.04, -15.3°; 59.45, -24.1°; 50.36, -32.6°; 40.31, -42°; 29.70, -53°; 20.00, -68°; 9.85, -81°; 0, -94°. Benzene-ethyl alcohol: 89.91, +2.5°; 79.92, +1.1°; 70.00, -0.4°; 59.97, -2.6°; 49.90, -6.1°; 39.90, -11.1°; 29.96, -21.0°; 20.02, -39.5°; 9.97, -66°; 0, -114°. Benzene-petroleum ( $d_{4}^{15}$  0.7159, Grozni): 90, +0.1°; 80, -4.5°; 70, -9.0°; 60, -14.2°; 50, -22.2°; 40, -26.5°; 30, -37.2°; 20, -43.5°; 10, -61.5°; 0, -160°.

CHEMICAL ABSTRACTS.

**Silver-cadmium alloys.** E. R. THEWS (Deut. Goldschmiede-Ztg., 1930, 33, 56—58; Chem. Zentr., 1930, i, 1857).

**X-Ray study of the nickel-chromium system.** S. SEKITO and Y. MATSUNAGA (J. Study Met., Japan, 1929, 6, 229—233).—The alloys containing 0—45% Cr are of the face-centred cubic structure, chromium dissolving in the nickel to form a solid solution. In the alloys containing 95—100% Cr the structure is body-centred cubic, the nickel dissolving in the chromium. Alloys containing 45—95% Cr consist of a mixture of these two solid solutions.

CHEMICAL ABSTRACTS.

**Electrical conductivity of Cu<sub>3</sub>Au alloys at low temperatures with and without superstructure.** H. J. SEEMANN (Z. Physik, 1930, 62, 824—833).—The electrical resistance of copper-gold alloys containing approximately 25 at.-% Au has been determined at low temperatures, (1) after heating for 50 hrs. at 860° (without superstructure), and (2) with the same test-piece cooled slowly through the range 400—300° (with superstructure). Alloys without superstructure show a linear fall in resistance, but those with superstructure show a considerably greater decrease at lower temperatures. The shape of the resistance-composition curve for the alloys without superstructure indicates the formation of an intermetallic compound of the formula Cu<sub>3</sub>Au, whereas the curve for alloys with superstructure suggests the existence of solid solutions of copper and gold. The decrease of resistance of the pure compound at low temperatures corresponds with that of the pure metal.

A. J. MEE.

**Equilibrium diagram of the iron-tungsten system.** S. TAKEDA (J. Study Met., Japan, 1929, 6, 298—308).—The eutectic of the  $\epsilon$ - (corresponding with Fe<sub>3</sub>W<sub>2</sub>) and  $\delta$ -phases is at 33% W; the peritectic reaction, in which the  $\epsilon$ -phase is formed, occurs in alloys containing more than 43% W. The existence of a phase  $\alpha$ , which is formed peritectically from the fused mass and tungsten (or  $\zeta$ -phase), is inferred.

CHEMICAL ABSTRACTS.

**Alloys of the ternary system iron-nickel-cobalt.** H. KÜHLEWEIN (Physikal. Z., 1930, 31, 626—640).—A review of the properties of alloys containing iron, cobalt, and nickel. Physical data for the pure metals are recorded and the properties of the binary and ternary systems are discussed. Various electrical, mechanical, thermal, and magnetic prop-

properties are considered. The discussion of these properties is given in detail with illustrative diagrams.

W. R. ANGUS.

**Solubility of silver chloride in aqueous solutions of potassium chloride.** A. PINKUS and N. BERKOLAÏKO (*J. Chim. phys.*, 1930, 27, 364—385).—The solubility of silver chloride in pure water is  $1.42 \times 10^{-5}$  mol./litre. On addition of potassium chloride the solubility passes through a minimum value of  $8.13 \times 10^{-7}$  mol./litre at 0.0196 mol./litre of potassium chloride, and rises rapidly with further increase in concentration of the latter. Activity coefficients and degrees of complex formation are calculated.

C. W. GIBBY.

**Solubility of magnesium neodymium nitrate in water, nitric acid, and magnesium nitrate solutions.** J. A. N. FRIEND (*J.C.S.*, 1930, 1903—1908).—The solubility of the salt in water rises steadily to the m. p., the solid phase being  $3\text{Mg}(\text{NO}_3)_2 \cdot 2\text{Nd}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ . Both nitric acid and magnesium nitrate reduce the solubility, the latter having the greater effect for equivalent concentrations. Indications are obtained of the possible existence of a higher hydrate at low temperatures. It is shown that on precipitation of neodymium as oxalate, adsorption of magnesium under the conditions employed is negligible.

H. I. DOWNES.

**Partition law in the fractional crystallisation of radium salts.** N. RIEHL and H. KÄDING (*Z. physikal. Chem.*, 1930, 149, 180—194).—The logarithmic partition formula of Doerner and Hoskins (*A.*, 1925, ii, 381) gives the distribution of radium between solution and precipitate more accurately when the experimental conditions correspond with the assumptions involved in the theory, viz., slow crystallisation by evaporation. The contrary results of Chlopin and his co-workers (*A.*, 1925, ii, 438; 1927, 1133; 1928, 830; this vol., 27) and of Henderson and Kracek (*A.*, 1927, 431) are explained by the difference in their experimental conditions. Well-developed crystals once precipitated do not show any marked subsequent change in radium content.

J. W. SMITH.

**Occlusion of hydrogen by platinum-black.** A. SEEVERTS and H. BRÜNING (*Festschr. Heraeus*, 1930, 97—114; *Chem. Zentr.*, 1930, i, 2226—2227).—For a particular temperature and pressure the sorption of hydrogen by platinum-black depends on the previous treatment of the latter. The isobars exhibit a change of direction between  $0^\circ$  and  $-20^\circ$ , becoming again rectilinear between  $-20^\circ$  and  $-120^\circ$ .

A. A. ELDRIDGE.

**Radiometer pressure and coefficient of accommodation.** M. KNUDSEN (*Ann. Physik*, 1930, [v], 6, 129—185).—The coefficient of accommodation of hydrogen and helium at a platinum surface has been deduced from measurements of radiometer pressure. The results for hydrogen at low pressures show that the value is the same for the internal energy as for the translational energy.

R. CUTHILL.

**Specific surface area of activated carbon and silica.** F. E. BARTELL and Y. FU (*Coll. Symp. Ann.*, 1929, 7, 135—149).—Data for the adsorption by sugar charcoal and silica gel of benzene, chloro-

form, carbon disulphide, ethyl carbonate, and carbon tetrachloride are recorded. The respective specific areas were 6.3 and  $4.5 \times 10^6$  cm.<sup>2</sup> With anhydrous silica gel values of the heat of wetting were: ethyl alcohol 16.64, acetone 16.83; the corresponding adhesion tensions are 3.5 and 2.77. The heat of wetting is a measure of the decrease in total surface energy; the free surface energy determines the adsorption.

CHEMICAL ABSTRACTS.

**Adsorption of vapours.** W. A. PATRICK (*Coll. Symp. Ann.*, 1929, 7, 129—133).—A summary and discussion. The total internal surface of silica gel is much less than  $6 \times 10^6$  cm.<sup>2</sup> Initially, the adsorbed water forms a unimolecular layer which, in tending towards a minimal surface, produces a capillary effect greatly exceeding that derived from the classical Kelvin equation.

CHEMICAL ABSTRACTS.

**Adsorption of sulphide and oxide films by metallic surfaces.** E. BEUTEL and A. KUTZELNIGG (*Z. Elektrochem.*, 1930, 36, 523—528).—The colouring of metals in solutions prepared from sodium thio-sulphate and a lead, silver, or copper salt is shown to be due to the adsorption of a film of insoluble compound formed by decomposition of complex salts deposited in the nascent state. The phenomena may be regarded as a particular case of the general adsorption at an interface wherein the factor determining above all the occurrence and velocity of adsorption is the electrochemical position of the metal; for the sixteen metals examined the adsorption is slower the nobler is the metal. Diagrams obtained by using photometers show that the series of interference colours obtained on the metals are dependent on the nature both of the adsorbing metal and of the precipitating sulphide.

H. I. DOWNES.

**Adsorption of fats from volatile solvents.** H. N. HOLMES and C. J. B. THOR (*Coll. Symp. Ann.*, 1929, 7, 213—222).—The results of experiments in which solutions of "oleostearin" in ether, acetaldelyde, carbon tetrachloride, light petroleum, benzene, cyclohexane, or toluene were shaken with norit, silica gel, hydrated ferric oxide, or hydrated alumina verified the prediction that the order of adsorption must be reversed when silica, instead of carbon, adsorbs fatty acids from toluene. The adsorption isotherms in general show that the order of the adhesion tension is that recorded by Bartell.

CHEMICAL ABSTRACTS.

**Adsorption capacity of starch and iodine-starch.** O. Y. MAGIDSON and A. G. BAITSCHKEV (*J. Chem. Ind., Russia*, 1929, 6, 1098—1103).—Measurements of the adsorbent power of starch and starch iodide towards iodine, alkalis, and naphthenic acids are described. The presence of various salts, especially in high concentration, considerably enhances the adsorption of potassium iodide, carbonates, and naphthenates. The substances are completely extracted by water.

CHEMICAL ABSTRACTS.

**Adsorption phenomena in solutions. XX. Chemical state of the surface of active charcoal.** N. SCHILOV, H. SCHATUNOVSKAJA, and K. TSCHMUTOV (*Z. physikal. Chem.*, 1930, 149, 211—222).—Besides the two basic oxides (oxide A and oxide B) previously reported (this vol., 991) an acidic oxide

*C* has been proved to exist on a carbon surface. The temperature limits of its formation from oxide *B* and also of its decomposition have been investigated. It readily adsorbs alkali. The adsorption of acid found with specimens of charcoal coated with this oxide is attributed to residual oxide *B*. Oxide *C* can be formulated as the anhydride of a carbon acid and is assumed to be an intermediate product in the oxidation of carbon dioxide and also in the equilibrium between carbon, carbon dioxide, and carbon monoxide at moderate temperatures. At higher temperatures the oxide *B* is the active intermediate compound in these reactions.

J. W. SMITH.

**Methyl-violet lake.** W. D. BANCROFT and J. W. ACKERMAN (J. Physical Chem., 1930, **34**, 1767—1776).—The function of sodium benzoate in the formation of lakes is to adsorb the methyl-violet: the alumina adsorbs the sodium benzoate. The aluminium sulphate employed forces the dye on the mordant, and is not used to adsorb the excess of the dye. Sodium sulphate is equally satisfactory in this respect. The adsorption of the sodium benzoate and the methyl-violet by alumina increases with rise in temperature up to 90°, and then decreases. On keeping for three months, methyl-violet lakes become stronger owing to increased adsorption. Alumina is the best mordant for lakes, those of iron, tin, and zinc being less satisfactory, whilst chromium is a good mordant for darker shades.

L. S. THEOBALD.

**Adsorption linking.** I. H. KAUTSKY and E. GAUBATZ (Z. anorg. Chem., 1930, **191**, 382—413).—The influence of the chemical constitution (*i.e.*, of the single atoms and ions) of various adsorbents with comparable surfaces on the adsorption of different gas molecules has been studied. Siloxen (*cf.* A., 1929, 257) and its mono-, tri-, and penta-bromo-derivatives were used as adsorbents. From X-ray measurements with calcium disilicide the surface per mol. of siloxen is taken to be 929,300 m.<sup>2</sup> The sp. gr. of these substances increases by a constant amount for each bromine atom introduced, and it may be assumed that all the bromine atoms are linked in the same way. Adsorption isotherms have been determined for ethane and for carbon dioxide. Ethane is more strongly adsorbed, and for both gases the adsorption (mols. gas./mol. adsorbent) increases in the order monobromosiloxen, siloxen, tribromosiloxen, pentabromosiloxen. The factors influencing adsorption are discussed and it is concluded that the degree of adsorption is determined by (a) the sign of the electric charge of the ions in the surface which influences the polarisability of the adsorbed gas molecule, (b) the constitution of the surface, *e.g.*, progressive substitution of hydrogen by bromine atoms, and (c) the spacial configuration of the surface. An apparatus suitable for the determination of adsorption isotherms through a wide range of pressures is described. The following values of *d* are recorded: siloxen, 1.58; mono-, tri-, and penta-bromosiloxen, 1.85, 2.39, and 2.917, respectively.

O. J. WALKER.

**Adsorption of amphoteric substances by collodion membranes.** G. ETTISCH, M. DOMONTOWITSCH, and P. VON MUTZENBECHER (Naturwiss., 1930, **18**, 447—448).—By means of refractivity

measurements the quantity of egg-albumin adsorbed by a collodion membrane has been determined as a function of the *p<sub>H</sub>* of the solution. There is a sharp peak in the *p<sub>H</sub>*-adsorption curve at the isoelectric point. Analogous results are obtained with hæmoglobin, serum-albumin, and serum-paraglobulin, and also with non-colloidal solutions of glycine. A maximum adsorption of gelatin at the isoelectric point is not shown by the refractometric method, but is rendered evident by the reaction of the adsorbed layer with auric chloride or silver nitrate solution. The existence of this maximum is explained by the decrease at the isoelectric point of the affinity of the colloid for the molecules of the disperse medium and the resulting decrease in the work necessary for the removal of the protein from the solution.

H. F. GILLBE.

**Thermodynamic study of surface tension, affinity, and speed of absorption.** VII. R. DEFAY (Bull. Acad. roy. Belg., 1930, [v], **16**, 741—754).—The formula connecting the vapour pressure of a liquid with the curvature of its surface is generalised so as to be applicable to the partial pressure of the several components of a liquid mixture.

N. M. BLIGH.

**Multimolecular films.** R. S. BRADLEY (Phil. Mag., 1930, [vii], **10**, 323—326).—The case of a dipole chain built up on the surface of the adsorber is theoretically investigated, regard being had to the polarisation at optical frequencies of the adsorbed molecules and the interaction between the latter and their electrical images in the surface. The latent heat of evaporation of the outside layer of molecules of a water film 3 molecules thick is evaluated, giving 8600 g.-cal. per mol., and this agrees well with Lenher's value for the case of a film 5 molecules thick, *viz.*, 9100 g.-cal.

W. GOOD.

**Phase diagram for unimolecular films.** C. G. LYONS and E. K. RIDEAL (Proc. Camb. Phil. Soc., 1930, **26**, 419—420).—The analogy between two- and three-dimensional systems is briefly shown.

W. GOOD.

**Density of ammonium nitrate solutions.** F. M. A. HOEG (Z. anal. Chem., 1930, **81**, 114—116).—The *d* of 20, 30, 40, 50, 60, 70, and 80% solutions of ammonium nitrate at 20°, 40°, 60°, 80°, and 100° are tabulated together with the composition and *d* of solutions saturated with the salt at these temperatures and at temperatures between 105° and 230°.

A. R. POWELL.

**Fluorescence of solutions. Variation of the polarisation with the concentration and the influence of a non-fluorescent dye.** (MLLE.) Y. CAUCHOIS (J. Chim. phys., 1930, **27**, 336—345).—The degree of polarisation of the fluorescent light emitted by solutions of fluorescein in glycerol and in dextrose decreases with increase of concentration. The fluorescence of aqueous fluorescein solutions diminishes, and the polarisation of the light increases, if the concentration of a co-existing non-fluorescent coloured substance such as ammoniacal copper sulphate is increased.

H. F. GILLBE.

**Cryoscopic study of the molecular equilibrium of resorcinol in aqueous solutions of calcium,**

barium, and magnesium chlorides and ammonium and magnesium sulphates. C. R. M. TUTTLE (J. Chim. phys., 1930, 27, 307—328).—In 0.25*M*-solutions of calcium, barium, and magnesium chlorides resorcinol exists as double and single molecules at concentrations from 0.25 to 0.625, 0.25 to 0.625, and 0.25 to 0.500*M*, respectively. Equilibrium between single and triple molecules exists at resorcinol concentrations from 1.0 to 2.0*M* for all three chlorides. In 0.625*M*-solutions of the chlorides the limiting equilibrium concentrations are but slightly different. The cryoscopic constants of the three chlorides have been measured and the degrees of hydration calculated at various concentrations. In 0.25*M*-solutions of ammonium and magnesium sulphates there exists an equilibrium between single and double molecules of resorcinol at concentrations from 0.25 to 0.625 and 0.25 to 0.50*M*, respectively, and between single and triple molecules at concentrations from 1.0 to 2.0 and 1.0 to 2.375*M*, respectively; at higher sulphate concentrations the equilibria are shifted slightly. The degrees of hydration of the two sulphates at various concentrations have been determined from the cryoscopic constants: although ammonium sulphate has a smaller constant than sodium chloride, it is hydrated to approximately the same extent at equivalent concentrations. H. F. GILLBE.

**Lyophile and lyophobic sols.** F. J. NELLENSTEYN (Chem. Weekblad, 1930, 27, 506—507).—The accepted colloid-chemical nomenclature is criticised, and it is proposed to divide sols according to the absence or presence of insoluble nuclei. The degree of hydration in hydrophilic sols is not regarded as highly characteristic; the most important factor for stability is the surface tension at the boundary between the micelle and the medium. S. I. LEVY.

**Optical analysis of some colloidal silver solutions and discussion of the results obtained.** F. RIMATTEI (Rev. gén. Colloid., 1930, 8, 145—160).—The extinction coefficients of aqueous solutions of "argyrol" have been measured and the variation of the values with the wave-length of light and with the concentration of the sol has been determined. The extinction coefficient is not affected by temperature over the range investigated, but decreases slowly when the sol is kept. The spectrophotometric method can be used for determining the concentration of silver sols; for "argyrol" solutions varying in concentration from  $0.6 \times 10^{-3}$  to  $0.00857 \times 10^{-3}$  the error of the method is 1—4%. This shows an advantage over determinations made in a colorimeter (error 4—8%) and those made by matching against a standard scale of tubes (error 13%). E. S. HEDGES.

**State of dispersion of cellulose in cuprammonium solvent as determined by ultracentrifuge.** A. J. STAMM (J. Amer. Chem. Soc., 1930, 52, 3047—3062).—The sedimentation by ultracentrifuge of pure cotton linters  $\alpha$ -cellulose in cuprammonium solvent (0.3—1.28% Cu, 14.8—22.0%  $\text{NH}_3$ ) has been studied at 20° by the refraction method (Lamm, A., 1929, 129, 1234). The specific sedimentation velocity is practically independent of the concentrations of copper and ammonia, but decreases slightly with increasing concentration of cellulose (0.025—0.5%). The diffusion

constant is independent of the concentration of copper, decreases with decrease of ammonia, and increases markedly with decrease of cellulose, but values for fresh solutions are considerably smaller than for old solutions. The apparent ageing of the solutions is due to the oxygen of the air, which causes a greater dispersion of the cellulose particles. The results are explained on the basis of the gelation of the system. The cellulose-cuprammonium complex is monodisperse and the mol. wt. is  $55,000 \pm 7000$ , which on a copper-free basis is  $40,000 \pm 5000$  (cf. Herzog and Krüger, A., 1926, 903). An experiment with 0.26% viscose in 2.2% sodium hydroxide indicates that the mol. wt. of cellulose xanthate is approximately the same as for the above cellulose.

The cuprammonium solvent contained polydisperse particles (copper hydroxide?) 6.5 to  $>20 \mu$  in diameter and with sedimentation velocities 10—100 times as great as that of the cellulose particles.

J. G. A. GRIFFITHS.

**Differences between the state of dispersion of isolated wood cellulose and cotton cellulose in cuprammonium solvent.** A. J. STAMM (J. Amer. Chem. Soc., 1930, 52, 3062—3067).—The ultracentrifuge method shows that absorbent cotton and cotton linters filter paper in cuprammonium solvent consist almost entirely of particles similar to those of cotton linters  $\alpha$ -cellulose (cf. preceding abstract), but the first also contains a small quantity and the second a somewhat larger quantity of constituents of finer dispersion the proportion of which decreases with increasing  $\alpha$ -cellulose content.

Sulphite pulp  $\alpha$ -cellulose, bleached sulphite pulp, Cross and Bevan aspen wood, and white spruce celluloses all contain in various proportions material of the same mol. wt. as that of cotton cellulose together with particles of one half this mol. wt. and molecular species of still finer dispersion.

J. G. A. GRIFFITHS.

**Formation of starch paste.** S. V. GORBATSCHEV (Biochem. Z., 1930, 224, 91—101).—The temperature of conversion of starch from the granular into the dispersed (paste) form is followed by the iodine reaction in different media and in presence of different ions. Alkali thiocyanates, iodides, and bromides facilitate the formation of the dispersed form, whilst the sulphates and chlorides of lithium, magnesium, calcium, and aluminium act as stabilisers. "Paste formation is not a specific reaction between starch and water, but may be effected with other media providing the dielectric constant is sufficiently large (glycerol). Using an aqueous medium, the effect of dissolved materials on the temperature of paste formation depends on whether they increase or diminish the adsorption of water by starch. Substances which neutralise the electric field of the hydrogen ions which are adsorbed on the surface of the starch increase the power of starch to adsorb water and thereby depress the temperature of paste formation (cf. A., 1927, 722, 1174). P. W. CLUTTERBUCK.

**Heating of solutions and emulsions by electrostatic fields.** W. H. MARSHALL (J. Gen. Physiol., 1930, 13, 637—646).—The rate of rise of temperature of sodium chloride solutions and water was found to



depend on the potential gradient employed as well as on the frequency. For potential gradients greater than about 70 volts per mm. the absorption increases rapidly with increase of frequency. For low potential gradients this relationship does not hold. The absorption figures for water decrease with exposure, dropping to about 40% of the original values. This decrease of absorption is not shown by the sodium chloride solutions. Emulsions of cottonseed oil in sodium oleate gave very high absorption values. This is due to their colloidal structure. G. F. MARRIAN.

**Stability of colloids.** H. R. KRUYT (Rev. gén. Colloid., 1930, 8, 200—209).—A summary of recent work carried out in the author's laboratory on the general problem of the stability of colloids and the relation of lyophobic to lyophilic colloids. The main conclusions are that lyophobic sols owe their stability to their electric charge, whilst lyophilic colloids depend mainly on their hydration for the stability and partly also on electric charge. In some cases, however, such as aqueous sols of gelatin and albumin, hydration alone is sufficient, since the sol persists in the isoelectric state, but in a colloid like casein, hydration alone is insufficient to keep the sol stable and the particles have to be charged by addition of acid or alkali. This constitutes a change in the direction of lyophobic properties. A reply is made to the criticisms of Lumière (A., 1929, 392). Recent work confirms the idea of discontinuous charges distributed at points on the surface of the particles, and the hydration factor of stabilisation is rendered more definite by recent experiments on coacervation and the effect of hydrated colloids on the depression of the f. p.

E. S. HEDGES.

**Structure of colloids.** A. LUMIÈRE (Rev. gén. Colloid., 1930, 8, 209—211).—A reply to the arguments of Kruyt (cf. preceding abstract). The properties of the typically hydrophobic and hydrophilic colloids copper ferrocyanide and gelatin are contrasted and it is maintained that there is as great a physico-chemical divergence as between colloids and crystalloids. It is not feasible, therefore, to treat lyophilic and lyophobic sols on the same lines. E. S. HEDGES.

**Stability of organo-metallic sols. I. Influence of electrolytes and non-electrolytes on coagulation.** N. A. YAFNIK, D. N. GOYLE, and C. BARN (J. Chim. phys., 1930, 27, 386—397).—The coagulation of zinc-acetone and copper-alcohol sols prepared by Bredig's method has been investigated. The order of influence of electrolytes is the same as for hydrosols. Addition of ethyl alcohol, ethyl ether, and chloroform accelerates the coagulation of the zinc-acetone sol, and ethyl ether and glycerol behave similarly with the copper-alcohol sol. The non-electrolytes exert their greatest influence at concentrations of 30—60%.

C. W. GIBBY.

**Coagulation of von Weimarn's Au<sub>2</sub> sols. II.** E. IWASE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 1—11).—The stability of von Weimarn's gold sols towards coagulation by sodium and barium chlorides has been studied with reference to the hydrogen-ion concentration, and the effect of varying the concentrations of potassium hydroxide and of formaldehyde has been determined. The results are

presented in the form of a graph in which the co-ordinates are the amounts of reducing agent and of alkali used in preparing the sols. The graph shows that the sols fall into three regions: (1) a region of incomplete reduction, where the sols are blue or violet, (2) a stable region, where reduction is complete and the sols remain red, and (3) an unstable region, where reduction is complete, but the sols turn violet when kept. The finest red gold sols are obtained in the region 0.001—0.0035*N*-potassium hydroxide, and in this region the concentration of the formaldehyde is of little importance. The most stable gold sols are generally acidic or almost neutral. E. S. HEDGES.

**Measurement of the forces operating during coagulation.** A. VON BUZÁGH (Naturwiss., 1930, 18, 444—447).—The forces operating during the coagulation of a colloid have been investigated by determining the number of particles which on sedimentation adhere to a horizontal surface under specified conditions and also the force required for their displacement as derived from the minimum angle  $\alpha$  to which the plate must be tilted to cause movement of the particles. This type of adherence is essentially an interfacial phenomenon, since there exists a maximum particle size above which it ceases to exist; there is also a lower limit governed by the inability of the particle to approach sufficiently near to the surface on account of its surrounding solvent envelope remaining undeformed by the weight of the particle. In course of time, however, the deformation of those particles nearest to the surface increases, mainly on account of thermal movements. The adherence of the smaller particles thus increases with age, whereas that of the larger particles remains unaltered, since by reason of their mass the envelope is easily deformed and the particle is less readily influenced by thermal movements. The specific adherence  $p$  may be calculated for a certain range of particle sizes from the equation  $p = l(\sigma - \sigma_s) = g \sin \alpha$ , where  $l$  is the length of side of the particle (assumed cubical), and  $\sigma$  and  $\sigma_s$  are the densities of the particles and of the medium, respectively. It is possible also by application of this equation to decide as to the nature of the envelope surrounding any given type of colloidal particle. Simultaneous measurements of the adherence and cataphoresis indicate that on addition of electrolyte the Freundlich potential varies on account of changes both of the charge and of the envelope thickness. In certain cases these two variables change in the same sense, and the variations of the potential and of the adherence follow a parallel course, the latter being a maximum when the former is a minimum, i.e., at the isoelectric point; in such cases only is the potential an indication of the stability of the colloid. On the other hand, the stability of lyophobic colloids at the isoelectric point is due to changes in the opposite sense of the charge and the envelope thickness. H. F. GILLBE.

**Swelling of cellulose, and its affinity relations with aqueous solutions. II. Acidic properties of regenerated cellulose illustrated by the absorption of sodium hydroxide and water from dilute solutions, and the consequent swelling.** S. M. NEALE (J. Text. Inst., 1930, 21, T225—230).—

The value for the ionisation constant of regenerated cellulose chosen arbitrarily (this vol., 417) has been fixed more precisely, and the reality of such a constant is confirmed by confining observations to dilute solutions of sodium hydroxide (below 0.5 molal) for which precise thermodynamic measurements have been made by other workers. The value  $1.84 \times 10^{-14}$  at 25° is now obtained, but the adoption of this in place of the approximate figure assumed earlier is without serious effect on the quantitative relations discussed previously. The swelling/concentration curve for cellulose and dilute sodium hydroxide has been established, and its shape is in accordance with the theoretical considerations previously laid down.

B. P. RIDGE.

**Osmotic pressure of gelatin solutions in equilibrium with magnesium chloride.** G. S. ADAIR and E. H. CALLOW (J. Gen. Physiol., 1930, 13, 819—830).—The osmotic pressures of solutions of gelatin of different concentrations (1—10 g. per 100 c.c.), in equilibrium with 4*N*-, 6*N*-, and 9*N*-solutions of magnesium chloride have been determined. The osmotic pressure was found to increase more rapidly than the concentration of gelatin, representing a high *b* value in the equation  $p(V-b)=RT$ . Measurement of the membrane potentials showed that this effect could not be due to an unequal distribution of diffusible ions. Hydration of the protein molecules is insufficient to account for the high *b* term. It is suggested that inter-ionic or inter-molecular faces may cause these high osmotic pressures in concentrated solutions.

G. F. MARRIAN.

**X-Ray structure of gelatin micelles.** W. ABITZ, O. GERNGROSS, and K. HERRMANN (Naturwiss., 1930, 18, 754—755).—The X-ray diagram of gelatin is very complex, but moderately swollen gels on dilution give a fibre-type diagram similar to that of collagen. Careful work has shown that undiluted gels exhibit a similar, although less intense, diagram, and, further, that preliminary dilatation is not necessary to produce these effects. The splitting up of amorphous rings and the origin of dilatation diagrams are obviously cohesive processes. These results are considered together with the available chemical data, and it is suggested that in gelatin the polypeptide chains are linked by amino-acid residues by means of a van der Waals cohesion to form a crystalline substance. This assumption is used to elucidate the X-ray diagrams and to explain many of the properties of gelatin.

W. R. ANGUS.

**Unequal distribution of hydrogen and hydroxyl ions in cubes of gelatin in diffusion equilibrium with an electrolyte solution.** E. J. BIGWOOD (Compt. rend. Soc. Biol., 1929, 102, 600—601; Chem. Zentr., 1930, i, 1946).—When gelatin cubes, prepared with phenol-red solution, are kept at 0° in an alkaline solution of the same indicator, the thickness of the red zone around the yellow centre of the cubes is practically constant for several days and is independent of the volume of the cube.

A. A. ELDRIDGE.

**Electrokinetic phenomena. II. Relation between cataphoretic and electroendosmotic mobilities.** H. A. ABRAMSON (J. Gen. Physiol., 1930, 13, 657—668).—It is shown that van der

Grinten's data (cf. A., 1926, 467) relating to the electroendosmotic velocity ( $V_E$ ) of a liquid past a surface, and the cataphoretic velocity ( $V_P$ ) of a particle of that surface through the liquid, lead to  $V_E/V_P=2.1-2.8$  instead of the recorded value 1.59. For a flat or round glass surface, and glass or quartz particles, both covered with a layer of gelatin or egg-albumin,  $V_E/V_P$  is found to be about 1.00.

G. F. MARRIAN.

**Methods of the kinetic theory of gases.** G. JAFFÉ (Ann. Physik, 1930, [v], 6, 195—252).—Mathematical. It is shown that Boltzmann's fundamental equation of motion for a simple gas can be transformed so as to become formally identical with the author's fundamental equation of motion of radiation in an anisotropic field of radiation (*ibid.*, 1922, [iv], 68, 583; 1923, [iv], 70, 457; Physikal. Z., 1922, 23, 500). The methods of the radiation theory are then utilised in working out the kinetic theory, and it has proved possible to bring the behaviour of gases at both moderate and low pressures within the scope of a single theory.

R. CUTHILL.

**Historical note on equilibrium between methyl alcohol and its decomposition products.** J. A. CHRISTIANSEN (J. Amer. Chem. Soc., 1930, 52, 3165).—Mainly a correction of statements by Lacy and others (this vol., 542).

J. G. A. GRIFFITHS.

**Kinetics of the solvation of iodine and the sexatomic iodine molecule.** J. GRÖN and E. TAKÁCS (Z. physikal. Chem., 1930, 149, 195—210). The addition of iodine to crucic acid in carbon tetrachloride and carbon disulphide solutions occurs less readily in the presence of ether than in the pure solvents. This is explained by assuming that in the iodine solution an equilibrium exists  $3I_2 \rightleftharpoons I_6$  and that only the sexatomic iodine molecules react with the crucic acid, this reaction being expressed  $E+I_6 \rightleftharpoons EI_2+2I_2$ . Solvation of the  $I_2$  molecules by ether is supposed to reduce the concentration of  $I_6$  molecules, and in pure ether they are practically non-existent. From the change in the reaction velocity with the ether concentration the equilibrium constant of the solvation of the iodine with ether has been calculated. The velocity of decomposition of di-iodoerucic acid has also been investigated. This dissociation is dependent on the presence of a trace of iodine and therefore supports the view that these reactions occur according to the above equation and also supports the conclusion reached previously (A., 1927, 728) concerning the existence of the sexatomic iodine molecule.

J. W. SMITH.

**Hydrolysis of thorium chloride.** E. CHAUVENET and J. TONNET (Bull. Soc. chim., 1930, [iv], 47, 701—703).—Conductivity and calorimetric measurements made during the addition of sodium hydroxide to a solution of thorium tetrachloride indicate the existence of a "thoryl" radical  $ThO$  in the solution. Hydrolysis takes place according to the equation  $ThCl_4+2H_2O=Th(OH)_2Cl_2+2HCl$ .

C. W. GIBBY.

**Apparent dissociation constants of arginine and of lysine; apparent heats of ionisation of certain amino-acids.** C. L. A. SCHMIDT, P. L. KIRK, and W. K. APPLEMAN (J. Biol. Chem., 1930, 88, 285—293).—At 25° arginine has  $K'_a$ ,  $3.32 \times 10^{-13}$ ,

$K'_a$ ,  $1.10 \times 10^{-5}$ ,  $K'_b$ ,  $1.05 \times 10^{-12}$ , isoelectric point at  $p_H$  10.75 (at  $0^\circ$  the corresponding figures are  $4.9 \times 10^{-14}$ ,  $7.09 \times 10^{-6}$ ,  $2 \times 10^{-13}$ , and 11.55). Lysine has  $K'_a$ ,  $2.95 \times 10^{-11}$  at  $25^\circ$ ,  $4.9 \times 10^{-12}$  at  $0^\circ$ ,  $K'_b$ ,  $0.89 \times 10^{-5}$  at  $25^\circ$ ,  $7.4 \times 10^{-6}$  at  $0^\circ$ ,  $K'_b$ ,  $1.52 \times 10^{-12}$  at  $25^\circ$ ,  $1.82 \times 10^{-13}$  at  $0^\circ$ , isoelectric point  $p_H$  9.74 at  $25^\circ$  and 10.56 at  $0^\circ$ . From these and similar figures are calculated the heats of ionisation of the various groups of arginine, histidine, lysine, and also of aspartic and glutamic acids. C. R. HARRINGTON.

**Conductance and activity coefficients of glutamic and aspartic acids and of their monosodium salts.** W. M. HOSKINS, M. RANDALL, and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 88, 215—239).—Measurements of the conductivity ( $0^\circ$ ) and of the depression of the f. p. are recorded. The conductivity data indicate that the free amino-acids are but little ionised, whilst the sodium salts are highly dissociated. The figures for the f.-p. depression have been subjected to thermodynamic interpretation leading to the derivation of the activity coefficients of the free amino-acids and of their salts considered as univalent electrolytes, and also of the undissociated portions of the amino-acids. The results suggest that the undissociated portions of the free acids exist in solution as neutral micelles, whilst the ionised parts of the salts exist to a small extent as ionic micelles. For the characterisation of a weak acid which forms micelles the use of the "overall" activity coefficient is to be preferred to that of the dissociation constant. C. R. HARRINGTON.

**Stability of cyanohydrins. II. Dissociation constants of cyanohydrins derived from methyl alkyl and phenyl alkyl ketones.** A. LAPWORTH and R. H. F. MANSKE (J.C.S., 1930, 1976—1981; cf. A., 1928, 1245).—A number of methyl alkyl ketones and phenyl alkyl ketones have been prepared in pure condition and the dissociation constants of their cyanohydrins determined at  $20^\circ$ . Replacement of an  $\alpha$ -hydrogen atom in the alkyl group usually increases the stability of the corresponding cyanohydrin; a decrease is observed in passing from methyl isopropyl ketone to methyl *tert.*-butyl ketone. Replacement of a  $\beta$ -hydrogen atom by methyl usually decreases the stability of the cyanohydrin. A direct influence of the substituent on the CO or C(OH)·CN groups is suggested, comprising a stabilising "steric effect" and a destabilising "electropolar effect," the former possibly being connected with the function  $a$  in van der Waals' equation. H. I. DOWNES.

**Dependence of the osmotic coefficient on the structure of the ions. II. Thermo-electric apparatus for measurement of f.-p. depression in dilute solutions of electrolytes.** L. EBERT and J. LANGE (Z. physikal. Chem., 1930, 149, 389—407; cf. A., 1929, 266).—The construction and manipulation of a modified form of Randall and Vanselow's apparatus (A., 1925, ii, 33) suitable for determining f.-p. depressions in 0.001—0.1N aqueous solutions are described. R. CUTHILL.

**Activity of ions in concentrated solutions.** J. PROSZT (Mitt. berg.-hütt. Abt. Hochsch. Soprow, 1929, 6 pp.; Chem. Zentr., 1930, i, 1830—1831).—Crocein-scarlet 3B is a suitable indicator for the

interval  $p_H$   $-0.3$  to  $-1$ , and neutral-red for the interval  $p_H$   $+1.0$  to  $-0.3$ . A rise in the acidity with increasing concentration of hydrochloric acid is indicated, whilst the specific conductivity curve exhibits a maximum at 5.5N. Crocein-scarlet remains red in 96% acetic acid, whilst neutral red indicates increasing acidity (blue) with increasing concentration. The indicators are no longer dissociated in media of low dielectric constant. Many acid indicators in organic solvents of low dielectric constant and free from acid exhibit their acid colour.

A. A. ELDRIDGE.

**Ionic entropy and solvation.** H. ULICH (Z. Elektrochem., 1930, 36, 487—506).—A new method for calculating the hydration numbers of monatomic ions is described. The values obtained agree with those calculated from the ionic mobilities. The connexion established between partial ionic entropy and ionic mobility permits the calculation of the one quantity from the other. H. I. DOWNES.

**Complexity of phosphorus pentoxide.** I. A. SMITS [with H. W. DEINUM] (Z. physikal. Chem., 1930, 149, 337—363).—The results previously obtained for the vapour pressure of the metastable volatile form of phosphorus pentoxide (A., 1925, ii, 268; Hoeflake and Scheffler, A., 1926, 342) have been confirmed. This form represents, not a polymorphic modification, but a mixed crystal not in internal equilibrium, for by rapid heating it can be superheated far above the unary stable triple point, and moreover its vapour pressure can be considerably reduced by partial distillation. The rate at which equilibrium, represented by the stable form, is approached is slow even at  $400^\circ$ . By assuming the existence of two kinds of molecules forming a pseudobinary system with a eutectic, the behaviour of the system is satisfactorily explained by the author's theory of allotropy, and the equilibrium diagram has been constructed. R. CUTHILL.

**Phase-rule study of the cobalt chloride colour change.** H. BASSETT and (in part) H. H. CROUCHER (J.C.S., 1930, 1784—1819).—The systems  $\text{CoCl}_2\text{--HCl--H}_2\text{O}$ ,  $\text{CoCl}_2\text{--MgCl}_2\text{--H}_2\text{O}$ ,  $\text{CoCl}_2\text{--HgCl}_2\text{--H}_2\text{O}$ , and  $\text{CoCl}_2\text{--ZnCl}_2\text{--H}_2\text{O}$  have been examined at  $25^\circ$  and the first also at  $0^\circ$ ,  $-15^\circ$ , and  $-20^\circ$ . No compound of cobalt chloride and hydrogen chloride could be isolated, but the blue compound  $\text{CoCl}_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$  and the red compound  $\text{CoCl}_2\cdot\text{HgCl}_2\cdot 4\text{H}_2\text{O}$  are obtained. Cobalt and zinc chlorides yield five series of red solid solutions, each containing as one constituent a hydrate  $\text{ZnCl}_2\cdot n\text{H}_2\text{O}$ , wherein  $n$  is respectively 3,  $2\frac{1}{2}$ ,  $1\frac{1}{2}$ ,  $1\frac{1}{3}$ , and  $1\frac{1}{4}$ . It appears from consideration of these complex salts that all cobalt chloride solutions contain in equilibrium the red cations:  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$ ,  $[\text{Co}_2(\text{H}_2\text{O})_{10}]^{4+}$ ,  $[\text{Co}_2(\text{H}_2\text{O})_6]^{4+}$ ,  $[\text{Co}(\text{H}_2\text{O})_3]^{3+}$ , and the blue anions:  $[\text{CoCl}_3]^{-}$ ,  $[\text{CoCl}_4]^{-}$ ; in some cases the blue non-ionised cobalt chloride is indicated. No evidence of other theoretically possible ions was obtained. The simple dehydration theory and the "variable co-ordination" theory of the colour change are not supported by the data, and the phenomena are regarded as being determined by the possibility of electron transfer between

different quantum levels. The electronic shifts responsible for the red and blue colours are considered and suggestions made. Some previous statements relative to the hydrates of zinc chloride are corrected.

H. I. DOWNES.

**Equilibrium between acetone and salts.** W. R. G. BELL, C. B. ROWLANDS, I. J. BAMFORD, W. G. THOMAS, and W. J. JONES (J.C.S., 1930, 1927—1931).—The solubilities of calcium chloride, iodide, and nitrate, strontium bromide, barium bromide, sodium iodide, lithium chloride and bromide, nickel bromide, cobalt chloride and bromide, and zinc bromide in absolute acetone, and the composition of the solid phases in equilibrium with the saturated solutions have been determined. For barium, lithium, and sodium bromide the solid phases are the non-solvated salts; for the remainder the solid phases are represented by acetates. Transition points at which the acetates of cobalt chloride, zinc bromide, lithium bromide, and sodium iodide are converted into the non-solvated salts, and the sesquiacetate of strontium bromide into the monoacetate have been established. The dissociation pressures of the acetates of sodium iodide, magnesium chloride, strontium bromide, calcium nitrate, cobalt chloride and bromide have been determined between 0° and -30°; the data show that  $\log P$  is a rectilinear function of  $1/T$ . This relation permits the calculation of heats of dilution and affinities of salts for acetone.

H. I. DOWNES.

**Solubility curves of mixtures and solid solutions.** J. H. NORTROP and M. KUNITZ (J. Gen. Physiol., 1930, 13, 781—791).—Systems of two solid components (mixture or solid solution) in contact with a liquid phase are considered from a theoretical point of view. Assuming that such systems follow the phase rule and Raoult's law, the relative amounts and solubilities of the two solid components may be calculated from the solubility curve of the mixture or solid solution.

G. F. MARRIAN.

**Equilibrium in the molten state between calcium, sodium, and their chlorides.** E. RINCK (Compt. rend., 1930, 191, 404—406).—Contrary to the results of Lorenz and Winzer (A., 1929, 650, 1229), which are based on defective analysis, it is shown that the equilibrium data for  $\text{Ca} + 2\text{NaCl} \rightleftharpoons 2\text{Na} + \text{CaCl}_2$  at 850—1100° conform to the requirements of the phase rule. The liquid phase contains 71%  $\text{CaCl}_2$  and the solid phases 13% Ca and 17% Na, respectively.

J. GRANT.

**Ternary system carbamide-ammonium nitrate-sodium nitrate.** W. J. HOWELLS (J.C.S., 1930, 2010—2017).—The equilibrium diagram shows three main areas or saturation surfaces in the largest of which sodium nitrate is precipitated as the solid phase. The curves afford evidence of the transition of regular to rhombohedral ammonium nitrate. The transition of rhombohedral to  $\alpha$ -rhombohedral ammonium nitrate at 83° is not observed, possibly because the latter is not readily formed in the presence of carbamide. The composition at the ternary eutectic point (37.1°) is, in mol.-%: 52.4%  $\text{CO}(\text{NH}_2)_2$ , 41.5%  $\text{NH}_4\text{NO}_3$ , 6.1%  $\text{NaNO}_3$ , and these are in the inverse order of the m. p.

H. I. DOWNES.

**Equilibria in the ammonium carbamate-carbamide-water-ammonia system.** H. J. KRASE and V. L. GADDY (J. Amer. Chem. Soc., 1930, 52, 3088—3093; cf. Fichter, Steiger, and Stanisch, A., 1919, i, 69).—Equilibria at 155° have been reached both from the ammonium carbamate and the carbamide sides in the presence of excess of ammonia. The conversion of carbamate ammonia into carbamide is increased from 44% to about 84% when the excess of ammonia is raised from 0 to 280%, but further additions are likely to have little effect. Carbon dioxide does not have a dehydrating action similar to ammonia.

J. G. A. GRIFFITHS.

**Heat of combustion of salicylic acid.** P. E. VERKADE and J. COOPS (Rec. trav. chim., 1930, 49, 864—865).—Polemical against Keffler (this vol., 702).

J. A. V. BUTLER.

**Calorimetric researches.** E. BERNER (Rec. trav. chim., 1930, 49, 861—863).—Some of the figures given by Keffler (this vol., 702) for the heat of combustion of salicylic acid are incorrectly quoted. It is pointed out that Keffler's results support the author's value.

J. A. V. BUTLER.

**Heat of formation of molecular oxygen.** L. C. COPELAND (J. Amer. Chem. Soc., 1930, 52, 2580—2581).—A provisional value afforded by direct measurement is  $165,000 \pm 5000$  g.-cal.

J. G. A. GRIFFITHS.

**Heat of formation of molecular oxygen.** W. H. RODEBUSH and S. M. TRONEL (J. Amer. Chem. Soc., 1930, 52, 3467; cf. Copeland, preceding abstract).—When precautions are taken to eliminate spurious heat effects in the calorimeter, the heat of formation of molecular oxygen by direct determination is 131,000 g.-cal. Metastable atoms do not reach the calorimeter.

J. G. A. GRIFFITHS.

**Heat of formation of zinc oxide.** C. G. MAIER (J. Amer. Chem. Soc., 1930, 52, 2159—2170; cf. Parks and others, A., 1928, 22).—A calorimeter with special features and involving the use of tantalum and bakelite, which are resistant to corrosion, is described. The heats of dissolution of zinc oxide and zinc in hydrochloric acid have been redetermined (cf. Richards and Thorvaldson, A., 1922, ii, 475; Richards and Burgess, A., 1910, ii, 391). The most probable value of the heat of formation of zinc oxide at 25° is computed to be  $83,270 \pm 50$  g.-cal. (15°), in good agreement with thermodynamic estimates (Millar, A., 1929, 21).

J. G. A. GRIFFITHS.

**Heat of dissolution of sparingly soluble electrolytes. II.** E. LANGE and Z. SHIBATA (Z. physikal. Chem., 1930, 149, 465—469).—Measurement of the heat of precipitation of silver iodide at 25° has given the value  $-26.71 \pm 0.05$  kg.-cal. per mol. AgI for the heat of dissolution. The heat of flocculation or the content of metastable modifications does not affect the result to an extent greater than the experimental error.

E. S. HEDGES.

**Heats of dissolution and of formation of  $\text{CuCsCl}_3$ .** A. BOUZAT and E. CHAUVENET (Bull. Soc. chim., 1930, [iv], 47, 697—698).—The heat of dissolution in water of caesium cupric chloride, prepared by concentrating a solution of equimolecular proportions of cupric chloride and caesium

chloride in a current of hydrogen chloride, can be represented between  $10^\circ$  and  $20^\circ$  by the formula  $Q = -0.65 + 0.12(t-15)$  g.-cal./mol. The heat of the reaction  $\text{CuCl}_2\text{aq} + \text{CsCl} = \text{CuCsCl}_3$  is 6.96 g.-cal. and that of the reaction  $\text{CuCl}_2(\text{solid}) + 2\text{CsCl}(\text{solid}) = \text{CuCs}_2\text{Cl}_4$  is 6.88 g.-cal. C. W. GIBBY.

**J. Thomsen's isodynamic principle and W. Thomson's rule.** J. SEBOR (Chem. Listy, 1930, 24, 322—325).—The above are valid for a number of soluble salts, but not for fluorides and sulphates.

R. TRUSZKOWSKI.

**Thermal data for organic compounds. VIII. Heat capacities, entropies, and free energies of the isomeric heptanes.** H. M. HUFFMAN, G. S. PARKS, and S. B. THOMAS (J. Amer. Chem. Soc., 1930, 52, 3241—3251).—The following heats of fusion are recorded (g.-cal. per g.):  $n$ -heptane, 33.78;  $\beta$ -methylhexane, 21.16;  $\gamma$ -ethylpentane, 22.56;  $\beta\beta$ -dimethylpentane, 13.98;  $\beta\delta$ -dimethylpentane, 15.97;  $\gamma\gamma$ -dimethylpentane, 16.86;  $\beta\beta\gamma$ -trimethylbutane, 5.25. The specific heats of the above hydrocarbons,  $\gamma$ -methylhexane, and  $\beta\gamma$ -dimethylpentane have been measured over a wide range of temperature by the method previously described (A., 1925, ii, 491). The entropies of the hydrocarbons, calculated from the heat capacity data, agree fairly well with those obtained from the equation  $S_{298} = 25.0 + 7.7n - 4.5r$  (this vol., 677). Increased branching in this series of hydrocarbons results in a free energy increase of 600 g.-cal./mol. for each side-chain.

H. BURTON.

**Electrolytic resistance with alternating current.** S. RAY (Z. Elektrochem., 1930, 36, 545—550).—A theoretical and mathematical treatment in which both high- and low-frequency alternations are considered.

H. I. DOWNES.

**Electrical conductivity of phenol solutions.** R. M. DOLBY and P. W. ROBERTSON (J.C.S., 1930, 1711—1721).—Phenolic solutions of sodium acetate, anilino hydrochloride, sodium phenoxide, picric acid, acetic acid, and hydrochloric acid at  $50^\circ$  show large differences in the equivalent conductivities. The conductivity of the acids increases more rapidly than required by the mass-action law, whereas the salts show the opposite behaviour. Although addition of toluene to solutions of the salts causes a decrease, addition of ethyl malonate and methyl acetate causes a considerable increase in the conductivity. Measurements of the dielectric constants, conductivities, and viscosities of phenol-ethyl malonate mixtures contribute no explanation for such an increase, which, in view of the agreement of the results with cryoscopic and molecular volume measurements (A., 1928, 947) may be due to intermolecular forces induced by internal pressures and polarities of the liquid.

H. I. DOWNES.

**Mobility of a number of ions containing iron. II. Influence of substitution in co-ordinated groups.** F. HÖLZL (Monatsh., 1930, 56, 79—96; cf. this vol., 862).—Further measurements of conductivity with complex ferro- and ferri-cyanides at  $5^\circ$  (to avoid decomposition) gave the following values for the mobility and apparent ionic radius:  $[\text{Fe}(\text{CN})_6]^{4-}$ , 62.5, 100;  $[\text{Fe}(\text{CN})_6]^{3-}$ , 61.7, 101;

$[\text{Fe}(\text{CN})_5\text{CO}]^{3-}$ , 62.1, 101;  $[\text{Fe}(\text{CN})_5\text{NO}_2]^{3-}$ , 51.6, 122;  $[\text{Fe}(\text{CN})_5\text{SO}_3]^{4-}$ , 51, 123;  $[\text{Fe}(\text{CN})_5\text{AsO}_2]^{4-}$ , 47.4, 134;  $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ , 45.8, 136;  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$ , 41.4, 151;  $[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$ , 41.1, 152. The change in mobility with variation of temperature is not identical for different ions and this is probably connected with hydration; the respective figures at  $5^\circ$  and  $25^\circ$  for  $[\text{Fe}(\text{CN})_6]^{4-}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ , and  $[\text{Fe}(\text{CN})_5\text{NO}]^{3-}$  are 100, 102, 142, and 100, 101, 151. The completely symmetrical ion  $[\text{Fe}(\text{CN})_6]^{4-}$  has the highest mobility, which appears to be practically independent of the valency of the central atom, and to be uninfluenced by substituting a neutral group (e.g., CO) for a negative group (e.g., CN). The large effect produced by the nitroso- or amino-group is attributed to a destruction of the symmetry of the ion, producing a looser binding and increased hydration.

J. R. I. HEPBURN.

**Change in the direction of migration of the alkali and other metals during electrolysis of the corresponding amalgams, in relation to the concentration.** R. KREMANN, F. BAUER, A. VOGGIN, and H. SCHEIBEL (Monatsh., 1930, 56, 35—65).—An extension of earlier work on sodium amalgams (A., 1926, 801) to amalgams of potassium, lithium, barium, and bismuth. With these amalgams in which the conductivity of the mercury is diminished (viz., sodium, potassium, and barium) the metal migrates to the anode up to concentrations of 2% Na, 2.5% K, and 2.7% Ba; beyond these concentrations a reversal of the direction of migration occurs in each case towards the cathode. In lithium amalgams the migration is always towards the cathode; bismuth always migrates to the anode. The theory of Lewis, Adams, and Lanman (A., 1916, ii, 76) is not confirmed by these results. It is suggested that the migration to the anode of bismuth, with its strong metalloid character, makes it probable that the polarity of the components of an alloy is an important factor in determining the direction of migration; with dilute amalgams of sodium, potassium, or barium, the effect suggested by Lewis may be the prominent factor, whilst at higher concentrations the difference in polarity of the components may assert itself through complex formation, giving rise to the reversal point.

J. R. I. HEPBURN.

**Electrolytic flow in fused silver-lead alloys.** R. KREMANN, B. KORTH, and E. I. SCHWARZ (Monatsh., 56, 16—25; cf. A., 1925, ii, 679; 1926, 802).—An extension of previous work. Alloys containing 50 at.-% or 35 wt.-% Ag were electrolysed at  $1000^\circ$  in fireclay capillary tubes for 6 hrs. with a high current density, using steel electrodes. A stationary state is set up in the centre of the capillary; silver migrates towards the cathode, and lead towards the anode. Slight changes in the concentration of the alloy as a whole are explained by evaporation of lead. Further experiments with varying percentages of lead and silver indicate that the maximum migration effect is shown with the equiatomic alloy.

J. R. I. HEPBURN.

**Electrolysis of bronzes with addition of silver.** R. KREMANN and E. I. SCHWARZ (Monatsh., 1930, 56, 26—34). **Electrolysis of bronzes with addition**

of lead. R. KREMAN and W. PIWETZ (Monatsh., 1930, 56, 71—78).—Complete data in connexion with an earlier paper (A., 1929, 1402) are given, with a series of photomicrographs illustrating the metallographic study of the system. J. R. I. HERBURN.

**Sodium and potassium amalgam electrodes in solutions containing sodium chloride, potassium chloride, and sodium and potassium chlorides.** E. W. BIRD and R. M. HIXON (J. Physical Chem., 1930, 34, 1412—1423).—A new type of flowing junction and a modified alkali amalgam electrode are described. The flow of the solutions of potassium chloride and calomel through the calomel half-cells used has no effect on their *E.M.F.* The sodium amalgam electrode gives abnormal readings in solutions of sodium chloride to which potassium chloride has been added, and the potassium electrode is similarly affected by the presence of sodium ions. The data obtained in these cases agree with those of Ringer (Z. physiol. Chem., 1923, 130, 270) and Neuhausen (A., 1922, ii, 610). Constant and reproducible *P.D.* are obtained with the sodium electrode in solutions of potassium chloride, and with the potassium electrode in solutions of sodium chloride.

L. S. THEOBALD.

**Voltage effect for solutions of electrolytes in acetone.** F. BAUER (Ann. Physik, 1930, [v], 6, 253—272; cf. Wien, A., 1929, 401).—The voltage effect,  $\Delta\lambda$ , for acetone solutions of various uni-univalent and uni-bivalent electrolytes has been measured. Up to high values of the field strength,  $X$ , the equation  $\Delta\lambda = AX^2(1 - BX^2)$  (Blumentritt, *ibid.*, 512) is valid. The value of  $A$  is approximately proportional to the product of the valencies of the ions of the particular salt and increases with increasing dilution, whilst as the theory requires  $A$  is greater and  $B$  is smaller than for the corresponding aqueous solution. For potassium iodide the limiting value of  $\Delta\lambda$  at high field strength has been obtained and found to correspond approximately with the conductivity at infinite dilution. R. CUTHILL.

**Polarographic studies with the dropping mercury cathode. XIV. The discontinuities on the curves which are obtained with solutions of mercuric cyanide.** W. KEMULA (Coll. Czech. Chem. Comm., 1930, 2, 502—519).—The first discontinuity is due to the adsorption of mercuric cyanide, the second to the exhaustion of reducible matter. C. W. GIBBY.

**Constitution of the aqueous pink and blue cobaltous chloride solutions. I. Electrodeposition at the dropping mercury cathode.** R. BRDIČKA (Coll. Czech. Chem. Comm., 1930, 2, 489—501).—The deposition of cobalt from solutions of cobalt chloride of various concentrations has been determined polarographically, using the dropping mercury cathode. In the presence of much calcium chloride the red solution becomes blue and the deposition potential more positive. Heating the solution has a similar effect on the potential, the colour changing if calcium chloride is present. Cobalt deposits reversibly only from blue solutions, the cathodic deposition potential being about 0.3 volt greater than for a pink solution with an equal cobalt

content. It is suggested that the irreversible deposition is due to slow dehydration of the pink hydrated ions, and that the reversible deposition from the blue solutions is facilitated by the ease with which the blue complexes give free cobaltous ions. C. W. GIBBY.

**Formation of free hydrogen atoms during the cathodic polarisation of metals.** N. KOBOSEV and N. I. NEKRASSOV (Z. Elektrochem., 1930, 36, 529—544).—The omission of free hydrogen atoms from the cathode surface of platinised platinum, polished platinum, palladium, nickel, copper, tin, zinc, lead, and mercury during polarisation is demonstrated by the reducing action on a tungstic oxide suspension, and a complete parallelism is found between this emission and the overvoltage of the metal. Theoretical considerations are adduced to support this fact and to show that both factors must vary inversely with the energy of combination of the hydrogen atom with the metal. The varying capacities of the metals to accelerate the recombination of hydrogen atoms and the relation between this and overvoltage receives consequential explanation. The results are in good agreement with a relation derived from a thermodynamical treatment of the overvoltage phenomena employing the assumption that the transition of hydrogen ion to molecular hydrogen through combination with metal ion is an irreversible step. This relation connects overvoltage with the energy of combination of metal with hydrogen and the concentration of the latter, and a temperature relation for overvoltage derived from this gives good agreement with experimental values. Calculation of the dissociation energy of the hydrogen molecule from the hydrogen overvoltage value with a mercury cathode agrees well with the experimental value. The energy of combination of hydrogen with the cathode is shown to be from 10 to 50 g.-cal. over the series. It is found that addition of mercuric chloride or hydrogen sulphide when using a platinised platinum cathode increases both the overvoltage and the hydrogen emission, and that the latter is also much increased by rise of temperature when using a polished platinum cathode. H. I. DOWNES.

**Unidirectional and photo-effects at the interface of cuprous oxide and deposited metal layers.** E. DUHME and W. SCHOTTKY (Naturwiss., 1930, 18, 735—736).—The rectifying action of the combination copper-washed cuprous oxide is due to the behaviour of a unidirectional layer of submicroscopic thickness at the interface; a unidirectional effect is also observed at the boundary of massive cuprous oxide plates and all loose or compact metals and also with graphite. The effect is more pronounced if the cuprous oxide is etched than if it is polished and has thin layers of gold deposited on it. It was expected that light in the neighbourhood of the unidirectional interface between oxide and electrode would give a photo-effect, as in the case of copper-cuprous oxide. The effect was demonstrated by using cuprous oxide plates which had been etched and on which gold or silver layers had been deposited cathodically. The photo-stream gave  $5 \times 10^{-8}$  A. for light from an incandescent gas-filled lamp. The



photo-effect comes from the front of the oxide exposed to the light—a front-wall effect—in contrast with the case of copper-cuprous oxide, which shows a back-wall effect. The spectral sensitivity of the front-wall effect differs from that of the back-wall effect. In the latter case it is determined by an absorption of the thin metal layer, and in the former by the light arriving at the surface. The direction of the photo-stream is the same, electrons being liberated in the oxide which then pass through the unidirectional layer to the adjacent electrode. Only etched material shows a good effect with the deposited layers. It appears that the primarily produced photo-stream is independent of a potential applied to the cell and that the observed dependence is due for the greater part to the dependence of the resistance of the unidirectional layer on the potential. The technical applicability of the new photo-cell depends on how far the deposited metal surface remains unaltered.

J. E. MILLS.

**Explosive gas reactions.** I. J. BOOY (Rec. trav. chim., 1930, 49, 866—875).—Theoretical. A reaction mechanism is proposed which accounts both for the existence of explosion limits in explosive gas mixtures and for the two pressure limits of the oxidation of phosphorus.

J. A. V. BUTLER.

**Speed of flame in a closed tube.** Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 243—244B).—The speed of flame propagation in a horizontal closed glass tube containing mixtures in various proportions of hydrocarbon vapour and air was measured. It was much higher than in an open tube and varied rapidly with concentration. The maximum speed was with about 2.25% of hydrocarbon, the figure for complete combustion being 1.92%. This result is connected with the dissociation of carbon dioxide at high temperatures, which is nevertheless less than in an open tube. Flame photographs showed very irregular forms.

C. IRWIN.

**Chain reaction theory of rate of explosion in detonating gas mixtures.** B. LEWIS (J. Amer. Chem. Soc., 1930, 52, 3120—3127).—The concept of reaction chains is employed in an attempt to calculate from thermal data the velocity of propagation of gaseous explosions. It is assumed that the energy liberated in each reaction in the chain is equi-parted among all the degrees of freedom of the products and hence the velocity of the propagating molecule (i.e., the velocity of propagation of the explosion) can be calculated. For thirteen different explosive mixtures a suitable choice of reaction mechanism and propagating molecule generally leads to calculated velocities in good agreement with the experimental determinations of other observers.

J. G. A. GRIFFITHS.

**Chain reactions.** (A) Remarks on a paper by Lenher and Rollefson on the kinematics of carbonyl chloride. (B) Mechanism of formation and decomposition of ethylene iodide. H. J. SCHUMACHER (J. Amer. Chem. Soc., 1930, 52, 3132—3139).—A. The mechanism proposed by Lenher and Rollefson (this vol., 433) for the photochemical reaction between carbon monoxide and chlorine is held to be improbable and a reply is

given to their objections to the mechanism suggested by Bodenstein and others (A., 1929, 894).

B. The observed kinetics of the decomposition of ethylene iodide (Polissar, this vol., 548) are explained by the following mechanism: (1)  $I_2 \rightleftharpoons 2I$ , (2)  $C_2H_4I_2 + I \rightarrow C_2H_4I + I_2$ , (3)  $C_2H_4I \rightleftharpoons C_2H_4 + I$ . The heats of activation of reactions (2) and (3) are computed to be 11,500 and 200 g.-cal., respectively. From the thermal and kinetic data the energy difference between the  $^5S$  and  $^3P$  state of the carbon atom is calculated to be 74 kg.-cal.; that between the valency linkings C-C and C-I is about 48, which is equal to the energy of the C-I linking in ethylene iodide.

J. G. A. GRIFFITHS.

**Reaction regions. XX. Influence of various circumstances on the extension of explosion regions.** W. P. JORISSEN, J. BOOY, and J. VAN HEININGEN (Rec. trav. chim., 1930, 49, 876—883).—The explosion limits of ternary mixtures are different for upward and downward propagation of the explosion wave. The difference at the lower explosion limit is greater with substances of small mol. wt., but at the upper explosion limit no such relation is observed.

J. A. V. BUTLER.

**Ignition of hydrogen-oxygen mixtures at low pressures by heated quartz.** H. N. ALYEA and F. HABER (Naturwiss., 1930, 18, 441—443).—The ignition by quartz at 500—600° of hydrogen-oxygen mixtures over a certain range of low pressures is caused by the production at the quartz-gas interface of hydroxyl, which on evaporation from the solid surface initiates the reactions  $OH + H_2 = H_2O + H$  and  $H + O_2 + H_2 = OH + H_2O$ . The lower pressure limit of the low-temperature ignition is governed mainly by the second of these reactions, whilst when the pressure is above the upper limit, evaporation of the hydroxyl is retarded by reflexion from adjacent gas molecules.

H. F. GILLBE.

**Decomposition of nitrogen peroxide at low pressures.** H. J. SCHUMACHER (Proc. Nat. Acad. Sci., 1930, 16, 554).—A correction (cf. this vol., 708).

**Thermal decomposition of nitrous oxide.** M. VOLMER and H. KUMMEROV (Z. physikal. Chem., 1930, B, 9, 141—153).—The thermal decomposition of nitrous oxide at 640° and under pressures of 25—300 mm. has been shown to be a unimolecular reaction, and not, as other authors have affirmed, bimolecular (cf. Hinshelwood and Burk, A., 1924, ii, 751). As the pressure falls the unimolecular velocity coefficient diminishes, but this is probably due to a decrease in the number of molecular impacts transmitting energy. The mean life of the active molecule is calculated to be about  $10^{-10}$  sec., which gives 57,500 g.-cal. per mol. for the heat of activation. If the latter is assumed to represent the energy of separation of the oxygen atom, the value of 154,500 g.-cal. is obtained for the molecular heat of dissociation of oxygen.

R. CUTHILL.

**Oxidation and ignition of mixtures of pentane and air.** M. PRETTRE, P. DUMANOIS, and P. LAFFITTE (Compt. rend., 1930, 191, 329—331).—Gaseous mixtures of pentane and air were passed at the rate of 6.5 litres per hr. into a glass receiver,

heated progressively by an electric furnace to 800° in about 2.5 hrs., in such a way that the effects of the products of combustion on the ignition point were not eliminated (cf. A., 1929, 271, 771). With less than 2.5 vol.-% of pentane (the quantity necessary for complete combustion) a luminescence appeared at 250–300°, and ignition occurred at 670°. With greater proportions (up to 13%) an intense blue luminescence occurred at 259–263° (depending on the composition) and ignition at 670–680°. It is concluded from changes in the nature of the luminescence in the latter case that two spontaneous ignitions may occur, at 260–300° and above 660–670°, and that in the interval (300–660°) such mixtures do not ignite but only luminesce.

J. GRANT.

**Ignition and combustion of mixtures of pentane and air.** M. PRETTRE, P. DUMANOIS, and P. LAFFITTE (Compt. rend., 1930, 191, 414–416).—Antidetontants raise the first ignition temperature observed in the authors' experiments (cf. preceding abstract) and, if sufficiently powerful or present in sufficient amount, suppress it or decrease the flame propagation velocity. Thus, 7 vol.-% of benzene or 1% of tin tetrathyl in the liquid pentane raises the temperature by 25°, and 0.4% of ethyl fluid (55% of lead tetrathyl) completely suppresses the first ignition. Prodetontants (e.g., 1 vol.-% of amyl nitrite) also raise the first ignition temperature, but increase the rate of flame propagation. J. GRANT.

**Determination of the explosion pressure for acetylene saturated with water and acetone vapours.** ANON. (Jahresber. VII Chem.-Tech. Reichsanst., 1928, 56–63; Chem. Zentr., 1930, i, 2037).—Water and acetone vapours depress the explosion pressure according to their tension, but the difference is the smaller the greater is the initial pressure. The explosion pressure of pure acetylene is about eleven times the initial pressure.

A. A. ELDRIDGE.

**Minimum concentration of carbon tetrachloride giving non-inflammable mixtures with carbon disulphide and the effect of combustion suppressors thereon.** Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 242B).—5.2 Vols. of carbon tetrachloride are required to give a non-inflammable mixture with 1 vol. of carbon disulphide. This figure is considerably reduced by adding to the carbon disulphide from 5 to 20% of ethyl bromide, tin tetramethyl, or petrol (b. p. 45–50°).

C. IRWIN.

**Effect of a hydrocarbon and ethyl ether on the spontaneous ignition temperature of carbon disulphide.** Y. NAGAI (J. Soc. Chem. Ind. Japan, 1930, 33, 241B).—A mixture of dimethylcyclopentane and isoheptane raises the ignition temperature of carbon disulphide markedly, whilst ethyl ether does so only slightly. Addition of 9% of the former gives a mixture which ignites spontaneously at 525°, whilst carbon disulphide with 9% of ether ignites at 240°.

C. IRWIN.

**Neutral salt effect of the ferric-iodide ionic reaction.** A. VON KRIS and I. BOSSANYI (Z. anorg. Chem., 1930, 191, 289–308).—In dilute solution the

order of the reaction between ferric and iodide ions is unimolecular with respect to the ferric ions and bimolecular with respect to the iodide ions. The hydrolysed ferric ions do not react with measurable velocity. The process is purely ionic, and up to an ionic strength of 0.15 follows almost quantitatively the neutral salt rule of Brönsted, but sodium iodide has a specific effect. The retarding effect of ferrous and sulphate ions found by Sasaki (A., 1924, ii, 765) has been confirmed, and it is shown that hydrogen, nitrate, bromide, and chlorate ions have a feeble catalytic effect.

O. J. WALKER.

**Rapid reactions. Velocity and heat effects involved in neutralisation of sodium dichromate by sodium hydroxide.** V. K. LAMER and C. L. READ (J. Amer. Chem. Soc., 1930, 52, 3098–3111).—The velocities of rapid chemical reactions have been investigated by a modification of the method of Hartridge and Roughton (A., 1925, ii, 47). The courses of the reactions are followed by means of thermocouples which measure the temperature change due to the heat of reaction evolved (cf. Roughton, this vol., 426). The reaction between 0.05*N*-ammonia and acetic acid is 95% complete in 0.002 sec. The velocity of neutralisation of 0.02–0.06*M*-sodium dichromate by sodium hydroxide at 25° is unaffected by the concentration of hydroxyl ions, but is a function of that of the dichromate ions. The reaction follows the unimolecular law with respect to dichromate ( $k=529 \text{ min.}^{-1}$ ) and the heat of reaction is 15,320 g.-cal. per g.-mol. of dichromate ion. The data are best interpreted by the following series of reactions: (a)  $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$  (slow), (b)  $\text{HCrO}_4^- \rightleftharpoons \text{H}^+ + \text{CrO}_4^{2-}$  (rapid), and (c)  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$  (rapid) (cf. Saal, A., 1928, 374). The heats of reaction involved in steps (a) and (b) have been evaluated:  $q_a$ , –13,640 g.-cal. per g.-mol. of  $\text{Cr}_2\text{O}_7^{2-}$  and  $q_b$ , 780 g.-cal. per g.-mol. of  $\text{HCrO}_4^-$ . J. G. A. GRIFFITHS.

**Velocity of inversion of sucrose. III. Inversion by Koji-invertase.** N. TAKETOMI (J. Soc. Chem. Ind. Japan, 1930, 33, 272–274B).—The velocity coefficient of inversion of sucrose and the effect of temperature using purified Koji-invertase were determined. In general the coefficient decreases as inversion proceeds. The optimum temperature is 48–50° and the action of the enzyme is not affected by the presence of alkali salts in dilute solution or by ultra-violet rays. It is poisoned by mercuric, lead, and copper salts and to a smaller degree by formaldehyde, ethyl alcohol, etc. C. IRWIN.

**Velocity measurements on the opening of the furan ring in hydroxymethylfurfuraldehyde.** H. P. TEUNISSEN (Rec. trav. chim., 1930, 49, 784–826).—When a 1% solution of hydroxymethylfurfuraldehyde in 0.5*N*-hydrochloric or -sulphuric acid is heated at 100° for 10 hrs., an equimolecular mixture of formic and lactic acids is produced; a small amount of humin is also formed. The reaction does not occur in water alone at 100°, but in presence of oxalic, sulphuric, hydrochloric, hydrobromic, or hydriodic acid the (pseudo-unimolecular) velocity coefficient increases in the above order. The coefficient also increases when more concentrated acid is used. Formic and lactic acids have no influence

on the hydrolysis, showing that the reaction is not autocatalytic. The probable course of the reaction is discussed with respect to the above example, furfuraldehyde, furfuryl alcohol, and pyromucic acid.

Formic acid was determined by the reduction of mercuric chloride, and lœvulic acid by conversion into iodoform. H. BURTON.

**Reaction between organic bromo-compounds and silver nitrate.** H. VON EULER and A. ÖLANDER (Z. Elektrochem., 1930, 36, 506—511).—The reaction between sodium bromoacetate and silver nitrate in aqueous solution at 50° has been investigated. Three reactions occur simultaneously: (a)  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Ag} + \text{H}_2\text{O} = \text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{AgBr}$ ; (b)  $\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Ag} + \text{CH}_3\text{Br}\cdot\text{CO}_2' = \text{CH}_3\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2' + \text{AgBr}$ ; (c)  $2\text{CH}_3\text{Br}\cdot\text{CO}_2\text{Ag} = \text{CH}_3\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Ag} + \text{AgBr}$ .

The reaction velocities when followed argentometrically and acidimetrically are recorded. The reaction between ethyl bromide and silver nitrate in 10% ethyl-alcoholic solution at 35° proceeds simultaneously in two ways:  $\text{EtBr} + \text{Ag}^+ + \text{H}_2\text{O} = \text{EtOH} + \text{AgBr} + \text{H}^+$ ;  $\text{EtBr} + \text{AgNO}_3 + \text{H}_2\text{O} = \text{EtOH} + \text{AgBr} + \text{HNO}_3$ , and the reaction velocity determined argentometrically or acidimetrically is recorded. H. I. DOWNES.

**Formation of acetanilide in aqueous solution.** H. VON EULER and A. ÖLANDER (Z. physikal. Chem., 1930, 149, 364—370).—The rate of formation of acetanilide from acetic acid and aniline in aqueous solution at 90° has been measured, the value  $6.48 \times 10^{-5}$  being obtained for the bimolecular velocity coefficient. The results indicate that the mechanism of the reaction is  $\text{AcOH} + \text{PhNH}_2 \rightleftharpoons \text{AcNH}_2\cdot\text{Ph} + \text{H}_2\text{O}$ . Measurements of the rate of the reverse reaction give 1070 for the value of the equilibrium constant  $[\text{AcOH}][\text{PhNH}_2]/[\text{H}^+][\text{AcNHPh}]$  at 90°.

R. CUTHELL.

**Decomposition of perchlorates by alkali nitrites.** A. TIAN and SILVARICH (Bull. Soc. chim., 1930, [iv], 47, 698—701).—The velocity of decomposition of potassium perchlorate when heated between 444.5° and 520° is increased by adding sodium nitrite. The effect diminishes on further raising the temperature and disappears at about 600°.

C. W. GIBBY.

**Theoretical significance of passivity.** W. J. MÜLLER (Z. Elektrochem., 1930, 36, 550—551).—Polemical against Smits (this vol., 999).

H. I. DOWNES.

**Theoretical significance of passivity.** A. SMITS (Z. Elektrochem., 1930, 36, 551).—Polemical (cf. preceding abstract).

H. I. DOWNES.

**Effect of movement in the system metal-nitric acid.** E. ABEL (Z. angew. Chem., 1930, 43, 734).—The author reaches the same conclusion as Hedges (this vol., 549) as to the cause of the reduction of the rate of dissolution of metals in nitric acid by movement.

A. R. POWELL.

**Interface potential and reactions at surfaces.** I. Reduction of permanganate by charcoal. A. WASSERMANN (Z. physikal. Chem., 1930, 149, 223—239).—The actions of different charcoal preparations on potassium permanganate solution have been com-

paratively investigated. If the velocity of reduction of the potassium permanganate is a measure of the diffusion of the permanganate ion to the interface, the surface charge on the charcoal should influence the velocity of decomposition. The effect of  $p_{\text{H}}$  on the reaction velocity in the acid region confirms this assumption. Also potassium permanganate is reduced about equally readily by normal and activated sugar charcoal in alkaline solution where both charcoal surfaces are negatively charged, whereas in acid solution the positively-charged active charcoal is the more active. The fact that the velocity of reaction in alkaline solution is independent of the concentration of the alkali is explained by supposing that the carbon adsorbs hydroxyl ions only in small amounts. J. W. SMITH.

**Action of mixed catalysts in the decomposition of nitrous oxide.** G. M. SCHWAB and H. SCHULTES (Z. physikal. Chem., 1930, B, 9, 265—288).—The decomposition of nitrous oxide under the catalytic influence of various metallic oxides has been studied as a function of temperature and the oxides studied can be arranged in the following order of decreasing effectiveness: copper > magnesium > aluminium > zinc > titanium > chromic > ferric oxide. The activity of mixtures of the basic white oxides of magnesium, zinc, and aluminium in pairs is in each case an additive property of the components; mixtures of cupric oxide, alumina, and magnesium oxide respectively with chromic oxide have a reduced activity, but mixtures of cupric oxide with the oxides of aluminium, zinc, or magnesium exhibit an enhanced reactivity. The rate of decomposition of nitrous oxide is proportional to its concentration. A more detailed examination of the effect of cupric, magnesium, and zinc oxides and of their mixtures in pairs was made. After ignition the activity of cupric oxide is reduced without alteration of the heat of activation. Ignited mixtures of cupric and magnesium oxides show a sharp maximum activity at a certain composition, the heat of activation at this stage being less than that of either component. With mixtures of zinc and magnesium oxides the velocity of decomposition and the heat of activation vary continuously from the values of one component to those of the other. From a consideration of these results it is concluded that the varied effects of the mixtures of catalysts can be separated into structural and energetic causes. E. S. HEDGES.

**Promoter action in reactions of oxidation concomitant with the catalytic decomposition of hydrogen peroxide.** I. Oxidation of hydrazine. D. P. GRAHAM (J. Amer. Chem. Soc., 1930, 52, 3035—3045; cf. Bohnson and Robertson, A., 1924, ii, 29; Robertson, A., 1925, ii, 690).—The decomposition of hydrogen peroxide and the concomitant oxidation of hydrazine to nitrogen in the presence of ferric and cupric sulphates are found to be comparatively free from side reactions and have been studied by means of the gases evolved. Copper sulphate alone is a much more effective catalyst for both reactions than is ferric sulphate. Promoter action is exhibited when a mixture of the two sulphates is used; in general when the concentration of one catalyst is

varied, the rate of decomposition of hydrogen peroxide and the rate of oxidation of hydrazine follow the general trends observed when the catalyst the concentration of which is being varied is used alone. In all cases, sulphuric acid has an inhibitory action. Promotion factors are computed. It is suggested that the hydrazine is oxidised by the oxygen liberated in the reaction between the catalytic intermediates (cupric or ferric acid) and hydrogen peroxide, and also by the catalytic intermediates themselves.

J. G. A. GRIFFITHS.

**Effect of sodium salts of monohydroxy-acids on rate of saponification of methyl acetate by sodium hydroxide.** F. L. ALLEN (Trans. Faraday Soc., 1930, 26, 527—533).—The hydrolysis of methyl acetate in 0.0125*N*-solution by sodium hydroxide at 20° is markedly retarded by sodium salicylate at a concentration of 0.1*N* or even 0.05*N*, and sodium glycolate, mandelate, lactate,  $\beta$ -hydroxy- $\beta$ -phenylpropionate, and  $\alpha$ -hydroxy- $\beta$ -phenylpropionate at a concentration of 0.1*N* have a similar, but much less pronounced effect. The position of the hydroxyl and phenyl groups in the salt molecule bears little relation to its retarding action, which is ascribed to the formation of hydrogen ions by ionisation of the hydroxyl group. By means of this assumption the dissociation constant of the hydroxyl group can be calculated from the velocity data, the neutral salt effect apparently being small.

R. CUTHILL.

**Catalysis of thermal decomposition of silver oxalate by silver sulphide.** S. E. SHEPPARD and W. VANSELOW (J. Amer. Chem. Soc., 1930, 52, 3468—3470).—Silver sulphide nuclei produced on silver oxalate are very effective catalysts in the thermal decomposition of the latter and cause a marked curtailment of the induction period (cf. Macdonald and Hinshelwood, A., 1926, 134).

J. G. A. GRIFFITHS.

**Potassium dichromate as catalyst in the dissolution of copper in sulphuric acid.** M. M. NARKEVICH (J. Chem. Ind., Russia, 1929, 6, 1438—1439).—The acceleration, which is observed in the first period of dissolution, is not catalytic but is due to oxidation.

CHEMICAL ABSTRACTS.

**Sputtered nickel films and the synthesis of ammonia.** L. R. INGERSOLL (Nature, 1930, 126, 204).—By heating to 150° in hydrogen a film sputtered from a nickel cathode in an atmosphere of nitrogen, ammonia is produced. Heating in an excess of hydrogen with added nitrogen does not appear to increase the yield.

L. S. THEOBALD.

**Heterogeneous catalysis and ultra-violet irradiation.** A. A. BALANDIN (Z. physikal. Chem., 1930, B, 9, 319—328).—The catalytic dehydrogenation of cyclohexane and of ethyl alcohol in the presence of metallic palladium has been studied both with and without irradiation from a mercury lamp in order to determine whether the rate of decomposition is influenced by absorption of radiation having quanta greater than the heat of activation of the catalytic reaction. The results show that this reaction is not appreciably affected by the radiation.

E. S. HEDGES.

**Passivity of metals. VI. Comparison between penetrating powers of anions.** S. C. BRINTON and U. R. EVANS (J.C.S., 1930, 1773—1784).—The penetrating power of various ions has been determined by constructing the current-time and potential-time curves when aluminium and lead electrodes are immersed in a solution containing a film-forming salt (potassium chromate) and the desired ion, subjected to a small *E.M.F.* (2 volts). The curves obtained fluctuate generally violently at low current densities, but less so at higher values, and these fluctuations are explained by the breakdown and repair of the anode film, which adequately explains the order of reproducibility of the results. The penetrating power of the ions is in the following decreasing order (aluminium)  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HPO}_4^{2-}$  and (lead)  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ .

J. O. CUTTER.

**Explosive antimony.** H. VON STEINWEHR and A. SCHULZE (Z. Physik, 1930, 63, 815—823).—This modification prepared electrolytically from antimony trichloride explodes when heated, and has a large specific electric resistance, showing electrolytic conductivity. X-Ray photographs showed it to be a mixture of antimony trichloride and amorphous antimony. The amorphous form exists only in the presence of the chloride, and on explosion returns to the ordinary metallic crystal. Energy changes during the explosion are calculated.

A. B. D. CASSIE.

**Physico-chemical studies of so-called explosive antimony. IV.** E. COHEN and C. C. COFFIN (Z. physikal. Chem., 1930, 149, 417—433).—The conditions of formation of explosive and non-explosive antimony in the electrolysis of aqueous solutions of antimony chloride have been studied. The most important factor is current density, increase of which favours the formation of the explosive form, whereas variation of the concentration of the solution produces a comparatively small effect. Rise of temperature favours the formation of non-explosive antimony and for each solution there is a temperature limit below which the product is explosive. The critical temperature varies with the concentration. The facts that rise of temperature and decrease of current density favour the production of the non-explosive form suggest that this modification is produced under conditions when the rate of transformation of the metastable explosive form exceeds its rate of deposition.

E. S. HEDGES.

**Dissociation of carbon dioxide in the electrodeless discharge.** H. HUNT [with W. C. SCHUMPE] (J. Amer. Chem. Soc., 1930, 52, 3152—3159).—Carbon dioxide at pressures less than 0.25 mm. in the electrodeless discharge is completely decomposed into oxygen and carbon monoxide, but at total pressures between 0.25 and 3 mm. the equilibrium  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$  is established from either side in 2 min. This is unaffected by change of wave-length from 34 to 51 m. Distinctive afterglows are observed. The results obtained by varying the percentage composition of the mixtures are not in accord with the law of mass action. The equilibrium constant decreases with increasing equilibrium pressures. Excess of oxygen decreases the amount of decomposition to a greater

extent than does carbon monoxide, but does not increase the synthesis of carbon dioxide. Helium displaces the equilibrium in the direction of increased decomposition. In qualitative agreement only with the law of mass action, increased pressure decreases the extent of decomposition of carbon dioxide and increases the synthesis.

J. G. A. GRIFFITHS.

**New group of photo-effects.** F. WEIGERT (Physikal. Z., 1930, 31, 806).—Anomalous photochemical processes, such as the fading of dyes, biological photo-effects, and phototropic phenomena, are distinguished from normal photochemical processes. It is suggested that two kinds of elementary particles are responsible for the production of these effects. In the normal process an absorbing molecule is required and such a process may be termed a "photomolecular" process, whilst anomalous effects are due to a "photomicellar" process, in which the elementary particle is a complicated micelle arising from many molecules.

W. R. ANGUS.

**Photochemical oxygen-carbon monoxide reaction.** W. F. JACKSON and G. B. KISTIAKOWSKY (J. Amer. Chem. Soc., 1930, 52, 3471—3472).—When a mixture of oxygen and carbon monoxide at the ordinary temperature is illuminated by light which produces oxygen atoms, ozone and carbon dioxide are formed. The reaction  $O + O_2 + X = O_3 + X$  proceeds at least 100 times as fast as the reaction  $O + CO + X = CO_2 + X$ , where X is a non-reacting molecule. At 575°, water vapour has a marked accelerating effect on the reaction (cf. Coehn and Tramm, A., 1921, ii, 476).

J. G. A. GRIFFITHS.

**Photochemical dissociation of nitrogen peroxide.** L. H. DAWSEY (Proc. Nat. Acad. Sci., 1930, 16, 546—552).—By means of a specially devised apparatus, which is described, the ultra-violet absorption spectra of nitrogen dioxide and nitrogen tetroxide have been photographed at the ordinary temperature and at -182° (liquid air), respectively, and compared with previous results (cf. Harris, A., 1928, 1305). The complex banded absorption attributed to nitrogen dioxide begins in the visible region, rises to a maximum at approximately 3900 Å., and then decreases to minimum intensity at approximately 3200 Å. Nitrogen dioxide absorbs radiation very feebly in the region 3200—2495 Å. With solid nitrogen tetroxide absorption begins at about 3820 Å. and increases in intensity towards the shorter wavelengths. This long wave-length limit corresponds with 74.6 kg.-cal. for the least heat of optical activation. From known thermochemical data it is calculated that the total change in thermal energy between -182° and 25° is approximately 4.5 kg.-cal., and hence 70.2 kg.-cal. is obtained as the value of the least energy of optical activation at the higher temperature. This value corresponds with light of wave-length 4060 Å. at the ordinary temperature. The continuous character of the absorption spectrum of nitrogen tetroxide suggests that the primary photochemical decomposition in nitrogen peroxide (which consists of nitrogen dioxide and tetroxide) is due to the tetroxide constituent (cf. Urey, Dawsey, and Rice, A., 1929, 864). The threshold for complete photochemical equivalence is

calculated to be about 3800 Å. On the basis of these results the mechanism  $N_2O_4 \xrightarrow{h\nu} 2NO + O_2 (^1S)$  is proposed to account for the primary photochemical dissociation and the continuous absorption spectrum of nitrogen tetroxide, where  $h\nu = 74.6/N$  kg.-cal., corresponding with a wave-length of 3820 Å. The corresponding energy for the thermal change is 39.6 kg.-cal., whilst the energy necessary to excite an oxygen molecule in the normal  $^3S$  to the  $^1S$  state is 1.62 volts (Mulliken, A., 1928, 1165), which is equivalent to 35 kg.-cal. Thus the sum of the energy of thermal change and the energy of excitation of the oxygen molecule is 74.6 kg.-cal., in good agreement with the above value obtained from the short wave-length limit of the continuous absorption spectrum.

J. W. BAKER.

**Atomic hydrogen. II. Behaviour of pentane in ultra-violet light and of its polymerisation products towards oxygen. Influence of mercury.**

Å. KLEMENC and F. PATAT (Z. physikal. Chem., 1930, 149, 449—464).—Both decomposition and polymerisation occur when pentane is irradiated without the presence of mercury (cf. A., 1929, 892). Under the influence of ultra-violet light the polymerisation products readily take up oxygen, carbon monoxide appearing among the gaseous products, or carbon dioxide in the presence of excess of oxygen. Further rupture of the carbon chain occurs and lighter hydrocarbons, such as methane, are formed. Carbon monoxide and hydrogen are oxidised to carbon dioxide and water, respectively, under the influence of the radiation in the absence of mercury, but under these conditions there is no formation of formaldehyde. The presence of mercury does not affect the oxidation of carbon monoxide, but exerts a marked influence on the oxidation of hydrogen and on the production of hydrogen from pentane.

E. S. HEDGES.

**Use of light of short wave-length in quantitative chemical investigations. "Strong" and "weak" fluorescences and new fluorescence reactions.** J. EISENBRAND (Pharm. Ztg., 1930, 75, 1033—1036).—In the examination of the fluorescence of solid substances in ultra-violet light, the small amount of visible violet light which passes through the best light filter often gives a violet colour to the compounds. This is due to reflexion and not to fluorescence. The violet light may also cause solutions to show a small Tyndall effect. When the same strength of fluorescence is obtained from a diluted solid as from a solution of the same dilution, the fluorescence from the solid is probably 1000 times as powerful as that from the solution owing to the difference in thickness of the layers used. The development of fluorescence analysis requires the provision of a wide range of specific fluorescence reactions, and also the development of methods for strengthening weak reactions (cf. A., 1929, 528; this vol., 34). A suitable method for increasing the fluorescence of a compound is the addition of salts. Thus, solutions of 8-hydroxyquinoline exhibit only weak fluorescence, but the solid derivatives with zinc, magnesium, or cadmium show brilliant fluorescence. Addition of a few drops of an alcoholic solution of 8-hydroxyquinoline to alcoholic solutions

of calcium chloride, cadmium acetate, lanthanum nitrate, lithium chloride, magnesium, strontium, or thorium nitrates, or zinc acetate gives strongly fluorescing solutions; no precipitation of metallic complex occurs. These phenomena allow the determination of the amount of 8-hydroxyquinoline in quinosol and the micro-determination of zinc to be made. 6-Hydroxyquinoline and apoquinine also show enhanced fluorescence in presence of some metallic salts.

H. BURTON.

#### Photochemical sensitisation in the ultra-violet.

L. FARKAS and P. HARTECK (Naturwiss., 1930, 18, 443—444).—In view of the photochemical sensitising action of ammonia on hydrogen-oxygen mixtures, that of other hydrogen compounds has been studied. Hydrogen bromide catalyses the combination of hydrogen with oxygen at 280° in the dark, and to a greater extent when the mixture is irradiated by zinc arc light; at 440° the reaction is very rapid in the dark. Hydrogen sulphide catalyses the reaction at 280° in the light, but not appreciably in the dark; at 330° the mixture readily explodes, but under certain conditions of concentration sulphur dioxide is formed rapidly in the dark, so that the reaction in the light is probably complicated by the presence of this substance, which at 350° causes rapid combination in the light, but has no influence on the dark reaction at temperatures below 480°. A mixture of hydrogen and oxygen containing a trace of nitrogen peroxide and heated to just below the ignition temperature is unaffected by light, since insufficient activated oxygen atoms are present, and no photosensitisation is observed until the nitrogen peroxide concentration is raised nearly to that which induces a rapid reaction in the dark; the action of nitrous oxide resembles that of sulphur dioxide.

H. F. GILLBE.

#### Precision actinometry with uranyl oxalate.

W. G. LEIGHTON and G. S. FORBES (J. Amer. Chem. Soc., 1930, 52, 3139—3152).—The quantum efficiency,  $\gamma$ , of the photolysis of 0.01–0.05*M*-oxalic acid in presence of 0.001–0.02*M*-uranyl sulphate has been investigated at 9.8° and 25° with monochromatic light of nine different wave-lengths between 494 and 254  $\mu\mu$ , inclusive. The liquid in the actinometer must be stirred and details of the analytical procedure are recorded. The solution used in the actinometer must be 0.010*M* with respect to uranyl sulphate and 0.050*M* with respect to oxalic acid. At 25°,  $\gamma$  then varies from 0.60 with light of wave-length 254  $\mu\mu$  to 0.58 for 435  $\mu\mu$  and has a minimum of 0.49 at 366  $\mu\mu$ .  $\gamma$  is diminished by the presence of sodium sulphate, sodium hydroxide, or sulphuric acid, and the temperature coefficient per 10° between 10° and 25° for light of wave-lengths 313 and 366  $\mu\mu$  is 1.03 (cf. Pierce, A., 1929, 1404). Evidence is adduced that the reaction probably proceeds by the decomposition of a complex of the type  $\text{UO}_2\text{H}_2\text{C}_2\text{O}_4$  or  $\text{UO}_2\text{C}_2\text{O}_4$  rather than by collisions of the second kind between activated uranyl ions and acid molecules.

J. G. A. GRIFFITHS.

**Photochemical isomerisation of allocinnamic acid in presence of iodine.** A. BERTHOUD and C. URECH (J. Chim. phys., 1930, 27, 291—306).—The transformation, in benzene solutions containing

iodine, of allocinnamic acid into cinnamic acid by visible radiation has been studied by observation of the change of *m. p.* The reaction is unimolecular and has a temperature coefficient at 25–35° of 1.3. For wave-lengths from 4580 to 5260 Å., over which range the absorption is almost complete, the reaction velocity *k* is independent of the iodine concentration, but for red light, which is only partly absorbed, *k* varies with the square root of the iodine concentration. The quantum yields at 4350 and 5600 Å. are 1.3 and 0.33, respectively. The suggested mechanism of the reaction, which accords well with the experimental data, is (1) a molecule of iodine is dissociated by the light, (2) an atom of iodine combines with a molecule of allocinnamic acid to form an unstable monoiodide containing a tervalent carbon atom, (3) mutual rotation of the two doubly-linked carbon atoms takes place with the formation of an iodine derivative of cinnamic acid, (4) the iodine atoms dissociate and reform iodine molecules. The ratio of formation of cinnamic acid is given by  $kaI_0^{1/2}[I_2]^{1/2}$  for weak absorption and by  $kaI_0^{1/2}$  for practically complete absorption, *a* being the initial concentration of allocinnamic acid,  $[I_2]$  the mol. iodine concentration, and  $I_0$  the radiation intensity.

H. F. GILLBE.

#### Determination of effect of light on dyes.

P. KRAIS (Kolloid-Z., 1930, 52, 173—174).—An indicator paper suitable for measuring the amount of sunlight may be made as follows. 200 G. of white kaolin are stirred with 200 c.c. of water, and 400 c.c. of a solution containing 1 g. of Victoria-blue B per litre are added, the mixture being stirred and filtered with suction. The residue is dried in air in the dark, powdered, and sieved, and then applied to paper by means of gum arabic. On exposure to light the paper becomes pure white and not grey as in most other indicators. Directions for the quantitative use of the paper are given.

E. S. HEDGES.

**Quantum yield in the photo-bromination of organic hydroxy-acids in relation to the frequency of the exciting light.** J. C. GHOSH and R. M. PURKAYASTHA (Z. physikal. Chem., 1930, B, 9, 128—132).—The quantum yields in the photo-bromination of mandelic, lactic, and phenyl-lactic acids (cf. this vol., 718) increase in a continuous manner from about 3.1 to 6, 3 to 5, and 2.2 to 3.5, respectively, as the wave-length of the light diminishes from 545 to 366  $\mu\mu$ .

R. CUTHILL.

**Differences in mechanism of addition and substitution reactions in photo-bromination of organic compounds.** J. C. GHOSH and R. M. PURKAYASTHA (Z. physikal. Chem., 1930, B, 9, 154—156).—It appears probable that in both the photo-bromination of hydroxy-acids (this vol., 718) and the photochemical addition of bromine (A., 1928, 256) continuance of the reaction chain is due to the secondary formation of bromine atoms in one of the constituent reactions. In the addition reactions it is likely that triatomic bromine molecules are formed.

R. CUTHILL.

**Irradiation reaction of protein.** B. RAJEWSKY (Strahlenther., 1929, 34, 582—586; Chem. Zentr., 1930, i, 1748—1749).—The coagulation of protein by ultra-violet light is only slightly affected by rise of



temperature, the curve being linear up to the coagulation temperature of the protein; the slight rise is attributed to the increased agglomeration of the denatured protein particles with increased molecular movement. The coagulation of protein by X-rays increases exponentially with rise of temperature.

A. A. ELDRIDGE.

**Energy yield in the decomposition of chloroform by X-rays and the mechanism of this and similar X-ray reactions.** G. CRONHEIM and P. GÜNTHER (Z. physikal. Chem., 1930, B, 9, 201—228; cf. A., 1928, 1340).—In the formation of hydrogen chloride from chloroform under the influence of X-rays the amount produced is proportional to the amount of energy absorbed in the form of secondary electrons, and 21 kg.-cal. are required per mol. of acid formed. Since this is small compared with the energy required to sever C-Cl and C-H linkings it is concluded that the reaction has a chain mechanism. Possibly the chloroform molecule is first shattered by a secondary electron with the formation of free chlorine atoms and a hydrogen atom which react with unchanged molecules,  $\text{Cl} + \text{CHCl}_3 = \text{HCl} + \text{CCl}_3$ ,  $\text{H} + \text{CHCl}_3 = \text{H}_2 + \text{CCl}_3$ , the  $\text{CCl}_3$  then continuing the chain by the reaction  $\text{CCl}_3^* + \text{CHCl}_3 = \text{Cl} + \text{CCl}_2 \cdot \text{CHCl}_2$ , and it is likely that the reactions  $\text{H} + \text{CHCl}_3 = \text{HCl} + \text{CHCl}_2$ ,  $\text{CHCl}_2^* + \text{CHCl}_3 = \text{Cl} + \text{CHCl}_2 \cdot \text{CHCl}_2$  also occur. In presence of water and oxygen, chlorine monoxide or hypochlorous acid is also formed, and the yield of hydrogen chloride is increased. It is uncertain how the water acts, but a possible mechanism for the action of oxygen is  $\text{CCl}_3 + \text{O}_2 = \text{COCl} + \text{Cl}_2\text{O}$ ,  $\text{COCl} + \text{CHCl}_3 = \text{COCl}_2 + \text{CHCl}_2$ ,  $\text{CHCl}_2 + \text{O}_2 = \text{HClO} + \text{COCl}$ ,  $\text{COCl}_2 + \text{H}_2\text{O} = 2\text{HCl} + \text{CO}_2$ . The retarding action of hydrocarbons such as petroleum on the decomposition may then depend on their interfering with the reaction of the chloroform with oxygen. In the formation of hydrogen chloride from mixtures of petroleum and carbon tetrachloride a chain of reactions is probably initiated by hydrogen atoms from the hydrocarbon as well as by chlorine atoms. In all the X-ray reactions examined it appears that the action of a secondary electron on a single molecule corresponds with the first step in the absorption of visible light in an ordinary photochemical chain reaction.

R. CUTHILL.

**Mechanism of the chemical action of X-rays in aqueous solutions.** O. RISSE (Strahlenther., 1929, 34, 578—581; Chem. Zentr., 1930, i, 1748).—Ultra-violet irradiation of water, whether in presence or absence of oxygen, did not lead to the formation of hydrogen peroxide unless zinc oxide was present; X- or  $\beta$ -irradiation of pure water leads, however, to its formation. Hydrogen peroxide is decomposed by all three radiations. The reaction depends on the dissolved oxygen; hence the presence of dissolved oxygen in irradiated solutions may cause changes dependent on the primary formation of hydrogen peroxide. The conversion of ferrous into ferric salts is an example. The mechanism of the formation of hydrogen peroxide is discussed. A. A. ELDRIDGE.

**Formation of periodic structures.** E. S. HEDGES (Rev. gén. Colloid., 1930, 8, 193—199).—A summary. Existing theories of Liesegang ring formation are inadequate. Periodic structures are

differentiated from periodic reactions and experiments are described in which the Liesegang phenomenon is separated into two stages, the banding occurring after the chemical reaction has been completed. Similar structures can be produced by the coagulation of colloids by electrolytes and also in the salting-out of simple salts such as sodium chloride. This particular manifestation of periodicity is considered in relation to the periodic dissolution of metals, periodic passivity, and periodic phenomena in electrolysis, both at the anode and at the cathode, and it appears that the essential condition for periodicity is the existence of a critical condition determining a change which takes place to completion every time the critical value is reached. E. S. HEDGES.

**Behaviour of sodium sulphate crystals towards cold ethyl and methyl alcohols.** M. A. RAKUSIN (Z. Krist., 1930, 73, 115—116; Chem. Zentr., 1930, i, 2228).—Treatment with 95% ethyl alcohol affords a powder consisting of thenardite; with methyl alcohol dehydration, but not powder formation, occurs. A. A. ELDRIDGE.

**Complex fluoborates.** A. TRAVERS and L. MALAPRADE (Bull. Soc. chim., 1930, [iv], 47, 788—801).—Fluoboric acid and normal fluoborates corresponding with the formula  $\text{MBF}_4$  decompose slowly in aqueous solution, giving complex fluoborates which are readily decomposed by alkalis. When hydrofluoric and boric acids react in aqueous solution an acid is formed which is not normal fluoboric acid, but when kept is slowly transformed into an equilibrium mixture containing the latter. A complex fluoborate is formed when boric acid reacts with potassium fluoride in aqueous solution. Two new fluoborates which are decomposable by alkalis have been isolated. The compound  $\text{K}_2\text{BF}_5$  is obtained when normal potassium fluoborate is heated at  $580^\circ$ . The compound  $\text{K}_2\text{B}_2\text{F}_6 \cdot 1.5\text{H}_2\text{O}$  may be prepared by the following method: 50 g. of potassium hydrogen fluoride and 25 g. of boric acid are dissolved in 100 c.c. of cold water, the solution is filtered and kept for about 4 hrs., when a crystalline deposit of the substance will have formed. E. S. HEDGES.

**Preparation of silver-free copper.** B. PARK (J. Amer. Chem. Soc., 1930, 52, 3165—3166).—Copper, spectrographically free from silver (i.e.,  $<0.0002\%$ ), is obtained by fractional electrolytic deposition on platinum electrodes from copper sulphate in 5% nitric acid. The first fractions contain the bulk of the silver.

J. G. A. GRIFFITHS.

**Cæsium borates.** A. P. ROLLET and L. ANDRÉS (Compt. rend., 1930, 191, 375—378).—Precipitates obtained by mixing various proportions of alcoholic solutions of boric acid and cæsium oxide have approximately the same compositions as the initial mixtures for 0.25—4 mols. of boric acid to 1 mol. of cæsium oxide, but for larger proportions of the former an amorphous precipitate of composition  $5\text{B}_2\text{O}_3 \cdot \text{Cs}_2\text{O}$  is produced. An isothermal diagram of the system  $\text{B}_2\text{O}_3 - \text{Cs}_2\text{O} - \text{H}_2\text{O}$  is shown for  $18^\circ$ , the following solid phases being identified by the method of residues: cæsium pentaborate,  $5\text{B}_2\text{O}_3 \cdot \text{Cs}_2\text{O} \cdot 8\text{H}_2\text{O}$ , small orthorhombic crystals; cæsium diborate,  $2\text{B}_2\text{O}_3 \cdot \text{Cs}_2\text{O} \cdot 5\text{H}_2\text{O}$ , large orthorhombic crystals which lose water at  $80^\circ$ ,

and are often contaminated with pentaborate; *cæsium monoborate*,  $B_2O_3 \cdot Cs_2O \cdot 7H_2O$ , orthorhombic prisms, losing water at  $45^\circ$ . J. GRANT.

**Reactions of ammonia on the system  $ZnCl_2-NH_4Cl-H_2O$ .** R. FRIESS (J. Amer. Chem. Soc., 1930, 52, 3083—3087).—The  $p_H$  of aqueous zinc chloride-ammonium chloride solutions in the range of solubility at  $20^\circ$ , the concentrations of ammonia requisite to produce precipitates, and the  $p_H$  of the liquids in equilibrium with the precipitates have been determined. The precipitate has the composition  $ZnCl_2 \cdot 2NH_3$  when the concentration of ammonium chloride is 15% or more, but a basic precipitate, probably  $ZnCl_2 \cdot 4ZnO$ , is formed when the concentration of ammonium chloride is less than 15%. The results are explained by the effect of ammonium chloride on the ionisation of the constituents of the system. J. G. A. GRIFFITHS.

**Composition of deposit forming on zinc immersed in cupric sulphate solution.** I. A. GALECKI and J. TOMASZEWSKI.—Sec B., 1930, 822.

**Action of hydrogen and hydrocarbons on barium.** P. REMY-GENNETÉ (Compt. rend., 1930, 191, 413—414).—Redistilled barium in contact with pure dry hydrogen at  $20^\circ$  and 639 mm. pressure for 2.5 months produces a fall in pressure to about 1 mm. Methane and acetylene are not adsorbed (1 month), and a method of separation of hydrogen from these gases is therefore indicated. J. GRANT.

**Preparation of mercuriammonium bromides and chlorides.** Crystalline dimercuriammonium bromide and chloride. M. FRANÇOIS (Bull. Soc. chim., 1930, [iv], 47, 825—833).—See this vol., 1006. E. S. HEDGES.

**Reaction mechanism in the precipitation of radium preparations rich in emanation.** O. ERBACHER and H. KÄDING (Z. physikal. Chem., 1930, 149, 439—448).—Radioactive preparations were made by precipitating a mixture of ferric chloride and barium radium chloride by the addition of an excess of ammonia solution containing ammonium carbonate, sulphate, or chromate. The emanating power of the precipitate was almost 100% when ammonium carbonate or sulphate was used, but only about 65% when the chromate was used. When the barium radium salt was added after precipitation of the ferric hydroxide the emanating power was unaltered in the presence of carbonate or sulphate, but was raised to about 75% in the presence of chromate. It is supposed that the sparingly soluble radium carbonate and sulphate are adsorbed at the outer surface of the ferric hydroxide gel, giving a highly emanating preparation, but the almost insoluble radium chromate is adsorbed so rapidly that a portion becomes enmeshed in inner surfaces of the gel, with reduction of the emanating power of the preparation. Similar phenomena were observed using aluminium hydroxide as the adsorbent. This conclusion is supported by the reduction of emanating power on ageing of the gel or on drying with alcohol. E. S. HEDGES.

**Action of calcium hydroxide solution on aluminium.** G. ASSARSON (Z. anorg. Chem., 1930,

191, 333—339).—The action of calcium hydroxide solution (0.040—0.125% CaO) on aluminium has been investigated at  $0-90^\circ$ . Analysis and crystallographic measurements of the resulting crystalline deposits show that the following calcium aluminates are formed under appropriate conditions:  $Al_2O_3 \cdot 4CaO \cdot 12H_2O$ ;  $Al_2O_3 \cdot 3CaO \cdot 12H_2O$ ; and  $Al_2O_3 \cdot 3CaO \cdot 6H_2O$ . O. J. WALKER.

**Volatility of silica in water vapour.** C. J. VAN NIEUWENBURG and H. B. BLUMENDAL (Rev. trav. chim., 1930, 49, 857—860).—Amorphous silica, quartz, tridymite, and cristobalite were heated at 300 atm. at  $395^\circ$  in the presence of water for periods of 9 and 24 hrs. An appreciable loss of weight was observed in each case. The metastable forms, cristobalite and tridymite, are more volatile than quartz, but less volatile than amorphous silica. Vaporised silica combined with zinc oxide to form a crystalline zinc silicate, identical in properties with willemite. Wollastonite was obtained from lime in the same way. J. A. V. BUTLER.

**Preparation of hypophosphoric acid.** M. SPETER (Chem.-Ztg., 1930, 54, 599).—Priority is claimed for the author's preparation of hypophosphoric acid from red phosphorus and alkali or alkaline-earth hypochlorites (A., 1927, 1156). In using alkali hypochlorites the solution should be added gradually to the aqueous suspension of red phosphorus. E. LEWKOWITSCH.

**Constitution of hyposulphurous acid.** O. VON DEINES and G. ELSTNER (Z. anorg. Chem., 1930, 191, 340—381).—When solid sodium hyposulphite is heated it decomposes suddenly at about  $190^\circ$ . The action is exothermal and evolves 10,350 g.-cal./mol. of hyposulphite, and can be represented by the equation:  $2Na_2S_2O_4 = SO_2 + Na_2SO_3 + Na_2S_2O_3$ , accompanied by the secondary reactions,  $SO_2 + 3Na_2SO_3 = 2Na_2SO_4 + Na_2S_2O_3$  and  $SO_2 + 2Na_2SO_3 = 2Na_2SO_4 + S$ . The main reaction probably takes place through the following stages:  $2Na_2S_2O_4 = 2Na_2SO_3 + 2SO$ ;  $2SO = S_2O_2$ ;  $S_2O_2 + Na_2SO_3 = Na_2S_2O_3 + SO_2$ . The decomposition of sodium hyposulphite solutions with hydrochloric acid solution at the ordinary temperature gives sulphur dioxide, oily hydrogen persulphide, and polythionic acids (cf. Meyer, A., 1903, ii, 285). With concentrated acid solution at  $40^\circ$ , however, no polythionic acids are formed and the main reaction is  $2H_2S_2O_4 = 3SO_2 + S + 2H_2O$ . The structure of the hyposulphites is discussed in detail and it is suggested that they are complex salts of the type  $M_2[SO_3SO]$ . This structure accounts for the above-mentioned decomposition of solid sodium hyposulphite and agrees also with the other reactions of hyposulphites. O. J. WALKER.

**Structure of the tungstic acids.** A. M. MORLEY (J.C.S., 1930, 1987—1999).—Four tungstic acids have been prepared and examined. The conditions of preparation were so chosen that the products obtained may be considered typical. Each type of acid was subjected to various ageing conditions, and all products were fully analysed during such ageing processes. An X-ray study (powder method) was also made of many of the products, and other tungsten compounds for comparison (photographs reproduced).

It is concluded from the combined evidence of X-ray structure and analysis that two definite compounds,  $\text{H}_2\text{WO}_4$  and  $\text{H}_2\text{WO}_3 \cdot \text{H}_2\text{O}$ , exist, but that other compounds exist which it is suggested may be condensed compounds, or compounds physically impure (*i.e.*, imperfectly or not crystalline). J. O. CUTTER.

**Technical preparation of rhenium.** W. FEIT.—See B., 1930, 822.

**Ferric hydroxide in the rusting process.** G. SCHIKORR (Z. anorg. Chem., 1930, 191, 322—332).—The conditions under which the two forms of ferric hydroxide,  $\text{FeO}_2\text{H}$ , are formed in the rusting process have been investigated. The  $\gamma$ -hydroxide is formed when the oxidation takes place through the intermediate ferrous ferrite stage, *e.g.*, when the rusting takes place directly on the iron under water. Rust which has been formed under water at a distance from the iron consists of the  $\alpha$ -hydroxide and is due to the direct oxidation of ferrous ions. Dehydration experiments show that slowly-formed rust corresponds closely with  $\text{FeO}_2\text{H}$  in its water content up to 160°, but that at higher temperatures the loss of water is rapid. Rust which has been formed rapidly has a considerably smaller percentage of water even at low temperatures. O. J. WALKER.

**Separation on iron of carbon from carbon monoxide. III. Formation of iron oxides and iron carbides in the solid phase.** U. HOFMANN and E. GROLL (Z. anorg. Chem., 1930, 191, 414—428; cf. A., 1928, 1341).—When carbon monoxide is passed not too rapidly over iron, magnetite is found in the solid phase up to 560° and ferrous oxide up to 655°. The presence of these oxides is shown by X-ray examination. Above 655° or with too rapid a gas stream no oxides are formed. At lower temperatures (275—320°), at which separation of carbon takes place only very slowly, formation of the carbide  $\text{Fe}_3\text{C}$  occurs. These facts, along with an examination of the equilibria in the system iron-carbon-oxygen, suggest that the reaction between iron and carbon monoxide proceeds as follows. At first iron carbide and carbon dioxide are formed. When the concentration of the latter in the gas phase is sufficiently high it oxidises the iron to oxides, which then react with carbon monoxide with further formation of carbide. The separation of carbon is due to decomposition of the carbide. In this decomposition cementite is always formed as well as iron.

O. J. WALKER.

**Analytical sublimation with special reference to micro-sublimation.** H. HOFFMANN, jun., and W. C. JOHNSON (J. Assoc. Off. Agric. Chem., 1930, 13, 367—377).—Sublimation points of numerous substances were determined at atmospheric pressure in a vacuum in the Hortvet sublimator (B., 1923, 805). Sublimation depends on vapour pressure and is more comparable with evaporation than with boiling. Typical procedure is described and photomicrographs are given. Sublimation possesses advantages in both qualitative and quantitative analysis.

A. G. POLLARD.

**Optical method for the detection of substances in mixtures, residues, etc.** H. WAGNER (Z. angew. Chem., 1930, 43, 686—687).—Immersion of various

transparent substances in liquids having refractive indices nearly the same as the solids causes them to appear various shades of blue when observed through the microscope by means of diffused transmitted light; thus calcium sulphate appears violet in a mixture of benzaldehyde and xylene, quartz bluish-violet in benzaldehyde and bronze-green in phenol, aluminium hydroxide light blue in toluene, and tricalcium phosphate, barium and strontium sulphates, and amphibole asbestos blue in phenylthiocarbimide. These tests serve to distinguish, *e.g.*, quartz and barium sulphate, and calcium and barium sulphates from one another when only small amounts of substance are available. A. R. POWELL.

**Application of the neon lamp to photometric titrations.** T. SOMIYA and S. SHIRAIISHI (J. Soc. Chem. Ind. Japan, 1930, 33, 300B).—Light from a powerful tungsten lamp passes through the solution which is being titrated, and falls on the filament of a neon lamp. The photo-electric current generated in the latter is measured, and can be used to indicate the end-point of titrations involving colour changes or precipitations. C. W. GIBBY.

**Sources of error in the determination of hydrogen in gases.** H. R. AMBLER.—See B., 1930, 816.

**Potentiometric determination of acids and bases.** F. L. HAHN (Z. angew. Chem., 1930, 43, 712—714).—The views of Jander (this vol., 51) are criticised and the potentiometric titration method for acids and bases is defended. H. I. DOWNES.

**Determination of active chlorine in hypochlorite liquors.** J. D. BLAKELEY, J. M. PRESTON, and F. SCHOLEFIELD.—See B., 1930, 860.

**Rapid determination of free sulphur by means of silver.** V. ALEKSANDROV (J. Chem. Ind., Russia, 1929, 6, 1114—1117).—The method is based on the formation of silver sulphide. If 0.3 g. of sulphur is present the minimal silver surface (wire or net) must be 28.5 cm.<sup>2</sup> If the sample is solid it must be dissolved in a solvent of b. p. higher than the m. p. of sulphur. The metal is immersed at 60°, washed with toluene or ether, and dried at 50° for 15—20 min. The silver is cleaned by ignition in air, followed by washing with ammonia solution and water.

CHEMICAL ABSTRACTS.

**Sensitive test for ammonia.** K. G. MAKRIKIS (Z. anal. Chem., 1930, 81, 212—214).—A freshly prepared mixture of 20% silver nitrate solution (5 vols.) and 5% tannin solution (1 vol.) is impregnated in a suitable substrate, the presence of a trace of gaseous ammonia being indicated by a lustrous deposit of silver. The method is capable of showing the presence of 0.005 mg. of gaseous ammonia. J. O. CUTTER.

**Volumetric determination of phosphoric acid.** W. H. ROSS.—See B., 1930, 816.

**Modified Gutzeit arsenic apparatus.** A. J. LINDSEY (Analyst, 1930, 55, 503—504).—The glass apparatus affords arsenic stains of uniform size, and avoids loss of gases. A flanged tube is ground to form a plane surface with the hole of the original bore; two ears are sealed to the flange. The disc of mercuric chloride paper is secured between the ground surface

of the cap and tube, and these are held together by rubber bands.

D. G. HEWER.

**Separation and identification of alkali and alkaline-earth metals using isoamyl alcohol.** H. YAGODA (J. Amer. Chem. Soc., 1930, **52**, 3068—3076).—In the absence of sulphates and other metals, a qualitative separation of sodium, potassium, barium, magnesium, strontium, and calcium may be effected by converting the chlorides or nitrates of the metals into bromides by heating with 1 c.c. of 8*N*-hydrobromic acid until dryness is attained and then boiling the residue for 0.5 min. with 3 c.c. of isoamyl alcohol. The bromides of the first three metals are almost insoluble, and any sodium and barium in the dried residue is extracted by boiling with 1—2 c.c. of 0.2*N*-hydrobromic acid in 95% ethyl alcohol. The two metals are then precipitated as chlorides by the addition of 1 c.c. of 12*N*-hydrochloric acid. The separation of the metals with isoamyl alcohol-soluble bromides (magnesium, strontium, calcium) depends on the relatively facile decomposition of magnesium nitrate on ignition and the solubility of calcium nitrate in 16*N*-nitric acid. Relevant solubility data at 25° are recorded.

J. G. A. GRIFFITHS.

**Quantitative spectrum analysis of alkali metals.** H. LUCAS (Physikal. Z., 1930, **31**, 803—804).—In the arc spectrum of potassium and sodium the intensity relations of two lines, the higher terms of which have approximately the same excitation potential but are members of different series, are constant within the limits of experimental error. The ratio of the intensities of any two lines, the initial levels of which are different, shows a marked dependence on the experimental conditions. The necessary precautions for maintaining the constancy of the arc are dealt with. The spark spectra of sodium and potassium are characterised by a strong retrogression of the subsidiary series. The intensity relation between the principal and subsidiary series in the arc and spark spectra is 1 : 100.

W. R. ANGUS.

**Determination of sodium [in water].** E. R. CALEY and C. W. FOULK.—Sec B., 1930, 884.

**Volumetric determination of very small quantities of silver.** J. GOLSE (Bull. Soc. chim., 1930, [iv], **47**, 760—768).—Silver is precipitated as a compound of the formula  $\text{HgI}_2 \cdot 2\text{AgI}$  by adding excess of a dilute solution of potassium iodide saturated with mercuric iodide. The iodine in the precipitate is determined volumetrically.

C. W. GIBBY.

**Detection of magnesium in minerals.** H. LEITMEIER and F. FEIGL (Tsch. Min. Petr. Mitt., 1930, **40**, 325—334).—A simple test for magnesium (A., 1929, 669) consists in warming the powdered mineral in a solution of nitrobenzeneazoresorcinol containing an excess of sodium hydroxide. In the presence of even a small amount of magnesium the powder acquires a blue colour. Silicates must be first decomposed, and if much iron is present this must be separated.

L. J. SPENCER.

**Iodometric determination of small amounts of zinc.** H. A. PAGEL and O. C. AMES (J. Amer. Chem. Soc., 1930, **52**, 3093—3098).—Minute details are given

for the iodometric determination of 3.3—33 mg. of zinc in 100 c.c. of solution. The metal is precipitated as the pyridine thiocyanate,  $\text{Zn}(\text{C}_5\text{H}_5\text{N})_2(\text{SCN})_2$ , which is then dissolved in about 125 c.c. of boiling water, 6 g. of borax are added, and the cooled liquid is poured into a volume of 0.1*N*-iodine at least 5 c.c. in excess of that required for the reaction  $\text{NCS}' + 4\text{I}_2 + 8\text{OH}' = \text{SO}_4'' + 7\text{I}' + 4\text{H}_2\text{O} + \text{ICN}$ . After 10—15 min., 10 c.c. of 6*N*-hydrochloric acid are added and the excess of iodine is immediately titrated slowly with thiosulphate. The quantitative relation is given by  $\text{NCS}' + 3\text{I}_2 + 4\text{H}_2\text{O} = \text{SO}_4'' + 8\text{H}' + 6\text{I}' + \text{CN}'$ . Chlorides and metals having insoluble pyridine thiocyanates interfere, but sulphates and nitrates are without effect.

J. G. A. GRIFFITHS.

**Potentiometric titrations using mercurous nitrate and sodium oxalate as titrating solutions.** C. MAYR and G. BURGER (Monatsh., 1930, **56**, 113—115; cf. A., 1929, 1413).—Correct results are obtained only if the sparingly soluble compound formed is crystalline. In determining phosphoric acid mercurous nitrate solution is added, precipitating mercurous phosphate; the excess is determined by potentiometric titration of an aliquot portion of the filtered solution against 0.1*N*-sodium oxalate solution. The method is not applicable to pyrophosphates, even if the salt is previously boiled with nitric acid to convert it into the ortho-acid. Nitrates of calcium, strontium, cerium, cadmium, and lead in solution are precipitated with 0.1*N*-sodium oxalate, the excess being determined by electrometric titration of an aliquot portion of the filtrate against 0.1*N*-mercurous nitrate solution.

J. R. I. HEPBURN.

**Separation and determination of gallium. II. Separation of gallium and aluminium from one another, and determination of these elements.** S. ATO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **14**, 35—47; cf. this vol., 564).—Three methods for the separation and determination of gallium and aluminium are described, the third being the most practicable. (1) An aqueous solution containing only the chlorides of the two metals is evaporated almost to dryness, and a solution of acetyl chloride in acetone (1 : 4) added with stirring. The precipitate of hydrated aluminium chloride is washed by decantation with the acetyl chloride solution. The solution is evaporated to dryness and heated repeatedly with nitric acid, evaporated again, ignited, and dissolved in hydrochloric acid, then evaporated to dryness, taken up in water, and the gallium is precipitated by adding acetic and camphoric acids, ignited, and weighed as trioxide. The filtrate is evaporated and ignited to remove organic matter, aluminium is precipitated as chloride, and, together with that precipitated at the beginning, weighed after conversion into oxide. (2) A solution containing only the chlorides is evaporated to dryness on the water-bath, the residue is dissolved in a mixture of 6*N*-hydrochloric acid and acetone (1 : 1), and the ice-cold solution saturated with hydrogen chloride. The precipitate of hydrated aluminium chloride is washed by decantation with a mixture of acetone and hydrochloric acid saturated with hydrogen chloride. Further procedure is as in (1). (3) A solution con-

taining only the chlorides is evaporated to dryness, redissolved in 6*N*-hydrochloric acid, treated with ether, and the ice-cold solution saturated with hydrogen chloride. The precipitate of aluminium chloride and the filtrate are treated as in (1) and (2).

C. W. GIBBY.

**Influence of cobalt on the determination of manganese by the bismuthate method.** Separation of manganese from cobalt by ammonium persulphate. T. SOMIYA (*J. Soc. Chem. Ind. Japan*, 1930, 33, 255—256B).—Cobalt is oxidised by sodium bismuthate and nitric acid even when the concentration of the latter is reduced to 5% and the solution ice-cooled. It is therefore not possible to determine manganese by this method without complete separation from cobalt. Ammonium persulphate will not precipitate manganese entirely free from cobalt either in ammoniacal or in neutral solution. In ammoniacal solution the precipitate is difficult to filter; in nearly neutral solution in presence of zinc it is readily filtered and contains very little cobalt, but repeated precipitation by boiling with ammonium persulphate is necessary to yield a filtrate free from manganese.

C. IRWIN.

**Delicate reagent for cobalt.** E. A. LUM (*Pharm. J.*, 1930, 125, 147).—When a cobalt nitrate solution is treated with 20% ammonium thiocyanate solution and the mixture shaken with acetone or a mixture of ether and amyl alcohol a bluish-green solution is obtained. The application of this test to the analysis of group IIIB is indicated.

A. R. POWELL.

**Potentiometric determination and separation of chromium, vanadium, and molybdenum in steel.** W. TRZEBIATOWSKI.—See B., 1930, 821.

**Separation of tungstates from arsenates, using benzidine hydrochloride.** J. LUKAS and A. JILEK (*Chem. Listy*, 1930, 24, 320—322).—Tungstic acid can be quantitatively separated from arsenic acid by the addition of benzidine hydrochloride to a feebly acid solution of the two salts.

R. TRUSZKOWSKI.

**Potentiometric determination of gold.** E. ZENZL (*Z. Elektrochem.*, 1930, 36, 551—552).—The high values obtained in the determination of gold with titanous chloride by Müller, Weisbrod, and Stein (*A.*, 1928, 388) are attributed to details of their experimental procedure. A note by E. MÜLLER is appended.

H. I. DOWNES.

**Use of micro-analysis in the streak test [for precious metal alloys].** R. STREBINGER and H. HOLZER.—See B., 1930, 867.

**M.-p. determinations.** A. WINSTANLEY (*Pharm. J.*, 1930, 125, 147).—The substance is placed at the bottom of a capillary tube 6 in. long and the upper half is then bent at right angles to the lower to form a handle by which the tube may be held against the thermometer bulb; the use of rubber bands is thus rendered unnecessary.

A. R. POWELL.

**Apparatus for determination of m. p.** L. M. DENNIS and R. S. SHELTON (*J. Amer. Chem. Soc.*, 1930, 52, 3128—3132).—A bar of copper 61×2.5×2.5 cm. has one end connected with a potentiometer by means of copper wire and the other end wound with an electrical heater through which the current

is adjusted so that the range of temperature of the bar between the hotter and cooler ends includes the temperature of the m. p. of the substance under examination. The finely-powdered material is spread along the bar, and a constantan wire, connected with the potentiometer, is brought into contact with the bar at the sharply-developed line between the melted and unmelted substance. In this way m. p. between the ordinary temperature and 300° are determined within 30 sec. to within 0.25°. M. p. of substances which decompose when heated are: phthalic acid, 228.5°; alloxan, 210°; barbituric acid, 250°; glycine, 297.2°; fumaric acid, 297°, and phenylboric acid, 222.5°.

J. G. A. GRIFFITHS.

**Valve-operated coreless induction furnace for high-temperature research.** F. ADCOCK (*Trans. Faraday Soc.*, 1930, 26, 544—560).—The construction and manipulation of a furnace of the above type are described.

R. CUTHILL.

**Electric muffle with chromium-nickel wire heaters.** H. SIEBERT (*Chem.-Ztg.*, 1930, 54, 499).—A readily replaceable heating unit composed of chromium-nickel spirals is described. Temperatures of 1000—1100° can be attained.

E. LEWKOWITSCH.

**Velocity meters for gases.** A. P. J. HOOGEVEEN (*Chem. Weekblad*, 1930, 27, 508—509; cf. *Nicolas*, this vol., 885).—To admit of the use of a differential pressure instrument in a circuit in which the absolute pressure may vary, without requiring repeated calibrations, the instrument is provided with two gas taps, at the inlet and exit ends, respectively, and an absolute pressure manometer just before the exit tap.

S. I. LEVY.

**Photo-electric density meter.** F. C. TOY (*J. Sci. Instr.*, 1930, 7, 253—256).—An instrument already described (*B.*, 1927, 60) has been improved.

C. W. GIBBY.

**Distillation apparatus.** W. SWIENTOSLAWSKI (*J. Chim. phys.*, 1930, 27, 329—335).—A modified form of Engler's distillation apparatus is described wherein a feed back of the distillate to the still may be effected by means of a by-pass drip feed from a vertical condenser; the distillation may be interrupted at any moment and the condensation temperature of the vapour determined, whilst the rate of evaporation and the degree of fractionation may be readily controlled.

H. F. GILLBE.

**Adiabatic calorimeter.** W. H. BARNES and O. MAASS (*Canad. J. Res.*, 1930, 3, 70—79).—A modification of earlier adiabatic calorimeters is described (cf. Maass and Barnes, *A.*, 1926, 668; Maass and Waldbauer, *A.*, 1925, ii, 492). A radiation thermoclement which is capable of detecting a difference in temperature of 0.00014° between the calorimeter and the outer bath is employed. The probable error in measurements of heat capacity is 0.2% when the change in temperature of the outer bath is 2°. The specific heat of platinum, in g.-cal. per g., between +25° and -78.5° is given by the equation,  $C_p = 0.013215 + 0.00010148T - 0.00000012543T^2$ . The heat capacity of ice between -78.5° and -3° is recorded.

T. H. MORTON.

**Aspirator for constant gas pressure.** F. FRIEDRICHS (Chem.-Ztg., 1930, 54, 667).—A simple improvement of the gas-holder described previously (*ibid.*, 1929, 53, 760), by which refilling of the aspirator bottle may be avoided, is depicted.

E. LEWKOWITSCH.

**Thermo-spring balance.** Y. OSHIMA and Y. FUKUDA (J. Soc. Chem. Ind. Japan, 1930, 33, 251—252B).—The balance consists of a quartz fibre helical spring to the lower end of which is attached an iron core carrying a sample container. The spring and core are contained in a vertical glass tube with cooling jacket and the sample container in a heating tube connected to it. A solenoid surrounds the core, and the elongation of the spring caused by the change in weight of the sample is balanced by the solenoid current. The apparatus can be used at temperatures up to 1000°.

C. IRWIN.

**Light filters for the isolation of narrow spectral regions.** L. A. JONES.—See B., 1930, 840.

**Elliptical reflector for intensifying optically excited mercury radiation.** R. N. WOLFE (Rev. Sci. Instr., 1930, 1, 471—472).—The reflector consists of a nickel elliptical cylinder, at one focus of which is placed the mercury arc and at the other the tube to be irradiated.

C. W. GIBBY.

**Thin sulphur layers.** D. K. BERKEY (Rev. Sci. Instr., 1930, 1, 479).—Layers of sulphur as thin as 0.0075 cm. have been obtained by the following method. Melted sulphur is poured on to a warmed piece of zinc about 1 in. square and 1/32 in. thick, and pressed out after placing a piece of cellophane over it. The cellophane is then removed and the sulphur ground down with emery cloth. A circular hole is dissolved in the zinc with dilute hydrochloric acid, the remainder being coated with protective paint. The layers crack spontaneously in a few days.

C. W. GIBBY.

**Untrustworthiness of photographic emulsions on glass for recording distances and a method of minimising this defect.** D. COOKSEY and C. D. COOKSEY (Physical Rev., 1930, [ii], 36, 80—84).—In order to determine the effect of development on the position of a latent image, superficial motions of double-coated emulsions were investigated, and the positions of developed images with respect to corresponding latent images were studied for singly-coated plates. The results indicate that there are stresses in undeveloped gelatin emulsions; these can be relieved before the plates are used photographically by soaking them in water and dehydrating in alcohol. This process of normalising gives increased trustworthiness for recording distances. N. M. BLIGH.

**Laboratory shaking machines.** E. BERL and A. SCHMIDT (Chem. Fabr., 1930, 302—304).—One type described depends on a wheel weighted on one side and driven by a motor the speed of which is so regulated that the oscillations produced by the weight are in resonance with a spring. Several variations in construction are given, and the wheel and drive may

be either vertical or horizontal with corresponding alteration in the position of the shaking bottle.

C. IRWIN.

**Shaking table.** F. KÖNIG (Chem. Fabr., 1930, 311).—A table is supported on six spiral springs and oscillated by the rotation of a brass disc carrying six projecting teeth which make and break a circuit from the lighting supply operating through a condenser and solenoid.

C. IRWIN.

**Viscosimeter.** A. KÄMPF; O. SCHRENK.—See B., 1930, 844.

**Correction in viscosimetry when using capillary tubes which have trumpet-shaped openings.** E. C. BINGHAM and R. R. THOMPSON (J. Rheology, 1930, 1, 418—423).—New evidence has been obtained for the validity of the customary value of  $m$  for capillaries which are squarely cut off at the ends. Capillary viscosimeters having trumpet-shaped openings must not be treated as if the ends of the capillary were square, for the kinetic energy correction may be greatly different. When the ends of the capillary are trumpet-shaped the kinetic energy correction cannot be neglected, but it is easy to determine what is the appropriate value of  $m$  for the given capillary.

E. S. HEDGES.

**Ultrafilters.** S. R. ZINZADZE.—See B., 1930, 844.

**Cryostat for moderately low temperatures.** J. BARBAUDY and A. LALANDE (Rec. trav. chim., 1930, 49, 850—856).—A cryostat for temperatures between 10° and —25° is described. The refrigerating agent is ethyl chloride. Constancy to 0.1° is attained.

J. A. V. BUTLER.

**Cryostat for use at temperatures from 0° to —160°.** W. E. MACGILLIVRAY and J. C. SWALLOW (J. Sci. Instr., 1930, 7, 257—260).—Pentane contained in a large silvered Dewar vessel is cooled by a continuous stream of liquid air flowing through a submerged coil at a rate sufficient to keep the temperature slightly lower than is required. Heat is supplied by a heating coil controlled by a hydrogen regulator, and the temperature may be kept constant to 0.01° down to —100° and to 0.02° down to —160°. The consumption of liquid air is comparatively low.

C. W. GIBBY.

**Tables for volumetric analysis.** J. LUKÁCS (Biochem. Z., 1930, 224, 151—156).—Two tables are given which serve for reading the factor of a solution from its titration value and the corrected titration value on applying a factor. P. W. CLUTTERBUCK.

**Lecture demonstration of spectrograms.** G. LASÈGUE and (Mlle.) T. COLLIN (Bull. Soc. chim., 1930, [iv], 47, 910—912).—The apparatus enables an enlarged image of the spectrum to be projected on to a screen simultaneously with a reference spectrum which shows the position of the principal lines of several elements.

E. S. HEDGES.

**Dschâbir [Geber].** E. O. VON LIPP MANN (Chem.-Ztg., 1930, 54, 677—678).

**Theodore William Richards Memorial Lecture.** —(Sir) H. HARTLEY (J.C.S., 1930, 1937—1969).



## Geochemistry.

**Annual variation of upper atmospheric ozone.** S. CHAPMAN (Phil. Mag., 1930, [vii], 10, 345—352).—The hypothesis that the temperature,  $T$ , of the upper atmosphere may be high enough to produce thermal decomposition of the ozone and so generally account for the annual fluctuations of ozone content of the atmosphere is examined. If it were certain that the annual variation of temperature is symmetrical about the solstices, then this hypothesis together with the observed annual ozone variation lead to the conclusion that the rate of production of ozone in the spring is nearly three times that in the autumn. This is considered unlikely. Agreement with observed data is, however, arrived at by assuming that the maximum of  $T$  occurs about 1 month after the summer solstice. The probability of this mode of variation of  $T$  is discussed as well as existing estimates of  $T$  between 30 and 40 kilometres.

W. GOOD.

**Radium content of petroliferous waters of Baku and of Daghestan.** B. NIKITIN and L. KOM LEV (Compt. rend., 1930, 191, 325—326; cf. Vernadsky, this vol., 886).—The richest group of the 72 samples of Baku well-water examined (by the emanation method) contained  $3 \times 10^{-10}\%$  of radium by weight ( $1.6 \times 10^{-10}$  in one case). Waters of similar chemical compositions from neighbouring wells of the same depth had varying radium contents, although waters from layers 600 m. deep were usually the richest. The 22 waters from Daghestan contained as a rule  $1.2 \times 10^{-10}\%$  of radium (decreasing with time) and 0.03% of barium, but no proportionality between these quantities was traceable. It is calculated that in some cases 0.2 g. of dissolved radium is delivered per annum.

J. GRANT.

**Clay minerals.** E. T. WHERRY, C. S. ROSS, and P. F. KERR (Coll. Symp. Ann., 1929, 7, 191—193).—The main types of clay minerals (kaolins, montmorillonites, and potash-bearing clays) indicated by X-ray examination are discussed.

CHEMICAL ABSTRACTS.

**Properties of chabazite.** Y. TANAKA and M. NAKAMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 274—275B).—The loss of weight on ignition proceeds continuously with rise of temperature up to about  $1000^\circ$ , when it amounts to 22%. Chabazite has no adsorptive power even if dehydrated. Although slightly alkaline to litmus, it does not interact with neutral salts and gives no colour reaction with vitamin-A. The silica gel obtained from chabazite by treating with 5N- or 10N-hydrochloric acid at  $50^\circ$  showed the best adsorptive power. C. IRWIN.

**Mariupolite and its related rocks.** J. MOROZEWICZ (Prace Polsk. Inst. Geol., 1929, 2, 217—350; Tsch. Min. Petr. Mitt., 1930, 40, 335—436).—Mariupolite (Morozewicz, 1902) from Mariupol, Ukraine, is an extreme member of the nepheline-syenite series. It consists of albite, nepheline, and aegirine, with sometimes lepidomelane, sodalite, or cancrinite, and

accessory magnetite, beckelite, and pyrochlore. The order of intrusion of this and the associated rocks was that of increasing basicity:

	Mean $d$ .	Mean SiO <sub>2</sub> (mol.-%).
1. Upper biotite-granite .....	2.632	80.0
2. Diabase- and amphibole-granite .....	2.678	74.4
3. Alkali-syenites .....	2.699	70.5
4. Mariupolites .....	2.712	63.9
5. Foyaites .....	2.718	60.6
6. Wehrlite .....	3.359	46.2

Many chemical analyses (some of them previously published; A., 1902, ii, 668; 1905, ii, 177; 1908, ii, 201; 1909, ii, 404; 1929, 45) are given of these rocks and their constituent minerals, and the relations are discussed in detail.

L. J. SPENCER.

**Sands of the Lower Austrian Marchfeld.** H. WIESENEDER (Tsch. Min. Petr. Mitt., 1930, 40, 303—324).—The alluvial plain east of Vienna and north of the Danube consists of gravel with beds of sand. These sands and the Danube sands and those of the dunes are compared. Determinations have been made of the grain size, specific gravity fractions, and chemical composition. The sands consist mainly of quartz grains with some muscovite, calcite, etc., and 1% of heavy minerals (iron ores, zircon, tourmaline, etc.).

L. J. SPENCER.

**Absorption and refraction of red, blue, and violet spinels of Ceylon.** K. SCHLOSSMACHER (Z. Krist., 1930, 72, 447—475; Chem. Zentr., 1930, i, 1900).—The degree of dispersion, as well as the concentration, of the colouring matter affects the absorption; with violet spinels the effects of the chromic and ferrous oxides were only approximately additive. The blue spinels have a somewhat higher refractivity than red, greater density of colour affording higher values. The violet spinels give intermediate values.

A. A. ELDRIDGE.

**Colloidal nature of some finely-divided natural phosphates.** K. D. JACOB, W. L. HILL, and R. S. HOLMES (Coll. Symp. Ann., 1929, 7, 195—204).—Chemical and mechanical analyses of Florida and Tennessee phosphate are recorded; the colloidal fractions (11.5—63.0%) resemble soil colloids in physical properties.

CHEMICAL ABSTRACTS.

**Chigrovskoye phosphorite deposit.** E. B. ORLOVA (Min. Suiv. Tzvet. Met., 1929, 4, 437—445).—The average phosphoric anhydride content is 16.38% and the insoluble residue 43.64%.

CHEMICAL ABSTRACTS.

**Popinskoye phosphorite deposit.** M. P. FIBEG and L. A. RUSINOV (Min. Suiv. Tzvet. Met., 1929, 4, 446—452).—Concentration by selective disintegration gives a product containing 17—19% P<sub>2</sub>O<sub>5</sub>.

CHEMICAL ABSTRACTS.

**New ideas of the genesis of petroleum.** F. FISCHER (Brennstoff-Chem., 1930, 11, 354—358).—A lecture.

H. BURTON.

## Organic Chemistry.

Theory of the meso-structure of organic compounds. III. Structural causes of optical activity. IV. Influence of ring formation on the molecular rotation. I. I. KOTYUKOV. V. Combined influence of radicals on optical activity. I. I. KOTYUKOV and M. N. YAKIMOV (Bull. Siberian Inst. Tech., 1928, 49, No. 4, 4 pp.; 1929, 50, No. 2, 37 pp., and 25 pp.).—If meso-linkings be assumed to exist in a number of substances new asymmetric atoms, not indicated by the classical formulæ, arise and can exhibit optical activity. All cases of optically active substances except complex inorganic compounds, the inositols, and certain diphenyl derivatives, are explainable by means of the meso-theory. Disregarding isolated exceptions, and taking into account the fact that according to the meso-formulation camphoric acid is tricyclic whilst the anhydride is dicyclic, it appears that ring formation is always associated with an increase in rotation. In 30 of 43 cases replacement of a hydroxyl by an amido-group decreased the rotation. In experiment on tartaric, malic, and lactic acids, and their R, R', and RR' derivatives, in only 13 of 48 cases could the rotations be predicted by means of an additivity formula  $M_{RR'} = M + (M_{R'} - M) + (M_R - M)$ .

## CHEMICAL ABSTRACTS.

Decomposition of hydrocarbons in the electrodeless discharge. J. B. AUSTIN (J. Amer. Chem. Soc., 1930, 52, 3026—3027; cf. Harkins and Gans, this vol., 1171).—The spectrum of the decomposition products obtained from chlorobenzene, pentane,  $\beta\gamma$ -trimethylpentane, acetylene, benzene, and cyclohexane in the electrodeless discharge has been examined. In all cases, except with cyclohexane, relatively large amounts of a reddish-brown solid were obtained.

J. G. A. GRIFFITHS.

Decomposition of the paraffin hydrocarbons. G. EGLOFF, R. E. SCHAAD, and C. D. LOWRY, jun. (J. Physical Chem., 1930, 34, 1617—1740).—The literature of the decomposition of the paraffin hydrocarbons by thermal means, with and without catalysts, by electrical means, by photosensitisation, and by  $\alpha$ -particles is extensively reviewed.

L. S. THEOBALD.

Production of hydrogen and gaseous, saturated hydrocarbons by the action of oxygen on saturated cyclic hydrocarbons containing side-chains at temperatures about 100°. G. CHAVANNE and O. MILLER (Bull. Soc. chim. Belg., 1930, 39, 287—297; cf. A., 1927, 452; this vol., 768).—Varying amounts of carbon monoxide and dioxide, hydrogen, methane, and (in some cases) homologues of methane are produced when 1:2-, 1:3-, and 1:4-dimethylcyclohexanes, 1:2- and 1:3-dimethylcyclopentanes, 1-methyl-3-*n*-butylcyclopentane, and 1:3-dimethylcyclopentanol are oxidised at 85—100° under the conditions previously described (*loc. cit.*). 1:3-Dimethylcyclopentane undergoes oxidation even at the ordinary temperature; hydrogen is produced.

H. BURTON.

Dissociation of methane at high temperatures and various pressures. F. DE RUDDER and H.

BIEDERMANN (Bull. Soc. chim., 1930, [iv], 47, 704—730).—Below 1000° the thermal decomposition of methane gives only minute quantities of ethylene and no acetylene. At 1000°/atmospheric pressure 2% of ethylene and 0.5% of acetylene can be obtained at suitable rates of flow. At higher temperatures and atmospheric pressure decomposition into carbon and hydrogen is practically complete; lower pressures are essential if any ethylene and acetylene are to be obtained. The maximum quantity of ethylene (4%) is produced at 1200°/100 mm., accompanied by 2.5% of acetylene. At 1300°/about 100 mm. 6.62% of acetylene and no ethylene are produced. At 1400° and 1500°/50 mm. no ethylene and 10.5% and 14.5%, respectively, of acetylene are produced. Quartz, Marquardt porcelain, and nickel exhibited no specific effects. Hydrogen chloride had no catalytic effect, and finely divided metallic thorium only a very slight one.

C. W. GIBBY.

Formation of ethane in the catalytic decomposition of ethyl alcohol. E. H. BOOMER and H. E. MORRIS (Canad. J. Res., 1930, 2, 384—387).—In the catalytic decomposition of alcohol by means of silica gel at 350—500°, the catalyst changes with rise of temperature from a dehydration catalyst to one possessing dehydrogenating powers, and the formation of ethane is explained as being due to the production of acetaldehyde and hydrogen by dehydrogenation, the hydrogen reacting with ethylene to form ethane.

T. T. PETTS.

Bromination of hexane. F. M. PARKER (J. Amer. Chem. Soc., 1930, 52, 3465—3466).—When hexane vapour diluted with nitrogen is passed into a mixture of bromine and water, no brominated benzene compound is produced. The reported formation of such derivatives (Blair, Ledbury, and Wheeler, A., 1924, i, 1277) is due to the presence of benzene in the hexane used.

H. BURTON.

Synthesis of higher isoparaffins. S. LANDA and R. RIEDL (Coll. Czech. Chem. Comm., 1930, 2, 520—530).—Ethyl palmitate, b. p. 185—187°/10 mm., and magnesium methyl bromide give dimethylpentadecylcarbinol, converted on distillation into  $\beta$ -methyl- $\Delta^3$ -heptadecene (I), b. p. 277°/100 mm.,  $d^{20}_4$  0.7953 (dibromide, b. p. 267—268°/28 mm.), which on oxidation with chromic acid in acetic acid yielded acetone and pentadecic acid, m. p. 51°. It is reduced by hydrogen and nickel at the ordinary pressure at 220—240° to  $\beta$ -methylheptadecane (II), b. p. 178.5°/15 mm.,  $d^{20}_4$  0.7838,  $n^{20}_D$  1.43942.

Ethyl behenate, m. p. 48.5°, is readily prepared in good yield by hydrogenation under pressure of colza oil in presence of nickel, followed by hydrolysis of the solid product with alcoholic potassium hydroxide, conversion of the resultant acid mixture into the esters, and separation of the fraction, b. p. 255°/15 mm. With magnesium methyl bromide it yields  $\beta$ -methyl- $\Delta^8$ -tricosene (III), b. p. 234—237°/10 mm., m. p. 41.5°,  $d^{20}_4$  0.8047, oxidised by chromic acid in acetic acid to acetone and an acid,  $C_{21}H_{42}O_2$ , m. p. 73.8°, which yielded heneicosane, m. p. 40.4°, when heated with hydriodic acid at 273—277°. The substance III

is only partly hydrogenated in the presence of nickel at 180° under pressure, and the  $\beta$ -methyltricosane (IV), m. p. 42°,  $d_{40}^{20}$  0.7882, is separated by dissolution of the hydrogenation product in ether and precipitation with cold alcohol.

The viscosities of I at 0—100°, of II at 10—100°, and of III and IV at 50—100°, have been determined.

A. I. VOGEL.

**Nuclear synthesis of unsaturated hydrocarbons. I.  $\Delta^{\alpha}$ -Olefines.** H. B. DYKSTRA, J. F. LEWIS, and C. E. BOORD (J. Amer. Chem. Soc., 1930, 52, 3396—3404).—*n*-Propyl  $\alpha\beta$ -dibromoethyl, b. p. 97°/27 mm.,  $d_{20}^{20}$  1.6554, and *n*-butyl  $\alpha\beta$ -dibromoethyl ethers, b. p. 115°/36 mm.,  $d_{20}^{20}$  1.5647, are obtained by the method previously described (this vol., 450). Treatment of ethyl  $\alpha\beta$ -dibromoethyl and the above ethers with magnesium alkyl (R) bromides affords  $\beta$ -alkoxyalkyl bromides, OAlk·CHR·CH<sub>2</sub>Br, in 34—81% yield. The following are described:  $\beta$ -ethoxy-*n*-butyl, b. p. 67°/34 mm.,  $d_{20}^{20}$  1.2312;  $\beta$ -ethoxy-*n*-amyl, b. p. 82°/34 mm.,  $d_{20}^{20}$  1.1812;  $\beta$ -ethoxy-*n*-hexyl, b. p. 98—99°/33 mm.,  $d_{20}^{20}$  1.1548;  $\beta$ -ethoxyisohexyl, b. p. 89—92°/38 mm.,  $d_{20}^{20}$  1.1578;  $\beta$ -ethoxyisohexyl, b. p. 106—109°/33 mm.,  $d_{20}^{20}$  1.1209;  $\beta$ -propoxy-*n*-propyl, b. p. 65°/32 mm.,  $d_{20}^{20}$  1.2205;  $\beta$ -propoxy-*n*-butyl, b. p. 66°/15 mm.,  $d_{20}^{20}$  1.1803;  $\beta$ -propoxy-*n*-amyl, b. p. 81—82°/13 mm.,  $d_{20}^{20}$  1.1439;  $\beta$ -propoxyisohexyl, b. p. 77—78°/14 mm.,  $d_{20}^{20}$  1.1349;  $\beta$ -propoxy-*n*-hexyl, b. p. 92—93°/14 mm.,  $d_{20}^{20}$  1.1226;  $\beta$ -propoxyisohexyl, b. p. 112—114°/28 mm.,  $d_{20}^{20}$  1.0872;  $\beta$ -propoxy-*n*-phenylethyl, b. p. 123°/12 mm.,  $d_{20}^{20}$  1.2518, and  $\beta$ -butoxyisohexyl bromides, b. p. 127—128°/27 mm.,  $d_{20}^{20}$  1.0686. Treatment of these bromides with zinc dust in 90% alcohol affords  $\Delta^{\alpha}$ -olefines,

OAlk·CHR·CH<sub>2</sub>Br  $\xrightarrow{\text{Zn}}$  CHR·CH<sub>2</sub> + OAlk·ZnBr. The following are prepared from the  $\beta$ -ethoxy-derivative in 65—90% yield:  $\Delta^{\alpha}$ -pentene, b. p. 29.5—31°,  $d_{20}^{20}$  0.6465 (dibromide, b. p. 84—85°/32 mm.,  $d_{20}^{20}$  1.6525);  $\Delta^{\alpha}$ -hexene, b. p. 61—64°,  $d_{20}^{20}$  0.6784 (dibromide, b. p. 103—105°/36 mm.,  $d_{20}^{20}$  1.5632);  $\Delta^{\alpha}$ -isohexene, b. p. 52.5—54.5°,  $d_{20}^{20}$  0.6718 (dibromide, b. p. 96—99°/38 mm.,  $d_{20}^{20}$  1.5507), and  $\Delta^{\alpha}$ -isohexptene, b. p. 84—86°,  $d_{20}^{20}$  0.6956 (dibromide, b. p. 110—113°/34 mm.,  $d_{20}^{20}$  1.4913). The preparation of  $\Delta^{\alpha}$ -pentene from magnesium ethyl bromide and allyl bromide, and its purification through the dibromide, are described.

When a mixture of allyl bromide and ethyl  $\alpha\beta$ -dibromoethyl ether is added gradually to magnesium in ether and the resulting product treated with bromine,  $\Delta^{\alpha}$ -pentadiene tetrabromide, m. p. 84—87°, is obtained. Treatment of this with zinc dust and alcohol gives  $\Delta^{\alpha}$ -pentadiene, b. p. 29—30° (corr.),  $d_{20}^{20}$  0.774.

H. BURTON.

**s-Dialkyltetra-tert.-butylethynylethanes.** H. B. GILLESPIE and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 3368—3376).—Magnesium tert.-butylethynyl bromide and ethyl trimethylacetate yield tert.-butyldi-tert.-butylethynylcarbinol, b. p. 103—107°/7 mm., m. p. 46—47°, converted by phosphorus tribromide in light petroleum into tert.-butyldi-tert.-butylethynyl-methyl bromide, b. p. 68—71°/13 mm. Treatment of this with "molecular silver" in ether affords s-di-tert.-butylethynylethane, m. p. 120—120.5°, which does not absorb oxygen when heated at 140° in *p*-dibromobenzene solution. The ethane linking is

broken only by sodium-potassium alloy (cf. A., 1929, 688) in ether; the resulting sodio-derivative gives with carbon dioxide tert.-butyldi-tert.-butylethynyl-acetic acid, m. p. 151.5—152.5°, also formed from the above bromide, sodium-potassium alloy, and carbon dioxide in ether.

Magnesium tert.-butylethynyl bromide and ethyl hexahydrobenzoate afford cyclohexyldi-tert.-butylethynylcarbinol, b. p. 123—128°/3 mm.,  $d_{20}^{20}$  0.8991,  $n_D^{20}$  1.4729 (acetate, m. p. 95—96°; methyl ether, b. p. 116—121°/3.5 mm.,  $d_{20}^{20}$  0.8680,  $n_D^{20}$  1.4640). Treatment of the crude bromide from this with "molecular silver," sodium-potassium alloy, or 40% sodium amalgam, the corresponding chloride with 40% sodium amalgam, or the above methyl ether with sodium-potassium alloy, gives varying amounts of s-dicyclohexyldi-tert.-butylethynylethane, m. p. 149—150°, which does not undergo fission even with sodium-potassium alloy. cyclohexyldi-tert.-butylethynylacetic acid has m. p. 125—126°.

Dehydration of cyclohexyldi-tert.-butylethynylcarbinol with potassium hydrogen sulphate at 125—130° yields cyclohexyldi-tert.-butylmethane, b. p. 105—110°/3 mm.,  $d_{20}^{20}$  0.8578,  $n_D^{20}$  1.4838, which with hydrogen chloride in alcohol gives an impure chloro-compound. Treatment of this with 40% sodium amalgam in ether regenerates the original hydrocarbon.

H. BURTON.

**Ethylene chlorohydrin. I.** G. BOZZA and L. MAMOLI (Giorn. Chim. Ind. Appl., 1930, 12, 283—292).—During the synthesis of ethylene chlorohydrin from ethylene and hypochlorous acid, direct attack of the ethylene by chlorine, and also action of the chlorine on the ready-formed chlorohydrin, become appreciable only with concentrations of chlorohydrin approaching normality. For lower concentrations, the yield of chlorohydrin remains about unity, but as the concentration is increased further the yield gradually diminishes. The velocity of the principal reaction, studied in solutions of pure hypochlorous acid, is independent of the concentration of this acid within wide limits, but is closely dependent on the surface area of the ethylene bubbles. The velocity coefficient, expressed in c.c. of ethylene absorbed per second by a surface of contact of area 1 sq. cm., with normal gas pressure is about 0.00312 under the conditions employed. This velocity is not altered by adding benzene or carbon tetrachloride or by starting with solutions already acid, but is progressively diminished by increasing proportions of sodium chloride, so that neutralisation of the acid with alkali is disadvantageous. Neutralisation with lead oxide is valueless, and if copper salts are present considerable formation of secondary products occurs. The action of chlorine on chlorohydrin solutions of medium concentration gives highly-chlorinated products very difficult to separate by distillation. To avoid marked losses owing to secondary reactions, the practical attainable limit of chlorohydrin concentration is 8—10%.

T. H. PORE.

**Optically active salts of  $\beta$ -nitro-octane.** R. L. SHRINER and J. H. YOUNG (J. Amer. Chem. Soc., 1930, 52, 3332—3340).—*d*- $\beta$ -Octanol is converted by phosphorus tribromide into *l*- $\beta$ -bromo-octane, b. p.

83—84°/18 mm.,  $n_D^{20}$  1.4500,  $\alpha_D^{25}$  -33.1°, and thence by treatment with silver nitrite in benzene into *d*- $\beta$ -nitro-octane, b. p. 102—105°/23 mm.,  $d_4^{20}$  0.9224,  $n_D^{20}$  1.4324,  $\alpha_D^{25}$  +15.84° in alcohol. 1- $\beta$ -Nitro-octane, b. p. 100—103°/18 mm.,  $d_4^{20}$  0.9165,  $n_D^{20}$  1.4292,  $\alpha_D^{25}$  -10.8° in alcohol, is prepared similarly from *d*- $\beta$ -bromo-octane, b. p. 83—84°/18 mm.,  $n_D^{20}$  1.4501,  $\alpha_D^{25}$  +29.8°. *d*- $\beta$ -Nitro-octane furnishes an optically active sodium salt when treated with 1 or 2 equivalents of sodium ethoxide; regeneration of the nitro-compounds at -10° affords a product retaining about 24% of its original activity. The product regenerated from the sodium salt of *l*- $\beta$ -nitro-octane at -70° retains 71% of its original activity. Treatment of this sodium salt with bromine furnishes 1- $\beta$ -bromo- $\beta$ -nitro-octane,  $d_4^{20}$  1.113,  $n_D^{20}$  1.4499,  $\alpha_D^{25}$  -2.22°. The sodium salts are considered to be mixtures of optically active and inactive forms (cf. Kuhn and Albrecht, A., 1927, 749; Branch and Deelman, *ibid.*, 852).

When *d*- $\beta$ -octyl nitrite, b. p. 86—90°/18 mm.,  $d_4^{20}$  0.852,  $n_D^{20}$  1.4279,  $\alpha_D^{25}$  +8.17° in alcohol, obtained as a by-product in the preparation of the nitro-octane, is dissolved in sodium ethoxide solution, the initial rotation is  $\alpha_D^{25}$  +3.46°. This gradually rises to  $\alpha_D^{25}$  +6.0° owing to hydrolysis. 1- $\beta$ -Octyl nitrite has b. p. 85—90°/18 mm.,  $d_4^{20}$  0.857,  $n_D^{20}$  1.4218,  $\alpha_D^{25}$  -10.8° in alcohol.

H. BURTON.

**Ferric ethoxide.** P. A. THIESSEN and O. KOERNER (Z. anorg. Chem., 1930, 191, 74—78).—A reply to Sutra (this vol., 318).

R. CUTHILL.

**Addition of halogens to allyl alcohol.** E. V. ZAPPI (Anal. Asoc. Quim. Argentina, 1930, 18, 43—46).—In the cold and in the dark solutions of allyl alcohol in carbon tetrachloride (0.1—1*N*) react quantitatively with solutions of chlorine in carbon tetrachloride (0.1—0.25*N*) or of bromine in carbon tetrachloride or absolute alcohol (2.5*N*), simple addition taking place.

R. K. CALLOW.

**Hydroxylation of double linkings.** S. SWANN, jun. (Univ. Ill. Eng. Exp. Sta. Bull., 1930, No. 204, 14 pp.).—Persulphuric acid may be used in dilute aqueous solution as a hydroxylating agent in the preparation of glycerol and *trans*-cyclohexane-1:2-diol.

CHEMICAL ABSTRACTS.

**Ether and ester. II. Formation of ether from alcohol.** J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 754—761).—Varying amounts of ether are formed when alcohol (96% except where stated otherwise) is heated with hydrated ferric chloride, anhydrous ferric sulphate, hydrated chromic chloride, chromic sulphate (60% alcohol), aluminium sulphate, copper sulphate (60% alcohol), copper chloride, or manganous chloride at 155—160°. When either 96% alcohol or an equimolecular mixture of ether and water is heated with ferric sulphate at 155—160°, the same equilibrium mixture is obtained; the value for the equilibrium constant is 6.1—6.2.

Varying amounts of ether are also produced when 96% alcohol is heated with sulphurous, phosphoric, arsenic, dichloroacetic, maleic, picric, or toluene-sulphonic acid at 150—160°. The yield of ether rises with increase in the strength of the acid. Hydrochloric acid is a better catalyst than sulphuric acid

under these conditions, and since ethyl chloride does not react with alcohol under the conditions used, it is unlikely that the chloride is an intermediate. The change  $2\text{EtOH} \rightleftharpoons \text{Et}_2\text{O} + \text{H}_2\text{O}$  is an equilibrium reaction, catalysed in the liquid state by hydrogen (hydrated hydrogen) ions. Salts of trivalent metals are the best catalysts; the sulphate is preferred to the chloride, since, with the latter, ethyl chloride is invariably produced.

H. BURTON.

**Esters of halogenated alcohols. III. Decomposition of trichloromethyl chloroformate with alcohols of different types.** W. NEKRASSOV and N. MELNIKOV (J. pr. Chem., 1930, [ii], 127, 210—218; cf. this vol., 1019).—The initial product from equimolecular quantities of trichloromethyl chloroformate and an alcohol (R-OH) is the alkyl trichloromethyl carbonate ( $\text{OR} \cdot \text{CO}_2\text{CCl}_3$ ). The following are isolated: *n*-propyl, b. p. 93°/12 mm.,  $d_4^{20}$  1.359,  $n_D^{20}$  1.4451; *iso*-butyl, b. p. 103°/14 mm.,  $d_4^{20}$  1.302,  $n_D^{20}$  1.4446;  $\beta$ -chloroethyl, b. p. 110°/12 mm.,  $d_4^{20}$  1.5664,  $n_D^{20}$  1.4748, and allyl, b. p. 89—90°/11 mm.,  $d_4^{20}$  1.4015,  $n_D^{20}$  1.4590 (dibromide, b. p. 163°/11 mm.,  $d_4^{20}$  1.9532,  $n_D^{20}$  1.5321). In some cases the alkyl trichloromethyl carbonate decomposes (partly or completely) into the alkyl chloroformate and carbonyl chloride; the alkyl chloroformate also decomposes into the alkyl chloride and carbon dioxide. Thus, benzyl alcohol gives some benzyl trichloromethyl carbonate which when distilled under ordinary pressure affords benzyl chloride. *iso*Propyl alcohol furnishes a mixture of *isopropyl* chloroformate and *isopropyl trichloromethyl carbonate*, b. p. 96°/23 mm., m. p. 29°,  $d_4^{20}$  1.3318,  $n_D^{20}$  1.4340, whilst *tert*-butyl alcohol, methyl-diethylcarbinol, and dimethylethylcarbinol all afford the corresponding carbonyl chloride.

H. BURTON.

**Chloromethionic [chloromethanedisulphonic] acid.** H. J. BACKER (Rec. trav. chim., 1930, 49, 729—734).—Decomposition of barium chloromethanedisulphonate (A., 1925, i, 359) with sulphuric acid gives *chloromethanedisulphonic acid* (+2H<sub>2</sub>O), m. p. 96—97°. Solubility and crystallographic data are given for most of the following salts: sodium (+H<sub>2</sub>O); potassium, anhydrous and +2H<sub>2</sub>O; rubidium; caesium; thallium; calcium (+H<sub>2</sub>O), and barium (+4.5H<sub>2</sub>O).

H. BURTON.

**Determination of the purity of acetic anhydride.** C. K. ROSENBAUM and J. H. WALTON (J. Amer. Chem. Soc., 1930, 52, 3366—3368; cf. Whitford, A., 1926, 189).—Acetic anhydride (1 g.) and anhydrous oxalic acid (1 g.) are treated with pyridine (2 c.c.), the mixture is cooled for 5 min., warmed at 50° for 10 min., and the excess of oxalic acid determined by titration with 0.1*N*-potassium permanganate. The results are calculated from the equation  $\text{Ac}_2\text{O} + (\text{CO}_2\text{H})_2 = 2\text{AcOH} + \text{CO}_2 + \text{CO}$ ; the method is accurate to 0.1%.

H. BURTON.

**Anaerobic oxidation of fatty acids.** S. L. NEAVE [with A. M. BUSWELL] (J. Amer. Chem. Soc., 1930, 52, 3308—3314).—The anaerobic oxidation of calcium acetate and sodium propionate by Söhngen cultures (A., 1910, ii, 798) gives methane, carbon dioxide, and a small amount of hydrogen; olefines, carbon monoxide, or homologues of methane are not produced in determinable amounts. The yield of carbon dioxide

from the propionate is higher than that required by simple decarboxylation; the additional oxygen is provided by water. The general equation for the change is  $C_nH_{2n}O_2 + (n-2)/2H_2O = (n+2)/4CO_2 + (3n-2)/4CH_4$ . Side reactions of the type  $AcOH + 2H_2O = 2CO_2 + 4H_2$  and  $CH_3R \cdot CO_2H + NH_3 = CHR(NH_2) \cdot CO_2H + H_2$  probably occur. The gas production is temporarily stopped by the addition of glycine.

H. BURTON.

**Oxidation of unsaturated compounds. II. Preparation and configuration of the  $\gamma$ -halogeno-derivatives of crotonic acid. III. Oxidation of  $\gamma$ -chlorocrotonic acid. Synthesis of *dl*-threonic acid. Proof of configuration of the *dl*- $\alpha\beta$ -dihydroxybutyric acids. IV. Oxidation of crotonic acid with hypochlorous and perbenzoic acids. V. Oxidation of conjugated systems. Oxidation of pentenoic and hexenoic acids. G. BRAUN (J. Amer. Chem. Soc., 1930, 52, 3167—3176, 3176—3185, 3185—3188, 3188—3191).—II.  $\gamma$ -Chloro- $\beta$ -hydroxy-*n*-butyronitrile is prepared either by Lespicau's method (A., 1905, i, 406) or, more conveniently, from  $\alpha\gamma$ -dichlorohydrin and aqueous sodium cyanide at 60—100°, and fractionation of the product formed. The nitrile is converted into ethyl  $\gamma$ -chloro- $\beta$ -hydroxy-*n*-butyrate by saturating an ethereal-alcoholic solution with hydrogen chloride at -15°, and the crude ester dehydrated with phosphoric oxide whereby a mixture of unsaturated chloro-esters is produced. Hydrolysis of this with barium hydroxide in 25% alcohol below 0° gives a mixture of  $\gamma$ -chlorocrotonic, m. p. 83°, and probably  $\gamma$ -chloro- $\Delta^8$ -butenoic acid, m. p. 10°.  $\gamma$ -Bromocrotonic acid, m. p. 74° (ethyl ester, b. p. 80—82°/2 mm.), is prepared similarly by way of  $\alpha\gamma$ -dibromohydrin (improved method of preparation given),  $\gamma$ -bromo- $\beta$ -hydroxy-*n*-butyronitrile, b. p. 154°/14 mm., and impure ethyl  $\gamma$ -bromo- $\beta$ -hydroxy-*n*-butyrate, b. p. 94—96° (slight decomp.)/2 mm.  $\gamma$ -Iodocrotonic acid, m. p. 108°, is obtained either from the chloro- or bromo-acid and sodium iodide in acetone, or by hydrolysis of ethyl  $\gamma$ -iodocrotonate, b. p. 90—92° (slight decomp.)/2 mm. Reduction of  $\gamma\gamma$ -dichlorocrotonic acid (improved method of preparation given) with hydrogen in presence of sodium hydroxide solution and palladised charcoal gives a mixture of products containing some  $\gamma$ -chlorocrotonic acid. Similar reduction of  $\gamma$ -chlorocrotonic acid affords *trans*-crotonic acid. Since the iodo-acid is obtained from both the chloro- and bromo-acids, it follows that all three compounds have the *trans*-configuration.**

III. Oxidation of  $\gamma$ -chlorocrotonic acid with barium chlorate in presence of a small amount of osmic acid below 30° gives 75—78% of *dl*-threo- $\gamma$ -chloro- $\alpha\beta$ -dihydroxybutyric acid, m. p. 100°. Treatment of this with silver acetate and oxidation of the product formed with nitric acid (*d* 1.21) at 55° afford *dl*-tartaric acid. The chloro-acid is converted by moist silver oxide into *dl*-threonic [ $\alpha\beta\gamma$ -trihydroxybutyric] acid (46% yield), m. p. 98°, also oxidised to *dl*-tartaric acid. Reduction of the chloro-acid with hydrogen in presence of sodium hydroxide solution and palladised charcoal furnishes 70% of *dl*-threo- $\alpha\beta$ -dihydroxybutyric acid, m. p. 74—75°. The configurations previously assigned (A., 1929, 293) to *dl*-

*threo*- and *dl*-erythro- $\alpha\beta$ -dihydroxybutyric acids (racemic and meso, respectively) are thus confirmed.

IV. Treatment of an aqueous solution of crotonic acid with chlorine at 0°, neutralisation with potassium hydrogen carbonate at 0°, and evaporation in a vacuum gives an 80% yield of potassium  $\alpha$ -chloro- $\beta$ -hydroxybutyrate; the free acid is obtained from the reaction mixture only in 30% yield. When the original reaction mixture is treated with an excess of potassium hydroxide solution at 0°, potassium  $\beta$ -methylglycidate (86% yield) is produced; the free acid, m. p. 88.5°, is isolated in 64% yield. Acidification of the alkaline solution with 10% hydrochloric acid and heating the mixture at 98° gives *dl*-erythro- $\alpha\beta$ -dihydroxybutyric acid, also obtained in 97% yield by hydrolysis of the glycidic acid with water at the ordinary temperature. Crotonic acid is oxidised by perbenzoic acid in chloroform to  $\beta$ -methylglycidic acid (20% yield).

V. Oxidation of  $\Delta^8$ -pentenoic acid with silver chlorate in presence of a small amount of osmic acid gives a *dl*- $\alpha\beta$ -dihydroxyvaleric acid (80% yield), m. p. 75° (phenylhydrazide +  $H_2O$ , m. p. 140.5°), whilst with perbenzoic acid in chloroform in presence of water, 75% of a *dl*- $\alpha\beta$ -dihydroxyvaleric acid, m. p. 106° (phenylhydrazide, m. p. 119—119.5°), results. Similar oxidations of  $\Delta^8$ -hexenoic acid furnish 86 and 46%, respectively, of *dl*- $\alpha\beta$ -dihydroxy-*n*-hexoic acids, m. p. 108.5° (phenylhydrazide +  $H_2O$ , m. p. 141.5—142°) and 99.5° (phenylhydrazide, m. p. 120—121°), respectively.

H. BURTON.

**Partial hydrogenation of linolenic acid. K. H. BAUER and F. ERMANN (Chem. Umschau, 1930, 37, 241—249; cf. Bauer and Mitsotakis, A., 1928, 1115).—**Examination of the "solid" acids obtained by the partial hydrogenation of linolenic acid (prepared from the solid hexabromide) showed that rise of temperature and speed of hydrogenation favoured the formation of solid unsaturated acids of the mono- and di-ethylenic series, whilst a low reaction temperature and slow hydrogenation increased the yield of stearic acid. The amount of diethylenic acids in the "liquid" acids was greater, and the amount of mono-ethylenic acids less, as the temperature and speed of hydrogenation were increased. The "liquid" acids were identified by ozonolysis as linolenic acid,  $\Delta^8$ -linoleic and  $\Delta^6$ -oleic acids. Ozonolysis of the "solid" acids of hydrogenation revealed the occurrence of stearic acid,  $\Delta^8$ - and  $\Delta^6$ -isooleic acids, and  $\Delta^8$ -octadecadienoic acid. These results indicate that linolenic acid is hydrogenated in stages, the  $\Delta^6$ - and  $\Delta^8$ -linkings being hydrogenated more readily than the  $\Delta^5$ -linkings; the latter appear to be capable of hydrogenation only after one of the others has been saturated, as no trace of adipic acid could be found among the oxidation products. No evidence was obtained of migration of the double linkings during hydrogenation, as postulated by Hilditch and Vidyarthi (A., 1929, 423), and it is suggested that the suberic acid recovered by these workers from the products of permanganate oxidation may have been due to destructive oxidation of the primary fission products.

E. LEWKOWITSCH.

**Polymerisation of methyl esters of highly unsaturated fatty acids.** III. Polymerised product. IV. *cyclo*Butane ester formed by the double linking in a molecule. K. KINO (J. Soc. Chem. Ind. Japan, 1930, 33, 305—310B, 311—312B; cf. this vol. 577, 741).—III. Observations on the polymerisation of methyl esters of the highly unsaturated acids obtained from sardine oil indicates that with those containing 4 or 5 double linkings formation of a *cyclobutane* ester by intramolecular coupling of unsaturated centres occurs independently of temperature, and that dimerisation of the cyclic ester takes place subsequently. In the case of esters of trebly unsaturated acids the formation of *cyclobutane* esters is also suspected. *cyclo*Butane ring formation appears to be more facile for esters with many double linkings.

IV. Portions of the methyl ester fraction, b. p. 207—220°/4 mm., were heated in hydrogen at 285—300° for 1 hr. and 20 min., respectively. The polymerised methyl esters after repeated fractionation furnished two products: (a) (?)  $C_{19}H_{31} \cdot CO_2Me$ , b. p. 190—195°/4 mm., iodine value 158.9, saponification value 177.9, and (b) (?)  $C_{21}H_{33} \cdot CO_2Me$ , b. p. 210—215°/3 mm., iodine value 223.4, saponification value 163. The products (a) and (b) when reduced by palladium-black and hydrogen in glacial acetic acid yielded saturated solid acids (a)  $C_{20}H_{36}O_2$ , m. p. 70—70.5°, and (b)  $C_{22}H_{40}O_2$ , m. p. 78—78.2°, which were isolated by the lead salt-alcohol method. It is not yet certain that these acids are homogeneous.

C. W. SHOPPEE.

**Existence of racemic compounds in solution and the application of circular dichroism to the synthesis of active compounds.** A. COTTON (Trans. Faraday Soc., 1930, 26, 377—383, and Ann. Physique, 1930, [x], 13, 453—470).—A more detailed discussion of work already noted (this vol., 193).

**Tautomeric forms of dimethylpyruvic acid.** C. FROMAGEOT and S. PERRAUD (Biochem. Z., 1930, 223, 213—221).—Dimethylpyruvic acid obtained by distillation is the pure keto-form. When this is dissolved in water an equilibrium between enolic and ketonic forms is obtained, an *M* solution containing 0.47%, a 0.1*M* solution 0.28%, and a 0.01*M* solution only a trace of the enolic form. After addition of a small amount of alkali a third form is detectable spectrographically.

P. W. CLUTTERBUCK.

***n*-Valerolactone.** III. Preparation. H. A. SCHUETTE and R. W. THOMAS (J. Amer. Chem. Soc., 1930, 52, 3010—3012).—Hydrogenation of lævulinic acid in presence of Adams' platinum catalyst at 2.3—3 atm. during 44 hrs. gives yields of valerolactone of 52%, 48%, and 87% in ethyl alcohol, acetic acid, and ethyl ether, respectively. In the last solvent two additions of fresh portions of catalyst during the reduction increase the yield to the theoretical. In ethyl alcohol the acid reacts to some extent with the solvent.

H. E. F. NOTTON.

**Detection of oxalic acid.** F. W. F. ARNAUD and J. W. FLINT (Analyst, 1930, 55, 501).—Oxalic acid dissolves appreciably in ether in the presence of free mineral (hydrochloric) acid but very sparingly in its absence. If 20 c.c. of concentrated hydrochloric acid

are added to 100 c.c. of a 0.1% solution of oxalic acid three extractions with ether will remove about one fifth of the oxalic acid.

D. G. HEWER.

**Polymerisation and ring formation.** V. Glycol esters of oxalic acid. W. H. CAROTHERS, J. A. ARVIN, and G. L. DOROUGH (J. Amer. Chem. Soc., 1930, 52, 3292—3300).—When ethylene glycol is heated with ethyl oxalate at 180—190°, *ethyl β-hydroxyethyl oxalate*, b. p. 108—110°/0.2 mm.,  $d_4^{20}$  1.2241,  $n_D^{20}$  1.4405, and polymeric ethylene oxalate, m. p. 153°, are produced. Distillation of the last-named substance in a vacuum gives monomeric ethylene oxalate, m. p. 143—144° (cf. Bischoff, A., 1907, i, 675), which when kept at the ordinary temperature undergoes polymerisation. The monomeric form is readily hydrolysed by 0.1*N*-alkali, and when heated at 135—140°, affords an acetone-insoluble polymeride, m. p. 172°. Extraction of a partly polymerised ester with warm acetonitrile gives soluble, m. p. 157—159°, and insoluble, m. p. 172°, forms; either of these modifications can arise spontaneously from the other by keeping at the ordinary temperature. The polymeric esters are readily hydrolysed (attempts to prepare sodium salts by the action of cold sodium hydrogen carbonate solution result in the formation of sodium oxalate) and when heated with *m*-bromobenzoic anhydride furnish *ethylene m*-bromobenzoate, m. p. 78—79°.

Propylene glycol and ethyl oxalate afford resinous material, converted by distillation at 5 mm. into monomeric *propylene oxalate*, m. p. 142°. This does not polymerise readily at the ordinary temperature, but at 140—150° it passes into a polymeride, m. p. 176—178°, insoluble in organic solvents. The trimethylene oxalate, m. p. 87—88°, of Tilitscheev (A., 1927, 340) is a linear condensation polymeride (A., 1929, 1165); when heated at 250°/3—4 mm., trimethylene carbonate and stable, dimeric (14-ring) *trimethylene oxalate*, m. p. 186—187° (cf. Tilitscheev, loc. cit.), are produced. *Hexamethylene*, m. p. 66°, and *decamethylene oxalates*, m. p. 79°, are prepared by heating ethylene oxalate with the appropriate glycol, first at atmospheric pressure and then in a high vacuum; they are both linear condensation polymerides.

H. BURTON.

**Association polymerisation and properties of adipic anhydride.** W. H. CAROTHERS (J. Amer. Chem. Soc., 1930, 52, 3470—3471).—Adipic anhydride, as prepared by the usual methods (cf. Farmer and Kracovski, A., 1927, 447), is a polymeride; the m. p. varies considerably with details of preparation. When heated in a vacuum partial depolymerisation occurs, and the resulting monomeric anhydride can be distilled as a colourless liquid, f. p. about 20°, which reverts spontaneously to the polymeric form. The monomeric form and aniline give adipanilic acid as the sole product, whereas the polymeride affords a mixture of adipic acid, adipanilic acid, and adipanilide. The formation of adipanilide proves that the polymeride is linear.

H. BURTON.

**Applicability of the quinhydrone electrode to unsaturated acids.** W. H. HATCHER and M. G. STURROCK (J. Amer. Chem. Soc., 1930, 52, 3233—3235).—The quinhydrone electrode cannot be used with



dihydroxymaleic acid; reduction of the acid to tartaric acid occurs.

H. BURTON.

**Sulphomaleic acid.** H. J. BACKER and J. M. VAN DER ZANDEN (Rec. trav. chim., 1930, 49, 735—744).—Maleic anhydride (1 mol.) and sulphur trioxide (1 mol.) react at about 50°, forming *sulphomaleic acid*, isolated and purified through the *barium* salt (+7H<sub>2</sub>O). The acid is also obtained from maleic or fumaric acid (1 mol.) and sulphur trioxide (3 mols.) (maleic anhydride is formed intermediately in each case) and in small amount from potassium acetylenedicarboxylate and potassium hydrogen sulphite (cf. A., 1928, 809). The free acid (potentiometric titration curve given) decomposes when heated without melting, decolorises permanganate slowly in the cold and rapidly in the hot, is decomposed by hydrochloric acid at 100°, and adds hydrogen sulphite, readily forming disulphosuccinic acid (*loc. cit.*). The following salts are also described: *lead* (+5H<sub>2</sub>O); *potassium dihydrogen* (+H<sub>2</sub>O), and *calcium* (+12H<sub>2</sub>O; loses 9H<sub>2</sub>O only at 200°).

H. BURTON.

**Metallic salts of ketones.** H. H. STRAIN (J. Amer. Chem. Soc., 1930, 52, 3383—3384).—*Sodium* salts of acetone (*calcium* salt), methyl propyl ketone, acetophenone (*calcium* salt), *p*-tolyl methyl ketone, camphor, and fenchone are prepared from the ketones and sodamide in liquid ammonia. Benzophenone affords with sodamide and potassamide the compounds C<sub>13</sub>H<sub>10</sub>O.NaNH<sub>2</sub> and C<sub>13</sub>H<sub>10</sub>O.NK<sub>3</sub>, respectively.

H. BURTON.

**Separate existence and stability of dihydroxyacetone and glyceraldehyde in aqueous solution.** C. NEUBERG and H. COLLATZ (Biochem. Z., 1930, 223, 494—501).—Pure dihydroxyacetone is stable in aqueous solution and does not spontaneously change either into an enolic form or into glyceraldehyde, nor is pure glyceraldehyde in aqueous solution spontaneously converted into dihydroxyacetone. Mixtures of the aqueous solutions of the two substances undergo no change on keeping. No interconversion occurs in aqueous solutions containing both substances. Glyceraldehyde does not spontaneously polymerise in aqueous solution to a hexose. *Dihydroxyacetone-2:4-dinitrophenylhydrazone*, m. p. 163—164° (corr.), *dl-glyceraldehyde-2:4-dinitrophenylhydrazone*, m. p. 167° (corr.), and the corresponding *osazone*, m. p. 265° (decomp.), are described.

W. MCCARTNEY.

**Alcoholysis of  $\alpha\gamma$ -diketones in presence of hydrogen chloride.** H. ADKINS, W. KUTZ, and D. D. COFFMAN (J. Amer. Chem. Soc., 1930, 52, 3212—3221).—The alcoholysis of 13  $\alpha\gamma$ -diketones has been studied in presence of (mainly) alcohol and hydrogen chloride at 60°. The rate is independent of the ratio diketone : alcohol, but it is a function of the amount of hydrogen chloride used. Alcoholysis of diacetylmethane proceeds to approximately the same extent with ethyl or butyl alcohol, but the rate falls appreciably with *isopropyl* or *tert*-butyl alcohol, duo to interaction of these alcohols with the hydrogen chloride. Diacetyl-mono- and -di-alkylmethanes are alcoholysed at a slower rate than diacetylmethane; the rate decreases in the following order: Bu, Pr, Et, Pr<sup>2</sup>, CH<sub>3</sub>Ph, Et<sub>2</sub>, (CH<sub>3</sub>Ph)<sub>2</sub>. Benzoylacetylmethane undergoes alcoholysis more slowly than diacetyl-

methane, whilst dibenzoylmethane is practically unaffected. Substitution of the ethyl, benzyl, and *iso*-propyl groups in benzoylacetylmethane causes a retardation (in the order mentioned) in alcoholysis.  $\alpha$ -Benzoyl- $\alpha$ -acetylisobutane, b. p. 146—149°/10mm., *d*<sub>4</sub><sup>25</sup> 1.043, is prepared from *isopropyl* iodide and sodium-benzoylacetylmethane at 150°.

H. BURTON.

**Structure of carbohydrates and their optical rotatory power.** W. N. HAWORTH (Nature, 1930, 126, 238—239).—Two recent communications of Hudson (this vol., 747) are criticised.

L. S. THEOBALD.

**Structure of chloraloses.**  $\beta$ -Xylochloralose. L. D. GOODHUE, A. WHITE, and R. M. HIXON (J. Amer. Chem. Soc., 1930, 52, 3191—3195).—Xylose and  $\beta$ -xylochloralose (Hanriot, A., 1910, i, 95) are converted by treatment with chloral hydrate and sulphuric acid into a mixture of *dichloralxylose*, m. p. 202°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +25.2° in acetone, and probably an isomeric compound, b. p. 200°/high vac.; the former of these could not be acetylated, indicating the presence of cyclic acetal groupings. Methylation of  $\beta$ -xylochloralose by the method previously described (A., 1929, 429) gives *dimethyl- $\beta$ -xylochloralose*, b. p. 135°/2 mm., m. p. about 53°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -41.08° in chloroform, which could not be methylated further. Reduction of the dimethyl derivative with sodium amalgam and alcohol at 60° affords indefinite products. When  $\beta$ -glucochloralose is boiled with alcoholic potassium hydroxide, a non-reducing compound is produced; this is hydrolysed by dilute acid to dextrose.

$\beta$ -Xylochloralose diacetate, m. p. 142°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -7.61° in chloroform, and  $\beta$ -glucochloralose triacetate, m. p. 108°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +22.72° in chloroform, are prepared by acetylation with acetic anhydride and pyridine.  $\beta$ -Glucochloralose penta-acetate, m. p. 151°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +46.12° in chloroform, is formed by using acetyl and zinc chlorides; fission of the oxide ring is presumed to occur. The  $\beta$ -glucochloralose tetra-acetate of Hanriot (*loc. cit.*) could not be prepared.

**Nomenclature of ring-isomeric forms of glucose as  $\alpha$ - or  $\beta$ -sugars.** K. JOSEPHSON (Svensk Kem. Tidskr., 1930, 42, 12—16).—A reply to Ohle, Euler, and Lichtenstein (this vol., 69) in defence of the author's previous conclusions (A., 1929, 1278). The designation of glucofuranoses with the 1- and 2-hydroxyl groups in the *cis*- and *trans*-positions as  $\alpha$ - and  $\beta$ -compounds, respectively, is analogous to that of the glucopyranoses (cf. Anderson, Charlton, and Haworth, A., 1929, 1044). The use of ring formulæ allows configuration to be shown unambiguously (cf. Drew and Haworth, A., 1926, 1125).

R. K. CALLOW.

**Action of perbenzoic acid on glucal and its derivatives.** C. TANAKA (Bull. Chem. Soc. Japan, 1930, 5, 214—222).—Glucal was rapidly oxidised by perbenzoic acid in chloroform solution to mannose; triacetylglucal under similar conditions required 4 days for complete oxidation and yielded 1-benzoyl-3:4:6-triacetylglucose, m. p. 141—142°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> +18.35° in benzene, further acetylation or benzoylation, respectively, of which produced 1-benzoyl-2:3:4:6-tetra-acetylglucose, m. p. 145—146°, [ $\alpha$ ]<sub>D</sub><sup>25</sup> -26.43° in chloroform, or 1:2-dibenzoyl-3:4:6-triacetyl-

glucose, m. p. 149°,  $[\alpha]_D^{20}$   $-15.7^\circ$  in chloroform (also formed by direct benzylation of triacetylglucose).

The filtrate from the slow oxidation on dilution with water gave some 1-deoxy-3:4:6-triacetylglucose, m. p. 122°,  $[\alpha]_D^{20}$   $+8.7^\circ$  in chloroform, accompanied by an isomeride, m. p. 168°, of 1-benzoyl-3:4:6-triacetylglucose. A cold chloroform solution of perbenzoic acid had practically no action on diacetyl- $\psi$ -glucal.

R. J. W. LE FÈVRE.

**Preparation of monomethyldiethylmercaptoglucose.** P. E. PAPADAKIS (J. Amer. Chem. Soc., 1930, 52, 3465).—Monomethyldiethylmercaptoglucose, m. p. 155°, is prepared from dry sodiodiethylmercaptoglucose and methyl iodide (cf. Fischer, A., 1894, i, 269).

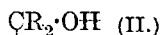
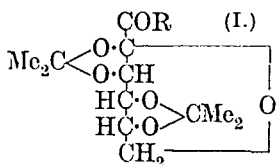
H. BURTON.

**Vicioside (vicin).** H. HÉRISSEY and J. CHEYMOL (Compt. rend., 1930, 191, 387–389).—Vicioside, obtained from the winter vetch by a method analogous to that described by Ritthausen (A., 1876, i, 936), suffers no loss in weight at 100°, and has  $[\alpha]_D^{20}$   $-11.93^\circ$  to  $-12.64^\circ$ , decreased by acidification with cold 4–5% sulphuric acid. Hydrolysis with 2% sulphuric acid gives a solution containing 57.7–58.5% of dextrose; hydrolysis with emulsin affords a similar solution containing 55% of dextrose, and it is concluded that the decomposition is the same in both cases. No trace of galactose was discovered (cf. Ritthausen, A., 1896, i, 696). The decomposition follows the general rule given by Bourquelot and Hérissé (A., 1908, i, 356).

C. W. SHOPPEE.

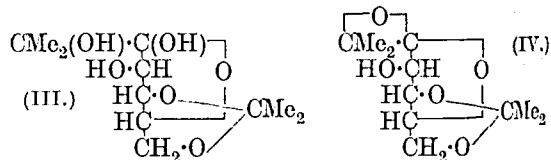
**New synthesis in the sugar group. I. Preparation of 1:1-dialkylfructose derivatives.** H. OHLE and O. HECHT (Annalen, 1930, 481, 233–254).

—By the action of the appropriate Grignard reagent on  $\alpha$ -ketodiisopropylidenegluconic acid (Ohle and Wolter, this vol., 744) or its methyl ester are obtained diisopropylidene-1:1-dialkylfructose derivatives (I) and diisopropylidene-1-alkylglucosone (II), the proportion of these two products formed depending on (1) the use of the acid or its ester, (2) the nature and



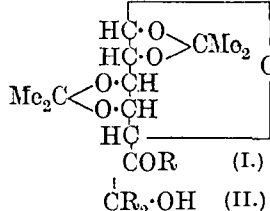
excess of the Grignard reagent used, and (3) the reaction temperature. Thus the free gluconic acid reacts with 4 mols. of magnesium methyl iodide to yield mainly  $\beta$ -diisopropylidene-1-methyl-d-glucosone (I; R=Me), b. p. 97.5–98.5°/0.05 mm.,  $d_4^{25}$   $-1.163$ ,  $n_D^{20}$   $1.4603$ ,  $[\alpha]_D^{20}$   $-40.6^\circ$  in chloroform, together with a small quantity of  $\beta$ -diisopropylidene-1:1-dimethylfructose (II; R=Me), m. p. 88°, b. p. 101°/0.05 mm.,  $[\alpha]_D^{20}$   $-22.9^\circ$  in chloroform. The latter is also obtained by further action of magnesium methyl iodide on the former and is the sole product when methyl  $\alpha$ -ketodiisopropylidenegluconate is treated with 4 mols. of the Grignard reagent in ether. On the other hand, excess of magnesium ethyl bromide converts either the acid or its ester solely into  $\beta$ -diisopropylidene-1:1-diethylfructose (II; R=Et), m. p. 83–84°, b. p. 102–105°/0.1 mm., 305–310°/760 mm.,  $[\alpha]_D^{20}$   $-19.0^\circ$  in chloroform. Similarly are obtained  $\beta$ -diisopropylidene-1:1-di-n-propyl-, m. p. 83°,  $[\alpha]_D^{20}$   $-166^\circ$  in chloroform, -di-n-butyl-, m. p. 64–

65°,  $[\alpha]_D^{20}$   $-14.1^\circ$  in chloroform, -diisopropyl-, m. p. 81–82°,  $[\alpha]_D^{20}$   $-19.2^\circ$  in chloroform, and -diisobutyl-, b. p. 125–126.5°/0.016 mm.,  $[\alpha]_D^{20}$   $-15.3^\circ$  in chloroform. Hydrolysis of these diisopropylidene-1:1-dialkylfructose derivatives with 2N-sulphuric acid occurs in two stages, the 4:5-isopropylidene group being much more readily removed to yield the intermediate  $\beta$ -monoisopropylidene-1:1-dialkylfructose, all of which are dextrorotatory and hence the hydrolysis-optical rotation curves all show a rapid rise to a maximum, followed by a fall as the equilibrium value of the dialkylfructose is approached. From the hydrolysis products are isolated:  $\beta$ -isopropylidene-1:1-dimethylfructose, m. p. 164°,  $[\alpha]_D^{20}$   $+2.7^\circ$  in water,  $+19.5^\circ$  in alcohol (reconverted by acetone and anhydrous copper sulphate into the parent diisopropylidene derivative), and 1:1-dimethylfructofuranose, m. p. 163° (decomp.), which has  $[\alpha]_D^{20}$   $-14.3^\circ$  in water but exhibits mutarotation  $[\alpha]_D^{20}$   $+11.0^\circ$  to  $-5.3^\circ$  in 80% alcohol [*phenylhydrazone*, m. p. 150° (decomp.)]. The furanose structure of this sugar is proved by the following reactions. It is converted by the action of acetone and anhydrous copper sulphate at the ordinary temperature into a mixture of 4:6-isopropylidene-1:1-dimethylfructofuranose (III), b. p. 155–162°/0.1 mm.,  $[\alpha]_D^{20}$   $+13.3^\circ$  in chloroform, and its 1:2-anhydride (IV), b. p. 137–139°/0.15 mm., m. p. 139–140°,  $[\alpha]_D^{20}$   $-8.9^\circ$  in chloroform, both of which possess strong reducing properties. The latter is the isopropylidene



derivative of the fructofuranose anhydride obtained by Ohle and Koller (A., 1924, i, 1168; cf. Schlubach and Flörshiem, A., 1929, 914). Similar hydrolysis of the diethyl derivative affords  $\beta$ -isopropylidene-1:1-diethylfructofuranose, m. p. 128°,  $[\alpha]_D^{20}$   $+28.1^\circ$  in alcohol (monobenzoyl derivative, m. p. 128°), but the 1:1-diethylfructose could be obtained only as an impure syrup which on hydrolysis with N-potassium hydroxide affords diethyl ketone in 21% yield.  $\beta$ -isoPropylidene-1:1-di-n-propylfructose, m. p. 105–106°,  $[\alpha]_D^{20}$   $+23.4^\circ$  in alcohol, is obtained similarly. J. W. BAKER.

**New syntheses in the sugar group. II. 6:6-Dimethylgalactose.** H. OHLE and C. DAXBERG (Annalen, 1930, 481, 255–262).—Extension of the Grignard syntheses (cf. preceding abstract) to diisopropylidenegalaconic acid, m. p. 148°,  $[\alpha]_D^{20}$   $-83.24^\circ$  (Ohle and Berend, A., 1926, i, 150, give m. p. 157°), affords mainly diisopropylidene derivatives of 6-alkyl-6-ketogalactose (I) and smaller yields of the diisopropylidene-6:6-dialkylgalactose (II). In these cases, however, the methyl ester of the galacturonic acid cannot be prepared owing to the ease of fission of the isopropylidene groups, and the Grignard reaction must be carried out in benzene instead of in ether. Thus from the appropriate Grignard



reagent are obtained: *diisopropylidene-6-methyl-*, b. p.  $120^{\circ}/1$  mm.,  $[\alpha]_D^{25}$   $-128.5^{\circ}$ , and *-6-ethyl-*,  $[\alpha]_D^{25}$   $-120.7^{\circ}$ , *-6-keto-d-galactose*, which on further treatment with the Grignard reagent are converted into *diisopropylidene-6:6-dimethyl-*, m. p.  $81-82^{\circ}$ ,  $[\alpha]_D^{25}$   $-62.3^{\circ}$ , and *-6:6-diethyl-*, m. p.  $87-88^{\circ}$ ,  $[\alpha]_D^{25}$   $-39.3^{\circ}$ , *-d-galactose* (all rotations in chloroform). Hydrolysis of derivatives of type I affords the corresponding 6-alkyl-6-ketogalactose, which, however, is too unstable to be isolated. Hydrolysis of derivatives of type II with 2*N*-alcoholic sulphuric acid affords 6:6-dimethyl-d-galactose as a syrup [osazone, m. p.  $214-215^{\circ}$  (decomp.)]. J. W. BAKER.

**Oxidation of lactal.** A. J. WATTERS and C. S. HUDSON (J. Amer. Chem. Soc., 1930, 52, 3472-3473).—The 4-galaetosidomannose of Bergmann and others (A., 1924, i, 265), obtained by the oxidation of lactal with perbenzoic acid, is a mixture of at least two sugars. H. BURTON.

**Cellulose and silicates.** L. MÉDARD (Rev. gén. Colloid, 1930, 8, 161-169).—The problem of the constitution of cellulose is discussed and several analogies with the corresponding problem of the silicates, particularly the zeolites, are pointed out. Classical structural formulæ have never been applicable to such compounds and in order to understand their properties the crystallographic structure is equally important. E. S. HEDGES.

**Reactions relating to carbohydrates and polysaccharides. XXIX. Constitution of alkali cellulose. XXXI. Behaviour of cellulose towards solutions of aluminium salts.** E. G. V. PERCIVAL, A. C. CUTHERBERTSON, and H. HIBBERT (J. Amer. Chem. Soc., 1930, 52, 3257-3269, 3448-3456).—XXIX. The absorption of sodium hydroxide by cellulose has been studied over the range of concentrations 0.32-46.4% (by weight) at  $25^{\circ}$ ; the amount of alkali absorbed is determined by washing the fibre with alcohol and then employing an extrapolation method. Evidence is obtained of the formation of a compound resulting from the interaction of 1 mol. of sodium hydroxide with each anhydroglucose unit of the cellulose. Calculation of the amount of water adsorbed by the cellulose during the alkali treatment indicates that there is a maximum with 14% sodium hydroxide; this agrees with the known point of maximum swelling. Quantitative analysis of an alkali-treated cellulose (washed free from adherent alkali) indicates that it is a mixture of the forms  $(C_6H_9O_5Na)_x$  and  $(C_6H_{10}O_5NaOH)_x$ . The suggestion is made that the equilibrium  $(C_6H_{10}O_5NaOH)_x \rightleftharpoons (C_6H_9O_5Na)_x + xH_2O$  may exist. A possible explanation of the changes occurring during the treatment of cellulose with sodium hydroxide is given.

XXXI. Small but definite amounts of aluminium hydroxide are adsorbed by "ash-free" cellulose when this is shaken with solutions of aluminium sulphate, chloride, or acetate at  $25^{\circ}$ . The amount adsorbed using the sulphate increases with rise in  $p_H$  and dilution of the solution, and adsorption is greatest with the acetate. The amount of aluminium hydroxide adsorbed depends on two factors: (a) a natural and (b) an exchange adsorption. The former factor depends on the specific nature of the fibre, hydrogen-ion

concentration, dilution, and extent of hydrolysis of the solution, and the anion; the latter appears to depend on the replaceable elements (calcium and iron) in the ash. The mechanism of the hydrolysis of aluminium acetate is shown to be the same as for the chloride and sulphate. H. BURTON.

**Lignin and related compounds. I. Isolation of spruce-wood lignin.** H. HIBBERT and H. J. ROWLEY (Canad. J. Res., 1930, 2, 357-363).—Spruce-wood meal is dried under reduced pressure, extracted with benzene and ethyl alcohol, dried, extracted with water, and again dried. The meal is mixed with ten times its weight of ethylene glycol, heated to  $110^{\circ}$ , 2% of iodine is added, and the mixture is maintained at  $110^{\circ}$  for 6 hrs., with vigorous agitation. The filtered solids are washed with hot glycol. The filtrate and washings are added to 10 vols. of water, a flocculent solid separating which is washed and dried over phosphoric oxide. The crude lignin may be purified by dissolving in 1.0% aqueous sodium hydroxide, followed by treatment with carbon dioxide until  $p_H$  8.8-8.9 is reached (this treatment is repeated). The main fraction of purified lignin gives on analysis C 64.65, H 6.14, O 29.21, OMe 18.79%. Methylated lignins are obtained from the purified lignin having methoxyl contents of 26-27%, repeated methylation increasing the methoxyl content to a maximum followed by a decrease. Methylated lignin treated with fuming nitric acid and acetic anhydride yields a nitrated product (C 43.15, H 3.45, N 10.65, OMe 14.1%). Purified lignin dissolved in ethylene glycol is chlorinated at  $0^{\circ}$ , yielding a product having C 45.11, H 4.14, Cl 20.77, OMe 12.22%. T. T. PORTS.

**Lignin and related compounds. II. Glycol lignin and glycol ether lignin.** H. HIBBERT and L. MARION (Canad. J. Res., 1930, 2, 364-375; cf. preceding abstract).—Spruce-wood meal, freed from resins as previously described, is treated at  $100-103^{\circ}$  with ten times its weight of ethylene glycol containing 0.05% of hydrogen chloride. Repeated extraction shows that the pentosan:lignin ratio remains constant in the wood and in the dissolved portion. The crude glycol lignin obtained by precipitation of the filtrate with water is purified by dissolution in 1.0% sodium hydroxide, acidified with sulphuric acid, and dissolved in 95% alcohol. The alcoholic solution is boiled under reflux with fresh zinc-copper couple, filtered, and poured into water. The washed lignin is dried over phosphoric oxide. Hydrolysis with 5% sulphuric acid reduces the methoxyl content to 16.42%, and formaldehyde is recognised as a product of the hydrolysis. Glycol could not be found in the hydrolysis liquors. Wood meal treated with ethylene glycol monomethyl ether, in the same way as above, yielded a product containing 21.4% OMe. It is concluded that the higher methoxyl content of the latter product is an indication that combination takes place between the lignin and the solvent. T. T. PORTS.

**Lignin and related compounds. III. Glycerol chlorohydrin lignin.** H. HIBBERT and J. B. PHILLIPS (Canad. J. Res., 1930, 3, 65-69).—From spruce-wood meal, previously extracted with water and with a mixture of alcohol and benzene, glycerol lignin and lactic acid lignin may be obtained by treat-

ment with glycerol and lactic acid, respectively, under conditions similar to those employed in the production of the glycol lignins (preceding abstract). In all these cases the lignin is apparently in combination with the solvent. A similar combination has been demonstrated when the lignin is extracted with glycerol  $\alpha$ -monochlorohydrin. Treatment of the wood meal with this substance, in the presence of 0.2–0.5% of hydrochloric acid as catalyst, for 6 hrs. at 80° yields a viscous mass from which "glycerol chlorohydrin lignin" may be isolated (5.5% Cl, 15.6% OMe). Comparison with glycol lignin indicates a mol. wt. of 309, if 1 mol. of solvent is combined in each case; cryoscopy in acetophenone gives a mol. wt. of 350. Hydrolysis with boiling 8% hydrochloric acid removes the glycerol chlorohydrin; the residue, which is substantially pure lignin as determined by the method of Klason (A., 1908, i, 717), is no longer soluble in dilute alkali, and it is suggested that, in addition to the removal of the chlorohydrin residue, the treatment has occasioned some fundamental change in the lignin molecule. Methylation of glycerol chlorohydrin lignin with methyl sulphate and alkali increases the methoxyl content to 23.2%, corresponding with an increase of methyl ether groups in a complex of mol. wt. 350 from 2 to 3. T. H. MORTON.

**Action of nitrosyl bromide on amino-acids.** Z. Csűrös (Magyar Chem. Fol., 1929, 35, 113–119; Chem. Zentr., 1930, i, 1461).—Substitution of the amino-group by bromine takes place only with  $\alpha$ - and  $\beta$ -substituted acids. The following substances are described:  $\gamma$ -benzamidobutyric acid, m. p. 79–80°;  $\epsilon$ -benzamido-n-hexoic acid, m. p. 80°;  $\zeta$ -benzamidooxymalonic acid, m. p. 115°;  $\zeta$ -aminoheptoic acid, m. p. 186° (benzoyl derivative, m. p. 81–82°).

A. A. ELDRIDGE.

**$\alpha$ -Methylbutenoamides.** P. BRUYLANTS, L. ERNOULD, and M. DEKOKER (Bull. Acad. roy. Belg., 1930, [v], 16, 721–740).—Dehydration of methyl ethyl ketone cyanohydrin with phosphoric oxide or thionyl chloride affords a mixture of unsaturated nitriles which after fractionation, saturation of the various fractions with hydrogen chloride, and re-fractionation gives  $\beta$ -chloro- $\alpha$ -methylbutyronitrile, b. p. 64–65°/12 mm., and  $\beta$ -chloro- $\alpha$ -ethylpropionitrile, b. p. 73–74°/12 mm. The former of these is converted by boiling with quinoline into a mixture of the nitriles, b. p. 121–122°/772 mm.,  $d_4^{20}$  0.81968,  $n_D^{20}$  1.42303, and b. p. 137–138°/772 mm., respectively, of  $\alpha$ -methylcrotonic acid, whilst the latter furnishes  $\alpha$ -ethylacrylonitrile, b. p. 115–116°/752 mm. The nitrile, b. p. 137–138°, is hydrolysed by cold 66% sulphuric acid to  $\alpha$ -methylcrotonamide, m. p. 75–76° (I), whilst the form of b. p. 121–122° gives  $\alpha$ -methylcrotonamide, m. p. 127–128° (II).  $\alpha$ -Ethylacrylamide has m. p. 86–87° (lit. 82°). Alkaline hydrolysis of II yields only tiglic acid, also formed by the action of nitrous acid in acetic acid solution. Tiglic acid is also obtained when either  $\alpha$ -methylcrotononitrile is hydrolysed with sulphuric acid. Prolonged treatment of methyl tiglate, b. p. 137–138°/758 mm., with concentrated ammonia at the ordinary temperature affords I, which undergoes 90% conversion into II when an acetone(?) solution is ex-

posed to ultra-violet light. These results show that the  $\alpha$ -methylcrotononitrile, b. p. 137–138°, and I are *trans*-compounds, whilst the nitrile, b. p. 121–122°, and II are *cis*-derivatives. Langseth's rule (A., 1926, 116) applies equally well to these compounds as to the corresponding crotonic acid derivatives.

$\alpha$ -Ethylacrylamide is converted by exposure to ultra-violet light into a mixture of unchanged material (42%), I (7%), and II (51%). Hydrolysis of methyl ethyl ketone cyanohydrin with sulphuric acid affords a mixture of  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acid and its amide. H. BURTON.

**Ultra-violet absorption spectra of  $\alpha$ -methylbutenoamides.** A. CASTILLE (Bull. Acad. roy. Belg., 1930, [v], 16, 811–816).—Ultra-violet absorption curves for aqueous solutions of the amides of *cis*- and *trans*- $\alpha$ -methylcrotonic and  $\alpha$ -ethylacrylic acids (cf. preceding abstract) and solutions of the nitriles of the same acids in hexane are given. The absorption of the *cis*-amide and -nitrile is less than that of the *trans*-isomerides, whilst the absorption of *cis*- $\alpha$ -methylcrotonic acid is greater than that of the *trans*-isomeride. H. BURTON.

**Ethylenethiocarbamide.** C. RUIZ and L. LIBENSON (Anal. Asoc. Quim. Argentina, 1930, 18, 37–42).—As usually prepared, ethylenethiocarbamide, m. p. 194°, contains labile sulphur, accounted for by the presence of 12–18% of *N*- $\beta$ -aminoethyl dithiocarbamate. Pure ethylenethiocarbamide, m. p. 199° (corr.), is prepared by heating ethylenediamine with carbon disulphide in alcohol at 100–105° for 4–5 hrs. It has no reducing properties and does not yield a precipitate with copper salts in the cold, as stated by Morgan and Burstall (A., 1928, 278).

R. K. CALLOW.

**Action of halogenohydrins and ethylene oxide on thiocarbamides.** J. F. OLIN and F. B. DAVIS (J. Amer. Chem. Soc., 1930, 52, 3322–3327).—Thiocarbamides react with halogenohydrins and their derivatives, forming isothiocarbamides,  $\text{OR} \cdot [\text{CH}_2]_n \cdot \text{SC}(\text{NR}') \cdot \text{NHR}''$ ; these are readily hydrolysed and when treated with amines give guanidines. Thus, ethylene chlorohydrin and thiocarbamide at 90–105° give  $\beta$ -hydroxyethylisothiocarbamide hydrochloride, m. p. 111°; with trimethylene chlorohydrin at 120–125°,  $\gamma$ -hydroxypropylisothiocarbamide hydrochloride, m. p. 130°, results. This is converted by ammonia and methylamine into guanidine and methylguanidine, respectively. Thiocarbamide and ethyl  $\beta$ -bromoethyl ether react at 100° in presence of a small amount of alcohol, furnishing  $\beta$ -ethoxyethylisothiocarbamide hydrobromide, m. p. 28–29°, hydrolysed by potassium hydroxide to  $\beta$ -ethoxyethyl mercaptan (phenylcarbimide derivative, m. p. 45°, also formed by heating the phenylthiocarbimide derivative, m. p. 42–43°, of  $\beta$ -ethoxyethyl alcohol with  $\beta$ -ethoxyethyl iodide at 130°), and converted by treatment with phenylcarbimide and potassium hydroxide into the compound  $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}(\text{N} \cdot \text{CO} \cdot \text{NHPh}) \cdot \text{S} \cdot \text{C}_2\text{H}_5 \cdot \text{OEt}$ , m. p. 132°. This is hydrolysed by potassium hydrogen sulphide (cf. A., 1929, 1055) to the thiocarbamide  $\text{CS}(\text{NH} \cdot \text{CO} \cdot \text{NHPh})_2$ , m. p. 202°. Thiocarbamide and

$\beta$ -bromoethyl acetate at 125° give  $\beta$ -acetoxyethyl-isothiocarbamide hydrobromide, m. p. 99° (the bis-phenylcarbimide, m. p. 134°, and di-*p*-nitrobenzoyl, m. p. 189°, derivatives of the free base are described), converted by aniline into phenylguanidine. Dibenzoylphenylguanidine is obtained similarly from the dibenzoyl derivative, m. p. 149°, of methyl-isothiocarbamide. The  $\beta$ -hydroxyethyl (hydriodide, an oil) and  $\beta$ -acetoxyethyl (hydrobromide, m. p. 158°; *p*-nitrobenzoyl derivative, m. p. 132°; phenylcarbimide derivative, m. p. 81–82°) derivatives, m. p. 69–70°, of phenylthiocarbamide are prepared similarly.

When thiocarbamide is heated with  $\beta$ -chloroethyl benzoate at 130–150°, a mixture of diphenylcarbamide, phenylthiocarbimide, benzanilide, benzoic acid, and 2:3-diphenylthiazolidine, m. p. 136°, is produced. The last-named compound is formed from the phenylthiocarbimide derivative, m. p. 145°, of  $\beta$ -anilinoethyl benzoate.

Ethylene oxide reacts with thiocarbamide in acetone at the ordinary temperature, forming carbamide and thioethylene glycol; the latter arises by hydrolysis of the unstable  $\beta$ -hydroxyethylisothiocarbamide. Diphenylthiocarbamide and ethylene oxide in acetone at 50–55° yield diphenyl- $\beta$ -hydroxyethylisothiocarbamide, m. p. 145° (phenylcarbimide derivative, m. p. 101°), hydrolysed by alkalis to diphenylcarbamide.

Hydrolysis of alkylisothiocarbamides with potassium hydrogen sulphide furnishes the corresponding thiocarbamides. The method is illustrated by the formation of 1:5-diphenyldithiobiuret, m. p. 149°, from the methyl derivative. Diacetylmethylisothiocarbamide, m. p. 107–108°, is, however, completely hydrolysed. The dicarbethoxy-derivative, m. p. 50–51°, of methylisothiocarbamide, prepared from the isothiocarbamide and ethyl chloroformate, is hydrolysed by potassium hydrogen sulphide to  $\beta$ -dicarbethoxythiocarbamide, m. p. 111–112°, whilst the carbethoxy-derivative, m. p. 128°, of phenyl-methylisothiocarbamide undergoes fission to phenylurethane.

H. BURTON.

**Constitution of cyanogen halides. I. Reactions of cyanogen chloride and iodide. II. Refractometry of cyanogen chloride and iodide.** E. V. ZAPPI (Anal. Asoc. Quím. Argentina, 1930, 18, 5–11, 12–30).—See this vol., 1027, 1171.

**Action of phosphine on formaldehyde. II.** A. HOFFMAN (J. Amer. Chem. Soc., 1930, 52, 2995–2998).—The action of alkaline hydroxides or carbonates on tetrahydroxytetramethylphosphonium chloride (I) (cf. A., 1922, i, 8) in aqueous solution takes place in two stages, hydrogen (1 mol.) and formaldehyde (1 mol.) being liberated at each stage. Sodium hydroxide or carbonate below 80° and barium carbonate at 100° give trihydroxytrimethylphosphine oxide (tribenzoate, m. p. 111°; cf. *loc. cit.*), whilst the first two give at 100° dihydroxydimethylphosphinic acid, isolated as the crystalline barium salt. The chloride, I, is converted by phosphorus pentachloride in boiling carbon tetrachloride into tetrachlorotetramethylphosphonium chloride, m. p. 192–193°, which is hydrolysed by alkalis and by sodium hydrogen carbonate to trichlorotrimethylphosphine, b. p. 100°/7 mm.,  $d_4^{20}$  1.414. This has only slight basic properties. It is stable in

air, does not combine with hydrogen chloride, and is oxidised by nitric acid ( $d$  1.2) to trichlorotrimethylphosphine oxide (+0.5H<sub>2</sub>O), m. p. 88–89°, which with sodium benzoate at 200° gives tribenzoyloxy-trimethylphosphine oxide. H. E. F. NOTTON.

**Preparation of mercury dialkyls from organo-magnesium halides.** H. GILMAN and R. E. BROWN (J. Amer. Chem. Soc., 1930, 52, 3314–3317; cf. A., 1929, 687).—Improvements in the preparation of mercury dimethyl (71% of the theoretical yield), diethyl (80–84%), and di-*n*-butyl (80%), involving (a) the use of approximately equivalent quantities of mercuric chloride and the organomagnesium halide and (b) reduction in the time of heating, are described. Mercury diethyl, di-*n*-butyl, and diphenyl do not afford appreciable quantities of organomagnesium halides when treated with magnesium bromide or iodide. Mercury dimethyl is more stable than the diethyl or di-*n*-butyl. H. BURTON.

**Determination of metal in organic compounds incapable of electrolysis.** K. DOSIOS and J. PIERRI (Z. anal. Chem., 1930, 81, 214–216).—The addition of excess of bromine water to lead tetraethyl dissolved in an inert solvent (carbon tetrachloride) causes quantitative formation of lead bromide. A similar method is applied for the determination of anti-knock substances in petrol, of tin in tin tetraphenyl, and of nickel and iron in their carbonyls.

J. O. CUTTER.

**Organic salts of lead triethyl hydroxide.** H. GILMAN and J. D. ROBINSON (Rec. trav. chim., 1930, 49, 766–768).—The following lead triethyl salts are prepared from lead tetraethyl and the appropriate acid in presence of silica gel (cf. Browne and Reid, A., 1927, 452): *salicylate*, m. p. 83–91°; *furoate*, m. p. 153–154°; *phenylacetate*, m. p. 101–106°;  $\beta$ -*furyl-acrylate*, m. p. 119–121°; *o*-*thiolbenzoate* (?), m. p. 97–99°; *p*-*toluenesulphonate*, m. p. 167–168°, and *monophosphate*, not melted at 250°. Lead triethyl acetate and sodium *p*-aminobenzoate in aqueous solution give lead triethyl *p*-aminobenzoate, m. p. 84–86°. These salts are only slightly soluble in water, and they are very irritant in the dry state.

H. BURTON.

**Organic gold compounds. I. Aurous chloride carbonyl; method of linking carbon to carbon.** M. S. KHARASCH and H. S. ISBELL (J. Amer. Chem. Soc., 1930, 52, 2919–2927).—Aurous chloride carbonyl (20% of the theoretical) is obtained by passing a rapid stream of carbon monoxide over dry auric chloride at 110°. Contrary to the statement of Manchot and Gall (A., 1925, ii, 1182), the simultaneous passage of carbon monoxide and chlorine produces little carbonyl compound, but much carbonyl chloride. The carbonyl compound is formed quantitatively from aurous chloride and carbon monoxide in benzene at 15°, or from auric chloride in tetrachloroethylene at 130–140°. It has a mol. wt. of 223 (calc. 260) in freezing benzene and dissociates in a vacuum or in hot solvents, giving pure aurous chloride. It reacts with nitrogenous bases, but not with amides or imides, the carbonyl group being displaced by 1 mol. of base. *Pyridine aurous chloride*,

m. p. 92° (decomp.), and *hexamethylenetetramine aurous chloride*, decomp. from 150°, are obtained thus. With bromine it gives auric chlorodibromide and with iodine aurous iodide. With alcohols it gives metallic gold, with mercury dialkyls, gold, alkyl-mercuric chlorides, and bis-hydrocarbons, and with Grignard reagents, gold and a quantitative yield of the bis-hydrocarbon. The view that a gold mono-aryl is formed intermediately in the last reaction is supported by the observation that the time elapsing before gold is precipitated increases with an increase in the electronegative character of the aryl radical. Thus, magnesium benzyl and phenyl halides cause an immediate precipitation, whilst magnesium  $\alpha$ -naphthyl bromide gives a solution from which gold is precipitated only on heating. H. E. F. NOTTON.

**Oxidation of unsaturated hydrocarbons by quadrivalent lead salts.** R. CRIEGEE (Annalen, 1930, 481, 263—302).—The oxidation of a number of unsaturated substances, mainly hydrocarbons, by lead tetra-acetate, tetrapropionate, tetrabutyrates, and *tetrabenzoate*, m. p. 168° (decomp.) (prepared by the action of the tetra-acetate on molten benzoic acid), in the corresponding acid as solvent, occurs mainly in two ways: (1) addition of two acetoxy-groups to the double linking, or (2) the double linking is un-attacked, whilst the adjacent hydrogen atom is replaced by an acetoxy-group. Thus *cyclohexene* is converted by lead tetra-acetate at 80° into a mixture of  $\Delta^2$ -*cyclohexenyl acetate*, *cyclohexane-1:2-diol diacetate* [identified after hydrolysis as the *cis*- and *trans*-diols, which are further oxidised with lead tetra-acetate to adipaldehyde (*diphenylhydrazone*, m. p. 140°, corr.)], and either  $\Delta^2$ -*cyclohexene-1:1-or-1:4-diol diacetate*. Indene yields 1-*hydroxyindene acetate*, b. p. 118—122°/12 mm.,  $d_4^{20}$  0.981 [hydrolysed with aqueous sodium hydroxide to  $\alpha$ -hydrindone, and with methyl-alcoholic sodium hydroxide to anhydro-bis- $\alpha$ -hydrindone; converted by further treatment with lead tetra-acetate into (?) *indone diacetate*, b. p. 166—172°/12 mm.,  $d_4^{20}$  1.165], hydrindene-2:3-diol diacetate (isolated as the glycol after reduction of the crude product with hydrogen and platinum-black in alcohol and subsequent hydrolysis), and an unsaturated ester which is probably the above indone diacetate. This in sodium or potassium hydroxide forms a pale yellow solution which is converted into a deep blue solution by addition of calcium, strontium, or barium salts. This blue solution is decolorised by shaking with air, the blue colour returning on keeping. *cyclopentadiene* with lead tetra-acetate at 30° yields a small fraction, b. p. 106—110°/12 mm.,  $d_4^{20}$  1.137, which consists mainly of the *diacetate* of  $\Delta^3$ -*cyclopentene-1:2-diol*, b. p. 110—114°/12 mm.,  $d_4^{17}$  1.152°, which is obtained on hydrolysis and is reduced to *cis-cyclopentane-1:2-diol*, and a main fraction, b. p. 119—124°/0.1 mm.,  $d_4^{20}$  1.215, which is the *monoacetate monoacetylglycollate* of  $\Delta^3$ -*cyclopentene-1:2-diol*,  $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{OAc} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OAc} \end{smallmatrix}$  since on hydrolysis it affords potassium glycollate and the diol (reduced to *cis-cyclopentane-1:2-diol*). The mechanism of the formation of derivatives of this type (other examples of which are described below) is discussed fully. It is

shown that the intermediate compound cannot be of the type of 1-acetoxycyclopentadiene, since lead tetrabenzoate in benzene at 30—35° converts *cyclopentadiene* into *trans- $\Delta^3$ -cyclopentene-1:2-diol dibenzoate*, m. p. 65.5—66° (corr.) (reduced to the *cyclopentene derivative*), further action in this case being precluded by the absence of an  $\alpha$ -hydrogen atom, for it is this atom which is involved, as is shown by the formation of similar derivatives when lead tetrapropionate or tetrabutyrates is used (cf. below). It is concluded that although the 1:2-diol diacetate cannot subsequently be converted into the acetylglycollate by further action of lead tetra-acetate, yet it is an activated enol form,  $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CH} \cdot \text{OAc} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{O} \cdot \text{C}(\text{OH}) \cdot \text{CH}_2 \end{smallmatrix}$  of this derivative which is the intermediate compound, the essential condition being the presence of such a double linking with high "addition energy." Such circumstances should arise when positive groups are attached, and, in agreement with this view, oxidation of either anethole or *isoeugenol methyl ether* with lead tetra-acetate yields, in addition to the normal additive product, compounds of the type under consideration, since on hydrolysis they yield potassium glycollate and the corresponding glycol. In the case of anethole this is further oxidised by lead tetra-acetate to anisaldehyde, whilst  $\alpha$ - and  $\beta$ -methyl-*isoeugenol glycols*, m. p. 122° and 88° (corr.), are actually isolated. Oxidation of various partly reduced aromatic hydrocarbons with lead tetra-acetate has been studied, the constitution of the products being proved by hydrolysis and reduction to known compounds in each case. Thus 9:10-dihydroanthracene in benzene at 80° gives a 30% yield of anthracene; 1:4-dihydronaphthalene affords naphthalene; 1:2-dihydronaphthalene gives the diacetate, b. p. 174—178°/12 mm., hydrolysed to *trans-1:2-dihydroxytetrahydronaphthalene*, whilst tetrahydronaphthalene affords mainly 1-acetoxy-1:2:3:4-tetrahydronaphthalene.  $\Delta^{1,3}$ -*cyclohexadiene* is converted into  $\Delta^3$ -*cyclohexene-1:2-diol diacetate*, and its *monoacetate monoacetylglycollate*, b. p. 132—135°/0.1 mm. Oxidation of the following aliphatic dienes was studied. Butadiene gives a mixture of oxidation and polymerisation products;  $\beta\gamma$ -dimethylbutadiene gives the *diacetate*, b. p. 92—102°/12 mm., of  $\beta\gamma$ -dimethyl- $\Delta^2$ -butene- $\alpha\beta$ -diol (reduced to the saturated diol, and oxidised to  $\alpha$ -hydroxy- $\alpha\beta$ -dimethylbutyric acid); and  $\Delta^{2,5}$ -hexadiene gives the *diacetate*, b. p. 67—71°/cathode vacuum, of a hexenediol the constitution of which is not determined. Oxidation of *cyclopentadiene* with lead tetrapropionate gives a 75% yield of the *monopropionate mono- $\alpha$ -propionoxypropionate* (cf. I), b. p. 125—135°/cathode vacuum,  $d_4^{20}$  1.119 (giving ethyl propionate and ethyl *dl*-lactate on treatment with alcoholic sodium ethoxide), of  $\Delta^3$ -*cyclopentene-1:2-diol*, together with its 2-*mono-propionate*, b. p. 110—115°/12 mm.,  $d_4^{20}$  1.101, and its *dipropionate*, b. p. 125—130°/12 mm.,  $d_4^{20}$  1.083. Similar oxidation of *cyclopentadiene* with lead tetrabutyrates affords the *mono-n-butyrates mono- $\alpha$ -n-butyryloxy-n-butyrates*, b. p. 149—154°/cathode vacuum,  $d_4^{20}$  1.068 (converted into ethyl butyrate and ethyl  $\alpha$ -hydroxybutyrate), of the same diol.

J. W. BAKER.



Parachors of two isomeric chlorodinitrobenzenes. D. V. SICKMAN and A. W. C. MENZIES (J. Amer. Chem. Soc., 1930, 52, 3327—3329).—Calculation of the parachor of 1-chloro-3:4-dinitrobenzene from the available data (Müller, A., 1914, ii, 188) gives a value differing greatly from that of 1-chloro-2:4-dinitrobenzene (348.2), using Jaeger's data (A., 1918, ii, 33). Re-determinations of the density and surface tension of the former compound lead to a value of 347.4 for the parachor. Both the above values are smaller than the calculated (358.3).

H. BURTON.

Reaction between *as*-diphenylethylene and a mixture of magnesium and magnesium iodide. H. GILMAN and S. A. HARRIS (Rec. trav. chim., 1930, 49, 762—765).—*as*-Diphenylethylene does not react to any appreciable extent with the binary system,  $Mg + MgI_2$ .

H. BURTON.

Tetracyclohexyldiphenylethane. S. S. ROSSANDER, L. H. BOCK, and C. S. MARVEL (J. Amer. Chem. Soc., 1930, 52, 2976—2981).—Dicyclohexylphenylcarbinol (Gray and Marvel, A., 1926, 43) and acetyl bromide yield dicyclohexylphenylmethyl bromide, m. p. 104—105°. The corresponding chloride gives, with 40% sodium amalgam in absence of air, red sodium dicyclohexylphenylmethyl and the chemically resistant substance  $C_{38}H_{54}$  (I), m. p. 209—211°. The sodio-derivative with carbon dioxide gives dicyclohexylphenylacetic acid, m. p. 242—244°; with water dicyclohexylphenylmethane, b. p. 145—148°/5 mm.,  $d_4^{20}$  0.9774,  $n_D^{20}$  1.5390, also prepared by hydrogenating cyclohexylcyclohexyldiphenylmethane (cf. Godchet, A., 1909, i, 19), and with dicyclohexylphenylmethyl chloride at 0° in absence of air, oily tetracyclohexyldiphenylethane. This is re-converted into the sodio-derivative by 1% sodium amalgam, gives with air dicyclohexylphenylmethyl peroxide, m. p. 186—188° (decomp.), and changes at 100° in xylene without development of colour into the hydrocarbon, I, and other products. In solution it decomposes in a few days at the ordinary temperature.

H. E. F. NOTTON.

Supposed existence of two stereoisomeric 9-phenyl-9-benzylfluorenes. W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 3290—3292).—Magnesium phenyldiphenylenemethyl bromide and benzyl chloride afford 9-phenyl-9-benzylfluorene, m. p. 140.3—140.8° (corr.), also obtained from magnesium benzyl chloride and 9-bromo-9-phenylfluorene. The same compound, and not the supposed isomeride, m. p. 125—126°, is produced by using Schlenk and Bergmann's method (A., 1929, 688).

H. BURTON.

Reactivity of halogenated hydrocarbons. IV. Transformations with halogenated condensed ring system hydrocarbons. J. LOEVENICH, W. BECKER, and T. SCHRÖDER (J. pr. Chem., 1930, [ii], 127, 248—259).—The reactivity of the halogen atoms in 2- and 9-bromofluorenes, 1- and 2-chloroanthracenes, and 9-bromoanthracene towards sodium acetate, potassium phenoxide, potassium phthalimide, lead oxide, potassium carbonate, benzamide, and ethyl chloroformate is studied by the methods previously described (A., 1927, 348, 538; this vol., 200).

9-Bromofluorene resembles cyclopentyl bromide whilst 2-bromofluorene is similar to an aryl halide. 9-Bromoanthracene is more reactive than the chloro-derivatives; the difference in reactivity is, however, not so marked as with the bromofluorenes, probably because of the aromatic nature of the 9-carbon atom in the anthracene molecule. 2-Phenoxyfluorene (?), m. p. above 260°; 9-phenoxyfluorene, m. p. 152—156°, and 9-benzamidoanthracene, m. p. 240—242°, are described. Mercury 9:9'-dianthryl, m. p. above 300°, is formed as a by-product during the interaction of 9-bromoanthracene, ethyl chloroformate, and sodium amalgam.

H. BURTON.

Action of  $Mg + MgBr_2$  on phenyldiphenylenemethyl. Formation of magnesium phenyldiphenylenemethyl bromide. W. E. BACHMANN (J. Amer. Chem. Soc., 1930, 52, 3287—3290).—9-Bromo-9-phenylfluorene (1 mol.) and magnesium (1 atom) react in *n*-butyl ether and benzene in an atmosphere of nitrogen, yielding magnesium phenyldiphenylenemethyl bromide. When 0.5 atom of magnesium is used, a mixture of magnesium bromide and phenyldiphenylenemethyl results; addition of a further 0.5 atom of magnesium to the mixture produces the Grignard reagent, also prepared directly from the free radical, magnesium, and magnesium bromide. The Grignard reagent reacts readily with 9-bromo-9-phenylfluorene forming the free radical, which is probably an intermediate in the production of the Grignard reagent.

Contrary to the statement of Schmidt-Nickels (A., 1929, 695), 9:9-diphenylfluorene is obtained from magnesium phenyl bromide and 9-chloro-9-phenylfluorene.

H. BURTON.

Halogenation of arylamines with the hydrogen halide and hydrogen peroxide mixture. A. LEULIER and G. ARNOUX (Bull. Soc. chim., 1930, [iv], 47, 730—737).—The following have been obtained in the yield indicated by the action of hydrogen peroxide and the hydrogen halide on the acetyl or benzoyl derivative of the toluidine or xylydine: 5-bromoaceto-*o*-toluidide, m. p. 156—157° (yield 91.5%); 5-chloroaceto-*o*-toluidide, m. p. 77.2° (yield 77.2%); 6-bromobenzoyl-*o*-toluidide, m. p. 175—176° (97%); 2:6-dibromoaceto-*m*-toluidide, m. p. 117°, and 4:5-dibromoaceto-*m*-toluidide, m. p. 161—162° (72.8%); 6-bromobenzoyl-*m*-toluidide, m. p. 97—98° (100%); 5:6-dibromobenzoyl-*m*-toluidide, m. p. 105—106° (97.7%); 3-bromoaceto-*p*-toluidide, m. p. 117° (83.5%); 3-bromobenzoyl-*p*-toluidide, m. p. 147—148° (87.5%), and 6-bromoaceto-*m*-4-xylydide, m. p. 168—169° (88%). Chlorination of aceto-*m*- and -*p*-toluidides and of the benzoyl derivatives of *o*- and *m*-toluidine gave indefinite products.

R. BRIGHTMAN.

Naphthalene series. I. Methylation of  $\alpha$ -naphthylamine. B. GOKHLE and F. A. MASON (J.C.S., 1930, 1757—1758).—Dimethyl- $\alpha$ -naphthylamine (25—50 g.) is conveniently prepared in 70% yield by methylating  $\alpha$ -naphthylamine with methyl sulphate and sodium hydroxide solution. When  $\alpha$ -naphthylamine sulphate is heated with methyl alcohol in a steel autoclave at 180° a mixture of dimethyl- $\alpha$ -naphthylamine (61%) and  $\alpha$ -naphthol

(26%) is obtained. The naphthol arises by hydrolysis of the tertiary base.  $\alpha$ -Naphthylamine hydrochloride and methyl alcohol at 180°/33 atm. give an 80% yield of the tertiary base (cf. Hantzsch, A., 1880, 813).

H. BURTON.

**Constitution of *p*-aminoazobenzene salts.** A. HANTZSCH and A. BURAWOY (Ber., 1930, 63, [B], 1760—1774).—Optical investigation of the salts of *m*-aminoazobenzene and the polyacidic salts of *p*-aminoazobenzene shows that the deeply-coloured salts of the latter bases cannot have the structure  $\text{NPh}(\text{HX})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2$  ascribed to them by Kehrman, since *m*-aminoazobenzene forms salts of the ammonium type,  $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_3\text{X}$ , in which the added acid molecule is normally united to the amino-group, quinonoid constitution being impossible. Vorländer's hypothesis that the acid molecule has no defined point of union and his arguments against the quinonoid formulation that the polyacidic salts of *p*-aminoazobenzene are appreciably lighter in colour than the monacid salts although a further quinonoid transformation is impossible cannot be maintained. Optical analogy with the di-acid salts of tetramethyl-yellow or dimethyl-yellow and the monacid salts of tetramethyl-yellow methochloride or dimethyl-yellow methochloride shows that an acid molecule is invariably attached to each amino-group. The di-acid salts of *p*-aminoazobenzene are lighter in colour than the monacid salts by reason of the diminished bathochromic action.

The quinonoid structure of the deeply-coloured *p*-aminoazobenzene salts is supported by the optical behaviour of auramine salts. The salt of *p*-dimethylaminobenzophenoneanil,  $\text{NHPh}\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{X}$ , absorbs more strongly than that of benzophenoneanil, whilst the absorption of the phenylauramine salt,  $\text{NHPh}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{X}$ , is not materially

changed on account of the introduction of a second dimethylamino-group; the auramine and anil salts have therefore the conjugated quinonoid constitution. Since the salts of *p*-aminoazobenzene and of the corresponding anils differ from one another solely by the replacement of the central nitrogen atom by the group CR and are therefore similarly constituted, the conjugated quinonoid structure must be common to both.

The spectra of the salt solutions of *p*-aminoazobenzene exhibited two markedly different bands. The short-wave ultra-violet bands of salts of the simple *p*-aminoazobenzenes are nearly identical with those of azobenzene or dimethyl-yellow methiodide; the short-wave bands of the salts of *p*-methoxydimethyl-yellow are very similar to those of *p*-methoxyazobenzene. The long-wave bands exhibit varying persistence. It follows, therefore, that equilibria between the yellow and red salts exist in the solutions of all *p*-aminoazobenzene salts and that the yellow compounds are ammonium salts. This view is confirmed by the observation that the spectra of salt solutions of azobenzene derivatives without amino-groups, which therefore cannot form ammonium salts, do not possess a second band in the ultra-violet. As

previously assumed, yellow azoid salts of the type  $\text{NAr}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\text{X}$  and red quinonoid salts,  $\text{NHAr}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2\text{X}$ , exist in the solid state. When

isomerism exists, the yellow salts can usually be transformed by pressure into the red compounds, whereby the mobile hydrogen atom is driven from the periphery to the centre of the molecule. H. WREN.

**Transformation of diazoamino- into aminoazo-compounds.** J. C. EARL (Ber., 1930, 63, [B], 1666; cf. this vol., 1033).—The action of very dilute alcoholic hydrochloric acid on diazoaminobenzene affords benzenediazoaminoazobenzene, m. p. 119.5°. Since the prolonged action of the reagent gives aminoazobenzene in good yield, the change may be formulated:  $2\text{NHPh}\cdot\text{N}_2\cdot\text{Ph} \rightarrow \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}_2\cdot\text{Ph} + \text{PhNH}_2 \rightarrow \text{Ph}\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 + \text{NHPh}\cdot\text{N}_2\cdot\text{Ph}$ . The scheme is supported by the observation of Rosenhauer and Unger (A., 1928, 407) that addition of aniline increases the yield of aminoazobenzene. H. WREN.

**Diazonium salts.** A. HANTZSCH (Ber., 1930, 63, [B], 1786—1789).—The constitution  $\text{Ar}\cdot\text{NX}\cdot\text{NHX}$  is not valid for "acid" diazonium salts, since the cryoscopic behaviour of benzenediazonium sulphate in sulphuric acid is similar to that of the sulphates of aniline bases and all other ammonium sulphates which contain only one nitrogen atom in the molecule. In the "acid" diazonium halides the added molecule of halogen hydride is not structurally united, but loosely attached to the cation. The compounds are therefore comparable with the additive products from hydrochloric acid and dimethylaniline hydrochloride and their greater stability is due to the less highly saturated condition of the central nitrogen atom.

Since diazonium salts and alcohols react with formation of hydrocarbons and aldehydes in strongly acidic solution at a rate which is independent of the concentration of the acid, only diazonium salts can be present, and the intermediate formation of *syn*-diazo-ethers is excluded. The change is considered to depend on the intermediate formation of adducts,  $\text{Ar}\cdot\text{NCl}\cdot\text{N}\cdots\text{H}\cdot\text{OEt}$ , which, in part, decompose with production of aryl ether, nitrogen, and hydrogen chloride, and, in part, become transformed into the non-electrolyte,  $\text{Ar}\cdot\text{NCl}\cdot\text{NH}\cdot\text{OEt}$ , which breaks down into ethyl hypochlorite (and thence aldehyde and acid), nitrogen, and hydrocarbon. H. WREN.

**Formation of diazo-oxy-compounds. Mechanism of azo-dye coupling.** H. T. BUCHERER and C. TAMA (J. pr. Chem., 1930, [ii], 127, 39—76).— $\beta$ -Naphthol-1-sulphonic acid couples in neutral or faintly alkaline solution with *p*-nitrobenzenediazonium chloride (best in equimolecular proportions in sodium hydrogen carbonate solution) to form sodium 2-*p*-nitrobenzeneazo-oxy-naphthalene-1-sulphonate (I) (decomp. 90—100°), which on acidification, or heating in aqueous solution at 70°, or in alcoholic or acetic acid solution at 50°, passes into 1-*p*-nitrobenzeneazo- $\beta$ -naphthol. In strongly alkaline solution very little para-red is formed owing to fission of the diazo-oxy-compound into  $\beta$ -naphthol-1-sulphonate and anti-diazotate. Aqueous solutions of the diazo-oxy-compound are stabilised by the addition of solutions

of sodium hydrogen carbonate and calcium chloride, any alkali formed reacting thus:  $\text{NaOH} + \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3$ ;  $\text{Na}_2\text{CO}_3 + \text{CaCl}_2 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$ . The reaction  $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH} + \text{ONa}\cdot\text{N}\cdot\text{NR} \rightleftharpoons \text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{O}\cdot\text{N}\cdot\text{NR} + \text{NaOH}$  is reversible.

A simple apparatus for measuring the rate of formation of I from its constituents is described, and the rates of formation under various conditions have been measured. The stability of the diazo-oxy-compound in the presence of aqueous sodium hydrogen carbonate, acetate, and carbonate solutions and of potassium carbonate and acetate solutions of specified concentrations was determined by adding aliquot parts of the solution after definite times to excess of hydrochloric acid ( $d$  1.185), weighing the precipitated para-red, then neutralising the filtrate with sodium carbonate, and further weighing the precipitated dye produced by coupling with a hydrogen carbonate solution of R-salt.

When  $\beta$ -naphthol-1-sulphonic acid is coupled with  $p$ -nitrobenzenediazonium chloride in strongly acid solution the sparingly soluble yellowish-orange diazonium sulphonate,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_3\cdot\text{O}\cdot\text{N}(\text{N})\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (cf. G.P. 280,371), is formed, which on dissolution in sodium carbonate or hydrogen carbonate solution and acidification yields para-red. This was hitherto assumed to be formed directly, but experimental evidence is now given showing that the diazonium sulphonate is first transformed into the diazo-oxy-compound, which isomerises into para-red.

Treatment of I (1 mol.) with 2 mols. of 30% sodium hydroxide solution yields a violet-red soluble compound, converted on keeping into a soluble yellow substance,  $\text{C}_{10}\text{H}_{10}\text{O}_6\text{N}_3\text{SNa}\cdot\text{H}_2\text{O}$ , m. p. 295–300°, in 40% yield, which on boiling for 6 hrs. with hydrochloric acid loses sulphur dioxide and yields a substance,  $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}_3\cdot 2\text{H}_2\text{O}$ , m. p. 310–315°.

Diazotised benzidine couples with 2 mols. of  $\beta$ -naphthol-1-sulphonic acid to yield diphenyl-4:4'-tetrazonium  $\beta$ -naphthol-1-sulphonate; 3:3'-dimethoxydiphenyl-4:4'-tetrazonium  $\beta$ -naphthol-1-sulphonate is obtained by using *o*-dianisidine and *m*-nitrotoluene-*p*-diazonium  $\beta$ -naphthol-1-sulphonate from *m*-nitro-*p*-toluidine. These give the corresponding diazo-oxy-compounds on treatment with aqueous sodium carbonate, and on further acidification the azo-compounds.

1-Chloro- $\beta$ -naphthol reacts with  $p$ -nitrobenzenediazonium chloride in sodium hydrogen carbonate solution to give an orange-brown solution, becoming violet-red with sodium hydroxide, and yielding para-red on acidification. The latter was also similarly produced from 2:2'-dihydroxydinaphthylmethane and  $p$ -nitrobenzenediazonium chloride. 2-Hydroxy-1-methylnaphthalene- $\omega$ -sulphonic acid does not couple with  $p$ -nitrobenzenediazonium chloride.

A. I. VOGEL.

**Decomposition of optically active diazo-compounds.** F. E. RAY (J. Amer. Chem. Soc., 1930, 52, 3004–3010).—It has already been shown that the *cis*- and *trans*-aminolauronic esters (3-amino-1:2:2-trimethylcyclopentane-1-carboxylic esters) yield different products when treated with nitrous acid under similar conditions (cf. Skinner, A., 1923, i, 791; Noyes and Skinner, A., 1918, i, 65). The diazo-compounds, presumably formed as intermediates, are

now shown to exhibit similar differences in behaviour, thus indicating that the carbon atom to which the diazo-group is attached retains, for a time at least, its asymmetry. Methyl *cis*-diazocamphonanate (Kendall and Noyes, A., 1926, 1134) is decomposed by dilute sulphuric acid to esters of hydroxy-acids (39.5%) and of unsaturated acids (60.5%) whilst the *trans*-ester at  $-20^\circ$  with this reagent gives 68% and 27%, respectively, of the esters and 5% of the methyl ether of *cis*-camphonolic acid. These yields are similar to those obtained from the corresponding amino-esters. Furthermore, spontaneous decomposition of the *cis*-diazo-ester yields the bishydrazone of Noyes and Taveau (A., 1904, i, 807), whilst the *trans*-derivative gives a compound, m. p.  $71^\circ$ , of mol. wt. 320–340.

H. E. F. NOTTON.

**Manufacture of diaminoazoanthraquinones.** I. G. FARBENIND. A.-G.—See B., 1930, 896.

**Nitrosation of phenols. X. Nitrosation of *m*-iodophenol.** H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 1969–1970).—The initial product of nitrosation of *m*-iodophenol is probably 3-iodo-4-nitrosophenol, decomp. about  $190^\circ$ , converted by treatment with acid or alkali (A., 1929, 1062; this vol., 910) into light-stable 3-iodo-*p*-benzoquinone-4-oxime (benzoate, m. p.  $166^\circ$ ; methyl ether, m. p.  $143^\circ$ ). 3-Iodo-4-nitrosoanisole, obtained from 3-iodo-*p*-anisidine and Caro's acid, has m. p.  $72.5^\circ$ . The *syn*- and *anti*-forms of 3-iodo-*p*-benzoquinone-4-oxime previously described by Hodgson and Moore (A., 1925, i, 1408) appear to correspond with the nitrosophenol and quinoneoxime tautomerides, respectively.

H. BURTON.

**Aromatic substitution. II. Action of fuming nitric acid on the 4-fluoro-2:6-dihalogenophenols and -anisoles. III. Action of fuming nitric acid on the 3-fluoro-2:4:6-trihalogenophenols and -anisoles.** H. H. HODGSON and J. NIXON (J.C.S., 1930, 1868–1869, 1870–1872).—II. *p*-Fluorophenol is converted by aqueous sodium hypochlorite into 2:6-dichloro-4-fluorophenol, m. p.  $42^\circ$ , methylated by Haworth and Lapworth's method (J.C.S., 1923, 123, 2986) to 2:6-dichloro-4-fluoroanisole, m. p.  $36^\circ$ . Both these substances are converted by nitric acid ( $d$  1.5) at  $0^\circ$  into 2:6-dichloro-*p*-benzoquinone. Treatment of a solution of *p*-fluorophenol in aqueous sodium hydroxide with iodine dissolved in aqueous potassium iodide affords 2:6-di-iodo-4-fluorophenol, m. p.  $67^\circ$ , methylated by methyl sulphate and sodium hydroxide solution to 2:6-di-iodo-4-fluoroanisole, m. p.  $61^\circ$ . The former of these is converted as above into 2:6-di-iodo-*p*-benzoquinone whilst the latter yields 6-iodo-4-fluoro-2-nitroanisole, m. p.  $53^\circ$ .

III. *m*-Fluorophenol is converted by bromine in aqueous potassium bromide into 2:4:6-tribromo-3-fluorophenol, m. p.  $90^\circ$ , and as above into 2:4:6-trichloro-, m. p.  $55^\circ$ , and 2:4:6-tri-iodo-3-fluorophenols, m. p.  $138$ – $139^\circ$ . Treatment of these with nitric acid at  $0^\circ$  affords 2:6-dibromo-, m. p.  $150^\circ$ , 2:6-dichloro-, m. p.  $145^\circ$ , and 2:6-di-iodo-3-fluoro-*p*-benzoquinones, m. p.  $195^\circ$ , respectively. Similarly, 2:4:6-trichloro-3-fluoroanisole, m. p.  $35^\circ$ , prepared by Haworth and

Lapworth's method, gives 3-fluoro-2:4:6-trinitroanisole, m. p. 180°; 2:4:6-tribromo-3-fluoroanisole, m. p. 55°, yields 2:4:6-tribromo-3-fluoro-5-nitroanisole, m. p. 87° (cf. Kohn and Rosenfeld, A., 1926, 282), whilst 2:4:6-tri-iodo-3-fluoroanisole, m. p. 107°, furnishes 2:4-di-iodo-3-fluoro-6-nitroanisole, m. p. 102°. The last-named compound is also obtained by methylation (Haworth and Lapworth's method) of 2:4-di-iodo-3-fluoro-6-nitrophenol, m. p. 106°, prepared by treatment of 3-fluoro-6-nitrophenol with iodine in presence of alcohol and yellow mercuric oxide.

H. BURTON.

**Action of freshly precipitated mercuric oxide on a suspension of 3:5-dinitrotoluene in aqueous sodium hydroxide.** Novel preparation of 3:5-dinitro-*p*-cresol. H. H. HODGSON and E. W. SMITH (J.C.S., 1930, 2035—2036).—When a mixture of mercuric chloride, 3:5-dinitrotoluene, and aqueous sodium hydroxide is boiled for 10 hrs., 3:5-dinitro-*p*-cresol is produced in approximately 50% yield together with amorphous material and mercury. Mercuric oxide alone has no action on the dinitrotoluene and sodium hydroxide alone gives no simple phenolic compound. No reaction occurs when the hydroxide is replaced by carbonate. H. BURTON.

**Migration of acyl groups in *o*-aminophenols.** F. BELL (J.C.S., 1930, 1981—1987).—Treatment of *o*-benzylidenaminophenol with acetyl, benzoyl,  $\alpha$ - and  $\beta$ -naphthoyl chlorides in pyridine at the ordinary temperature affords 2-hydroxy-acetanilide, -benzanilide, - $\alpha$ -naphthanilide, m. p. 194°, and - $\beta$ -naphthanilide, m. p. 194°, respectively. With *p*-toluenesulphonyl chloride a mixture of 2-benzylidenaminophenyl *p*-toluenesulphonate, m. p. 98°, and 2-*p*-toluenesulphonyl-1-phenyldihydrobenzoxazole, m. p. 138°, results. Hydrolysis of the ester with boiling water gives 2-aminophenyl *p*-toluenesulphonate [formed together with 5(?) -chloro-2-aminophenyl *p*-toluenesulphonate, m. p. 112° (acetyl derivative, m. p. 168°), by the reduction of the 2-nitro-ester with stannous chloride and alcoholic hydrochloric acid], whilst the oxazole is hydrolysed by alcoholic hydrogen chloride to 2-hydroxy-*p*-toluenesulphonanilide (prepared also from *o*-aminophenol and *p*-toluenesulphonyl chloride in pyridine). *m*-Nitrophenyl *p*-toluenesulphonate, m. p. 112°, is reduced as above to the *m*-amino-derivative, m. p. 98° (benzylidene derivative, m. p. 90°). 4-Benzylidene- and 2-*p*-dimethylaminobenzylidene-aminophenyl *p*-toluenesulphonates have m. p. 165° and 135°, respectively. *o*-Aminophenol and  $\beta$ -naphthoyl chloride in pyridine give a mixture of 2-hydroxy- $\beta$ -naphthanilide and 2- $\beta$ -naphthoxy- $\beta$ -naphthanilide, m. p. 150°. Since the above oxazole contains an asymmetric carbon atom, attempts to obtain the 2-camphorsulphonyl derivative have been made; viscous products are formed. 2-*p*-Dimethylaminobenzylidenaminophenol and *p*-toluenesulphonyl chloride afford a mixture of 2-hydroxy-*p*-toluenesulphonanilide and 2-*p*-toluenesulphonyl-1-*p*-dimethylaminophenyldihydrobenzoxazole, m. p. 188°. This oxazole is converted by dilute acetic or aqueous-alcoholic *d*-camphorsulphonic acid into the *N*-*p*-toluenesulphonyl derivative, m. p. 92°, of *p*-dimethylaminobenzaldehyde-*o*-hydroxyaniline; hydration of the oxazole occurs.

Hydrolysis of various diacylated *o*-aminophenols (cf. Raiford and others, A., 1924, i, 1304; 1925, i, 809) shows that the migration of acyl groups depends on some peculiarity of the  $\cdot\text{O}\cdot\text{CO}\cdot$  linking which is absent from the  $\cdot\text{O}\cdot\text{SO}_2\cdot$  linking. Substituents have also a marked influence in determining migration. Thus, 2-acetoxy- $\alpha$ -naphthanilide, m. p. 153°, and 2- $\alpha$ -naphthoxyacetanilide, m. p. 139°, are both hydrolysed by sodium hydroxide solution to 2-hydroxy- $\alpha$ -naphthanilide, also formed by hydrolysis of 2-benzoyloxy- $\alpha$ -naphthanilide, m. p. 176°, or 2- $\alpha$ -naphthoxybenzanilide, m. p. 170°. 2-*p*-Toluenesulphonoxyacetanilide, m. p. 134°, and 2-acetoxy-*p*-toluenesulphonanilide, m. p. 123°, are hydrolysed to 2-hydroxyacetanilide (formed also from 2-*d*-camphorsulphonoxyacetanilide, m. p. 133°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +60.9° in acetone) and 2-hydroxy-*p*-toluenesulphonanilide (*p*-toluenesulphonyl derivative, m. p. 143°), respectively. 2-*p*-Toluenesulphonoxy- $\alpha$ , m. p. 125°, and - $\beta$ -naphthanilides, m. p. 125°, are hydrolysed to 2-hydroxy- $\alpha$ - and - $\beta$ -naphthanilides (also formed from 2-acetoxy- $\beta$ -naphthanilide, m. p. 149°).

H. BURTON.

**2:5-Dibromo-*p*-anisidine.** G. BARGELLINI and A. GRIPPA (Atti R. Accad. Lincei, 1930, [vi], 11, 673—676; cf. this vol., 908).—Bromination of *p*-acetanisidide gives first 2-bromo-*p*-acetanisidide and then 2:5-dibromo-*p*-acetanisidide, m. p. 193—195°, Bureš and Nedělková's statement that the action of bromine on *p*-acetanisidide gives the 3:5-dibromo-compound (A., 1929, 1437) being thus inaccurate. 2:5-Dibromo-*p*-anisidine, m. p. 92—94°, forms a picrate, m. p. 133—134°, a benzoyl derivative, m. p. 170—172°, and a piperonylidene derivative, m. p. 171—172°. 2:5-Dibromo-2':4'-dinitro-4-methoxydiphenylamine, m. p. 182—188° (decomp.), is obtained by condensation of 2:5-dibromoanisidine and chlorodinitrobenzene in presence of sodium acetate. Treatment of 2:5-dibromo-*p*-acetanisidide with hydriodic acid yields 2:5-dibromo-4-aminophenol, which gives 2:5-dibromobenzoinquinone on oxidation with chromic acid (loc. cit.).

T. H. POPE.

**3:5- and 2:6-Dibromo-*p*-anisidines.** G. BARGELLINI and F. MADESANI (Atti R. Accad. Lincei, 1930, [vi], 11, 676—679; cf. preceding abstract).—Bromination of *p*-anisidine in acetic acid solution yields 3:5-dibromo-*p*-anisidine, m. p. 81—82° (cf. Wieland, A., 1910, i, 244), which forms an acetyl derivative, m. p. 225°, and a benzoyl derivative, m. p. 198°. 2:6-Dibromo-*p*-anisidine (cf. Robertson, J.C.S., 1902, 81, 1479) forms a piperonylidene derivative, m. p. 143°, and with chlorodinitrobenzene forms 3:5-dibromo-2':4'-dinitro-4-methoxydiphenylamine, m. p. 220°.

T. H. POPE.

**Sulphonation of  $\beta$ -naphthol in presence of boric acid;  $\beta$ -naphthol-1:6-disulphonic acid.** K. H. ENGEL (J. Amer. Chem. Soc., 1930, 52, 2835—2844).—Addition of boric acid changes the course of the reaction between  $\beta$ -naphthol and sulphuric acid (cf. Crossley and Simpson, B., 1926, 234), the greatest effect being produced when the proportion of boric acid reaches 0.33 mol. per mol. of naphthol. This, and the solid nature of the reaction product, suggests that formation of trinaphthyl borate precedes sulphonation. In general the effect of the catalyst is to

favour the production, or survival, of derivatives containing the 1-sulphonic acid group, and to minimise loss by destructive oxidation. Sulphuric acid (2 parts) and naphthol (1 part) at 20–28° for 4 min. give  $\beta$ -naphthol-1-sulphonic acid (90%) and -6-sulphonic acid (9%). In practice, it is better to continue the sulphonation for 24 hrs. at 30°, when 83% of 1 is formed and 74% can be isolated by precipitation with sodium chloride. In this case,  $\beta$ -naphthol-1:6-disulphonic acid, which forms the principal impurity, is more easily removed than the 6-sulphonic acid. When sufficient sulphuric acid to effect complete disulphonation is present, the 6-sulphonic, 8-sulphonic, and 1:6-disulphonic acids are formed in proportions varying from 2:7:81 at 0° to 20:27:53 at 85°. A further transformation of these products into the 3:6- and 6:8-disulphonic acids proceeds slowly at 35° and more rapidly at higher temperatures. For the preparation of the 1:6-disulphonic acid, naphthol (1 part) and sulphuric acid (3 parts) are heated in presence of boric acid at 45° for 30 hrs., when the ratio of products is 4:24:72 and 64% of 1:6-disulphonic acid is precipitated as the sodium salt (+3H<sub>2</sub>O) by sodium chloride. The potassium salt (+H<sub>2</sub>O) is obtained similarly. The 1-sulphonic acid group in the 1:6-disulphonic acid is displaced by coupling with the more reactive diazonium salts and by hydrolysis with dilute mineral acid at 85°.  $\beta$ -Naphthol-1-sulphonic acid is also obtained by very rapid sulphonation in absence of boric acid at 20–30°. Using more sulphuric acid and a reaction period of 24 hrs., the 1:6-disulphonic acid is obtained in yields decreasing from 74% at 2° to 23% at 25° and none at 85°. The yield of 8-sulphonic acid reaches a maximum (55%) at 25–30°, whilst that of 6-sulphonic acid increases from 3% at 0° to 74% at 85°. Boric acid also influences the course of sulphonations at 135°, increasing the yield of 1:6-disulphonic acid from 0 to 23%.

H. E. F. NOTTON.

Scission of diaryl ethers and related compounds by means of piperidine. V. Nitration of methyl, dimethyl, and polyhalogeno-derivatives of diphenyl ether. (Miss) D. L. FOX and E. E. TURNER (J.C.S., 1930, 1853–1867).—2-Chloro-2'-bromodiphenyl ether, b. p. 195–196°/10 mm., prepared by the usual method from the chloroamino-ether, is nitrated by nitric (*d* 1.5) and acetic acids to the 4:4'-dinitro-derivative, m. p. 150–151°. When nitration is effected with nitric acid at 100° some hydrogen halide is evolved (cf. this vol., 909). Introduction of a further nitro-group into diphenyl ethers substituted in the 2- and 4-positions of each nucleus with either two nitro-groups or one nitro-group and a halogen atom is not readily accomplished. The presence of methyl groups favours the introduction of more than one nitro-group. Chlorination of *p*-bromophenol in acetic acid affords 2-chloro-4-bromophenol, m. p. 50–51° (lit. 45°), the *p*-toluenesulphonate, m. p. 114–115°, of which gives with nitric acid (*d* 1.5) 2-chloro-4-bromo-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate, m. p. 107–108° (piperidine fission product 2-chloro-4-bromo-5-nitrophenol, m. p. 83°). Reduction of this ester with stannous chloride and hydrochloric and acetic acids, replace-

ment of the amino-groups by chlorine, and subsequent hydrolysis gives 2:5-dichloro-4-bromophenol, m. p. 71–72°, also obtained from 2:5-dichloro-4-bromoaniline, m. p. 91–92°, by Noelting and Kopp's method (A., 1905, i, 872). The last-named compound is prepared by the reduction with iron filings, 70% alcohol, and a small amount of hydrochloric acid of 1:4-dichloro-2-bromo-5-nitrobenzene, m. p. 57–58°, which is formed by nitrating 2:5-dichlorobromobenzene. 2-Chloro-4-bromophenol and 1-chloro-2:4-dinitrobenzene give a 95% yield of 2-chloro-4-bromo-2':4'-dinitrodiphenyl ether, m. p. 122–123°, which, like the 2:4-dichloro- and -dibromo-derivatives (A., 1929, 551; this vol., 907), undergoes nitration in the 5-position, yielding 2-chloro-4-bromo-5:2':4'-trinitrodiphenyl ether, m. p. 132–133° (piperidine scission products 2:4-dinitrophenylpiperidine and 2-chloro-4-bromo-5-nitrophenol). Treatment of 2:5-dichlorophenol (1 mol.) with bromine (1 mol.) in acetic acid containing sodium acetate (1 mol.) at 100° furnishes a mixture of 2:5-dichloro-4-bromo- and 2:5-dichloro-4:6-dibromo-phenol, m. p. 99–100°.

2:4:6-Trichloro-, m. p. 121–122°, 2:4:6-tribromo-, and 4-chloro-2:6-dibromo-2':4'-dinitrodiphenyl ethers, m. p. 145–146°, are all nitrated by nitric acid (*d* 1.5) at 100° to the corresponding 3:2':4'-trinitro-derivatives, m. p. 144–145°, 177–178°, and 157–159°, respectively; elimination of halogen does not occur. The trinitro-compounds show no tendency to undergo further nitration. They are decomposed by piperidine, forming 2:4-dinitrophenylpiperidine and the appropriate 2:4:6-trihalogeno-3-nitrophenol. 4-Chloro-2:6-dibromo-3-nitrophenol has m. p. 81–82°. 4-Chloro-2:6-dibromophenol, m. p. 89° (*p*-toluenesulphonate, m. p. 107–108°), is prepared by brominating *p*-chlorophenol in acetic acid. Bromination of 2:4-dichlorophenol or dichlorination of *o*-bromophenol affords 2:4-dichloro-6-bromophenol, b. p. 192°/12 mm., m. p. 68–69°, which with 1-chloro-2:4-dinitrobenzene yields 2:4-dichloro-6-bromo-2':4'-dinitrodiphenyl ether, m. p. 140–141°. Nitration of this at 100° gives a mixture (constant m. p. 149–149.5°) of 3:2':4'- and 5:2':4'-trinitro-derivatives, which were not separated but converted by piperidine into a mixture of 2:4-dichloro-6-bromo-3-, m. p. 78–79°, and -5-nitrophenols, m. p. 92–93°. These phenols are also obtained by bromination of the requisite dichloronitrophenol. Similar nitration of 2:4-dichloro-6-bromophenyl *p*-toluenesulphonate, m. p. 82–83°, yields a mixture (constant m. p. 122–125°) of 2:4-dichloro-6-bromo-3-, m. p. 122–122.5°, and -5-nitrophenyl *o*-nitro-*p*-toluenesulphonate, m. p. 134–135°, converted by piperidine into the above dichlorobromonitrophenols. These esters are also synthesised from the appropriate phenol and 2-nitro-*p*-toluenesulphonyl chloride. 2:3:4- and 2:4:5-Trichloro-6-bromophenols have m. p. 84–85° and 81–82°, respectively.

*p*-Cresol and 2:5-dibromonitrobenzene give 4-bromo-2-nitro-4'-methyldiphenyl ether, m. p. 109.5°, which with nitric and acetic acids yields an equimolecular compound (or mixture) of unchanged ether and 2:2'-dinitro-derivative. With nitric acid alone at

0°, a mixture of 4-bromo-2:6-dinitrophenol and a small amount of 4-bromo-2:2':3'-trinitro-4'-methyl-diphenyl ether, m. p. 166° (piperidine scission products 2:3-dinitro-*p*-cresol and 4-bromo-2-nitrophenyl-piperidine), results. 4-Bromo-2'-nitro-4'-methyl-diphenyl ether, m. p. 82°, and nitric acid give only 4-bromo-2:6-dinitrophenol. The last-named ether is converted by sulphuric acid at 100° into 2'-nitro-4'-methyl-diphenyl ether 4-sulphonic acid, m. p. 131—132°; under similar conditions the 2-nitro-isomeride is unaffected. These results are the reverse of those obtained with the analogous chloro-derivatives (this vol., 909). 2:4-Dinitro-4'-methyl-diphenyl ether, m. p. 97—98°, is nitrated to the 2:4:2'-trinitro-, m. p. 175—176°, and 2:4:2':3'-tetranitro-derivatives, m. p. 184°, whilst 2:4-dinitro-2':4'-dimethyl-diphenyl ether, m. p. 106°, affords 2:4:5'-trinitro-, m. p. 129—130° (piperidine scission products 2:4-dinitrophenyl-piperidine and 6-nitro-*m*-4-xylene), and 2:4:3':5'-tetranitro-derivatives, m. p. 198°. Piperidine scission of the tetranitro-compound furnishes 2:4-dinitrophenyl-piperidine and 2:6-dinitro-*m*-4-xylene, m. p. 162—163° (*p*-toluenesulphonate, m. p. 110—111°). Nitration of 6-nitro-*m*-4-xylene with nitric acid (*d* 1.5) at the ordinary temperature gives 5:6-dinitro-*m*-4-xylene, m. p. 119—120°, also obtained by the action of piperidine on 5:6-dinitro-*m*-4-xylene *o*-nitro-*p*-toluenesulphonate, m. p. 140—141°, formed by nitrating 5-nitro-*m*-4-xylene *p*-toluenesulphonate, m. p. 111—112°.

4-Chloro-2-nitro-2':4'-dimethyl-diphenyl ether, m. p. 77—78°, undergoes nitration, yielding the 2:5'-dinitro-, m. p. 88—89°, and 2:3':5'-trinitro-derivatives, m. p. 140°. 4-Bromo-2-nitro-2':4'-dimethyl-diphenyl ether, m. p. 89—90°, affords the 2:5'-dinitro-derivative, m. p. 98—99°, but further nitration causes elimination of halogen with the production of 2:4:5'-trinitro- and 2:4:3':5'-tetranitro-2':4'-dimethyl-diphenyl ethers. H. BURTON.

**Reaction between glyoxal and resorcinol.** J. MIKŠIĆ, A. REŽEK, and Z. PINTEROVIĆ (J. pr. Chem., 1930, [ii], 127, 189—194).—Glyoxal reacts with 4 mols. of resorcinol in presence of ether and phosphoric oxide, forming 16% of the theoretical yield of *s*-tetra-(2:4-dihydroxyphenyl)ethane (+0.5H<sub>2</sub>O), m. p. (anhydrous) 235—236° (decomp.) (octa-acetate, m. p. 270°), also obtained in 5% yield when condensation is effected with dry hydrogen chloride. Dissolution of the hydroxy-compound in sulphuric acid gives a fluorescent solution (xanthene formation); a solution of the acetyl derivative shows no fluorescence. Xanthene formation also occurs when the hydroxy-compound is heated with zinc chloride at 150° or alone at 180° for a long time. H. BURTON.

**Action of nitrous acid on resorcinol diethyl ether.** H. H. HODGSON and H. CLAY (J.C.S., 1930, 1872—1875).—Nitrosation of resorcinol diethyl ether in acetic acid containing hydrogen chloride (cf. Kraus, A., 1892, 44) or sulphuric acid gives an 80—90% yield of 4-nitroso-3-ethoxyphenol; reaction does not occur in acetic acid alone. Since 4-nitrosoresorcinol diethyl ether, m. p. 104°, prepared by oxidising 4-aminoresorcinol diethyl ether with persulphuric acid, is converted into the above phenol by treatment with

cold, dilute hydrochloric or sulphuric acid (not by 5% potassium hydroxide solution), it is probable that the first product of nitrosation is the diethyl ether. The decomposition of this by mineral acid probably proceeds with a greater velocity than the nitrosation, since no 4-nitrosoresorcinol diethyl ether could be isolated. H. BURTON.

**Primary additive products in indirect substitution in the benzene nucleus.** (Nitration and bromination of 4:4'-dialkoxydiphenyls.) J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 769—783).—Treatment of a solution of 4:4'-dimethoxydiphenyl in cold carbon tetrachloride with an emulsion of absolute nitric acid (2 mols.) in carbon tetrachloride affords an impure, indigo-blue additive dinitrate, also formed when finely-divided 4:4'-dimethoxydiphenyl is exposed to nitric acid vapour at the ordinary temperature. The dinitrate is decomposed by water, regenerating the reactants; it reacts with phenol forming *o*-nitrophenol, and when heated at 50—100°, or dissolved in acetone, acetic acid, or acetic anhydride, affords 3:3'-dinitro-4:4'-dimethoxydiphenyl, m. p. 221°. Bromination of 4:4'-dimethoxydiphenyl in boiling acetic acid gives the 3:3'-dibromo-derivative, m. p. 167°, which on exposure to bromine vapour in the dark forms a green additive dibromide. The dibromo-compound also forms a green mononitrate, which when heated to 100° passes into 3:3'-dibromo-5-nitro-4:4'-dimethoxydiphenyl, m. p. 178°, also prepared by nitration of the dibromo-derivative in boiling carbon tetrachloride. When 4:4'-dimethoxydiphenyl is exposed to bromine vapour for 24 hrs., a tetrabromo-derivative, m. p. 139°, is produced. This is not identical with 3:5:3':5'-tetrabromo-4:4'-dimethoxydiphenyl, m. p. 209°, obtained by methylation of the 4:4'-dihydroxy-compound. 4:4'-Dihydroxy- and 4:4'-diethoxy-diphenyls also furnish coloured dinitrates, which when heated pass into the 3:3'-dinitro-derivatives. The above additive compounds are formulated as oxonium salts; their isolation supports the theory previously proposed (A., 1928, 57).

3:5:3':5'-Tetranitro-4:4'-dimethoxydiphenyl has m. p. 255° (lit. 242° and 244.6°). H. BURTON.

**Mixed aromatic hydroxysulphones.** II. **Hydroxyphenyl-*o*-hydroxytolylsulphones.** J. ZEHESTER and F. PLASS (J. pr. Chem., 1930, [ii], 127, 263—268).—When a mixture of phenol and *o*-cresol is heated with fuming sulphuric acid (8—10% SO<sub>3</sub>) at 175—180° there are formed 4:4'-dihydroxydiphenylsulphone, di-*o*-hydroxyditolylsulphone, phenol- and *o*-cresol-sulphonic acids, and three hydroxyphenyl-*o*-hydroxytolylsulphones. These isomerides are designated  $\alpha$ -, m. p. 246—247° [main product; diacetate, m. p. 129°; dibenzoate, m. p. 188°; tribromo-derivative, m. p. 266—267°; dinitro-derivative, m. p. 210—212°, obtained by the action of nitric acid (*d* 1.1) at 100°];  $\beta$ -, m. p. 237° (diacetate, m. p. 134—135°; dibenzoate, m. p. 196°; dinitro-derivative, m. p. 214—215°; tribromo-derivative, m. p. 270—271°), and  $\gamma$ -, m. p. 204° (diacetate, m. p. 120°; dibenzoate, m. p. 155°). Hydrolysis of the  $\beta$ -diacetate or -dibenzoate affords the  $\alpha$ -compound, which on prolonged treatment with sulphuric acid at the



ordinary temperature yields a disulphonic acid (barium salts +3 and  $7\text{H}_2\text{O}$ ). Sulphonation of the  $\alpha$ -derivative at  $100^\circ$  gives phenol- and *o*-cresol-4-sulphonic acids, indicating that the  $\alpha$ -compound is *p*-hydroxyphenyl-4-hydroxy-*m*-tolylsulphone.

H. BURTON.

Reduction of organic halogen compounds and compounds of the tetra-arylbutane series. X. Compounds of the tetra-arylbutane series. K. BRAND and W. BAUSCH. XI. Electrochemical preparation of  $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- and  $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\beta}$ -butinenes. K. BRAND, O. HORN, and W. BAUSCH (J. pr. Chem., 1930, [ii], 127, 219–239, 240–247).—X. Reduction of  $\beta\beta\gamma$ -tribromo- $\alpha\alpha$ -di-*p*-phenetylene with hydrogen in presence of alcoholic pyridine and palladised calcium carbonate at  $45$ – $50^\circ$  gives about 32% of  $\beta\gamma$ -dibromo- $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\beta}$ -butene, m. p.  $184.5^\circ$  (cf. Brand and Kercher, A., 1921, i, 787), together with a small amount of 4:4'-diethoxystilbene. In some of the above reduction experiments hydrogen is not absorbed, but  $\beta\beta$ -dibromo- $\alpha\alpha$ -di-*p*-phenetylene is formed, probably by dehydrogenation of the alcohol and subsequent reduction of the tribromo-compound. The dibromoethane and alcoholic sodium ethoxide afford  $\beta$ -bromo- $\alpha\alpha$ -di-*p*-phenetylene, whilst the tribromo-compound and 10% alcoholic potassium hydroxide give  $\beta\beta$ -dibromo- $\alpha\alpha$ -di-*p*-phenetylene, m. p.  $118.5^\circ$ . Reduction of  $\beta\gamma$ -dibromo- $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\beta}$ -butene with zinc dust and alcohol or acetic acid yields  $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\beta}$ -butinene, m. p.  $96^\circ$  (see below). Bromine is not eliminated from the above dibromobutene by catalytic reduction or treatment with copper-bronze in benzene or sodium iodide in acetone. Treatment of the dibromobutene with amyl-alcoholic sodium ethoxide affords  $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\beta\gamma}$ -butatriene (A., 1927, 549) together with a small amount of 5-ethoxy-1-*p*-phenetyl-3-di-*p*-phenetylmethyleneindene (*loc. cit.*).

$\beta\beta\gamma$ -Trichloro- $\alpha\alpha$ -di-*p*-chlorophenylethane is reduced similarly to the above tribromoethane, yielding either a mixture of  $\beta\gamma$ -dichloro- $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\beta}$ -butene (I), m. p.  $229^\circ$  (35.6%), and a small amount of an isomeride (II), m. p.  $174^\circ$ , or  $\beta\beta\gamma\gamma$ -tetra-*p*-chloro- $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenylbutane, m. p.  $271.5^\circ$ . The last-named compound is reduced further to I by the same process; with zinc dust and acetic acid  $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\beta}$ -butinene, m. p.  $174^\circ$ , results. Treatment of I or II with amyl-alcoholic sodium ethoxide gives  $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\beta\gamma}$ -butatriene, m. p.  $288^\circ$  (decomp.), together with a small amount of low melting material. Oxidation of this butatriene with chromic and acetic acids yields 4:4'-dichlorobenzophenone, whilst reduction with zinc dust and acetic acid affords a mixture of the above butinene and  $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\beta\gamma}$ -butadiene, m. p.  $244^\circ$  (also formed when the butinene is treated with alcoholic sodium ethoxide solution). Reduction of the butatriene with sodium and amyl alcohol yields impure  $\alpha\alpha\delta\delta$ -tetraphenylbutane, whilst prolonged treatment with a saturated solution of hydrogen chloride in acetic acid at  $100^\circ$  furnishes a mixture of 5-chloro-1-*p*-chlorophenyl-3-di-*p*-chlorophenylmethyleneindene, m. p.  $222^\circ$ , and an additive compound,  $\text{C}_{28}\text{H}_{17}\text{Cl}_5$ , m. p.  $158^\circ$ . Treatment of the last-named

compound with alcoholic sodium ethoxide regenerates the above butatriene, which under the influence of sunlight passes into a dimeride, m. p.  $323.5^\circ$  (decomp.).

XI. Electrolytic reduction of  $\beta\beta\gamma$ -trichloro- $\alpha\alpha$ -di-*p*-phenetylene with a lead cathode and alcoholic hydrochloric acid as the cathode solution gives 4:4'-diethoxystilbene (8%) and  $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\beta}$ -butinene (35%). Treatment of the butinene with alcoholic sodium ethoxide affords  $\alpha\alpha\delta\delta$ -tetra-*p*-phenetyl- $\Delta^{\beta\gamma}$ -butadiene, m. p.  $202^\circ$ . Similar reduction of  $\beta\beta\gamma$ -trichloro- $\alpha\alpha$ -di-*p*-chlorophenylethane yields 4:4'-dichlorostilbene (trace) and  $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\beta}$ -butinene (13%). This butinene and  $\alpha\alpha\delta\delta$ -tetra-*p*-chlorophenyl- $\Delta^{\beta\gamma}$ -butadiene are both oxidised by chromic and acetic acids to 4:4'-dichlorobenzophenone; the butadiene is not affected by treatment with zinc dust and acetic acid.

H. BURTON.

Pyrolysis of aryl allyl sulphides. C. D. HURD and H. GREENGARD (J. Amer. Chem. Soc., 1930, 52, 3356–3358).—When phenyl allyl sulphide, b. p.  $215$ – $218^\circ/750$  mm.,  $104$ – $106^\circ/25$  mm.,  $n_D^{20}$  1.4772, obtained from sodium thiophenoxide and allyl bromide in alcohol, is refluxed for 6 hrs., about 25% of *o*-allylthiophenol, b. p.  $183$ – $190^\circ/17$  mm.,  $n_D^{20}$  1.6098 (lead salt), is produced together with a small amount of 2-methyl-2:3-dihydrothionaphthen, b. p.  $103$ – $108^\circ/8$  mm.,  $n$  1.5811. Oxidation of *o*-allylthiophenol with potassium permanganate gives *o*-sulphobenzoic acid. Similarly, *p*-tolyl allyl sulphide, b. p.  $123$ – $127^\circ/25$  mm.,  $n_D^{20}$  1.5711, affords some 2-allyl-*p*-thiocresol, b. p.  $190$ – $196^\circ/11$  mm.,  $n_D^{20}$  1.6921 [lead salt, m. p.  $330^\circ$  (decomp.)], oxidised to 4-sulphoisophthalic acid, sublimes at  $320^\circ$ .

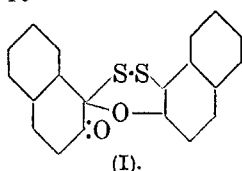
H. BURTON.

Derivatives of diphenyl sulphide and diphenyl ether. R. B. SANDIN and W. V. DRAKE (J. Amer. Chem. Soc., 1930, 52, 3353–3356).—3:4:5-Triiodonitrobenzene and *p*-methoxythiophenol react in presence of methyl ethyl ketone and anhydrous potassium carbonate, forming 2:6-di-iodo-4-nitro-4'-methoxydiphenyl sulphide (60% yield), m. p.  $138$ – $139^\circ$  (all m. p. are corr.), reduced to 2:6-di-iodo-4-amino-4'-methoxydiphenyl sulphide, m. p.  $172$ – $173^\circ$  [hydrochloride, m. p.  $200^\circ$  (decomp.)]; acetyl derivative, m. p.  $230^\circ$ . 2:6-Di-iodo-4-nitro-2'-(25% yield), m. p.  $149$ – $150^\circ$ , and -3'-methoxydiphenyl ethers (45–50%), m. p.  $139$ – $140^\circ$ , are obtained similarly, using guaiacol and resorcinol monomethyl ether, respectively. These are reduced to 2:6-di-iodo-4-amino-2', m. p.  $178$ – $179^\circ$  [hydrochloride, m. p.  $236$ – $237^\circ$  (decomp.)]; acetyl derivative, m. p.  $227$ – $228^\circ$ ; benzoyl derivative, m. p.  $239$ – $240^\circ$ , and 2:6-di-iodo-4-amino-3'-methoxydiphenyl ethers, m. p.  $124$ – $125^\circ$  [hydrochloride, m. p.  $132$ – $134^\circ$  (decomp.)]; acetyl derivative, m. p.  $177$ – $178^\circ$ ; benzoyl derivative, m. p.  $201$ – $202^\circ$ , respectively.

H. BURTON.

$\beta$ -Naphtha-1-thioquinone and dehydro-2-naphthol 1-disulphide. H. A. STEVENSON and S. SMILES (J.C.S., 1930, 1740–1745).—Treatment of a mixture of  $\beta$ -naphthol and sodium thiocyanate in 96% acetic acid with a solution of bromine in acetic acid (cf. Kaufmann, A., 1926, 392; 1929, 436) affords 2-naphthyl 1-thiocyanate. Reduction of this with zinc dust and acetic acid containing a small amount

of hydrochloric acid, separation of the 2-naphthylene 1-thiolcarbonate,  $C_{10}H_6\langle\overset{\text{S}}{\text{O}}\rangle\text{CO}$ , m. p.  $106^\circ$ , formed, and oxidation of the residual solution with hydrogen peroxide affords 2-naphthol 1-disulphide. Hydrolysis of the thiolcarbonate with aqueous-alcoholic sodium hydroxide affords the disulphide; with cold alcoholic sodium ethoxide, 2-naphthol-1-ethylthiolcarbonate, m. p.  $127^\circ$ , results. The above thiolcarbonate is also formed when a solution of 2-naphthyl 1-thiocyanate in acetic acid containing a small amount of sulphuric acid is boiled for 15 min. Reduction of 2-naphthol 1-disulphide with zinc dust and acetic-hydrochloric acids gives 1-thiol-2-naphthol, m. p.  $55^\circ$ , whilst treatment with bromine in carbon tetrachloride furnishes 1-bromothiol-2-naphthol, m. p.  $93\text{--}95^\circ$ . Treatment of this bromothiol with 2 mols. of  $\beta$ -naphthol in carbon tetrachloride affords 2-naphthol 1-sulphide; with 6-bromo-2-naphthol, 6-bromo-2:2'-dihydroxy-1:1'-dinaphthyl sulphide, m. p.  $131^\circ$ , results. 1-Bromo-2-naphthol and the bromothiol react in presence of carbon tetrachloride and pyridine forming about 30% of dehydro-2-naphthol 1-sulphide (this vol., 908). Treatment of the bromothiol with pyridine in carbon tetrachloride affords dehydro-2-



naphthol 1-disulphide (I), m. p.  $171^\circ$ , presumably by spontaneous polymerisation of the intermediate  $\beta$ -naphtha-1-thioquinone. The same disulphide is also produced by oxidation of 2-naphthol 1-disulphide with alkaline potassium ferricyanide in presence of benzene. Reduction of I with zinc dust and acetic and hydrochloric acids furnishes hydrogen sulphide and iso-2-naphthol sulphide (*loc. cit.*). Dehydro-2-naphthol 1-sulphide cannot be prepared from 1-thiol-2-naphthol and  $\beta$ -naphthaquinone; the normal type of nuclear additive product (G.P. 175,070) is formed.

H. BURTON.

**Synthesis of cinnamyl alcohol and homologues.** L. BERT and P. C. DORIER (*Compt. rend.*, 1930, **191**, 378—380).—Cinnamyl chloride (for synthesis see this vol., 1290) by treatment with fused sodium acetate in boiling glacial acetic acid yields cinnamyl acetate, b. p.  $138^\circ/15$  mm.,  $d_4^{25}$  1.0603,  $n_D^{25}$  1.555. The following substituted cinnamyl acetates are obtained similarly: o-methyl-, b. p.  $147^\circ/15$  mm.,  $d_4^{25}$  1.043,  $n_D^{25}$  1.544; p-methyl-, b. p.  $149^\circ/15$  mm.,  $d_4^{25}$  1.0153,  $n_D^{25}$  1.541; 2:4-dimethyl-, b. p.  $161^\circ/15$  mm.,  $d_4^{25}$  1.033,  $n_D^{25}$  1.540; 2:5-dimethyl-, b. p.  $160^\circ/15$  mm.,  $d_4^{25}$  1.018,  $n_D^{25}$  1.541; p-isopropyl-, b. p.  $164^\circ/15$  mm.,  $d_4^{25}$  0.994,  $n_D^{25}$  1.533; 2:5-methylisopropyl-, b. p.  $174^\circ/15$  mm.,  $d_4^{25}$  0.990,  $n_D^{25}$  1.530. By hydrolysis with potassium hydroxide cinnamyl alcohol, b. p.  $139^\circ/15$  mm.,  $d_4^{25}$  1.032,  $n_D^{25}$  1.576, and the following substituted cinnamyl alcohols are obtained: o-methyl-, b. p.  $149^\circ/15$  mm.,  $d_4^{25}$  1.0302,  $n_D^{25}$  1.578; p-methyl-, b. p.  $152^\circ/15$  mm.,  $d_4^{25}$  1.005,  $n_D^{25}$  1.565; 2:4-dimethyl-, b. p.  $155^\circ/15$  mm.,  $d_4^{25}$  1.020,  $n_D^{25}$  1.569; 2:5-dimethyl-, b. p.  $156^\circ/15$  mm.,  $d_4^{25}$  1.004,  $n_D^{25}$  1.564; p-isopropyl-, b. p.  $161^\circ/15$  mm.,  $d_4^{25}$  0.977,  $n_D^{25}$  1.548; 2:5-methylisopropyl-, b. p.  $164^\circ/15$  mm.,  $d_4^{25}$  0.974,  $n_D^{25}$  1.547.

C. W. SHOPPEE.

**Amino-alcohols. II. Homologues and analogues of phenylpropanolamine.** W. H. HARTUNG, J. C. MUNCH, W. A. DECKERT, and F. CROSSLEY (*J. Amer. Chem. Soc.*, 1930, **52**, 3317—3322).—The following aryl  $\alpha$ -oximoalkyl ketones are prepared by the method previously described (A., 1929, 1066): phenyl  $\alpha$ -oximopropyl, m. p.  $49^\circ$ ; p-tolyl  $\alpha$ -oximopropyl, m. p.  $78^\circ$ ; phenyl  $\alpha$ -oximobutyl, m. p.  $69^\circ$ ; phenyl  $\alpha$ -oximinoamyl, m. p.  $53\text{--}54^\circ$ , and phenyl  $\alpha$ -oximoheptyl ketones, m. p.  $38.5^\circ$ . These are reduced by hydrogen in presence of palladium and alcoholic hydrogen chloride to the following amino-alcohols:  $\beta$ -amino- $\alpha$ -phenylbutyl alcohol, m. p.  $80.5\text{--}81^\circ$  (lit.  $76\text{--}78^\circ$ ) (hydrochloride, m. p.  $242^\circ$ );  $\beta$ -amino- $\alpha$ -p-tolylbutyl alcohol, m. p.  $85^\circ$  (hydrochloride, m. p.  $255^\circ$ );  $\beta$ -amino- $\alpha$ -phenylamyl alcohol, m. p.  $70\text{--}71^\circ$  (hydrochloride, m. p.  $222^\circ$ );  $\beta$ -amino- $\alpha$ -phenylhexyl alcohol, m. p.  $72\text{--}72.5^\circ$  (lit.  $65\text{--}66^\circ$ ) (hydrochloride, m. p.  $197.5\text{--}198^\circ$ ), and  $\beta$ -amino- $\alpha$ -phenyloctyl alcohol, m. p.  $79^\circ$  (hydrochloride, m. p.  $157.5^\circ$ ).  $\beta$ -Amino- $\alpha$ -diphenylethyl alcohol, m. p.  $165^\circ$  (hydrochloride, m. p.  $235^\circ$ ), is prepared by similar reduction of  $\alpha$ - or  $\beta$ -benziloxime. Phenyl heptyl ketone, b. p.  $150\text{--}153^\circ/7$  mm. (semicarbazone, m. p.  $125\text{--}125.5^\circ$ ), is obtained by the Friedel-Crafts reaction. Pharmacological data for the amino-alcohols are given; the toxicities of the alcohols increase with lengthening of the carbon chain.

H. BURTON.

**Preparation of cyclopentane derivatives.** W. R. EDWARDS, jun., and E. E. REID (*J. Amer. Chem. Soc.*, 1930, **52**, 3235—3241).—The following cyclopentylalkylcarbinols are prepared from magnesium cyclopentyl bromide and the requisite aldehyde: methyl, b. p.  $85\text{--}85.5^\circ/52.5$  mm.,  $d_4^{25}$  0.9163 (3:5-dinitrobenzoate, m. p.  $86^\circ$ );  $\alpha$ -naphthylcarbinol derivative, m. p.  $104^\circ$ ; ethyl, b. p.  $97.5\text{--}98.5^\circ/52.5$  mm.,  $d_4^{25}$  0.9035,  $n$  1.4502 (3:5-dinitrobenzoate, m. p.  $83.5^\circ$ );  $\alpha$ -naphthylcarbinol derivative, m. p.  $91^\circ$ ; n-propyl, b. p.  $114.5\text{--}115.5^\circ/52$  mm.,  $d_4^{25}$  0.8970,  $n$  1.4510 (3:5-dinitrobenzoate, m. p.  $85^\circ$ );  $\alpha$ -naphthylcarbinol derivative, m. p.  $85^\circ$ ; n-butyl, b. p.  $114\text{--}115^\circ/23$  mm.,  $d_4^{25}$  0.8935,  $n$  1.4548 (3:5-dinitrobenzoate, m. p.  $63.5^\circ$ ); n-hexyl, b. p.  $129.5\text{--}130.5^\circ/12\text{--}12.5$  mm.,  $d_4^{25}$  0.8848,  $n$  1.4562. Phenylcyclopentylcarbinol has b. p.  $129\text{--}131^\circ/5$  mm.,  $d_4^{25}$  1.0346. All m. p. and b. p. are corr. 2:5-Dibenzylidene- and 2:5-dianisylidene-cyclopentanones are formed as by-products when the reaction mixtures from magnesium cyclopentyl bromide and benzaldehyde and anisaldehyde, respectively, are decomposed with hydrochloric acid. These probably arise from cyclopentanone (in the cyclopentyl bromide used) which does not appear to react with the Grignard reagent.

H. BURTON.

**Isomerisation of ergosterol.** C. E. BILLS and F. G. McDONALD (*J. Biol. Chem.*, 1930, **88**, 337—346).—Fractional crystallisation from alcohol of the isomerides of ergosterol described by the author (this vol., 84) as also of the isoergosterol of Heilbron and Spring (*ibid.*, 210) afforded a number of (still impure) products with varying optical rotations, molecular extinction coefficients, and m. p.; the existence of numerous isomerides is thus indicated.

C. R. HARTINGTON.

**ωωω-Trifluoro-*o*-toluic acid and ωωω-trifluoro-6-nitro-*m*-cresol.** S. DE BROUWER (Bull. Soc. chim. Belg., 1930, 39, 298—308).—Prolonged hydrolysis of *o*-cyanobenzotrifluoride (Rouché, A., 1928, 876) with 10% sodium hydroxide solution affords **ωωω-trifluoro-*o*-toluic acid**, b. p. 247° (corr.)/753 mm., m. p. 108.5° [sodium (+2H<sub>2</sub>O), lead (+2H<sub>2</sub>O), barium (+2H<sub>2</sub>O), calcium (+2H<sub>2</sub>O), and silver salts; *amide*, m. p. 161°, prepared from the *methyl ester*, b. p. 207°/757 mm., 106°/20 mm., *d*<sub>15</sub> 1.3062, and saturated ammonia solution at 110°]. The acid (*k*=2.57×10<sup>-3</sup>) is 15.7 times as strong as the *m*-isomeride and twice as strong as phthalic acid.

During the hydrolysis of the nitration product of *m*-acetamidobenzotrifluoride with 20% sodium hydroxide solution (Rouché, *loc. cit.*), some **ωωω-trifluoro-6-nitro-*m*-cresol**, b. p. 173°/14 mm., m. p. 78.5—79°, *k*=4.4×10<sup>-7</sup> (barium salt), is produced. This is unaffected by chlorosulphonic acid at the ordinary temperature, sulphuric acid at 130—140°, or 75% hydrobromic acid in presence of silica at 140°.

H. BURTON.

**Walden inversion. XIV. Influence of substituent groups on optical rotation in  $\alpha$ -phenyl-aliphatic acids.** P. A. LEVENE, L. A. MIKESKA, and K. PASSOTH (J. Biol. Chem., 1930, 88, 27—59).—The order of effect of substituent groups on optical rotation in the  $\alpha$ -methyl-aliphatic acid series (this vol., 63) does not hold good for the corresponding  $\alpha$ -phenyl series, in which the descending order is ·CO<sub>2</sub>H, ·CHOH, ·CH<sub>2</sub>Hal, ·CN; thus in the nitriles, substitution of methyl by phenyl actually reverses the direction of rotation. The *l*-nitriles obtained from *d*- $\alpha$ -phenylpropionic and *d*- $\alpha$ -phenylbutyric acids yield *l*- and *d*-amines, respectively, which apparently represents a case of reversal of rotation accompanying substitution of ethyl for methyl. *d*- $\alpha$ -Phenyl-*n*-valeric acid (itself related to *d*- $\alpha$ -phenyl-*n*-butyric and *d*- $\alpha$ -phenylpropionic acids) when hydrogenated gives *l*- $\alpha$ -cyclohexyl-*n*-valeric acid, from which the unexpected result follows that the latter is configuratively related to *d*- $\alpha$ -cyclohexyl-*n*-butyric and *d*- $\alpha$ -cyclohexylpropionic acids. In all series conversion of the *d*-carbinol into the halide has been accompanied by change of rotation towards the left, which confirms the conclusions of Levene and Mikeska (A., 1928, 170).

*dl*- $\alpha$ -Phenylpropionic acid was resolved with the aid of quinine to give the *l*-acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -59.7° in ether; this was converted successively into the *l*-chloride, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -68.8° in ether, *l*-amide, m. p. 92°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -26.3° in 75% alcohol, *d*- $\alpha$ -phenylpropionitrile, b. p. 109°/8 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12.7° in ether, *d*- $\beta$ -phenyl-*n*-propylamine, b. p. 90°/12 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12.4° in ether (*hydrobromide*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +16.4° in water). The latter amine gave, with nitrosyl chloride, *d*- $\alpha$ -chloro- $\beta$ -phenylpropane, b. p. 52—54°/1 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +0.33° in ether, and *l*- $\beta$ -phenyl-*n*-propyl alcohol, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -16.3° in ether (isolated through the *hydrogen phthalate*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -16.5° in ether). The above chloro-compound yielded *d*- $\alpha$ -thiol- $\beta$ -phenylpropane, b. p. 70—71°/1.5 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +9.3° in ether, whilst *d*- $\alpha$ -phenylpropionyl chloride, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +44.9° in ether, afforded *d*- $\alpha$ -phenylthiopropionic acid, b. p. 136—138°/3 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +61.6° in ether. *dl*- $\alpha$ -Phenyl-*n*-butyric acid was converted through the cinchonidine salt into the *d*-acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +81.0° in ether (*sodium*

salt, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +8.2° in water; *ethyl ester*, b. p. 80—85°/3 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +72.2° in ether). From the *d*-acid were derived successively the *d*-chloride, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +89.0° in ether, *d*-amide, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +19.9° in 75% alcohol, *l*- $\alpha$ -phenylbutyronitrile, b. p. 56—57°/4.1 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -27.6° in ether, and *d*- $\beta$ -phenyl-*n*-butylamine, b. p. 74°/2.6 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +9.7° in ether (*hydrobromide*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -2.1° in water). The amine yielded, with nitrosyl chloride, *d*- $\alpha$ -chloro- $\beta$ -phenyl-*n*-butane (87% pure), b. p. 62—64°/1 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +11.2° in ether, and, with nitrous acid, *d*- $\beta$ -phenyl-*n*-butyl alcohol, b. p. 95—96°/4 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +30.0° in ether; the chloro-compound afforded *d*- $\alpha$ -thiol- $\beta$ -phenyl-*n*-butane, b. p. 81°/1.3 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +7.0° in ether (with the corresponding *disulphide*, b. p. 178—180°/1.5 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -31.1° in ether), which was oxidised to *l*- $\beta$ -phenyl-*n*-butane- $\alpha$ -sulphonic acid (impure), [ $\alpha$ ]<sub>D</sub><sup>20</sup> -32.7° in water (*barium salt*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -27.6° in water); *l*- $\beta$ -phenyl-*n*-butyryl chloride, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -23.7° in ether, gave *l*- $\beta$ -phenylthio-*n*-butyric acid, b. p. 124—125°/13 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -35.2° in ether. *l*- $\alpha$ -Phenylpropionic acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -54.6° in ether, was reduced with hydrogen and platinum to *l*- $\alpha$ -cyclohexylpropionic acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -12.5° in ether (*sodium salt*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -1.9° in water), from which were prepared the *l*-chloride, b. p. 54°/12 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -7.6° in ether, *l*-amide, m. p. 138—139°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -9.9° in 75% alcohol, *l*- $\alpha$ -cyclohexylpropionitrile, b. p. 80°/3 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> -13.3° in ether, and  $\beta$ -cyclohexyl-*n*-propylamine, b. p. 65—66°/2 mm., which was optically inactive. *d*- $\alpha$ -Phenyl-*n*-butyric acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +79.8° in ether, yielded *d*- $\alpha$ -cyclohexyl-*n*-butyric acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +2.4° in ether, and *l*- $\alpha$ -phenyl-*n*-valeric acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -16.3° in ether (from the *dl*-acid through the cinchonidine salt), gave *d*- $\alpha$ -cyclohexyl-*n*-valeric acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +2.2° in ether. *d*- $\alpha$ - $\beta$ -Diphenylpropionic acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +36.6° in ether (from the *dl*-acid through the quinine salt), was converted successively into the *d*-chloride, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +43.0° in ether, *d*-amide, m. p. 134°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +41.2° in 95% alcohol (partly racemised), and *l*-nitrile, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -7.9° in alcohol. The inactive nitrile was reduced to  $\alpha$ - $\beta$ -diphenylpropylamine, which was resolved with the aid of tartaric acid to give the *l*-amine, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +40.1° in ether; a preparation with [ $\alpha$ ]<sub>D</sub><sup>20</sup> +27.1° in ether gave, with nitrous oxide, *d*- $\alpha$ - $\beta$ -diphenylpropanol, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +18.6° in ether, and with nitrosyl chloride *d*- $\alpha$ -chloro- $\beta$ - $\gamma$ -diphenylpropane, b. p. 130—132°/0.3 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +12.2° in ether; the latter yielded *l*- $\alpha$ -thiol- $\beta$ - $\gamma$ -diphenylpropane, b. p. 123—127°/0.3 mm., [ $\alpha$ ]<sub>D</sub><sup>20</sup> +13.3° in ether, which was oxidised to *d*- $\beta$ - $\gamma$ -diphenylpropane-sulphonic acid, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +11.2° in water (*barium salt*, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +11.5° in water). C. R. HARRINGTON.

**Optical resolution of 2:4-dinitro-2'-methyl-diphenyl-6-carboxylic acid.** (MISS) M. S. LESSLIE and E. E. TURNER (J.C.S., 1930, 1758—1765).—When equimolecular quantities of ethyl 2-chloro-3:5-dinitrobenzoate and iodobenzene are heated with copper-bronze at 220—240°, *ethyl 2:4-dinitrodiphenyl-6-carboxylate*, m. p. 84—85°, is produced as the sole product. The free acid, m. p. 193—194°, obtained only by hydrolysis of the ester with sulphuric and acetic acids, is converted by sulphuric acid at 100° into 2:4-dinitrofluorenone. *m*-Iodobenzene, ethyl 2-chloro-3:5-dinitrobenzoate, and copper-bronze at 220—230° give the *ethyl ester*, m. p. 120—121°, of

2:4-dinitro-3'-methylphenyl-6-carboxylic acid, m. p. 118—119°. The above acids could not be resolved by brucine. When they are incompletely esterified with *l*-menthol, the unesterified acid is optically inactive. Ethyl 2:4-dinitro-2'-methylphenyl-6-carboxylate, m. p. 95—96°, is hydrolysed as above to the free acid (I), m. p. 156—157°, which is resolved by brucine (using the fractional crystallisation method) into *d*- and *l*-isomerides, m. p. 158—159°,  $[\alpha]_{D}^{25} \pm 18.7^\circ$  in alcohol. Crystallisation of these from benzene gives optically active acids ( $[\alpha]_{D}^{25} \pm 7.8^\circ$  in alcohol) containing 0.5 mol. of benzene of crystallisation, which is not removed by repeated evaporation of alcoholic solutions. The acid remaining unesterified during partial esterification of I with *l*-menthol at 140° has  $[\alpha]_{D}^{25} + 2.8^\circ$  in acetone. Esterification of 2-chloro-3:5-dinitrobenzoic acid with *l*-menthol at 150° affords *l*-menthyl 2-chloro-3:5-dinitrobenzoate, m. p. 113—114°,  $[\alpha]_{D}^{25} - 53.6^\circ$  in acetone, which with *o*-iodotoluene and copper-bronze gives an ester, hydrolysed to 2:4-dinitro-2'-methylphenyl-6-carboxylic acid,  $[\alpha]_{D}^{25} + 4.4^\circ$  in acetone; with iodo-benzene, only a very small amount of product results.

The above facts suggest that it is unnecessary to replace the theory explaining the resolution of 2-phenylnaphthylene-1:3-diamine (A., 1929, 1061) by a purely stereochemical one. H. BURTON.

**Activated silica gel in the esterification of salicylic acid and of  $\beta$ -naphthol.** R. CHELBERG and G. B. HEISIG (J. Amer. Chem. Soc., 1930, 52, 3023).—Commercial "silica gel" activated by treatment with air at 150°, unlike the product of Korolev (A., 1928, 637), failed to catalyse the reaction between methyl alcohol and salicylic acid or  $\beta$ -naphthol.

H. E. F. NOTTON.

**Mutarotation of optically active esters of  $\alpha$ -keto-acids.** A. MCKENZIE and A. G. MITCHELL (Biochem. Z., 1930, 224, 242—252).—The authors' previous paper (A., 1929, 877) is extended. Both cinchonine and cinchonidine give crystalline derivatives with phenylglyoxylic acid; cinchonidine phenylglyoxylate has m. p. 176—177°,  $[\alpha]_{D}^{25} - 88^\circ$ ; cinchonine phenylglyoxylate, m. p. 258°,  $[\alpha]_{D}^{25} + 148.5^\circ$ . Evidence of the existence in these products of two optically isomeric forms could not be obtained. The rates of mutarotation of the *d*- and *l*-bornyl pyruvates are the same after careful fractionation of these esters in a vacuum, the previous quicker mutarotation of the *d*-ester being due to the presence of a trace of some catalyst. The acceleration of mutarotation by hydrochloric acid and by pyridine of *l*-menthyl phenylglyoxylate and *d*- and *l*-bornyl pyruvate is followed. When two drops of 1.47*N*-ethyl-alcoholic potassium hydroxide are added to an alcoholic solution of *l*-menthyl phenylglyoxylate, an acceleration of mutarotation first occurs, followed by a gradual exchange of the menthyl for the ethyl radical.

P. W. CLUTTERBUCK.

**Unsaturated 1:4-diketones. V. Configurations of unsaturated dibromo-1:4-diketones and -ketonic acids. Synthesis and structure of *cis*- and *trans*- $\alpha\beta$ -dibromo- $\beta$ -benzoylacrylic acids and derivatives. VI. Synthesis and configurations of unsaturated 1:4-diketones and**

**ketonic acids, and the stereochemical mechanism of the addition of bromine.** R. E. LUTZ (J. Amer. Chem. Soc., 1930, 52, 3405—3422, 3423, 3436).—V. Dibromomaleic anhydride and benzene in presence of aluminium chloride give *cis*- $\alpha\beta$ -dibromo- $\beta$ -benzoylacrylic acid, m. p. 92° (all m. p. and b. p. are corr. except where stated otherwise), esterified by methyl-alcoholic hydrogen chloride to the methyl ester, m. p. 71.5°. Hydrolysis of the ester with alcoholic sodium ethoxide at the ordinary temperature regenerates the acid, but with aqueous sodium hydroxide benzoic acid results. The dibromo-acid is stable towards reagents which usually effect isomerisation, it is reduced by zinc dust and acetic acid to  $\beta$ -benzoyl-propionic acid, and gives with phosphorus pentachloride the  $\psi$ -chloride,  $\text{C}_6\text{H}_5\text{Cl} \cdot \text{CBr} \cdot \text{CBr} \cdot \text{CO}$ , m. p. 82.5°, which is hydrolysed only slowly by water. This chloride reacts with benzene in presence of aluminium chloride forming 2-bromo-1:1-diphenylindene-3-carboxylic acid, m. p. 242—243° (decomp.), oxidised by alkaline potassium permanganate to diphenylphthalide. The indene is also formed in small amount from benzene and dibromomaleic chloride. The  $\psi$ -chloride, m. p. 76°, from *cis*- $\alpha\beta$ -dibromo- $\beta$ -2:4:6-trimethylbenzoylacrylic acid, m. p. 157°, obtained by the Friedel-Crafts reaction with dibromomaleic anhydride and mesitylene, reacts with mesitylene in presence of aluminium chloride and carbon disulphide, forming a small amount of a compound,  $\text{C}_{21}\text{H}_{22}\text{O}_3\text{Br}$ , m. p. 240—242° (uncorr.).

Treatment of dibromofumaryl chloride with 1 equivalent of methyl alcohol in benzene gives the chloride, b. p. 83—86°/3.5 mm., of methyl hydrogen dibromofumarate (the dimethyl ester has b. p. 113—114°/5 mm., m. p. 41.5°), which gives with benzene and aluminium chloride the methyl ester, m. p. 80.5°, of *trans*- $\alpha\beta$ -dibromo- $\beta$ -benzoylacrylic acid, m. p. 108° [normal acid chloride, b. p. 164° (uncorr.)/7 mm., m. p. 37°]. The methyl ester, m. p. 115.5—116°, of *trans*- $\alpha\beta$ -dibromo- $\beta$ -2:4:6-trimethylbenzoylacrylic acid, m. p. 139° (acid chloride, m. p. 73—73.5°), is prepared similarly, using mesitylene diluted with carbon disulphide. The Friedel-Crafts reaction with dibromofumaryl or *trans*- $\alpha\beta$ -dibromo- $\beta$ -benzoylacrylyl chloride and benzene affords the less fusible (*trans*) form of  $\alpha\beta$ -dibromo- $\alpha\beta$ -dibenzoyl-ethylene (Conant and Lutz, A., 1925, i, 681), also obtained as the main product from dibenzoylacetylene and bromine in boiling chloroform. *cis*- $\alpha\beta$ -Dibromo- $\alpha\beta$ -dibenzoyl-ethylene (*loc. cit.*) is not rearranged into the *trans*-isomeride by treatment with aluminium chloride in benzene. *trans*- $\alpha\beta$ -Dibromo- $\alpha\beta$ -di-2:4:6-trimethylbenzoyl-ethylene, m. p. 198.5°, and *trans*- $\alpha\beta$ -dibromo- $\alpha$ -benzoyl- $\beta$ -2:4:6-trimethylbenzoyl-ethylene, m. p. 102.5°, are prepared from mesitylene and dibromofumaryl and *trans*- $\alpha\beta$ -dibromo- $\beta$ -benzoylacrylyl chloride, respectively, in presence of aluminium chloride and carbon disulphide.

VI. The chloride, b. p. 69.5°/14 mm., m. p. 16°, of methyl hydrogen fumarate, m. p. 144.5°, is converted as above into the methyl ester of *trans*- $\beta$ -benzoylacrylic acid. The unstable chloride from this acid gives with benzene and aluminium chloride *trans*- $\alpha\beta$ -dibenzoyl-ethylene; the *cis*-form is isomerised under the same conditions. Methyl *trans*- $\beta$ -2:4:6-tri-

*methylbenzoylacrylate*, m. p. 53°, is also described; when the free acid is esterified with methyl-alcoholic hydrogen chloride *methyl α-chloro-β-2:4:6-trimethylbenzoylpropionate*, m. p. 78°, is produced. *trans-α-β-2:4:6-trimethylbenzoyl-ethylene* is obtained together with a small amount of an acid, m. p. 217° (uncorr.), when *trans-β-2:4:6-trimethylbenzoylchloride* reacts with mesitylene in presence of benzene and aluminium chloride.

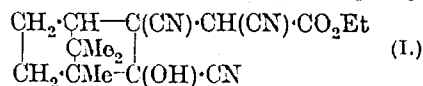
The normal  $\alpha\beta$ -dibromo- $\beta$ -benzoylpropionic acid, m. p. 150° (decomp.) (cf. Bougault, A., 1909, i, 102), obtained as the main product when bromine is added to *trans-β-benzoylacrylic acid* in acetic acid, is converted into the chloride and thence by the Friedel-Crafts reaction with benzene into *meso-αβ-dibromo-αβ-dibenzoyl-ethane* (cf. A., 1927, 565). *iso-αβ-Dibromo-β-benzoylpropionic acid*, m. p. 150° (decomp.) (cf. Bogert and Ritter, A., 1925, i, 816), gives by the same series of reactions *dl-αβ-dibromo-αβ-dibenzoyl-ethane*. These results show that under certain controlled conditions the addition of bromine to the dibenzoyl-ethylenes is *trans*; addition to dibenzoyl-acetylene is *cis*. A third *bromo-β-benzoylacrylic acid*, m. p. 105°, is formed together with the known  $\beta$ -bromo-derivative when  $\alpha\beta$ -dibromo- $\beta$ -benzoylpropionic acid is treated with sodium acetate and carbonate in acetone containing a small amount of methyl alcohol.

The Friedel-Crafts reaction with diphenyl ether and fumaryl chloride yields *trans-αβ-di-p-phenoxybenzoyl-ethylene*, m. p. 170.5–171°, reduced by zinc and acetic acid to *αβ-di-p-phenoxybenzoyl-ethane*, m. p. 160°. A small amount of *dl-αβ-dibromo-αβ-di-p-toluoylethane*, m. p. 138°, is obtained with much *meso*-form when *trans-αβ-di-p-toluoylethane* is treated with bromine in acetic acid. The Friedel-Crafts reaction with benzene and *trans-β-2:4:6-trimethylbenzoylacrylyl chloride* affords *trans-α-benzoyl-β-2:4:6-trimethylbenzoyl-ethylene*, m. p. 61.5°, whilst benzene and maleic chloride furnish a small amount of *trans-γ-hydroxy-γγ-diphenyl-Δ<sup>α</sup>-butenoic acid*, m. p. 224° (decomp.). *αβ-Di-α-naphthoylethane* has m. p. 130–131°.

H. BURTON.

**Condensation of benzoin and benzil with ethyl cyanoacetate.** J. A. McRAE and A. L. KUEHNER (J. Amer. Chem. Soc., 1930, 52, 3377–3382).—Benzoin condenses with ethyl cyanoacetate in presence of alcoholic sodium ethoxide, forming  $\alpha$ -cyano- $\gamma$ -hydroxy- $\beta\gamma$ -diphenylcrotonolactone, m. p. 141°, and not  $\alpha\delta$ -dicyano- $\beta\gamma$ -diphenyl- $\Delta^{\beta}$ -butene- $\alpha\delta$ -dicarboxylic acid as stated by Haworth (J.C.S., 1909, 95, 480). The lactone is hydrolysed by slightly diluted sulphuric acid at 130–140° to  $\beta$ -benzoyl- $\beta$ -phenylpropionic acid, and converted by boiling nitric acid into  $\alpha$ -cyano- $\beta$ -benzoyl- $\beta$ -m-nitrophenylacrylic acid, m. p. 218–220° (decomp.) after softening at 212°, which is oxidised by potassium permanganate in aqueous acetone to 3-nitrobenzil. Oxidation of the lactone with dilute nitric acid gives  $\alpha$ -cyano- $\beta$ -benzoylcinnamic acid (+0.5C<sub>6</sub>H<sub>6</sub>), m. p. 116–117° after softening at 112°, m. p. (benzene-free) 135–136°, also obtained by hydrolysis of *ethyl α-cyano-β-benzoylcinnamate*, m. p. 141°, which is prepared from benzil and ethyl cyanoacetate in presence of alcohol and a small amount of piperidine. The last-named ester and the above

lactone do not add hydrogen cyanide, but ethyl camphorylidene cyanoacetate (Forster and Withers, J.C.S., 1912, 101, 1327) does so, yielding *ethyl 2:3-*



*dicyano-2-hydroxy-1:7:7-trimethyldicyclo-(1:2:2)-heptane-3-cyanoacetate* (I), m. p. 202–204°, [ $\alpha$ ]<sub>D</sub> +115.1°. Benzoin methyl ether and ethyl cyanoacetate do not condense.

H. BURTON.

**Reaction of sodium phenoxide with  $\alpha$ -chloro- $\beta$ -hydroxypropionic acid.** C. F. KOELSCH (J. Amer. Chem. Soc., 1930, 52, 3364–3366).—The formation of  $\alpha$ -hydroxy- $\beta$ -phenoxy- (main product) and  $\beta$ -hydroxy- $\alpha$ -phenoxy-propionic acids from  $\alpha$ -chloro- $\beta$ -hydroxypropionic acid and sodium phenoxide is confirmed (cf. this vol., 1038).

H. BURTON.

**Physical identity of enantiomerides.** A. N. CAMPBELL and F. C. GARROW (Trans. Faraday Soc., 1930, 26, 560–564; cf. A., 1929, 1370).—Slight differences in m. p., solubility in water, rotatory dispersion, and numerical value of the rotatory power between *d*- and *l*-mandelic acids have been detected.

R. CUTHILL.

**Anthracene-1-carboxylic and -1:5-dicarboxylic acids and their derivatives.** E. A. COULSON (J.C.S., 1930, 1931–1936).—1:5-Dicyanoanthraquinone, obtained in 83% yield when 1:5-dichloroanthraquinone, phenylacetonitrile, and cuprous cyanide are heated at 230° (bath), is hydrolysed with slightly diluted sulphuric acid to the 1:5-dicarboxylic acid. Reduction of this with zinc dust and ammonia gives *anthracene-1:5-dicarboxylic acid*, m. p. above 360°, converted by way of the chloride (formed only by the action of phosphorus pentachloride at 150°) into the ethyl ester, m. p. 185°, which with magnesium methyl iodide yields 1:5-di- $\alpha$ -hydroxyisopropylantracene, m. p. 182.5°; no reaction occurs with magnesium benzyl chloride. This diol is dehydrated by dissolution in boiling acetic acid to 1:5-diisopropenylantracene, m. p. 121°, oxidised by chromic oxide in acetic acid to 1:5-diacetylanthraquinone, m. p. 317° after darkening above 280°. *Methyl anthracene-1-carboxylate*, m. p. 108°, forms resinous products with the above Grignard reagents. When treated with bromine in cold carbon disulphide it gives the unstable 9:10-dibromo-9:10-dihydro-derivative, which when crystallised from acetic acid passes into *methyl 10(or 9)-bromoanthracene-1-carboxylate*, m. p. 130°, and on treatment with pyridine furnishes unstable 1-carbomethoxy-9:10-dihydroanthranlyl-9:10-dipyridinium dibromide, m. p. 180°. This passes readily by loss of pyridine hydrobromide into 1-carbomethoxyanthranlyl-10(or 9)-pyridinium bromide, m. p. 271° (decomp.) (dichromate, m. p. 192°, from the bromide and aqueous potassium dichromate). Bromination of ethyl anthracene-1:5-dicarboxylate in boiling acetic acid gives a small amount of *ethyl 9-bromoanthracene-1:5-dicarboxylate*, m. p. 117°; prolonged action of chlorine in carbon tetrachloride furnishes impure, unstable 9:10-dichloride, m. p. 125°. *Ethyl anthraquinone-1:5-dicarboxylate* has m. p. 155°. The above anthracenecarboxylic esters and the diol show

brilliant purple fluorescence when illuminated by the carbon arc.

H. BURTON.

**Scission of the methylenedioxy-group with aluminium bromide.** E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1930, 52, 2988—2994).—Methylene ethers give the corresponding dihydroxy-derivatives when treated with aluminium bromide in nitrobenzene at 0° or 15° and subsequently with water. The highest yields are obtained when sufficient of the bromide is used to allow of the intermediate formation of a compound of the type  $R\langle\begin{smallmatrix} O(AlBr_3) \\ O(AlBr_3) \end{smallmatrix}\rangle CH_2$ .

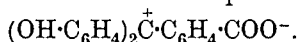
Methoxyl and ester groups are stable under these conditions and the ethylene ethers of pyrocatechol and protocatechuic acid are not attacked even at 130°. Dihydroxy-derivatives have been obtained, in the yields given in parentheses, from piperonaldehyde (82% of the theoretical), piperonylic acid (92%), methyl piperonate (58%), acetopiperone (48%), and 4-nitropyrocatechol methylene ether (65%). *i*-Tetrahydroberberine is converted into the base,  $C_{17}H_{13}N(OH)_2(OMe)_2$  (Späth and Mosettig, A., 1926, 965). 6-Nitropiperonaldehyde (Ekeley and Klemme, A., 1928, 1375), sodium phenylacetate, and zinc chloride in acetic anhydride give 2-nitro-4:5-methylenedioxy- $\alpha$ -phenylcinnamic acid, m. p. 193—195°, reduced by ferrous hydroxide and ammonia to the 2-amino-derivative, yellow, m. p. 201—203° (decomp.) (pink modification, yellow at 100°). This with nitrous acid and finely divided copper gives 2:3-methylenedioxyphenanthrene-9-carboxylic acid (I), m. p. 259—260° (methyl ester, m. p. 151—151.5°), from which by the new method 2:3-dihydroxyphenanthrene-9-carboxylic acid (97%), decomp. 280°, is obtained. When distilled under reduced pressure, this gives 2:3-dihydroxyphenanthrene, m. p. 158.5—159°. Decarboxylation of I gives 2:3-methylenedioxyphenanthrene, m. p. 93—94° (picrate, m. p. 151—152°), which, like safrole, isosafrole, piperonyl alcohol, and its benzoate, fails to give a crystalline product after treatment with aluminium bromide and water. H. E. F. NOTTON.

**Constitution of phenolphthalein. II. Fading of phenolphthalein in alkaline solution.** H. LUND (J.C.S., 1930, 1844—1852).—The velocity coefficients of the reversible reaction  $C_{20}H_{12}O_4'' + OH' \xrightleftharpoons[k_{-1}]{k_1} C_{20}H_{13}O_5'''$ , assumed to occur during the fading of phenolphthalein in alkaline solution, have been determined at 18° by spectrophotometric measurements. It is assumed that the concentration of the bivalent ion is proportional to the colour intensity, i.e., the extinction. In aqueous sodium hydroxide solution  $k_1$  increases more rapidly than the hydroxyl-ion concentration (cf. Biddle and Porter, A., 1915, ii, 539); in presence of 2*N*-sodium chloride  $k_1$  is proportional to the hydroxyl-ion concentration and the absolute values are more than twice those in aqueous solution. The value of  $k_1$  increases from 0.0015 in aqueous solution to 0.0043 in *N*-sodium chloride for 0.01*N*-sodium hydroxide, whereas  $k_{-1}$  increases only from 0.00065 to 0.00090. It is predicted that the forward reaction is rather sensitive to the presence of salts, whilst the reverse change is nearly independent of electrolytes.

Dimethylanilinephenolphthalein in an excess of

alkali fades considerably faster than phenolphthalein; the reverse reaction is slower. The salt effect is evaluated as being approximately half that for phenolphthalein. The above salt effects are in agreement with Bronsted's theory.

Various anomalies in the behaviour of phenolphthalein are explained by assuming that it has the character of an amphoteric ion,



H. BURTON.

**Pyrocatecholsulphonaphthalein.** C. B. WOOD (J. Amer. Chem. Soc., 1930, 52, 3463—3464).—The colours obtained with pyrocatecholsulphonaphthalein (cf. Moir, A., 1920, ii, 628) and solutions of varying  $\mu_a$  show a marked tendency to change, in some cases even after a few minutes. It is essential that the phthalein be prepared at a relatively low temperature; at 130—160° insoluble products result. H. BURTON.

**Synthesis of cinnamaldehyde and its homologues.** L. BERT and P. C. DORIER (Compt. rend., 1930, 191, 332—333).— $\gamma$ -Chloroallylbenzene (A, 1925, i, 803) is converted by heating with potassium hydroxide (3 mols.) and an alcohol into a cinnamyl alkyl ether, from which cinnamyl chloride is formed by heating with concentrated hydrochloric acid under pressure. The cinnamyl chloride yields cinnamaldehyde when heated with hexamethylenetetramine in aqueous alcohol. The following homologues prepared by these methods are described: cinnamyl chlorides: *o*-methyl-, b. p. 123°/9.5 mm.,  $d_4^{25}$  1.071,  $n_D^{25}$  1.575; *p*-methyl-, b. p. 132°/13 mm.,  $d_4^{25}$  1.0465,  $n_D^{25}$  1.571; 2:4-dimethyl-, b. p. 135°/13 mm.,  $d_4^{25}$  1.110,  $n_D^{25}$  1.566; 2:5-dimethyl-, b. p. 141°/17 mm.,  $d_4^{25}$  1.042,  $n_D^{25}$  1.570; *p*-isopropyl-, b. p. 150°/13 mm.,  $d_4^{25}$  1.007,  $n_D^{25}$  1.551; 2-methyl-5-isopropyl-, b. p. 154°/13 mm.,  $d_4^{25}$  1.002,  $n_D^{25}$  1.550; cinnamaldehydes: *o*-methyl-, b. p. 137°/16 mm.,  $d_4^{25}$  0.9855,  $n_D^{25}$  1.5623 (semicarbazone, m. p. 217°); *p*-methyl-, b. p. 147°/16 mm.,  $d_4^{25}$  0.967,  $n_D^{25}$  1.547 (semicarbazone, m. p. 243°); 2:4-dimethyl-, b. p. 147°/15 mm.,  $d_4^{25}$  1.005,  $n_D^{25}$  1.540 (semicarbazone, m. p. 231°); 2:5-dimethyl-, b. p. 151°/11 mm.,  $d_4^{25}$  0.9577,  $n_D^{25}$  1.534 (semicarbazone, m. p. 256°); *p*-isopropyl-, b. p. 156°/17 mm.,  $d_4^{25}$  0.952,  $n_D^{25}$  1.537 (semicarbazone, m. p. 219°); 2-methyl-5-isopropyl-, b. p. 162°/11—15 mm. (All b. p. are corrected, and m. p. by Maquenne block.)

R. K. CALLOW.

**Ring enlargement with diazomethane in the hydroaromatic series.** E. MOSETTIG and A. BURGER (J. Amer. Chem. Soc., 1930, 52, 3456—3463).—Treatment of cyclohexanone with ethereal methyl-alcoholic diazomethane first at 0° and then at the ordinary temperature gives cycloheptanone (main product), cyclooctanone, and the oxide,  $C_5H_{10} > C \begin{smallmatrix} O \\ \diagup \diagdown \\ CH_2 \end{smallmatrix}$ . The oxide (not obtained pure) is isomerised by distillation over a small amount of zinc chloride into hexahydrobenzaldehyde, and gives with piperidine at 95—100°, 1-hydroxy-1-piperidinomethylcyclohexane (?) (hydrochloride, m. p. 194.5—195°). cyclopentanone is converted similarly into cycloheptanone (main product) and -octanone. The ketones do not react with diazomethane in absence of the methyl alcohol.

H. BURTON.



**Action of aluminium chloride on arylaliphatic, aliphatic, and hydroaromatic ketones in presence of tertiary aromatic amines.** C. COURTOT and V. OUPEROFF (Compt. rend., 1930, 191, 416—418; cf. this vol., 1184).—Acetophenone and aluminium chloride in the presence of dimethylaniline yield 50% of triphenylbenzene, styryl methyl ketone gives non-basic resins, whilst phenyl styryl ketone at 30—40° affords a double compound with dimethylaniline (cf. A., 1923, i, 683), which undergoes fission at 91—92° to give leuco-malachite-green;  $\alpha$ -indanone gives exclusively anhydrobisindanone and truxene. Acetone, with aluminium chloride and dimethylaniline at 10°, yields the ketal,  $C_9H_{16}O_2$ , which is probably the precursor of phorone (cf. Grignard and Fluchaire, A., 1928, 396); propione (diethyl ketone) at 40—50° gives 20% of dipropione alcohol identical with that obtained by Grignard and Fluchaire. Of the hydroaromatic ketones examined, only cyclohexanone reacts at 40—50° to give 1:1-tetramethyldiaminodiphenylcyclohexane, m. p. 158°; at 10—20° cyclohexylene-2-cyclohexanone is formed exclusively. cyclopentanone at 15° yields no isolable product, but at 0° furnishes anhydrobiscyclopentanone; cycloheptanone yields cycloheptylenecycloheptanone, but camphor is unaffected.

C. W. SHOPPEE.

#### Cleavage of carbonyl compounds by alkalis.

**I. Trihalogenomethyl ketones of the mesitylene series.** R. C. FUSON and J. T. WALKER (J. Amer. Chem. Soc., 1930, 52, 3269—3275).—The fission of ketones by alkali is presumed to involve the addition of hydroxyl ion to the carbonyl carbon atom. If the substituents on the adjacent carbon atom are sufficiently "negative," dissociation then occurs. The 2:4:6-trimethylphenyl trihalogenomethyl ketones have been prepared and found to be stable towards alkali; this is attributed to inhibition of addition reaction at the carbonyl group through the presence of two *ortho*-substituents.

Treatment of acetomesitylene with sodium hypobromite solution at the ordinary temperature affords  $\omega\omega\omega$ -tribromo-2:4:6-trimethylacetophenone (I), m. p. 68.5—69°, which with nitric acid (*d* 1.6) at 0° gives the 3:5-dinitro-derivative, m. p. 114.6—115.1° (corr.), also obtained from 3:5-dinitroacetomesitylene, m. p. 139.6—140.6° (corr.), and sodium hypobromite. Similar treatment of 2:4:6-trimethylphenacyl bromide also furnishes I, which when boiled with alcoholic silver nitrate and the mixture then decomposed with sodium hydroxide solution gives  $\beta$ -isodurylic acid.  $\omega\omega\omega$ -Trichloro-2:4:6-trimethylacetophenone, b. p. 130—140°/5 mm., and its 3:5-dinitro-derivative, m. p. 100.1—100.6° (corr.), are prepared by analogous methods using sodium hypochlorite. H. BURTON.

**Synthesis by means of magnesium amyl halides. II. Reduction of benzophenone.** W. C. DAVIES, R. S. DIXON, and W. J. JONES (J.C.S., 1930, 1916—1921).—Treatment of magnesium *n*-amyl, *dl*- $\beta$ -methylbutyl, or isoamyl bromide with benzophenone in ether gives benzhydrol (main product), benzpinacol, and the appropriate decane. The formation of these products is explained by the following changes (cf. Gomberg and Bachmann, A., 1927, 245, 1190; Blicke and Powers, this vol., 85; Gilman

and Brown, *ibid.*, 778):  $R_2CO + C_nH_{2n+1} \cdot MgX \rightarrow \cdot C_nH_{2n+1} + \cdot CR_2 \cdot O \cdot MgX$  (I);  $2 \cdot CR_2 \cdot O \cdot MgX \rightleftharpoons (CR_2 \cdot O \cdot MgX)_2 \rightarrow \begin{matrix} CR_2 \cdot O \\ | \\ CR_2 \cdot O \end{matrix} > Mg + MgX_2$ ;  $2 \cdot C_nH_{2n+1} \rightarrow C_{2n}H_{4n+2}$ ;  $C_nH_{2n+1} + \cdot CR_2 \cdot O \cdot MgX \rightarrow C_nH_{2n} + \cdot CHR_2 \cdot O \cdot MgX$ . In the above reactions a deep red coloration is first produced, probably due to the formation of the ketyl I. H. BURTON.

#### Attempts to resolve derivatives of fluorene.

***p*-Aminobenzophenonehydrazone.** C. W. BENNETT and W. A. NOYES (J. Amer. Chem. Soc., 1930, 52, 3437—3440).—Reduction of 2-aminofluorenonehydrazone with zinc dust and acetic acid gives the *monoacetyl* derivative, m. p. 219°, of 2:9-diaminofluorene, which could not be resolved by means of *d*-camphorsulphonic acid, *d*- $\alpha$ -aminophenylacetic acid, or *d*-hydroxymethylcyclohexanone. Nitration of 9-acetamidofluorene with nitric and sulphuric acids affords probably 1:8-dinitro-9-acetamidofluorene, m. p. 236—238° (cf. Schmidt and Stützel, A., 1910, i, 29).

***p*-Aminoacetophenonehydrazone**, m. p. 139—140° (corresponding *azine*, m. p. 225°), is oxidised by mercuric oxide or mercury acetamide in various solvents forming a purple solution of the corresponding diazo-compound; this decomposes readily to the above *azine*. H. BURTON.

#### Electrolytic reduction of ketones. II. Formation of hydrocarbons.

G. SHIMA (Mem. Coll. Sci. Kyōtō, 1930, A, 13, 315—322).—Optimum yields (60—90%) of hydrocarbons are obtained when ketones are reduced electrolytically in a modified form of the apparatus previously described (A., 1929, 521) using an amalgamated zinc cathode, a mixture of 70—85% sulphuric acid and alcohol as the cathode solution, a current strength of 15 amp., and a temperature of 65—75°. Thus, benzoin affords mainly dibenzyl together with small amounts of stilbene and deoxybenzoin (*p*-nitrophenylhydrazone, m. p. 163°); dibenzyl is also produced from benzil or deoxybenzoin. Benzophenone, *p*-methoxybenzophenone, phenyl *p*-tolyl, phenyl *p*-cymyl, and phenyl  $\alpha$ -naphthyl ketones all give the corresponding methanes. The yield of benzyl-*o*-xylene, m. p. 33—34° (from phenyl *o*-xylyl ketone), is much smaller than those of benzyl-*m*- and -*p*-xylenes. H. BURTON.

#### Reduction of benzoin with sodium amalgam and alcohol.

A. WEISSBERGER and H. BACH (J. pr. Chem., 1930, [ii], 127, 260—262).—Reduction of benzoin with 4% sodium amalgam and aqueous alcohol at 50° in an atmosphere of nitrogen gives much improved yields of hydro- and isohydro-benzoin. The small amount of by-product formed during the reduction (cf. Breuer and Zincke, A., 1880, 116) is probably benzoinpinacol, m. p. 249—250° (corr.) (lit. 233°), since when this is heated alone or with alcoholic potassium hydroxide, a mixture of benzoin and probably hydrobenzoin is obtained. H. BURTON.

#### Reactions of quinol and constitution of quinhydrone.

T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, 52, 3204—3206).—Treatment of quinol with sodium iodate in cold, aqueous solution affords an almost quantitative yield of quinhydrone.

The yield is not so good in presence of acetic acid, whilst in presence of sodium hydroxide a brown dye results. Varying amounts of quinhydrone are also produced when quinol is oxidised with potassium permanganate and acetic acid, alkaline potassium ferricyanide, potassium persulphate, and potassium bromate. When quinol is treated with a hot solution of sodium iodate, a 40% yield of *p*-benzoquinone is produced.

Addition of dioxan to a saturated solution of quinol in ether precipitates an additive compound, probably  $O_2C_2H_4 \cdot O \cdot OH \cdot C_6H_4 \cdot OH$ , m. p. (sealed tube) 93–100°, the existence of which supports the analogous oxonium formula for quinhydrone (Richter, A., 1911, i, 136).

H. BURTON.

**New synthesis in the 1:2-naphthanthraquinone series.** H. WALDMANN (J. pr. Chem., 1930, [iii], 127, 195–200).—1:2-Naphthanthraquinones are prepared by ring closure of 1-benzoyl-2-naphthoic acids, which are obtained by the Friedel-Crafts reaction with benzene derivatives and naphthalene-1:2-dicarboxylic anhydride.

[With U. WEISS].—1:2-Dicyanonaphthalene is formed in 50% yield when small amounts of sodium 1-chloronaphthalene-2-sulphonate and dry potassium ferrocyanide are distilled in a current of carbon dioxide. Hydrolysis of the dinitrile with aqueous-alkaline potassium hydroxide at 150° gives naphthalene-1:2-dicarboxylic acid, the anhydride of which reacts with benzene in presence of aluminium chloride, forming 1-benzoyl-2-naphthoic acid, m. p. 219–220°. Fusion of this with potassium hydroxide at 300° affords benzoic and  $\beta$ -naphthoic acids. Ring closure of the keto-acid is accomplished by phosphorus pentachloride at 120°, whereby 1:2-naphthanthraquinone, m. p. 168°, results. With sulphuric acid, ring closure is accompanied by sulphonation. The Friedel-Crafts reaction with naphthalene-1:2-dicarboxylic anhydride and chlorobenzene yields 1-*p*-chlorobenzoyl-2-naphthoic acid, m. p. 249° (potassium hydroxide fusion product,  $\beta$ -naphthoic acid), which when heated with phosphoric oxide gives 6-chloro-1:2-naphthanthraquinone, m. p. 222°. The chloro-compound gives a red vat with alkaline sodium hyposulphite.

H. BURTON.

**Derivatives of naphthanthraquinone.** H. WALDMANN (J. pr. Chem., 1930, [ii], 127, 201–209).—Various halogeno- and amino-naphthanthraquinones and condensation products of 6(or 7)-bromo-1:2-naphthanthraquinone with 1-amino- and 1:5-diamino-anthraquinones are described.

[With G. STESKAL].—4-Bromophthalic anhydride and naphthalene react in presence of benzene and aluminium chloride, forming 4(or 5)-bromo-2-naphthoylbenzoic acid, m. p. 208°, which when warmed with sulphuric acid at 58–60° gives (6 or 7)-bromo-1:2-naphthanthraquinone, m. p. 228°, together with a small amount of sulphonated product. Prolonged interaction of this bromo-derivative with 1-amino- and 1:5-diamino-anthraquinone in presence of naphthalene, sodium acetate, and copper chloride affords 6-(1-anthraquinonylamino)-1:2-naphthanthraquinone and 1:5-di-(6-naphthanthraquinonylamino)anthraquinone, respectively. These secondary amines dye

cotton with a red shade from an alkaline vat. Prolonged treatment of the bromo-derivative with concentrated ammonia and copper chloride at 190° yields 6(or 7)-amino-1:2-naphthanthraquinone, m. p. 240°. 3-Amino-1:2-, m. p. 254°, and 1:6(or 7)-diamino-2:3-naphthanthraquinones, m. p. 307°, are prepared similarly from 3-chloro-1:2-, m. p. 207.5° (Heller, A., 1912, i, 357), and 6(or 7)-chloro-1-hydroxy-2:3-naphthanthraquinones, respectively. The Friedel-Crafts reaction with 4-chlorophthalic anhydride and 1-chloronaphthalene gives 4(or 5)-chloro-2-*l*-chloronaphthoylbenzoic acid, m. p. 199°, converted by treatment with sulphuric acid at 65–75° into 3:6(or 7)-dichloro-1:2-naphthanthraquinone, m. p. 155°. Treatment of 4(or 5)-chloro-2-naphthoylbenzoic acid (G.P. 234,917) with sulphuric acid at 58–60° furnishes a chloronaphthanthraquinonesulphonic acid, which with sodium chlorate and dilute hydrochloric acid affords a dichloro-1:2-naphthanthraquinone, m. p. 204°. When 3:4:5:6-tetrachloro-2-naphthoylbenzoic acid is heated with phosphoric oxide and kieselguhr at 250°, 5:6:7:8-tetrachloro-1:2-naphthanthraquinone, m. p. 253°, results. The last-named substance is formed in small amount, together with a substance, m. p. 150°, when the keto-acid is heated in a current of carbon dioxide.

H. BURTON.

**Bilirubin. II. Coloured oxidation stages of bilirubin and their behaviour with changes in hydrogen-ion concentration. III. Effect of radiated energy on bilirubin. IV. Solubility of bilirubin and of its coloured oxidation products, and their treatment with reducing and condensing agents. V. Properties of the bile pigments. VI. Detection and determination of bilirubin and of the coloured oxidation products.** W. KERPPOLA and E. LEIKOLA (Skand. Arch. Physiol., 1929, 55, 70–77, 78–86, 87–90, 258–259, 260–265; Chem. Zentr., 1929, i, 1571–1572).—II. The colour of bilirubin varies with the  $p_H$  of the solution. On treating a solution in chloroform with increasing amounts of hydrochloric acid and sodium nitrite, the colour changes from reddish-yellow, through shades of violet, to ochre-yellow; finally, the solution is decolorised. The  $p_H$  values corresponding with each colour have been determined.

III. The colour of air-dried bilirubin and of a solution in glycerol is unchanged by exposure to ultra-violet light for many hours. In chloroform, the solution is decolorised in a few minutes. The same changes occur in all liquids, but the velocities are different. Daylight acts most strongly in alkaline solution. X-Rays and the radiations from radium act more slowly. The colours vary with the  $p_H$  of the solution.

IV. The effect of reducing and condensing agents on the colour of the oxidation products of bilirubin is tabulated.

V. In strongly alkaline solution, bilirubin reduces photophotungstic acid to the blue pentoxide. Bilirubin and biliverdin both migrate to the anode.

VI. A critical discussion of the usual methods of determination.

L. S. THEOBALD.

**Partial dehydrogenation of  $\alpha$ - and  $\beta$ -amyrin.** W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1930,

88, 137—152).— $\beta$ -Amyrin benzoate, when heated with sulphur at 220—230°, yielded a compound,  $C_{37}H_{48}O_2S$ , m. p. 224—225°,  $[\alpha]_D^{25} +96^\circ$  in pyridine, which was hydrolysed to a compound,  $C_{30}H_{41}OS$ , m. p. 200—201°,  $[\alpha]_D^{25} +88^\circ$  in pyridine (also obtained directly by heating  $\beta$ -amyrin with sulphur at 200—210°). The above dehydroamyrin benzoate by oxidation with permanganate and hydrolysis with potassium hydroxide gave a lactone,  $C_{30}H_{44}O_4$ , m. p. 299—300° (decomp.),  $[\alpha]_D^{25} -14^\circ$  in pyridine, and a ketone,  $C_{30}H_{46}O_3$ , m. p. 274—275°,  $[\alpha]_D^{25} -127^\circ$  in pyridine. The lactone afforded an acetate, m. p. 269—271°, and a benzoate, m. p. 292—293° (also isolated from the crude oxidation product), and was hydrolysed with difficulty to the acid, m. p. 237—238°,  $[\alpha]_D^{25} +96^\circ$  in pyridine. The ketone [oxime, m. p. 234—236° (decomp.); acetate, m. p. 231—232°; benzoate (also from above oxidation product), m. p. 261—262°,  $[\alpha]_D^{25} -77^\circ$  in pyridine] was reduced with zinc and hydrochloric acid to a compound,  $C_{30}H_{48}O_2$ , m. p. 155—160° (impure), and was hydrogenated to a mixture of isomerides having the approximate empirical composition of amyrin. Dehydro- $\alpha$ -amyrin benzoate,  $C_{37}H_{52}O_2$ , m. p. 171—172°,  $[\alpha]_D^{25} +304^\circ$  in pyridine, was obtained by heating  $\alpha$ -amyrin benzoate with sulphur at 220—230° or by benzoylating the product which resulted from heating  $\alpha$ -amyrin with sulphur at 200—210°, and was hydrolysed with alcoholic potassium hydroxide to dehydro- $\alpha$ -amyrin,  $C_{30}H_{48}O$ , m. p. 162—163°,  $[\alpha]_D^{25} +358^\circ$  in pyridine; this was oxidised with chromic acid to dehydro- $\alpha$ -amyrone,  $C_{30}H_{46}O$ , m. p. 133—134°,  $[\alpha]_D^{25} +412^\circ$  in pyridine [oxime, m. p. 233—235°]. C. R. HARRINGTON.

**Saponins. V. Partial dehydrogenation of hederagenin.** W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1930, 88, 153—161).—Hederagenin methyl ester and methyl hedraganate,  $C_{31}H_{50}O_2$  (A., 1926, 1250), have both been hydrolysed by heating with 10% alcoholic potassium hydroxide at 120—130°, yielding in the latter case hedraganic acid, m. p. 242—243°. Methyl hedraganate gave, when heated with sulphur at 215—220°, a compound,  $C_{31}H_{44}O_2S$ , m. p. 137—138°, in which the sulphur and the ester group were both stable towards boiling alkali; oxidation of this compound with permanganate afforded a lactone ester,  $C_{31}H_{44}O_5$ , m. p. 274—275°,  $[\alpha]_D^{25} -16^\circ$  in pyridine, and a keto-ester,  $C_{31}H_{46}O_4$ , m. p. 202—204°,  $[\alpha]_D^{25} -184^\circ$  in pyridine [oxime, m. p. 236—237°]. Treatment of the lactone ester with dilute sodium hydroxide yielded the lactone acid, m. p. 255—256°, whilst hydrolysis with 10% potassium hydroxide also eliminated carbon dioxide giving the acid,  $C_{29}H_{44}O_4$ , m. p. 209—210°. Neither the lactone ester nor the keto-ester could be acylated. The keto-ester was hydrolysed with dilute sodium hydroxide to the acid, m. p. 184—185° (decomp.), and, with 10% potassium hydroxide, lost carbon dioxide to give a neutral compound,  $C_{29}H_{42}O_2$ , m. p. 262—264°. The degradation is evidently closely analogous to that of  $\beta$ -amyrin (cf. preceding abstract). The increased lability of the ester group in the products obtained by oxidative removal of sulphur from the compound  $C_{31}H_{44}O_2S$  suggests that the sulphur in the latter is attached to that carbon atom which forms the lactone

and the carbonyl groups of the respective oxidation products. C. R. HARRINGTON.

**Optical activity and the polarity of substituent groups. XIV. Influence of substituent poles and dipoles on the rotatory power of menthyl acetate.** H. G. RULE, R. H. THOMPSON, and (in part) A. ROBERTSON (J.C.S., 1930, 1887—1894).—The values previously obtained (A., 1925, ii, 1120) for the rotatory powers of *l*-menthyl esters of mono-substituted acetic acids are discussed in conjunction with the dipolar character of the substituents. Introduction of an electronegative substituent is regarded as creating a positive field, and an electropositive substituent a negative field, in that part of the molecule to which it is attached. The magnitude of the negative rotatory power of a *l*-menthyl acetate rises with increasing strength of the positive field exerted at the asymmetric atom by the substituent; conversely, a negative field will lead to a diminished rotatory power. These deductions are illustrated by the following observations. The rotatory power of sodium *l*-menthyl malonate (superimposed negative field caused by ionisation) is lower than that of the hydrogen ester. The value for *l*-menthyl dimethylaminoacetate, b. p. 132°/9 mm.,  $d_4^{20}$  0.9357,  $[M]_{5461}^{20} -185.5^\circ$ ,  $-201^\circ$  in alcohol, is slightly lower than that for *l*-menthyl acetate, but increases for the hydrochloride, m. p. 169°,  $[M]_{5461}^{20} -207^\circ$  in alcohol, and the methiodide, m. p. above 250°,  $[M]_{5461}^{20} -208^\circ$  in alcohol. A similar relationship exists for *l*-menthyl diethylaminoacetate, b. p. 142.5—143°/9 mm., its hydrochloride, m. p. 127° (lit. 108°), and methiodide, m. p. 161—162° (lit. 157°). *l*-Menthyl chloroacetate and aqueous-alcoholic sodium sulphite give *l*-menthyl sulphoacetate (+2H<sub>2</sub>O),  $[M]_{5461}^{20} -210^\circ$  in water, the rotatory power of which is somewhat high. This relatively high value may be partly due to the powerful electronegative character of the sulpho-group, which contains two semipolar double linkings arranged with their positive poles directed towards the menthyl group. H. BURTON.

**Optical activity and the polarity of substituent groups. XV. Phenyl-substituted esters and ethers of *l*-menthyl and  $\beta$ -octyl alcohol.** H. G. RULE and J. BAIN (J.C.S., 1930, 1894—1903).—The *l*-menthyl and  $\beta$ -octyl ethers of mono-, di-, and tri-phenylcarbinol, and the  $\beta$ -octyl esters of mono-, di-, and tri-phenylacetic acid have been prepared and their rotatory powers determined for light of four different wave-lengths. Comparison with the analogous non-phenylated compounds shows that the rotatory power increases with successive introduction of two phenyl groups and then decreases with a third phenyl group. With the exception of *l*-menthyl triphenylmethyl ether, this decrease is so pronounced that an inversion of sign results. The variations in rotatory powers of the phenylated acetic acids do not correspond with alterations in the strengths of the acids; molar conductivity determinations with aqueous-alcoholic solutions of the acids at 20° show that triphenylacetic acid is the strongest of the series. The statements in the literature (Elbs and Toller, A., 1886, 352; Schmidlin and Hodgson, A., 1908, i, 170) describing it as an extremely weak

acid are, therefore, incorrect. The diminished rotatory powers of compounds containing the triphenylmethyl group are assumed to be due to the close proximity of this group and the active complex. The abnormally low rotatory power of *l*-menthyl  $\delta$ -phenylvalerate (Rupe and Münter, A., 1909, i, 928) is probably due to the proximity of the phenyl and menthyl groups, owing to the normal bending of the carbon chain.

The following ethers are prepared from the requisite chloride and alcohol: *l*-menthyl triphenylmethyl, m. p. 136°; triphenylmethyl 1- $\beta$ -octyl, b. p. 178°/0.3 mm.,  $d_4^{20}$  1.026; *d*-bornyl triphenylmethyl, m. p. 116°; 1-menthyl diphenylmethyl, m. p. 67°; diphenylmethyl 1- $\beta$ -octyl, b. p. 202°/10 mm.,  $d_4^{20}$  0.9675; benzyl 1- $\beta$ -octyl, b. p. 154°/18 mm.,  $d_4^{20}$  0.8974. 1- $\beta$ -Octyl phenylacetate, b. p. 174°/12 mm.,  $d_4^{20}$  0.9578, *d*- $\beta$ -octyl diphenylacetate, b. p. 221°/17 mm.,  $d_4^{20}$  0.9974, and *d*- $\beta$ -octyl triphenylacetate, b. p. 206°/0.03 mm., are obtained by the acid chloride method.

H. BURTON.

**Preparation of thymol from piperitone.** S. KIMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 301b).—Pure *l*-piperitone may be extracted from eucalyptus oil by treatment with a concentrated solution of resorcinol or sodium salicylate followed by steam-distillation.

The oxidation of piperitone with ferric chloride in acetic acid solution using manganese salts as catalyst gives a maximal yield of 48–53% of thymol during 5–6 hrs. heating with gentle boiling. The concentration of acetic acid had no influence at above 20%, and the yield of thymol at first increased with increasing amount of ferric chloride, but decreased with a large excess.

C. W. SHOPPEE.

**Reduction of piperitone with aluminium amalgam.** S. KIMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 301–302b).—*l*-Piperitone is reduced by aluminium amalgam to a ketone,  $C_{20}H_{34}O_2$ , m. p. 125–126°, but sodium amalgam affords the ketone  $C_{20}H_{34}O_2$ , m. p. 166–167°, also obtained together with the isomeride, m. p. 135–136°, from *dl*-piperitone by reduction with aluminium amalgam; the isomerides, m. p. 166–167° and 135–136°, are identical with the ketones previously obtained by Smith and Penfold (1921) by reduction of piperitone with sodium or sodium amalgam. The use of aluminium amalgam appears to avert racemisation.

C. W. SHOPPEE.

**Oxidation of *d*- $\Delta^3$ -carene and  $\alpha$ -pinene with benzoyl hydrogen peroxide and peracetic acid.** B. A. ARBUSOV and B. M. MICHAÏLOV (J. pr. Chem., 1930, [ii], 127, 1–15).—Partly an account of work previously reviewed (this vol., 1044). The following is new. Oxidation of *d*- $\Delta^3$ -carene with peracetic acid in acetic acid solution gives mainly the acetate, b. p. 134–141°/11 mm. (probably a mixture), of *d*- $\Delta^3$ -carene  $\beta$ -glycol. When the oxidation is carried out in ether the chief product is *d*- $\Delta^3$ -carene oxide, b. p. 75.5–77°/10 mm., identical with that previously described (*loc. cit.*); a very small amount of glycol acetate is produced. These results do not agree with Böeseken's views (A., 1928, 734) of the mode of action of peracetic acid. It is, however, pointed out that,

unlike Böeseken, the authors have used peracetic acid free from sulphuric acid.

$\alpha$ -Pinene is oxidised by peracetic acid in ether to the oxide (88.6% of the theoretical); in chloroform, a mixture of the oxide (main product), glycol acetate, and high-boiling material results. Similar high-boiling products are formed when  $\alpha$ -pinene oxide is treated with acetic acid. Prolonged treatment of *d*- $\Delta^3$ -carene oxide with acetic acid containing a small amount of sulphuric acid gives mainly unchanged material together with a small amount of high-boiling material (not identical with the glycol acetate).

H. BURTON.

**Transformation of camphene into isobornyl esters and decomposition of bornyl and isobornyl esters to camphene.** G. BRUS and J. VÉBRA (Compt. rend., 1930, 191, 267–270).—The reaction between camphene and formic or acetic acid in presence of phosphoric or 50% sulphuric acid is shown to be reversible. Quantitative yields of isobornyl formate or acetate are, therefore, not obtained. The yields of crude products are, however, 94–98%. When isobornyl formate (10 parts) is distilled with phosphoric acid (1 part) at 20 mm., formic acid, camphene (86% of the theoretical amount), and a small amount (7%) of a diterpene,  $C_{20}H_{32}$ , b. p. 125–130°/1 mm., are obtained. Bornyl formate and acetate, and isobornyl acetate are decomposed similarly, and sulphuric acid, zinc chloride, or antimony trichloride can be used in place of phosphoric acid.

H. BURTON.

**Solubilisation of some metallic salts of camphorcarboxylic acid in organic solvents.** M. PRION (Compt. rend., 1930, 191, 137–139).—The neutral anhydrous camphorcarboxylates of neodymium, cerium, bismuth, gold, and uranium are soluble in the usual organic solvents and in olive oil. The camphorcarboxylates of calcium, copper, zinc, lead, and mercury become soluble after treatment with boiling benzene; such treatment does not increase the solubilities of the sodium, magnesium, and manganese salts.

C. C. N. VASS.

**Treatment of cedrene with mercuric acetate.** J. BELL (J.C.S., 1930, 1908–1910).—Prolonged treatment of cedrene with aqueous mercuric acetate affords an organo-mercury compound,  $C_{16}H_{28}O_6Hg_2$ , m. p. 193–195° (decomp.), which is possibly a mixture, mercurous acetate being precipitated. Oxidation of cedrene with mercuric oxide in glacial acetic acid gives a saturated alcohol,  $C_{15}H_{26}O$ , b. p. 140–150°/10 mm.,  $d_4^{20}$  0.9872,  $n_D^{20}$  1.5071, which is probably the same product as is obtained by oxidation of cedrene with hydrogen peroxide (Henderson and Sword) and apparently identical with  $\psi$ -cedrol (Semmler and Mayer, A., 1912, i, 479).

J. W. BAKER.

**Sagittol.** A new sesquiterpene alcohol. E. YANOVSKY (J. Amer. Chem. Soc., 1930, 52, 3446–3448).—Distillation of the roots of *Balsamorhiza sagitta* (Pursh), Nutt., with steam gives about 0.5% (of dry cortex) of sagittol,  $C_{15}H_{26}O$ , m. p. 77–78°,  $[\alpha]_D^{25} +26.15^\circ$  in alcohol (acetate).

H. BURTON.

**Caryophyllene series. III. Clovene alcohol and  $\alpha$ -caryophyllene alcohol.** J. BELL and G. G. HENDERSON (J.C.S., 1930, 1971–1975).—The liquid

by-product obtained in the preparation of caryophyllene dihydrochloride (A., 1929, 931) is now shown to be a monohydrochloride, since it is converted by the action of silver acetate in glacial acetic acid and subsequent hydrolysis into a mixture of clovene and a tricyclic sesquiterpene alcohol,  $C_{15}H_{26}O$ , b. p. 146–154°/10 mm.,  $d_4^{20}$  0.9934,  $n_D^{20}$  1.5039. The same alcohol is obtained by similar action of silver acetate on the product obtained by saturating clovene in dry ether with dry hydrogen chloride at 0°. Dehydration of  $\alpha$ -caryophyllene alcohol either with phosphoric oxide or anhydrous oxalic acid yields a hydrocarbon the physical constants of which, b. p. 118–123°/12 mm.,  $d_4^{20}$  0.9252,  $n_D^{20}$  1.5000, are closely similar to those of clovene. The action of phosphorus pentachloride on  $\alpha$ -caryophyllene alcohol affords no crystalline chloro-derivative similar to that obtained from the  $\beta$ -alcohol (Wallach and Walker, A., 1893, i, 101), indicating that the  $\alpha$ - and  $\beta$ -alcohols are structural isomerides. This view is confirmed by oxidation of the two alcohols with Beckmann's chromic acid mixture.  $\beta$ -Caryophyllene alcohol gives a viscous oily acid,  $C_{10}H_{12}O_3$  (methyl ester, b. p. 170–180°/10 mm.; silver salt), whilst  $\alpha$ -caryophyllene alcohol yields a crystalline dicarboxylic acid,  $C_{13}H_{24}O_4$ , m. p. 187° (yielding an anhydride, m. p. 49.5°, when heated above its m. p.), identical with an acid obtained by similar oxidation of the sesquiterpene by-product formed in the hydration of caryophyllene (Ruzicka). J. W. BAKER.

**$\alpha$ -Tetrahydrofurfuryl chloride and ethers.** W. R. KIRNER (J. Amer. Chem. Soc., 1930, 52, 3251–3256).— $\alpha$ -Tetrahydrofurfuryl chloride, b. p. 149–149.5°/721 mm.,  $d_4^{20}$  1.1102,  $n_D^{20}$  1.4560, prepared from the corresponding alcohol by Darzens' method, is more stable and less reactive than furfuryl chloride. The following  $\alpha$ -tetrahydrofurfuryl alkyl ethers are prepared from tetrahydrofurfuryl alcohol and the requisite alkyl halide (usually bromide) in presence of powdered potassium hydroxide: methyl, b. p. 140–141°/715.5 mm.,  $d_4^{20}$  0.9640,  $n_D^{20}$  1.4292; ethyl, b. p. 152–154°/726 mm.,  $d_4^{20}$  0.9386,  $n_D^{20}$  1.4298; n-propyl, b. p. 175–176.5°/728 mm.,  $d_4^{20}$  0.9248,  $n_D^{20}$  1.4313; n-butyl, b. p. 194.5–196°/721 mm.,  $d_4^{20}$  0.9150,  $n_D^{20}$  1.4357; isoamyl, b. p. 209–210° (corr.)/718 mm., 86.5–87.5°/10 mm.,  $d_4^{20}$  0.9040,  $n_D^{20}$  1.4370; n-hexyl, b. p. 231–233°/708 mm., 107.5–108.5°/10 mm.,  $d_4^{20}$  0.9019,  $n_D^{20}$  1.4407; allyl, b. p. 179.5–181°/707 mm.,  $d_4^{20}$  0.9571,  $n_D^{20}$  1.4498, and benzyl, b. p. 141.5–143°/10 mm.,  $d_4^{20}$  1.0484,  $n_D^{20}$  1.5174. Several of the ethers show anæsthetic action when injected peritoneally into mice and guinea-pigs. H. BURTON.

**Methylfurfuraldehyde oxide as a by-product in the preparation of hydroxymethylfurfuraldehyde.** J. P. C. CHANDRASENA (J.C.S., 1930, 2035).—In the preparation of hydroxymethylfurfuraldehyde by heating together sucrose and oxalic acid in aqueous solution under 3 atm. pressure (Troje, A., 1925, ii, 1210) a by-product,  $C_{12}H_{10}O_5$ , m. p. 120°, apparently identical with methylfurfuraldehyde oxide (Kiermayer, A., 1896, i, 144), is obtained. Oxidation with cold alkaline permanganate or 2N-nitric acid converts it into oxalic acid, but hot alkaline permanganate gives an unidentified substance, not melting at 250°.

J. W. BAKER.

**Preliminary formation of additive compounds in substitution reactions of aromatic types.** **Bromination of ethyl 2-furylacrylate.** H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1930, 52, 3349–3353).—When ethyl  $\beta$ -2-furylacrylate (1 mol.) is treated with bromine (1 mol.) in carbon disulphide at the ordinary temperature and the solution cooled to –10°, a dibromide, m. p. 70°, separates. Treatment of this with zinc dust and alcohol regenerates the original ester, whilst decomposition with alcoholic potassium hydroxide and subsequent hydrolysis affords 5-bromofurylacrylic acid (this vol., 479). The dibromide readily loses hydrogen bromide yielding ethyl 5-bromofurylacrylate. H. BURTON.

**Tea tannin from green tea.** M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 63–69).—From green tea a new tannin has been isolated (procedure described in detail) closely resembling that described by Deuss (A., 1923, i, 1046). Tea tannin,  $C_{22}H_{18}O_{10} (+2H_2O)$ ,  $[\alpha]_D^{25}$  –162.5° in alcohol, gives a blue colour with ferric chloride, but not the flavone reaction with magnesium and hydrochloric acid; it is gradually oxidised in air. By hydrolysis with 5% sulphuric acid it affords gallic acid, m. p. 237°, and a reddish-brown substance which yields phloroglucinol when heated with 50% potassium hydroxide at 180°. Treatment of the tannin with cold acetic anhydride and a trace of sulphuric acid or with acetic anhydride and anhydrous sodium acetate at 100° yields a hepta-acetyl derivative,  $C_{22}H_{11}O_3(OAc)_7$ ,  $[\alpha]_D^{25}$  –100° in benzene, which appears to contain 0.5–1 mol.  $H_2O$ . It is suggested that tea tannin is the gallic ester of tea catechin (cf. A., 1929, 934). C. W. SHOPPEE.

**Synthesis and constitution of scutellarein.** F. WESSELY and G. H. MOSER (Monatsh., 1930, 56, 97–105; cf. Robinson and Schwarzenbach, this vol., 785).—2:5-Dimethoxyresorcinol (Baker, Nodzu, and Robinson, A., 1929, 326) is converted into 2:4-dihydroxy-3:6-dimethoxyacetophenone, m. p. 129°, by condensation with acetonitrile in presence of zinc chloride and ethereal hydrogen chloride. When this is heated with anisic anhydride and potassium anisate at 180–185° and the resulting product hydrolysed with aqueous-alcoholic sodium hydroxide, 5:7-dihydroxy-6:4'-dimethoxyflavone, m. p. 219° (slight decomp.) (diacetate, m. p. 149–150°), is obtained. This is demethylated by boiling hydriodic acid (d 1.7) to 5:6:7:4'-tetrahydroxyflavone, the tetra-acetate of which is identical with natural scutellarein acetate. Methylation of the dimethoxy-derivative with ethereal methyl-alcoholic diazomethane affords 5-hydroxy-6:7:4'-trimethoxyflavone, m. p. 188–189° (acetate, m. p. 169°), identical with the trimethyl ether from scutellarein, whilst methylation with an excess of methyl sulphate and potassium hydroxide in acetone at 60° furnishes 5:6:7:4'-tetramethoxyflavone, two modifications, m. p. 142° and 161°.

7-Hydroxy-5:8:4'-trimethoxyflavone, m. p. 258° (slight decomp.) (acetate, m. p. 194.5°), was isolated in one case from the condensation of the above acetophenone with anisic anhydride and potassium

anisate. When this was demethylated with hydriodic acid ( $d$  1.7) and the product then acetylated, scutolarenin tetra-acetate was obtained. 5:7:8:4'-*Tetra-methoxyflavone* has  $m. p.$  207—208°. H. BURTON.

**5-Thiofluoran.** II. Action of phthaloyl chloride on *p*-bromoanisole and *p*-bromophenyl methyl sulphide. W. KNAPP (Monatsh., 1930, 56, 106—112).—*p*-Bromophenyl methyl sulphide reacts with phthaloyl chloride in presence of carbon disulphide and aluminium chloride at 40—50°, forming 2:8-dibromo-5-thiofluoran,  $m. p.$  214—216° (cf. A., 1929, 186). Reduction of this with sodium amalgam and sodium in boiling alcohol affords 5-thiohydrofluoranic acid,  $m. p.$  215—216°, both bromine atoms being replaced by hydrogen. When an aqueous-alkaline solution of this acid is boiled for a long time in presence of air, 5-thiofluoran,  $m. p.$  174—175° (corresponding sulphoxide,  $m. p.$  266—268°), is obtained.

*p*-Bromoanisole and phthaloyl chloride react as above furnishing 3':3'-dibromo-6':6'-dimethoxydiphenylphthalide,  $m. p.$  214—216°. H. BURTON.

**Pyrrolidine derivatives from ethyl  $\alpha\alpha'$ -dibromoadipate and secondary amines.** R. C. FUSON and R. A. CONNOR (J. Amer. Chem. Soc., 1930, 52, 2985—2987).—The failure of dimethylamino to effect the cleavage of ethyl  $\alpha\alpha'$ -dibromoadipate (cf. von Braun, Leistner, and Münch, A., 1926, 1128) is explained by the fact that the main product in this case is a salt-like substance, believed to be 2:5-dicarboxy-1:1-dimethylpyrrolidinium bromide, which, when distilled under reduced pressure, yields ethyl 1-methylpyrrolidine-2:5-dicarboxylate (cf. von Braun and Seeman, A., 1923, i, 1242; Le Sueur and Haas, J.C.S., 1910, 97, 173). H. E. F. NOTTON.

**Action of Grignard reagents on *N*-methylpyrrolidone.** Synthesis of substituted pyrrolines. R. LUKES (Coll. Czech. Chem. Comm., 1930, 2, 531—544).—Grignard reagents react with *N*-methylpyrrolidone to give generally a mixture of monoalkyl- $\Delta^2$ -pyrrolines (separated first as perchlorates) and dialkylpyrrolidines (subsequently isolated as picrates); a mechanism for the reaction is suggested. Thus magnesium methyl bromide and *N*-methylpyrrolidone,  $b. p.$  200°,  $d_4^{25}$  1.0450,  $n_D^{25}$  1.47118 (best prepared by electrolytic reduction of *N*-methylsuccinimide), at the ordinary temperature give 1:2-dimethyl- $\Delta^2$ -pyrroline,  $b. p.$  125—127° [perchlorate,  $m. p.$  238°; chloroaurate,  $m. p.$  135—182° (decomp.: depends on the rate of heating); chloroplatinate], and 1:2:2-trimethylpyrrolidine,  $b. p.$  130—135° (picrate, decomp. about 250°); if the reaction mixture is warmed for several hours a small quantity of a base,  $C_8H_{17}N$ ,  $b. p.$  146° (perchlorate, decomp. about 234°), is also formed. Magnesium ethyl bromide similarly yields 1-methyl-2-ethyl- $\Delta^2$ -pyrroline,  $b. p.$  40—41°/10 mm.,  $d_4^{25}$  0.8779,  $n_D^{25}$  1.48422 (perchlorate,  $m. p.$  209°; chloroaurate,  $m. p.$  115—117°), and 1-methyl-2:2-diethylpyrrolidine,  $b. p.$  168° (corr.) [hydrochloride; picrate,  $m. p.$  about 235° (decomp.); chloroaurate,  $m. p.$  159—163°; chloroplatinate], whilst magnesium *n*-propyl bromide gives 1-methyl-2-*n*-propyl- $\Delta^2$ -pyrroline,  $b. p.$  82°/30 mm.

(perchlorate), and 1-methyl-2:2-di-*n*-propylpyrrolidine,  $b. p.$  206.8°/738 mm. (corr.) (picrate).

Interaction between *N*-methylpyrrolidone (1 mol.) and magnesium phenyl bromide (3 mols.) yields only 2-phenyl-1-methylpyrroline,  $b. p.$  112°/15 mm.,  $d_4^{25}$  1.0083,  $n_D^{25}$  1.57578 (hydrochloride +  $H_2O$ ,  $m. p.$  about 96°; perchlorate,  $m. p.$  117—118°; chloroaurate +  $H_2O$ ,  $m. p.$  95—97°; chloroplatinate; picrate,  $m. p.$  140—141°). A. I. VOGEL.

**Preparation of oxindoles and iodoindoles.** Q. MINGOIA (Gazzetta, 1930, 60, 509—515).—Indole and aqueous mercuric acetate give indole 2:3-dimercuriacetate, converted by hot saturated sodium chloride solution into indole 2:3-dimercurichloride, which with iodine in potassium iodide solution affords 2:3-di-iodoindole,  $m. p.$  220° (decomp.). 3-Methylindole similarly gives 3-methylindole 2-mercuroacetate, converted successively into the chloride and 2-iodo-3-methylindole,  $m. p.$  197—198°, and 2-methylindole yields 2-methylindole mercuroacetate, giving successively the chloride and 3-iodo-2-methylindole,  $m. p.$  82°. These iodoindoles are unaffected by moist silver oxide or by aqueous or alcoholic alkali; the above mercury compounds all decompose without melting.

C. W. SHOPPEE.

**ortho- and para-Bz-Chloronitroquinolines.** E. FOURNEAU, (M.) TRÉFOUEL, (MME.) TRÉFOUEL, and A. WANCOLLE (Bull. Soc. chim., 1930, [iv], 49, 738—755).—Seven of the eight possible chloronitroquinolines containing the chlorine and nitro-group in *o*- or *p*-positions to one another in the benzene ring have been synthesised by the Skraup-Knueppel reactions. 8-Chloro-5-nitroquinoline,  $m. p.$  145°, was obtained in 63% yield from 6-chloro-3-nitroaniline, or in 82.5% yield by nitration at 0° to -5° of 8-chloroquinoline,  $b. p.$  288°/760 mm., 163°/20 mm., similarly obtained in 55% yield from *o*-chloroaniline. 6-Chloro-3-nitroaniline,  $m. p.$  119°, was obtained in 77% yield by nitration of *o*-chloroaniline sulphate at 0°. 6-Chloro-5-nitroquinoline,  $m. p.$  129°, is similarly obtained from *p*-chloroaniline either together with an orange-yellow sulphate (?),  $m. p.$  155°, and a basic precipitate,  $m. p.$  126°, by nitration of 6-chloroquinoline,  $m. p.$  41—42°,  $b. p.$  159°/45 mm. (obtained in a yield of 85—88%), or together with 6-chloro-7-nitroquinoline,  $m. p.$  160°, by the Skraup reaction on 4-chloro-3-nitroaniline,  $m. p.$  103°, obtained in 70% yield by nitration of *p*-chloroaniline sulphate at 0°. 5-Chloro-8-nitroquinoline,  $m. p.$  136°, is obtained from *m*-chloroaniline,  $b. p.$  127°/33 mm., 230°/767 mm., either by nitration of the *m*-chloroacetanilide,  $m. p.$  78°, at -10° to 15°, hydrolysis of the 5-chloro-2-nitroacetanilide,  $m. p.$  118° (after separation of the 3-chloro-4-nitroacetanilide,  $m. p.$  144°, also formed), with 50% hydrochloric acid and condensation of the 5-chloro-2-nitroaniline,  $m. p.$  125° (yield 80.3%), or together with 7-chloro-8-nitroquinoline,  $m. p.$  186°, by nitration of the mixture of 5- and 7-chloroquinolines,  $b. p.$  144°/16 mm., obtained in 86.6% yield from *m*-chloroaniline. The constitution of 5-chloro-8-nitroquinoline is confirmed by its synthesis from 2:5-dichloroaniline. 5-Chloro-6-nitroquinoline,  $m. p.$  153°, is obtained, together with 7-chloro-6-nitroquinoline,  $m. p.$  155—156°, from 3-chloro-



4-nitroaniline, m. p. 157°, obtained by hydrolysis of 3-chloro-4-nitroacetanilide, m. p. 144°, also formed in the nitration of *m*-chloroacetanilide. On reduction and elimination of the amino-group it is converted into 5-chloroquinoline, a reaction which establishes its structure. The structure of 7-chloro-6-nitroquinoline is similarly established by its conversion into 7-chloroquinoline and 7-chloro-8-nitroquinoline.

R. BRIGHTMAN.

**Stereoisomerism in polycyclic systems. VII. Reduction of 7 : 8 : 9 : 10-tetrahydroheptaquinoline.** S. G. P. PLANT and R. J. ROSSER (J.C.S., 1930, 1840—1844).—Reduction of 7 : 8 : 9 : 10-tetrahydroheptaquinoline with sodium and boiling alcohol yields approximately equal amounts of the two stereoisomeric (*cis*- and *trans*-) forms, *A*, m. p. 61·5° (hydrochloride, m. p. 244—245°; *picrate*, m. p. 167—168°; *phenylcarbamyl*, m. p. 144°, and *benzoyl*, m. p. 139—140°, derivatives), and *B*, an oil (Perkin and Plant, A., 1928, 1258) (hydrochloride, m. p. 143—145°; *picrate*, m. p. 196°; *phenylcarbamyl*, m. p. 112·5°, and *benzoyl*, m. p. 146·5°, derivatives) of 5 : 7 : 8 : 9 : 10 : 11 : 14 : 15-octahydroheptaquinoline, separated by fractional crystallisation of their hydrochlorides from ethereal-alcoholic solution. Electrolytic reduction affords the two forms *A* and *B* in the ratio 3 : 4, whilst with zinc and alcoholic hydrogen chloride the ratio is 3 : 5. Re-investigation of the product obtained by reduction with tin and alcoholic hydrogen chloride (Perkin and Plant, *loc. cit.*) by the improved method of separation indicates the presence of a small quantity of the *A* form (ratio 1 : 6). Similarly, re-examination of the product obtained by the reduction of 11-keto-5 : 7 : 8 : 9 : 10 : 11-hexahydroheptaquinoline with sodium amalgam and boiling alcohol (*loc. cit.*) reveals the presence of a small amount of the *A*-isomeride, isolated as its hydrochloride, m. p. 244—245°.

J. W. BAKER.

**Thiohydantoins from cystine and cysteine. Action of alkali.** B. H. NICOLET (J. Biol. Chem., 1930, 88, 395—401, 403—407).—A solution of cystine in sodium hydroxide was treated with acetic anhydride (1 mol.), neutralised with hydrochloric acid, and evaporated; the residue containing *N*-acetylcystine was heated with ammonium thiocyanate and acetic anhydride to give a mixture of free sulphur, *cystine-bis*-NS-diacetyl-2-thiohydantoin,  $C_{12}H_{14}O_4N_4S_4$ , m. p. 208° (decomp.), and *cysteine*-NS-diacetyl-2-thiohydantoin,  $C_8H_{10}O_3N_2S_2$ , m. p. 142°; the latter compound was obtained also by the direct action of ammonium thiocyanate and acetic anhydride on cysteine, and its production (together with liberation of sulphur) from cystine was favoured by the presence of sodium acetate.

The above cysteine derivative when kept in solution in *N*-sodium hydroxide for 30 min. at the ordinary temperature yields a polymeride of 2-thio-5-methylenehydantoin,  $(C_4H_4ON_2S)_n$ ; the same compound together with *cystine-bis*-N-acetyl-2-thiohydantoin,  $C_8H_{10}O_2N_4S_4$ , is formed by the action of 0·1*N*-sodium hydroxide on the cystine derivative described above for 5 min. at the ordinary temperature.

C. R. HARRINGTON.

**Synthesis of iminazole derivatives from  $\alpha$ -amino-acids. I. Synthesis of  $\beta$ -iminazolypropionic acid.** S. AKABORI (Proc. Imp. Acad. Tokyo, 1930, 6, 260—261).—Reduction of ethyl  $\alpha$ -aminoglutarate with 2·5% sodium amalgam in cold, dilute hydrochloric acid and treatment of the semi-aldehyde formed with potassium thiocyanate affords  $\beta$ -2-thioliminazolypropionic acid ( $+H_2O$ ), m. p. 205—206·5°. This is converted by mild oxidising agents into  $\beta$ -iminazolypropionic acid, m. p. 206—207° (lit. 208—209°).

H. BURTON.

**Structure of the veronal molecule.** C. M. ESCOLAR (Anal. Fis. Quim., 1930, 28, 495—500).—The changes of structure of the veronal molecule on addition of alkali to a 3·28% aqueous solution have been followed by measurements with the interferometer: the reading at first falls rapidly until about one equivalent of alkali has been added, and thereafter rises to approximately the initial value. The partition coefficient of veronal between water and ether diminishes from 5·8 to 0·7 as the  $p_H$  of the solution rises from 5 to 8. The physiological significance of these results is discussed with reference to the distribution of the hypnotic between the lipins and the blood. Analogous measurements with barbituric acid indicate that its structure differs from that of veronal.

H. F. GILLBE.

**Skraup reaction with 4-aminoresorcinol dimethyl ether.** K. MATSUMURA (J. Amer. Chem. Soc., 1930, 52, 3196—3198).—The Skraup-Knueppel reaction with 4-aminoresorcinol dimethyl ether gives, unexpectedly, *p*-phenanthroline [*picrate*, m. p. 255—256°; *chloroplatinate*, m. p. above 310°; *dihydrochloride*, not melted at 315°; *sulphate* ( $+H_2O$ ), m. p. 233—234°; *chromate* ( $+2·5H_2O$ ), m. p. 225—230°; *methiodide* ( $+H_2O$ ), m. p. 268—269°; *dimethiodide* ( $+H_2O$ ), m. p. 271°], oxidised to 3 : 3'-dipyridyl-2 : 2'-dicarboxylic acid, m. p. 215° (decomp.) [*sulphate* ( $+2H_2O$ ), m. p. 218°].

H. BURTON.

**Electrolytic reduction of 4-keto-3-phenyl-3 : 4-dihydroquinazoline.** H. ITOMI (Mem. Coll. Sci. Kyōtō, 1930, A, 13, 311—313).—Electrolytic reduction of 4-keto-3-phenyl-3 : 4-dihydroquinazoline with a lead cathode and aqueous-alcoholic sodium carbonate as the cathode solution at 25° gives 4-hydroxy-3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline, m. p. 170—171°, in 40% of the theoretical yield. Both the above quinazolines are reduced to 3-phenyl-1 : 2 : 3 : 4-tetrahydroquinazoline, m. p. 118—119°, when the cathode consists of copper coated with platinum-black and reduction is carried out at 50—60°.

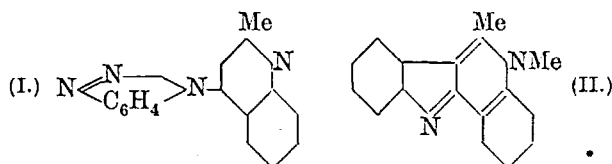
H. BURTON.

**Formation of a phenazine compound from a diphenyl ether derivative.** K. MATSUMURA (J. Amer. Chem. Soc., 1930, 52, 3199—3204).—Nitration of diphenyl ether with potassium nitrate and sulphuric acid at 10—70° gives an 80% yield of 2 : 4 : 2' : 4'-tetranitrodiphenyl ether, which when reduced with stannous chloride and hydrochloric acid at 115—120° furnishes a mixture of 2 : 4 : 2' : 4'-tetra-aminodiphenyl ether, m. p. 129° (tetrahydrochloride, not melted at 310°; *tetrabenzoyl* derivative, m. p. 232—233°), and a small amount of a diaminophenazine, not melted at 320° (*sulphate*, anhydrous and  $+7·5H_2O$ ;

triacetyl derivative, not melted at 320°). The tetraaminodiphenyl ether could not be converted into a phenoxazine derivative. H. BURTON.

**Optical and photographic properties of sensitising and desensitising dyes of the cyanine and related types.** O. BLOCH and F. M. HAMER.—See B., 1930, 928.

**Synthesis in the indole series. IV. Derivatives of 2:3-benz- $\gamma$ -carboline.** W. O. KERNACK and J. F. SMITH (J.C.S., 1930, 1999—2010).—Condensation of 4-chloro-2-methylquinoline with *o*-phenylenediamine at 140°/20—30 mm. gives 4-*o*-aminophenylamino-2-methylquinoline, m. p. 220°, isolated as its *dihydrochloride*, m. p. 301°, and converted by nitrous acid into 4-(benztriazolyl-3')-2-methylquinoline (I), m. p. 149° (*hydrochloride*, m. p. 210°), which affords 5-methyl-2:3-benz- $\gamma$ -carboline, m. p. 298° (for nomenclature, cf. Gulland, Robinson, Scott, and Thornley, this vol., 219), when heated in syrupy phosphoric acid. By similar methods are obtained 4-*o*-aminophenylamino-, m. p. 188° (*hydrochloride*, m. p. 294°), and 4-(benztriazolyl-3')-, m. p. 144° (*hydrochloride*, m. p. 221°), -6-methoxy-2-methylquinoline; and 15-methoxy-5-methyl-2:3-benz- $\gamma$ -carboline + MeOH, m. p. 236°.



Condensation of *p*-anisidine with ethyl methylacetate at 37° for 3—4 days followed by heating to 250° gives 4-hydroxy-6-methoxy-2:3-dimethylquinoline + H<sub>2</sub>O, m. p. 294°, converted by heating with phosphoryl chloride at 130—140° into the corresponding 4-chloro-derivative, m. p. 111°. This is converted as before into 4-*o*-aminophenylamino-, m. p. 193° [*monohydrochloride*, m. p. 125° (decomp.); *dihydrochloride*, m. p. 284° (decomp.)], and 4-(benztriazolyl-3')-, m. p. 201°, -6-methoxyl-2:3-dimethylquinoline. The latter does not yield a crystalline base when heated with phosphoric acid, thus confirming the view that in the previous cases ring closure occurs not in the 5-, but in the 3-position as postulated. When 4-chloro-2-methylquinoline and phenylmethylhydrazine are heated together at 160—180°, 4-( $\beta$ -phenyl- $\beta$ -methylhydrazino)-2-methylquinoline, m. p. 237° (*hydrochloride*, m. p. 172°), is obtained, but cyclisation to 1:5-dimethyl-2:3-benz- $\gamma$ -carboline, m. p. 173—174°, could not be effected. This derivative is, however, obtained when the phenylmethylhydrazone, m. p. 131—132°, of *o*-acetamidoacetophenone is treated with phosphorus oxychloride in boiling toluene. The constitution of this compound is proved as follows. Methyl sulphate in boiling benzene converts 5-methyl-2:3-benz- $\gamma$ -carboline (above) into its *methosulphate*, m. p. 277° (decomp.), which is converted by ammonium hydroxide into the *monohydrate*, m. p. 262°, of the anhydronium base 4:5-dimethyl-2:3-benz- $\gamma$ - $\psi$ -carboline (II), the *methosulphate*, m. p. 292°, of which is identical with the *methosulphate* of 1:5-dimethyl-2:3-benz- $\gamma$ -carboline. J. W. BAKER.

**Ring synthesis of porphyrins with substituted and unsaturated side-chains.** H. FISCHER and W. KUTSCHER (Annalen, 1930, 481, 193—214).—The yield of 4-carbethoxy-2:3-dimethylpyrrole-5-carboxylic acid (hydrolysed by 20% potassium hydroxide to the dicarboxylic acid, which is converted by heating in glycerol at 210° into 2:3-dimethylpyrrole) obtained by Piloty's method (A., 1912, i, 899) is much improved by careful control of the hydrogen-ion concentration. It is converted by chloroacetyl and acetyl chlorides and aluminium chloride in carbon disulphide into ethyl 4-chloroacetyl-, m. p. 103°, and 4-acetyl-, m. p. 137°, -2:3-dimethylpyrrole-5-carboxylate, respectively, the latter being reduced by the Wolff-Kishner method (sodium ethoxide and hydrazine hydrate in a sealed tube at 165°) to haemopyrrole, identified as its picrate. Ethyl 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate is converted by methyl-alcoholic sodium methoxide at 100° into methyl 3-methoxyacetyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 139° [free acid, m. p. 188° (decomp.)], decarboxylated to 3-ethoxyacetyl-2:4-dimethylpyrrole, m. p. 89°, reduced by aluminium amalgam in ether to methyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 154—155°. Similar reduction of the ethyl ester of the 3-ethoxyacetyl derivative (free acid, m. p. 175—180°) affords ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate; ethyl 3-dimethylaminoacetyl-2:4-dimethylpyrrole-5-carboxylate is reduced to the 3- $\alpha$ -hydroxyethyl derivative (Fischer and Zeile, A., 1928, 902), but ethyl 3- $\beta$ -dimethylaminopropionyl-2:4-dimethylpyrrole-5-carboxylate is reduced to ethyl 3-( $\gamma$ -dimethylamino- $\alpha$ -hydroxypropyl)-, m. p. 122°, converted by anhydrous hydrogen chloride in ether or by benzoyl chloride into ethyl 3- $\gamma$ -dimethylaminoethyl-, m. p. 95° (picrate, m. p. 182°; *hydrochloride*, m. p. 187°), -2:4-dimethylpyrrole-5-carboxylate. Bromination of ethyl 3-chloroacetyl-2:4-dimethylpyrrole-5-carboxylate affords a monobromocompound, C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>NCIBr, m. p. 147°, the constitution of which is uncertain. By the action of formaldehyde and hydrogen chloride on the appropriate pyrrole derivative are obtained bis-(4-methoxyacetyl-3:5-dimethylpyrrolyl)methane, m. p. 245° (decomp.), and bis-(4-ethoxyacetyl-3:5-dimethylpyrrolyl)methane, m. p. 174°, which could not be converted into methenes. 3-Methoxyacetyl- and 3-ethoxyacetyl-2:4-dimethylpyrroles are converted by hydrogen cyanide in ether, in the presence of hydrogen chloride, into 3-methoxyacetyl-, m. p. 127°, and 3-ethoxyacetyl-, m. p. 121°, -2:4-dimethylpyrrole-5-aldehyde, respectively, whilst condensation of these products with the parent substances in the presence of 50% hydrobromic acid affords (4-methoxyacetyl-3:5-dimethylpyrrolyl)-(4-methoxyacetyl-3:5-dimethylpyrrolyl)methene hydrobromide, m. p. 174° (free base, m. p. 143°), and (4-ethoxyacetyl-3:5-dimethylpyrrolyl)-(4-ethoxyacetyl-3:5-dimethylpyrrolyl)methene hydrobromide, m. p. 169° (decomp.) (free base, m. p. 129°). Reduction of ethyl 3-cyanoacetyl-2:4-dimethylpyrrole-5-carboxylate with aluminium amalgam converts it into ethyl 3-( $\alpha$ -hydroxy- $\beta$ -cyanoethyl)-2:4-dimethylpyrrole-5-carboxylate, m. p. 134—136°, dehydrated by hydrogen chloride in dry ether to ethyl 3- $\beta$ -cyanovinyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 201°. Ethyl 3- $\beta$ -cyanopropionyl-2:4-dimethylpyrrole-5-carboxylate,

m. p. 173° (obtained by heating the 3- $\beta$ -chloropropionyl derivative with aqueous sodium cyanide), is similarly converted successively into ethyl 3-( $\alpha$ -hydroxy- $\gamma$ -cyanopropyl)-, m. p. 113–115°, and ethyl 3- $\gamma$ -cyanoallyl-, m. p. 160°, 2:4-dimethylpyrrole-5-carboxylate. Hydrolysis of the 3- $\beta$ -cyanopropionylpyrrole ester with 20% sodium hydroxide converts it into 3- $\beta$ -carboxypropionyl-2:4-dimethylpyrrole-5-carboxylic acid, m. p. 188° (dimethyl ester, m. p. 131°), which is decarboxylated to 2:4-dimethylpyrrole-3- $\gamma$ -ketobutyric acid, m. p. 175°, which is also obtained by reduction of ethyl 3- $\beta$ -cyanopropionyl-2:4-dimethylpyrrole-5-carboxylate by the Wolff-Kishner method. 2:4-Dimethylpyrrole-5-aldehyde is converted by sulphuryl chloride in ether into 4-chloro-3-methylpyrrole-2:5-dialdehyde, m. p. 145° (diphenylhydrazone, m. p. 178°). Condensation of ethyl 2:3-dimethylpyrrole-5-carboxylate with propionyl chloride in the presence of aluminium chloride in carbon disulphide gives ethyl 4-propionyl-2:3-dimethylpyrrole-5-carboxylate, m. p. 102°, hydrolysed to the free acid, m. p. 187°. The same acid is obtained by condensation of methyl  $\alpha$ -aminoethyl ketone and propionylpyruvic acid. By the action of magnesium ethyl bromide on cryptopyrrole and treatment of the product with 5-chloroacetyl-2:4-dimethyl-3-ethylpyrrole is obtained 3:5-dimethyl-4-ethylpyrrolmethyle 3:5-dimethyl-4-ethylpyrrol ketone, m. p. 142–143° (corr.). In the conversion of ethyl 2:4-dimethylpyrrole-5-carboxylate into the 3-aldehyde-derivative a dimeride,  $C_{18}H_{24}O_4N$ , m. p. 236°, is obtained as a by-product, whilst in the preparation of ethyl 2:3-dimethylpyrrole-5-carboxylate by the Grignard reaction a polymeride,  $C_{21}H_{26}O_2N_3$ , m. p. 274–275°, probably a molecular compound of 2 mols. of the dimethylpyrrole with 1 mol. of the 5-carboxylate, is also obtained.

J. W. BAKER.

**Chlorophyll series. III. Products of the phase test.** J. B. CONANT and W. W. MOYER (J. Amer. Chem. Soc., 1930, 52, 3013–3023).—When methylphæophorbide is dissolved in a little pyridine and the solution diluted to about 0.1% with ether and shaken with one tenth of its volume of 25% methylalcoholic potassium hydroxide at 23° (phase-test reaction) for 5–10 min., products of two kinds are obtained: (a) a mixture of chlorins (acid numbers, 6–12) which cannot be isolated pure, since they change rapidly in ethereal solution into the purplish-brown compounds (acid numbers 7 and 18, respectively), phæopurpurin-7 (10–12% yield),  $C_{35}H_{38}O_7N_4$ , m. p. 200–205° on the block (dimethyl derivative, m. p. 233–235°), and phæopurpurin-18 (35–43% yield),  $C_{34}H_{36}O_5N_4$ , sinters at 250–280° (monomethyl ester, m. p. 275–278°); (b) chlorin-e and a monomethylchlorin (combined yield, 15%) of acid number 5. This is not identical with chlorin-e monomethyl ester, since further methylation gives an ester which differs in crystalline form from chlorin-e trimethyl ester. The formation of chlorin-e is completely repressed by replacing the methyl alcohol by ethyl or  $n$ -propyl alcohol, or by carrying out the reaction at –10°, whilst in boiling pyridine (Willstätter's conditions; cf. A., 1911, 1, 659) chlorin-e is the main product and no unstable chlorins are formed. The unstable chlorins probably comprise two compounds

differing by a methoxyl group, one of which, the precursor of phæopurpurin-18, is identical with phytochlorin-g. On methylation, both yield dimethylphæopurpurin-7. Towards alkali the trimethyl ester of chlorin-e behaves very similarly to methylphæophorbide, yielding unstable chlorins at the ordinary temperature and chlorin-e at the b. p. Phæopurpurin-7 contains one methoxyl and one free propionic acid group. Phæopurpurin-18 has no methoxyl, but one free carboxyl and probably one lactone and one lactam group. It is hydrolysed in ether by methylalcoholic potassium hydroxide to a product,  $C_{34}H_{38}O_6N_4$ , apparently identical with Willstätter's chlorin-a (trimethyl ester, m. p. 239–240°). This reverts rapidly in solution at 140° and slowly at the ordinary temperature to phæopurpurin-18. Both phæopurpurins are almost completely converted by alkali at 150° under the conditions used by Treibs and Wiedemann (A., 1929, 941) into rhodoporphyrin. Details of the absorption spectra of the new compounds are given and their probable constitutions are discussed (cf. this vol., 225, 793). The formulæ given for phæopurpurin-18, chlorin-a, chlorin-e,  $C_{34}H_{40}O_7N_4$ , and their methyl esters differ by +4H from those obtained by assuming that these products are formed by simple hydrolysis and agree much better with the analytical results than do the latter.

H. E. F. NOTTON.

**Glutathione.** B. H. NICOLET (J. Biol. Chem., 1930, 88, 389–393).—Glutathione with ammonium thiocyanate and acetic anhydride yielded a compound,  $C_{16}H_{19}O_6N_5S_3$ , m. p. 155° after sintering at 140°; the product obtained by condensing this compound with benzaldehyde in presence of acetic acid and sodium acetate afforded, when hydrolysed with sodium hydroxide, a 50% yield of benzylidenethiohydantoin. The compound  $C_{16}H_{19}O_6N_5S_3$  is therefore regarded as a bithiohydantoin in the formation of one of the thiohydantoin groups of which glycine must have taken part. It follows that glycine occupies a terminal position in the molecule of glutathione, and in conjunction with the evidence adduced by Hopkins (A., 1929, 1491) and by Kendall and others (this vol., 113, 945), that the latter compound is  $\gamma$ -glutamylcysteinylglycine.

C. R. HARRINGTON.

**Glutathione. IV. Determination of structure.** E. C. KENDALL, H. L. MASON, and B. F. MCKENZIE (J. Biol. Chem., 1930, 88, 409–423).—Evidence is adduced that glutathione is not hydrolysed during esterification with alcohol and hydrogen chloride and the previous work (this vol., 945) on the reaction between the ethyl ester hydrochloride and magnesium phenyl bromide is confirmed. By heating in aqueous solution at 62° for 120 hrs. glutathione was hydrolysed to glutamic acid and a dipeptide of glycine and cysteine, only a small amount of the latter having undergone conversion into the anhydride. After treatment of this dipeptide with sodium hypobromite or with nitrous acid the product still gave glycine (although in poor yield) on hydrolysis. The dipeptide was oxidised to the disulphide, the latter was condensed with 2:3:4-trinitrotoluene, and the product was hydrolysed with hydrochloric acid to a product, m. p. 190–195°, and glycine; the dipeptide was therefore cysteinyl-

glycine, which confirms the previously suggested (*loc. cit.*) constitution of  $\gamma$ -glutamylcysteinylglycine for glutathione. Whilst direct treatment of glutathione with hydrogen peroxide yields a product from which no glycine and only small amounts of succinic acid can be obtained by hydrolysis, large amounts of these compounds result from hydrolysis of the product of oxidation with hydrogen peroxide of the sulphonic acid corresponding with glutathione. C. R. HARRINGTON.

**Condensation of 2:4-diketo-3-phenylthiazole with aromatic aldehydes.** K. S. MARKLEY and E. E. REID (J. Amer. Chem. Soc., 1930, 52, 2981—2984).—All the aldehydes examined except resoreyl-aldehyde,  $\gamma$ -phenylpropaldehyde, and 2:4:6-trinitrobenzaldehyde give high yields of derivatives suitable for purposes of characterisation when refluxed with this reagent in glacial acetic acid in presence of sodium acetate (cf. Andreasch, A., 1918, i, 80; Ruhemann, J.C.S., 1909, 95, 117). The following 2:4-diketo-3-phenyl-5-arylidenethiazoles are described: -*p*-methylbenzylidene-, m. p. 192°; -*p*-hydroxybenzylidene-, m. p. 257.5°; -*o*-chlorobenzylidene-, m. p. 169—170°; -*vanillylidene*-, m. p. 234—235°; -*veratrylidene*-, m. p. 208—209°; -*furfurylidene*-, m. p. 218—219°; -*p*-anisylidene-, m. p. 199—200°; -*o*-anisylidene-, m. p. 138—139°; and -*m*-nitrobenzylidene-, m. p. 188°.

H. E. F. NOTTON.

**Catalytic reduction of nicotine and metanicotine.** W. R. HARLAN [with R. M. HIXON] (J. Amer. Chem. Soc., 1930, 52, 3385—3388).—Catalytic reduction (Adams) of nicotine hydrochloride in 95% alcohol gives a mixture of 25% of hexa- and 75% of octa-hydronicotine hydrochlorides. A mixture of nicotine and its hexa- and octa-hydro-derivatives can be separated by fractional crystallisation of the hydrochlorides and picrates. Similar reduction of metanicotine affords the dihydro-derivative; this can be reduced further to octahydrometanicotine.

H. BURTON.

**Sparteine.** III. K. WINTERFELD and W. IPSEN (Arch. Pharm., 1930, 268, 372—380).—Sparteine  $\alpha$ -methoacetate, from the methiodide and silver acetate, is oxidised by mercuric acetate to a mercuri-derivative, which with hydrogen sulphide gives syrupy *dehydrosparteine methoacetate*. Attempts to convert this into crystalline salts were unsuccessful. It is oxidised by chromic and sulphuric acids to carbon dioxide and two products of amphoteric nature. These are obtained in better yield by oxidation and subsequent demercuration of the mercuri-derivative. The first is isolated as the *chloroplatinate*, m. p. 250° (also +H<sub>2</sub>O), after removal of chromium and sulphate. The free base, C<sub>7</sub>H<sub>13</sub>O<sub>2</sub>N, [ $\alpha$ ]<sub>D</sub><sup>20</sup> -51.6°, gives a positive pine-shaving reaction, contains a methylimino-group, and must therefore be derived from the nucleus which is concerned in methiodide formation. Since this nucleus has already been degraded to 2-methylpyrrolidine (A., 1929, 1186), the new product must be a 1:2-dimethylpyrrolidine-3-, -4-, or -5-carboxylic acid. The second product, a hygroscopic, optically inactive oil, gives a dark blue copper salt (N, 8.5%). H. E. F. NOTTON.

**Strychnine and brucine.** XI. Dihydrobrucine and some derivatives. O. ACHMATOWICZ, R. C. FAW-

CETT, (the late) W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1930, 1769—1772).—Catalytic reduction of brucine with palladised charcoal affords *dihydrobrucine*, m. p. 179—181°, +4H<sub>2</sub>O, m. p. 70—72°, +1.5AcOEt, m. p. 48—50° [*methosulphate* +2H<sub>2</sub>O, m. p. 242—244° after sintering at 215°; *methiodide* +H<sub>2</sub>O, m. p. 283—285° after sintering at 245°, when prepared by the action of sodium iodide on the methosulphate, direct combination of dihydrobrucine with methyl iodide yielding a compound, m. p. 242—245° (decomp.)], and converted into *bisapomethylidihydrobrucine*, not melting at 320°, by a method similar to that used by Leuchs and Anderson (A., 1911, i, 746) for *bisapomethylbrucine*. The dihydrobrucine, m. p. 115°, described by Skita and Franck (A. 1911, i, 1017) cannot have been homogeneous (cf. Wieland and Münster, this vol., 936). Similar reduction of brucidine affords *dihydrobrucidine*, m. p. 172—172.5° (retains acetone of crystallisation tenaciously) [*dimethosulphate*, m. p. 270°], which is also obtained by electrolytic reduction of dihydrobrucine, whilst tetrahydrobrucine is reduced to *hexahydrobrucine*, m. p. 133°.

J. W. BAKER.

**Sinomenine and disinomenine.** XVII. Methylsinomeninone. K. GOTO, T. NAMBO, and R. INABA (Bull. Chem. Soc. Japan, 1930, 5, 223—227).—Treatment of methylsinomenine with 2*N*-hydrochloric acid at 100° gives methylsinomeninone, m. p. 188°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +18.65° in chloroform (*oxime*, sinters at 100°, m. p. 170°, decomp. 213°; *methiodide*, decomp. 225—227°), in 70% yield; this with hydrogen and palladised charcoal yields dihydromethylsinomeninone, m. p. 128°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +71.05° in chloroform [*oxime*, m. p. 177°; *methiodide*, m. p. 248° (decomp.)], but with concentrated aqueous ammonia gives an amorphous substance.

The reactions of methylsinomenine are therefore not completely analogous with those of either sinomenine or its 1-bromo-derivative. An improved preparation of benzoylsinomenine [*oxime*, m. p. 249° (decomp.); *methiodide*, m. p. 237° (decomp.)] is given.

R. J. W. LE FÈVRE.

**Direct arsenation of benzene derivatives.** C. S. HAMILTON and C. G. LUDEMANN (J. Amer. Chem. Soc., 1930, 52, 3284—3286).—The formation of *o*-carboxyphenylarsinic acid (Rosenmund, A., 1921, i, 370) and acetophenone-4-arsinic acid (G.P. 468,403) by the action of potassium arsenite on *o*-bromobenzoic acid and *p*-bromoacetophenone, respectively, is confirmed. *p*-Carboxyphenylarsinic and *o*-phenylenediarsinic acids are similarly prepared from *p*-bromobenzoic and *o*-bromophenylarsinic acids, respectively. Little or no arsenic acid was obtained using halogenonitrobenzenes and *p*-bromobenzenesulphonic acid.

H. BURTON.

**Arsinic acids of *p*-aminophenol.** M. A. PHILLIPS (J.C.S., 1930, 1910—1916).—Nitration of *o*-acetamidophenylarsinic acid with mixed acids at 5° affords 5-nitro-2-acetamido-, reduced by sodium hyposulphite and 2*N*-sodium hydroxide at 10° to 5-amino-2-acetamido-, and converted by boiling 50% sodium hydroxide into 5-nitro-2-hydroxy-phenylarsinic acid. The last-named is reduced by various reagents to the corresponding 5-amino-acid, acetylated

to 5-acetamido-2-hydroxyphenylarsinic acid (cf. Benda, A., 1912, i, 61; Balaban, this vol., 354). 3-Oxalylaminophenylarsinic acid (G.P. 261,643; cf. Fourneau and others, A., 1923, i, 983) is converted by potassium nitrate and sulphuric acid into the 2-nitro-5-oxalylamino-acid, hydrolysis of which with boiling 2*N*-hydrochloric acid to 2-nitro-5-aminophenylarsinic acid is accompanied by considerable fission of arsenic. Much less separation of arsenic occurs in the similar hydrolysis of 2-nitro-5-acetamidophenylarsinic acid, prepared as follows. 4-Nitro-*m*-phenylenediamine is converted by boiling acetic acid and acetic anhydride into a mixture of 4-nitro-3-aminoacetanilide, m. p. 200° (Kehrmann and Mermod, A., 1927, 260, give m. p. 178°) (deaminated to *p*-nitroacetanilide, and converted by the Sandmeyer reaction and subsequent hydrolysis into 3-chloro-4-nitroaniline), and the 1:3-diacetamido-compound. After diazotisation of the mixture, unchanged 4-nitro-1:3-diacetamidobenzene is removed and the diazonium salt converted into the required acid by the action of copper arsenite (cf. Bart, G.P. 250,264). Reduction of the 2-nitro-acid with sodium hyposulphite affords 2-amino-5-acetamidophenylarsinic acid. 2-Nitro-5-aminophenol (acetyl derivative, m. p. 200°; diacetyl derivative, m. p. 118°) is obtained either by diazotisation of 4-nitro-3-aminoacetanilide and subsequent treatment with 2*N*-solutions of sulphuric acid and copper sulphate, or by refluxing 4-nitro-1:3-diacetamidobenzene with 40% potassium hydroxide. It is converted by the Sandmeyer reaction into 5-chloro-2-nitrophenol. Application of the modified Bart method (above) to 4-nitro-3-aminophenol gives a 37% yield of 2-nitro-5-hydroxyphenylarsinic acid, monohydrate, m. p. 175°, resolidifying and melting again at 205°, which is also obtained by boiling 2-nitro-5-aminophenylarsinic acid with 25% sodium hydroxide. Reduction with ferrous sulphate and sodium hydroxide converts it into the corresponding 2-amino-acid (*N*-acetyl derivative, m. p. 230°; magnesium, barium, and calcium salts). 2:5-Diaminophenylarsinic acid, m. p. 220° (calcium and magnesium salts), is obtained by acid hydrolysis of either of its monoacetyl derivatives and on acetylation affords 2:5-diacetamidophenylarsinic acid + H<sub>2</sub>O, m. p. 225° (decomp.) (calcium, barium, and magnesium salts). Nitration of 2-methoxyphenylarsinic acid (Johnson and Adams, A., 1923, i, 724) with mixed acids at 5° affords the 5-nitro-acid, reduced by ferrous sulphate and sodium hydroxide to 5-amino-2-methoxyphenylarsinic acid, decomp. 240—245° (acetyl derivative, decomp. 260—262°; monosodium + H<sub>2</sub>O salt). Nitration of *m*-acetamidophenol with nitric acid (*d* 1.45) at 0° and hydrolysis of the two products (separated by fractional crystallisation from alcohol) so obtained affords 4-nitro-3-aminophenol and a nitroaminophenol, m. p. 163°, which is not 2-nitro-5-aminophenol, the constitution of which is under investigation (Meldola and Stephens, J.C.S., 1906, 89, 925, state it to be 6-nitro-3-aminophenol).

J. W. BAKER.

Properties and molecular state of organic arsenicals. F. F. BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1930, 52, 2946—2951).—Contrary

to many published statements (cf., however, Palmer and Scott, A., 1928, 433; Steinkopf and Dudek, A., 1929, 1471), arsenobenzene and its *pp'*-dimethyl, m. p. 218—219°, and *pp'*-dimethoxy-, m. p. 230—232°, derivatives, obtained from the dichloroarylsarsines and hypophosphorous acid in hot acetone, are colourless and do not absorb oxygen. In presence of traces of catalysts, such as the strong mineral acids, iodine, halogenoarylsarsines, and triphenylmethyl bromide, they react rapidly, the amount of oxygen absorbed (1—2 mols. per mol. of arsenobenzene) depending on the catalyst chosen. Mol. wt. determinations show that aromatic arsenicals may be divided into three classes. (I) Compounds in which the arsenic atom is attached by single linkings to atoms other than arsenic, e.g., halogenoarylsarsines, triarylsarsines, and diarylsarsine oxides or sulphides, are colourless, unimolecular in solution, and stable towards oxygen. (II) Compounds in which arsenic is doubly linked to arsenic or some other atom, e.g., arylarsenious oxides, sulphides, and imides, and arsenobenzenes, are stable towards oxygen when pure and are associated (di- to quadrimolecular) in solution. (III) Compounds in which arsenic is singly linked to arsenic, e.g., tetraaryldiarsines and di-iododiarylsarsines, react instantly with oxygen and in solution may be partly dissociated into free radicals. Phenylarsenious sulphide has m. p. 174—176°.

H. E. F. NOTTON.

#### Diarsines. III. Di-iododiaryldiarsines. F. F.

BLICKE and F. D. SMITH (J. Amer. Chem. Soc., 1930, 52, 2937—2946).—*Di-iodo- $\alpha$ -naphthylarsine*, m. p. 106—108°, and *di-iodo-*p*-diphenylarsine*, m. p. 104—106°, are obtained from the arylarsenious oxide and hydriodic acid (*d* 1.7) at 100°. The following di-iododiaryldiarsines are prepared by the method of Michaelis and Schulte (A., 1881, 722): *-diphenyl-*, m. p. 176—177°, *-di-*p*-tolyl-*, m. p. 149—150°; *-di-*p*-anisyl-*, m. p. 135—137°; *-di- $\alpha$ -naphthyl-*, m. p. 176—178°, and *-di-*p*-diphenyl-*, m. p. 244—246° (decomp.). The mol. wt. of these derivatives does not deviate sufficiently from the normal to afford evidence of dissociation into free radicals. Di-iododiphenylarsine (I) is also formed (a) from phenylarsenious oxide, hydriodic acid, and phosphorous acid in absolute alcohol, (b) from arsenobenzene (1 mol.) and di-iodophenylarsine (2.5 mols.) in alcohol, (c) from arsenobenzene (1 mol.) and iodine (1 mol.) in benzene, and (d) from di-iodophenylarsine and mercury in bromobenzene, the apparatus and methods being similar to those used in the isolation of free radicals. The diarsine rapidly absorbs oxygen, probably forming first a peroxide which decomposes liberating iodine. This with I yields di-iodophenylarsine, the final result being given by the scheme  $2(\text{AsPhI})_2 + \text{O}_2 \rightarrow 2\text{AsPhO} + 2\text{AsPhI}_2$ . In presence of mercury twice this volume of oxygen is absorbed, owing to the occurrence of reaction (d). The oxygen absorptions of the products obtained in reactions (b) and (c) are in accordance with expectation, but in presence of a trace of iodine arsenobenzene (4 mols.) absorbs 5—6 mols. of oxygen, and in presence of a trace of di-iodophenylarsine 4—5 mols., instead of 4 mols. *Dibromodiphenylarsine* (2 mols.), m. p. 122—124° in nitrogen, from dibromophenylarsine and

arsenobenzene at 135°, absorbs between 1 and 2 mols. of oxygen in bromobenzene solution. Dichlorophenylarsine and arsenobenzene give a solution which absorbs oxygen, although no dichlorodiphenyl-diarsine can be isolated from it. The diarsine I in benzene is slowly converted by mercury into arsenobenzene (95% of the theoretical) and triphenylarsine.

H. E. F. NOTTON.

**Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. V. Nitration of benzyldiethylsulphonium picrate.** A. POLLARD and R. ROBINSON (J.C.S., 1930, 1765—1769).—Treatment of benzyldiethylsulphonium picrate, m. p. 115—116°, prepared from the corresponding bromide, with nitric acid (*d* 1.51), first at 0° and then at the ordinary temperature, gives a mixture of *o*-, m. p. 118—120°, *m*-, m. p. 147—148° (about 28%), and *p*-nitrobenzyldiethylsulphonium picrates, m. p. 112—114° (about 61%). The nitro-salts are synthesised from nitrobenzyl halides, diethyl sulphide, and sodium picrate. It is now considered that the relatively greater deformation of the ionic centres in the sulphonium salt renders the sulphonium cation less effective than the ammonium in distributing a positive field over the nucleus (cf. A., 1928, 71).

*o*-Nitrobenzyldiethylsulphonium chloride develops an intense bluish-violet coloration when treated with sodium hydroxide in acetone solution. A solution of *p*-nitrobenzyldiethylsulphonium chloride in acetone gives an intense eosin-red coloration with aqueous-alcoholic potassium hydroxide. These colorations may be due to the formation of quinonoid betaines,  $-\text{[NO}_2\text{:C}_6\text{H}_4\text{:CH:SR}_2\text{]}+$ .

H. BURTON.

**Alternating effect in carbon chains. XXXIII. Nitration of aromatic sulphonium and selenonium salts.** J. W. BAKER and W. G. MOFFITT (J.C.S., 1930, 1722—1733).—Nitration of phenyldimethylsulphonium and -selenonium picrates with a mixture of nitric (*d*<sub>4</sub><sup>15</sup> 1.53) and 95% sulphuric acids at 60° gives 94 and 99%, respectively, of the *m*-nitro-derivatives; no trace of the *o*- or *p*-nitro-compounds could be detected. The exclusive *m*-nitration shows that the possible influence of *op*-directive tautomeric electron displacements due to the presence of unshared electron pairs in the outer group of electrons is inoperative in orientation; the unshared pairs are effectively restricted by the charge on the atom. The damping effect of the extra electron group present in selenium is, however, clearly indicated by the formation of only 16% of the *m*-nitro-derivative by nitration of benzyldimethylselenonium picrate with nitric acid (*d*<sub>4</sub><sup>15</sup> 1.53) at -15°, whereas the corresponding sulphonium compound affords 52% of *m*-nitro-compound. The relationship between the directive action of various elements and their position in the periodic classification is discussed. The amounts of isomerides formed during nitration are determined by the bromination method (Goss, Ingold, and Wilson, A., 1926, 1132), or by oxidation to the nitrobenzoic acids and subsequent reduction and bromination (Flürscheim and Holmes, A., 1928, 403).

Prolonged treatment of phenyl methyl sulphide with methyl sulphate at 100° and addition of aqueous

sodium picrate to the resulting methosulphate give phenyldimethylsulphonium picrate, m. p. 101—102°. *m*- and *p*-Nitrophenyldimethylsulphonium picrates, m. p. 163° and 137°, respectively, are prepared similarly. Phenyldimethylselenonium picrate, m. p. 87—89°, is obtained by the same process from phenyl methyl selenide. When a large excess of sodium picrate solution is used in the preparation of this salt, there is also obtained the double picrate,

$[\text{SePhMe}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{O}]_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{ONa}$ , m. p. 136—144° (decomp.). Treatment of an alcoholic solution of *p*-chloronitrobenzene with the product from phosphorus pentaselenide, selenium, and aqueous-alcoholic sodium hydroxide affords *pp'*-dinitrodi-phenyl selenide, m. p. 170—171°. Reduction of this with alkaline sodium sulphide and subsequent methylation with methyl sulphate gives *p*-nitrophenyl methyl selenide, m. p. 54—56°, converted as above into *p*-nitrophenyldimethylselenonium picrate, m. p. 122—123°. Methylation of the product from *m*-nitrophenyl selenocyanate and aqueous-alcoholic sodium hydroxide furnishes *m*-nitrophenyl methyl selenide, m. p. 30—31°, convertible into *m*-nitrophenyldimethylselenonium picrate, m. p. 156°. Benzyl bromide and dimethyl sulphide afford a hygroscopic bromide which with aqueous sodium picrate yields benzyldimethylsulphonium picrate, m. p. 134°. *o*-, *m*-, and *p*-Nitrobenzyldimethylsulphonium picrates, m. p. 150—153°, 167.5—168.5°, and 148.5—149°, respectively, are prepared similarly from the appropriate nitrobenzyl iodides. Prolonged digestion of dibenzyl diselenide with an excess of methyl iodide, conversion of the resulting tri-iodide into the hydroxide by the action of silver oxide in sulphurous acid, and treatment of this with aqueous picric acid gives benzyldimethylselenonium picrate, m. p. 118°, also formed from benzyl bromide, dimethyl selenide, and aqueous sodium picrate. *o*-, *m*-, and *p*-Nitrobenzyldimethylselenonium picrates have m. p. 145—148°, 132—134°, and 152°, respectively.

H. BURTON.

**Triorgano-thallium compounds; thallium triethyl and thallium triphenylmethyl.** H. P. A. GROLL (J. Amer. Chem. Soc., 1930, 52, 2998—3002).—Thallium diethyl chloride and lithium ethyl in light petroleum in complete absence of air and moisture (cf. Schlenk and Holtz, A., 1917, i, 255) at the ordinary temperature give 79% of the theoretical of thallium triethyl, b. p. 54.6—54.8°/1.50—1.55 mm., decomp. 129°/760 mm. without boiling, f. p. between -80° and -183°, *d*<sub>4</sub><sup>25</sup> 1.971. It is also formed in small yield from alloys of thallium with 7%, 10%, or 15% of sodium and ethyl chloride at the ordinary temperature. It is stable towards oxygen, but is slowly decomposed by water to thallium diethyl hydroxide and ethane. The slowness of reaction arises from the immiscibility of the two liquids, since the trialkyl is violently decomposed by absolute alcohol. Syrupy thallium triphenylmethyl, obtained in an impure state from thallium diethyl chloride and sodium triphenylmethyl, gives in moist air thallium diethyl carbonate and triphenylmethane.

H. E. F. NOTTON.

**Preparation of magnesium phenyl chloride in absence of solvent.** H. GILMAN and R. E. BROWN



(J. Amer. Chem. Soc., 1930, 52, 3330—3332).—When magnesium (0.15 atom) is heated with chlorobenzene (0.1 mol.) in an evacuated, sealed tube at 150—160° for 3 hrs., magnesium phenyl chloride is obtained in 85% yield. The solid Grignard reagent is dissolved in ether before use.

H. BURTON.

**Combination of iron with proteins, amino-acids, and related compounds.** C. V. SMYTHE and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 88, 241—269).—The mode of combination of iron with the compounds named has been investigated (a) by determination of the concentration of ferric iron in solution in presence of the substance under test, for which the intensity of colour produced with thiocyanate was utilised, (b) by determining whether the iron compound is anodic or cathodic in character. The first method showed that marked reduction in the concentration of ferric iron in a solution (*i.e.*, formation of an undissociated iron compound) occurred on addition of  $\alpha$ -hydroxy-aliphatic acids, unsubstituted and hydroxy-dicarboxylic acids, hydroxy- and dicarboxylic amino-acids, phosphoric and arsenic acids, glycerophosphoric and nucleic acids, caseinogen and gelatin; ordinary amino-acids had no effect. These results were confirmed by electrical transference experiments which showed the iron to be in the anodic condition in solutions of the above-mentioned compounds at suitable  $p_{\text{H}}$ ; in some cases (*e.g.*, the dicarboxylic acids) the iron is held in the undissociated complex at reactions as acid as  $p_{\text{H}}$  2.0. The extra force necessary for the formation of this complex is thought to be derived from the residual negative charge of the substituent group; thus in the simplest case, lactic acid, the compound is formulated  $\text{OH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Fe}(x)_n$ ; the explanation is

elaborated to cover the more complex cases. The amount of iron bound in the complex with caseinogen can be accounted for by the dicarboxylic amino-acids and the phosphoric acid contained in the protein.

C. R. HARRINGTON.

**Combination between dyes and gelatin granules.** L. M. C. RAWLINS and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 88, 271—284).—The amount of Biebrich scarlet or of tropæolin-O which is taken up by gelatin granules at  $p_{\text{H}}$  2.2 or 3.5 at a fixed temperature depends on the time of contact; the ultimate amount of dye taken up corresponds, however, with that which combines with the same amount of gelatin in solution at the same reaction. Logarithmic plotting of the absorption data fails to give curves approximating to straight lines. The process is therefore regarded as one of chemical combination rather than of adsorption. In the case of the gelatin solutions a "protective colloidal" region was observed in which precipitation of the normally insoluble protein-dye complex failed to occur. On the assumption that the solubility of the protein is due to the orientation of its polar group to water, this phenomenon is ascribed to the progressive neutralisation of the polar groups by the dye; until a certain concentration of the latter is attained the number of free polar groups may suffice to maintain the complex in the soluble condition.

C. R. HARRINGTON.

**Mol. wt. of legumin.** B. SJÖGREN and T. SVEDBERG (J. Amer. Chem. Soc., 1930, 52, 3279—3283).—Solutions of legumin show an absorption maximum at 280  $\mu$  and a minimum at 255  $\mu$  both at  $p_{\text{H}}$  6.5 and 12.4. Determinations of the mol. wt. by the method of sedimentation equilibrium give a mean value of  $208,000 \pm 5000$  at  $p_{\text{H}}$  6.5—8.0 in phosphate buffers. The protein is stable at  $p_{\text{H}}$  5—9, but at  $p_{\text{H}} < 5$  and  $> 9$  the molecules are disrupted. The molecules are spherical with a radius of 3.96  $\mu$ .

The mol. wt., sedimentation constant, molar frictional constant, and molecular radius of legumin are identical, within the limits of experimental error, with the corresponding constants for edestin (A., 1929, 1092), amandin and excelsin (this vol., 356), and *R*-phycocyan, *C*-phycocyan, and *R*-phycocerythrin (*ibid.*, 233).

H. BURTON.

**Determination of organic halogen.** P. W. ROBERTSON (J. Amer. Chem. Soc., 1930, 52, 3023—3024).—The method of Thompson and Oakdale (this vol., 799) is similar to that of the author (J.C.S., 1915, 107, 902; 1916, 109, 218), the latter being preferred.

H. E. F. NORTON.

**Determination of halogens in organic compounds.** J. J. THOMPSON and U. O. OAKDALE (J. Amer. Chem. Soc., 1930, 52, 3466—3467).—The authors' method (this vol., 799) for the determination of halogen in organic compounds is preferred to that of Robertson (preceding abstract) since it is more rapid, more accurate, and applicable to iodo- as well as to chloro- and bromo-compounds.

H. BURTON.

**Determination of sulphur in organic compounds.** H. ZAHND and H. T. CLARKE (J. Amer. Chem. Soc., 1930, 52, 3275—3279).—The substance is oxidised with potassium nitrate and nitric acid, the nitric acid evaporated, the residue fused, and the amount of sulphate determined. The method can be used for the determination of sulphur in material containing as little as 0.02%, but fails with compounds yielding volatile sulphones.

H. BURTON.

**Identification and determination of methyl alcohol in presence of ethyl alcohol.** A. IONESCO-MATIU and C. POPESCU (J. Pharm. Chim., 1930, [viii], 12, 63—79).—A critical account and bibliography of existing methods are given, together with the results of experimental examination. The colour reactions of formaldehyde and formic acid with mercury compounds afford the foundation for the most suitable qualitative and quantitative methods. The redistillation in presence first of acid and then of alkali of the original distillate is necessary to obtain trustworthy results.

S. I. LEVY.

**Micro-determination of cholesterol.** R. OKEY (J. Biol. Chem., 1930, 88, 367—379).—Blood or other tissue is extracted with a mixture of alcohol and ether (*cf.* Bloor, A., 1928, 662); an aliquot portion of the filtered extract is evaporated in presence of excess of digitonin, the residue is washed with ether and then with warm water, and the remaining cholesterol digitonide is oxidised with standard potassium dichromate and sulphuric acid, the excess of dichromate being determined iodometrically. If cholesteryl esters are to be included the extract is hydrolysed with sodium hydroxide and the residue obtained on

evaporating the alkaline solution in an atmosphere of carbon dioxide is treated with slight excess of sulphuric acid and extracted with light petroleum. The latter is evaporated and the residue is taken up in alcohol and treated as above.  
C. R. HARRINGTON.

**Rapid determination of furfuraldehyde.** A. NOLL, F. BOLZ, and W. BELZ (Papier-Fabr., 1930, 28, 565—568).—Furfuraldehyde in aqueous or alcoholic solution is treated with a 7% solution of hydroxylamine hydrochloride,  $\alpha$ -furfuraldoxime being formed, and an equivalent amount of hydrochloric acid liberated. The reaction is complete after shaking for 30 min. at the ordinary temperature or 1 hr. on the water-bath. The free acid is then titrated with 0.1N-sodium hydroxide, 1 c.c. being equivalent to 0.0096 g. of furfuraldehyde. The method has been applied to the determination of furfuraldehyde in the condensates and residual liquors in the sulphite pulp process. The furfuraldehyde is liberated from its hydrogen sulphite compound, the lignin residues are precipitated with alcohol, and the furfuraldehyde is determined as above.  
T. T. POTTS.

**Colorimetric determination of tryptaflavin and rivanol.** M. J. SCHULTE (Pharm. Weckblad, 1930, 67, 809—811).—The same colour is obtained with red fuming nitric acid as with nitrous acid. In strong sunlight the colour disappears within a minute.  
S. I. LEVY.

**Micro-detection of alkaloids.** G. D. LANDER (Analyst, 1930, 55, 474—476).—Fränkel's method of isolation and purification of alkaloids, primarily in saliva, is described in detail and the sensitivity of the colour tests with various alkaloids is recorded.  
D. G. HEWER.

**Apparatus for micro-catalytic hydrogenation.** J. F. HYDE and H. W. SCHERP (J. Amer. Chem. Soc., 1930, 52, 3359—3363).—The apparatus described involves the use of the same principle as that of Warburg (A., 1925, i, 321). An accuracy of  $\pm 2\%$  is obtained for the micro-scale hydrogenation of *d*-pinene, maleic, and dimethylacrylic acids. The apparatus can also be used for the determination of small amounts of gas absorbed or evolved during a reaction.  
H. BURTON.

## Biochemistry.

**Determination of blood [in blood-stained materials].** M. WAGENAAR (Z. anal. Chem., 1930, 81, 207—212).—Quantitative results are possible by the determination of nitrogen and iron content. Tabulated results of the ratio of nitrogen to iron of bloods of different mammalian origin are given.  
J. O. CUTTER.

**Determination of hæmoglobin. Hæmoglobinometer.** F. F. SCHWENTKER (J. Lab. Clin. Med., 1929, 15, 247—259).—A spectroscopic method is described.  
CHEMICAL ABSTRACTS.

**Position of the violet band of oxy- and carbon monoxide-hæmoglobin.** F. R. BERG and W. SCHWARZACHER (Z. physiol. Chem., 1930, 190, 184—188).—The violet band in the absorption spectrum of oxyhæmoglobin is at  $4137 \pm 2$  and that of carbon monoxide-hæmoglobin is at  $4180 \text{ Å}$ . No difference in this respect is discernible in the product from various animal species and that from man.  
J. H. BIRKINSHAW.

**Decomposition of blood-pigments by dilute acids.** G. BARKAN (Biochem. Z., 1930, 224, 53—62).—The view of Lintzel and Radeff (A., 1929, 338) that treatment of oxyhæmoglobin with dilute acid decomposes part of the pigment, liberating iron, is denied, since the amount of iron set free does not correspond with the amount of pigment disappearing. The iron liberated is the "labile" iron investigated previously by the author (A., 1928, 537; 1929, 87).  
P. W. CLUTTERBUCK.

**Additive power of hæmatin.** A. HAMSÍK (Z. physiol. Chem., 1930, 190, 199—221).—"Active" hæmatin like the  $\alpha$ -metahæmins probably contains acetone or alcohol combined as a complex. This  $\alpha$ -metahæmatin is converted into the anhydride

and inactivated by the loss of the additive substance. It is considered that acetone and alcohol (a) can drive out the oxygen from oxyhæmoglobin, whereby formation of methæmoglobin is induced, (b) can convert native globin into paraglobin, whereby cathæmoglobin is formed, (c) can drive out paraglobin from the complex and give acetone- and alcohol-hæmatin. The preparation and properties of the  $\alpha$ -metahæmins and  $\psi$ -hæmins are described and the inactivation of active hæmatin is followed under various conditions. The coupling of globin with various hæmatin preparations in presence of pyridine and potassium cyanide is described.  
J. H. BIRKINSHAW.

**Structure of hæmocyanin.** A. SCHMITZ (Naturwiss., 1930, 18, 798).—When hæmocyanin is hydrolysed by N-sodium hydroxide and the precipitate extracted with alcohol, there is obtained a solution of the sodium salt of a complex copper compound. The free acid (C 44.9, H 7.1, N 12.5, Cu 6.3%) is obtained by acidification and purified by reprecipitation. It is greenish-blue, amorphous, yields no copper ion, and has an absorption spectrum similar to that of oxyhæmocyanin, with a maximum at  $495 \text{ m}\mu$  and complete absorption below  $425 \text{ m}\mu$ . It is decomposed by hot concentrated hydrochloric acid with conversion of all the nitrogen into amino-nitrogen. Hæmocyanin is also similarly decomposed by trypsin. It is suggested that hæmocyanin consists of a protein combined with a complex copper compound which is of peptide nature and not a porphyrin.  
R. K. CALLOW.

**Nature of the prosthetic group in *Limulus* hæmocyanin.** J. B. CONANT and W. G. HUMPHREY (Proc. Nat. Acad. Sci., 1930, 16, 543—546).—The copper complex of the prosthetic group of the hæmo-

cyanin of the horseshoe crab (*L. polyphemus*) is isolated as a black powder (Cu 21.5, N 9.2, C 39.5, H 5.6, S 8.0%) by treatment of the whole blood with potassium hydroxide (10% of the blood) at 40–50°, washing the precipitate, dissolving in 50% acetic acid, removing copper sulphide by filtration, and reprecipitating with alkali. It is soluble in alkaline solutions only if ammonia or an amine is present to give green or brown solutions the spectra of which exhibit one broad band in the blue which extends into the extreme violet. Treatment of its solution in 50% acetic acid with concentrated hydrochloric acid removes the copper, hydrogen sulphide is evolved, and an amphoteric substance containing sulphur, insoluble at the neutral point, and a water-soluble, non-crystalline substance are formed. A similar amphoteric compound is obtained by precipitation with acetic acid after aerating a solution of the pigment in ammonia. The original material does not give either a pine splint or an Ehrlich test for pyrrole, but on fusion with potassium hydroxide a volatile substance giving a strong positive test is obtained. Reduction of the pigment with hydrogen iodide and phosphonium iodide, however, gave no trace of pyrroles. The pigment appears to be a complex salt of an unknown amino-acid containing sulphur, which forms highly-coloured complexes with amines, its function probably resembling that of protoporphyrin in haemoglobin.

J. W. BAKER.

**Plasma-protein in relation to suspension stability of erythrocytes and precipitation of serum-protein with aluminium sulphate.** L. R. JONES (J. Lab. Clin. Med., 1929, 15, 209–215).—An increase in the sedimentation rate of erythrocytes is often associated with an increase in the fibrinogen content of the blood or with a decrease in the albumin: globulin ratio. An increase in the precipitability of the serum-proteins with aluminium sulphate is associated with various pathological conditions; it does not appear to be related to the quantitative distribution of the plasma-proteins.

## CHEMICAL ABSTRACTS.

**Chemical constitution of serum- and tissue-proteins. II.** A. BLANKENSTEIN and A. FISCHER (Biochem. Z., 1930, 224, 211–222).—Further fractionation by salt solutions of serum-proteins (cf. this vol., 943) and of the proteins of pancreas, skeletal and heart muscle, spleen, liver, kidney, lung, thyroid, and brain is described together with determinations of the amounts of tryptophan, tyrosine, and cystine and of the nitrogen of the fractions in its various states of combination. Both the pseudoglobulin and the acid albumin of the serum-proteins are capable of separation into two fractions and the muscle-proteins into three fractions, the amino-acid contents of which are very different. It was not possible to identify any of the muscle-protein fractions with those of the serum-proteins. P. W. CLUTTERBUCK.

**Specific refraction increments of serum-albumin and serum-globulin.** G. S. ADAIR and M. E. ROBINSON (Biochem. J., 1930, 24, 993–1011).—Crystalline horse serum-albumin (N, 15.6%) has been prepared by a method based on that of Hopkins. The specific refraction increment is a constant un-

affected by recrystallisation. In aqueous solution it is 0.00183 for the crystalline protein, but uncrystallised fractions of albumin show a higher increment. The refractive indices of solutions of alkali albuminates equilibrated with phosphate buffers have been measured and are represented by a simple empirical formula which can be used for calculations of the protein concentration from refractometric measurements. A calculation of the specific refraction increment of the protein from measurements of the refractive indices of the solution and the dialysate has been made by the application of Donnan's theory of membrane equilibrium. The preparation of clear solutions of horse serum-globulin (N 15.13%) is described. The refractive indices of solutions of isoelectric and of alkaline globulins equilibrated with phosphate buffers have been measured and the specific refraction increment of the protein has been calculated after making corrections for the effects due to the unequal distribution of ions. The mean value obtained for total globulin is 0.00186. Measurements have been made of the refractive indices of solutions of glycine, alanine, valine, and tryptophan.

S. S. ZILVA.

**Determination of arginine in blood.** C. J. WEBER (J. Biol. Chem., 1930, 88, 353–359).—The method for the determination of arginine recently described (this vol., 755) has been applied to tungstic acid blood filtrates which, in the case of dog's blood, give a colour corresponding with 2–3 mg. of arginine per 100 c.c. of blood. That the chromogenic substance is in fact arginine is shown by its destruction by arginase and by the fact that arginine has been isolated (as the monoflavinate) from such blood filtrates.

C. R. HARRINGTON.

**Determination of carbamide in blood.** O. FOLIN and A. SVEDBERG (J. Biol. Chem., 1930, 88, 77–83).—Improvements in the technique of the urease method for determination of carbamide in blood (cf. Folin and Wu, A., 1919, ii, 308) are described.

C. R. HARRINGTON.

**Determination of blood-carbamide-nitrogen by direct Nesslerisation.** J. M. LOONEY (J. Biol. Chem., 1930, 88, 189–195).—Protein-free blood filtrate is treated with urease and, when conversion of carbamide into ammonium carbonate is complete, with gum ghatti solution and with Nessler's reagent; the colour is compared with that produced on Nesslerisation of a standard solution of ammonium sulphate containing similar amounts of gum ghatti and of urease.

C. R. HARRINGTON.

**Micro-determination of non-protein-nitrogen, carbamide, uric acid, and sugar in unclaked blood.** O. FOLIN and A. SVEDBERG (J. Biol. Chem., 1930, 88, 85–96).—The application of standard micro-methods for the determination of the above-named substances in blood filtrates free from material of corpuscular origin (this vol., 630) is described; 0.1–0.2 c.c. of blood is required for each of the determinations.

C. R. HARRINGTON.

**Determination of blood-sugar.** E. R. NORRIS and W. E. GIBB (J. Lab. Clin. Med., 1929, 15, 281–284).—Folin's micro-method gives results which agree closely with Folin and Wu's macro-method and with

Myers and Bailey's modification of Lewis and Benedict's method. Gibson's micro-method gives inconsistent results. CHEMICAL ABSTRACTS.

**Determination of blood-sugar. I. Reduction of alkaline copper reagents by dextrose and other substances. II. Effect of different deproteinising agents on the determination of blood-sugar.** S. L. TOMPSETT (Biochem. J., 1930, 24, 1148—1163, 1164—1171).—I. The amount of reduction of the Shaffer-Hartmann alkaline copper reagent by pure dextrose is greater when carried out in an atmosphere of nitrogen than when carried out in air. When the potassium salts are not incorporated in the reagent but added as a separate solution after reduction, the reduction is the same whether carried out in an atmosphere of nitrogen or air and the results are identical with those obtained when the reduction of the reagent containing the potassium salts is carried out in an atmosphere of nitrogen. The amount of reduction by dextrose of alkaline copper solutions containing copper sulphate, tartaric acid, and sodium carbonate depends on the relative concentrations of the two latter substances. Hydrogen carbonates can replace tartrates in alkaline copper solutions. Glycine, aspartic acid, glutamic acid, tryptophan, and cystine affect the reduction of alkaline copper reagents by dextrose only under certain conditions. Uric acid and creatinine in concentrations found in pathological bloods do not appreciably affect the determination of blood-sugar. Urea when present in a concentration of 200 mg. per 100 c.c. of blood has no influence on blood-sugar determinations. Potassium oxalate used as an anti-coagulant in a concentration of 1% in blood has no influence on the reduction values. The composition of a modified alkaline copper reagent and a modified technique for the determination of dextrose in blood filtrates are described. The method is based on the reduction of an alkaline copper solution, dissolution of the cuprous oxide in an acid iodide-iodate-oxalate solution, and titration with thiosulphate.

II. The non-sugar substances present in the tungstic acid filtrates in the method described above do not appreciably affect the results. The sugar content of tungstic acid filtrates as determined by the Folin-Wu, Folin, and Shaffer-Hartmann methods is low. Part of the sugar in a tungstic acid filtrate is in combination with other substances in the filtrate.

S. S. ZILVA.

**Reducing power of a mixture of two kinds of sugar in equal concentrations.** P. SCHWARTZ (Biochem. Z., 1930, 224, 193—201).—The amounts of copper (mg.), as determined by Benedict's method, equivalent to various amounts of pure dextrose, lævulose, galactose, arabinose, and maltose, and the similar values for the reducing power of mixtures of equal concentrations of dextrose and lævulose, dextrose and galactose, dextrose and arabinose, dextrose and maltose, are tabulated. The total reducing power of the mixtures is not equal to the sum of the separate reducing powers of the two sugars, but is much more nearly equal to half the sum of the reducing power of each sugar in double the concentration. P. W. CLUTTERBUCK.

**Nature of blood-sugar.** L. B. WINTER (Biochem. J. 1930, 24, 851—855).—Blood-sugar consists mainly of  $\alpha$ -glucopyranose, which can be obtained in crystalline form from the deproteinised blood by precipitation with lead acetate and then with barium hydroxide in methyl alcohol and subsequent decomposition of the barium compound. S. S. ZILVA.

**Determination and regulation of blood-clotting function in childhood.** I. N. KUGELMASS, F. W. BANCROFT, and M. STANLEY-BROWN (Amer. J. Dis. Children, 1930, 39, 471—486).—The index of the clotting function of the blood ( $I = [\text{prothrombin}]/[\text{fibrinogen}]/[\text{antithrombin}]$ ) is normally  $0.5 \pm 2$ . Tendencies to clot ( $I > 1.0$ ) or bleed ( $I < 0.2$ ) may be influenced by diet. CHEMICAL ABSTRACTS.

**Action of simple hæmolysins.** E. PONDER and J. F. YEAGER (Proc. Roy. Soc., 1930, B, 106, 506—531).—Time-dilution and percentage hæmolysis curves were determined for simple hæmolytic systems (saponin, sodium taurocholate, sodium oleate, and washed erythrocytes) over greater ranges of dilution than in previous work. It is shown that the reaction should be expressed by an equation of the  $n$ th order rather than by one of the first order, as has been previously supposed. It is tentatively suggested that a reaction between the cell component and aggregates of different numbers of lysin molecules would explain this. The value for  $n$  was 1.0—3.0 under normal conditions, but varied with the nature of the lysin, the type of the erythrocyte, the temperature, and with the presence of different electrolytes in the system. The application of these findings to the calculation of the "resistance constant"  $R$  for the comparison of different systems containing the same lysin is discussed. It is pointed out that the values for  $R$  previously obtained must be less than the true values when the reactions are considered as of the  $n$ th order, and that the effects of different inhibitors must be greater than has been previously supposed. G. F. MARRIAN.

**Effect of variations in cell content of hæmolytic systems.** E. PONDER (Proc. Roy. Soc., 1930, B, 106, 532—542).—The author's hypothesis (A., 1926, 969) of a limited zone of action round the erythrocyte to explain the relation between the quantity of lysin used and the number of cells present is revised in view of the fact that hæmolysis must be considered as an  $n$ th order reaction (see preceding abstract), and to include experiments covering a greater range of cell concentration. Equations showing this relationship are developed. The observed values for the quantity of lysin used were found to agree closely with those predicted. The value ( $\rho$ ) for the radius of the "zone of action" was found to be larger than previously given. Calculations of  $\rho$  for different types of red cells and various simple lysins confirmed the author's previous conclusion that the magnitude of  $\rho$  depends on the resistance to hæmolysis of the cells in the system, although this relationship is not so exact as was supposed. G. F. MARRIAN.

**Chlorohæmoglobin reaction in cadaverous tissues.** A. D. VOLTA (Boll. Soc. Ital. sperim., 1928, 3, 37—39; Chem. Zentr., 1929, i, 1591).—The colour

reaction previously described (A., 1929, 459) is intense and rapid with putrescent parts which already show traces of cadaverous decomposition. The reaction detects incipient sepsis when other signs of decomposition are lacking. L. S. THEOBALD.

**Fibrillar structures in the albuminous layer of the egg of the fowl.** G. C. HERINGA and S. H. VAN KEMPE VALK (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 530—532).—The albuminous layer surrounding the egg yolk consists of a series of strata, the outer layers being clear and transparent, whilst the rest is opaque. The membranes are of fibrillar structure. The fibrils are dissolved on digestion with pepsin and hydrochloric acid at 37°, when the albumin of a hard-boiled egg is dissolved completely. In a raw egg the membranes are dissolved less readily than the remainder of the albumin, and when sections are prepared from a frozen egg the membranous structures remain in connexion even after digestion. The membranes are completely soluble in alkaline trypsin. Evidence is obtained that the fibrils are composed of a keratinic substance. J. W. SMITH.

**Glutathione content of organs, especially of muscle.** E. GABBE (Klin. Woch., 1930, 9, 169—170; Chem. Zentr., 1930, i, 1952).—Of the glutathione in the lungs and arterial blood, 50—70% is present in the thiol form, whilst of that in the liver and spleen 98—100% is present in the thiol form. In resting animals the glutathione content of the muscle was 32—41 (average 37) mg. per 100 g., being depressed by vigorous exercise to 12—30 (average 23) mg. per 100 g. A. A. ELDRIDGE.

**Glutathione. IV. Determination of structure.** E. C. KENDALL, H. L. MASON, and B. F. MCKENZIE.—See this vol., 1299.

**Glutathione.** B. H. NICOLET.—See this vol., 1299.

**Internal secretion in insects. III. Digestive enzymes of the silkworm.** O. SHINODA (J. Biochem. Japan, 1930, 11, 345—367).—Optimal  $p_H$  values for the proteases, amylase, maltase, and invertase are recorded. Cellulase and cytase are absent. The disaccharide and dipeptide enzymes are localised in the intestinal epithelium.

#### CHEMICAL ABSTRACTS.

**Co-zyrnase content of various animal tissues.** E. SYM, R. NILSSON, and H. VON EULER (Z. physiol. Chem., 1930, 190, 228—246).—The co-zyrnase content of various animal organs was determined and an attempt made to correlate this with the sugar metabolism. Striped muscle shows the highest co-zyrnase content, unaffected by stimulation. Nerve substance has a high co-zyrnase content compared with connective tissue. The cortex of the kidney and adrenal has about double the co-zyrnase content of the medulla. The muscular layer of the intestine contains co-zyrnase. J. H. BIRKINSHAW.

**Structure of simple nucleic acids.** E. ANNAU (Z. physiol. Chem., 1930, 190, 222—227).—Guanylic acid from pancreas is identical in crystalline form of the tertiary sodium salt, specific rotation of the secondary sodium salt, and velocity of hydrolysis with the product obtained from yeast.

J. H. BIRKINSHAW.

**Microchemical tests for phenolic substances in the exoskeleton.** H. SCHMALFUSS and H. BARTHMEYER (Mikrochem., 1930, 8, 245—251).—A minute quantity of the substance is powdered and then moistened with 0.008—0.25 c.c. of water and the suspension transferred to a test-tube. After heating for 2 min. in a water-bath the liquid is filtered. Into the filtrate is dipped a strip of filter-paper impregnated with at least a day-old preparation of the enzyme obtained from the larvae of *Tenebrio molitor*, L. The preparation is kept for 3 days at 38° in a sealed tube; in the presence of melanogenic substances a grey or brown colour develops in the test paper. For the detection of *o*-dihydroxybenzene derivatives a drop of the filtrate is rubbed on a white tile with a fine rod which has been dipped in a 5% solution of ferric chloride; a green colour which becomes red on addition of a trace of sodium carbonate indicates the presence of the above-named compounds. Phenolic substances may be detected in a similar way by the blue to green colour produced with sodium hydrogen carbonate and a suspension of 2:6-dichloro-1-quinono-4-chloroimide in water or by means of Millon's reaction. A. R. POWELL.

**Determination of lactic acid in muscle.** E. ERNST and I. TAKÁCS (Biochem. Z., 1930, 224, 145—150).—The muscle is frozen in carbon dioxide snow-ether mixture, pulverised, extracted with ether, and the ether removed. The lactic acid in the filtered aqueous extract of the residue is then determined by permanganate titration (see following abstract). The recovery of added lactic acid is 90—94%.

P. W. CLUTTERBUCK.

**Permanganate titration in a heated medium.** E. ERNST and G. HORVÁTH (Biochem. Z., 1930, 224, 135—144).—In carrying out determinations by permanganate oxidation in hot acid solution, an error is caused by the fact that the permanganate is itself oxidised as well as the substance to be determined. The amount of self-reduction is shown to be proportional to the total amount of permanganate used and a standardisation curve is constructed which permits the reading off from the total permanganate used of the amounts concerned with self-reduction and oxidation of the substance. With this modification small amounts (10  $\gamma$ ) of lactic acid can be determined. P. W. CLUTTERBUCK.

**Detection of ergosterol in human skin.** H. HENTSCHEL and L. SCHINDEL (Klin. Woch., 1930, 9, 262; Chem. Zentr., 1930, i, 1952).—The sterol obtained from the cutis and epidermis of cadavers contained 0.42% (adult) or 0.15% (new-born) of ergosterol. A. A. ELDRIDGE.

**Absorption spectrum of cholesterol from human brains.** I. H. PAGE and W. MENSCHICK (Naturwiss., 1930, 18, 735).—Cholesterol from adult brains exhibits in the ultra-violet an "end" absorption similar to the purified product, whilst cholesterol from the brain of young and newly-born infants and of foeti shows a certain amount of absorption due to the presence of other substances. Two absorption maxima at 2820 and 2930 Å. are assigned to ergosterol, but the third maximum due to ergosterol (at 2700 Å.) is completely masked by unknown substances or

mixtures. The brain may absorb ergosterol along with nourishment or vitamin-*D* may accumulate during the period of bone formation, increasing the amount of ergosterol in cholesterol-rich organs. The regularity of the occurrence of considerable absorption at 2500—2600 Å. in the cholesterol from infant and foetal brains but not from adult brains seems to substantiate the latter hypothesis.

W. R. ANGUS.

**Cholesterol in the earth-worm.** A. DE WAELE (Bull. Acad. roy. Belg., 1930, [v], 16, 592—597).—After keeping for several days in sand, worms were extracted with ether, the extract being then evaporated and the residue twice saponified with 15% alcoholic potassium hydroxide. The material obtained by ethereal extraction of the resultant soap gave, after recrystallisation, the reactions of pure cholesterol. The results obtained by Dorée (cf., B., 1909, 373) are vitiated by the presence of impurities, probably phytosterol. The cholesterol content of earth-worms is 0.922 g. per kg. H. J. DOWDEN.

**Fat from *Cypridina*.** M. KOTAKE and Y. KIMOTO (Proc. Imp. Acad. Tokyo, 1930, 6, 237—238).—The fats extracted from *Cypridina* by light petroleum were hydrolysed with alcoholic potassium hydroxide. The portion insoluble in alcohol consists essentially of cholesterol (40% of total fats). The portion soluble in alkali yielded by extraction with ether a small crystalline fraction (6%),  $C_{17}H_{34}O_2$ , m. p. 53—56°, possibly mixed crystals of palmitic and stearic acids, and a residue which on hydrogenation afforded a crystalline acid (20%),  $C_{20}H_{40}O_2$ , m. p. 68.5—70°, which showed no depression of m. p. when mixed with dihydrologanic acid. The principal acid of *Cypridina* fat is probably laganic acid. No significant amount of highly unsaturated acids is present. T. H. MORTON.

**Composition of the fatty acids present as glycerides in the liver oil of the thresher shark (*Alopias vulpes*).** J. A. LOVERN (Biochem. J., 1930, 24, 866—869).—The amount of squalene (if any) must be very low in this oil. In this respect and in the composition of the fatty acids, namely, the absence of unsaturated acids of the  $C_{21}$  group and the high content of unsaturated acids of the groups  $C_{20}$  and  $C_{22}$ , it resembles skate-liver oil.

S. S. ZILVA.

**Radium in aquatic organisms.** W. VERNADSKY (Compt. rend., 1930, 191, 421—423).—The extent and significance of the presence of radium in aquatic organisms (*Lemna*) are discussed. F. O. HOWITT.

**Colorimetric determination of proteins of the cerebrospinal fluid.** P. B. MATZ (J. Lab. Clin. Med., 1930, 15, 370—385).—Colorimetric modifications of Hewitt's and Wu's methods for the determination of albumin, globulin, and total protein are described. Non-meningitic and non-syphilitic cerebrospinal fluid contains albumin (average) 3.4, globulin 0.13, total protein 48 mg. per 100 c.c. Markedly higher values and a lower albumin : globulin ratio are associated with paresis and multiple sclerosis.

CHEMICAL ABSTRACTS.

**Vitamin content of milk used in infant feeding.** I. G. MACY and J. OUTHOUSE (Amer. J. Dis. Children,

1929, 37, 379—400).—Human milk contains about the same amount of vitamin-*A*, but only half as much -*B*, as cow's milk; it is deficient in the anti-rachitic factor, whereas cow's milk contains a small quantity.

CHEMICAL ABSTRACTS.

**Variations in component fatty acids of butter due to changes in seasonal and feeding conditions.** T. P. HILDITCH and J. J. SLEIGHTHOLME (Biochem. J., 1930, 24, 1098—1113).—The influence of added fat in the diet of cows, although definite, is small. Much more profound changes in fatty acid composition appear to be caused by conditions such as change from outdoor to indoor life, character of diet, and seasonal changes in temperature. These differences lie mainly in the variation of the amount of unsaturated acids present and the amount of the lower saturated acids—butyric to lauric; palmitic acid appears to be the most constant, whilst the stearic acid content varies somewhat erratically from one butter to another. Butter-fat is characterised by amounts of butyric to myristic acids more or less specific to cow's milk-fat, and of palmitic, oleic, and linoleic acids not widely dissimilar from the proportions of the same acids found in the body or storage fats of the same class of animal. S. S. ZILVA.

**Solubility of cholesterol in the bile.** O. MERKEL-BACH (Schweiz. med. Woch., 1929, 59, 12 pp.; Chem. Zentr., 1930, i, 1963).—By precipitation with digitonin after esterification the variable cholesterol content of the bile was confirmed. The solubility of cholesterol in the bile is favoured by a high content of bile acids. The mechanism of formation of cholesterol and cholic acid in the organism is discussed. A. A. ELDRIDGE.

**Determination of bile acids. Bile salts in urine.** C. L. DUCCO and P. T. PANZA (Semana med., 1930, 37, 1193—1198).—With body fluids Petteukofer's reaction is not sensitive to 1 in 1000. In sodium glycocholate solution traces of impurities cause considerable variations in surface tension, rendering the stalagmometric method inexact. The determination is most exact when performed at  $p_H$  2.0. In solutions less concentrated than 0.1% practically all of the bile salt is adsorbed on charcoal. Hence the surface tension is determined at  $p_H$  2 and after treatment with charcoal, the bile salt content being determined by reference to a table. Urine contains 0.10—0.25 g. per 1000 calculated as sodium glycocholate. CHEMICAL ABSTRACTS.

**Mechanism of sugar excretion. I. Dextrose.** T. G. NI and P. B. REHBERG (Biochem. J., 1930, 24, 1039—1046).—There is no difference between sugar excretion after one sugar injection and a second following shortly after. The content of dextrose in the reabsorbed fluid is very variable. The reabsorption of dextrose goes on even when the blood-sugar is far above normal and is not decreased with increasing blood-sugar. The increase in reabsorption becomes less as the blood-sugar rises. Glycosuria must be due to the failure of the reabsorption of the sugar to increase as fast as its filtration increases with rising blood-sugar. The concentration difference between urine and blood at the site of reabsorp-



tion is probably the limiting factor of reabsorption of dextrose. S. S. ZILVA.

**Fastness of dyes to perspiration. I. Composition of human perspiration.** C. C. N. VASS and B. A. MCSWINEY (J. Soc. Dyers and Col., 1930, 46, 190—195).—The maximum and minimum values for freshly-shed sweat from normal males and females were:  $p_H$ , 7.35 and 5.10 (females, 6.80 and 6.35); ammonia-nitrogen, 7.00 and 2.55 mg. per 100 c.c. (11.1 and 2.6); urea-nitrogen, 32.92 and 11.10 mg. per 100 c.c. (27.72 and 13.63); amino-acid-nitrogen, 9.2 and 2.4 mg. per 100 c.c. (8.7 and 4.7); dextrose, 26.4 and 9.4 mg. per 100 c.c. (35.0 and 12.0); and chlorides calc. as NaCl, 5.01 and 2.65 g. per 1000 c.c. (3.87 and 2.23). The dextrose content of sweat from stout healthy women is about twice that of sweat from normal women; the amount of dextrose in the sweat of stout men is only about 50% greater than in that of normal men. With few exceptions freshly-shed sweat is faintly acid, but on keeping its reaction becomes alkaline owing to decomposition, which results in a marked increase of the ammonia-nitrogen content and a disappearance of the urea-nitrogen, these changes being due to bacteria normally associated with freshly-shed perspiration. A. J. HALL.

**Plasma-proteins [in disease].** H. J. WIENER and R. E. WIENER (Arch. Int. Med., 1930, 46, 236—265).—The fibrinogen, serum-globulin and -albumin contents of human plasma have been determined in health and in a number of diseases, including cirrhosis of the liver, diabetes mellitus, benign glycosuria, and liver, gall-bladder, and renal affections. Cholesterol, chlorides, non-protein-nitrogen, uric acid, and calcium have also been determined. In mild infections, the albumin is slightly decreased and the fibrinogen content is increased, whilst in more severe infections the albumin is more markedly decreased and the globulin increased. In cirrhosis of the liver there is a decrease in the albumin and an increase in the globulin. No significant change in the serum-proteins occurs in diabetes mellitus and benign glycosuria.

W. O. KERMACK.

**Excretion of chloride in achlorhydria.** R. S. HUBBARD (J. Biol. Chem., 1930, 88, 361—366).—Patients with achlorhydria show a high rate of urinary excretion of chloride on awakening and a low rate of excretion for 1 hr. after breakfast.

C. R. HARINGTON.

**Blood-serum-proteins in anæmic conditions.** C. ACHARD and M. HAMBURGER (Compt. rend., 1930, 191, 309—311).—An abnormally low content of all fractions of proteins (albumin, globulin, and myxoprotein) is observed in the serum in cases of pernicious anæmia and also, although not invariably, in anæmias accompanying other pathological conditions. When cure takes place both the amount of serum-protein and the erythrocyte count rise to normal.

R. K. CALLOW.

**Crystalline derivatives of an acid present in liver, active in pernicious anæmia.** R. WEST and M. HOWE (J. Biol. Chem., 1930, 88, 427—431).—Concentrated liver extract was saturated with picric acid and extracted with a mixture of butyl alcohol and ether; the aqueous solution, after removal of

picric acid and organic solvents, was cleared with excess of lead hydroxide and with lead acetate and barium hydroxide. The filtrate was freed from lead and barium and precipitated with phosphotungstic acid; the solution obtained by decomposition of the precipitate with barium hydroxide was concentrated in a vacuum, treated with excess of barium hydroxide, and precipitated with alcohol. The barium salt was decomposed to give an alcohol-insoluble water-soluble product with C 46.6%, H 6.9%, N 10.6%; none of the nitrogen is in the amino-condition, but after acid hydrolysis one half is found in this form and in fact to be present as  $\beta$ -hydroxyglutamic acid. The other (unidentified) hydrolysis product is a neutral compound which is precipitated with phosphotungstic acid. The acid is highly active therapeutically in pernicious anæmia and gives a crystalline *quinine* salt,  $C_{20}H_{24}O_2N_2 \cdot C_{10}H_{18}O_6N_2$ ,  $[\alpha]_D -97^\circ$ , which retains the therapeutic activity. C. R. HARINGTON.

**Anæmic lipæmia.** M. HEKI (J. Biochem., Japan, 1930, 11, 369—390).—The distribution of total fatty acids, total cholesterol, and lipid phosphorus in the blood, liver, lung, kidney, spleen, heart, and skeletal muscles of anæmic rabbits has been determined. CHEMICAL ABSTRACTS.

**Preputial calculus.** COUILLAUD (J. Pharm. Chim., 1930, [viii], 11, 31—34).—A calculus weighing 645 g., found in a case of phymosis, was separated into four concentric layers. The outermost contained calcium carbonate, phosphate, and oxalate and magnesium ammonium phosphate (I), the second (120 g.), a larger proportion of I, but no calcium oxalate, the third (20 g.), almost entirely I, with uric acid, sodium urate, and traces of calcium salts, and the centre (4 g.), uric acid with traces of I and of calcium carbonate. The urine contained crystals of calcium oxalate and phosphate and of uric acid.

H. E. F. NOTTON.

**Effect of vitamin injury on the origin of cancer.** R. ERDMANN and E. HAAGEN (Arb. Reichsgesundh.-Amt, 1929, 61, 141—152; Chem. Zentr., 1930, i, 1323).—Alternating nutrition with food rich in vitamin and with the vitamin content enriched by vitamin-B favours the formation of tumours.

L. S. THEOBALD.

**Cancer chemotherapy. IX. Reaction of the blood in cancer.** F. BISCHOFF, M. L. LONG, and E. HILL (J. Pharm. Exp. Ther., 1930, 39, 425—433).—The mean  $p_H$  value of the plasma of 15 untreated cancerous subjects was 7.50, whilst that of 15 normal individuals was 7.46. Statistical analysis shows that the difference is probably significant. The carbon dioxide tension for the cancer group was lower than that of the normal group, the hydrogen carbonate content of the two groups being very nearly the same.

W. O. KERMACK.

**Comparison of effects of arginine and thyroxine on tumour growth-rate in the mouse.** E. GILROY (Biochem. J., 1930, 24, 1181—1187).—Injections of thyroxine into mice retard the rate of tumour growth without an accompanying loss of body-weight during a 12-day period of treatment. Substitution of arginine for thyroxine causes a renewal of rapid growth, but if arginine be given previously

the substitution of thyroxine does not cause a permanent deflexion of the curve. If both are given to the same animal the rate of growth is similar to that of untreated controls if arginine is given daily, but if less often, the effect of thyroxine predominates.

S. S. ZILVA.

**Fluid exchange. VIII. Fluid and gas exchange in diabetes insipidus.** K. KIMURA, S. ABE, and T. YAMAGUCHI (Tohoku J. Exp. Med., 1930, 15, 70—90).—Circulation of fluid between tissues and blood is abnormally active in diabetes insipidus. Chlorides tend to accumulate in the tissues, and tissue respiration is decreased.

CHEMICAL ABSTRACTS.

**Hypophysectomy and pancreas diabetes in the toad.** B. A. HOUSSAY and A. BIASOTTI (Semana Méd., 1930, 37, 1207).—Pancreatectomy produces hyperglycemia and glycosuria, but with simultaneous hypophysectomy the former does not develop unless part of the pituitary gland is reimplanted under the skin.

CHEMICAL ABSTRACTS.

**Chemistry and metabolism in experimental yellow fever in *Macacus rhesus*.** A. M. WAKEMAN and C. A. MORRELL (Arch. Int. Med., 1930, 46, 290—305).—Blood from *M. rhesus* in the final stages of yellow fever infection has a high concentration of non-protein-nitrogen, and usually an increase in urea concentration which is small in proportion to the non-protein-nitrogen. It also shows an increase of amino-acid-nitrogen large in proportion to that of non-protein-nitrogen, and of residual nitrogen, and a normal uric acid content. The creatinine content of the blood is usually increased.

W. O. KERMACK.

**Cholesterol content of blood in filaria.** T. C. BOYD and A. C. ROY (Indian J. Med. Res., 1930, 17, 949—953).—Values were 0.12—0.22 (average 0.146)%, instead of (normally) 0.116%.

CHEMICAL ABSTRACTS.

**Disturbance of metabolism produced by bony and non-bony injury, with notes on certain abnormal conditions of bone.** D. P. CUTHBERTSON (Biochem. J., 1930, 24, 1244—1263).—In normally healing fractures there is little change in the metabolism of calcium. There is, however, a marked loss of nitrogen, phosphorus, and sulphur, the rate of loss following the injury reaching a maximum about the second to sixth day and then gradually declining, but persisting even after 1 or 2 months. This loss can be traced mainly to the catabolism of muscle. The administration of irradiated ergosterol to these cases does not alter their metabolism apart from a slight increase in the urinary excretion of calcium, nor does it improve the clinical condition of the patient. Irradiated ergosterol can have a beneficial effect in certain types of pathological fracture and abnormal bone conditions. There is a catabolic loss of sulphur, nitrogen, and phosphorus resulting from the injury of tissue other than bone. There is no coincident increase in the non-protein-nitrogen and inorganic phosphorus of the blood corresponding with the increased catabolism in the cases of fracture and non-bony injury. Changes occur later which appear to involve a raising of the level of these elements. A

few cases of abnormal bone metabolism are discussed in so far as they illustrate some phases of calcium and phosphorus metabolism.

S. S. ZILVA.

**Lactic acid content of blood in hepatic disease.** E. MASSOBRIO and M. MICHAÏLOV (Minerva Med., 1930, 1, 650—656).—In mild cases not involving the parenchyma the blood-lactic acid is unchanged; it is considerably increased in severe cases, in heart disease, and in liver stasis.

CHEMICAL ABSTRACTS.

**Action of the cinchona and certain other alkaloids in bird malaria.** J. A. GOODSON, T. A. HENRY, and J. W. S. MACFIE (Biochem. J., 1930, 24, 874—890).—Only alkaloids belonging to or derived from the cinchona series showed marked remedial action in canaries infected with *Plasmodium inconspicuum*. Of the natural alkaloids the most active was hydroquinine, followed by quinidine, quinine, cinchonidine, and cinchonine in descending order, differing, however, little in activity. Hydrogenation of quinidine, cinchonidine, and cinchonine, unlike that of quinine, does not increase the activity. Among alkaloidal drugs having some reputation as remedies for malaria slight activity was observed only in *Alemania scholaris* and *A. constricta*. The former species probably owes its activity to echitamine, which showed slight action. Activity is restored to quinine and the analogous carboxylic acids derived from quinidine, cinchonidine, and cinchonine by esterification; the activity rises as the mol. wt. of the alcohol used for esterification is increased, and reached a maximum at butyl- or amyl-quinine. The following esters were prepared by passing dry hydrogen chloride into a mixture of the acid and the alcohol and heating: *methylquitenine* (not obtained crystalline), m. p. 170°,  $[\alpha]_D^{25}$  —130° in chloroform (*monohydrochloride*, m. p. 153°,  $[\alpha]_D^{25}$  —189° in water); *n-propylquitenine*, m. p. 170°,  $[\alpha]_D^{25}$  —143° in chloroform (*monohydrochloride*, m. p. 187°,  $[\alpha]_D^{25}$  —225° in water); *isopropylquitenine*, m. p. 189°,  $[\alpha]_D^{25}$  —142° in chloroform (*monohydrochloride*,  $[\alpha]_D^{25}$  —231° in water); *n-butylquitenine*, m. p. 142°,  $[\alpha]_D^{25}$  —143° in chloroform (*monohydrochloride*,  $[\alpha]_D^{25}$  —227° in water); *dihydrochloride*,  $[\alpha]_D^{25}$  —250° in water); *isobutylquitenine*, m. p. 154°,  $[\alpha]_D^{25}$  —144° in chloroform (*monohydrochloride*, m. p. 248°,  $[\alpha]_D^{25}$  —223° in water); *n-amylquitenine*, m. p. 135°,  $[\alpha]_D^{25}$  —135° in chloroform (*monohydrochloride*, m. p. 195°,  $[\alpha]_D^{25}$  —217° in water); *isoamylquitenine*, m. p. 160°,  $[\alpha]_D^{25}$  —136° in chloroform (*monohydrochloride*,  $[\alpha]_D^{25}$  —222° *octylquitenine monohydrochloride*, m. p. 181°,  $[\alpha]_D^{25}$  —191° in water, and *dihydrochloride* not crystalline, m. p. 164°; *benzylquitenine*, m. p. 161°,  $[\alpha]_D^{25}$  —128° in chloroform (*monohydrochloride*, m. p. 233°,  $[\alpha]_D^{25}$  —175° in water); *ethylquitenidine*, m. p. 139°,  $[\alpha]_D^{25}$  +163° in chloroform (*monohydrochloride*, m. p. 242°,  $[\alpha]_D^{25}$  +151° in water); *isoamylquitenidine monohydrochloride*, m. p. 245°,  $[\alpha]_D^{25}$  +132° in water; *ethylcinchotenidine*, m. p. 180°,  $[\alpha]_D^{25}$  —115° in chloroform (*monohydrochloride*,  $[\alpha]_D^{25}$  —165° in water); *isoamylcinchotenidine monohydrochloride*, m. p. 152°,  $[\alpha]_D^{25}$  —151° in water; *ethylcinchotenine monohydrochloride*,  $[\alpha]_D^{25}$  +130° in water; *isoamylcinchotenine*, m. p. 147—149° (*monohydrochloride*, m. p. 145°,  $[\alpha]_D^{25}$  +117° in water).

S. S. ZILVA.

**Constituents of blood-serum in myxœdema.** C. ACHARD and I. ORNSTEIN (Compt. rend., 1930, 191, 311—312).—In twelve cases of myxœdema the blood-serum had the normal content of proteins, cholesterol, and sodium, but the total lipin content was slightly high, and calcium content slightly low.

R. K. CALLOW.

**Fat metabolism. I. Fat tolerance in obesity.** H. R. RONY and A. J. LEVY (J. Lab. Clin. Med., 1929, 15, 221—228).—The blood-fatty acid normally increases after ingestion of cream; obese subjects behave irregularly. The plasma-cholesterol is normal in both cases. A high or low fat tolerance in obese subjects is usually associated, respectively, with a high or low sugar tolerance. CHEMICAL ABSTRACTS.

**Liberation of a histamine-like substance from the lung in œdema.** E. PESERICO (Minerva Med., 1930, 1, 692—700).—The presence in the blood of a substance behaving like histamine is discussed.

CHEMICAL ABSTRACTS.

**Experimental production of pellagra in rats.** I. V. R. LEADER (Biochem. J., 1930, 24, 1172—1180).—Pellagra can be induced in rats in 17—25 days on a synthetic diet containing starch and sucrose and just sufficient marmite to prevent polyneuritis, administered when the animals begin to manifest the deficiency of the vitamin-B complex. In the absence of sucrose from the diet pellagra does not appear, but all the rats develop polyneuritis. Increased amounts of sucrose do not increase the severity of the symptoms. Rats suffering from polyneuritis develop pellagra after the marmite dose is raised sufficiently to protect them from the disease, and in the case of those on a sugar-free diet when sugar is added. Rats, like human beings, have a seasonal immunity from pellagra.

S. S. ZILVA.

**Nature of the sugar in pentosuria.** I. GREENWALD (J. Biol. Chem., 1930, 88, 1—7).—The urine was cleared with lead acetate, and the filtrate was further precipitated with basic lead acetate and sodium hydroxide; the precipitate was decomposed with carbon dioxide, and the filtrate, after removal of traces of lead with hydrogen sulphide, was concentrated. The resulting solution was treated with mercuric sulphate (in molecular proportion to the nitrogen content) and neutralised with barium hydroxide, and the filtrate, freed from mercury, was concentrated to small bulk and treated with excess of alcohol; after filtration, the concentration and precipitation with alcohol were repeated. The final filtrate was concentrated and treated with an amount of *p*-bromophenylhydrazine equal in weight to the apparent dextrose content. Application of this procedure to the urines of four patients exhibiting pentosuria resulted in the isolation of xyloketose-*p*-bromophenylhydrazone. The conclusions of Levene and La Forge (A., 1914, i, 1027) are therefore confirmed.

C. R. HARRINGTON.

**Post-mortem blood chemistry in renal disease.** S. H. POLAYES, E. HERSHEY, and M. LEDERER (Arch. Int. Med., 1930, 46, 283—289).—Blood from patients who died from various diseases has been analysed in respect of urea and creatinine, and the results have been compared with those obtained from the same

patient before death. No definite relation was found between the urea contents of the blood before and after death. The *post-mortem* creatinine figures in various diseases were on an average 0.5—1.7 mg. per 100 c.c. higher than those obtained during life.

W. O. KERMAK.

**Absorption spectrum of blood and its relation to rickets.** R. C. GIBBS, J. R. JOHNSON, and C. V. SHAPIRO (Naturwiss., 1930, 18, 764).—Suhmann's statement (this vol., 132) that solutions of blood from rachitic rats give a different absorption spectrum from that obtained with a solution of blood from normal animals was not confirmed. It is therefore concluded that his results were accidental and that no effective change in the blood-pigments results from a change in pathological state.

W. R. ANGUS.

**Effect of administration of phosphorus, anti-rachitic treatment, and spontaneous healing on calcium of the blood-serum of rachitic rabbits.** B. HAMILTON, L. KAJDI, and D. MEEKER (J. Biol. Chem., 1930, 88, 331—336).—The increase in the phosphorus of the blood-serum of rachitic rabbits which occurred in cases of spontaneous healing, or was brought about by administration of phosphate, cod-liver oil, or irradiated ergosterol, or by the action of ultra-violet light, was frequently accompanied by diminution in the blood-calcium.

C. R. HARRINGTON.

**Anomaly of copper metabolism.** F. HAURWITZ (Z. physiol. Chem., 1930, 190, 72—74).—In two cases of Wilson's disease (pseudosclerosis) the liver contained 5.9 and 4.8 mg. of copper per 100 g. (normal value about 0.3) and the abdominal ganglia 2.8 and 3.1 mg. (normal value about 0.55). The iron content of the liver was normal.

J. H. BIRKINSHAW.

**Metabolism of the lung-fish, *Protopterus aethiopicus*.** H. W. SMITH (J. Biol. Chem., 1930, 88, 97—130).—Lung-fish were induced to aestivate under artificial conditions, and, after varying periods, were transferred to a metabolism chamber. The fasting but active lung-fish utilises oxygen at the rate of about 20 c.c. per kg. per hr., of which about 50% is employed in the oxidation of protein, the nitrogen appearing almost equally as carbamide and as ammonia. Of the total metabolism of the active fish about 15% is estimated to be due to muscular tone and movement. During aestivation the fish is completely immobilised and is enveloped, except for the oral aperture, by an impervious cocoon; secretion of urine is entirely suspended. The oxygen consumption of the aestivating fish falls, at 20°, to about 8 c.c. per kg. per hr.; the metabolic rate may be raised by rise of temperature or by injection of thyroxine without awaking the fish. The reduction of the metabolism must involve non-mechanical as well as muscular processes. Energy during aestivation is derived largely from the catabolism of protein, of which the nitrogen accumulates in the tissues almost exclusively as carbamide; this, together with sulphate which also accumulates, is excreted at a very high rate during the first days of the post-aestivation period. No significant accumulation of ammonia, creatine, or phosphate is observed; acetone sub-

stances and uric acid were absent from the tissues during aestivation. C. R. HARRINGTON.

**Carbohydrate metabolism of normal and tumour tissue. I. Measurement of the respiratory quotient.** F. DICKENS and F. ŠIMER (Biochem. J., 1930, 24, 905—913).—Thin slices of tissue are suspended in carbon dioxide-free Ringer solution buffered by means of phosphate and in equilibrium with pure oxygen. The carbon dioxide formed in respiration is absorbed by barium hydroxide solution and the diminution in pressure which occurs is used for the calculation of respired oxygen. After a definite time all the carbon dioxide is expelled from the barium hydroxide, phosphate, and tissue by addition of excess of strong acid, and the resulting positive pressure is used for the calculation of the total carbon dioxide at the end of the experiment. This figure corrected for the carbon dioxide present at the beginning of the experiment gives the amount formed in respiration during the experimental period. The greatest error to be expected in the value of R.Q. is 0.02.. S. S. ZILVA.

**Oxidations in central and peripheral nervous tissue.** E. G. HOLMES (Biochem. J., 1930, 24, 914—925).—Various types of tissue composing the central nervous system have different rates of oxygen consumption; the activity of grey matter whether in the central system or in the peripheral nerve is much higher than that of the white matter. The distributions of indophenol oxidase and of cytochrome run approximately parallel both to each other and to the rate of oxygen consumption of the different types of tissue. The greatly increased oxygen uptake which grey matter displays in the presence of dextrose depends on the conversion of the sugar into lactic acid and disappears if this conversion is prevented by fluoride. Other substances besides lactic acid, probably not of a carbohydrate nature, which are not easily removed by washing are also responsible for some of the oxygen uptake by brain-tissue. S. S. ZILVA.

**Lactic acid oxidation in brain with reference to the "Meyerhof cycle."** E. G. HOLMES and C. A. ASHFORD (Biochem. J., 1930, 24, 1119—1127).—Although a "Meyerhof quotient" (total lactic acid disappearing/lactic acid oxidised) was obtained, no synthesis of carbohydrate from that portion of the lactic acid which disappeared, but was not accounted for by the oxygen uptake, could be demonstrated in brain. S. S. ZILVA.

**Transformation of pyruvic acid into lactic acid in the liver.** Y. KHOUVINE, E. AUBEL, and L. CHEVILLARD (Compt. rend., 1930, 191, 446—448).—The addition of pyrophosphate to macerated liver with sodium pyruvate incubated at  $p_{\text{H}}$  7.4 favours the formation of lactic acid, but has no influence on the amount of lactic acid derived from pyruvic acid. The carbon dioxide evolution and oxygen consumption lead to the conclusion that an enzyme allows pyruvic acid to function as a hydrogen acceptor and thus form lactic acid. F. O. HOWITT.

**Energetics of muscular contraction with increased formation of lactic acid.** O. MEYER-

HOF, E. LUNDGAARD, and H. BLASCHKO (Naturwiss., 1930, 18, 787—788).—When creatinephosphoric acid is hydrolysed, a considerable amount of energy is liberated which during muscular activity is employed partly for anaërobie contraction. When the muscle is poisoned with iodoacetic acid, formation of lactic acid is inhibited without affecting anaërobie contraction and the whole of the phosphagen is simultaneously decomposed, even more quickly than in normal muscle. By a comparison of the total anaërobie development of tension with the decomposition of phosphagen, it is shown that the whole of the energy for anaërobie contraction with the poisoned muscle is derived from phosphagen. P. W. CLUTTERBUCK.

**Methylglyoxal as an intermediate product of carbohydrate degradation.** E. WIDMANN and E. SCHNEIDER (Biochem. Z., 1930, 224, 157—169).—Macerates of normal and diabetic human blood-corpuscles, of red and white corpuscles separately, and of acetone preparations of human red cells, are able to convert magnesium hexosediphosphate into methylglyoxal in the same way as macerates of the blood cells of sheep, horses, and rabbits (this vol., 360). Human red and white cells have per c.c. the same glycolytic power but per cell the glycolytic power of the white cell is about twenty times that of the red cell. Macerates of red and white cells give with magnesium hexosediphosphate yields of methylglyoxal corresponding with 71.5 and 70.3% of the sugar used. Macerates of pus, on the other hand, gave negative results. P. W. CLUTTERBUCK.

**Use of sodium sulphite as fixing agent for acetaldehyde in surviving tissues and hearts.** M. KORTSCHAGIN and M. LEVITOV (Biochem. Z., 1930, 224, 63—68).—A buffered mixture containing sodium sulphite can be used for fixing acetaldehyde in surviving tissues and hearts. P. W. CLUTTERBUCK.

**Carbohydrate metabolism of the normal newborn infant. II. Effect on the concentration of blood-sugar of feeding various sugars.** H. M. GREENWALD and S. PENNEL (Amer. J. Dis. Children, 1930, 39, 493—503).—The blood-sugar in infants does not increase after breast-feeding during the first 48 hrs., but may do so after the second day. Dextrose is most readily absorbed. CHEMICAL ABSTRACTS.

**Passage of carbohydrate through the animal organism.** F. HOLTZ and E. SCHREIBER (Biochem. Z., 1930, 224, 1—52).—After administration of dextrose solutions to dogs, the absorption in the stomach, the emptying of the stomach, the filling of and the absorption in the intestine, and the amount and character of the fluids secreted and absorbed are studied and the movements of these organs followed by the usual barium-X-ray technique. Stomach absorption was investigated both in normal and in anaesthetised animals in which the stomach was ligatured above and below. Dextrose solutions of known concentration and containing a known amount of colloidal silicic acid are introduced into the stomach. Changes in silicic acid concentration indicate the changes due to dilution by secretions and permit the calculation of the sugar concentration after allowing

for these dilutions. Comparisons of this with the actual sugar concentration indicates whether or not absorption has occurred. In twelve experiments with normal animals three showed no absorption and nine an absorption of about 2 g. of dextrose per hr. per m.<sup>2</sup> body-surface, whilst in all of seven experiments of the second type, smaller but positive absorption was obtained. The volumes of gastric juice, its  $p_H$ , and content of chloride, nitrogen, etc. are tabulated.

P. W. CLUTTERBUCK.

**Intermediate metabolism of foreign sugars.** E. H. FISHBERG and B. T. DOLIN (Arch. Int. Med., 1930, 46, 321—332).—A method is given for the determination of galactose or xylose in the presence of dextrose in 0.2 c.c. of blood, the principle being to remove the dextrose by treatment with a suitably-prepared yeast suspension. In normal human subjects the reducing non-fermentable fraction is approximately 28 mg. per 100 c.c., but is increased in uremia, diabetes, and lactation. Galactose and xylose introduced into the blood-stream of a rabbit disappear at a rate proportional to their concentration in the blood. Xylose disappears much more slowly from the blood-stream of rabbits suffering from uranum nephritis and more quickly from rabbits made diabetic by phloridzin. Galactose disappears abnormally slowly from the blood-stream of rabbits suffering from uranum nephritis and from the blood of those gradually poisoned by phosphorus. In human beings, galactose disappears slowly from the blood of patients with nephritis and diabetes.

W. O. KERMACK.

**Embryos. IV. Accumulation of glycogen in the bodies of developing chick embryos. V. Accumulation of glycogen in the liver of developing chick embryos.** G. E. VLADIMIROV (Biochem. Z., 1930, 224, 69—78, 79—82).—IV. [With M. J. DANILINA.] The increase in the absolute amount of glycogen in the embryo follows the same law as the increase in weight and is calculable from the expression  $\log G = 6.31 \log t - 6.01$ . This holds even before the internal secretory glands have become active. Part of the glycogen is utilised at hatching. Fat may serve as a source of glycogen in the second half of the incubation period. The liver is very rich in glycogen and heart-muscle is richer than skeletal.

V. The ratio of the weight of the liver to the total weight of the embryo is constant from the 13th day to the time of hatching, the growth of the liver following the same law as that of the whole body. Liver-glycogen forms 40% of the total glycogen of the embryo (cf. A., 1926, 1268).

P. W. CLUTTERBUCK.

**Metabolism of tributyrin.** R. E. DAVIS (J. Biol. Chem., 1930, 88, 67—75).—When tributyrin was administered orally to hens it was digested to the extent of about 90% in the first experiment and less in subsequent experiments with the same bird owing to the toxicity of the material. Tributyrin was stored to some extent by rats after injection but not after oral administration of the fat, although in the latter case it was digested and absorbed; the butyric acid was probably largely synthesised into higher acids during absorption. Administration of tri-

butyrin to normal and phloridzinised rats on a carbohydrate-free diet increased the ketonuria.

C. R. HARRINGTON.

**Lipins of blood-plasma in normal dogs in the post-absorptive state and in fasting dogs.** D. GLUSKER (J. Biol. Chem., 1930, 88, 381—387).—Figures are given for the total fatty acids and the total cholesterol of the blood-plasma of 10 dogs in the above-named conditions.

C. R. HARRINGTON.

**Effects of cystine diet on keratin composition in rabbit wool.** J. BARRITT, A. T. KING, and J. N. PICKARD (Biochem. J., 1930, 24, 1061—1065).—There was a large increase in the sulphur content of the fur of individual Angora buck rabbits between two successive 3-month periods, January to April and April to July, whether fed on a normal diet or on a diet containing added cystine. The weight of the fleece was also not influenced by the inclusion of cystine in the diet.

S. S. ZILVA.

**Comparative biochemistry. V. Behaviour of 2-methylquinoline in the organism of the rabbit and the hen. VI. Behaviour of nitrocinnamic acid in the animal organism.** M. TAKAHASHI (J. Biochem. Japan, 1930, 11, 437—441, 441—444).—2-Methylquinoline is partly oxidised and partly paired with glycine to form pyridine-2 : 3-dicarboxylic acid. In rabbits *o*-nitrocinnamic acid is only sparingly oxidised or paired; in the hen it is oxidised to nitrobenzoic acid and then to succinic acid.

CHEMICAL ABSTRACTS.

**Carbamide of rat's blood in pregnancy and lactation on diets containing varying amounts of protein.** H. T. PARSONS (J. Biol. Chem., 1930, 88, 311—330).—Large increases were observed in the concentration of carbamide in the blood of pregnant and lactating rats as the result of diets rich in protein, particularly if this dietary treatment were preceded by partial nephrectomy. The greatest increase was observed during lactation and appeared to be associated with an effect (possibly emotional) of the act of suckling.

C. R. HARRINGTON.

**Nitrogen and calcium metabolism in calves during the period of milk feeding.** E. A. SOKOLOV (Nauch. Agron. Zhur., 1929, 6, 429—437).

CHEMICAL ABSTRACTS.

**Calcium and phosphorus metabolism in older children on mixed diet containing a large or small quantity of milk.** A. M. COURTNEY and A. BROWN (Arch. Dis. Childhood, 1930, 5, 17—22).—A diet which contains eggs and vegetables but only a small quantity of milk does not provide sufficient calcium and phosphorus. Marked individual differences in the amounts secreted were observed.

CHEMICAL ABSTRACTS.

**Calcium and phosphorus concentration in the large and small intestines of children.** A. M. COURTNEY (Arch. Dis. Childhood, 1930, 5, 23—27).—The contents of the large intestine, *post mortem*, contained more calcium and less phosphorus than those of the small intestine.

CHEMICAL ABSTRACTS.

**Effect of the contents of the radicle of germinated grain on calcium and phosphorus metabolism.** M. RUBNER (Deut. med. Woch., 1930, 56,

295—297; Chem. Zentr., 1930, i, 2271).—The normal organism is enriched in calcium and phosphorus. A. A. ELDRIDGE.

**Influence of bile acids on calcium metabolism.** T. SEKITO (J. Biochem. Japan, 1930, 11, 390—406).—Laparotomy alone has no effect on the blood-calcium of the rabbit. Hypocalcaemia resulting from the discharge of bile from a gall-bladder fistula can be remedied by administration of bile acids. In experimental obstructive icterus hypercalcaemia alternates with hypocalcaemia.

CHEMICAL ABSTRACTS.

**Retention of calcium on diets rich and poor in fat.** M. C. MALLON, R. JORDAN, and M. JOHNSON (J. Biol. Chem., 1930, 88, 163—167).—No constant effect of dietary fat on the retention of calcium in normal young women could be observed.

C. R. HARRINGTON.

**Behaviour of potassium in the organism. I. Potassium and sodium contents of different organs. II. Fluctuations in excretion of potassium, sodium, and chlorine by the kidney. III. Fluctuation in potassium concentration of the plasma after administration of potassium salts and in diuresis, and its relation to the elimination of potassium in urine.** M. NORN (Skand. Arch. Physiol., 1929, 55, 162—183, 184—210, 211—229; Chem. Zentr., 1930, i, 1580).—I. The potassium content of the heart is less than that of the skeletal muscles, but the sodium content is greater. The sodium content of the kidney compared with that of muscle is very high.

II. The excretion of potassium, sodium, and chlorine by the kidneys is lower during the night than the day; with persons awake at night and asleep during the day, the reverse is the case. Muscular activity has no effect on the secretion. The reduction in secretion is not attributable to a general depression of renal activity, since the secretion of calcium is unchanged, whilst that of magnesium is greater at night than during the day. Narcosis appears to exert an influence similar to that of sleep.

III. The administration of potassium chloride to rabbits is accompanied by a marked increase in the potassium content of the plasma; this brings about an increase in the excretion of potassium by the kidneys.

L. S. THEOBALD.

**Value of potassium iodide as a supplement to the ration of growing chicks.** T. S. HAMILTON and C. H. KICK (J. Agric. Res., 1930, 41, 135—137).—Addition of potassium iodide to chicken food, at the rates of 0.5 and 1.0 mg. per 100 g. body-weight, in no way affected the rate of growth of chicks.

A. G. POLLARD.

**Ionic theory of nerve excitation.** N. VON RASCHEVSKY (Z. Physik, 1930, 63, 660—665).—The observations of Hill on the motion of ions in an electric field between two parallel impermeable membranes are brought into line with the theory of nerve excitation.

A. J. MEE.

**Hysteresis in biophysics.** N. VON RASCHEVSKY (Z. Physik, 1930, 63, 666—671).—A heterogeneous system with several equilibria, possessing the property

of reacting to certain "configurations" brought about by external conditions, is considered. A. J. MEE.

**Biological significance of intermediate compounds.** E. ABDERHALDEN (Naturwiss., 1930, 18, 429—431).—The importance in biological processes of intermediate compounds such as the polypeptides, hexosephosphates, and the enzyme-substrate complexes is discussed; such compounds may have considerable bearing on the action of hormones, vitamins, and immunising agents.

H. F. GILLBE.

**Physiological reaction of salts.** M. GÓRSKI (Rocz. Nauk. Roln. Lés., 1929, 22, 27—32).—The dependence of the adsorption of salts on  $p_n$  is expressed diagrammatically.

CHEMICAL ABSTRACTS.

**Iodine investigations at Bad Hall in Upper Austria.** T. VON FELLEBERG (Biochem. Z., 1930, 224, 176—192).—Water from the various bore-holes at Bad Hall gave in one case only 1.23 mg. but in all others values between 11.1 and 47.5 mg. of iodine per litre. The soil of Bad Hall is rather poor in iodine and the iodine-containing water must come from low-lying strata. The drinking water and stream-water are very rich in iodine and must also be enriched by water from deep strata. The Hall water gives off small amounts of iodine into the air. The milk supply is rich in iodine. By bathing for  $\frac{1}{2}$  hr. in the water (63 g. of salts with 13.3 mg. of iodine per litre) an absorption of iodine through the skin is detected by subsequent urine analysis of about 0.48 mg. corresponding with 36 c.c. of bath water. Iodine can be detected in sweat.

P. W. CLUTTERBUCK.

**Determination of traces of iodine in organic materials.** T. VON FELLEBERG (Biochem. Z., 1930, 224, 170—175).—Various modifications of the author's method of determining traces of iodine in which ashing in an open vessel is replaced by ashing in a tube (McClendon, A., 1928, 607; Reith, A., 1929, 337, 414, 1410; Schwaibold, A., 1929, 337, 1256) are examined and gave low results, it being often difficult either to avoid formation of tarry material or to absorb quantitatively the whole of the fumes developed. Details are given of an improved method which combines a preliminary fusion with potassium hydroxide in a nickel dish with subsequent burning of carbon in a heated tube after removal of water-soluble material. The fumes from the tube are collected in potassium hydroxide and together with the residual ash are combined with the water-soluble material and the iodine is finally determined by titration. Using the method, calf's blood is shown to contain 1.2 and 1.14  $\gamma$  per 10 c.c. and the mean of six determinations of 142  $\gamma$  of iodine added to the blood was 144.5  $\gamma$ .

P. W. CLUTTERBUCK.

**Effect of organic fluorine compounds on the animal organism. I. Action of fluorobenzene, *p*-fluorotoluene, and *p*-fluoroacetanilide and the state of fluorine in the blood.** K. LANG (Arch. exp. Path. Pharm., 1930, 152, 361—376).—Feeding organic fluorine compounds to rabbits does not increase the fluorine content of the blood, which is almost entirely inorganic, nor does it increase the time required for clotting. Feeding of fluorobenzene,



*p*-fluorotoluene, or *p*-fluoroacetanilide causes no accumulation of fluorine in the various organs except the heart and, in smaller degree, the lungs. Dogs fed regularly with fluorobenzene grow thin and show intense salivation, but no definite product of metabolism can be isolated. The fate of *p*-fluoroacetanilide is also obscure, but *p*-fluorotoluene gives rise to *p*-fluorobenzoic acid, of which 5 g. are obtained from the urine on feeding 26 c.c. of *p*-fluorotoluene in small daily doses.

P. G. MARSHALL.

**Pharmacology of gold compounds.** I. B. VON ISSEKUTZ and M. LEINZINGER. II. B. VON ISSEKUTZ and Z. DIRNER. III. B. VON ISSEKUTZ and I. MÉHES (Arch. exp. Path. Pharm., 1930, 152, 238—305, 306—317, 318—340).—I. Sodium chloraurate has a characteristic affinity for proteins and will cause agglutination of blood-corpuscles and check the swelling of gelatin. The hæmolytic action is strongly inhibited by blood-serum, falling from 1:150,000 to 1:15,000 in the presence of 2% of serum. Potassium auricyanide, which is lipid-soluble, produces no inhibition of the swelling of gelatin and has no appreciable hæmolytic activity. "Sanocrysin" resembles it in this respect and is bound only to the extent of 20% by serum. Most other gold compounds resemble gold chloride and sodium chloraurate in their properties.

II. A study of the toxicity of gold compounds on various organisms such as bacteria, yeast, and paramoecium. Gold chloride is a general protoplasmic poison and is more effective in killing bacteria than is "sanocrysin." Potassium auricyanide shows the strongest antiseptic action, probably by virtue of the inhibiting action of the cyanogen group on oxidative processes. Its toxic effect on frogs and rats is only slightly diminished by sodium thiosulphate. "Krysolgan" and "triphal" have a toxicity similar to that of "sanocrysin," whilst "solganal" has only one tenth the toxicity.

III. Neutralised gold chloride solutions in a concentration greater than 1:2500 produce a digitalis-like action on the isolated frog's heart, a considerable proportion of the gold being bound in the surface layers of the heart-muscle. Frog's gastrocnemius is similarly contracted. In cats gold chloride produces a lowering of blood-pressure and increase in the respiration rate. "Krysolgan" and "solganol" produce similar effects in smaller degree. The tonus of isolated rabbit's gut is raised by gold chloride (and by "sanocrysin" in larger doses) and lowered by gold cyanide.

P. G. MARSHALL.

**Influence of crystalline glutathione on the physiological action of arsenic compounds.** S. M. ROSENTHAL and C. VOEGTLIN (J. Pharm. Exp. Ther., 1930, 39, 347—367).—Intravenous injection into rats of the minimum lethal dose of 3-amino-4-hydroxyphenylarsenious oxide or of sodium arsenite does not cause death if the animals have previously received an injection of a solution of glutathione in the ratio of 10 mols. of the tripeptide to 1 g.-atom of arsenic. Trypanosomes exposed *in vitro* to the action of arsenious oxide retain their power to infect rats if glutathione is present, and the inflammation produced in the ear of the rabbit by injection there of solutions

of arsenious oxide is prevented if glutathione is added to the solutions. The rate of oxidation of glutathione by oxygen with hæmin as catalyst is reduced if arsenious oxide or its 3-amino-4-hydroxyphenyl derivative is present in concentrations of the same order as that of the glutathione. Lower concentrations of arsenic compound have no effect, although there may be more than sufficient arsenic compound present to combine with all the hæmin used. Concentrations of sodium cyanide, very low in relation to the concentration of glutathione, produce marked inhibition of the oxidation. It is probable that the action of compounds of trivalent arsenic on living cells involves chemical reaction between the compounds and glutathione and possibly also between the compounds and other constituents of the protoplasm which contain thiol groups.

W. MCCARTNEY.

**Local anæsthetics derived from dialkylamino-propanediols.** I. Phenylurethanes. T. H. RIDER (J. Pharm. Exp. Ther., 1930, 39, 457—467).—The local anæsthetic activity of the hydrochlorides of the phenylurethanes and diphenylurethanes of dialkylaminopropanediol (cf. this vol., 897) has been investigated on the sciatic nerve of the frog and on the rabbits' cornea. With increase in the size of the alkyl group the local anæsthetic action increases. In the lower homologues it is greater in the diphenyl than in the monophenyl series, whereas in the higher homologues the reverse is the case. The compounds have a marked precipitating action on proteins, and this probably masks the local anæsthetic action to some extent, especially in the diphenyl series, where precipitating power is very pronounced. Diisobutylaminopropanediol monophenylurethane hydrochloride is six times as strong as cocaine on the rabbit's cornea and more than three times as strong as either novocaine or cocaine in an interdermal wheal, whilst it appears to be less toxic than either of these two drugs.

W. O. KERMACK.

**Comparison of the effect on the circulation and the narcotic action of barbituric acid derivatives.** M. VOGT (Arch. exp. Path. Pharm., 1930, 152, 341—360).—The action of the following compounds is reported: diethyl- (veronal), dipropyl- (proponal), phenylethyl- (luminal), cyclohexenylethyl- (phanodorm), diallyl- (dial, curral), isopropylallyl- (numal), isobutylallyl- (sandoptal), isoamylethyl- (amytal), isopropylbromoallyl- (noctal), and sec.-butylbromoallyl- (pernocton)-barbituric acids. The whole group produces lowering of blood-pressure and reduction of the respiratory volume. Veronal has the least and pernocton the greatest circulatory effect in the dosage necessary to produce narcosis, other derivatives being intermediate. The lethal dose for a 20-g. rat is 9.0 mg. of veronal and 1.8 mg. of pernocton. The therapeutic ratio is greatest (3.0) for phanodorm and least (1.2) for noctal.

P. G. MARSHALL.

**Pharmacological actions of harmalol.** J. A. GUNN and A. J. L. SIMONART (Quart. J. Pharm., 1930, 3, 218—237).—Investigation of the pharmacological actions of harmalol and comparison with harmaline show that the replacement of the methoxyl group in the latter by hydroxyl is accompanied by a reduction of the toxicity by subcutaneous injection

to 40% for laboratory mammals, but the toxicity for frogs is unchanged. Harmalol does not produce the clonic convulsions characteristic of harmaline. Harmaline is 30–60 times as toxic for protozoa (*Colpidia*) as harmalol. Otherwise the action of the two alkaloids on voluntary and involuntary muscle runs parallel with their toxicity. R. K. CALLOW.

**Pyrethrum flowers. IV. Relative toxicity of pyrethrins I and II.** C. B. GNADINGER and C. S. CORL (J. Amer. Chem. Soc., 1930, 52, 3300–3307).—The toxicity of pyrethrins I and II, isolated from Japanese *Pyrethrum* flowers and partly purified through their semicarbazones (cf. Staudinger and Ruzicka, A., 1924, i, 700), has been determined towards house flies (*Musca domestica*) using the oil-spray method of Peet and Grady (J. Econ. Entomol., 1928, 21, 612). Pyrethrin II is about 80% as toxic as pyrethrin I. The determination of the total pyrethrin content of *Pyrethrum* flowers by the authors' copper reduction method (B., 1929, 996) is an accurate index of their toxicity. H. BURTON.

**Study of toxicity [of rotenone] using goldfish.** W. A. GERSDORFF (J. Amer. Chem. Soc., 1930, 52, 3440–3445).—The toxicity of rotenone to goldfish in concentrations of 0.015–4 mg. per litre of water (containing 1 part of acetone in 1000) is studied at  $27 \pm 0.2^\circ$ . H. BURTON.

**Histamine and alkalosis.** R. RAFFLIN and P. SARADJICHVILI (Compt. rend. Soc. Biol., 1929, 102, 559; Chem. Zentr., 1930, i, 1325).—The subcutaneous injection of histamine into mentally-deficients is accompanied by alkalosis of the blood and urine, the result of elimination of chlorine in the gastric and urinary secretions. L. S. THEOBALD.

**Chemotherapy of quinoline compounds. I. Action of certain quinoline compounds on *Paramacia*.** U. BRAHMACHARI, T. BHATTACHARYYA, R. BANERJEA, and B. B. MAITY (J. Pharm. Exp. Ther., 1930, 39, 413–415).—8-Aminoquinoline and quinolyl-8-glycineamide are without toxic action on paramacia in concentration of 1–2000, whereas 6-aminoquinoline and quinolyl-6-glycineamide kill at a concentration of 1–2000, but not at a concentration of 1–4000. 8-Amino-6-hydroxyquinoline and 6-hydroxyquinolyl-8-glycineamide are highly lethal, but 8-amino-6-methoxyquinoline (1–2000) is without action. W. O. KERMACK.

**Idiosyncrasy to quinine, cinchonidine, and ethylhydrocupreine and other laevorotatory alkaloids of the cinchona series. Further chemical delimitation of the idiosyncrasy; alteration in sensitiveness.** W. T. DAWSON and F. A. GARBADE (J. Pharm. Exp. Ther., 1930, 39, 417–424).—A male subject exhibiting sensitiveness to quinine and related alkaloids is not sensitive to quinine and cinchonidine, but is sensitive to the ethyl, amyl, and isoamyl esters of quinine. Sensitiveness is shown to laevorotatory propyl-, isopropyl-, isobutyl-, and isoamyl-hydrocupreine and to quinoline. The sensitiveness to isoamylhydrocupreine did not exist at the beginning of the experiments, but set in later, indicating apparently an increase of sensitiveness of the subject. W. O. KERMACK.

**Fate of apomorphine after subcutaneous injection.** F. BAMFORD (Analyst, 1930, 55, 502–503).—Four rabbits were injected subcutaneously with (1) 160 mg. of morphine hydrochloride, (2) 160 mg. of apomorphine hydrochloride, (3) as (2), and (4) 6 mg. of apomorphine hydrochloride. After 1 hr. the rabbits were killed and the stomachs and contents of (1) and (2) and the contents only of (3) and (4) extracted by the Stas-Otto process. Only the extracts from (1) and (2) gave precipitates with the usual alkaloid precipitants and the colour reactions of the morphine group, and in (2) the extracted apomorphine was free from morphine.

D. G. HEWER.

**Enzyme purification; pancreatic amylase.** H. C. SHERMAN, M. L. CALDWELL, and M. ADAMS (J. Biol. Chem., 1930, 88, 295–304).—Commercial pancreatin is extracted with 10 parts of 87% glycerol at the ordinary temperature, the mixture is centrifuged, and the supernatant fluid is diluted at  $0^\circ$  with 5 parts of a phosphate buffer solution so that the final  $p_H$  is 5.8; the solution is again centrifuged and the mother-liquor is treated with an alcoholic suspension of aluminium hydroxide at  $0^\circ$ . The enzyme is eluted from the precipitate with dilute sodium hydroxide (final  $p_H$  7.0–7.3) and is again precipitated by addition of a mixture of equal parts of alcohol and ether. The resulting preparation (0.7 g. from 10 g. of pancreatin) has an amylolytic activity about eight times as great as that of the original material. Control of the  $p_H$  is important throughout and is checked by electrometric determinations, which can be made in presence of alcohol or glycerol. The purified preparation has the properties of a protein and is free from carbohydrate; it exhibits proteolytic activity. C. R. HARRINGTON.

**Action of powdered organs on pancreatic amylase.** A. BADREAU (J. Pharm. Chim., 1930, [viii], 11, 20–31).—Desiccation of salivary glands of the ox, stomach mucosa of the pig, pancreas of the pig, ox, and horse, bile, and pig's intestine gives powders of  $p_H$  6–6.2, all of which, except the bile and stomach powders, show amylolytic power. The amount of starch hydrolysed by a mixture of pancreas powder (0.05 g.) with 0.2 g. of one of the others is greater than that hydrolysed under similar conditions by the two glands separately. Addition of larger quantities of the second gland, or of a mixture of glands, does not produce a further exaltation. Similarly, the amylolytic action of mixtures of any two of the other glands, whether both or only one is active, is greater than that of the two separately. The activity of pancreatic amylase is also increased by thymus and liver powders and by glycine and tyrosine, whilst peptone causes the greatest increase of any of the substances tried. It is suggested that the effect of all these products is due to the amino-acids which they contain, and that the latter may be co-enzymes necessary for the activity of this enzyme. H. E. F. NORRIS.

**Enzymic hydrolysis of phloridzin.** E. A. MOELWYN-HUGHES (J. Gen. Physiol., 1930, 13, 807–817).—Data on the velocity of hydrolysis of phloridzin by acids (A., 1928, 374), compared with those of

other glucosides, showed that the lability of phloridzin towards acids resembles the fructosides rather than the normal glucosides. Emulsin had no action on phloridzin, whereas maltase and maltase-free invertase hydrolysed it. The action of maltase is considered to be due to small amounts of invertase known to be present. The phloridzin sugar prepared by hydrolysis had  $[\alpha]_D +44.61^\circ$ . *B. pestis* fermented phloridzin sugar less readily than dextrose. It is concluded that phloridzin is not a normal glucoside, and the tentative suggestion that it is a derivative of a  $\gamma$ -hexose is put forward. G. F. MARRIAN.

**Inactivation of pancreatic lipase by heat.** I. H. MCGILLIVRAY (Biochem. J., 1930, 24, 891—904).—Purified pancreatic lipase is inactivated by heat in accordance with the unimolecular law, the optimum stability being at  $p_H$  6.0. The critical increment for the heat-inactivation process in 50% glycerol is sensibly the same, namely of the order of 46,000 g.-cal., at  $p_H$  6.0, 8.01, and 5.0. In 25% glycerol and at  $p_H$  6.0 the critical increment is 47,800 g.-cal. With unpurified lipase the course of inactivation by heat in 80% glycerol is unimolecular, whereas in the water extract of the dried gland powder the unimolecular coefficient decreases with time. The unpurified lipase is also most stable at about  $p_H$  6.0. At  $p_H$  6.0 and in 80% glycerol the critical increment for the process in unpurified extracts is of the order of 100,000 g.-cal., whereas in 50% glycerol the value is 57,500 and in water 35,000. At  $p_H$  9.3 the critical increment of unpurified extract containing 80% glycerol is of the order 92,000 g.-cal. S. S. ZILVA.

**Action of arsenate on hexosephosphatase.** M. G. MACFARLANE (Biochem. J., 1930, 24, 1051—1057).—Hexose-mono- and di-phosphate can be hydrolysed by washed dried yeast in the absence of co-enzyme. Arsenate accelerates the rate of production of phosphate from hexosediphosphate only in the presence of yeast extract and the acceleration has not been obtained without an accompanying fermentation. Fluoride inhibits this acceleration. Fractionation of the boiled yeast extracts used indicates that some other factor besides the co-enzyme is necessary for the reaction. S. S. ZILVA.

**Crystalline pepsin.** I, II. Isolation and properties. J. H. NORTHROP (J. Gen. Physiol., 1930, 13, 739—766, 767—780).—I. Commercial pepsin was dissolved in dilute sulphuric acid and precipitated by half saturation with magnesium sulphate. The precipitate was suspended in water, dissolved by the addition of sodium hydroxide, so that the  $p_H$  did not rise above 5.0, reprecipitated by the addition of sulphuric acid to  $p_H$  3.0, and dissolved in sodium hydroxide at  $45^\circ$ . After inoculation and slow cooling a crystalline paste separated. The proteolytic activity of the crystals was about 5 and 2.5 times that of the original pepsin when measured by the hydrolysis of caseinogen and the liquefaction of gelatin. It had the characteristic properties of a protein; the nitrogen content, optical rotation, and proteolytic activity were constant for six different preparations and remained unchanged throughout seven crystallisations. Data from solubility determinations in differ-

ent salt solutions, the rate of activation by heat and alkali, and the determination of its diffusion coefficient suggest that it is a pure substance. The possibility that it is a solid solution is not, however, excluded. The rate of inactivation at  $65^\circ$  ( $p_H$  3.0) was found to follow the course of a unimolecular reaction.

Sera of rabbits injected with active and denatured preparations gave precipitin reactions with either active or denatured pepsin solutions. Both sera inhibited the action of the enzyme.

II. The effects of temperature,  $p_H$ , and varying concentrations of sodium sulphate on the solubility of crystalline pepsin were studied. The substance has a minimum solubility at  $p_H$  2.75 corresponding with its isoelectric point. Migration experiments and a titration curve confirm this figure. Different methods of determining the mol. wt. (osmotic pressure, diffusion coefficient, phosphorus content, chlorine content, and sulphur content) gave values ranging from 33,000 to 40,000. A summary of the chemical and physical properties of the substance is given. G. F. MARRIAN.

**Action of pepsin on gelatin.** R. K. CANNAN and E. MUNTWYLER (Biochem. J., 1930, 24, 1012—1020).—The changes in acid- and in base-binding capacities which accompany the digestion of gelatin by pepsin have been determined with the aid of hydrogen electrode titration curves, and it was found that the main chemical effect of pepsin is the hydrolysis of peptide linkings between the  $\alpha$ -amino- and  $\alpha$ -carboxyl groups of amino-acids. Pepsin produced marked changes in the physical condition of gelatin before any increase in titratable groups could be demonstrated. Each peptide linking hydrolysed rendered 14—15 atoms of nitrogen soluble in 80% alcohol. S. S. ZILVA.

**Action of the latex of *Ficus carica* on proteins.** S. VISCO (Atti R. Accad. Lincei, 1930, [vi], 11, 688—691).—The action of the latex on the proteins of egg-white does not proceed further than the formation of secondary proteoses. T. H. POPE.

**Rate of liberation of arginine in tryptic digestion.** J. A. DAUPHINEE and A. HUNTER (Biochem. J., 1930, 24, 1128—1147).—In the case of caseinogen and gelatin the initial rate of liberation by arginase of arginine or of an arginine complex is so great that half of their total potential arginine is easily set free within 3 hrs. With Witte peptone this liberation is only slightly slower, whilst with edestin and fibrin free arginine appears much more gradually. Egg-albumin exhibits a peculiar behaviour in that the liberation of arginine, like that of free amino-groups in general, commences only after a latent period of one or two days. With fibrin the total amount of arginine liberated by trypsin was only two thirds of the amount obtainable on complete hydrolysis, and with caseinogen, gelatin, edestin, egg-albumin, or Witte peptone four fifths. These fractions appear to be characteristic. In the acid hydrolysis of gelatin arginine is liberated less rapidly and at a more regular rate than in its tryptic digestion. S. S. ZILVA.

**Protein constituents and their enzymic conversions.** M. BERGMANN (Naturwiss., 1930, 18,

465—468).—The structure and reactions of certain amino-acids and related compounds are described with special reference to the action of enzymes.

H. F. GILLBE.

"Activation" of proteolytic enzymes. H. A. KREBS (Naturwiss., 1930, 18, 736).—Priority of publication is claimed over Waldschmidt-Leitz, Purr, and Balls (this vol., 1217). W. R. ANGUS.

[Biochemical factors in] heredity. IV. H. VON EULER, H. DAVIDSON, and D. RÜNEHJELM (Z. physiol. Chem., 1930, 190, 247—261; cf. A., 1929, 1497).—The catalase content of chlorophyll-normal and chlorophyll-defective mutants of barley was determined at different stages of germination. One strain had a ratio green : white of 2.5, another 2.2, another green : light green 1.5 (etiolated, yellow : light yellow, 1.4). A further strain green : yellowish-green had a similar ratio. J. H. BIRKINSHAW.

Cytochrome and the catalase action of yeast. H. VON EULER and H. HELLSTRÖM (Z. physiol. Chem., 1930, 190, 189—198).—Hæmochromogen of yeast shows absorption bands at 557 and 525  $m\mu$  coinciding with those of pyridine hæmochromogen and a third at 586  $m\mu$  unaffected by oxidation and reduction. 60% pyridine extracts hæmochromogen, the extract giving a strong band at 586  $m\mu$  and a very weak one at 557  $m\mu$  which is strengthened by reduction. The 586  $m\mu$  band disappears on the addition of hydrazine hydrate. Cytochrome on addition of pyridine is apparently resolved into two different porphyrin or porphyratin complexes of which one is hæmin. Heating yeast to 65° or treatment with chloroform or acetone causes three of the five cytochrome bands to disappear, 550 and 521  $m\mu$  remaining. The catalase action is strengthened.

J. H. BIRKINSHAW.

Selective fermentation. I. Alcoholic fermentation of dextrose, lævulose, and mannose mixtures. H. SOBOTKA and M. REINER (Biochem. J., 1930, 24, 926—931).—All the types of yeast examined fermented dextrose and lævulose at a rate of 2 to 1 or higher. This rate is influenced by the nature of the culture medium. There is no correlation between selective fermentation and invertase or maltase content. Dextrose and mannose were fermented at a rate of about 2—3 : 1, whilst in the case of lævulose and mannose the ratio was about 1.4 : 1.

S. S. ZILVA.

Fourth and fifth fermentation processes of sugar. C. NEUBERG and M. KOBEL (Naturwiss., 1930, 18, 427—429).—The existence has been established of a fourth mode of fermentation of hexoses, which follows the second and third processes and results in the production of pyruvic acid and glycerol, whilst in a fifth mode of decomposition, according to the equation  $C_6H_{12}O_6 = 2H_2O + 2CMe \cdot CHO$ , an 85% yield has been obtained by employment of 2:4-dinitrophenylhydrazine to isolate the methylglyoxal formed. The significance of these reactions in plant and animal organisms is indicated.

H. F. GILLBE.

Co-zymase. XVII. H. VON EULER and K. MYRBÄCK (Z. physiol. Chem., 1930, 190, 93—100; cf. A., 1929, 1340).—The best preparations of co-

zymase show an activity coefficient of about 70,000—80,000 units. The composition corresponds with an adenine-carbohydrate (pentose)-phosphoric acid complex. On this basis about 80% of the co-zymase is accounted for. Further fractionation of a highly active preparation yields some inactive fractions, the total activity of all fractions being considerably less than that of the original. Co-zymase may also be inactivated by enzymes, e.g., liver nucleotidase, but the phosphoric acid liberated is much less than corresponds with the amount of co-zymase rendered inactive. The activating action of boiled yeast juice is probably the resultant of several factors. In the determination of the activity of co-zymase different preparations of apozymase give different results, although with fresh apozymase from a given strain of yeast the results are comparable.

J. H. BIRKINSHAW.

Effect of different amounts of toluene on the fermentation of sugar by fresh and dried yeast. G. SELIBER (Biochem. Z., 1930, 224, 202—210).—The intensity of fermentation by living yeast is depressed by 10—50% in presence of toluene, but increasing the amount of toluene from 2 to 40% does not affect the extent of inhibition. A greater effect is obtained by triturating yeast with toluene. Dried yeast is more sensitive to toluene except when drying has been prolonged, when the total fermenting power is very low and toluene has little effect.

P. W. CLUTTERBUCK.

Growth acceleration in protozoa and yeast. H. H. DARBY (J. Exp. Biol., 1930, 7, 308—316).—The allelocatalytic phenomena in the growth of *Paramecium* do not occur if a small volume of suitable medium is used. The optimum growth of yeast is at  $p_H$  4.4.

E. BOYLAND.

Oxalic acid as a reagent for isolating tubercle bacilli. Growth of acid-fast, non-pathogenic organisms on different media, and their reaction towards chemical reagents. H. J. CORPER and N. UYER (J. Lab. Clin. Med., 1930, 15, 348—369).

CHEMICAL ABSTRACTS.

Oxidation of hydrogen and hydrocarbons by bacteria. J. TAUSZ and P. DONATH (Z. physiol. Chem., 1930, 190, 141—168).—Both *B. aliphaticum liquefaciens* and the methane bacterium are able to oxidise hydrogen in presence of air. The former organism oxidises all the longer-chain paraffins beginning with pentane. The olefines are not attacked nor are the cyclic hydrocarbons except those with a long side-chain (e.g., cetylbenzene). The methane bacterium oxidises all the paraffins and propylene and butylene, but not benzene or cyclohexane. The bacterial oxidation of hydrogen proceeds with methylene-blue as acceptor, indicating hydrogen activation. In the oxidation of hexane, the intermediate formation of unsaturated hydrocarbons was established.

J. H. BIRKINSHAW.

Culture media containing urea. III. A. J. J. VANDE VELDE (Natuurwetensch. Tijds., 1930, 12, 141—145; cf. this vol., 503).—Two series of experiments have been carried out on the influence of urea on the fermentation of milk. The acidity developed, determined by titration, is somewhat less in presence

of urea; it is concluded that lactic acid bacteria can decompose urea to give ammonia, and that *B. fluorescens liquefaciens* can ferment lactose to lactic acid.

S. I. LEVY.

**Oxidation-reduction studies in relation to bacterial growth.** I. Oxidation-reduction potential of sterile meat broth. II. Method of poisoning the oxidation-reduction potential of bacteriological culture media. B. C. J. G. KNIGHT (Biochem. J., 1930, 24, 1066—1074, 1075—1079).—I. The oxidation-reduction potential of completely deaerated sterile, buffered meat broths has been measured over a range  $p_H$  4—10.5. The potentials indicated by Clark's dyes are more negative than those shown by an electrode in broth alone. When oxygen is removed the potential of the broth drifts to a definite level depending on  $p_H$ .

II. The negative potential drift is balanced by passing into the medium a controlled stream of very dilute oxygen in nitrogen, the concentration and rate of flow of the gas mixture being adjusted until there is equilibrium between the rate of reduction of the broth system and its rate of oxidation by the oxygen. Much greater precision can be given to the electrode readings and the poisoning of the potential is made more refined by the addition of small quantities of oxidation-reduction dyes with a span of potential covering the desired level.

S. S. ZILVA.

**Mechanism of opsonin and bacteriotropin action.** IV. Isoelectric points of certain sensitised antigens. M. McCUTCHEON, S. MUDD, M. STRUMIA, and B. LUCKÉ (J. Gen. Physiol., 1930, 13, 669—681).—The isoelectric points of *Mycobacterium avium* and *M. chelonae*, determined by cataphoresis, showed a progressive shift from about  $p_H$  2.5 to 5.7 after sensitisation with increasing amounts of homologous rabbit immune serum, the mean isoelectric point of the globulins of the sera used being  $p_H$  5.1—5.2. This phenomenon was not due to the deposition of residual fibrinogen on the bacteria since when plasma was used instead of serum slightly, lower results were obtained. The shift in isoelectric point was accompanied by agglutination, and changes in surface properties of the bacteria.

G. F. MARRIAN.

**Possible mechanism of diphtheria toxoid formation.** L. F. HEWITT (Biochem. J., 1930, 24, 983—992).—Eighty-five % of the amino-nitrogen present in fresh diphtheria toxins remains free in completely detoxified toxoids prepared by incubation with formaldehyde. Reducing and oxidising agents and methyl alcohol failed to produce a detoxified toxoid. Slight reducing conditions are maintained when toxin is incubated with formaldehyde.

S. S. ZILVA.

**Effect of intravenous injection of urethane on the secretion of adrenaline in cats.** S. KODORNA (Tohoku J. Exp. Med., 1930, 15, 11—16).—Hypersecretion of adrenaline is observed; it is prevented by cutting the splanchnic nerves.

CHEMICAL ABSTRACTS.

**Calcium of cerebrospinal fluid and of blood-serum with reference to parathyroid hormone.** S. MORGULIS and A. M. PERLEY (J. Biol. Chem., 1930,

88, 169—188).—Oral administration of calcium salts and production of experimental jaundice were without effect on the calcium of the blood-serum or cerebrospinal fluid of dogs. Increase in the serum-calcium of dogs by direct injection of calcium salts or by their oral administration in combination with parathyroid hormone and decrease in the serum-calcium brought about by parathyroidectomy had little or no effect on the calcium of the cerebrospinal fluid. No evidence was obtained of the transfer of calcium to the red blood-corpuscles as the result of parathyroidectomy, or of the existence in blood of a slowly dissociable organic calcium compound. The diffusible calcium determined by dialysing blood-serum against cerebrospinal fluid was practically constant in amount irrespective of whether the dogs were normal, or had received injections of calcium salts with or without parathyroid hormone, or had been parathyroidectomised. The parathyroid hormone has therefore no apparent effect on the distribution of calcium between the blood-serum and the cerebrospinal fluid.

C. R. HARRINGTON.

**Influence of the thyroid on the protein metabolism of individual organs.** O. STEFFERN and A. SMIRNOVA (Biochem. Z., 1930, 224, 83—90).—The authors' previous work on the autoprocolysis of entire animal bodies (A., 1926, 1174) is extended to individual tissues, the autolysis of rabbits' liver, muscle, heart, and brain being investigated at  $p_H$  3.4, 7.4, and in water after 24 and 48 hrs. incubation at 37°, the tissues being obtained from normal animals and animals to which had been administered thyroid gland either as dry preparation by stomach tube or thyroxine by injection. Changes in the rate of autolysis are exceptionally marked in the case of liver and heart-muscle pulp, much less with skeletal muscle, and scarcely appreciable with brain.

P. W. CLUTTERBUCK.

**Effect of secretin on blood-sugar.** M. YASUDA (J. Biochem. Japan, 1930, 11, 479—503).—Insulin hypoglycaemia is accompanied by a corresponding fall in inorganic phosphorus; hyperglycaemia causes a fall in plasma-phosphorus. Under the influence of thyroxine and amino-acids the effect of sympathetic stimulation is manifested in so far as both hyperglycaemia and hypophosphataemia are produced. Only with injection of pancreatic secretin is the former accompanied by the latter. The internal secretion of the pancreas is not promoted by its external secretory activity.

CHEMICAL ABSTRACTS.

**Hormones of the anterior pituitary lobe.** I. B. ZONDEK (Klin. Woch., 1930, 9, 245—248; Chem. Zentr., 1930, i, 1955).—A description of biological tests for the hormones, and a definition of units.

A. A. ELDRIDGE.

**Effect of posterior pituitary extract on respiratory metabolism.** E. SCHILL and J. VON FERNBACH (Z. ges. exp. Med., 1929, 67, 551—557; Chem. Zentr., 1930, i, 1955).

**Stability of aqueous solutions of the oxytocic principle of the pituitary gland.** J. H. GADDUM (Biochem. J., 1930, 24, 939—944).—The rate of destruction of the principle in the aqueous extract has

been measured at different hydrogen-ion concentrations and at different temperatures.

S. S. ZILVA.

**Pituitary gland. VII. Separate identity of the pressor and melanophore principles.** L. HOGGEN and C. GORDON (J. Exp. Biol., 1930, 7, 286—292).—By the action of sodium hydroxide the pressor activity of pituitary extracts can be removed whilst the melanophoric activity remains. E. BOYLAND.

**Isolation and preparation of vagotonin, a new pancreatic hormone.** H. PÉNAU and D. SANTE-NOISE (Compt. rend., 1930, 191, 342—344).—Extraction of minced pancreas with 0.05*N*-alcoholic sulphuric acid, followed by processes of fractional precipitation and ultra-filtration to remove compounds of low mol. wt., yields vagotonin as a white, water-soluble powder, with properties quite distinct from those of insulin. It acts on the oculo-cardiac reflex in doses of less than 0.1 mg. per kg., and has a slow hypoglycaemic effect.

R. K. CALLOW.

**Crystalline insulin. XI. Does insulin cause an initial hyperglycaemia?** E. M. K. GELLING and A. M. DE LAWDER (J. Pharm. Exp. Ther., 1930, 39, 369—385).—The initial temporary hyperglycaemia which immediately follows injection of commercial insulin is caused by non-dialysable impurities which are present. The impurities are not completely destroyed by alkali solutions of sufficient concentration to render insulin inactive. Crystalline insulin does not cause initial hyperglycaemia.

W. MCCARTNEY.

**Insulin. XII. Crystalline insulin.** H. JENSEN and A. DE LAWDER (Z. physiol. Chem., 1930, 190, 262—272).—A non-crystalline preparation of pig's insulin showing activity equal to that of crystalline ox insulin had a lower sulphur content (2.7 instead of 3.1%). Crystalline insulin precipitated by heating with 0.1*N*-hydrochloric acid cannot be reconverted into the crystalline form. An attempt was made to account for the low activity of acetylinsulin. Part of the acetyl is probably attached to an amino-group. Acetylation at higher temperatures yields a product of lower activity than acetylation at 0°. Compounds of insulin formed with benzaldehyde and benzoyl chloride are inactive and the activity cannot be regenerated. The action of dilute alkali hydroxide eliminates not only sulphide-sulphur but also ammonia or an amine. The ammonia removed seems to be related to the loss of activity which also occurs.

J. H. BIRKINSHAW.

**Determination of insulin secretion.** B. A. HOUSSAY, J. T. LEWIS, and V. G. FOGLIA (Rev. soc. Argentina biol., 1929, 5, 15—31).—Determinations of blood-sugar were made on fasting dogs anaesthetised with chloralose; the pancreas was removed and insulin injected into the jugular vein. In a fasting anaesthetised animal with normal blood-sugar the pancreas secretes about 0.01 unit per kg. per hr. to maintain the blood-sugar at the normal level. When the blood-sugar is high, 0.1 unit is at first secreted, the quantity falling when the normal level is reached.

CHEMICAL ABSTRACTS.

**Action of insulin on the glycogen distribution in normal animals.** M. W. GOLDBLATT (Biochem.

J., 1930, 24, 1199—1209).—The observation made on young rabbits (A., 1929, 609) that insulin produces a very large rise in hepatic glycogen without any simultaneous considerable fall in muscle-glycogen is confirmed on kittens. This rise is not a necessary sequel of a high degree of hypoglycaemia. The increase in liver-glycogen consequent on the injection of insulin into starving young rabbits cannot be explained by changes occurring in glycogen and free sugar in other parts of the body nor is it associated with changes in blood constituents other than diminution in sugar and inorganic phosphorus. Under the conditions described glycogen formation from endogenous sources is definitely increased.

S. S. ZILVA.

**Oestrin. IV. Chemical nature of crystalline preparations.** G. F. MARRIAN (Biochem. J., 1930, 24, 1021—1030; cf. this vol., 821).—Of the total oestrus-producing material in the ethereal extract of acidified urine, 32% has been obtained as a pure crystalline substance,  $C_{18}H_{24}O_3$ , m. p. 264—266°,  $[\alpha]_{5461}^{20} + 38^\circ$ . The substance is feebly acidic, being soluble in aqueous alkali. It is precipitated from alkaline solution by carbon dioxide. A triacetate, m. p. 120—122°, insoluble in aqueous alkali, has been prepared. Determinations of the base-binding power and approximate  $p_K$  of the substance show that one hydroxyl group is acidic; it gives colour reactions characteristic of phenolic substances. The activities and m. p. of the material precipitated from alkaline solution by carbon dioxide and of the material obtained by regenerating the acetate are the same as those of the original substance. It is not appreciably volatile at 165°/0.001 mm.

S. S. ZILVA.

**Crystalline menoformone.** E. DINGEMANSE, S. E. DE JONGH, S. KOBER, and E. LAQUEUR (Dent. med. Woch., 1930, 56, 301—304; Chem. Zentr., 1930, i, 1954).—Menoformone, dissolved in a little benzene, was adsorbed on fuller's earth, which was then boiled with benzene, the residue from which was extracted with much light petroleum. The precipitate obtained on cooling was treated with potassium hydroxide and extracted with 70% alcohol and the solution shaken with benzene. The menoformone was then recovered by shaking the acidified solution with benzene, and was recrystallised as needles or plates from 70% alcohol. The substance contains not more than 25 carbon atoms in the molecule; it gives only a faint coloration with antimony pentachloride in chloroform solution.

A. A. ELDRIDGE.

**Relaxative hormone of the corpus luteum. Purification and concentration.** H. L. FEVOLD, F. L. HISAW, and R. K. MEYER (J. Amer. Chem. Soc., 1930, 52, 3340—3348).—Details are given for the extraction of the relaxative hormone (named relaxin) from the corpus luteum tissue of sows' ovaries. The method involves extraction with acidified alcohol, removal of proteins and fats from the extract, and subsequent treatment of the resulting water-soluble extract as follows: (a) the evaporated extract is dissolved in acetic acid and the relaxin (contaminated with sodium chloride) crystallises, or (b) the extract is treated with picric acid whereby the active material is precipitated. This is freed from picric acid by dissolving in acetic acid, re-precipitating with ether,



dissolution of the solid in water, adjusting the solution to  $p_H$  5.4, and centrifuging the precipitated active material. The purified product contains about 11% N and 0.035 mg. constitutes a guinea-pig unit. Relaxin is soluble in acetic acid, slightly soluble in water, and insoluble in organic solvents. Acid and neutral solutions are stable, whilst alkaline solutions are unstable. The activity of aqueous solutions is destroyed by boiling for 10–15 min., and the solid gradually loses its activity when heated above 50° in the air. Relaxin is oxidised by potassium permanganate (with loss of activity) and it is destroyed by pepsin and trypsin. Relaxin can be isolated from the serum of pregnant rabbits; it is associated with the pseudoglobulin fraction.

H. BURTON.

**Effect of cryptorchidism and of castration on the chemical composition of rats.** V. KOREN-CHEVSKY and M. DENNISON (Biochem. J., 1930, 24, 954–960).—The amount of intra-abdominal fat is increased in cryptorchid and to a greater extent in castrated rats. The nitrogen content is slightly decreased in both-sided cryptorchid and in castrated rats. This decrease, however, is chiefly due to the increased proportion of fat in these animals. There is a slight increase in the content of solid matter in both-sided cryptorchid and in castrated rats.

S. S. ZILVA.

**Properties of the comb-growth-promoting substance obtained from testes and urine.** E. C. DODDS, A. G. H. ALLAN, and E. J. GALLIMORE (Biochem. J., 1930, 24, 1031–1038; cf. Dodds, Greenwood, and Gallimore, Lancet, 1930, i, 683).—The activity of this factor is destroyed by pepsin, trypsin, and oxidation, but survives with acids and alkalis. The benzene solution of the active substance can be washed with concentrated acids and alkalis and the active substance can be extracted from a 50% aqueous alcohol solution with light petroleum. The hormone can be distilled in a high vacuum, but only after previous purification and drying. When injected into male castrated rats or mice the atrophied seminal vesicles regain their normal size. The extracts from testes do not produce oestrus.

S. S. ZILVA.

**Carotene and vitamin-A. Transformation of carotene into vitamin-A as shown by a study of the absorption spectra of rat-liver oils.** N. S. CAPPER (Biochem. J., 1930, 24, 980–982; cf. Moore, this vol., 962).—The band at 325  $m\mu$  attributed to vitamin-A is absent from the absorption spectra of liver oils of rats suffering from vitamin-A deficiency, but is shown by liver oils of similar rats which have been subsequently cured by massive doses of carotene, which does not show this band.

S. S. ZILVA.

**Vitamin-A of butter.** R. A. MORTON and I. M. HEILBRON (Biochem. J., 1930, 24, 870–873).—The unsaponifiable matter from butter shows ultra-violet absorption similar to that of carotene, an increasing absorption on the ultra-violet side of 380  $m\mu$ , identical with that of the vitamin-A of liver oils, and an ultra-violet absorption of an unidentified substance characterised by a maximum near 272  $m\mu$ . Carotene and vitamin-A can be determined spectroscopically with

some degree of accuracy. The blue colour given by the unsaponifiable matter from New Zealand butter with antimony trichloride was characterised by a band at 592  $m\mu$  (carotene) and at 624  $m\mu$  (vitamin-A). In the case of a Danish butter the latter band was very sharp whilst the former was absent.

S. S. ZILVA.

**A diatom (*Nitzschia closterium*, W. Sm.) as a source of vitamin-A.** B. AHMAD (Biochem. J., 1930, 24, 860–865).—The oil obtained from the diatom possesses a very high vitamin-A activity and gives a strong colour reaction with antimony trichloride. The greater part of the biological activity of the oil is probably due to carotene synthesised by the organism and extracted with the oil.

S. S. ZILVA.

**Vitamin content of marine plankton.** J. C. DRUMMOND and E. R. GUNTHER (Nature, 1930, 126, 398).—An examination of phytoplankton and zooplankton for vitamin-A and vitamin-D showed positive tests for vitamin-A in the former and for vitamin-D in the latter. The small amount of vitamin-D present in zooplankton appears to result from irradiation in surface waters and not from a prolonged diet of phytoplankton.

L. S. THEOBALD.

**Isolation of the antineuritic vitamin.** N. STECHOW and L. WAMOSCHER (Arch. Pharm. Inst. Univ. Berlin, 1927, 13, 145–147; Chem. Zentr., 1930, i, 1961–1962).—In experiments with rice bran, precipitation with potassium bismuth iodide, but not that with lead acetate, afforded active preparations.

A. A. ELDRIDGE.

**Heat-stability of the (antidermatitis, "anti-pellagra") water-soluble vitamin-B<sub>2</sub>.** II. H. CHICK and A. M. COPPING (Biochem. J., 1930, 24, 932–938).—An extract made from washed brewer's yeast by boiling in dilute acetic acid after being heated in acid solution ( $p_H$  2.5) for 4 hrs. at 119° retained its power to cure the skin affection in rats, due to deprivation of vitamin-B<sub>2</sub>, completely in doses equivalent to 0.5 g. of yeast (dry wt.) and less completely in doses equivalent to 0.16–0.33 g. of yeast. The same extract treated in alkaline solution ( $p_H$  10.3–9.6) failed to cure the skin affection in doses equivalent to 0.5 g. or 1.0 g. in three out of four cases. The acid extract promoted the growth of rats on diets deficient in vitamin-B<sub>2</sub>, whilst the alkaline extract did not.

S. S. ZILVA.

**Experimental scurvy. VII. Effect of vitamin-C given parenterally to guinea-pigs fed on a vitamin-free diet.** T. NAGAYAMA and T. TAGAYA. **VIII. Carbohydrate metabolism of guinea-pigs fed on a diet free from vitamin-C.** Y. KOZA (J. Biochem. Japan, 1930, 11, 445–460, 461–477).—**VII. Hypodermic administration of vitamin-C prevents experimental scurvy.**

**VIII. Lack of vitamin-C has no direct effect on the liver- or muscle-glycogen of the guinea-pig.**

CHEMICAL ABSTRACTS.

**Vitamin-C and the rat's diet.** G. A. HARTWELL (Biochem. J., 1930, 24, 967–972).—The addition of vitamin-C to a synthetic diet produces no improvement in the rate of growth or reproduction of the rat.

S. S. ZILVA.

**Fat-soluble vitamins. XXX. Effect of feeding with irradiated yeast on antirachitic value of cow's milk.** H. STEENBOCK, E. B. HART, F. HANNING, and G. C. HUMPHREY (J. Biol. Chem., 1930, **88**, 197—214).—Daily administration to cows of 10 g. of irradiated yeast had no effect on the milk but increased the vitamin-A content of the butter; 50 g. of irradiated yeast daily caused definite increase in the vitamin-A of the milk, and as much as 200 g. could be given daily without adverse effect on the amount or the fat-content of the milk.

C. R. HARRINGTON.

**Is vitamin-D a single substance?** G. VON WENDT (Klin. Woch., 1930, **9**, 166—167; Chem. Zentr., 1930, i, 1961).—Experiments on the massive feeding of rats with "vitophos" suggest the possibility that several different substances may exhibit the effects of vitamin-D.

A. A. ELDRIDGE.

**Sinkage [of pulp-wood]. II. Seasonal distribution of water and gas in trees.** R. D. GIBBS (Canad. J. Res., 1930, **2**, 425—439; cf. B., 1930, 907).—The distribution of water and gas, together with the seasonal changes, in balsam, jack pine, birch, and poplar have been investigated. The water content of freshly-cut soft woods, with the exception of balsam, is relatively uniform, very high in sapwood, and low in heartwood. The gas content of heartwood is higher than that of sapwood; thus the higher is the proportion of heartwood the lower is the tendency of logs to sink. An apparatus for the measurement of volume of wood samples is described, and the seasonal distribution of water and gas is illustrated by means of curves and tables.

T. T. POTTS.

**Effect of turbulence [of the atmosphere] on the carbon dioxide exchange in plants.** P. LEHMANN (Forts. Landw., 1929, **4**, 745; Bied. Zentr., 1930, **59**, 312—318).—Variations in the carbon dioxide content of the air at short intervals and under varying conditions are recorded. The effect of wind velocity, temperature, and environmental conditions on local changes in the moisture and carbon dioxide in air, and the resulting influence on the carbon dioxide assimilation of plants, are discussed.

A. G. POLLARD.

**Assimilation of carbon dioxide under the influence of radioactivity in the development of cells containing chlorophyll.** J. STOKLASA, J. ČAKIR, and J. PĚNKAVA (Biochem. Z., 1930, **224**, 102—134).—The amounts of carbon dioxide assimilated and expired by a cell containing chlorophyll changes with its age. The action simultaneously of  $\beta$ - and  $\gamma$ -rays and the action of  $\gamma$ -rays alone increase the assimilation of carbon dioxide, the increase being different for cells at different stages of development. Simultaneous action of  $\beta$ - and  $\gamma$ -rays using 200 and 250 g. of "nasturan" ( $=0.0354$  and  $0.04425$  mg. of radium) causes a decrease in the respiration of young cells. Radium emanation causes a decrease of assimilation at all stages of the cell development, the greatest effect being obtained with a young cell and decreasing with age. Emanation also causes an increased respiration, the increase being greatest with the young cell.

P. W. CLUTTERBUCK.

**Photosynthesis. I. The formaldehyde hypothesis. II. First sugar of carbon assimilation and nature of the carbohydrates in the narcissus leaf.** E. C. BARTON-WRIGHT and M. C. PRATT (Biochem. J., 1930, **24**, 1210—1216, 1217—1234).—I. The production of formaldehyde in Klein and Werner's experiments (A., 1926, 439) is not due to photosynthetic activity of the plant, but to the action of light on carbonic acid and hydrogen carbonates in their solutions.

II. Only hexoses and sucrose are formed in the leaf of the daffodil *Narcissus pseudonarcissus*, L. Investigation of the carbohydrates indicates that the hexose and not sucrose is the first sugar of photosynthesis.

S. S. ZILVA.

**Storage and other carbohydrates in a Natal succulent and a Natal geophyte and their behaviour before, during, and after the winter resting season.** J. W. BEWS and J. E. VANDERPLANK (Ann. Bot., 1930, **44**, 689—719).—The succulent type studied was *Portulacaria afra* (Jacq) and the geophytic type, *Hypoxis rooperi* (Moore). The pentosan content of the leaves of the former is 49.9% and the hexosan content 45.5% higher on the north (sunny) side than on the south side. The carbohydrate content of *H. rooperi* is highest in the spring and least in dying leaves, except for the hexosan fraction, for which the reverse is true. The hexosans, the chief products of photosynthesis, increase largely during the day and decrease by night. In neither plant does the water content directly affect the carbohydrates. The large carbohydrate reserves are drawn on only to a small extent for the production of spring leaves.

P. G. MARSHALL.

**Influence of temperature on composition and quality of peas (*Pisum sativum*, L.).** V. R. BOSWELL (Proc. Amer. Soc. Hort. Sci., 1928, **25**, 21—26).—The sugar:starch ratio, the temperature during development, and the time of maturity were studied.

CHEMICAL ABSTRACTS.

**Enzymic change in ripening barley.** H. LÜERS, II. FINK, and W. RIEDEL (Woch. Brau., 1930, **47**, 393—397, 405—409).—With progressive ripening the catalase content of barley shows an increase which is followed by a decrease at the resting stage, and finally reaches a value which remains constant during storage. The content of catalase appears to be dependent on external influences such as climate. During ripening the diastatic power of the barley increases steadily, but decreases at the conclusion of that condition. At  $p_H$  4.6 there is an optimum for the diastatic action. Apart from slight changes with the barely ripe barley, the oxidation-reduction system shows no appreciable quantitative changes during the ripening process. Post-mortal respiration decreases markedly during ripening.

**Significance of glutamine in germination.** R. NUCCORINI (Annali Chim. Appl., 1930, **20**, 239—244).—Comparison of the proportions of glutamic and aspartic acids in the proteins of *Ricinus* seeds and wheat with those of the glutamine and asparagine extractable from the germinating seeds indicates that, unlike asparagine, glutamine may be regarded

as a direct product of the hydrolysis of the proteins during germination. T. H. POPE.

**Transport of nitrogenous substances in the cotton plant. V. Movement to the boll.** E. J. MASKELL and T. G. MASON (Ann. Bot., 1930, 44, 657—688; of this vol., 965).—Of six samples, three had the bolls removed and after 5 days the increase of the various nitrogen fractions was determined. In the upper regions of the leaves, wood, and bark the nitrogen response is always significant, and that of the crystalloid nitrogen is greater than that of the protein. The carbohydrate concentration is also increased, in the leaves chiefly on account of sucrose and in the bark entirely so. The  $p_H$  of the sap is increased in all tissues except the bark of the upper regions. Fertilisation of the bolls causes a marked increase in carbohydrate and water uptake and a much smaller increase in nitrogen uptake, such increase being greater in the ovules than in the carpels. After the fourth day the concentrations of all nitrogen fractions except amino-acid are higher in unfertilised than in fertilised ovules. The  $p_H$  of the sap of normal ovules continues to rise after the fourth day but falls in unfertilised ovules, whilst in the carpels no difference is detectable until after the sixth day. The nitrogen gradients into the boll during growth indicate that organic nitrogen enters from the sieve-tubes as residual rather than asparagine-nitrogen. P. G. MARSHALL.

**Physiological reaction of ammonium salts and nitrates.** A. MAKSIMOV (Rocz. Nauk Rol. Lés., 1929, 22, 33—88).—Plants altered the reaction of a solution of single salts only to a certain value which varied for different plants. With physiologically acid salts the final values were for grain crops  $p_H$  3.3, and for leguminous crops  $p_H$  4.1. The course of the change was irregular. Between 0.001 and 0.02N the concentration of the salt solution does not affect the final value. The physiological reaction of ammonium nitrate is not definite, but is determined by the reaction of the medium. CHEMICAL ABSTRACTS.

**Improvement of the metabolism of plants by physiological culture without change in the soil.** N. A. BARBIERI (Atti R. Accad. Lincei, 1930, [vi], 11, 712—717).—Improved results are obtained with *Cattleya*, maize, beans, potatoes, sugar beet, tobacco, and tomato plants supplied with a mixture of the soluble and insoluble salts actually existing in the plants and in doses corresponding with the requirements of the whole crop. T. H. POPE.

**Development of seedlings from seeds treated with solutions of nitrates.** B. N. AXENTSEV (Biochem. Z., 1930, 223, 387—393; cf. A., 1929, 1345).—Although the early development of seeds of *Amaranthus retroflexus*, L., is stimulated by treatment with solutions of sodium nitrate, later stages of the growth of seeds so treated may be either more or less vigorous than those of untreated seeds, and the effect of treatment with the nitrate may be modified according as growth takes place in the dark or in light. W. MCCARTNEY.

**Ripening and composition of the Texas magnolia fig.** H. P. TRAUB and G. S. FRAPS (Proc. Amer. Soc. Hort. Sci., 1928, 306—310).

CHEMICAL ABSTRACTS.

**Leaves of *Solanum pseudocapsicum*.** M. G. BREYER-BRANDWIJK (Bull. Sci. pharmacol., 1929, 36, 541—550; Chem. Zentr., 1930, i, 1163).—Alcohol extracts an alkaloid (0.25—0.53% of the dry substance) which is not volatile with steam. Solanine is not present. A. A. ELDRIDGE.

**Alcohol-soluble proteins of varieties of *Holcus sorghum*.** D. B. JONES and F. A. CSONKA (J. Biol. Chem., 1930, 88, 305—309).—The seeds of dwarf yellow milo and of feterita contain alcohol-soluble proteins which are closely similar in composition to each other and to that derived from kafir (Johns and Brewster, A., 1917, i, 108) except that tryptophan is absent from the protein of milo. C. R. HARRINGTON.

**Crystalline globulin of banana seeds.** G. L. KEENAN and J. D. WILDMAN (J. Biol. Chem., 1930, 88, 425—426).—Banana seeds contain a crystalline globulin similar in properties to those previously observed in squash and cantaloupe seeds (cf. Jones and Gersdorff, A., 1923, i, 883). C. R. HARRINGTON.

**Carotenoid from the seed-hulls of the spindle-tree (*Euonymus europæus*).** L. ZECHMEISTER and K. SZILÁRD (Z. physiol. Chem., 1930, 193, 67—71).—The arillus of the seeds on extraction with ether and treatment with alkali yields a carotenoid, red crystals, m. p. 201° (corr.),  $[\alpha]_D^{25}$  —63° ( $\pm 20\%$ ). The absorption spectrum is identical with that of zeaxanthin. The natural pigment appears to be an ester of which the substance described is the alcoholic component. J. H. BIRKINSHAW.

**African *Chaulmoogra* species.** E. PERROT and M. T. FRANÇOIS (Bull. Sci. pharmacol., 1929, 36, 551—554; Chem. Zentr., 1930, i, 1163).—*Caloncoba Welwitschii* seeds afford an oil (44%) having m. p. 38°,  $d_4^{20}$  0.942,  $n_D^{20}$  1.4750,  $[\alpha]_D^{20}$  +54.8°, acidity (oleic%) 7, saponification value 184; iodine value (Hanus) 84; the fatty acids had m. p. 56°, acid value 203, average mol. wt. 275, iodine value (Hanus) 90,  $[\alpha]_D^{20}$  +55.5°. Oil from *Oncoba echinata* and *Caloncoba glauca* (yield 19%) is similar. A. A. ELDRIDGE.

**Composition of wallflower-seed oil.** J. VAN LOON (Rec. trav. chim., 1930, 49, 745—753; cf. Matthes and Boltze, A., 1912, i, 601).—The oil, obtained in 20% yield by extraction of the ground seeds of the wallflower (*Cheiranthus cheiri*, L.) with light petroleum, has  $d_4^{15}$  0.9155,  $n_D^{20}$  1.4718, acid value 2.5, saponification value 176.4, ester value 173.9, iodine value (Wijs) 137.0, Reichert-Meissl value 0.5. The total fatty acids (94.5% of the oil) consist of saturated (mainly palmitic) (4.9%), erucic (40.6%), oleic (4.9%), linoleic (24.7%), and linolenic (19.4%). The oil contains glycerol (3.9%) and solid unsaponifiable matter (1.1%). H. BURTON.

**Composition of soya beans under the conditions prevailing in the middle Volga district.** V. KHARICHKOV and E. VAGANOVA (Masloboino Zhir. Delo, 1930, No. 2, 64—66).—Variations of the oil and protein contents with the soil and climatic conditions are recorded. Early or dense sowing increases the protein and decreases the oil content; humidity increases the oil content. CHEMICAL ABSTRACTS.

**Cephalins of soya bean.** B. SUZUKI and U. NISHIMOTO (Proc. Imp. Acad. Tokyo, 1930, 6, 262—265).—Details are given for the extraction of the cephalins from the oil-free alcoholic extract of soya bean. Hydrolysis of these with 3% sulphuric acid gives choline, stearic, linoleic, linolenic, and  $\beta$ -glycerophosphoric acids. Treatment of the cephalins with bromine in light petroleum affords (a) soluble and (b) insoluble fractions, hydrolysed to (a) stearic and tetrabromostearic acids, and (b) stearic and hexabromostearic acids. The original mixture contains, therefore,  $\alpha$ -stearyl- $\gamma$ -linoleo- and  $\alpha$ -stearyl- $\gamma$ -linolenol- $\beta$ -cephalins. H. BURTON.

**Occurrence of lysolecithin in polished rice.** M. IWATA (Proc. Imp. Acad. Tokyo, 1930, 6, 212—215).—Washed, polished rice contains 0.2% of lysolecithin which may be extracted by repeated digestion with 94% alcohol, evaporating to a syrup, and pouring into ether. The crude material is purified by precipitating the alcoholic solution with warm alcoholic cadmium chloride, removing the cadmium, and recrystallising from absolute alcohol and chloroform. Lysolecithin,  $[\alpha]_D^{25}$   $-4.52^\circ$ , softens at  $100^\circ$ , decomposes at  $262$ – $264^\circ$ , and on hydrolysis yields palmitic acid, choline, and glycerophosphoric acid, the first two being obtained in almost theoretical yield. P. W. CLUTTERBUCK.

**Phototoxic substance from *Hypericum crispum*.** Z. MÉLASJOANNIDÈS (Arch. Inst. Pasteur Hellén., 1928, 2, 161—165; Chem. Zentr., 1929, i, 1576).—In an attempt to isolate the phototoxic substance from *Hypericum crispum*, 0.16 g. of a red, amorphous substance, slightly soluble in water and giving a characteristic spectrum, was obtained from 100 g. of the dried plant. L. S. THEOBALD.

**Rice starch.** V. Comparative studies on rice, boiled rice, and mochi. W. S. TAO (Bull. Chem. Soc. Japan, 1930, 5, 209—214).—The chemical change undergone by rice during cooking (either simple boiling with water, or steaming and pounding into mochi-cake) is mainly hydrolysis to water-soluble reducing sugars and polysaccharides. Both boiled rice and mochi give large quantities of soluble sugars when treated with diastase or saliva; with the former enzyme both maltose and dextrose are obtained but with the latter only maltose. In both reactions dextrin is produced.

The chemical changes caused in rice starch by cooking resemble those in the germination of rice seeds except that the velocity of conversion of starch into soluble sugars is greater in the former, and the change of starch into carbon dioxide and water takes place only in the latter. R. J. W. LE FÈVRE.

**Biochemical relations between formaldehyde, sugars, and plant acids.** H. SCHMALFUSS (Z. angew. Chem., 1930, 43, 500—503).—A lecture.

A. R. POWELL.

**Variations in content of sugars and related substances in olives.** P. F. NICHOLS (J. Agric. Res., 1930, 41, 89—96).—The picric acid determination of reducing sugars and sucrose in the water extract of olives is unsatisfactory if basic lead acetate is used for clarification. After clarification with mercuric nitrate, the remaining reducing substances can be

removed by yeast. All of the 17 varieties of olive studied showed a maximum total sugar content about midway in their production season, and the ratio of simple to total sugars usually declined as the season progressed. E. HOLMES.

**Constitution of the principal sugar of *Rhodymenia palmata*.** H. COLIN and E. GUGUEN (Compt. rend., 1930, 191, 163—164).—The principal sugar of *Rhodymenia palmata* is an  $\alpha$ -monogalactoside of glycerol (secondary alcohol group) and is the typical sugar of many *Florideae*. C. C. N. VASS.

**Biochemical studies on the bamboo.** I. S. KOMATSU (Reprint Chikashige Anniversary Vol., Kyoto, 1930, 119—138).—An investigation of the carbohydrates and nitrogenous substances of the mature mandrake (*Phyllostachys quilioides*) and its shoots is recorded. The polysaccharide content of the nodes increases with age, whilst the water, ash, and total nitrogen decrease. The pentose content is constant throughout the life of the shoot, but the pentosan-hemicellulose decreases. Crystalline *l*-xylose (m. p.  $145$ – $150^\circ$ ,  $[\alpha]_D^{25}$   $+19.21^\circ$ ) and glycuronic acid isolated from the shoot-juice indicate the course of the hexose catabolism. The juice also contains oxalic, tartaric, citric, and lactic acids. The variation in moisture, carbon dioxide, oxygen, and gaseous nitrogen in the culm runs parallel with the total reducing sugar content of the aqueous extracts. F. O. HOWITT.

**Hydrolytic products of oroboside: dextrose and orobol.** M. BRIDEL and C. CHARAUX (Bull. Soc. Chim. biol., 1930, 12, 765—772).—See this vol., 456.

**Hexacosanol, a new  $C_{26}$  alcohol of the fatty series extracted from the bark of *Amelanchier vulgaris*, Moench.** J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 758—764).—The bark is dried, extracted with boiling 60% alcohol, and the residue digested with boiling 95% alcohol. The lipid and fatty matter thus obtained is saponified, the benzene-soluble substances are separated, and hexacosanol, m. p.  $77.5^\circ$  (corr.), is obtained in the pure state by crystallisation from ethyl acetate. The acetate, iodo-derivative, and the acid formed on oxidation are described. F. O. HOWITT.

**Piceoside in the bark of the black willow.** M. BRIDEL and J. RABATÉ (J. Pharm. Chim., 1930, [viii], 11, 561—572).—See this vol., 825.

**Constituents of corncockle seed. III. Githagoic acid and githagonolic acid. Degradation of githagenin.** E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1930, 190, 1—14; cf. A., 1929, 857).—Githagenin on oxidation with permanganate in acetone yielded the dibasic githagoic acid,  $C_{25}H_{44}O_8$ , m. p.  $359^\circ$ ,  $[\alpha]_D^{25}$   $+91.6^\circ$  (methyl ester,  $C_{30}H_{48}O_8$ , m. p.  $247^\circ$ ,  $[\alpha]_D^{25}$   $+77^\circ$ ). The presence of an alcoholic or a ketonic group could not be detected. Alkali fusion of githagenin gave githagonolic acid,  $C_{25}H_{38}O_4 \cdot H_2O$ , m. p.  $364^\circ$  [methyl ester, m. p.  $234$ – $235^\circ$ ; acetyl derivative, m. p.  $328^\circ$  (decomp.); methyl ester of acetyl derivative, m. p.  $171^\circ$ ]. Acetyl-githagonolic acid was produced as a by-product in the acetylation of githagenin. Oxidation of acetyl-githagenin with chromic acid in aqueous acetic acid at  $60$ – $70^\circ$  gave

acids I and II (methyl ester of I,  $C_{29}H_{42}O_6$ , m. p.  $279^\circ$ ; methyl ester of II, m. p.  $189^\circ$ ). Treatment of the methyl ester I with hydroxylamine hydrochloride yielded the oxime,  $C_{29}H_{43}O_6N$ , m. p.  $222^\circ$ . Oxidation of githagoic acid with chromic acid in boiling acetic acid gave an acid (dimethyl ester,  $C_{46}H_{38}O_6$ , m. p.  $265^\circ$ ).  
J. H. BIRKINSHAW.

Determination of the saponin content of indigenous *Gypsophila paniculata*, L. G. MATOLCSY (Ber. Ungar. pharm. Ges., 1929, 5, 33—42; Chem. Zentr., 1929, i, 1592).—A method for the determination of the foam number (1667 in this case) is described. The viscosity and surface tension increase with concentration, whilst the former decreases with temperature. Different parts of the root contained from 0.15 to 8.36% of saponin (mean 7.06%). Haemolytic indices are recorded.

L. S. THEOBALD.

Microscopical and chemical examination of the tissue of the bamboo stalk. S. OGIURI and M. NARA (J. Soc. Chem. Ind. Japan, 1930, 33, 236—238B).—Photomicrographs of longitudinal and transverse sections of bamboo stalk are shown and the proportions of the main constituents (cellulose, lignin, and pentosans) are determined.  
F. R. ENNOS.

Jute fibre. II. Hemicelluloses. J. K. CHOWDHURY and T. M. SAHA (J. Indian Chem. Soc., 1930, 7, 347—356).—Jute fibre is extracted with chloroform to remove resin and fat and delignified by treatment with a slow current of chlorine dioxide gas. The residue is extracted successively with benzene, 95% alcohol, boiling water, and 17.5% sodium hydroxide. The extracted material is isolated by evaporation of the solvent or by concentration and addition of alcohol. The hemicelluloses are precipitated repeatedly from their solutions by alcohol and subsequently hydrolysed by 2.5% sulphuric acid. Galactose, lavulose, arabinose, xylose, uronic acids, and pectins are identified among the products of hydrolysis. It appears improbable that the insoluble calcium salt method gives a quantitative measure of the pectin.

Pectins and hemicelluloses of jute may be removed almost completely by treatment in an autoclave with water at 2—3 atm. for 4 hrs. The residue is similar in properties to  $\alpha$ -cellulose.  
H. WREN.

Hemicelluloses. II. Hemicelluloses of maize cobs. I. A. PREECE (Biochem. J., 1930, 24, 973—979).—Hemicellulose of maize cobs has been separated into four fractions, hemicellulose A which yields on hydrolysis xylose and uronic acid, B1 and C1 yielding varying proportions of xylose, uronic acid, and methylpentose, and C2 which gives arabinose, uronic acid, and methylpentose. In all cases the proportion of pentose residues present far exceeded the combined proportions of residues of methylpentose and uronic acid. The separation was carried out by Norris and Preece's method (cf. this vol., 383). Hemicellulose C was fractionated by precipitation of C1 directly with Fehling's solution and C2 with acetone from the filtrate.  
S. S. ZILVA.

Preparation of skeletal substances from incrustated cell walls of plants by means of chlorine

dioxide. E. SCHMIDT, Y. C. TANG, and W. JANDEBEUR (Naturwiss., 1930, 18, 734).—Preparations of these skeleton substances have previously been made by a two-stage reaction with chlorine dioxide. It has been found that direct preparation may be effected at the ordinary temperature in presence of suitable inorganic or organic compounds which are stable towards chlorine dioxide. The new method gives a better insight into the constitution of the cell wall and results on red beech are recorded. The method is applicable to the determination of cellulose in lignin.  
W. R. ANGUS.

[Impurities in] wood and animal charcoals. D. I. MACHT (J. Pharm. Exp. Ther., 1930, 39, 343—346).—Saline extracts of animal charcoal and of blood charcoal, but not those of wood charcoal, had a detrimental effect on the growth of seedlings of *Lupinus albus*. This effect may be due to the presence in the animal charcoal of substances which could modify the effects produced by solutions of compounds having powerful physiological actions.

W. MCCARTNEY.

Kinetics of penetration. II. Penetration of carbon dioxide into *Valonia*. A. G. JACQUES and W. J. V. OSTERHOUT (J. Gen. Physiol., 1930, 13, 695—713; cf. this vol., 110).—The rate of penetration of carbon dioxide is believed to be of the first order, although the velocity coefficient decreases. The latter phenomenon was found not to be due to differences in the shape and size of the cells. It is suggested that individual differences in the permeability of the cells used is the cause. The velocity coefficients at  $p_n$  4.8 (carbon dioxide undissociated) and at  $p_n$  6.8 (carbon dioxide 75% dissociated) were nearly the same. The rate of penetration of carbon dioxide depends on the concentration of the undissociated carbon dioxide in the sea-water, rather than the concentration of ions. It is concluded that there is little penetration of ions.

G. F. MARRIAN.

Bioelectric potentials. I. Effects of potassium and sodium chlorides on *Nitella*. W. J. V. OSTERHOUT (J. Gen. Physiol., 1930, 13, 715—732).—Experiments on the concentration effects of potassium and sodium chloride solutions in *Nitella* were carried out by the technique previously described (cf. A., 1929, 1112). When it was assumed that diffusion potentials predominated, the calculated P.D. agreed closely with the observed values. On the basis of phase boundary potentials the calculated figures were not satisfactory. It is concluded that diffusion potentials predominate.  
G. F. MARRIAN.

Cell sap of *Halicystis*. L. R. BLINKS and A. G. JACQUES (J. Gen. Physiol., 1930, 13, 733—739).—Analyses of the sap obtained from growing cells of *Halicystis* gave the following results expressed in mols. per litre: Cl 0.6028, Na 0.5570, K 0.0064, Ca 0.0080, Mg 0.0167, and a trace of sulphate. The  $p_n$  of the fresh sap was 6.2.  
G. F. MARRIAN.

Mineral content of mushrooms. H. RAMAGE (Nature, 1930, 126, 279).—All parts of a button mushroom have a high potassium and low calcium content; the skin contains lithium and most of the

iron present. Phosphorus varies from 1 to 3% in the dried material, the gills containing most. Silver and copper are present in all parts, the stem containing least. The skin, the white, and the gills (dried material) contain more than 0.02% of copper and more than 0.01% of silver (gills  $\leq 0.05\%$ ). L. S. THEOBALD.

**Separation from *Laminaria* of a complex compound containing labile iodine.** P. DANGEARD (Compt. rend., 1930, 191, 337—339).—If a stalk of *Laminaria flexicaulis* is immersed in sea-water, small amounts of iodine are liberated in the first few hours. At the end of two or three days iodides appear from which iodine is liberated by acids. In fresh water iodides are also set free in the initial period. The labile iodine is supposed to be in the form of a complex compound, decomposed by acids, of an iodide and a thermo-stable oxidising agent. R. K. CALLOW.

**Boron content of oranges.** C. S. SCOFIELD and L. V. WILCOX (Science, 1930, 71, 542).—A relationship between the boron content of irrigation water and that of the leaves and fruit is established.

L. S. THEOBALD.

**Potassium and sodium contents of plants growing in salt lagoons or on the sea shore.** G. BERTRAND and M. ROSENBLATT (Bull. Soc. chim., 1930, [iv], 47, 639—642).—See this vol., 823.

**Biology of metals. III. Localisation of lead within the cell of the growing root. IV. Influence of lead on mitosis and cell size in the growing root. F. S. HAMMETT. V. Selective fixation of lead by root nuclei in mitosis. F. S. HAMMETT and E. S. JUSTICE. VI. Nature of the lead compound deposited in the growing root. F. S. HAMMETT (Protoplasma, 1928, 5, 135—141; 1929, 535—542, 543—546, 547—562).—In plants grown for 24 hrs. in lead nitrate solution (1 in  $10^4$ ) the lead was combined in especially high concentration with the nuclei and walls of the cells. The deposit is a compound of lead with an organic thiol compound, possibly glutathione.**

CHEMICAL ABSTRACTS.

**I. Precipitation of silicic acid in plants. II. Comparison of the precipitation of silicic acid and of calcium salts in plants. A. FREY-WYSSLING (Ber. deut. bot. Ges., 1930, 48, 179—183, 184—191).—I. The phenomenon of silica precipitation in plants is represented as the elimination of non-assimilable matter and is characteristic of tropical and sub-tropical flora. The higher temperature at which rock disintegration occurs leads to a higher silica content in the soil solution than occurs in temperate and polar zones. Silica is precipitated mainly in the peripheral tissues of transpiratory organs and is localised along the conducting vessels.**

**II. The deposition of silica in plant-tissue occurs in a similar manner and in corresponding tissues to that of calcium salts. In warmer regions plants take up amounts of calcium and silica in excess of their physiological requirements. Calcium hydrogen carbonate enters the plant from the soil solution and its subsequent deposition as calcium carbonate represents merely the elimination of unutilisable surplus. Oxalic**

**acid, however, is a product of plant metabolism and its precipitation as calcium oxalate is an excretory function.** A. G. POLLARD.

**Toxicity of some aliphatic alcohols [to plants]. W. S. EISENMENGER (Plant Physiol., 1930, 5, 131—156).—Ethyl alcohol (up to 0.0012*M*) stimulated, but other aliphatic alcohols retarded, the growth of soyabean seedlings. Low concentrations of calcium nitrate also had a stimulating effect, but increased the toxicity of some of the alcohols. The toxicity does not increase regularly with increase in the number of carbon atoms in the molecule, and *n*-alcohols are not more toxic than *iso*-alcohols.**

CHEMICAL ABSTRACTS.

**Simple instrument for micro-manipulations. A. N. RICHARDS (J. Biol. Chem., 1930, 87, 463—466).—Technical.** C. R. HARRINGTON.

**Micro-determination of mercury in organic material. K. O. MÖLLER (Biochem. Z., 1930, 223, 379—386).—Unless precautions are taken, mercury is lost by volatilisation during the destruction of organic matter when determinations of the metal are carried out by the usual methods. A satisfactory method is described.** W. MCCARTNEY.

**Determination of manganese in animal material. J. T. SKINNER and W. H. PETERSON (J. Biol. Chem., 1930, 88, 347—351).—The material is incinerated, the ash is extracted with dilute phosphoric acid, the filtered extract is treated with potassium periodate, and the permanganate formed is determined colorimetrically; 0.01 mg. of manganese may be determined with an error of about  $\pm 10\%$ , the use of phosphoric acid avoiding the difficulties otherwise encountered owing to precipitation of calcium sulphate.** C. R. HARRINGTON.

**Determination of sulphur and phosphorus in plants. G. BERTRAND and L. SILBERSTEIN (Bull. Soc. chim., 1930, [iv], 47, 95—99).—See this vol., 120.**

**Improved design of Van Slyke apparatus for the determination of amino-nitrogen. S. J. FOLLEY (Biochem. J., 1930, 24, 961—964).—Rubber connexions are obviated in the deaminising chamber and in the Hempel pipette of this design.**

S. S. ZILVA.

**Should lipins be calculated as fat? H. FINCKE (Chem.-Ztg., 1930, 54, 598).—Polemical against Rewald (cf. *ibid.*, 134); the author supports his opinion that lipins should not be included in determinations of "fat content" of materials.**

E. LEWKOWITSCHE.

**Analysis. X. Determination of fats. L. PRINCUSSEN and S. KOLODNY (Biochem. Z., 1930, 223, 347—351).—The acids obtained from fats by hydrolysis under pressure with water, zinc, and zinc oxide are converted into lead salts. The salts of unsaturated acids are dissolved in ether and of the ether-insoluble salts some are dissolved by chloroform. After the organic matter in the three fractions has been destroyed by treatment with nitric acid and hydrogen peroxide, the lead is determined colorimetrically as sulphide.** W. MCCARTNEY.



# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

NOVEMBER, 1930.

### General, Physical, and Inorganic Chemistry.

**Extension of Balmer series in laboratory.** T. TAKAMINE and T. SUGA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 14, 117—122).—By passing a condensed discharge through a neon tube containing a trace of hydrogen which had been liberated from the various parts of the tube during discharge, the Balmer series could be followed up to  $H_{25}$  with an exposure of a few hours. The pressure of the neon was 1 mm. or less. Addition of hydrogen to a tube containing pure neon was not effective owing to the appearance of the continuous and the secondary spectra of hydrogen. An explanation is suggested of the fact that in a neon tube the Balmer series of hydrogen is much better developed than in an argon tube.

W. GOOD.

**Fine structures in the band spectra of hydrogen and helium examined under high resolution.** S. IMANISHI (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 14, 105—115).—Using suitably cooled sources and an interference spectrograph of high resolving power, hydrogen and helium bands were examined for fine structures due to multiplicity of various electronic levels in the molecules. The accuracy of existing data for helium is much exceeded, but still no separation of the  $2p^3\Sigma$  level was observed. Fulcher bands as well as some newly-reported bands of hydrogen were also examined.

W. GOOD.

**Energy distribution in the continuous spectrum of hydrogen.** Y. HUKUMOTO (Sci. Rep. Tôhoku, 1930, 19, 301—305).—The energy distribution in the continuous spectrum of hydrogen in the range 4800—2900 Å. was investigated and compared with the known energy distribution in the spectrum from a tungsten-filament lamp. The experimental results agree qualitatively with those derived theoretically by Winans and Stueckelberg (A., 1929, 118).

A. J. MEE.

**Structure and spectra of the molecules of hydrogen and helium.** W. WEIZEL (Z. Elektrochem., 1930, 36, 599—603).—A description is given of the manner whereby the band spectra of the hydrogen and helium molecules may be developed by consideration of the arrangement of the electrons and protons, and the physical significance and method of determining the quantum numbers of the individual electrons are indicated. The origins of the ortho- and para-hydrogen spectra by symmetrical and asymmetric rotations are described.

H. F. GILLBE.

**Polarisation of two hydrogen atoms in the ground state.** G. PODOLANSKI (Physikal. Z., 1930,

31, 803).—The polarisation of two hydrogen atoms in the ground state is derived from the principles of wave mechanics and the results are compared with those found by Eisenschitz and London (this vol., 525).

W. R. ANGUS.

**Corona discharge in hydrogen.** J. H. BRUCE (Phil. Mag., 1930, [vii], 10, 476—480; cf. Huxley, A., 1928, 567).—A study of the corona discharge between coaxial cylinders in carefully purified hydrogen shows that, as in other gases, the relation  $\alpha X = f(\alpha p)$  (where  $\alpha$  is the radius of the smaller cylinder,  $X$  the electric force at its surface, and  $p$  the gas pressure) is valid except at low pressures. The current between the cylinders is proportional to the applied potential when the smaller cylinder is positive. The velocity of the positive ions in the direction of the electric force increases rapidly with the ratio  $X/p$ , as with the monatomic gases.

F. L. USHER.

**Fine structure of He as a test of the spin interactions of two electrons.** G. BREIT (Physical Rev., 1930, [ii], 36, 383—397).—Mathematical. The quantum Hamiltonian of two electrons (cf. A., 1929, 1125) is discussed, and is applied to the calculation of the fine structure of the He  $2^3P$  level. Results are in agreement with experimental data. The calculation is applied to  $Li^+$ .

N. M. BLIGH.

**Optical excitation function of helium.** W. C. MICHELS (Physical Rev., 1930, [ii], 36, 604; cf. Hanle, A., 1929, 1116; Elenbaas, this vol., 387).—The optical excitation function of helium was investigated, using a variation of the photographic method permitting intensity measurements and elimination of secondary electron emission and ionisation effects. Intensity and pressure or current are linearly related. For the triplets, double maxima were found at 28 volts, and on correction are found to be at the excitation potentials.

N. M. BLIGH.

**Helium spectrum in the presence of an electric field.** Y. ISHIDA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 14, 49—61).—Theoretical considerations are advanced to explain the appearance of more lines than expected at higher fields in investigations of the Stark effect in helium and also the non-crossing and peculiar intensity relations of two helium spectral lines in the Lo Surdo field.

W. GOOD.

**Relative intensities of Stark components in helium.** G. O. LANGSTROTH (Proc. Roy. Soc., 1930, A, 129, 70—91).—By employing higher fields than have been used previously, and comparatively high

dispersion, a quantitative study has been made of the intensity relations in the fine analysis of the Stark effect in helium. The theoretical intensities are more "stable" in high fields. A special type of Lo Surdo tube is described; the Stark components which are produced branch out from the main line until they reach maximum field and then run parallel for an appreciable distance. In this region the intensities may be measured with some precision. The measurements are carried out by means of a modification of the photographic-photometric method described by Dorgelo (*Z. Physik*, 1925, 26, 756). The lines investigated include the parhelium groups  $2P-4Q$  and  $2P-5Q$  and the orthohelium groups  $2p-4q$  and  $2p-5q$ . The experimental results are mostly in good agreement with theory; definite discrepancies are found, however, which are of two general types: those which appear to the same degree in all the components of a line, and those which appear only in certain components. The discrepancies of the first class are explained on the assumption that the selection rule for impact transitions breaks down in the presence of an electric field to no greater extent than is indicated by the Stark effect in emission.

L. L. BIRCUMSHAW.

**Spark potential in helium.** F. LEVI (*Ann. Physik*, 1930, [v], 6, 409—433).—The experiments of Zuber (*ibid.*, 1925, [iv], 76, 231; 1926, 81, 205) on the transition time of the spark discharge in an inert gas have been repeated, using carefully-purified helium and brass or nickel electrodes; the values obtained with the brass electrodes are always higher than with nickel, indicating that the state and composition of the electrodes play an important rôle in the determination of the spark potential of helium. Very slight traces of foreign gases also influence the values greatly. The theories advanced by Penning (*A.*, 1928, 214) and Taylor (*Proc. Roy. Soc.*, 1928, A, 117, 508) to explain the increased values obtained for the spark potential when the helium is more thoroughly purified are discussed; preference is given to Penning's explanation. The results agree, within the limits of permissible error, with those of Townsend and MacCallum (*A.*, 1929, 969). The same degree of consistency in results cannot be obtained as in an examination of noble gases.

W. R. ANGUS.

**Spectrum of exploding lithium wires.** L. ECKSTEIN and (Miss) I. M. FREEMAN (*Z. Physik*, 1930, 64, 547—555).—The lines  $1s-md$ , forbidden in absorption, appear when lithium is exploded. The Anderson method of electrical explosion was applied to lithium. The spectrum obtained is comparatively simple.  $2p-md$ ,  $1s-mp$ ,  $1s-md$  lines were observed. Preliminary experiments with sodium and potassium also show  $1s-md$  lines, which are forbidden in absorption.

A. B. D. CASSIE.

**Effect of motion of the nucleus on the spectra of Li I and Li II.** D. S. HUGHES and C. ECKART (*Physical Rev.*, 1930, [ii], 36, 694—698).—Mathematical. The wave equation for a system of electrons and one nucleus is solved approximately. Results are compared with Schüller's experimental data (cf. this vol., 124) on Li II,  $\lambda$  5485 and Li I,  $\lambda$  6708, and show satisfactory agreement.

N. M. BLIGH.

**Band spectrum of nitrogen excited by a high-frequency discharge.** B. C. MUKHERJI (*Z. Physik*, 1930, 64, 698—707).—The nitrogen band spectrum, 6700—2813 Å., was excited by a low-voltage high-frequency discharge, using external electrodes. Photographs showed the second positive group intense, the more prominent bands of the first negative group, and the whole of the first positive. The second positive group was sometimes accompanied by a second system of unknown bands lying on the red side of the normal bands at a frequency interval of about  $20\text{ cm}^{-1}$ . The new band system cannot be attributed to impurities, and it is considered that the 9.35-volt  $^3\Pi$  level of the nitrogen molecule has a neighbouring  $^1\Pi$  level and the new system may be due to transitions to this level from the 13-volt  $^3\Pi$  level or a  $^1\Pi$  level close to it. The new band system may also be a satellite system or a further intense  $Q$  branch. An afterglow was observed during the course of the experiments; the high-frequency discharge gave it just as readily in air as in nitrogen. It is considered that metastable nitrogen atoms rather than metastable molecules are responsible for the observed effect.

J. E. MILLS.

**Singlet system of the oxygen arc spectrum and the origin of the green auroral line.** R. FRERICHS (*Physical Rev.*, 1930, [ii], 36, 398—409; cf. this vol., 2).—The oxygen arc spectrum was investigated under varied controlled conditions in the extreme ultraviolet. Results and classifications for a number of lines in the singlet system are tabulated. Values of the low terms  $^1D_2$  and  $^1S_0$  have been fixed. The green auroral line  $\lambda$  5577.35 is probably the forbidden combination between these low metastable terms.

N. M. BLIGH.

**Presence of neutral oxygen in the gaseous nebulae.** I. S. BOWEN (*Physical Rev.*, 1930, [ii], 36, 600).—The reason for the occurrence of the  $^3P-^1D$  lines alone of neutral oxygen in nebulae, and the  $^1D-^1S$  line alone under auroral conditions, is discussed. In the former case the mean time between impacts is large; the  $^1D-^1S$  should therefore be weaker than the  $^3P-^1D$  transition; in the latter case the  $^1D-^1S$  transition has a probability such that it can take place before a collision of the second kind removes the atom from the  $^1S$  state.

N. M. BLIGH.

**Electronic states in the visible halogen bands.** R. S. MULLIKEN (*Physical Rev.*, 1930, [ii], 36, 699—705).—Theoretical. The type of transition corresponding with the visible iodine absorption bands and the analogous bands of the other halogens is discussed. On the interpretation deduced the upper level of the halogen bands is paramagnetic, in agreement with observed phenomena. Electron configurations for the normal and excited states of fluorine are suggested.

N. M. BLIGH.

**Spark spectrum of neon (Ne II).** S. FRISCH (*Z. Physik*, 1930, 64, 499—501).—The spark spectrum of neon in a discharge tube with a hollow cathode was measured from 2200 to 1500 Å. by means of a concave grating of dispersion 16.5 Å. per mm. The lines are fitted to energy levels agreeing with those of other authors.

A. B. D. CASSIE.

**Actinic power and spectrum temperature of the light of magnesium ribbon and flash powder.** H. ARENS and J. EGGERT (Z. wiss. Phot., 1930, **28**, 169—177).—A reply to Eder's criticisms (this vol., 388). The discrepancy between the value for the actinic power of the flame of burning magnesium ribbon previously recorded (Z. wiss. Phot., 1927, **24**, 368) and that obtained by Eder is to be attributed to differences in the experimental conditions, *e.g.*, in the plates used. The value previously obtained for the spectrum temperature of the flame of flash powder is, however, in error, the correct value being 3350° Abs.

R. CUTHILL.

**Vibrational quantum analysis of the potassium infra-red absorption bands.** W. O. CRANE and A. CHRISTY (Physical Rev., 1930, [ii], **36**, 421—429).—By re-measurement of the red system of the potassium molecule 26 new bands were found; bands of the infra-red system for the region  $\lambda$  7735—8850 were measured and a new vibrational analysis is given. Results are tabulated, and vibrational constants given. The upper state of each system dissociates into a normal and a  $^2P$  excited atom. The average value of the dissociation energies for the upper level of the two systems is 2.41 volts, giving 0.81 volt for the heat of dissociation of the lower level.

N. M. BLIGH.

**Shifts in spectral lines of ionised titanium by disruptive discharge.** H. NAGAOKA, T. FUTAGAMI, and I. MACHIDA (Proc. Imp. Acad. Tokyo, 1930, **6**, 252—255).—Lines in the range 5000—2500 Å. were observed. Some disagreement with existing observations is found, especially in the reversal of some of the lines. The values of the displacements are given.

W. GOOD.

**Partial analysis of the Cr II spectrum.** M. A. CATALÁN (Anal. Fis. Quím., 1930, **28**, 611—631).—240 Lines in the Cr II spectrum have been classified in 33 multiplets formed by the combination of 67 levels derived from 9 low and 6 medium terms, and 7 levels not yet grouped. All 15 terms are in agreement with Hund's theory and conform to the  $d^3$ ,  $d^4s$ , and  $d^4p$  configurations, although some of the lower terms are missing. The Zeeman factor  $g$ , calculated from Babcock's measurements, is in all cases greater than that calculated from Lande's formula; the discrepancy is greatest for the  $a^6D$  and  $a^4D$  terms, and is almost negligible for the  $a^4F$  and  $b^4F$ , *i.e.*, for the lower terms. Thus  $\Sigma g$  cannot be constant in this spectrum. The anomaly is not due to experimental error.

H. F. GILLBE.

**Character of shifts in different series of iron lines by disruptive discharge.** H. NAGAOKA, T. FUTAGAMI, and I. MACHIDA (Proc. Imp. Acad. Tokyo, 1930, **6**, 224—227; cf. this vol., 970).—The changes in intensity and in wave-length of iron lines produced by disruptive discharge have been investigated over the wave-length range 5500—2500 Å. Series showing the same type of shifts have been identified and are classified into six groups, the characteristics of which are detailed.

J. W. SMITH.

**Shifts in spectral lines of nickel by disruptive discharge.** H. NAGAOKA, T. FUTAGAMI, and I. MACHIDA (Proc. Imp. Acad. Tokyo, 1930, **6**, 248—

251).—The spectrum of nickel, ranging from 5000 to 2400 Å., was examined in the same manner as previously described for iron. The various types of shifts are described and the data tabulated. (See preceding abstract.)

W. GOOD.

**Intensity measurements in the spectrum of nickel and cobalt.** L. S. ORNSTEIN and T. BOUMA (Physical Rev., 1930, [ii], **36**, 679—693).—Quantitative intensity measurements were made in the Ni I and II and Co I spectra; results for a large number of lines are tabulated. The analyses used were: Ni I (cf. Bechert, A., 1925, ii, 913; Russell, A., 1929, 1351); Ni II (cf. Shenstone, A., 1927, 998); Co I (cf. Catalán, A., 1925, ii, 611). Large divergences are found on application of the summation rules for multiplets and supermultiplets, and of the intensity ratio for singlets and triplets, doublets and quadruplets.

N. M. BLIGH.

**Wave-lengths in the vacuum copper arc.** A. G. SHENSTONE (Physical Rev., 1930, [ii], **36**, 602—603).—Spark spectra lines are satisfactory standards for the measurement of Cu II low level spark lines, but introduce an error of about 2.7 wave-numbers into the results for high-level lines.

N. M. BLIGH.

**Intensity measurements in copper arcs.** L. S. ORNSTEIN and D. VERMEULEN (Z. Physik, 1930, **64**, 657—659).—The ratio of the intensities of the  $1^2S$ — $2^2P_1$  and  $1^2S$ — $2^2P_2$  lines was determined for different currents, and was found to vary with the current, having a maximum at 0.9 amp. This shows that reversal affects the intensity of these lines, and accordingly, Nottingham's calculations (J. Franklin Inst., 1929, **207**, 209) are probably incorrect.

A. B. D. CASSIE.

**Arc spectrum of palladium.** A. G. SHENSTONE (Physical Rev., 1930, [ii], **36**, 669—678).—A practically complete analysis of the spectrum Pd I is based on previous analyses (cf. McLennan, A., 1926, 875; Bechert, *ibid.*, 214). A number of new terms has been found, some being identified as second series members of the  $d$ -electron series. The spectrum in the ultra-violet has been measured and new lines have been found by long exposures. The electron structures are  $d^{10}$ ,  $d^95s$ ,  $6s$ ,  $7s$ ,  $8s$  (part of),  $d^8s^2$  (incomplete),  $d^95p$ ,  $d^8sp$ ,  $d^96p$  (parts of),  $d^95d$ ,  $d^96d$ . The presence of an unidentified level  $k_1$  is discussed; its only explanation on the Hund theory as a hyperfine structure component of  $5d^3P_1$  is unsatisfactory.

N. M. BLIGH.

**Hyperfine structure of some lines in the arc and first spectrum of indium.** J. C. McLENNAN and (Miss) E. J. ALLIN (Proc. Roy. Soc., 1930, **A**, **129**, 208—211).—The spectra were excited in stages by altering the pressure of the vapour in the discharge tube. The structure of the nine strongest lines of the  $3D^1D$ — $3F^0F^0$  multiplet and of the arc lines  $\lambda$  4511 and 4102 Å. was studied. The fact that all the lines have either two or three components suggests that the indium nucleus possesses a moment of momentum of  $\frac{1}{2}h/2\pi$ .

L. L. BIRCUMSHAW.

**First spark spectrum of xenon.** P. K. KICHLO (Z. Physik, 1930, **64**, 697).—Attention is directed to an anomalous series of terms the members of which

fit a Ritz formula when the frequency of each is increased by approximately  $10,500 \text{ cm}^{-1}$ .

A. B. D. CASSIE.

**Intensity and natural width of the blue caesium doublets.** I. W. SCHÜTZ (Z. Physik, 1930, 64, 682—696).—The total absorption of radiation by a given spectral line depends on the natural width of the line and on the Doppler effect. This leads to three distinct regions of absorption, as the number of absorbing atoms is increased; in the intermediate region the absorption is independent of the number of absorbing atoms. This may explain the inconsistent results of observations on the ratio of the intensities of the two component lines. The number of absorbing electrons was determined from the magneto-rotation of the vapour at two different temperatures. The natural width of the lines is calculable when the total absorption and the number of absorbing electrons are known, but, because of hyperfine structure, the results are not conclusive.

A. B. D. CASSIE.

**Optical dissociation of caesium iodide.** G. H. VISSER (Z. Physik, 1930, 63, 402—403).—By irradiating caesium iodide vapour with light from the spark spectrum of iron (which contains strong lines in the region  $2600 \text{ Å}$ .) emission of the line  $8521 \text{ Å}$ . of caesium was detected. This supports Sommermeyer's interpretation of the absorption spectrum of caesium iodide vapour in which dissociation to give caesium in the  $2P$  state is postulated, with which would correspond emission of the caesium doublet  $8943, 8521 \text{ Å}$ .

H. A. JAHN.

**Measurement of the life period of the visible mercury triplet,  $2^3S_1-2^3P_{0,1,2}$ .** E. F. RICHTER (Physikal. Z., 1930, 31, 824).—The life period of the excited mercury states can be determined by observation of the polarisation and the influence of a magnetic field on the lines. The life period of the visible mercury triplet  $2^3S_1-2^3P_{0,1,2}$  has been determined by using a magnetic field, the lines of force of which are perpendicular to the electric vector of the light from a fluorescent tube containing 1—2 mm. of nitrogen. The functional relation between the life period and the presence of nitrogen furnishes interesting data on the mechanism of excitation. Values for  $\lambda 4047$  with a pressure of nitrogen above 1.5 mm. are in good agreement with those obtained from the decay of illumination with canal rays.

W. R. ANGUS.

**Absorption spectra of dissolved mercury.** H. REICHARDT and K. F. BONHOEFFER (Z. Elektrochem., 1930, 36, 753).—The solubility of mercury in water at temperatures below  $130^\circ$  is too small for the absorption spectrum of the metal to be detected, but at about  $140^\circ$  two absorption bands of about 20—30 Å. width, due to the mercury atom, occur at 2600 and 2520 Å. They are not derived by broadening and displacement of the normal lines at 2650 and 2537 Å., since in the solvents methyl alcohol and hexane, both of which contain dipoles, the bands occur at 2575 and 2530 Å. and 2575 and 2545 Å., respectively; they may result from division of the line at 2537 Å. by the action of the electric fields surrounding the solvent molecules.

Mercury is appreciably soluble in hexane, from which it may be removed by shaking with gold foil; the solubility, determined gravimetrically by this method, is 0.65 mg. per 100 c.c., corresponding with a partial pressure of about 0.5 mm.

H. F. GILLBE.

**Intensity modifications in the spectrum of mercury.** S. TOLANSKY (Proc. Phys. Soc., 1930, 42, 536—562).—The singlet series is strengthened in the high-frequency spectrum of mercury in the region 7000—2400 Å. The first members of the triplet series are weakened by self-absorption. Intercombination lines show both types of behaviour. The degree of modification can be made to vary by alteration of the current density in the discharge tube. Mercury films are produced by the discharge driving mercury into the walls of the tube. The line  $6^1P_1-8^1S_0$ , i.e., 4916 Å., was examined for fine structure with a resolving power greater than  $3 \times 10^6$ . It is single and narrow, the half width being less than 0.004 Å.

W. E. DOWNEY.

**Fine structure in the singlet series of mercury.** S. TOLANSKY (Nature, 1930, 126, 434).—Many strengthened lines involving singlet levels show a complex structure.

L. S. THEOBALD.

**Intensity measurements in the band spectrum of mercury hydride.** II. J. G. EYMERS (Z. Physik, 1930, 63, 396—401; cf. Kapuściński and Eymers, A., 1929, 740).—The intensity distribution in three further bands (at 3647, 4050, and 4150 Å.) of mercury hydride are given. From the results of the previous paper the ratio of the total intensities of the bands of a group (4017, 4219, 4394, 4520 Å.) having a common initial level ( $n=0$ ) are determined, and for a second group (3500, 3647, 3785 Å.) with the same initial vibration state (i.e.,  $n=0$ ) but a different electronic state the same ratio was found; for a group (3900, 4050, 4150 Å.) with a different initial vibration state ( $n=1$ ) the ratio was, however, quite different. Values for the broadening of the last lines of the 4394 and 4219 Å. bands are given; the broadening is different for the two bands, but is the same for the separate branches of the individual bands.

H. A. JAHN.

**Fine structure of some lines in the visible region of the spectrum of thallium.** III. J. C. McLENNAN and (Miss) E. J. ALLIN (Proc. Roy. Soc., 1930, A, 129, 43—47).—A quartz tube with aluminium electrodes was used and the metal to be studied was vaporised in the tube by external heating. The light was analysed by a glass transmission echelon grating. A table of measured wave-lengths and their classifications is given. Goudsmit and Bacher's formula  $a \sim Z_1^2/n^2$ , (this vol., 265) is applied to calculating the magnitude of the separation of a number of terms; the theoretical and experimental values are found to be in good agreement.

L. L. BIRUMSHAW.

**Zeeman effects for fine structure components of thallium spectral lines.** J. C. McLENNAN and A. M. I. A. W. DURNFORD (Proc. Roy. Soc., 1930, A, 129, 48—70).—By means of an improved form of the apparatus previously described (A., 1928, 1295), an examination has been made of the magnetically

resolved components from 18 wave-lengths of the various thallium spectra. Special consideration is given to the five strong lines in Tl II, 5949, 5152, 5079, 4981, and 4737 Å. Except in the case of 5152 Å., the Zeeman patterns observed differed widely from the predicted effects. The wave-length 5949 Å. was studied extensively, Zeeman patterns being obtained for five different magnetic field strengths. With a very weak field the Zeeman components converge to three separate and sharp wave-lengths, and it is concluded that fine structure in the thallium spark lines is the factor causing the observed patterns to deviate from the predicted types.

L. L. BIRCUMSHAW.

#### Spectra of doubly and trebly ionised thallium.

A. L. NARAYAN, P. PATTABHI, and A. S. RAO (*Nature*, 1930, 126, 434).—The inverted  $^2D$  term ( $5d^96s^2$ ) with an interval of 18,618 cm.<sup>-1</sup> and the quadruplet terms of ( $5d^96s6p$ ) and ( $5d^96s6d$ ) configurations have been identified. A few combinations due to transitions  $6p \rightarrow 7s$  have also been established. In the spectrum of Tl IV the supermultiplet due to the combination of  $6p^3PFD$  with  $7s^3D$  and  $^1D$  has been identified.

L. S. THEOBALD.

**Moving striations in the positive column in rare gases.** R. WHIDDINGTON (*Nature*, 1930, 126, 470—471).—The moving striations travelling from anode to cathode are supposed to be due to a regular sequence of dark spaces travelling at constant speed in a uniform positive column away from the anode. Attempts to follow the flashes up to the cathode in argon are described. L. S. THEOBALD.

#### Spectroscopy of auroral green line radiation.

J. C. McLENNAN and H. J. C. IRETON (*Proc. Roy. Soc.*, 1930, A, 129, 31—43).—Details are given of a spectrograph used for photographing the spectrum of the light from the night sky. It is found that the intensity of the non-polar radiation corresponding with the auroral green line coming to earth from a moonless cloudless sky is roughly the same for observations made at ground level in the south of England and in Ontario and Saskatchewan, or at 2300 m. above sea level on Sulphur Mountain at Banff, Alberta. The view is confirmed that the non-polar auroral green line radiation from the moonless night sky acquires a maximum intensity shortly after midnight. Details are given of experiments designed to obtain the yellowish-green line 5577-341 Å. by gradually reducing the voltage of an argon discharge tube containing a trace of oxygen. With the exception of the argon line 6965 Å. an exact replica of the spectrum of the light of the non-polar aurora can be obtained, and it is concluded that the green line originates in the transition of oxygen atoms from the metastable  $^1S_0$  energy state to the metastable  $^1D_2$  state, but that molecules of nitrogen in an excited metastable energy state of approximately 10.5—11.8 volts also play a part. L. L. BIRCUMSHAW.

**Effective temperatures in a discharge tube determined from intensity measurements of band spectra.** W. LOCHTE-HOLTGREVEN (*Z. Physik*, 1930, 64, 443—451).—Discharges in acetylene and in methane gave the 3852 Å. band of carbon and the 3900 Å. band of CH. The rotation structure showed

a Boltzmann distribution of intensity corresponding with temperatures of 4700° Abs. for the carbon molecule, and of 2000° Abs. or 1400° Abs. for CH, according as the discharge is in acetylene or methane. This difference in effective rotation temperature occurs whether or not emission of the two bands is from the same volume of gas.

A. B. D. CASSIE.

**Resonance and damping in the theory of atomic nuclei.** R. D'E. ATKINSON (*Z. Physik*, 1930, 64, 507—519).—Gamow's conception of  $\alpha$ -particle emission corresponds exactly with optical resonance, so that the natural damping (disintegration constant) is calculable from the equivalent of the width of a spectral line. The effect of this resonance on the probable entry of an  $\alpha$ -particle into a nucleus is discussed.

A. B. D. CASSIE.

#### Notation for spectra of diatomic molecules.

R. S. MULLIKEN (*Physical Rev.*, 1930, [ii], 36, 611—629).—A report.

N. M. BLIGH.

**Band spectra intensities for symmetrical diatomic molecules.** E. HUTCHISSON (*Physical Rev.*, 1930, [ii], 36, 410—420; cf. Condon, A., 1929, 235).—Mainly mathematical. The intensity of a spectral line is calculated quantum-mechanically by evaluating the integral of the product of the electric moment and the wave functions of the initial and final states. By approximate integration for vibration electronic transitions in symmetrical diatomic molecules a formula is deduced for the intensity of any band in the electronic vibration spectra of these molecules. Comparison is made with experimental intensities of certain spectral bands of sodium, potassium, iodine, and hydrogen.

N. M. BLIGH.

**Quanta exchanges in collisions of the second order.** H. BEUTLER and W. EISENSCHIMMEL (*Z. Elektrochem.*, 1930, 36, 746—747).—By study of the intensity variations of the mercury spectral lines the action of excited krypton atoms in the  $2^3P_2$  state at pressures from 0.004 to 0.58 mm. on normal ( $1^1S_0$ ) mercury atoms has been investigated. The intensity of the mercury emission at low krypton pressures exhibits a sharp maximum at the resonance position, indicating that under certain conditions of resonance the  $5^3D_n$  and  $5^1D_2$  mercury terms are capable of absorbing energy from the krypton atoms; the resulting excited mercury atoms in turn reactivate the krypton atoms if the concentration of the latter be sufficiently high, and the process of energy exchange thus becomes continuous. Despite the almost identical resonance positions of the single and triple terms, the probability of excitation of the latter is 15—30 times as great as that of the former.

H. F. GILLBE.

**Variation with temperature of molecular polarisation and its relationship to free rotation.** L. MEYER (*Z. Elektrochem.*, 1930, 36, 743—746).—A survey; see A., 1929, 980; this vol., 980.

H. F. GILLBE.

**Chemical combination and the line emission of solid bodies.** R. TOMASCHEK (*Z. Elektrochem.*, 1930, 36, 737—743).—A survey of work on the spectrum of samarium in phosphors. See A., 1925, ii, 12, 354; 1927, 1125.

H. F. GILLBE.

**Permitted and forbidden quantum jumps.** R. LADENBURG (*Z. Elektrochem.*, 1930, **36**, 631—640).—A survey. H. F. GILLBE.

**Abnormal lines and series in atomic spectra.** H. DESLANDRES (*Compt. rend.*, 1930, **191**, 7—11).—The differences between the observed and calculated frequencies for the principal spectral series of lithium and potassium are given. The displacement of the lines towards the red, caused by, but not always proportional to, the pressure appears to be greatest for lines of which the frequency is a multiple of the elementary frequency ( $1062.5\text{ cm}^{-1}$ ). H. F. GILLBE.

**Line spectra of crystals [potassium permanganate and potassium chlorate.]** K. SCHNETZLER (*Physikal. Z.*, 1930, **31**, 802—803).—At the temperature of liquid air mixed crystals of potassium permanganate and chlorate show the absorption spectrum of manganate ions between 4000 and 6000 Å. This spectrum consists of seven equidistant doublets with a wave-number difference of  $767\text{ cm}^{-1}$ , corresponding with a fundamental vibration at  $13.0\text{ }\mu$ . The intensity relation in the doublet is as 2:1 and the short-wave component is the weaker. The spectrum cannot be explained by arrangement of separate components into ordinary and extraordinary rays. It is much more likely that the doublet arises from a double electron term.

In spite of the complete optical isotropy of potassium chromiselenate its Zeeman effect shows a marked dependence on orientation. Sometimes the  $\sigma$  components are influenced and sometimes the  $\pi$  components. It appears that the optical symmetry is not conclusive, but belongs to the grating itself.

W. R. ANGUS.

**Carriers of some flame spectra.** V. KONDRATIEV (*Z. Physik*, 1930, **63**, 322—333).—Measurements were made with a Fuess quartz spectrograph of the ultra-violet band spectra of the carbon monoxide-oxygen flame, from 2784 to 5020 Å., at a pressure of about 30 mm. The bands are arranged in six series having a frequency difference of about  $600\text{ cm}^{-1}$ , which is compared with the frequency difference of  $672\text{ cm}^{-1}$  occurring in the infra-red and Raman spectra of carbon dioxide. The infra-red bands of carbon dioxide have a doublet structure, and this and the other considerations lead to the conclusion that the carbon dioxide molecule is the origin of the flame spectrum. The change in the frequency difference from 672 to  $600\text{ cm}^{-1}$  could be explained by the excitation of the higher vibration levels in the flame. The flame spectrum was also examined in the visible region under large dispersion, but was too complicated to be analysed; the background consisted of a line spectrum, which casts doubt on the really continuous nature of the backgrounds occurring in the flame spectrum. The spectrum of a sulphur-oxygen flame measured from 2377 to 4530 Å. was shown to consist of two groups of bands, one in the visible and one in the ultra-violet, the two being separated by a continuous region. The spectrum is thus the same as that of the carbon disulphide-oxygen flame and of the phosphorescent (cold) carbon disulphide flame, and the measured wave-lengths are shown to agree with those made on the latter flames by Emeléus and

by Strutt and Fowler. The visible group is shown to be in good agreement with the calculated bands for the  $\text{S}_2$  molecule, and the ultra-violet group with those for the SO molecule, and to these molecules the origin of the spectrum is therefore ascribed. The spectrum of the phosphorescent flame of ether is shown to be due to the formaldehyde molecule, for the absorption band spectrum of formaldehyde can be arranged in series with the identical frequency difference occurring in the flame spectra ( $1150\text{ cm}^{-1}$ ). H. A. JAHN.

**Visible temperature radiation of colourless oxides.** G. LIEBMANN (*Z. Physik*, 1930, **63**, 404—436).—It is shown that by Skaupy's method (*Z. Physik*, 1922, **12**, 177) a single pyrometer determination can give the temperature correctly to  $\pm 10^\circ$ . The temperature radiation of the oxides of aluminium, beryllium, chromium, magnesium, and thorium as dependent on grain size and temperature is investigated for temperatures from  $1208^\circ$  to  $2000^\circ\text{ Abs}$ . The emissive power for red light of wave-length  $0.665\text{ }\mu$  was shown to decrease with decrease in the size of grain. For the colourless oxides the emissive power increased rapidly with rise of temperature for practically all visible wave-lengths, whilst that of chromium oxide was independent of temperature. The emissive power of the colourless oxides increases rapidly with decreasing wave-length, whilst for chromium the emissive power decreases for green light. The dependence of the emission on the angle of emission was investigated for aluminium and magnesium oxides, large deviation from Lambert's law being found. H. A. JAHN.

**Spectra of solidified gases and their interpretation by the atomic theory.** L. VEGARD (*Ann. Physik*, 1930, [v], **6**, 487—544).—The author's investigations on the spectra of solidified gases, excited by cathode or canal rays, are reviewed and collated for solid nitrogen and its mixtures with inert gases. Recent investigations have revealed new series and these are discussed. The recent determination of the crystal structure of  $\alpha$ -nitrogen has furnished a valuable criterion for the interpretation of the observed light processes. A brief summary of the theory of spectra arising from atomic and molecular vibration and the calculation of line frequencies and dissociation energy are given.

The band systems are divided up into six families and each is fully discussed. In the  $N_1$  family four bands ( $N_1, N_2, N_3, N_4$ ) are observed, each consisting of three components and all corresponding with green and red auroral lines. The wave-number separations of the components in  $N_1$  and  $N_3$  are of the same order, whilst the separations of the components in  $N_2$  and  $N_4$  are also of the same order but considerably less than in  $N_1$  and  $N_3$ . The wave-number differences between  $N_1$  and  $N_3$ , and  $N_2$  and  $N_4$ , are the same, indicating that they belong to two vibration series of the same band system. The  $\epsilon$  family consists of four sub-groups, of which the  $\epsilon$  system is observed when a small amount of nitrogen is present in argon, with the  $\eta$  series of this system predominating. In a mixture of neon and nitrogen the  $\eta$  series appears strong, but the  $\epsilon$  series is often completely missing. All members of the  $\epsilon$  family belong to the same



electron transition. The other families are called the  $\zeta$  series, the  $C$  series, the  $A$  family, and the  $\theta$  family. The  $A$  series is found in the afterglow and in solid nitrogen. The  $\alpha$  series is given by mixtures of argon and nitrogen and neon and nitrogen, giving singlets with argon and doublets with neon. A new series belonging to the  $A$  family has been found by excitation of solid argon with cathode rays. The lines of this ( $\psi$ ) series are mostly triplets with a wave-number difference of  $56\text{ cm}^{-1}$  and are not observed in the afterglow. The  $G$ - $G'$  system of the  $A$  family is identical with the  $\gamma$  bands or third positive nitrogen group, and is due to nitric oxide produced by the action of the canal rays on traces of oxygen present in the argon-nitrogen mixture, whilst the  $E$ - $e$  series is identical with the  $\beta$  bands of nitric oxide. These two series have the same end state but different initial states. The  $A$ ,  $\alpha$ , and  $\psi$  series belong to the solid state, whereas the  $G$  and  $E$  series belong to the gaseous state. Recently it has been shown that admixture with air considerably enhances the  $\alpha$  series. Reinvestigation of the  $\theta$  family has revealed, in addition to the  $\theta$ ,  $\delta$ , and  $\chi$  series, a new ( $\pi$ ) series; and has also revealed the splitting of the  $\theta$  lines into doublets and triplets and the splitting of the  $\delta$  lines into doublets only.

The intensity distribution of lines within a system is considered, the energy functions and nuclear separations are numerically evaluated, and the intensity distribution of lines in several series is explained by an application of the theory of Condon.

The classification of the lines falls into two chief groups: (a) series which arise essentially from solid  $\alpha$ -nitrogen, and (b) series which are due to nitric oxide. The energy values of the electronic transitions of the different band systems, the vibration constants of the initial and final states, and the dissociation energies of these states are tabulated. The electronic levels of solid nitrogen are discussed, term symbols are assigned, and the various series are interpreted. The analogies between the spectrum of solid nitrogen and the arc spectrum of magnesium, and of solid nitric oxide and the arc spectrum of aluminium, are discussed. The electronic levels of the nitrogen molecule in the solid and gaseous states are compared.

W. R. ANGUS.

**Multiplex-interference spectroscope.** E. LAU (Z. Physik, 1930, 63, 313—317).—A multiplex-interference spectroscope is described. It consists of two parallel silvered glass plates of thicknesses 3 and 9.9 mm. respectively, placed at a distance of about 20 cm. apart. A preliminary photograph of the  $5769.6\text{ \AA}$ . mercury line is given, and it is shown that the satellite line about  $0.05\text{ \AA}$ . shorter in wave-length is at least double, the separation being about  $0.004\text{ \AA}$ . Preliminary investigations of the green krypton line are briefly described.

H. A. JAHN.

**Absorption of X-rays by lithium.** K. C. MAZUMDER (Physical Rev., 1930, [ii], 36, 457—459).—The mass scattering coefficient of lithium was measured for the wave-length range  $0.587$ — $0.100\text{ \AA}$ ., and an expression is given for the coefficient in the long-wave region. A curve is given for the mass absorption coefficient plotted against the cube of the corre-

sponding wave-length; it drops sharply below the wave-length  $0.2\text{ \AA}$ .

N. M. BLYTH.

**Fine structure in the X-ray absorption spectra of the  $K$  series of the elements calcium to gallium.** B. KIEVIT and G. A. LINDSAY (Physical Rev., 1930, [ii], 36, 648—666).—The  $K$  X-ray absorption spectra of the elements calcium, chromium, manganese, cobalt, nickel, copper, and zinc, using the element as the absorbing screen, were photographed, and showed a fine structure of six or seven secondary edges extending over an energy range of more than 200 volts. The relation between the  $K\beta_2$  emission line and the principal  $K$  absorption limit for iron, cobalt, nickel, and copper was investigated; the main edge is probably produced by the ejection of a  $K$  electron to an optical level rather than to infinity. Kossel's theory is inadequate to explain all the secondary edges. On the basis of multiple ionisation the probable electron transitions have been determined and tabulated to account for the observed separations of the secondary edges from the principal  $K$  edge. The energy values found are not in agreement with transitions proposed by Ray (cf. A., 1929, 868).

N. M. BLYTH.

**False lines in X-ray grating spectra.** J. M. CORK (Physical Rev., 1930, [ii], 36, 665—668).—False lines, additional to those due to defects in the grating, are described, and are due to a non-uniform focal spot or reflexion from slit faces. An unexplained type of companion line is present at wave-lengths about 13% greater than that of the parent line.

N. M. BLYTH.

**Scattering power of elementary silicon for molybdenum and copper rays.** R. W. G. WYCKOFF (Z. Krist., 1930, 73, 181—186; Chem. Zentr., 1930, i, 2686).

**Axiality of light emission and atomic structure.** VIII. Normal and polarised X-ray emission from a crystal. IX. Axiality of the valency fields of the carbon and nitrogen atoms. J. STARK (Ann. Physik, 1930, [v], 6, 637—662, 663—680; cf. this vol., 512, 654).—VIII. For observation of the X-ray emission from a crystal  $\gamma$ -dibromoanthracene was selected, since it has one axis of molecular symmetry lying in the plane of the benzene rings and one asymmetric axis perpendicular thereto and passing through the bromine atoms. The intensity of the  $K$  radiation of the bromine atoms, measured in the direction of the long axis of the needle-shaped crystal, is considerably different from the intensity in a direction perpendicular to this axis; at an angle of  $10^\circ$  from the axial direction the difference between the intensities is about 20%, and at  $40^\circ$  about 5%. The difference is independent of the excitation potential between 30 and 60 kilovolts, but it has not been ascertained whether this is true also for potentials comparable with the excitation potential of the  $K$  radiation of the bromine atoms. The existence of axial polarisation of the tertiary X-rays emitted has been demonstrated by comparative measurements of the intensities of the rays in two directions, which show, having regard to Barkla's observation relating the intensity of the emission with the direction of the electric field, that the electrical axis of the pre-

dominant  $K$  radiation is parallel to the axis of the crystal. The intensity of the tertiary radiation orthogonal to the axis of the crystal, and therefore of the secondary radiation having its electrical axis parallel to the crystal axis, is greater by about 16% of the mean intensity than the intensity perpendicular to the axis. Analogous measurements of the axiality of the intensity and of the polarisation of  $p$ -dibromobenzene gave negative results, probably because the molecules in the crystal are not oriented with all their axes parallel to one principal axis. The phenomenon of axiality is therefore not due primarily to crystallographic symmetry, since the crystals of both substances exhibit the same type of symmetry. The axial nature of the transference of an electron from one level to another and the accompanying emission of radiation must be bound up with the internal structure of the atom and not with the valency field operating at the surface of the atom. From the observed axiality of the secondary radiation it follows that the electrons in the shell of the bromine atom are arranged, not in concentric spheres, but around a principal axis. Further, the dibromoanthracene molecules must be oriented in the crystal with the Br—Br axes parallel, and the bromine atoms must be axially positioned in the molecule; these conditions can exist only if the valency field holding each bromine atom to its adjacent carbon atom possesses a rigid axis approximately parallel to the electronic axis in the shell of the atom.

IX. The orientation of the atoms in a molecule is considered. The formation of optically active compounds of carbon, and of complex ring systems, is discussed in support of the view that chemical valency is due to axial electronic arrangements, and in opposition to the concept of a spherically symmetrical atom. A distinction is drawn between axial valency such as is operative in the majority of carbon compounds, and spatial valency, which is due to the establishment of an equilibrium distance between oppositely charged particles and is operative in the sodium chloride lattice and in co-ordination compounds. The nitrogen atom possesses four axial valencies, oriented as in the carbon atom, and one spatial valency which is capable of ionisation from quinquivalent nitrogen compounds. In a tervalent nitrogen compound two of the axial valencies can remain non-operative, and the fifth valency then behaves as a non-ionisable axial valency. The principal axis of the nitrogen atom passes through the nucleus and bisects the angles between each pair of valency axes; the fifth valency lies on this principal axis. Sommerfeld's theory of the spherically symmetrical atom is further criticised. H. F. GILLBE.

**Relationship between chemical constitution and  $K$  X-ray spectra.** O. STELLING (Z. Elektrochem., 1930, 36, 605—611).—The purely constitutive displacement of the  $K$  absorption spectrum of an element according to the type of molecule of which it forms part is described; the chief factors influencing the displacement are the interionic distances, the lattice type, and the electronic configuration. Complex salts containing chlorine, and chlorinated organic acids and nitro-compounds, are cited in illustration of the influence of the distance in the molecule

between the chlorine atom and the other negative group. H. F. GILLBE.

**Intensity of total scattering of X-rays by monatomic gases.** Y. H. WOO (Nature, 1930, 126, 501—502).—Theoretical. L. S. THEOBALD.

**X-Ray interference with thin films.** H. KRIESSIG (Naturwiss., 1930, 18, 847—848).—The total reflexion of X-rays by thin films of nickel, formed by precipitation of nickel vapour on glass, have been investigated with the  $\text{Cu } K\alpha_1$  lines. Reflexion curves for thin nickel films have been obtained also by the ionisation method. The effects of the limiting angle and time of illumination are considered. For small angles the reflective power is very great, but as the angle is increased a sharp diminution in reflexion occurs accompanied by the appearance of two maxima in the reflexion curve. The appearance of these maxima and minima is explained. The thickness of the films can be calculated from the position of these maxima.

W. R. ANGUS.

**Differences in the intensity of X-ray reflexion from the two different (111) faces of zinc blende.** D. COSTER, K. S. KNOL, and J. A. PRINS (Z. Physik, 1930, 63, 345—369).—It is deduced theoretically from semi-classical considerations that it should be possible to detect a difference in the intensity of reflexion of X-rays from the bright, well-developed (111) face of zinc blende of which the outermost layer consists of sulphur atoms, as compared with reflexion from the matt, less developed ( $\bar{1}\bar{1}\bar{1}$ ) face for which zinc atoms form the outermost layer, so long as two X-ray lines having wave-lengths lying on both sides of the  $K$  absorption edge of zinc are used for comparison. The  $L\alpha_1$  and  $L\alpha_2$  lines of gold satisfy this condition, and the relative intensities of the reflexion of these lines from the two (111) faces of commercial plates of zinc blende were measured both for the first- and for the third-order reflexions so as to eliminate the special properties of the surface. Agreement with the theory was found, and also for reflexion of the  $L\beta_1, \beta_2, \beta_3$ , and  $\beta_4$  lines of tungsten reflected from the faces of a natural crystal. The disagreement in detail of the reflexion results with the simple theory is shown to lead to the conclusion that not only the amplitude but also the phase of the radiation scattered by a single atom varies with the angle of scattering, and an extension of the theory giving better agreement with the experiments was made by considering the scattering of the two  $K$  electrons of zinc separately.

H. A. JAHN.

**Scattering of X-rays by bound electrons.** S. BHARGAVA (Nature, 1930, 126, 398—399).—The phenomenon observed by Ray (this vol., 833, 972) is not a case of scattering but is an experimental verification of photo-ionisation. L. S. THEOBALD.

**Scattering of X-rays by bound electrons.** B. B. RAY (Nature, 1930, 126, 399; cf. this vol., 972 and preceding abstract).—Further modified lines of the  $K\beta_1$  radiations of nickel and iron scattered by carbon and nitrogen are recorded. The effects which have been observed (*loc. cit.*) are more correctly described as modifications due to part absorption of the incident radiation by atoms. L. S. THEOBALD.

**Effect of irradiation on cathode-ray reflexion at aluminium and platinum surfaces and the reality of the positive and negative currents thereby produced.** W. KOHL (Ann. Physik, 1930, [v], 6, 391—407).—The effect of irradiation on the reflexion of cathode rays at aluminium and platinum surfaces is to produce currents of two kinds. The total radiation is either greater or less than the sum of the single components, i.e., the thermo-electric and the photo-electric currents. It can be shown that the diminution in the total current observed by Frey when a foil was simultaneously radiating electrons and being radiated with ultra-violet light in a homogeneous field is dependent only to a small extent on the velocity of the primary electrons, but to a much greater extent on the gas content of the foil. Foils containing gas can give rise to a positive addition current in a homogeneous field, a fact which is explained by the diminution of the space charge effect. This positive addition current may amount to 50% of the photo-electric current according to the conditions of the experiment. It is possible to obtain currents of greater strength than the photo-electric current if the field is not homogeneous and the foil is free from gas.

A. J. MEE.

**Ionisation of gases by short-wave X-rays.** K. SCHOCKEN (Z. Physik, 1930, 64, 458—464).—Photo-electric emission is proportional to the cube of the effective atomic number, whilst recoil-electron emission is independent of the effective atomic number. The two effects are therefore separable when the rate of ionisation of two gases by a given homogeneous X-ray beam is known. Homogeneous radiation was obtained spectroscopically, and the ionisation of oxygen, argon, and methyl chloride was studied. The recoil-electron ionisation is negligible for wave-lengths greater than 0.35 Å. Correction of these results for the different ionisation potentials of different substances gives lower values for the photo-electric ionisation, but this correction is not of importance.

A. B. D. CASSIE.

**Effect of intense electric fields on the photo-electric properties of metals.** E. O. LAWRENCE and L. B. LINFORD (Physical Rev., 1930, [ii], 36, 482—497).—The photo-electric effect from thin films of potassium and oxygen on tungsten was studied as a function of strong accelerating fields up to 63,000 volts per cm., which shifted photo-electric thresholds towards the red. The shift at 36,000 volts per cm. for a potassium layer on tungsten was from 5620 to 5880 Å. A film of potassium on a thick layer of oxygen on tungsten showed a threshold at 6800 Å.; for a thin layer of oxygen at 7350 Å. for small applied fields, which shifted to 7575 Å. with 18,600 volts per cm.; for a thinner layer, monatomic or less, at 5830 Å. in small fields, shifting to 5960 Å. with 18,600 volts per cm. From observed variations of shifts with applied field calculations of the surface fields were made (cf. Becker and Mueller, A., 1928, 453). Outside the film of potassium on a thin oxygen layer on tungsten the field closely followed the Schottky image law for  $1.5 \times 10^{-6}$  to  $10^{-7}$  cm. from the surface, and for potassium on tungsten for  $8 \times 10^{-7}$  to  $1.5 \times 10^{-6}$  cm.

from the surface. The relation of shifts of photo-electric thresholds to changes of the work function of a surface is discussed. The form of the photo-electric sensitivity-frequency curve remains unchanged, and shifts with the thresholds in intense fields. Results are in good agreement with wave mechanics and Fermi-Dirac statistical theory of the photo-electric effect.

N. M. BLIGH.

**Photo-electric behaviour of solid and liquid mercury.** D. ROLLER (Physical Rev., 1930, [ii], 36, 738—742; cf. Grutzmann, A., 1929, 229).—An apparatus is described for the investigation of the effects of temperature and changes in the state of aggregation on the photo-electric threshold and current for mercury and of any allotropic change in mercury in the region  $-190^\circ$  to the m. p. With monochromatic light the photo-electric threshold for solid mercury was  $2750 \pm 25$  Å. for all temperatures in this region; for the ordinary temperature it was  $2753 \pm 10$  Å. The photo-electric current excited by each of the lines 2537, 2653, and 2700 Å. was independent of temperature from  $-190^\circ$  to  $-125^\circ$ , with a gradual small decrease in the current from  $-125^\circ$  to  $-39^\circ$  probably due, however, to contamination or secondary causes. No other indication of allotropic change was found. The photo-electric current was always higher for the solid than for the liquid phase at the ordinary temperature. The emission curves showed marked hysteresis between  $-39^\circ$  and  $0^\circ$ .

N. M. BLIGH.

**Ionisation potential of radon.** F. HOLWECK and L. WERTENSTEIN (Nature, 1930, 126, 433).—The ionisation potentials for krypton, xenon, and radon are 13.3, 11.4, and 10.6 volts, respectively; the last value is in agreement with that of Rasmussen (10.7 volts; cf. this vol., 1076).

L. S. THEOBALD.

**Energy losses of electrons in mercury vapour.** D. C. ROSE (Canad. J. Res., 1930, 3, 174—185).—A more detailed account of work already published (this vol., 513).

**Avoidance of the infinite singularity at an electron.** V. AMBARZUMIAN and D. IVANENKO (Z. Physik, 1930, 64, 563—567).—The representation of an electron by a point leads to difficulties equivalent to the classical infinite inertia of a point charge. This is avoidable by assuming a discontinuous space, where difference calculus replaces differential calculus. This hypothesis resolves Klein's paradox. The effect of a discontinuous time is also discussed.

A. B. D. CASSIE.

**Application of the Fermi-Thomas statistical model to the calculation of potential distribution in positive ions.** E. B. BAKER (Physical Rev., 1930, [ii], 36, 630—647).—Mathematical. The Fermi-Thomas statistical calculation of atomic potential distributions is extended to positive ions; a table of potentials for any positive ion is given. Results are applied to the calculation of ionic radii, successive ionisation potentials, and deviations from the Moseley law in optical spectra.

N. M. BLIGH.

**Metastable atoms and electrons produced by resonance radiation in neon.** I. LANGMUIR and C. G. FOUND (Physical Rev., 1930, [ii], 36, 604—

605).—Investigations of arcs in neon at low pressures indicated that the resonance radiation from the arc can travel through the non-ionised neon beyond the end of the arc for 20 or 30 cm., and on absorption produces, by excitation of the gas and by subsequent collisions of the second kind, metastable atoms at the rate of at least  $10^{13}$  cm.<sup>-3</sup> sec.<sup>-1</sup> These diffuse into contact with the walls or electrodes and liberate electrons. The effects and properties of these electrons are discussed.

N. M. BLIGH.

**Scattering of low-velocity electrons by gases, and its bearing on experimental methods.** H. BARTELS and H. NOACK (*Z. Physik*, 1930, **64**, 465—498).—Bartels' scattering theory (A., 1929, 1125) is modified to fit the four conditions: (i) the scattering substance lies between two infinite planes; (ii) the electrons enter normally to the first plane; (iii) there is no favoured direction of reflexion of electrons by a scattering atom; (iv) the scattering atoms occupy a field-free space. This theory is also generalised to include reflexion at bounding surfaces and the effect of inelastic collisions. The calculations are used to modify interpretations of experimental observations on electron collisions in gases. Pose (A., 1929, 231) used electrons satisfying condition (ii) in measurements of the effective collision area of an atom, and so obtains values which, when corrected, agree with Ramsauer's. The optical excitation function is not explicitly observed in experiment, but rather the product of this and other factors, which vary with the velocity of the exciting electrons and with the gas pressure. Curves showing the variation of the true optical excitation function with velocity are given for the 3888 and 5048 Å. lines of helium. The curve for 5048 Å. shows no subsidiary maximum (cf. A., 1929, 1116). Ornstein and Elenbaas' results (this vol., 392) on the optical determination of effective collision areas also require correction for scattering. The effect of scattering on electrons moving in a homogeneous magnetic field normal to their path is discussed. Such a magnetic field does not modify results of collision experiments. Finally, the correspondence of Rayleigh and Raman scattering of radiation with elastic and inelastic scattering of electrons is noted.

A. B. D. CASSIE.

**Space distribution of X-ray photo-electrons from a solid film.** L. SIMONS (*Phil. Mag.*, 1930, [vii], **10**, 387—401; cf. Watson and van den Akker, this vol., 128).—Experiments having for their object the investigation of the law according to which the probability of a photo-electron being ejected at an angle  $\xi$  to the electric vector of a plane polarised wave is proportional to  $\cos^2 \xi$  are described. A retarding electric field was used to discriminate between the fast and slow groups of electrons, and the photo-electric current was measured at various angles of incidence of a beam of X-rays applied to a thin film of gold. The emitted electrons are divisible into those that have and those that have not suffered a further disturbance after production. The former have a uniform radial distribution, whilst the latter conform to the  $\cos^2 \xi$  probability law. Approximately equal numbers of fast or  $\beta$ -electrons are emitted from each side of the film, but they originate

chiefly at the surface on which the X-rays are incident.

F. L. USHER.

**Determination of molecular structure by diffraction of an electron stream.** H. MARK and R. WIERL (*Z. Elektrochem.*, 1930, **36**, 675—676).—The measurement of interatomic distances by observation of the diffraction of a stream of electrons through a column of vapour is described.

H. F. GILLBE.

**Lecture experiment to demonstrate the influence of a monatomic film of sodium on the glowing electron emission of a tungsten wire.** R. SUHRMANN and F. BREYER (*Physikal. Z.*, 1930, **31**, 823—824).—A diminution of electron emission is produced when a thin film of an electro-positive metal is deposited on an electro-negative metal. The method of depositing a monatomic film of sodium on a tungsten wire and a simple lecture demonstration of the photo-electric effect thereby produced are described.

W. R. ANGUS.

**Secondary emission from metals by impact of metastable atoms and positive ions.** W. UYTENDHOEVEN and M. C. HARRINGTON (*Physical Rev.*, 1930, [ii], **36**, 709—725).—The secondary electron emission from nickel electrodes due to bombardment of positive ions and metastable atoms in a neon discharge under conditions simulating those at the cathode in a glow discharge was investigated by three methods. Values of 15—50% were found for the proportion of apparent positive ion current carried by secondary electrons, and 14—20% for the number of free electrons per positive ion. The greater part of the emission is ascribable to the metastable atoms.

N. M. BLIGH.

**Mobility of ions in pure gases.** A. M. TYNDALL and C. F. POWELL (*Proc. Roy. Soc.*, 1930, **A**, **129**, 162—180).—A metal-glass apparatus which can be subjected to a rigorous bake-out has been designed for measuring the mobility of ions in gases by the method previously described (Tyndall, Starr, and Powell, A., 1929, 5). Tested with dry air at various pressures the results obtained for positive ions are in agreement with Langevin's law. Under a field of 180 volts per cm. in dry air at 66 mm. all the negative carriers were electrons, but at higher pressures "normal" ions appeared. Results in nitrogen and helium indicate the importance of the effect of small traces of impurities on the mobility of positive ions; in the former gas the negative ions were all electrons, and in the latter the maximum mobility recorded for a positive ion was of the order of 17, which is roughly three times that previously obtained and agrees as regards order of magnitude with the value deduced from classical theory for the mobility of the positive monatomic helium ion moving through helium. Results obtained in the present work agree with the principle of electron capture advanced by Kallmann and Rosen (this vol., 514). Residual impurity in the gas used has been reduced to values not hitherto obtained, and the omission of this in previous work is considered to vitiate the results obtained.

L. L. BIRCUMSHAW.

**Relation between charge and size of ions.** G. VON HEVESY (*Z. physikal. Chem.*, 1930, **149**, 472—474).—The diffusion constants and sizes of ions are

discussed and it is shown from a consideration of the available data that in a large number of instances there is an inverse proportionality between diffusion coefficient and valency.

E. S. HEDGES.

**Artificial  $\gamma$ -radiation.** A vacuum discharge tube for  $2.4 \times 10^6$  volts. A. BRASCH and F. LANGE (Naturwiss., 1930, 18, 765—766).—A discharge tube for voltages up to  $1.2 \times 10^6$  volts recently described by the authors (*ibid.*, 16) has been modified so as to be used for the acceleration of corpuscular rays, to increase the working voltage to the region of the transition of elements, and to determine more favourably the dimensions of the tube employed. A tube has been made for voltages up to  $2.4 \times 10^6$  volts, capable of producing artificial  $\gamma$ -radiation.

W. R. ANGUS.

**Behaviour of positive ions in hydrogen.** A. C. G. MITCHELL (J. Franklin Inst., 1930, 210, 269—286).—The rate of decrease of pressure has been measured for hydrogen at low initial pressures (0.01—0.06 mm.) in presence of a glowing filament, and when cooled in liquid air. In the absence of positive ions a decrease in pressure occurs due to thermal dissociation on the hot filament and subsequent condensation on the cold walls of the containing vessel. With positive ions (lithium or caesium) of energies from 15 to 320 volts flowing through the tube, the rate of decrease of pressure is greater, indicating the probable formation of a hydride. The rate of pressure decrease with voltage applied is proportional to the ion current flowing; the rate for unit current is proportional to the pressure, and the rate per unit current per unit pressure is practically independent of the voltage, for lithium and caesium ions of energies from 15 to 320 volts, contrary to the results of Leipunski and Schechter (this vol., 392).

J. R. I. HEBURN.

**Atomic diameters of hydrogen and the inert gases with respect to electrons of very low velocity.** H. L. BROSE and E. H. SAAYMAN (Nature, 1930, 126, 400—401).—Using assumptions similar to those made by Sommerfeld, the atomic diameters of hydrogen, helium, neon, and argon have been calculated with respect to electrons of vanishingly small velocity; it is found that the atomic diameters should vary inversely as the atomic numbers.

L. S. THEOBALD.

**Measurement of the effective cross-section of gases and vapours.** F. SCHMIEDER (Z. Elektrochem., 1930, 36, 700—704).—Measurements with a number of organic vapours indicate that, despite the disturbing influence of dipoles, the relationships among certain groups of chemical compounds classified according to Grimm's law, such as hydrogen cyanide, acetylene, nitrogen, and methyl ether, dimethylamine, *n*-propane, are manifested by both the form and the position of the effective cross-section-electron velocity curves. Of isomeric substances, the curves of *n*- and *iso*-butane are almost identical, those of *n*-pentane and tetramethylmethane exhibit small differences at low electron velocities, whilst those of methyl ether and ethyl alcohol are of quite different forms, probably on account of the existence of dipole moments. The similarities between the curves given by various

alcohols and water are discussed in reference to the specific influence of the hydroxyl group.

H. F. GILLBE.

**Isotope effect in the spectrum of neon.** H. NAGAOKA and T. MISHIMA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1930, 13, 293—316).—Every strong line in the yellow and red portion of the neon spectrum shows the presence of a faint component when analysed by interferometers of resolving power greater than  $0.5 \times 10^6$ . The wave-number differences of the doublets are nearly constant for the same series and a little greater than the isotope effect of  $\text{Ne}^{20}$  and  $\text{Ne}^{22}$  given by Bohr's formula. The term values  $I_s$  for the  $\text{Ne}^{22}$  components are slightly greater than those for  $\text{Ne}^{20}$ , whilst  $2p_i$ 's are nearly the same. Zeeman effect of lines for  $\text{Ne}^{22}$  is the same as for  $\text{Ne}^{20}$ . The wave-lengths of neon lines require revision on account of their doublet character.

W. E. DOWNEY.

**Separation of isotopes.** K. P. JAKOVLEV (Z. Physik, 1930, 64, 378—391).—The different methods which have been used for the separation of isotopes are reviewed. None of them provides anything like a complete separation. The best method for obtaining specimens of isotopes in the pure state is that using positive rays. This has not been previously applied owing to the great experimental difficulties. An apparatus is described by which it is possible by using a bundle of positive rays to separate small quantities of isotopes. It is applied to the separation of the isotopes of neon. The quantity of pure isotope it is possible to obtain by this method is small (e.g., 0.1 c.c. of neon), but is sufficient for testing purposes where the sensitive physico-analytical methods can be used. The products obtained gave no difference in spectra to an accuracy of 0.006 Å. The analysis by the positive-ray method is not yet complete.

A. J. MEE.

**At. wt. of chromium. I. Preparation and analysis of chromyl chloride.** P. G. NÚÑEZ (Anal. Fis. Quím., 1930, 28, 579—586).—Preliminary analyses have been made of chromyl chloride, purified by distillation under reduced pressure, with a view to the revision of the at. wt. of chromium.

H. F. GILLBE.

**Synthesis of silver sulphide; at. wt. of sulphur.** O. HÖNIGSCHMID (Z. Elektrochem., 1930, 36, 689—690).—The synthesis of silver sulphide from its elements yields for the at. wt. of sulphur  $32.0685 \pm 0.0006$ , in agreement with Richards and Jones' value derived from the conversion of silver sulphate into the chloride. Reduction of silver sulphide by hydrogen does not yield satisfactory results, as the last traces of sulphur are extremely difficult to remove.

H. F. GILLBE.

**At. wt. of chlorine. Solubility of silver chloride.** A. F. SCOTT and C. R. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 3586—3587).—Direct nephelometric determinations were made of the solubility of flocculent silver chloride in 0—1M-nitric acid at 0.5°. The value accepted by Hönigschmid and Chan (A., 1927, 806) is too low and consequently their determination of the at. wt. of chlorine is too high by about 0.001 unit.

J. G. A. GRIFFITHS.

**At. wt. of rhenium. Analysis of silver perhenate.** O. HÖNIGSCHMID and R. SACHTLEBEN (Z. anorg. Chem., 1930, **191**, 309—317).—The various methods available for determining the at. wt. of rhenium have been investigated, and it is shown that Noddack's method (A., 1929, 21) is unsuitable, since complete reduction of the disulphide by means of hydrogen is difficult. Analysis of the chloride obtained by synthesis from the elements is also untrustworthy, because apparently a mixture of chlorides, which undergoes a complicated hydrolysis on being dissolved in water, is obtained. A suitable method is the precipitation of silver perhenate,  $\text{AgReO}_4$ , by means of hydrobromic acid and weighing the silver bromide. From seven determinations the ratio  $\text{AgReO}_4 : \text{AgBr}$  was found to be 1.90735, which gives  $\text{Re} = 186.31 \pm 0.02$ . O. J. WALKER.

**Constitution of molybdenum.** F. W. ASTON (Nature, 1930, **126**, 348).—Analysis of the carbonyl shows that molybdenum has 7 isotopes; the mass numbers and approximate abundances are 92 and 14.2, 94 and 10.0, 95 and 15.5, 96 and 17.8, 97 and 9.6, 98 and 23.0, and 100 and 9.8, respectively. The packing fractions of  $\text{Mo}^{98}$  and  $\text{Mo}^{100}$  are both approximately  $-5.5$ , giving an at. wt.  $95.97 \pm 0.05$ .

L. S. THEOBALD.

**Speculation concerning the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -rays of radium-B, -C, and -C'.** I. Revised theory of the internal absorption coefficient. R. H. FOWLER (Proc. Roy. Soc., 1930, A, **129**, 1—43).—An attempt is made to calculate the "internal conversion coefficient" of the  $\gamma$ -rays from radium-BC and radium-CC'D,  $\gamma$ -rays which are very strongly absorbed in a type of photo-electric effect by the planetary electrons of the parent atom giving rise to the sharp lines of the  $\beta$ -ray spectrum. The nucleus is supposed to contain a quantum-mechanical system carrying a charge, which possesses a series of stationary states and is not necessarily initially found in its ground state when  $\gamma$ -rays are about to be emitted. The external atomic system is considered to contain a single electron in a Coulomb field of a charge  $+Ze$ , and this electron is initially in its ground level, i.e., a  $K$ -ring electron. A simplified interaction coupling the nuclear system and the electron is given by  $Qe^2[(1/R) - (1/r_e)]$ , where  $R$  is the distance between the electron and the nuclear system and  $r_e$  that of the electron from the centre of the nucleus. It is suggested that the strong abnormally converted  $\beta$ -ray at  $14.26 \times 10^5$  volts results from an excited nuclear state from which a radioactive transition is impossible, and is due to a side product of the purely  $\alpha$ -ray disintegration of the special type yielding 9.2-cm. particles. The theory is further developed by a model of the nucleus which contains an oscillating system, which itself contains extra internal energy capable of transfer by radiation or collision. L. L. BIRCUMSHAW.

**Analysis of groups of  $\alpha$ -rays. I.  $\alpha$ -Rays from radium-C, thorium-C, and actinium-C.** (Sir) E. RUTHERFORD, F. A. B. WARD, and C. E. WYNN-WILLIAMS (Proc. Roy. Soc., 1930, A, **129**, 211—234).—A method, of the Greinacher type, of counting  $\alpha$ -particles, which involves the linear amplification by means of thermionic valves of the

ionisation current due to an  $\alpha$ -particle, is described. This has made possible the detection of the group of  $\alpha$ -particles of short range emitted in the dual disintegration of radium-C, although they are present in only about 1 part in 3000 parts, mixed with the main group of  $\alpha$ -particles of range 7 cm. By the use of a double ionisation chamber the number of particles with ranges between  $x$  and  $x + \partial x$ , where  $\partial x$  is of the order of a few mm., may be determined, and the disadvantages involved in the use of a Wilson chamber are avoided. The differential counter has been used to study the 8.6-cm.  $\alpha$ -particles from thorium-C', the 7.0-cm. particles from radium-C', and the 3.9-cm. particles from polonium, which all appeared to be homogeneous groups. The 5.5-cm. particles from actinium and the 4.8-cm. particles from thorium-C were found to be complex, the former consisting of two well-marked groups differing in range by 4.2 mm.

L. L. BIRCUMSHAW.

**Capture of electrons by swift  $\alpha$ -particles.** J. C. JACOBSEN (Phil. Mag., 1930, [vii], **10**, 401—412; cf. Thomas, A., 1927, 606).—Simple mechanical considerations show that the chance of capture of electrons by swift  $\alpha$ -particles in a substance possessing a small nuclear charge is very small compared with that in atoms where the nucleus has an important influence on the result of a collision. The distribution on a screen of  $\alpha$ -particles in a homogeneous beam after passing through a magnetic field either in hydrogen or in air is deduced on the general assumptions that (1) the probability of capture in hydrogen can be neglected and (2) the equilibrium between single- and double-charged particles is, for a given velocity, the same for mica and for air. Observations of the number of  $\alpha$ -particles striking a screen at different positions are in agreement with the calculation, and the assumptions are considered to be valid.

F. L. USHER.

**Photographic counting of  $\alpha$ -particles.** J. C. JACOBSEN (Phil. Mag., 1930, [vii], **10**, 413—416).—Photographic counting of  $\alpha$ -particles has been carried out by counting the blackened grains present in measured areas of a highly magnified image of the exposed plate. The number of grains is proportional to the number of  $\alpha$ -particles when the latter is between 10,000 and 200,000 per sq. mm. The lower limit is imposed by the number of grains due to "fog." The method is impracticable when the velocity of the particles is less than 0.3 of the velocity of those from radium-C. Within the limits stated the method has important advantages over that involving visual counting of scintillations. F. L. USHER.

**Disintegration of boron by means of  $\alpha$ -particles from radium-C'.** H. FRÄNZ (Z. Physik, 1930 **63**, 370—380).—The disintegration of boron by  $\alpha$ -rays from radium-C' and from polonium is investigated, using the adapted multiplication Geiger counter previously described (this vol., 130). With radium-C' the  $\beta$ -rays caused a broadening of the oscillograph trace so that very small deflexions could not be detected, but with polonium there were no  $\beta$ -rays to interfere. Hence assuming the curve to have the same nature in each case, from the nature of the curve relating size of deflexion to the number of deflexions



for polonium, that obtained for radium-*C'* could be extrapolated to small deflexions. By integration under the curves obtained the total emission under the given conditions is calculated. Two curves are given showing the total emission plotted against the thickness of absorption layer placed in the path of the emitted hydrogen particles. The first curve refers to experiments with the  $\alpha$ -particles of range 6.4 cm. from radium-*C'*, the second to those of range 3.93 cm. from polonium, both curves referring to hydrogen particles making a mean angle of  $143^\circ$  with the direction of the impinging  $\alpha$ -rays. Both curves show two groups of hydrogen particles for which the maximum range is calculated to be 24 and 43 cm. for the  $\alpha$ -particles from radium-*C'*, and 15 and 33 cm. for those from polonium. In the first case 0.6 long-range hydrogen particle per million  $\alpha$ -particles was obtained, but in the second case only 0.2 per million, showing that with decreasing range of the  $\alpha$ -particles the intensity of the longer-range hydrogen particles decreases more rapidly than does their range. From consideration of the fact that the range of emitted hydrogen particles decreases with increase in the angle between their direction and that of the impinging  $\alpha$ -particles, it is deduced that the 33-cm. range particles represent a new group of hydrogen particles not previously discovered by the old method, using small angles of emission. The 15-cm. particles are identified with the previous 32-cm. particles. H. A. JAHN.

**Decomposition of boron by means of  $\alpha$ -particles from polonium.** W. BOTHE (Z. Physik, 1930, **63**, 381—395; cf. preceding abstract).—The disintegration of pure amorphous boron was investigated, using the  $\alpha$ -particles of different ranges emitted from polonium, the apparatus being specially designed to permit the investigation of the hydrogen particles emitted at different angles relative to the impinging  $\alpha$ -particle stream. The existence of the third group of hydrogen particles discovered by Fränzl (see above) was verified, the yield being 0.17 per million  $\alpha$ -particles with the emission angle of  $0^\circ$ , compared with the 0.2 per million found by Fränzl at  $143^\circ$ , thus showing the small variation of yield with angle of emission. The range of these particles with 3.9-cm. range  $\alpha$ -particles was found to be 74 cm. at an angle of emission of  $0^\circ$ . The range of the second group of hydrogen particles (corresponding with the 15-cm. particles of Fränzl) was investigated at a series of emission angles from  $0^\circ$  to  $106^\circ$ , and found to diminish steadily with increase in the angle of emission, whilst the intensity varied only slightly and corresponded with a yield of 6.5 per million. In agreement with Fränzl the intensity of the hydrogen particles of the second group was found to decrease more rapidly than the range with decrease in the range of the  $\alpha$ -particles. H. A. JAHN.

**Fine structure of  $\alpha$ -rays.** G. GAMOW (Nature, 1930, **126**, 397).—Theoretical. An explanation of the five groups found by Rosenblum (A., 1929, 738; this vol., 837) in the  $\alpha$ -rays of thorium-*C* is advanced.

L. S. THEOBALD.

**Capture of electrons by  $\alpha$ -particles.** H. C. WEBSTER (Nature, 1930, **126**, 352).—When a beam of  $\alpha$ -particles is passed through a stream of electrons

moving parallel to it, the number of singly-charged particles is about 1% of the total; the numbers of doubly- and singly-charged particles are quite unaffected by the electron stream throughout the range 450—750 volts (cf. Barnes, this vol., 393).

L. S. THEOBALD.

**Period of "actino-uranium" and its bearing on the ages of radioactive minerals.** A. HOLMES (Nature, 1930, **126**, 348—349).—The ratio of accumulated  $\text{Pb}^{207}$  to accumulated  $\text{Pb}^{206}$  for Pre-Cambrian minerals is shown to vary between 2.5 and 3.3, indicating that throughout the greater part of geological time the proportion of  $\text{Pb}^{207}$  generated in minerals has been of the same order as that generated at the present time. It is also concluded that Aston's estimate (A., 1929, 370) of 9.3% for  $\text{Pb}^{207}$  in Norwegian bröggerite is too high, and that Rutherford's estimate (*ibid.*, 373) for the period of actino-uranium is too low. The periods of uranium-I and actino-uranium are probably of the same order and hence no correction to the calculated ages of minerals is at present required.

L. S. THEOBALD.

**$\beta$ -Radiation and the energy principle.** J. KUDAR (Z. Physik, 1930, **64**, 402—404).—Theoretical. The statistical accuracy of the energy principle, at least, can be relied on in the case of radioactive disintegration. The universal quantity  $e^2/mc^2$  appears to play a peculiar part in the theory of  $\beta$ -disintegration.

A. J. MEE.

**$\gamma$ -Rays from radium and its products.** L. T. STEADMAN (Physical Rev., 1930, [ii], **36**, 460—471).—The wave-lengths of the  $\gamma$ -rays in the spectrum of radium and of radium-*B*, -*C*, and -*D* were determined by the crystal diffraction method with the use of a Geiger counting chamber. Good agreement with existing data was obtained, and additional short wave-length rays, the shortest being 0.42 Å., were found, using a calcite crystal. With a diamond for the shortest wave-lengths a ray of wave-length 0.17 Å. was found. Changes in intensity with wave-length were investigated, and a determination of the background of the intensity curve showed that no continuous  $\gamma$ -radiation of appreciable intensity existed. N. M. Blich.

**Absolute intensities and internal conversion coefficients of the  $\gamma$ -rays of radium-*B* and -*C*.** C. D. ELLIS and G. H. ASTON (Proc. Roy. Soc., 1930, **A**, **129**, 180—207).—When the nucleus emits energy  $E$  this occurs in the form of radiation which has a frequency  $E/h$ , and if in a fraction  $\alpha$  of the cases the radiation is absorbed in the electronic structure and gives rise to a photo-electron, in the remaining fraction  $(1-\alpha)$  the  $\gamma$ -ray is emitted clear of the atom. The quantity  $\alpha$  is the coefficient of internal conversion. There is, however, neither need nor justification to consider the  $\gamma$ -ray to be emitted in the case of those atoms which give photo-electrons. Experiment shows that the atom as a whole is capable of emitting energy  $E$ , either in the form of a quantum of radiation  $h\nu=E$ , or as an electron of energy  $E-K$  or  $E-L$ , etc., followed by the appropriate excited *K*-, *L*-, *X*-radiations. The second point of view implies some type of collision interaction between the nucleus and the electronic structure of the atom. An attempt has been made to obtain information on this question by

an experimental investigation of the relative intensities of the  $\gamma$ -rays of radium-*B* and -*C*, and of the photoelectric groups associated with them. The results lead to the abandonment of the hypothesis of only radiative coupling between the nucleus and the electronic system, and indicate rather a direct action of the nucleus on the electronic structure.

L. L. BIRCUMSHAW.

**Emanation method in the study of salts of unstable surface.** H. MÜLLER (Z. physikal. Chem., 1930, 149, 257—278; cf. A., 1929, 737).—The emanation method has been applied to the study of surface changes, due to variations in humidity, in substances possessing very low aqueous tensions. Activated preparations (using radium salts) of hydrated barium chloride, anhydrous barium sulphate, barium glass, Jena glass, and of the zeolites chabasite and heulandite were investigated. In general it was found that the emanation activity (ratio of the emanation in the vapour phase to the total formed) remained constant so long as there was no change in the surface of the substance. Under conditions in which efflorescence was to be anticipated in substances such as hydrated barium chloride, chabasite, and heulandite, the surface changes were accompanied by a corresponding rise in emanation activity. In circumstances in which an aqueous film formed on the surface, whether due to surface dissolution as in the case of hydrated barium chloride, or to adsorption as in the case of barium glass, an increase in emanation activity was also found. No dependence of the emanation activity on humidity was found in conditions in which change in surface conditions was unlikely, as, for example, in the cases of barium sulphate and Jena glass. Effects due to ageing in the proper sense were absent. Apparent ageing effects were traced to causes such as the formation of a water film through surface crystallisation, to surface expansion through swelling as a result of water exchange in barium glass, and to changes of the water equilibrium in the cases of the zeolites.

F. G. TRYHORN.

**Compensated electrometer for radioactive measurements in buildings infected by radioactive material.** V. A. SOKOLOV (Z. Physik, 1930, 63, 318—321).—An arrangement is described consisting of two hermetically sealed electrometers with one common electrode and charged to opposite potentials, so that the effect of variation in the radioactivity of the surrounding air does not affect measurements made on one of the electrometers.

H. A. JAHN.

**Collisions of photons.** A. L. HUGHES and G. E. M. JAUNCEY (Physical Rev., 1930, [ii], 36, 773—777).—It is shown that if two photons of frequency  $\nu$  move along paths making an angle  $2\theta$  with each other they will on collision give rise to a photon of frequency  $\nu(1+\cos\theta)$  travelling forward along the bisector of the angle. This was investigated experimentally, with negative result, using two beams of sunlight, filtered by red glass, intersecting at the common focus of two lenses. No light was detected at this point. Results indicate a value of the order  $10^{-10}\lambda^2$  for the area of cross-section of a photon.

N. M. BLYTH.

**Mass action and the electronic configuration of atoms.** R. D. KLEEMAN (Z. anorg. Chem., 1930, 191, 201—208).—Theoretical considerations based on previous experimental work. H. F. GILLBE.

**Exchange of energy between gas atoms and solid surfaces.** J. K. ROBERTS (Proc. Roy. Soc., 1930, A, 129, 146—161).—If the average translational energy of the molecules of a gas corresponds with a temperature  $T_1$  before striking a surface at temperature  $T_2$ , and after leaving the surface corresponds with a temperature  $T_2'$ , then it can be shown that  $(T_2' - T_1)/(T_2 - T_1) = \alpha$  (the accommodation coefficient). Application of Knudsen's theory leads to the equation  $Q = 1.74 \times 10^{-4} [p\alpha(T_2 - T_1)] / \sqrt{\mu T}$  g.-cal. cm.<sup>-2</sup> sec.<sup>-1</sup>, where  $Q$  is the heat lost per unit area of the wire per sec. for a monatomic gas and for small temperature differences,  $p$  is the pressure in dynes per cm.<sup>2</sup>,  $\mu$  is the mol. wt. of the gas, and  $T$  is the mean temperature. An apparatus is described for the determination of  $\alpha$  for helium on tungsten and nickel wires by the measurement of the heat loss. With tungsten it was found that the value of  $\alpha$  for a cleaned wire is considerably smaller than for a wire which has been kept over-night and is covered with films of adsorbed gas, and that the value for a cleaned wire shows a definite drift with time, presumably owing to the gradual building up of adsorbed films by the residual impurities in the gas. For clean tungsten surfaces the values 0.05 and 0.07 were obtained, and 0.08 for nickel. The results are discussed both from the view-point of the classical collision theory and from that of the reflexion and diffraction of molecules by the grating action of the atoms on the surface of the solid.

L. L. BIRCUMSHAW.

**Electron states and chemical combination in diatomic molecules.** R. S. MULLIKEN (Z. Elektrochem., 1930, 36, 603—605).—The derivation of the electronic configuration of  $N_2^+$  in its two electronic states from that of the nitrogen molecule is described and correlated with the configurations of  $CN^-$ , CO, and  $NO^+$ . Chemical reaction is discussed in its relationship to the configuration of molecules such as NO,  $F_2$ , and  $O_2$ .

H. F. GILLBE.

**Characteristic values of an electronic dipole in the atomic field.** K. BASU (Z. Physik, 1930, 63, 304—312).—Mathematical. H. A. JAHN.

**Electrical properties of active nitrogen.** E. J. B. WILLEY and W. A. STRINGFELLOW (Nature, 1930, 126, 349—350).—Removal of all charged bodies from a stream of active nitrogen is without effect on its chemical properties, or the concentration of the chemically active species. When the electrodes are placed in a thin quartz vessel surrounded by, but not containing, glowing nitrogen, no current passes. When the electrodes are immersed in the glowing gas the current which passes depends on the area of the cathode and the nature of the metal composing it. By heating the gas before it reaches the electrodes to destroy the glow, the conductivity vanishes, but the concentration of chemically active nitrogen remains unchanged, indicating the presence of another modification of nitrogen which is chemically inactive

but able to cause emission of electrons from metals. The conductivity and glow intensity have been correlated with the nature and concentration of the photogens, or other gases, present in active nitrogen.

L. S. THEOBALD.

**Frequency numbers of elements, and existence of a new periodic system.** R. A. SONDER (*Z. anorg. Chem.*, 1930, **192**, 257—285).—Examination of geochemical data for the more commonly occurring elements shows that an element of even atomic number has a higher frequency number, *i.e.*, is more abundant, than either the preceding or succeeding element of odd atomic number, the ratio of the frequency numbers, however, rarely exceeding 100. Assuming this generalisation to be valid for all the elements, it would appear that the accepted frequency numbers of many of the rarer elements are considerably in error. If, now, the frequency numbers, corrected where necessary, are plotted against the atomic numbers for all the elements, the resulting curve is periodic in form, the principal maxima corresponding with the atomic numbers,  $8$ ,  $8+6\times 1^2$ ,  $8+6\times 2^2$ , and  $8+6\times 3^2$ . This is taken to indicate periodicity in the structure of the nucleus, a conclusion which receives further support from the observation that if the atomic number is plotted against the number of "additional electrons" in the atom, *i.e.*, the number obtained by subtracting from the atomic weight twice the atomic number, a stepped curve is obtained, the steps corresponding with  $1\times 4$ ,  $3\times 4$ ,  $6\times 4$ , and  $10\times 4$  additional electrons.

R. CUTHILL.

**Simple system of the elements.** H. HERIBERT (*Z. Elektrochem.*, 1930, **36**, 687—688).—A method of representing the periodic system for demonstration purposes.

H. F. GILLBE.

**Classical quantum theory and X-ray excitation by canal rays and  $\alpha$ -particles.** W. BAND (*Proc. Physical Soc.*, 1930, **42**, 541—546).—Mathematical theory of the experimental data.

W. E. DOWNEY.

**Some problems of nuclear physics according to wave mechanics.** A. C. BANERJI (*Phil. Mag.*, 1930, [vii], **10**, 450—464; cf. this vol., 837).—The theory of  $\gamma$ -ray production is developed on the basis of Schrödinger's equation. It is shown that the assumption of negative energy values leads to wavelengths comparable with those of cosmic rays. The existence of discrete and quantised positive energy values of  $\alpha$ -rays within the potential barrier accounts satisfactorily for the energy values of  $\alpha$ -rays and of nuclear  $\gamma$ -rays actually observed. Tables showing good agreement between observed and calculated characteristics of  $\gamma$ -rays from six elements are given.

F. L. USHER.

**Temperature radiation of non-metallic bodies, and especially of oxides.** F. SKAUPY and G. LIEBMANN (*Z. Elektrochem.*, 1930, **36**, 784—786).—The validity of the relation (A., 1928, 217; this vol., 660) between particle size and absorption has been established for particle sizes below that at which the absorption is a maximum.

H. F. GILLBE.

**Abundance of the chemical elements.** I. NODDACK and W. NODDACK (*Naturwiss.*, 1930, **18**, 757—

764).—Tables of the abundance of the chemical elements in the earth's crust and in meteorites are given. The values for the abundance in the earth's crust are compared with those obtained by Clarke and Washington.

W. R. ANGUS.

**Element classification of Corbino.** A. MAZZUCHELLI (*Gazzetta*, 1930, **60**, 531—534).—An elaboration of Corbino's representation of the elements (*Nuovo Cim.*, 1923, **61**) in which cognisance is taken of the secondary as well as the primary quantum numbers.

F. G. TRYHORN.

**Thermodynamic treatment of stationary states in non-isothermal systems. II.** C. WAGNER (*Ann. Physik*, 1930, [v], **6**, 370—390).—Theoretical. The law put forward previously that in a strictly neutral electrical state the potential of condensed phases with respect to a vacuum is independent of the addition of capillary active substances is extended. The structural change of a surface layer with change of charge and the heating effect bound up with it are analysed. The formulæ obtained agree completely with those of Eastman. A formula for the stationary heat of vaporisation of electrons emitted from a heated cathode is given.

A. J. MEE.

**Transition of kinetic into vibrational energy by collisions with particles.** N. SEMENOV and A. SHECHTER (*Nature*, 1930, **126**, 436—437).—Previous work on the dissociation of hydrogen (this vol., 392) is confirmed. The transition of kinetic into vibrational energy by collision and the reverse process do not readily occur.

L. S. THEOBALD.

**Application of the method of infinite determinants to calculation of "eigen"-values for the Stark effect.** K. BASU (*Z. Physik*, 1930, **64**, 708—713).—Mathematical.

A. B. D. CASSIE.

**Exclusion principle and intramolecular statistics.** L. GOLDSTEIN (*Compt. rend.*, 1930, **191**, 521—522; cf. this vol., 1093).—Fermi's function  $\phi$  showing the distribution of charge within the atom takes account of interactions between electrons and between electrons and the nucleus. If therefore  $\phi_1$ ,  $\phi_2$  are these functions for the two atoms of a molecule  $\phi_1 + \phi_2$  fails to take account of any interaction between the constituents of the two atoms. This is discussed and a method devised for obtaining a nearer approximation for the distribution in such cases.

C. A. SILBERRAD.

**Ultra-violet absorption of tartaric acid solutions: influence of the concentration.** G. BRUHAT and J. TERRIEN (*Compt. rend.*, 1930, **191**, 37—39).—Beer's law is valid for the ultra-violet absorption of tartaric acid solutions in concentrations from 0.16 to 3.3M at 2537 and 2804 Å. Since consistent absorption measurements cannot be made with tartaric acid solutions contained in glass tubes, on account of chemical action, it is necessary to employ quartz tubes. The measurements thus made afford no evidence of the existence in solution of two forms of the acid having different absorptive powers.

H. F. GILLBE.

**Absorption spectra of organic compounds at the temperature of liquid air.** J. B. CONANT and F. H. CRAWFORD (*Proc. Nat. Acad. Sci.*, 1930, **16**,

552—554).—The absorption spectra, in the visible region, of protoporphyrin dimethyl ester, chlorin *e*, bilirubin, and pinacyanol as gels in dilute alcoholic or ethereal solution at the temperature of liquid air have been examined and compared with the spectra obtained at the ordinary temperature. Visual observation shows that the widest bands in porphyrin are thus broken into uniformly spaced narrow bands. The narrow band of protoporphyrin dimethyl ester, with a centre near  $\lambda$  5363 Å., is broken up, at the low temperature, into three components of frequency 18,462, 18,648, 18,909  $\text{cm}^{-1}$ , whilst the wider band, centre at approximately  $\lambda$  5000, yields six components, 19,488, 19,668, 20,107, 20,328, and 20,544  $\text{cm}^{-1}$ .  
J. W. BAKER.

**Form of optical absorption bands of solutions.** W. KUHN and E. BRAUN (*Z. physikal. Chem.*, 1930, B, 9, 426; cf. this vol., 980).—One of the expressions given previously for the absorption curve of a solution is similar to that given by Bielecki and Henri (*Physikal. Z.*, 1913, 14, 516).  
J. W. SMITH.

**Absorption of the silver ion in the ultra-violet of short wave-length.** F. VOLBERT (*Z. physikal. Chem.*, 1930, 149, 382—388).—In the ultra-violet down to a wave-length of about 1770 Å. silver perchlorate in aqueous solution shows selective absorption in the region  $\lambda$  2240, 2105, and 1930 Å. On addition of ammonia the first band disappears and the third is practically completely masked by the characteristic absorption of the ammonia.  
R. CUTHILL.

**Analysis of the  $\beta$ -bands of boron monoxide.** A. ELLIOT (*Proc. K. Akad. Wetensch. Amsterdam*, 1930, 33, 644—648).—The  $\beta$ -bands in the arc spectrum of boron monoxide have been investigated in the region 2400—2600 Å. The 0 $\rightarrow$ 1 and 0 $\rightarrow$ 2 bands have been analysed, and doublet *P* and *R* branches found. The combination differences for the excited state in these two bands agree with each other, and the combination differences for the 0 $\rightarrow$ 2 band agree with those given by Scheib (cf. this vol., 395) for the 0 $\rightarrow$ 2 band in the  $\alpha$ -system of boron monoxide. A comparison of the  $\beta$ -bands excited in the arc and in active nitrogen confirms the view that it is the *R* branch which is present in the latter case, the *P* branch being usually absent.  
O. J. WALKER.

**Molecular absorption of chlorine, bromine, iodine chloride, and iodine bromide in the extreme ultra-violet.** I. H. CORDES and H. SPONER (*Z. Physik*, 1930, 63, 334—344; cf. Spomer and Watson, A., 1929, 978).—The absorption spectra of chlorine, bromine, iodine chloride, and iodine bromide at various pressures are investigated in the region 1560—3000 Å. With chlorine no absorption in this region was observed at pressures from 44 to 90 mm.; with increasing pressure a continuous region of absorption extending from the short wave-length end, reaching to 1800 Å. at 350 mm. and to 1900 Å. at 560 mm., was obtained. The absorption is explained by dissociation occurring by a transition from the ground state to an excited state (cf. Franck, A., 1925, ii, 1077), the liberated atoms having high kinetic energy. The dissociation probably gives rise to a normal atom and an excited atom in a metastable  $2^2P_{1/2}$

state. With bromine the similar region of continuous absorption extended to 1580 Å. at 0.08 mm. pressure, to 1790 Å. at 3.2 mm. and to 2700 Å. at 1.6 atm. This is explained in the same way by a dissociation into a normal bromine atom and a bromine atom in a  $2^2P_{1/2}$  state. A series of diffuse bands at 1657, 1671, and 1685 Å. was also observed at 0.08 mm., a further band at 1697 Å. appearing at 1.1 mm. These bands were probably due to bromine chloride, and in support of this, addition of chlorine was shown to increase the number of bands. The ground vibration quantum for BrCl is thus found to be 435  $\text{cm}^{-1}$ , an excited state existing with a vibration quantum of 495  $\text{cm}^{-1}$ . With iodine chloride a continuous region of absorption from 2300 to 2500 Å. was obtained at low pressures, extending to 2200—2650 Å. at the pressure corresponding with 40°, and at 45° to 2700 Å. and meeting the short wave-length continuous absorption region. The maximum absorption occurred at 2400 Å. A series of bands was observed and measured in the regions 1670—1730 Å. and 1796—1911 Å.; a third system still shorter in wave-length appeared at higher pressures, but it could not be measured as it occurred in the many-line spectrum of hydrogen. A region of continuous absorption extending from the short wave-lengths further towards the long wave-lengths with increasing pressure was given the same interpretation as before. This continuous absorption, extending to 1950 Å. at the high pressures, was also obtained with iodine bromide, and also two systems of bands in the regions 1736—1790 Å. and 1879—1975 Å., and from these the normal vibration quantum for IBr is found to be 270  $\text{cm}^{-1}$ , compared with the 276.2  $\text{cm}^{-1}$  of Loomis and Allen. From spectroscopic data the heat of dissociation of iodine bromide is calculated to be  $41.4 \pm 2.3$  kg.-cal. ( $1.8 \pm 0.1$  volts).  
H. A. JAHN.

**Photochemistry of alkali halide and silver halide crystals.** R. HILSCH and R. W. POHL (*Z. Physik*, 1930, 64, 606—622).—A summary of experimental results. The absorption bands of the colour centres are independent of the colouring wave-length. The number of colour centres per unit volume was determined from the dispersion and absorption of the crystals. The quanta of light absorbed to give this density of colour centres were determined for silver chloride and bromide; 0.4—0.33 centre arises per quantum absorbed. This is comparable with Smakula's value (this vol., 1234) of 0.9—0.6 for alkali halides, but the reaction products are different in the two cases. Irradiation of a crystal can give either irreversible colouring or reversible excitation. The first occurs largely in the colouring of alkali halides, where light absorption transfers an electron from the halide to form a neutral alkali atom, which absorbs within a narrow spectral range; the second occurs largely in the silver halide crystals, where absorption transfers an electron from the halide to no definite atom or ion, and gives absorption in a wide spectral range. Light absorption by a neutral alkali atom may again ionise it, and the colouring disappears, irreversibly. Absorption by the excited colour centres destroys it, but the colour reappears on heating; i.e., this process

is reversible. Experiments on denser colouring and on the colouring of tellurium chloride are described, but no definite conclusions are reached.

A. B. D. CASSIE.

**Influence of temperature on the absorption spectra of alkali halide crystals.** H. FESEFELDT (Z. Physik, 1930, 64, 623—629).—Absorption spectra of rubidium bromide and potassium iodide crystals were determined between 220° and —253°. The position of the shortest wave-length absorption region when measured in volts is displaced almost linearly towards shorter wave-lengths as the temperature diminishes. This displacement of the absorption region with diminishing temperature is almost four times that expected from thermal contraction of the crystal, and explains the large variation of refractive index of the alkali halides with temperature. Absorption bands become sharper at lower temperatures, and new bands due to impurities, or to a modification of the cubic crystal, appear. A. B. D. CASSIE.

**Structure of acetylene derived from spectroscopic investigations.** R. MECKE (Z. Elektrochem., 1930, 36, 803).—The absorption spectrum of acetylene between 7000 and 9000 Å., photographed with a dispersion of 2.6 Å./mm., shows three bands of similar structure at 7887, 7956, and 8623 Å.; a number of new bands have been discovered between 1 and 3  $\mu$ . The acetylene molecule is of an elongated form, since the band structure corresponds with that of a diatomic molecule with one moment of inertia, of which the mean value is  $23.509 \times 10^{-40}$ . On the assumption that the distance between the carbon and hydrogen atoms is the same as in the methane molecule, the distance between the carbon atoms in the acetylene molecule is  $1.19 \times 10^{-8}$  cm. The bands show an intensity variation of 1:3.

H. F. GILLBE.

**Significance and prediction of molecular spectra.** F. HUND (Z. Elektrochem., 1930, 36, 596—599).—The manner in which the various terms and multiplets originate in atomic spectra, and the developments of the rotational, vibrational, and translatory terms in molecular spectra, are described. The origin of the spectrum of a simple diatomic molecule such as that of hydrogen is considered in detail.

H. F. GILLBE.

**Aims and results of band spectra research.** R. MECKE (Z. Elektrochem., 1930, 36, 589—596).—A survey of the later developments of work on band spectra, with special reference to the study of polyatomic molecules, electron states and isotopes, dissociation energy, and photochemistry.

H. F. GILLBE.

**Spectroscopy and molecular structure. I. Determination of thermochemical magnitudes from spectroscopic data.** J. FRANCK (Z. Elektrochem., 1930, 36, 581—589).—The relationships between spectral types and molecular structure are described. The work of dissociation of a molecule may be determined from observations of band spectra in a manner analogous to the calculation of ionisation work from the line spectrum of a monatomic gas, and the method may be applied to unstable molecules which cannot be studied by purely chemical means.

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The theory of photochemical sensitisers and the related question of heats of activation are discussed.

H. F. GILLBE.

**Collision broadening of rotation-vibration spectra of gases.** V. LASAREV (Z. Physik, 1930, 64, 598—605).—The influence of argon, air, hydrogen bromide, and hydrogen chloride on the 3.46  $\mu$  band of hydrogen chloride, on the 3.9  $\mu$  band of hydrogen bromide, and on the 2.73  $\mu$  band of carbon dioxide was investigated. Polar gases increase the percentage absorption more than non-polar gases, but this difference is not great enough to suggest that intermolecular coupling appreciably affects the width of component rotation lines. A. B. D. CASSIE.

**Behaviour of the nuclear oscillation bands of the ammonium radical in the transition region.** L. WILBERG (Z. Physik, 1930, 64, 304—324; cf. A., 1929, 119).—Experiments on the anomalous behaviour of the specific heat of the ammonium halides between —30° and —50° have indicated that there is a change in the salt to a different state, conditioned by a transition in the ammonium radical. Further experiments have been made on crystal structure and the infra-red spectrum of ammonium halides in order to confirm this, the total spectral range covered being 3.10—16  $\mu$  for a temperature of approximately —50°, and 0.80—16.0  $\mu$  for the ordinary temperature. The variation, with temperature, of percentage of light transmitted, or the "isochromate," was determined for the wave-lengths 5.60 and 6.95  $\mu$ . The "isochromates" show a marked change in transmissibility at —30.3°. For the isotherms, three groups of bands could be separated: (a) those of which the intensity was practically unchanged at low temperatures, (b) those of which the intensity increased considerably at low temperatures, and (c) those of which the intensity diminished markedly under the same conditions. It is sought to explain the results on the assumption of the existence of two quantum states of the ammonium radical. For the bands placed in class a it is considered that both states exist; for those in class b it is the lower state that is effective, and for those in class c it is the higher state that is concerned. A. J. MEE.

**Possibility of separating two forms of the ammonia molecule.** R. M. BADGER (Nature, 1930, 126, 310).—Three of the absorption bands of ammonia in the red and the near infra-red afford evidence for two forms of the ammonia molecule. A spectroscopic examination of the gas drawn from a cylinder in different ways and submitted to various treatments failed, however, to detect a separation of the two forms (cf. Baly and Duncan, J.C.S., 1922, 121, 1008).

L. S. THEOBALD.

**Infra-red spectroscopy.** M. CZERNY (Z. Elektrochem., 1930, 36, 615—618).—A historical survey of the development of modern methods of infra-red spectroscopy, with some experimental details.

H. F. GILLBE.

**Raman effect in solutions of weakly ionised salts.** L. A. WOODWARD (Physikal. Z., 1930, 31, 792—793).—Approximately saturated solutions of mercuric chloride and mercuric cyanide were examined, using the mercury lines at 4047 and 4358 Å. Mercuric chloride gave two Raman lines with a wave-number

separation of  $320\text{ cm}^{-1}$ . This is a proof that the molecule is undissociated; otherwise no lines would be found. The cyanide radical has a characteristic Raman spectrum. Dadiou and Kohlrausch (this vol., 664) have examined acetonitrile and benzonitrile, in which the CN group is bound, and found wave-number separations of  $2246$  and  $2227\text{ cm}^{-1}$ , respectively. A concentrated solution of potassium cyanide gave a spectrum with a wave-number difference of  $2081\text{ cm}^{-1}$ , which is attributed to the dissociated CN group. The wave-number separation for a saturated solution of mercuric cyanide was found to be  $2195\text{ cm}^{-1}$ , which indicates that mercuric cyanide is only slightly dissociated. W. R. ANGUS.

**Polarisation of Raman radiation in crystals.** C. SCHAEFER, F. MATOSI, and H. ADERHOLD (Physikal. Z., 1930, 31, 801–802).—The polarisation of Raman radiation has been observed in calcite, sodium nitrate, and gypsum. Small cubes (1 cm. side) of calcite and sodium nitrate and a flat polished piece of gypsum were used. Three axes are taken and the ratio of the intensities of the vibrating components along two axes is calculated for the infra-red wavelength corresponding with each Raman displacement. The results for calcite and sodium nitrate are not in complete agreement with the experimental values of Cabannes (this vol., 15) nor with the theoretical values of Leontovitch (cf. *ibid.*, 664), and reasons for the lack of agreement are given. The water of crystallisation in gypsum shows a different polarisation. W. R. ANGUS.

[Spectra of] solutions of nitrates and nitric acid. A. HANTZSCH (Z. physikal. Chem., 1930, 149, 161–178).—The changes in the spectra of dilute potassium nitrate solutions produced by the addition of foreign electrolytes can be explained as solvation and desolvation effects. Solutions of potassium nitrate in nearly absolute ether absorb continuously, selective absorption occurring only when an appreciable quantity of water is present. The continuous absorption is therefore regarded as the normal absorption spectrum of the unimolecular pseudo-acid  $\text{NO}_2\text{OH}$  and as such can be used in measuring the nitric acid equilibrium. The different forms of nitric acid and the derivatives obtained from them are discussed. J. W. SMITH.

**Raman effect and its significance for the spectroscopic study of molecular structure.** A. SIEKAL (Z. Elektrochem., 1930, 36, 618–631).—A survey of recent work. H. F. GILLBE.

**Raman effect in hydrogen sulphide.** S. BHAGAVANTAM (Nature, 1930, 126, 502).—Liquid hydrogen sulphide shows a single, intense, and sharp line shifted from the exciting mercury radiation by  $2578\text{ cm}^{-1}$ ; with the gas, the line is more diffuse and is shifted by  $2615\text{ cm}^{-1}$ . In both cases, indications of other faint lines or bands adjacent to the exciting radiations and ascribable to a rotational Raman effect were obtained. L. S. THEOBALD.

**Physical methods in chemical laboratories.** XIV. **Raman effect and its applications in organic chemistry.** A. DADIEU (Z. angew. Chem., 1930, 43, 800–805).—A lecture. A. R. POWELL.

**Intensities of the lines in Raman spectra.** S. C. SIKKAR (Indian J. Physics, 1930, 5, 159–168).—The method developed by Merton and Nicholson was used to compare the intensities of the different Raman lines due to carbon tetrachloride, as well as those of the corresponding undisplaced scattered lines. There is a deviation from Rayleigh's fourth-power law, the deviation increasing as the exciting frequency approaches that of the ultra-violet absorption line of the liquid. W. GOOD.

**Raman spectra under high dispersion.** W. M. DABADGHIAO (Indian J. Physics, 1930, 5, 207–217).—The Raman effect in benzene, chloroform, and carbon tetrachloride has been reinvestigated, using a high-dispersion spectrograph. A few new lines have been discovered. Details of the spectra are recorded. The nebulosity accompanying the Hg lines in benzene and chloroform is again noticed; its relation to molecular anisotropy is to be further investigated. W. GOOD.

**Raman spectra of inorganic sulphates and nitrates.** C. RAMASWAMY (Indian J. Physics, 1930, 5, 193–206).—The Raman effect in powdered crystals of inorganic sulphates and nitrates and in their aqueous solutions was studied. It appears that in the crystal lattice the cation has a definite influence on the oscillations within the anion, whilst in the case of the solutions the oscillations remain unaffected whatever is the nature of the free cation. A qualitative explanation of the large intensities of the inactive frequencies in the spectra is given. W. GOOD.

**Raman spectra of crystalline inorganic sulphates.** P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 183–191).—The Raman spectra of 15 inorganic sulphates in the form of coarse powders were examined systematically to obtain information on the influence of the cation on the frequencies and relative intensities of the lines due to the sulphate radical. The strong Raman line at about  $10\ \mu$  ( $\nu_1$ ) was observed in all cases except those of ferrous and nickel sulphates. The line was observed faintly with weaker paramagnetic cations (copper and manganese). In an aqueous solution of ferrous sulphate the line appeared strongly, showing that the magnetic influence of the cation was very small in solution. The shift of  $\nu_1$  for sulphates with cations in the same group of the periodic table follows ionic size when the salts are similarly hydrated. W. GOOD.

**Raman spectra of crystalline inorganic chlorides.** P. KRISHNAMURTI (Indian J. Physics, 1930, 5, 113–128).—Observations of the Raman spectra of crystalline inorganic halides in the form of coarse powders have been made. The results lead to the conclusion that the presence of co-valent linkings is necessary to give the Raman effect. The effect is not shown by compounds possessing only electrovalent linkings. W. GOOD.

**Raman effect with solutions of mercuric chloride and bromide.** H. BRAUNE and G. ENGELBRECHT (Z. physikal. Chem., 1930, B, 10, 1–6).—The Raman effect has been observed with solutions of mercuric chloride and bromide in ethyl acetate and also with aqueous solutions of the chloride, the



influence of the solvent on the frequency being negligible. Values for the characteristic frequencies calculated by means of Eucken's relationship (A., 1925, ii, 207) are in fair agreement with the experimental values. Aqueous solutions of cadmium chloride and iodide exhibit no effect. R. CUTHILL.

**Raman displacements and the infra-red absorption bands of carbon disulphide.** C. R. BAILEY and A. B. D. CASSIE (Nature, 1930, 126, 350).—The absorption spectrum of carbon disulphide vapour has been examined in the region 1–22  $\mu$ . Of the four bands at 878, 1522, 2179, and 2335  $\text{cm}^{-1}$ , the second is probably a fundamental band,  $\nu_2$ . Two additional fundamental frequencies,  $\nu_3=655 \text{ cm}^{-1}$  and  $\nu_1=150 \text{ cm}^{-1}$ , approximately, are postulated. The spectra are summarised. Two of the bands have been resolved into *P* and *R* branches with a frequency difference of 12–13  $\text{cm}^{-1}$ . Carbon disulphide is a rectilinear molecule with one moment of inertia, approximately  $312 \times 10^{-40} \text{ g.-cm}^2$ .

L. S. THEOBALD.

**Relation between the Raman spectra and the structure of organic molecules.** D. H. ANDREWS (Physical Rev., 1930, [ii], 36, 544–554).—Theoretical. The type of vibration in the molecule with which an observed Raman frequency corresponds is identified on the basis of certain assumptions regarding the intramolecular forces, by which the observed frequencies may be regarded as due to the variation in mass of the atoms concerned and their space relation. The number of Raman lines and respective frequencies can thus be calculated for any compound. Fair agreement with experiment for a number of compounds is shown.

N. M. BLIGH.

**Raman spectra of the mercaptans.** S. VENKATESWARAN (Indian J. Physics, 1930, 5, 219–236).—A study of the Raman spectra of methyl, ethyl, propyl, butyl, isobutyl, isoamyl, and phenyl mercaptans has been made and the results are recorded. A prominent line appears in all the spectra at about 2573  $\text{cm}^{-1}$  and is attributed to the SH oscillation. Two strong frequencies at about 659 and 739  $\text{cm}^{-1}$  are also present and are attributed to the oscillations of the CS group. Among the higher members of the aliphatic mercaptans the spectra show a number of broad bands the origin of which may be supposed to lie in the C–C oscillations. Unlike the groups C–O and C=O, the groups C–S and C=S (the latter in carbon disulphide) show no large difference in magnitude of their oscillation frequencies. The results are compared with the infra-red absorption data.

W. GOOD.

**Raman effect and crystal structure of diamond.** S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 169–182).—A discussion of previous results (this vol., 1092) of a study of the Raman effect in 9 different specimens of diamond is given in relation to crystal structure, infra-red absorption, specific heat, colour, and other physical properties.

W. GOOD.

**Raman spectra of aliphatic amines and alcohols.** S. VENKATESWARAN and S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 129–143).—Results of investigations of the Raman effect in methylamine, ethylamine, and triethylamine and in

methyl, ethyl, propyl, and the butyl alcohols are given. A comparison is made with existing data for paraffins and fatty acids, attention being specially directed to the characteristic common configurations of the substances. The viewpoint that the prominent frequencies are due to the particular linkings in a radical, whilst the less conspicuous ones are due to the group as a whole, is adopted. W. GOOD.

**Raman effect in organo-metallic and heterocyclic compounds.** S. VENKATESWARAN (Indian J. Physics, 1930, 5, 145–158).—Raman spectra of zinc methyl, zinc ethyl, thiophen, and pyrrole have been examined. The origins of the various Raman lines are indicated. The similarities and differences in the spectra of  $\text{SO}_2$  and  $\text{ZnX}_2$  are discussed.

W. GOOD.

**Splitting of spectral lines at scattering of light by liquids.** E. GROSS (Nature, 1930, 126, 400).—Further details and experiments are described (cf. this vol., 1237).

L. S. THEOBALD.

**Intensity of lines in the Raman effect in diatomic molecules.** E. SEGRÉ (Atti R. Accad. Lincei, 1930, [vi], 9, 825–831).—Excellent agreement is found between experimental values of the intensity of the Raman lines for oxygen and those calculated by the application of quantum mechanics. From a microphotometric determination of the maximum of intensity the value of  $h/k$  may be determined within 10%.

F. G. TRYHORN.

**Fluorescence in organic compounds.** S. DUTT (J. Indian Chem. Soc., 1930, 7, 505–508).—Quinine, resacetophenone, anthracene, methylacridine, cosin, anthranilic acid, and dicyanoquinol become non-fluorescent on exhaustive purification. With the exception of dicyanoquinol, which under no conditions regains its fluorescence, they recover on keeping in air for periods varying from several days to a few years or on heating at their m. p. for a short time. Fluorescein on exhaustive purification loses its fluorescence to a very considerable extent, but not entirely. It recovers completely on heating at 200° for 10 min., or when a current of air is passed through the alkaline solution for 12 hrs. M. p. given for the highly purified substances are a little higher than those usually recorded.

H. A. PIGGOTT.

**Reversible phototropic phenomena.** J. R. MOURELO (Anal. Fis. Quim., 1930, 28, 572–578).—The change of colour of phosphorescent calcium sulphide from greyish-white to violet on exposure to direct light has been demonstrated to be a true case of reversible phototropy.

H. F. GILLBE.

**Properties of resistance cellules.** W. SCISLOWSKI (Bull. Acad. Polonaise, 1930, A, 151–158).—The method used was that of previous workers (Reboul, A., 1926, 1072; 1927, 604), except that the current traversing the pastille (mercuric sulphate, 5–7 mm. thick and 15 mm. diam.) was measured simultaneously with the intensity of radiation. The effect varied with the material of the electrodes. With silver or brass, radiation was emitted only when the perforated electrode was connected with the anode; with aluminium, when connected with either pole, but

much more strongly when this was the cathode. Luminescence is visible in the portion of the pastille emitting radiation, at pressures below 12 cm. of mercury, increasing as pressure decreases, and developing into scintillation below 6 cm. Curves showing variation with time of current, and of intensity of radiation, for the different electrodes, and for current for different *P.D.* are given. The current in 2–4 min. attains a maximum which increases with the *P.D.*, but falls to approximately the same limit in 7–8 min., irrespective of the *P.D.* C. A. SILBERRAD.

**Extinction of calcium phosphors, with particular reference to mixed phosphors.** F. BANDO (Ann. Physik, 1930, [v], 6, 434–457).—A number of CaS-Bi- $\alpha$  phosphors were prepared with slight modifications of temperature and cooling. The addition of small quantities of fluoride to these phosphors gave a light-sum three times as great as that of a phosphor containing no fluoride. The rate of cooling plays an unimportant part in the value of the light-sum. The values of the maxima of the long-wave extinction of these CaS-Bi- $\alpha$  phosphors do not seem to be influenced by the methods of preparation, although other properties of the phosphors are considerably affected.

Calcium oxide-sulphide mixed phosphors are compared with pure phosphors. The total light-sum of mixed phosphors is very small. The Bi- $\alpha$  light-sum in oxide phosphors is very much less than in calcium sulphide, but with Bi- $\alpha$  the colour of the afterglow of oxide and sulphide centres is not very different. In mixed phosphors (CaO:CaS=1:1) the sulphide extinction is diminished; each of the oxide centres is increased five times compared with the trustworthy value for the pure phosphor. A sulphide phosphor prepared in an atmosphere of sulphur exhibits the same extinction as ordinary calcium sulphide. The results are compared with those obtained by previous investigators. The centres create a mutual impedance in the absorption of the extinguishing light. Irrespective of the method of preparation, all phosphors having the same central configuration give identical values of extinction; these values are also independent of the total light-sum of the phosphor and of the mutual separation of neighbouring centres. The influence of the excitation state of different centres on each other has been considered. Some subnormal bismuth phosphors and some pure and mixed copper phosphors are discussed. W. R. ANGUS.

**Phosphorescence of gelatin and fluorescein at low temperatures.** K. OCHIAI (Bull. Chem. Soc. Japan, 1930, 5, 203–209).—Gels of photographic gelatin of different concentration were exposed to a reproducible light source while immersed in a cryostat which could be cooled to the temperature of liquid air. After the removal of the light source the duration of the period of phosphorescence, determined visually, increased suddenly for all gels at a temperature of 220° Abs. and further cooling had no effect. Increasing concentration of gelatin raises this temperature. This concentration effect is correlated with the manner of freezing of the gelatin. Fluorescein was examined in a similar manner in various media, chiefly acidic substances. The phosphorescence observed is ascribed

to the presence of complex compounds in the media used. J. O. CUTTER.

**Luminescence at the electrodes during electrolysis.** M. FRAYMANN (Rech. et Inv., 1930, 11, 36–41; Chem. Zentr., 1930, i, 1902).—Three phenomena are differentiated: electrolytic luminescence confined to a thin layer surrounding the electrodes and affording a continuous spectrum, electrolytic sparking, and cathodic violet luminosity. The last two depend on the presence of a thin gaseous layer. With sulphuric acid as electrolyte the arc spectrum of the cathode metal and the *C* and *F* lines of hydrogen may be observed. A. A. ELDRIDGE.

**Ionisation of carbon dioxide by electron impact.** H. D. SMYTH and E. C. G. STUECKELBERG (Physical Rev., 1930, [ii], 36, 472–477; cf. Kallmann, this vol., 514).—Using an improved mass spectrograph, of glass except for the electrodes, and designed to reduce thermal dissociation to a minimum, the products of ionisation in carbon dioxide were studied. Primary ions were  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{O}^+$ , and  $\text{C}^+$  appearing at 14.4, 20.4, 19.6, and 28.3 volts, respectively; a secondary product was  $\text{O}_2^+$  at 20.0 volts. Experimental minimum values for the ionisation potentials were in good agreement with calculation. N. M. Blich.

**Ionisation of nitrous oxide, and nitrogen dioxide by electron impact.** E. C. G. STUECKELBERG and H. D. SMYTH (Physical Rev., 1930, [ii], 36, 478–481).—With the apparatus previously described (cf. preceding abstract) the products of ionisation in nitrous oxide and nitrogen peroxide were investigated. In the latter gas  $\text{NO}_2^+$ ,  $\text{N}^+$ , and  $\text{O}_2^+$  were found as primary ions; owing to thermal dissociation, ionisation potentials could be determined only approximately. In nitrous oxide the ionisation potentials 12.9, 16.3, 15.3, and 21.4 were found for the primary ions  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{N}^+$ , respectively, and are in good agreement with calculated values. N. M. Blich.

**Effect of gas pressure on photo-electric conductivity of organic dyes.** A. PETRIKALN (Z. physikal. Chem., 1930, B, 10, 9–21).—The photo-electric conductivity of solid triphenylmethane dyes in thin layers is largely dependent on the nature and pressure of the gas with which they are in contact. The conductivity of most of the dyes examined increased as the gas pressure decreased, and was greater in hydrogen than in oxygen at the same pressure. With the eosins and erythrosins, however, the conductivity increased with increasing pressure, and was greater in oxygen than in hydrogen. These effects are attributed to adsorption of gas by the dye, and if the conductivity of the eosins and erythrosins is assumed to be directly proportional and that of the other dyes inversely proportional to the amount of gas adsorbed, the results correspond with the requirements of the Freundlich isotherm. R. CUTHILL.

**Electrostatic impedance of free rotation.** L. MEYER (Z. angew. Chem., 1930, 43, 747–749).—A brief discussion of the above problem with special reference to the experiments of Debye and of Wierl on  $\alpha\beta$ -dichloroethane. F. G. TRYHORN.

**Dielectric constant of supercooled sulphur and of some solutions of sulphur.** S. ROSENTHAL (Bull. Acad. Polonaise, 1930, A, 247—248; cf. A., 1929, 242).—Allowing for an error in the density of molten sulphur, its polarisation is corrected to 0.2628—0.2630; the polarisation of soluble sulphur is calculated to be approximately 0.318. C. A. SILBERRAD.

**Electric moments of some organic molecules in benzene solution.** A. E. EIDE and O. HASSEL (Tids. Kjemi, 1930, 10, 93—95).—A series of results of determinations of electric moments of various organic molecules in benzene solution is given. The small value obtained for *p*-nitrobenzonitrile ( $0.72 \times 10^{-18}$ ) seems to be due to a negative effect of the nitrogen when associated with carbon. The two hydrobenzoin isomers were investigated as examples of two compounds standing to each other in the relationship of *meso*-form and racemic form. The moments are almost the same. The dipole moment of *p*-chloroaniline is  $2.9 \times 10^{-18}$ , whilst the calculated value is about  $3.0 \times 10^{-18}$ . A. J. MEE.

**Electric moments of organic molecules. IV.** O. HASSEL and E. NÆSHAGEN (Tids. Kjemi, 1930, 10, 81—84).—The structure of ring systems is discussed on the basis of the electric moments of the molecules. Results are given for a number of cyclic compounds in benzene solution, and these are in general agreement with those of other observers. The moments of some methylated sugars are given, but from these data it is not possible to arrive at any accurate conclusions concerning the structure of sugars. For thiophen, the maximum value found for the electric moment was  $0.63 \times 10^{-18}$ , which may be compared with that for furan. The moment of carvone is  $3.17 \times 10^{-18}$ , which is somewhat different from that for menthone ( $2.80 \times 10^{-18}$ ). A. J. MEE.

**Dielectric constant of carbon dioxide as a function of temperature and density.** F. G. KEYES and J. G. KIRKWOOD (Physical Rev., 1930, [ii], 36, 754—761).—The dielectric constant of carbon dioxide was measured, using a heterodyne beat method, for a wide range of densities at temperatures of 35°, 70°, and 100°, and for the liquid at 0°. The Clausius-Mosotti function is independent of temperature, but increases slowly with increasing density. N. M. BLIGH.

**Electric moments of certain molecules. H.** MÜLLER and H. SACK (Physikal. Z., 1930, 31, 815—822).—Dilute solutions of a number of substances have been investigated in non-polar solvents (carefully dried and distilled benzene and hexane), using an apparatus which is fully described. A table is given showing the concentrations, the densities, dielectric constants, refractive indices, molecular polarisations, and molecular refractions of the solutions. The values for bromobenzene, chlorobenzene, and methylene chloride are in good agreement with those of previous investigators. Eight organic acetates show electric moments of the same order of magnitude. The values for 6-di- and tri-substituted halogen derivatives of methane are discussed; the agreement with the results of Mahanti and Das-Gupta (A., 1929, 994) is not good. Cetyl alcohol, 9-bromoanthracene, and *trans*- and *cis*-dichloroethylene have also been

measured. Solutions of iodine in benzene and carbon disulphide have been found by Williams (A., 1928, 578) to possess an electric moment approximately  $1.2 \times 10^{-18}$ ; this value has been verified for a benzene solution (red in colour). It has been found that solutions of iodine in hexane and cyclohexane (violet in colour) have a zero moment. W. R. ANGUS.

**Dielectric polarisation of liquids. X. Polarisation and refraction of the normal paraffins.** R. W. DORRTE and C. P. SMYTH (J. Amer. Chem. Soc., 1930, 52, 3546—3552).—Refractive indices and mol. refractions at 20°, dielectric constants, densities, and polarisations at temperatures between -90° and 210° of the normal paraffins in the series pentane to dodecane are tabulated. An approximately linear increase of polarisation with rise of temperature, about 1% per 100° rise, is observed in all cases. The polarisation of the CH<sub>2</sub> groups is constant throughout the series. The electric moments are zero within the accuracy of experiment and it is concluded that the valency linkings of alkyl radicals have no polarity detectable from electric moments arising from them. J. G. A. GRIFFITHS.

**Dielectric constant of liquid bromine. D.** DOBORZYNSKI (Bull. Acad. Polonaise, 1930, A, 97—111).—A modification of the resonance method of Jezewski (J. Phys. Radium, 1920, [vi], 3, 293) was used. The dielectric constant ( $\epsilon$ ) thus determined is  $3.334 \pm 0.019$  at 0°, and for the interval 0—53.8° is  $1.0730 + 617.42/T$  ( $T$  in Abs.). These results differ by about 3% from those of Anderson (A., 1928, 347). The specific polarisation,  $p = (\epsilon - 1)v/(\epsilon + 2)$ , where  $v$  is specific volume, is given by  $pT = 0.10307T + 9.338$ . Bromine is a dipole liquid, with moment  $0.49 \times 10^{-18}$ . C. A. SILBERRAD.

**Influence of strong electric fields on the dielectric constants of liquids. H.** GUNDERMANN (Ann. Physik, 1930, [v], 6, 545—573).—Measurement of the dielectric constant of a number of liquids and liquid mixtures by the Wien-Malsch method demonstrates that the dielectric constant diminishes with the square of the applied field strength, in accordance with the Debye theory. For liquids of high dielectric constant the effect is less than is required by the simple theory, whilst for mixtures of polar liquids the effect is anomalous and bears no direct relationship to the dielectric constant of the components, owing to the interaction of the dipoles; the effect is entirely absent from benzene, owing to its freedom from dipoles. The influence of concentration on mixtures of ethyl or butyl alcohol with benzene shows the effect with the latter to be in accordance with the Debye theory, whereas the ethyl alcohol mixtures are anomalous; at low concentrations too high values are obtained, whereas at high concentrations the discrepancy is in the reverse direction. Association in the alcohol is the probable cause of the anomaly, especially as the pure alcohol exhibits a much smaller effect than theory would require. H. F. GILLBE.

**Relationship between the dielectric and optical properties of substances having the sodium chloride lattice. J.** ERRERA [with B. M. BLOCH] (Z. Elektrochem., 1930, 36, 818—823).—The total polarisation of the alkali metal halides increases with

increase of the at. wt. of both the anion and the cation. The atomic polarisation has been calculated in each case with the aid of Spangenberg's values for the electronic polarisation. The proportion of the total dielectric constant contributed by atomic vibrations decreases with increase of the at. number of the anion, and, in the case of the bromides and iodides, with increase of that of the cation; the chlorides and fluorides show irregular variations. Comparison of the characteristic infra-red frequencies calculated by the dispersion formula from the observed values of the dielectric constant with those calculated by Born on the theory of electrostatic cohesion permits the determination of the factor  $p$  of the infra-red term of the dispersion formula, and enables also the infra-red branch of the dispersion curve to be constructed.

H. F. GILLBE.

**Electric moments.** O. HASSEL (Z. Elektrochem., 1930, 36, 735—737; cf. this vol., 979, 1093).—Measurements have been made of the moments of two kinds of polar molecules simultaneously present in solution in solvents free from dipoles, such as benzene, and also of dipolar substances in dilute solution in solvents containing dipoles. For the first case the equation  $c_1 P'_{A+O} + c_2 P''_{A+O} = 1000[(e-1)/(e+2) - (e'-1)/(e'+2) - (n^2-1)/(n^2+2) - (n'^2-1)/(n'^2+2)]$  where  $c_1$  and  $c_2$  are the concentrations of the two solutes,  $P_{A+O}$  the apparent sum of the atomic and orientation polarisations, when the solutes are present separately, and  $e$  and  $e'$ , and  $n$  and  $n'$  are the dielectric constants and refractive indices of the solutions and solvents, respectively, has been derived. Comparison of the value of the left-hand side of the equation, calculated from measurements of the moments, with that of the right-hand side, calculated from measurements of  $e$  and  $n$ , shows that in general, and, e.g., for benzene solutions of chloroform containing chlorobenzene, the moments of the two solutes have no disturbing influence on one another; the reverse is true for benzene solutions of chloroform containing ether. In view of the general absence of such a disturbing factor the possibility of employing solvents containing dipoles in the measurement of electric moments has been investigated; provided that certain precautions in the choice of solvents be taken, the procedure yields satisfactory results.

H. F. GILLBE.

**Variation of the ionisation current in ceresin with temperature.** D. N. NASLEDOV and P. V. SCHARAVSKI (Ann. Physik, 1930, [v], 6, 574—580).—The variation with temperature of the ionisation current in ceresin (A., 1929, 1356; this vol., 984) at an applied potential of 985 volts is expressed by the equation  $I_T = I_0 e^{\alpha T}$ , where  $I_T$  is the current at  $T^\circ$  and  $\alpha$  is a constant. The quantity of electricity furnished by the dielectric also increases with rise of temperature, indicating that the current effect is due primarily to an increase of ionisation at the higher temperature.

H. F. GILLBE.

**Passage of electric current through solid paraffin in the dark and during irradiation by X-rays.** V. M. TUTSCHKEVITSCH (Ann. Physik, 1930, [v], 6, 622—636).—Time-current curves show the existence of residual currents in paraffin in the

dark which remain constant for periods up to 48 hrs. after the application of the *E.M.F.* The relationship between the current at any time and the applied potential is not linear for short times, although it becomes nearly linear at 13 min. after the time of application; the polarisation *E.M.F.* is therefore proportional to the applied potential only when the former has attained its maximum value. Both for conduction in the dark and during irradiation the similarity principle of Kurtshatov has been verified for paraffin thicknesses between 5 and 20 mm. On irradiation by X-rays after the steady state has been attained, the current-time curve rises rapidly to a constant value, and is not influenced by further irradiation, indicating that the conduction is not a surface phenomenon. As observed by Nasledov and Scharavski for ceresin (A., 1929, 1356) the ionisation current of paraffin is independent of the period between the application of the field and the commencement of the irradiation, and, further, Ohm's law is valid during the irradiation for all thicknesses of the dielectric.

H. F. GILLBE.

**Magnetic birefringence of phenol, naphthalene, and phenanthrene liquefied by fusion.** C. SALCEANU (Compt. rend., 1930, 191, 487—488).—The author's method (this vol., 668) has been applied to the measurement at 47—169° of (1) the ratio ( $\beta g/\beta y$ ) of the birefringences of phenol, naphthalene, and phenanthrene for the green and yellow mercury lines; (2) the ratio of the latter value to the birefringence of nitrobenzene (at 20°); (3) the Cotton-Mouton constant ( $C_m$ ) taking the value  $2.46 \times 10^{-12}$  for nitrobenzene at 20°; (4) the quotient  $C_m/\text{density}$ . The values  $\beta g/\beta y = 1.045$  (phenol at 49°), 1.10 (naphthalene at 106°), and 1.075 (phenanthrene at 104°) were found.  $\beta$  increases with increase in the number of benzene nuclei in the molecule, but decreases only slightly with rise in temperature, the resulting curves (straight lines for phenol and phenanthrene) being characteristic of the normal thermal variation of  $\beta$ .

J. GRANT.

**Refractivity of anhydrous alkali hydrogen phthalates.** E. WIDMER (Z. Krist., 1930, 72, 442—446; Chem. Zentr., 1930, i, 1900—1901).—The potassium salt is abnormal; optical data are recorded.

A. A. ELDRIDGE.

**Light refraction and mol. volume of crystalline salts.** W. HERZ (Z. anorg. Chem., 1930, 191, 320—321).—For 12 univalent halides the mol. volume calculated from the refraction data of the solid salt ( $V_n$ ) is compared with the mol. volume obtained by addition of the ionic volumes ( $V_i$ ). The ratio  $V_n : V_i$  has a value between 1.3 and 2.1.

O. J. WALKER.

**Geometrical configuration of molecules showing a structural group periodicity.** R. O. HERZOG and O. KRATKY (Naturwiss., 1930, 18, 732—734).—A macro-molecule is defined as a complex formed of principal valency chains or rings characterised by a periodicity in their structure. The repetition of a group occurs at constant intervals (a binding group) and between these periodical groups lie groups either identical or chemically related (a structural group kernel). The binding group divides into two parts, the halves of two neighbouring ones going with the

structural group kernel to form the structural group itself. One-, two-, and three-dimensional molecules are differentiated depending on the form of the line skeleton obtained by uniting the centres of gravity of neighbouring structural groups. For a one-dimensional molecule it is a single line, for a two-dimensional molecule the lines are on a single surface. All other cases are three-dimensional.

J. E. MILLS.

**Geometrical configuration of the molecules showing structural group periodicity.** R. O. HERZOG and O. KRATKY (*Naturwiss.*, 1930, 18, 788).—The authors' definition of the binding groups (cf. preceding abstract) is supplemented, periodically recurring groups which are homologous or isomeric being differentiated from those which are identical with one another.

P. W. CLUTTERBUCK.

**Representation of the dynamic properties of molecules by mechanical models.** C. F. KETTERING, L. W. SHUTTS, and D. H. ANDREWS (*Physical Rev.*, 1930, [ii], 36, 531–543).—Assuming that the intramolecular forces lie along lines associated with the chemical linkings, and that for small vibrations they obey Hooke's law and have the mechanical character of spiral springs, models have been constructed for some of the simpler non-polar molecules, the forces and masses being represented by steel balls and spiral springs. The characteristic frequencies correspond closely with those observed in Raman spectra, and the Raman lines can be identified with definite types of motion of particular atoms in the molecule, in agreement with the view that Raman lines correspond closely with characteristic fundamental molecular frequencies.

N. M. BLIGH.

**Elastic character of the homopolar chemical linking.** R. C. YATES (*Physical Rev.*, 1930, [ii], 36, 555–562; cf. preceding abstract).—Mathematical. Dynamical equations of motion are set up for systems of three particles, assuming the forces of restitution to be elastic. Calculated wave-numbers for the molecules  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{EtOH}$  are compared with observed data from Raman spectra, and fair agreement is obtained.

N. M. BLIGH.

**Small vibrations of six particles in a system analogous to the benzene ring.** R. C. YATES (*Physical Rev.*, 1930, [ii], 36, 563–567; cf. preceding abstract).—Mathematical. The system of six particles is allowed to vibrate under certain restrictions, assuming an elastic nature for the restoring forces. Frequencies of vibration are obtained and compared with Raman data.

N. M. BLIGH.

**Modern molecular theories.** H. A. KRAMERS (*Chem. Weekblad*, 1930, 27, 406–411).—The earlier theories of molecular structure are reviewed and the manner in which modern ideas of quantum mechanics have developed is discussed.

H. F. GILLBE.

**Quantum theory of homopolar compounds.** W. HEITLER (*Z. Elektrochem.*, 1930, 36, 640–641).—Chemical combination and valency are interpreted in terms of atomic structure. The significance of energy of activation is demonstrated by consideration of the forces operating when the hydrogen atoms in the hydrazine molecule are removed to infinite

distance, and when they again approach the nitrogen residue.

H. F. GILLBE.

**Quantum theory of the double linking and its stereochemical relationships.** E. HÜCKEL (*Z. Elektrochem.*, 1930, 36, 641–645).—The nature of the double linking is described in terms of the electronic configuration of the component atoms, and the modern view is compared with the earlier tetrahedral conception of van 't Hoff.

H. F. GILLBE.

**Nature of extramolecular forces.** D. H. ANDREWS (*Coll. Symp. Ann.*, 1930, 7, 119–128).—Comparison of observed and calculated values of specific heat indicates that the attractive force around the molecule of an organic compound becomes small, and insufficient to hold two molecules together, when the molecules have been displaced from their normal positions in the lattice by a distance comparable with the diameter of a carbon atom. Purely chemical forces cannot extend over a sufficiently great distance to produce a multimolecular adsorbed layer.

CHEMICAL ABSTRACTS.

**Division and calculation of the parachor.** A. SIFFEL (*Ber.*, 1930, 63, [B], 2185–2188).—The parachor  $P$  of a compound  $\text{C}_x\text{H}_y\text{O}_z\text{N}_t$  may be calculated from the expression  $P = wc_2 + xh_2 + yo_2 + zn_2 + 23.2$ . The new constants,  $c_2$ ,  $h_2$ ,  $o_2$ ,  $n_2$ , can be calculated from any non-cyclic compounds without reference to the mode of linking. Increments are taken into account only with cyclic structures, and are always negative (three, four, five, and six members have the values  $-6.5$ ,  $-11.6$ ,  $-14.7$ ,  $-17.1$ , respectively). The method of calculation accords with experience except in the cases of mercury and the thallous compound of ethyl acetoacetate. If the atomic constants are increased by 23.2, the expression becomes  $P = wc_3 + xh_3 + yo_3 + zn_3 - 23.2v$  and the factor  $v$  is the number of linkings in a non-cyclic compound with  $w+x+y+z$  atoms. For cyclic compounds the value of  $v$  increases by 1 for each ring present. If 23.2 for each pair of external electrons is subtracted from the atomic constants calculated by the modified equation, the "core constants" of the atoms are obtained. The new possibilities of division show that the octet rule is not necessarily a guiding principle.

For practical purposes the first modified mode of calculation is recommended on account of its extreme simplicity. The value of the parachor lies essentially in the detection of ring formation and in the examination of molecular formulæ in particular instances.

H. WREN.

**Theory of molecular forces in dipole gases.** H. MARGENAU (*Z. Physik*, 1930, 64, 584–597).—Theoretical. London's method is used to calculate the exchange energy of rigid rotating dipoles in different energy levels, and from this the second virial coefficient for low temperatures is determined. Polarizable and quadrupole molecules are also considered. In all cases the quantum value of this virial coefficient coincides, at sufficiently high temperatures, with the classical value.

A. B. D. CASSIE.

**Aromatic disulphides and Sugden's parachors.** IV. S. S. BHATNAGAR and B. SINGH (*J. Indian Chem. Soc.*, 1930, 7, 663–668).—The following parachors

were determined from density and surface tension measurements made at various temperatures in the fused state: diphenyl disulphide, 477.9; 4:4'-dichlorodiphenyl disulphide, 550.6; 4:4'-dibromodiphenyl disulphide, 575.9; di-*p*-tolyl disulphide, 552.9; 4:4'-dimethoxydi-*m*-tolyl disulphide, 666.1; di- $\beta$ -naphthyl disulphide, 689.6; dibenzyl disulphide, 557.1, and 2:2'-dinitrodibenzyl disulphide, 665.7. These values are in good agreement with those calculated for the structure (SR)<sub>2</sub>. H. BURTON.

**X-Ray examination of higher normal primary alcohols.** T. MALKIN (J. Amer. Chem. Soc., 1930, 52, 3739—3740; cf. this vol., 1161).—Crystals of normal primary alcohols containing numbers of carbon atoms between 12 and 25, inclusive, per molecule have long spacings which increase with number of carbon atoms and may be arranged in two linear series. Molecules with less than 18 or an odd number of carbon atoms belong to one series in which the chains of carbon atoms are vertical, whilst molecules with an even number of carbon atoms greater than 16, inclusive, constitute the other series in which the long axes of the molecules are tilted at an angle of 55° 40'. Thus the C<sub>16</sub> and C<sub>18</sub> alcohols exhibit both spacings. The alcohols crystallise in double molecules with the hydroxyl groups in juxtaposition. J. G. A. GRIFFITHS.

**Corresponding state of maximum surface tension of saturated vapours.** J. L. SHERESHEFSKY (J. Physical Chem., 1930, 34, 1947—1950).—The surface tension of a saturated vapour is connected with temperature by the expression  $d \log \rho_v / dT = 0.4343 / [T_c(1 - T_m/T_c)]$ , where  $T_m$  is the absolute temperature at which the surface tension of the saturated vapour is a maximum and  $\rho_v$  is the density of the saturated vapour. For all substances  $T_m/T_c$  is 0.910, and  $d \log_e \rho_v / d \log_e T$  is a universal constant 10.1. L. S. THEOBALD.

**Determination of crystallite orientation.** G. TAMMANN (Inst. Metals, Sept. 1930. Advance copy. 45 pp.).—The three principal methods used at present for the determination of the orientation of the crystallites in metals are described and their relative value in certain cases is discussed. Recent work on the crystallographic behaviour of numerous metals during mechanical working and heat treatment is reviewed in detail and critically discussed.

A. R. POWELL.

**Lattice distortion as a factor in the hardening of metals.** W. L. FINK and K. R. VAN HORN (Inst. Metals, Sept., 1930. Advance copy. 7 pp.).—Measurements of the Rockwell hardness and examination of the X-ray diffraction patterns of an externally stressed aluminium alloy and of an  $\alpha$ -brass show that lattice distortion can be accompanied by an appreciable decrease in hardness. Thus for duralumin the decrease of hardness rises with increasing stress to a maximum of 6.8% at the elastic limit, whilst the diffraction rings become gradually broader. In some cases distortion of the lattice caused by stresses set up during quenching does not produce a hardening effect, and in other cases lattice distortion reaches a maximum and partly disappears before

the maximum hardness is reached during the process of age-hardening.

A. R. POWELL.

**Simple graphical method of interpreting Debye-Scherrer diagrams.** W. EULITZ (Z. Physik, 1930, 64, 452—457).—It is shown how, by use of a nomograph, Debye-Scherrer diagrams due to cubic crystals are readily interpreted. A. B. D. CASSIE.

**Determination of the inner structure of liquids by means of X-rays.** P. DEBYE and H. MENKE (Physikal. Z., 1930, 31, 797—798).—Knowledge of the intensity of the radiation scattered when a liquid is irradiated with X-rays and of the probability of two atoms of a monatomic liquid being in a unit volume has been used in determining the inner structure of mercury. The distances from a central atom can be obtained from the values of the probability factor. W. R. ANGUS.

**Metastability of matter.** E. COHEN [with H. ADDINK] (Z. Elektrochem., 1930, 36, 726—727).—Red and yellow lead monoxides are ill-defined mixtures of two modifications. Pure specimens of the red form, which is stable up to 587°, and of the yellow form, which is stable at lower temperatures, have been prepared. H. F. GILLBE.

**Interferometric determination of the structure of individual molecules.** P. DEBYE (Z. Elektrochem., 1930, 36, 612—615).—The theory of the determination of molecular structure by the X-ray interferometer is described, and measurements with organic compounds such as the four chlorinated derivatives of methane are cited in illustration of the method. H. F. GILLBE.

**Pure crystalline iron for the study of ferromagnetism.** W. GERLACH (Festschr. Heraeus, 1930, 27—33; Chem. Zentr., 1930, i, 2223).—A discussion. A. A. ELDRIDGE.

**Crystalline structure of hydrogen sulphide and of hydrogen selenide.** G. NATTA (Atti R. Accad. Lincei, 1930, [vi], 11, 679—684, 749—754).—A form of X-ray spectrograph applicable to the examination of substances having very low m. p. is described. A fine filament of the substance is obtained on a capillary tube which forms the lower extremity of a Dewar vessel containing liquid ammonia or liquid air by plunging the capillary into the liquid or gaseous substance. The Dewar vessel is then mounted so that the cooled capillary tube has its axis parallel with that of the camera. By these means hydrogen sulphide was examined and found to crystallise in a cubic lattice, with an elementary cell of edge  $5.778 \pm 0.003$  Å., containing 4 mols.; hydrogen sulphide has  $d_{\text{calc.}}^{179} 1.166$ . The intensities of the spectral lines for this substance agree with those calculated on the basis of an ionised molecule.

Hydrogen selenide at  $-170^\circ$  has a cubic structure, with an edge of  $6.020 \pm 0.005$  Å. The unit cell, of volume  $218.2 \times 10^{-24}$  c.c., contains 4 mols.;  $d_{\text{calc.}} 2.456$ . Perfect isomorphism is to be anticipated between these two hydrides in consequence of their identical crystal structure (fluorite type; space-group  $O_h^2$ ) and their approximately equal cell dimensions. As in the case of hydrogen sulphide, the calculated intensities of the spectral lines of hydrogen



selenide agree best with the experimental ones when they are derived on the basis of an ionised molecule.

F. G. TRYHORN.

**Carbides. I. Crystal structure of the carbides  $\text{MeC}_2$ .** M. VON STACKELBERG (Z. physikal. Chem., 1930, B, 9, 437—475).—The crystal structures of the derivatives  $\text{CaC}_2$ ,  $\text{SrC}_2$ ,  $\text{LaC}_2$ ,  $\text{CeC}_2$ ,  $\text{PrC}_2$ ,  $\text{NdC}_2$ ,  $\text{ThC}_2$ ,  $\text{NaHC}_2$ , and  $\text{KHC}_2$  have been determined by the powder method. The evidence indicates a tetragonal face-centred lattice with 4 mols. in the elementary cell. The lattice constants are tabulated. The structures of  $\text{ThC}_2$ ,  $\text{CaC}_2$ ,  $\text{NaHC}_2$ , and  $\text{KHC}_2$  in particular are discussed with respect to the arrangement of the atoms in the primary cell.

J. W. SMITH.

**Crystal grating of iron silicide,  $\text{FeSi}$ .** H. MOLLER (Naturwiss., 1930, 18, 734—735).—X-Ray measurements on iron silicide by the Debye-Scherrer method showed that the atoms are arranged in a single, cubic translation grating with a side of 4.467 Å. The intensity and intensity distribution were measured and results were obtained in good agreement with calculated values. From the values of the intensity the atomic separations of Fe—Si, Fe—Fe, and Si—Si were found to be approximately 2.34, 2.74, and 2.76 Å., respectively.

W. R. ANGUS.

**Structure of cementite.** S. SHIMURA (Proc. Imp. Acad. Tokyo, 1930, 6, 269—271).—The crystal structures of cementite and spiegeleisen were investigated by X-ray examination by the Bragg, Laue, Debye-Scherrer, and the rotating-crystal methods. It was confirmed that the two structures are the same except for a slight contraction in the lattice constants of spiegeleisen. The structural data are given.

W. GOOD.

**Relation between crystal structure and atomic properties in metallic compounds of the transition elements.** A. WESTGREN (Svensk Kem. Tidskr., 1930, 42, 193—203).—A theoretical discussion of the relationships between crystal structure and atomic properties shown by the nitrides, carbides, borides, and hydrides of Bohr's transition elements, and also by the metallic alloys formed by them.

H. F. HARWOOD.

**Internal structure of solid salts of oxy-acids at high temperatures. I. Theoretical foundations.**

**II. Tungstates and molybdates of bivalent metals.** W. JANDER (Z. anorg. Chem., 1930, 192, 286—294, 295—316).—I. A discussion of the lattice structure and reactivity in the solid state of salts of oxy-acids leads to the conclusion that it is probable that at high temperatures these salts have the "double-oxide" lattice, i.e., the oxygen atoms are so placed relatively to the other atoms that the effective constituents of the lattice are largely the acid and basic oxides, instead of the atoms or ions, as at lower temperatures.

II. This supposition has been verified for various molybdates and tungstates from the results of measurements of the conductivity in the solid state at 600—1100°, taken in conjunction with the results of diffusivity and reactivity measurements previously reported (this vol., 1006). Nickel, zinc, and manganese tungstates, and probably also magnesium

tungstate, are purely electronic conductors, and their diffusivity and reactivity point conclusively to the double-oxide lattice. Cadmium tungstate, on the other hand, is a mixed conductor, and its lattice possibly contains both ions and the oxides. The lattices of the tungstates and molybdates of calcium, strontium, and barium appear to be purely ionic, even at 1100°. Magnesium, zinc, manganous, and nickel molybdates, however, probably have the double-oxide lattice, although conductivity data are not available.

R. CUTHILL.

**Crystal structure of sodium perchlorate.** W. H. ZACHARIASEN (Z. Krist., 1930, 73, 141—146; Chem. Zentr., 1930, i, 2684).—The rhombic unit cell, containing 4 mols., has  $a$  6.48,  $b$  7.06,  $c$  7.08 ( $\pm 0.02$ ) Å.; space-group  $V_7^7$ .

A. A. ELDRIDGE.

**Crystal structure of sodium uranyl acetate.** W. F. DE JONG (Physica, 1930, 10, 101—108; Chem. Zentr., 1930, i, 2684).—The unit cell has  $a$  10.960  $\pm$  0.005 Å.

A. A. ELDRIDGE.

**Isomorphism and chemical homology.** P. C. RAY (Nature, 1930, 126, 310—311).—From a consideration of the ionic radii of certain elements and other factors, predictions of cases of isomorphism are possible. Sarkar has obtained further examples of isomorphism of the ion  $\text{PO}_3\text{F}$  with the sulphate ion. The following compounds have been isolated:  $\text{MSO}_4(\text{NH}_4)_2\text{PO}_3\text{F} \cdot 6\text{H}_2\text{O}$ , where M is Ni, Cu, Co, Zn, Mn, or Mg;  $\text{MPO}_3\text{F}(\text{NH}_4)_2\text{PO}_3\text{F} \cdot 6\text{H}_2\text{O}$ , where M is Ni or Co, isomorphous with the double sulphates of Locke;  $\text{NiPO}_3\text{F} \cdot 7\text{H}_2\text{O}$ ,  $\text{CuPO}_3\text{F} \cdot 5\text{H}_2\text{O}$ , and  $\text{CoPO}_3\text{F} \cdot 6\text{H}_2\text{O}$  isomorphous with the corresponding sulphates; and  $(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{PO}_3\text{F} \cdot \text{Al}_2(\text{PO}_3\text{F})_3 \cdot 24\text{H}_2\text{O}$  isomorphous with the alums.

L. S. THEOBALD.

**Structure of thortveitite,  $\text{Sc}_2\text{Si}_2\text{O}_7$ .** W. H. ZACHARIASEN (Z. Krist., 1930, 73, 1—6; Chem. Zentr., 1930, i, 2230).—The monoclinic unit cell, which contains 2 mols., has  $a$  6.56,  $b$  8.58,  $c$  4.74 Å.;  $\beta$  103° 8'; space-group  $C_{2h}^2$ .

A. A. ELDRIDGE.

**Structure of titanite.** W. H. ZACHARIASEN (Z. Krist., 1930, 73, 7—16; Chem. Zentr., 1930, i, 2230).—The monoclinic unit cell, which contains 4 mols. of  $\text{CaTiSiO}_5$  (the composition varies; the possibility of isomorphous replacement is discussed), has  $a$  6.55  $\pm$  0.01,  $b$  8.70,  $c$  7.43  $\pm$  0.01 Å.,  $\beta$  119° 43'; space-group  $C_{2h}^2$ .

A. A. ELDRIDGE.

**Crystal structure of pseudobrookite.** L. PAULING (Z. Krist., 1930, 73, 91—112; Chem. Zentr., 1930, i, 2230).—The rhombic unit cell has  $a$  9.79,  $b$  9.93,  $c$  3.725 Å.; space-group  $V_7^7$ . The formula  $\text{Fe}_2\text{TiO}_5$  accords with the structure. The formula  $\text{Fe}_4\text{Ti}_3\text{O}_{12}$ , obtained by analysis, is attributed to the presence of rutile.

A. A. ELDRIDGE.

**Lattice constants of ammonium cryolite.** G. MENZER (Z. Krist., 1930, 73, 113; Chem. Zentr., 1930, i, 2230).—The cubic, face-centred lattice has  $a$ , 8.90  $\pm$  0.003 Å.; space-group  $T^2$  or  $T_d^2$ . The unit cell contains 4 mols.

A. A. ELDRIDGE.

**Crystal structure of phenacite,  $\text{Be}_2\text{SiO}_4$ , and willemite,  $\text{Zn}_2\text{SiO}_4$ .** W. L. BRAGG (Z. Krist., 1930, 72, 518—528; Chem. Zentr., 1930, i, 1917).—The

structure is discussed and the co-ordinates of the beryllium atoms are calculated. The space-group of phenacite is  $C_{2h}^2$ . A. A. ELDRIDGE.

**Crystallographic relations between potassium and ammonium dichromates.** B. GOSSNER and F. MUSSGUTH (Z. Krist., 1930, 72, 476—481; Chem. Zentr., 1930, i, 1913).—The dimensions of the unit cells, containing 4 mols., are, respectively: potassium dichromate (triclinic),  $a$  7.50,  $b$  7.38,  $c$  13.40 Å.,  $\alpha$  82° 0',  $\beta$  96° 13',  $\gamma$  90° 51'; ammonium dichromate (monoclinic),  $a$  7.78,  $b$  7.54,  $c$  13.27 Å.,  $\beta$  93° 42'. The latter has space-group  $C_{2h}^2$ . The substances are not isomorphous. A. A. ELDRIDGE.

**Natural and artificial domeykite.** F. MACHATSONKI (Zentr. Min. Geol., 1930, A, 19—36; Chem. Zentr., 1930, i, 1918).—Crystals of composition  $Cu_3As$ , prepared by passing arsenic vapour over copper, have  $a$  7.200,  $c$  7.478 Å.,  $d$  7.9, 6 mols. in the unit cell; the substance is identical with unfused natural domeykite. Neither substance is isomorphous with dyskrasite,  $Ag_3Sb$ . A. A. ELDRIDGE.

**Crystal structure and chemical composition of the monoclinic amphiboles.** B. R. WARREN (Z. Krist., 1930, 72, 493—517; Chem. Zentr., 1930, i, 1917—1918).—The structure of tremolite is typical. The following values for  $a$ ,  $b$ , and  $c$  (Å.) are recorded: tremolite 9.78, 17.8, 5.26; kupperite 9.7, 17.8, 5.25; actinolite 9.8, 17.9, 5.27; hornblende 9.8, 17.9, 5.28; grunerite 9.4, 17.9, 5.27. The space-group is  $C_{2h}^2$ . A. A. ELDRIDGE.

**Chemical and X-ray study of silicates. Hornblende group.** B. GOSSNER and F. SPIELBERGER (Z. Krist., 1929, 72, 111—142; Chem. Zentr., 1930, i, 2532—2533).—Arfvedsonite has  $a$  9.87,  $b$  18.31,  $c$  5.33 Å.; barkevikite has  $a$  9.92,  $b$  18.30,  $c$  5.33 Å.; kärsutite has  $a$  9.85,  $b$  18.17,  $c$  5.39 Å. The unit cells contain 4 mols. Enigmatite and cossyrite are closely related. A. A. ELDRIDGE.

**Crystalline hydrates of mellitates and their significance in the theory of the combination of water of crystallisation.** M. A. RAKUSIN (Z. Krist., 1930, 73, 270—273; Chem. Zentr., 1930, i, 2680).—A discussion. A. A. ELDRIDGE.

**Stability of salt hydrates.** K. FAJANS (Z. Krist., 1930, 73, 273—274; Chem. Zentr., 1930, i, 2680).—A discussion (cf. preceding abstract). A. A. ELDRIDGE.

**Atopite and mauzeilite.** F. MACHATSCHKI (Z. Krist., 1930, 73, 159—175; Chem. Zentr., 1930, i, 2713).—Atopite,  $(Ca,Mn,Na_2)Sb_2O_7$ , face-centred, has  $a$  10.267±0.008 Å., with 8 mols. in the unit cell; space-group  $O_h^2$ . Mauzeilite also has the general composition  $X_2Z_2(O,OH,F)$ . A. A. ELDRIDGE.

**Berzeliite.** F. MACHATSCHKI (Z. Krist., 1930, 73, 123—140; Chem. Zentr., 1930, i, 2713—2714).—Berzeliite,  $NaCa_2Mn_2As_2O_{12}$ , body-centred, has  $a$  12.357±0.008 Å., with 8 mols. in the unit cell; space-group  $O_h^2$ . A. A. ELDRIDGE.

**Kaliophilite.** B. GOSSNER and F. MUSSGUTH (Z. Krist., 1930, 73, 187—201; Chem. Zentr., 1930, i, 2714).—Kaliophilite from Vesuvius had  $c$  8.59 Å.;  $a$  was 27.01 or 15.59 Å. A. A. ELDRIDGE.

**Crystal structure of germanite.** W. F. DE JONG (Z. Krist., 1930, 73, 176—180; Chem. Zentr., 1930, i, 2714).—Germanite,  $a$  5.290±0.005 Å., assumed to have 1 mol. of  $Cu_3(Fe,Ge)S_4$  in the unit cell, may be in space-group  $T^2$ ,  $T^2_h$ , or  $O_h^2$ . A. A. ELDRIDGE.

**Rare-earth silicates of the nepheline and anorthite type.** W. EITEL and G. TRÖMEL (Fortschr. Min. Kryst. Petr., 1929, 14, 28—33; Chem. Zentr., 1930, i, 2529).—The compounds have been characterised optically and by means of X-rays. Correspondence of a sodium and a calcium compound in the crystal structure is observed. A. A. ELDRIDGE.

**X-Ray examination of synthetic chromium spinels.** S. HOLGERSSON (Z. anorg. Chem., 1930, 192, 123—128).—X-Ray examination of magnesium and cadmium chromites has shown that each has the characteristic spinel lattice, the values of  $a$  being 8.29 and 8.59 Å., respectively. R. CUTHILL.

**Davynite and its relation to hainite and cancrinite.** B. GOSSNER and F. MUSSGUTH (Z. Krist., 1930, 63, 52—60; Chem. Zentr., 1930, i, 2230—2231).—Davynite,  $3NaAlSiO_4 \cdot Ca(SO_4, Cl_2)$ , has  $a$  12.80,  $c$  5.35 Å.; space-group  $D_{2h}^{10}$ . Cancrinite has  $a$  12.60,  $c$  5.18 Å. A. A. ELDRIDGE.

**Anthophyllite, grammite, and cummingtonite.** H. JOHANSSON (Z. Krist., 1930, 73, 31—50; Chem. Zentr., 1930, i, 2231).

**Crystal structure of feldspars.** E. SCHIEBOLD (Fortschr. Min. Kryst. Petr., 1929, 14, 62—68; Chem. Zentr., 1930, i, 2532).

**Structure of staurolite.** E. SCHIEBOLD and G. M. CARDOSO (Fortschr. Min. Kryst. Petr., 1929, 14, 69—70; Chem. Zentr., 1929, i, 2532).

**Chemical and X-ray study of substances and crystals of complex structures.** B. GOSSNER and M. ARM (Z. Krist., 1929, 72, 202—236; Chem. Zentr., 1930, i, 2514—2515).—Metavoltine,  $K_5H_7(SO_4)_6 \cdot Fe(OH)_3 \cdot H_2O$  (synthetic), hexagonal-prismatic, has  $a$  19.43,  $c$  18.60 Å., with 8 mols. in the unit cell. Voltaite,  $K_2H_{10}(SO_4)_6 \cdot 3Fe(OH)_3 \cdot 4FeSO_4 \cdot 4H_2O$  (synthetic), face-centred cubic, has  $a$  27.33 Å., with 20 mols. in the unit cell; space-group probably  $O_h^2$ . Mangano-voltaite and cobaltovoltaite,  $K_2H_{10}(SO_4)_6 \cdot 3Fe(OH)_3 \cdot 4XSO_4 \cdot 4H_2O$  ( $X=Mn,Co$ ), but not chromovoltaite ( $Cr^{+++}$  in place of  $Fe^{+++}$ ) or nickelovoltaite ( $Ni^{++}$  in place of  $Fe^{+++}$ ), could be prepared. Boleite,  $3PbCl_2 \cdot 3Cu(OH)_2 \cdot AgCl$ , space-group  $O_h^2$ , has 9 mols. in the unit cell. Cumengeite,  $PbCl_2 \cdot Cu(OH)_2$ , has  $a$  15.17,  $c$  24.71 Å., with 44 mols. in the unit cell. A. A. ELDRIDGE.

**X-Ray study of certain esters of cellulose and of dextrose.** A. NOWAKOWSKI (Compt. rend., 1930, 191, 411—413).—The Debye-Scherrer method alone is suitable for the X-ray examination of the micro-crystalline cellulose dilaurate and distearate, and shows that the internal structure of the cellulose is completely destroyed by fixation of the long aliphatic chains. The  $\alpha$ -penta-acetate and the  $\alpha$ -penta-laurate and -palmitate of dextrose have therefore been studied, the first by the rotating-crystal method, and the last two after crystallisation in fibrous form from

a mixture of chloroform and absolute alcohol at 20°. It is shown that the long aliphatic chains are always approximately perpendicular to the axis of the fibre (cf. Meyer and Mark, A., 1928, 621), and that the molecules are always oriented in the same direction corresponding with a cell unit of side 5.28–5.39 Å.

J. GRANT.

**Behaviour of cathode rays towards preparations of cellulose.** C. TROGUS, H. HALBERSCHADT, and K. HESS (Naturwiss., 1930, 18, 846–847; cf. Thomson and Reid, A., 1927, 605).—When sheets of ash-free cigarette paper (40  $\mu$  thick), manufactured from pure cellulose, were irradiated with cathode rays perpendicular to the surface of the paper, no diffraction pattern was observed, but when part of the electron bundle was passed through a pin hole in the paper, an electron diffraction pattern, due to the cellulose crystals at the edge of the pin hole, was formed, similar to that obtained by Kikuchi (A., 1928, 1174) with mica. The sharpness of the interference diminishes with decreasing voltage. It is suggested that the position of the interference is influenced by the voltage. Tangential irradiation of natural and artificial silk (cellulose acetate II) gave a similar diffraction effect.

W. R. ANGUS.

**Interferometer measurements of the carbon tetrabromide molecule.** E. RUMPF (Physikal. Z., 1930, 31, 791–792).—Carbon tetrabromide cannot be examined in the pure state owing to the closeness of its b. p. and the temperature at which it decomposes. Consequently 0.5*M* solutions of carbon tetrabromide in benzene were examined. By an application of Debye's formula to the interference ring the length of the side of the carbon tetrabromide molecule was calculated as 4.0 Å. The second maximum was masked by the interference produced by benzene which has not been fully investigated. It would appear that the side of the benzene hexagon is 2.6 Å. long.

W. R. ANGUS.

**Crystallographic properties of  $\alpha$ -methylbutenoic acid amides.** J. THOREAU (Bull. Acad. Roy. Belg., 1930, [v], 16, 823–828).—Crystallographic data are recorded for the amides of tiglic (*trans*- $\alpha$ -methylcrotonic), angelic (*cis*- $\alpha$ -methylcrotonic),  $\alpha$ -ethylacrylic, and  $\alpha$ -hydroxy- $\alpha$ -methylbutyric acids (Bruylants, Ernould, and Dekoker, this vol., 1276).

H. BURTON.

**Space-group of strychnine.** T. C. MARWICK (Nature, 1930, 126, 438).—The unit cell has a volume of 1634 Å<sup>3</sup>; *a* 11.9, *b* 12.1, *c* 11.3 Å.; *a*:*b*:*c*=0.983:1:0.931; the number of molecules is 4, and the space-group is *Q*<sub>1</sub>.

L. S. THEOBALD.

**Temperature dependence of Kerr constants for gases and the results for methyl and ethyl alcohol.** H. A. STUART (Physikal. Z., 1930, 31, 616–617, and Z. Physik, 1930, 63, 533–557; cf. A., 1929, 872).—The Kerr constants of several aliphatic compounds have been determined at temperatures between 18° and 100°. For carbon disulphide the constant varies as 1/*T* Abs. according to the Langevin-Born orientation theory; for ethyl chloride and methyl bromide, applying a correction for a small degree of anisotropy, the variation is propor-

tional to 1/*T*<sup>2</sup> Abs. The Kerr constants for methyl and ethyl alcohol at 760 mm. are, respectively,  $< \pm 0.4 \times 10^{-15}$  at 94.2° and  $< \pm 0.5 \times 10^{-18}$  at 102°. From these values it follows that the oxygen angle must be large, and further it may be concluded that the molecule does not possess an axis of symmetry with regard to its optical polarisation in the direction OC. The presence of an axis of symmetry would require the angle between the electric moment and the axis of greatest polarisation to have a value of 55°, which is contradictory to conceptions of classical structural chemistry.

W. R. ANGUS.

**Conception of the Hall effect.** H. ZAHN (Naturwiss., 1930, 18, 848–849).—Anomalous results for the Hall effect are discussed. The large positive value for antimony is converted into a small negative value by the addition of small quantities of tin. Measurements of the Hall effect on a liquid sodium-potassium alloy (in the ratio of the at. wt.) have been made and results of the expected magnitude and sign are given. It had been previously assumed, since no results had been found for liquid metals, that the Hall effect depended on the structure only. It now appears necessary to differentiate between an "Electronengas" Hall effect, which is exhibited only by liquid metals, and a structural Hall effect.

W. R. ANGUS.

**Electrical conductivity measurements at low temperatures.** J. C. McLENNAN, J. F. ALLEN, and J. O. WILHELM (Phil. Mag., 1930, [vii], 10, 500–511; cf. Trans. Roy. Soc. Canada, 1930, 24, Sect. III).—Measurements of electrical conductivity between 300° and 1.9° Abs. have been made with the following alloys: bismuth-silver, bismuth-copper, bismuth-cadmium, bismuth-manganese, arsenic-copper, arsenic-gold, antimony-silver, antimony-gold, lead-cerium, lead-lanthanum, cadmium-zinc, and Heusler alloy. None of these becomes superconducting at the lowest temperature reached, but the curves for bismuth-cadmium, bismuth-manganese, and the two arsenic alloys bend so sharply towards the temperature axis as to suggest that they might become superconducting at a still lower temperature. Cerium, lanthanum, polonium, silver chloride, and the sulphides of iron, silver, and bismuth were also examined, but showed no peculiarities.

F. L. USHER.

**New phenomenon in the change of resistance in a magnetic field of single crystals of bismuth.** L. SCHUBNIKOV and W. J. DE HAAS (Nature, 1930, 126, 500).—The curves showing the change of resistance as a function of the intensity of the magnetic field have a very complicated form under certain conditions.

L. S. THEOBALD.

**Change of resistance of nickel wire under tension with simultaneous heating.** S. ARZIBISHEV and V. J. U. JUSCHAKOV (Z. Physik, 1930, 64, 405–410).—The resistance of a nickel wire under tension decreases at first, reaches a minimum, and then increases. All the curves show discontinuities between 343° and 360°. The temperature corresponding with the inflexion point is about 353°, which is very near the Curie point for nickel. This value of the temperature appears to be a kind of critical temper-

ature, at which the character of the phenomenon changes. The diminution of resistance of a nickel wire under tension therefore seems to be intimately bound up with the ferromagnetism of the metal.

A. J. MEE.

**Tension coefficient of resistance of metals.** H. ROLNICK (Physical Rev., 1930, [ii], 36, 506—512).—A dynamic method for measuring the change in resistance of a metal under tension is described; a direct current is sent through the wire under test whilst longitudinal vibrations set up in the wire cause the resistance, and hence the potential drop, in the wire to fluctuate, these changes being amplified and measured. The method is applied to 15 metals. For bismuth, aluminium, manganin, and constantan the resistance decreases with the tension and increases for silver, gold, copper, molybdenum, lead, palladium, platinum, tin, tungsten, zinc, and nichrome.

N. M. Blich.

**Change of resistance of thin bismuth plates in a magnetic field.** F. GROSS (Z. Physik, 1930, 64, 520—536).—Plates of polished and grey bismuth about 6  $\mu$  thick have been examined in a field of 28,000 gauss. The specific resistance of the strips and the change in resistance increase to a limit with increasing thickness; this limit is the higher the higher is the temperature, and is affected also by the method of preparation. For plates of resistance of about 1 ohm there is a change in resistance of about 90—100% in contrast with the 140% change which has been found for a bismuth spiral. With increasing thickness of the plate the grain size increases; at a higher temperature, but below 270°, the m. p. of bismuth, the grains form large conglomerates and the plate is smooth and polished. When cast at about 270°, the plates are coarse and uneven. It is thought that the grain size is not responsible for the varying behaviour of the plates in the magnetic field. X-Ray examination revealed that the plates were always crystalline. The dependence of the change in resistance on the position of the plate relative to the magnetic lines of force is explained by the fibrous structure of the (111) plane. This structure is obtained under certain temperature conditions during casting.

J. FARQUHARSON.

**Structure of thin bismuth plates.** W. BÜSSEM, F. GROSS, and K. HERRMANN (Z. Physik, 1930, 64, 537—546).—Bismuth plates about 6  $\mu$  thick, made by cathodic sputtering in an atmosphere of hydrogen, have always a crystalline structure, having a rhombohedral lattice. White bismuth plates have a striated structure. In grey bismuth the crystals are not striated (cf. preceding abstract).

J. FARQUHARSON.

**Evidence of the impossibility of spontaneous magnetisation.** N. AKULOV (Z. Physik, 1930, 64, 559).—The Weiss-Heisenberg theory of ferromagnetism bears on the existence of spontaneous magnetisation. Experimental evidence shows that crystals of iron, nickel, and cobalt have sharp energetic anisotropy, and also vanishingly small hysteresis loss, which are irreconcilable with the theory.

J. FARQUHARSON.

**Change of electrical resistance produced in cold-worked metals by annealing.** K. TAKAHASHI

(Sci. Rep. Tôhoku, 1930, 19, 265—282).—The change of resistance produced in metals by cold drawing was investigated for copper and silver. For copper the resistance increased rapidly up to a reduction of about 40%, but this increase became gradually less as the reduction became greater, and for a reduction of more than 90% the resistance is slightly decreased. In the case of silver the resistance is increased by about 3% in a reduction of 50%, but a further reduction causes a decrease in resistance. The total increase in resistance produced by a reduction of 95% was only 1%. The change of resistance of metals annealed in an atmosphere of hydrogen was also investigated. For silver and copper the decrease in resistance is at first slow, the rate of decrease becoming a maximum at between 150° and 250°. The minimum resistance is attained at about 400°; after this the resistance begins to rise again. At 650° and 750° for copper and silver, respectively, the resistance becomes higher than that of the metal in the cold-drawn state, probably due to the occlusion of hydrogen. To test this view, experiments were also made with wires annealed in a vacuum. In the case of copper the increase is definitely due to the occlusion of hydrogen. In the case of other metals, as the annealing temperature is raised the resistance decreases at first slowly, then rapidly, reaching a minimum, and then increases.

A. J. MEE.

**Dependence of back-*E.M.F.* and true conductivity of ion crystals on field intensity.** A. SNEKAL (Physikal. Z., 1930, 31, 809—811).—The back-*E.M.F.* generated in rock-salt and sylvine crystals, when fields up to 300,000 volts per cm. were applied, was determined by Quittner's method. The true conductivity of these crystals was also determined in this range, and appears to follow Pohl's formula. The measurements were repeated at different temperatures in the range 0—300°; the conductivities follow van 't Hoff's exponential law.

A. B. D. CASSIE.

**Measurements with the aid of liquid helium.** X. W. MEISSNER (Z. Physik, 1930, 64, 581—583).—The resistance of the alloys  $\text{Cu}_x\text{Au}$  ( $x=1-3$ ) and  $\text{MnNi}_3$  was determined at different temperatures down to that of liquid helium. A tempered  $\text{Cu}_3\text{Au}$  alloy showed the greatest decrease in resistance with temperature. None became superconducting.

A. B. D. CASSIE.

**Change in resistance of metals in strong magnetic fields.** N. H. FRANK (Z. Physik, 1930, 64, 650—656).—Theoretical. An equation for the relative change in resistance of metals in any strong magnetic field is deduced. It appears to give a satisfactory explanation for Kapitza's linear region.

J. FARQUHARSON.

**Magnetic isotropy of copper crystals.** C. G. MONTGOMERY (Physical Rev., 1930, [ii], 36, 498—505).—In order to determine whether a cubic crystal is magnetically isotropic as demanded by theory, the variation in the magnetic susceptibility with the direction of the applied field was investigated for large single crystals of copper, using a modification of Curie's method (cf. Foëx, A., 1926, 932). A Fourier analysis of the results indicates no variation

of susceptibility larger than 1%, a result in agreement with the magnetic isotropy of cubic crystals.

N. M. Blich.

**Magnetic properties and the crystal lattice of the ferrites.** S. HOLGERSSON and A. SERRES (Compt. rend., 1930, 191, 35–37).—The considerable differences which exist between the magnetic properties of various ferrites, such as those of magnesium and zinc, are not due to differences of the lattice arrangements. The magnetic properties of the ferric iron are dependent on the nature of the atoms which occupy the nodes of the grating adjacent to the iron atoms in the lattice.

H. F. GILLBE.

**Magnetic characteristics of iron crystals.** W. GERLACH (Z. Physik, 1930, 64, 502–506).—A note on the appearance of remanence and coercivity in good and bad iron crystals. The magnitude of the remanence in iron crystals cannot be clearly expressed. The coercivity converges towards zero, the more the crystal lattice is chemically and physically perfect. This supplies a measure of any strain in a crystal.

J. FARQUHARSON.

**Diamagnetism of metals.** L. LANDAU (Z. Physik, 1930, 64, 629–637).—Heisenberg's commutation law applied to the motion of a free electron in a magnetic field leads to the Hamiltonian function for an oscillator of vibration frequency  $eH/mc$ . The corresponding "eigen" values and functions are deduced, and from them the diamagnetic susceptibility is calculated in the usual way. This appears, for the free electron, to be one third of the corresponding Pauli spin-paramagnetic susceptibility, but it may have very different values for an electron under the influence of the interionic fields of a crystal. Kapitza's linear law for the variation of electrical resistance with applied magnetic field applies only when the orbital radius of the motion of the electron in the magnetic field is less than its mean free path.

A. B. D. CASSIE.

**Magnetisation of nickel wire under strong tension.** R. BECKER and M. KERSTEN (Z. Physik, 1930, 64, 660–681).—By applying a correction for the distortion of the dipoles, it is possible to deduce, theoretically, the magnetisation of nickel wire under a strong external strain. Quantitative data are in agreement with theory. The magnetostriction of nickel wire under these conditions is about 50% greater than in nickel free from strain.

J. FARQUHARSON.

**Mechanism of steel hardening.** G. KURDJUMOV and G. SACHS (Z. Physik, 1930, 64, 325–343).—Large single crystals of austenite were tempered with water and submitted to X-ray examination. In the partly changed austenite crystal the particles of the tetragonal phase and of  $\alpha$ -iron are arranged quite regularly. The composition of the phases under different conditions of tempering is determined.

A. J. MEE.

**Thermal electron emission and heat energy.** M. VON LAUE and G. SILJEHOLM (Naturwiss., 1930, 18, 764–765).—In the vicinity of the transition point, A3 ( $T=1183^\circ$  Abs.), at which there is a transition from  $\beta$ - to  $\gamma$ -iron, it has been found by measurement of the thermal electron emission stream of iron

that a qualitative relationship exists between the changes in the electron stream and those occurring in the thermal energy. Thermodynamically this relationship has been determined quantitatively. Experimental and theoretical values are in close agreement.

W. R. ANGUS.

**Supposed allotropy of bismuth.** A. SCHULZE (Z. tech. Physik, 1930, 11, 16–23; Chem. Zentr., 1930, i, 1915).—Dilatometric measurements and determinations of electrical resistance afforded no evidence of allotropy. The resistance ratio  $W_{\text{liq.}}/W_{\text{solid}}$  is 0.489.

A. A. ELDRIDGE.

**Mesomorphic state.** G. FRIEDEL (Z. Krist., 1929, 72, 416–418; Chem. Zentr., 1930, i, 2351).—A discussion of nomenclature.

A. A. ELDRIDGE.

**Change of colour on cold working.** G. TAMMANN and E. JENCKEL (Z. anorg. Chem., 1930, 192, 245–248).—Change of colour on mechanical working is not restricted to metals, but is exhibited by such substances as zinc and lead oxides and phosphorescent alkaline-earth sulphides.

H. F. GILLBE.

**Conductivity of crystalline lead sulphide.** G. SÖN FREY (Z. Elektrochem., 1930, 36, 511–523).—Lead sulphide prepared by precipitation from a nitric acid solution of electrolytic lead, roasting in hydrogen sulphide, and subliming in a vacuum has  $d^{20}$  7.590. The resistance was determined by a compensation method and corrected for porosity. The specific resistance at  $20^\circ$  is  $0.00306 \text{ ohm cm}^{-1}$  and within the range  $-183^\circ$  to  $100^\circ$  is represented by  $0.00258(1 + 0.00895t + 0.000022t^2)$ . The specific conductivity at  $0^\circ$  is  $388 \text{ mho cm}^{-1}$ .

H. I. DOWNES.

**Electrical conductivity of sodium chloride crystals.** B. HOCHBERG and A. WALTHER (Z. Physik, 1930, 64, 392–401).—Sodium chloride is a typical dielectric crystal, for which, however, the expression  $\sigma = Ae - B/T$  (where  $\sigma$  is the specific resistance and  $A$  and  $B$  are constants) does not strictly hold. The electrical conductivity of sodium chloride crystals was determined over the temperature range  $25$ – $800^\circ$ . The ordinary relationship holds up to  $550^\circ$ , but above this ionic conductivity has to be taken into account, necessitating the introduction of a second term into the equation.

A. J. MEE.

**Specific heat and latent heat of fusion of ice.** W. H. BARNES and O. MAASS (Canad. J. Res., 1930, 3, 205–213).—The total heat of ice and resulting water has been determined for initial temperatures of  $-78.5^\circ$  to  $0^\circ$  and a final temperature of  $25^\circ$ ; the total heat from  $-80^\circ$  to  $0^\circ$  is expressed by the Barnes equation to within  $\pm 0.05\%$ . The values obtained for the specific heat of ice do not entirely accord with those of Maass and Waldbauer, probably on account of the different value taken for the sublimation point of carbon dioxide. The latent heat of fusion of ice is  $79.40 \text{ g.-cal./g.}$

H. F. GILLBE.

**Coupled vibrations with applications to the specific heat and infra-red spectra of crystals.** A. B. LEWIS (Physical Rev., 1930, [ii], 36, 568–586).—Mathematical. The free periods of  $p$  identical coupled groups, each group containing  $n$  identical linear oscillators, are investigated. From the equa-

tions obtained the specific heats of methyl, ethyl, butyl, and hexyl alcohols are calculated for low temperatures; fair agreement with experimental values is found.

N. M. BUGH.

Electrical differential method for the determination of  $C_p$  for gases. M. TRAUTZ and A. ZÜRN (Festschr. Heraeus, 1930, 115—138; Chem. Zentr., 1930, i, 2223).—Measurements were made with iron pentacarbonyl.

A. A. ELDRIDGE.

Relation of m. p. to crystal structure and to compressibility. J. H. CHESTERS (Trans. Ceram. Soc., 1930, 29, 169—176).—Mathematical.

R. J. CARTLIDGE.

Optical determination of high metallurgical temperatures. M. p. of iron. C. H. M. JENKINS and (Miss) M. L. V. GAYLER (Proc. Roy. Soc., 1930, A, 129, 91—114).—The adaptation of the optical pyrometer to the determination of melting, freezing, and transformation temperatures in metals and alloys by observation of a black body enclosure immersed in the metal is described. Observations are taken at regular time intervals and plotted in the usual way, and are preferably of the "time-temperature" type. Methods for the preparation of refractory containers of hard, pure alumina are described, and the precautions necessary to ensure black body conditions are discussed. The calibration of the optical pyrometer has been carried out by means of the m. p. of gold and palladium and intermediate temperatures by comparison with thermocouples. The use of the rotating sector has confirmed the shape of the calibration curve. In the case of iron, the rotating-sector method has confirmed the new value of the m. p. obtained in reference to that of palladium. The method has been found suitable for m.-p. determinations of alloys at high temperatures, but existing thermocouple methods appear to be preferable for determinations with alloys at low temperatures. The effect of metal vapour is described and a method is developed for counteracting the absorption of light from this cause. Iron of very high purity gives m. p.  $1527 \pm 3^\circ$ , referred to palladium  $1555 \pm 2^\circ$ .

L. L. BIRCUMSHAW.

Heats of evaporation at the absolute zero. W. HERZ (Z. anorg. Chem., 1930, 191, 318—319).—By substituting  $ML_0 = RA$  in the expression  $\log p = -A/T + C$  the mol. heat of evaporation at  $0^\circ$  Abs. ( $ML_0$ ) is calculated. This is compared with the mol. heat of evaporation at the ordinary b. p. ( $ML_s$ ) for 29 organic liquids. In most cases the ratio  $ML_0 : ML_s$  lies between 1.05 and 1.2. Ethyl alcohol gives a low ratio, formic and acetic acids give high ratios.

O. J. WALKER.

Properties of tellurium tetrachloride. J. H. SIMONS (J. Amer. Chem. Soc., 1930, 52, 3488—3493).—The preparation of pure tellurium tetrachloride (m. p.  $225^\circ$ , b. p.  $390^\circ/755.6$  mm.) is described. Vapour density and vapour pressure data are recorded and the latent heat of vaporisation is calculated to be 18,400 g.-cal. per mol. The vapour consists of single ( $\text{TeCl}_4$ ) molecules, but dissociation, accompanied by a darkening in colour, commences at about  $500^\circ$ . The density and surface tension of the liquid have

been determined at temperatures between about  $230^\circ$  and  $430^\circ$ , and the parachor has been calculated. It is concluded that the central (tellurium) atom has a shell of ten electrons, four pairs being shared with the chlorine atoms.

J. G. A. GRIFFITHS.

Properties of selenium tetrachloride. J. H. SIMONS (J. Amer. Chem. Soc., 1930, 52, 3483—3487).—The preparation of pure selenium tetrachloride (sublimation point  $196 \pm 1^\circ/760$  mm., m. p.  $305 \pm 3^\circ$ ) is described. The crystals are insoluble in carbon tetrachloride at  $100^\circ$  and react with acetonitrile. The vapour changes from light yellow to dark reddish-brown as the temperature is raised from  $208^\circ$  to  $600^\circ$  and within this range the vapour density (110.4) remains constant, indicating complete dissociation into chlorine and  $\text{SeCl}_2$  or  $\text{Se}_2\text{Cl}_2$ .

J. G. A. GRIFFITHS.

Vapour pressure and vapour constitution of mercurous bromide. G. JUNG and W. ZIEGLER (Z. physikal. Chem., 1930, 150, 139—144).—Measurements of the vapour density by the Dumas method give results consistent with the constitution  $[\text{HgBr}]$  or  $[\text{HgBr}_2 + \text{Hg}]$ . The latter constitution is confirmed by the fact that the absorption spectrum of mercurous bromide vapour corresponds qualitatively with that of bromine vapour. The vapour pressure between  $100^\circ$  and  $400^\circ$  is given by  $\log p = -4298/T + 9.338$ . The vapour-pressure curve leads to the equations  $2\text{HgBr}_{\text{solid}} = \text{Hg}_{\text{vap.}} + \text{HgBr}_{2\text{vap.}} - 39.2 \text{ kg.-cal.}$ ;  $\text{HgBr}_{\text{solid}} = \text{HgBr}_{\text{vap.}} - 52 \text{ kg.-cal.}$

F. G. TRYHORN.

Thermodynamical experiments on supercooled phases. H. SCHMOLKE (Z. Physik, 1930, 64, 714—716).—These experiments do not contradict the Nernst heat theorem, but indicate how it has been wrongly applied.

A. B. D. CASSIE.

Chemical constant of hydrogen. J. PALACIOS (Anal. Fis. Quím., 1930, 28, 587—602).—The equation  $\log p = -\lambda/4.571T + 2.5 \log T - (1/4.571) \int_0^T C_p dT/T + (1/4.571)(S'_0 - S'_s)$ , where  $p$  is the vapour pressure,  $\lambda$  the latent heat of vaporisation,  $T$  the absolute temperature,  $S'_0$  the entropy of the liquid phase at  $0^\circ$  Abs. and pressure  $p$ , and  $S'_s$  an integration constant, has been derived from purely thermodynamical considerations for substances obeying the gas law. A similar formula, but one which takes into account the equation of state of hydrogen, yields for this substance values of  $p$  which are in close agreement with those observed by Palacios, Onnes, and other workers; the value of the chemical constant of hydrogen derived from this modified equation is 1.105.

H. F. GILLBE.

[Physical] properties of absolute alcohol. J. BARBAUDY and A. LALANDE (Compt. rend., 1930, 191, 406—408).—The product was neutral, free from aldehydes and hydrocarbons, and had  $d_{25}^{25} = 0.02$  0.78523 (corresponding with 99.96 wt.-% of alcohol), b. p. (760 mm.)  $78.385 \pm 0.01^\circ$ ,  $dt/dP$  ( $754.3$ — $761.9$  mm.)  $0.034^\circ/\text{mm.}$ ,  $n_D^{25}$  ( $\lambda$  0.578  $\mu$ )  $1.3594_5$ ,  $dn/dt$  ( $20$ — $30^\circ$ , and  $\lambda$  0.436— $0.671$   $\mu$ )  $0.00042 \pm 0.00001$ , surface tension (Harkins and Jordan's method)  $22.10 \pm 0.05$  dynes per cm. at  $21^\circ$ . Spectra ( $\lambda$  2300—4356) of the sample are compared with those obtained in the presence of impurities, and demonstrate its transparency in the ultra-violet region. J. GRANT.



**Density and compressibility of ammonia.** Revision of the at. wt. of nitrogen. E. MOLES and T. BATUECAS (Anal. Fis. Quím., 1930, 28, 871—894).—The most probable value of the density of ammonia, in g./litre at S.T.P., derived from the mean of 31 measurements employing synthetic ammonia, and ammonia obtained by the decomposition of ammonium oxalate and by the hydrolysis of magnesium nitride, is  $0.77169 \pm 0.00005$ . This value, although nearly identical with that of Leduc after the application of the Crespi and Moles adsorption correction, is about 0.1% higher than that obtained by other observers. The values of the density, calculated from measurements made at 0.6667, 0.5000, and 0.3333 atm. pressure, are 0.76772, 0.76585, and 0.76383 g./litre, respectively, whilst the mean value of  $1+\lambda$ , calculated by the method of limiting densities, is 1.01552. The at. wt. of nitrogen, calculated from the density measurements, is 14.009.

H. F. GILLBE.

**Density of the vapours in equilibrium with water, ethyl alcohol, methyl alcohol, and benzene.** (EARL OF) BERKELEY and E. STENHOUSE (Phil. Trans., 1930, A, 229, 255—286).—An investigation of the validity of Dalton's law, the extent of the association among vapour molecules, and the dependence of this association on temperature has been made in order to put the vapour pressure method of determining osmotic pressure on a sound experimental basis. A method for determining the ratio of vapour densities in air and other gases is described and results are given for water, ethyl and methyl alcohols, and benzene. With ethyl alcohol and water, direct comparisons of the vapour density at  $0.75^\circ$  and  $30.02^\circ$  have been made. Considerable attention has been directed to the experimental errors involved, the means of calculating the effects caused by changes in temperature and pressure, and other corrections necessary for the highest accuracy. Diffusion is probably the cause of slight discrepancies, which can be avoided when the experiments are conducted with a relatively rapid air current for a sufficient time. With the aid of certain assumptions an approximate estimate of the concentrations of normal and associated molecules in the different vapours can be reached.

E. S. HEDGES.

**Calculation of the density of gases in the dry state.** L. ZIPPERER and G. MÜLLER (Gas- u. Wasserfach, 1930, 73, 802—804).—An accurate formula for the calculation of  $d$  for dry gas from experimental work with the Bunsen-Schilling apparatus is given and compared with a previously published approximate formula and with a further one proposed by Guman. It is shown that the divergence does not exceed 0.0001, which is in any case beyond the experimental accuracy, and that there is no advantage in using the more complicated exact formula nor that of Guman.

C. IRWIN.

**Rotational motion of molecules in crystals.** L. PAULING (Physical Rev., 1930, [ii], 36, 430—443).—Theoretical. The motion of a diatomic molecule in a crystal is discussed on the basis of the wave equation of the molecule. It is shown that crystalline hydrogen is a solid solution of symmetric and antisymmetric

molecules. At temperatures near  $5^\circ$  Abs. the solid solution becomes unstable relative to phases of definite composition. The change of entropy is discussed (cf. Giauque, A., 1929, 138). Transitions in thermal phenomena over a range of temperature for methane (cf. Clusius, *ibid.*, 635), the hydrogen halides (cf. Giauque, *ibid.*, 755), and other substances are interpreted as changes from oscillational to rotational motion.

N. M. BLIGH.

**Thermodynamic treatment of chemical equilibria in systems composed of real gases. I. Approximate equation for the mass-action function applied to the existing data on the Haber equilibrium.** L. J. GILLESPIE and J. A. BEATTIE (Physical Rev., 1930, [ii], 36, 743—753).—An equation for the mass-action function is deduced correlating all the equilibrium data on the ammonia synthesis reaction for a temperature range of  $325$ — $952^\circ$ , and a pressure range of 10—1000 atm. with the compressibility and heat capacity data on the pure reacting gases. The effects of temperature and pressure on the mass-action function are separated; for the former the relation is exact, for the latter certain approximations are made.

N. M. BLIGH.

**Vapour pressure of liquid. I. Vapour pressure, heat of vaporisation, and chemical constant of pure liquid substance.** K. WATANABE (Sci. Rep. Tokyo Bunrika Daigaku, 1930, 1, 1—13).—A theoretical paper in which general equations of vapour pressure and latent heat of vaporisation are derived.

W. GOOD.

**Zero volumes of crystallised organic substances.** W. BILTZ (Z. Elektrochem., 1930, 36, 815—818).—A discussion of mol. volume and its relationship to the additive and constitutive properties of at. volume.

H. F. GILLBE.

**Lattice energy and the combined state.** W. KLEMM (Z. Elektrochem., 1930, 36, 704—711).—Chemical combination is discussed from the viewpoint of the energy associated with the lattice. In analogy with characterisation by m. p., density, etc., a compound may be characterised by its "energy quotient," which is the ratio of the lattice energy derived experimentally from the Born cycle to that derived from an empirical formula applicable to ionic co-ordination lattices wherein the cations belong to the principal groups.

H. F. GILLBE.

**Zinc ethyl.** F. HEIN and H. SCHRAMM (Z. physikal. Chem., 1930, 149, 408—416).—An investigation of the physical properties of zinc ethyl has yielded the following results:  $d_{20}^{20}$   $1.207 \pm 0.001$ ; dielectric constant at  $20^\circ$ , 2.55; absolute viscosity at  $20^\circ$ , 0.008575. From measurements of the vapour pressure at  $26$ — $85^\circ$  the mol. heat of vaporisation has been calculated to be 8820 g.-cal. Application of Trouton's rule shows the liquid to be non-associated, and the mol. wt. in benzene solution, as determined by the cryoscopic method, is also normal.

R. CUTHILL.

**Volatility of liquids.** S. SAIJO and Y. NAGAI (J. Soc. Chem. Ind., Japan, 1930, 33, 299B).—The volatilities, in mg.-mols., of liquid vaporised per c.c. of air per sec. per sq. cm. for methyl alcohol, hexane,

benzene, ethyl alcohol, and water are in the order given. The corresponding specific volatilities (volatility/vapour pressure) are in the order methyl alcohol, water, hexane, ethyl alcohol, benzene, methylcyclohexane. This order is dependent on the amount of air used.

C. W. GIBBY.

**Viscosities of glyceryl trinitrate and related glycol nitrates.** J. M. PETERSON (J. Amer. Chem. Soc., 1930, 52, 3669—3676).—The viscosities of ethylene, propylene, trimethylene, and diethylene glycol dinitrates, and glyceryl trinitrate have been measured in c.g.s. units at 5° intervals from 10° to 60°. The values for ethylene and propylene glycol dinitrates are almost identical, but those for the isomeric propylene and trimethyl derivatives differ considerably. The corresponding fluidities are calculated.

H. BURTON.

**Diffusion of substances showing deviations from Fick's law.** D. KRÜGER and H. GRUNSKY (Z. physikal. Chem., 1930, 150, 115—134).—Details are given of a discontinuous method of investigating diffusion velocity, which, by the application of Boltzmann's formula, permits an evaluation of the results in cases in which the diffusion coefficients are functions of concentration. The method has been applied to the study of the diffusion of cellulose nitrate in acetone and of quinol in water. The results in the case of the cellulose nitrates are not entirely explained by a dependence of the diffusion coefficient on the concentration. A partial explanation is given by the assumption of forces of affinity between the cellulose ester particles themselves and between the particles and the molecules of solvent.

F. G. TRYHORN.

**Dielectric constants of liquids. III. Aqueous solutions of some organic compounds.** G. DEVOTO (Gazzetta, 1930, 60, 520—530).—Measurements have been made at 25° of the dielectric constants of solutions of benzoic acid, benzamide, carbamide, thiocarbamide, phenol, aniline, acetonitrile, acetanilide, glycine, phenylglycine,  $\alpha$ -alanine, aspartic acid, and asparagine. The dielectric constant-concentration coefficient is greatest in the case of phenol (—67) and is approximately constant (about 28) for the amino-acids. It is inferred that carbamide and thiocarbamide exist in aqueous solution mainly in the polar forms  $\text{NH}_3^+\text{C}(\text{NH})\text{O}^-$  and  $\text{NH}_3^+\text{C}(\text{NH})\text{S}^-$ .

F. G. TRYHORN.

**Viscosities of several aqueous solutions of organic substances. II.** H. M. CHADWELL and B. ASNES (J. Amer. Chem. Soc., 1930, 52, 3507—3518).—Relative viscosities have been determined for 1—20% solutions of carbamide between 5° and 25°, for 2—26% solutions of urethane at 10°, and for solutions of ethyl ether, methyl acetate, and ethyl acetate at 10° and at concentrations falling within the ranges of complete miscibility. A comparison with earlier data (Chadwell, A., 1926, 1006) shows that in all cases save that of carbamide the solutions have greater relative viscosities at 10° than at 25°, possibly owing to solvation effects or compound formation. The relative viscosities of all solutions increase as the concentration is increased and thus the effect of the depolymerisation of water on viscosities is not

apparent. The volume changes occurring on the dissolution of the esters remain unaltered when the temperature is changed from 25° to 10°. The contractions are greatest in the case of ether and are successively less for ethyl acetate, methyl acetate, and carbamide, thus affording confirmation of the hypothesis (Richards and Chadwell, A., 1925, ii, 1049) that cohesive forces and internal pressures in liquids largely determine the volume of the systems. A comparison of the viscosity and contraction curves shows that change of volume is not the only factor determining the viscosity. The bearing of compound formation and the orientation of polar molecules on the results is discussed.

J. G. A. GRIFFITHS.

**Behaviour of glasses in the softening interval.** G. TAMMANN (Z. Elektrochem., 1930, 36, 665—675).—The variations with temperature of numerous physical properties of glasses in the softening interval are summarised. See A., 1929, 649, 993, 1138; this vol., 404.

H. F. GILLBE.

**Variation with temperature of certain elastic properties of glasses over the softening interval.** G. TAMMANN and R. KLEIN (Z. anorg. Chem., 1930, 192, 161—178).—The elasticity coefficient of a vitreous layer of salicin, colophony, or phenolphthalein as measured by the height of rebound of a steel ball after being allowed to drop from a considerable height on to a steel plate coated with a thin film of the glass, diminishes rapidly as the temperature is raised above that at which threads may first be drawn from the glass, but it is not possible by this method to decide the temperature at which the material changes from a glass to a highly viscous liquid. The hardness of glasses, as measured by the pressure necessary to cause initial rupture of the surface, diminishes continuously over the softening range, the diminution commencing before softening begins; at the lowest temperature at which threads may be drawn from the glass the hardness vanishes. The types of surface fissure produced under various conditions of pressure and temperature are described, and the variations with pressure of the mean temperature of rupture, taken as the mean of the highest temperature at which scratching is possible and that at which a smooth groove is formed, have been measured for selenium and colophony glasses and for an ordinary silicate glass.

H. F. GILLBE.

**Specific heat, heat conductivity, and adiabatic temperature change of glasses over the softening interval.** G. TAMMANN and H. E. VON GRONOW (Z. anorg. Chem., 1930, 192, 193—209).—The specific heat of vitreous selenium rises abruptly from 0.089 at 29.6° to 0.132 at 31.2°, and that of colophony from 0.275 at 17.4° to 0.412 at 33.0°. Analogous sudden changes are exhibited by the heat-conductivity coefficients: in an interval of 5° above 29°, at which temperature selenium glass first loses its brittleness, there is a 40% decrease of the function  $k=\lambda/KdC$ , where  $\lambda$  is the heat-conductivity coefficient,  $d$  the density,  $C$  the specific heat, and  $K$  is a constant; with salicin glass there is a 40% fall of  $k$  over a 4° interval, and with colophony a 22% fall over 6°. Study of the adiabatic temperature changes which occur on sudden compression of a softening glass

indicates that very slow physical changes take place, especially in the highly viscous products of the softening process. H. F. GILLBE.

**Structure of glasses. Evidence of X-ray diffraction.** J. T. RANDALL, H. P. ROOKSBY, and B. S. COOPER (J. Soc. Glass Tech., 1930, 14, 219—229r).—As a result of experiments in which X-ray diffraction patterns (rings) were produced by Cu-K $\alpha$  and Mo-K $\alpha$  radiation, the authors consider that vitreous silica, wollastonite glass, and sodium borate consist of crystallites the distribution of which with regard to size in the glasses is not simple. A considerable proportion of the silica in a hard glass is said to be in the form of cristobalite crystallites, but in a softer glass (SiO<sub>2</sub> 70%, Na<sub>2</sub>O 5%, CaO 4%, MgO etc.) no evidence of a similar nature was found. The above results are shown to be compatible with the observed physical properties of glass and crystal phases of the compounds considered. M. PARKIN.

**Thermal expansion of boric oxide, arsenious oxide, metaphosphoric acid, and lead glasses, and the variation of the volume with the crystallisation pressure.** G. TAMMANN and G. BANDEL (Z. anorg. Chem., 1930, 192, 129—144).—The thermal expansion of a number of vitreous substances has been determined by measurement of the pressure variations which occur when the substance is heated at constant volume. Boric oxide yields a  $p$ - $T$  curve with a definite break which at low initial pressure occurs at 248°, rising to 280° for pressures in the neighbourhood of 3000 kg. per cm.<sup>2</sup>, the variation being expressed by  $T_{\text{break}} = 247^\circ + 0.02p - 3 \times 10^{-6}p^2$ ; below the break  $dp/dT$  is about 0.25, and above the break, 1.7—2.0. If the  $p$ - $T$  curve is determined at a pressure of 500 kg. per cm.<sup>2</sup> above that at which the glass is devitrified, a horizontal portion appears from 210° to 270°, whilst at higher pressures the curve assumes a negative slope between 200° and 300°, i.e., the glass has a negative coefficient of expansion over this interval. Vitreous arsenious oxide exhibits similar phenomena; when the glass devitrified at 150 kg. per cm.<sup>2</sup> is heated at 1900 kg. per cm.<sup>2</sup> and cooled, the volume increases by about 3.6%. Lead glass when heated at low initial pressures shows a linear increase of pressure up to about 460° and then a more rapid increase; at initial pressures of 500 kg. per cm.<sup>2</sup> and upwards the pressure diminishes up to about 200°, remains constant for the next 200—300°, and finally rises rapidly. It is uncertain whether lead glass has a negative expansion coefficient at high pressures, but the specific volume diminishes when the glass is devitrified at a high pressure. The  $p$ - $T$  curves of metaphosphoric acid resemble closely those of boric oxide; for a glass containing 12.4% of water the break occurs at  $T_{\text{break}} = 33.5^\circ + 0.0062p$ , and for a glass containing 9.9% of water,  $T_{\text{break}} = 85.5^\circ + 0.0053p$ . The change of specific volume with the devitrification pressure is only about 0.33 of that observed with boric acid glass, and diminishes as the water content of the acid increases. H. F. GILLBE.

**Glass. V. Heat capacity data for some complex organic glasses and liquids.** G. S. PARKS, S. B. THOMAS, and W. A. GILKEY (J. Physical Chem., 1930, 34, 2028—2034; cf. A., 1929, 1228).—

Data for the specific heats of the systems glycerol-dextrose (equal parts by weight) and propylene glycol-glycerol-dextrose (equal parts by weight) between 90° and 285° Abs. have been obtained by Nernst's method, using an aneroid calorimeter to obtain instantaneous values. The heat capacity curves are similar to those obtained for glycerol and dextrose (A., 1928, 1189), but the transition from glass to liquid is more gradual with the two- and three-component systems. In the case of the system glycerol-dextrose the transition occurs between 200° and 222° Abs., and in that of the second system the transition is more abrupt when the time between successive determinations of specific heat is lengthened.

L. S. THEOBALD.

**X-Ray analysis of the system lithium-silver.** S. PASTORELLO (Gazzetta, 1930, 60, 493—501).—Nine lithium-silver alloys, containing from 5.6 to 48% Li, prepared by fusion in an inert atmosphere have been examined by the Debye method. The existence of a compound, AgLi, inferred from the brisk evolution of heat attending the dissolution of silver in lithium near 500°, was confirmed by the X-ray spectrograms. This compound possesses a cubic lattice of the CsCl type with  $a$  3.22 Å., corresponding with  $d$  5.68. A second compound occurs of which the formula is probably AgLi<sub>3</sub>. In the case of the system sodium-silver, X-ray analysis failed to show any solubility of sodium in silver. F. G. TRYHORN.

**Constitution of the cadmium-zinc alloys.** D. STOCKDALE (Inst. Metals, Sept., 1930. Advance copy. 6 pp.).—A re-examination of the equilibria at the zinc end of the cadmium-zinc system has shown that the solid solubility of cadmium in zinc is 2.15% at 263° and 2.6% at 353°; these results are in good agreement with those of Jenkins (B., 1926, 831), but much lower than those of Grube and Burkhardt (B., 1929, 721). The solid solubility of zinc in cadmium increases linearly from 0.5% at 100° to 2.95% at the eutectic temperature; these values are intermediate between those found by the above-named authors. A. R. POWELL.

**X-Ray investigation of lead-antimony alloys.** D. SOLOMON and W. M. JONES (Phil. Mag., 1930, [vii], 10, 470—475).—X-Ray analysis by the powder method of alloys of lead and antimony containing, respectively, 30% and 80% Pb affords no evidence of the formation of either a compound or a solid solution. The size of the lattice of the pure elements is maintained unchanged in the alloys. This is contrary to the findings of Bronievski and Slivovski (A., 1928, 1085). F. L. USHER.

**Equilibrium diagram of the lead-tin system.** K. HONDA and H. ABÉ (Sci. Rep. Tôhoku, 1930, 19, 315—330).—The method of differential thermal analysis applied to the study of the above equilibrium diagram shows that the thermal change which takes place at about 160°, just below the eutectic line, is due to a rapid decrease of solubility of the  $\beta$ -phase in the  $\alpha$ -solid solution with fall of temperature. The horizontal line usually given on the equilibrium diagram can be omitted with advantage. In this way the diagram is considerably simplified. It is suggested

that other horizontal lines found in equilibrium diagrams for other systems could be omitted.

A. J. MEE.

**Transformation of solid metallic phases. I. The tetragonal gold-copper alloy, AuCu.** U. DEHLINGER and L. GRAF (Z. Physik, 1930, 64, 359—377).—The transformation of cubic mixed crystals containing 50 at.-% Au and 50 at.-% Cu into the tetragonal compound AuCu takes place in the case of single crystals by means of a direct change in the form of the lattice. After only a short time an intermediate state is reached. In this condition there is a lattice with tetragonal symmetry and with accurately defined lattice constants, in which, however, some of the atoms are in the mixed crystal state. Afterwards, when the alloy has been kept at a red heat for some time, the atoms become ordered, but during this process the lattice constants do not change. The change of electrical resistance with the temperature which has been established for this alloy can be explained on the basis of a slow decrease in tetragonal form before the transition point, and of the gradual arrangement of the atoms. The compound AuCu, with completely arranged atoms, is very soft, whilst the intermediate state is extraordinarily hard. On deformation the tetragonal form is destroyed. The theory of the change is discussed. The transformation from cubic mixed crystals to the tetragonal form must involve the free metal electrons. This is shown to be thermodynamically possible. The atoms, after reaching the tetragonal intermediate stage, become ordered by diffusion. The tetragonal distribution of atoms, which can hold only for an atomic ratio of 1:1, stabilises the tetragonal symmetry of the electrons, but this may easily change its axial direction.

A. J. MEE.

**Meaning of the equilibrium diagram [of iron-carbon alloys].** R. RUER (Stahl u. Eisen, 1930, 50, 1062—1067).—Polemical against Honda (Trans. Amer. Soc. Steel Treat., 1929, 16, 183). Simplification of the iron-carbon diagram by omitting the graphite lines is not permissible, as the diagram then does not represent the equilibria in the system and is not in accord with the theory of heterogeneous equilibria.

A. R. POWELL.

**Metallographic investigation of vanadium steels.** M. ŌYA (Sci. Rep. Tôhoku, 1930, 19, 331—364).—The structure and equilibrium diagrams of vanadium steels have been studied by dilatometric and magnetic analyses, and by microscopical observation. The equilibrium diagram shows that the solubility of carbon in the  $\gamma$ -phase decreases to a considerable extent on the addition of vanadium, and hence the existing range of the  $\gamma$ -phase in this system is very narrow. In the  $\gamma$ -phase region there exist three proeutectoid surfaces in which the  $\alpha$ -phase,  $\text{Fe}_3\text{C}$ , and  $\text{V}_4\text{C}_3$ , respectively, begin to separate. The eutectoid temperature in the  $\text{Fe}-\text{Fe}_3\text{C}$  system (the A1 point) is raised  $15^\circ$  by the addition of 0.5% V, and remains constant on further addition of vanadium. The binary eutectoid reaction  $\gamma \rightarrow \alpha + \text{V}_4\text{C}_3$  occurs in the temperature range  $745-1330^\circ$ . The non-variant reaction  $\text{V}_4\text{C}_3 + \gamma \rightleftharpoons \text{Fe}_3\text{C} + \alpha$  takes place in the neighbourhood of about 0.5% V and 0.9% C.

A. J. MEE.

**Change in electrical resistance and hardness of alloys of lead and of thallium with time.** G. TAMMANN and H. RÜDIGER (Z. anorg. Chem., 1930, 192, 1—44).—The change in hardness and resistance on keeping at  $20^\circ$  of binary alloys of lead with cadmium, bismuth, tin, sodium, potassium, mercury, and thallium and the change in resistance of binary alloys of thallium with lead, mercury, and tin have been studied. The concentrations examined varied from below to a little above that corresponding with the saturated solution in lead or thallium at  $20^\circ$  of the other component. Three specimens of each alloy were studied, one prepared by chilling the molten metal to  $20^\circ$ , another by heating for some time at a little below the m. p. to homogenise the alloy, which was then chilled, and the third by homogenising and then cooling slowly to  $20^\circ$ . The results in general are in agreement with the theory that the change in resistance is due to the relatively rapid diffusion which occurs in lead and thallium at  $20^\circ$ , permitting homogenisation of laminated crystals, crystallisation from super-saturated solid solutions, and, in the case of cold-drawn wires, recrystallisation. By working on this hypothesis approximate solubilities in solid lead and thallium may often be deduced from observations on the change of resistance with time. A further cause of changes in resistance of wires of thallium alloys is surface oxidation, resulting in a reduction of the effective cross-section. In this respect thallium-tin alloys, however, are exceptional, for even small amounts of tin have a marked protective action. The hardness is influenced by factors much the same as those which affect the resistance, but not always in the same direction. Crystallisation from super-saturated solid solutions, for instance, appears always to reduce the resistance and will usually reduce the hardness also, but if the crystals separating are very small, as in sodium-lead alloys, the hardness may be increased.

R. CUTHILL.

**Hardness of binary alloys rich in aluminium in relation to their composition.** K. RÖRN (Z. anorg. Chem., 1930, 191, 181—193).—For binary alloys of aluminium with copper, silicon, nickel, calcium, magnesium, manganese, and zinc the logarithm of the percentage by volume of the second component bears an approximately linear relation to the depth of impression made in the Ludwig hardness test; for alloys in which compound formation takes place the same relation applies to the concentration of the compound. In both cases there is a break in the curve above a certain concentration, and the linear relation does not hold for the regions over which mixed crystals exist. Analogous results are obtained if the Brinell hardness test is employed.

H. F. GILLBE.

**Molecular constitution of certain intermetallic solid solutions at temperatures below that of the eutectic examined thermodynamically.** F. H. JEFFERY (Trans. Faraday Soc., 1930, 26, 587—588).—By suitable choice of the molecular aggregation of the components X and Y in the two co-existing solutions it is found that  $\log(l-n')/n$  becomes a linear function of  $1/T$ , where  $n$  and  $n'$  are the molal fractions of Y in X in the one phase and of X in Y in

the other, respectively, and  $T$  is the absolute temperature; from this the molecular constitution of the solid solutions can be determined. H. F. GILLBE.

**Molecular constitution of the solid solution of tin in lead at temperatures below that of the eutectic.** F. H. JEFFERY (Trans. Faraday Soc., 1930, 26, 588—590).—The relation previously derived (cf. preceding abstract) has been verified for lead-tin alloys at temperatures below that of the eutectic. The solid solution of tin in lead contains only monatomic molecules of the two metals and remains of the same nature from the f. p. of lead to 130°. No evidence has been obtained for the existence of an isothermal at 149° starting within the region investigated. H. F. GILLBE.

**Solid solutions, isomorphism, and symmorphisms among oxides of bivalent metals. III. Systems MnO-CdO and MnO-MgO.** L. PASSERINI (Gazzetta, 1930, 60, 535—543; cf. A., 1929, 639).—An X-ray examination has been made by the powder method of solid solutions of metallic oxides prepared by the calcination at temperatures between 350° and 700° of mixtures of the hydroxides obtained by precipitating mixed solutions of the chlorides by potassium hydroxide solution. In seven preparations of the system MnO-CdO, prepared at 350°, and containing up to 90% MnO, partial miscibility was found, up to a maximum of 21% CdO in manganous oxide, and of 26% MnO in cadmium oxide. When the solid solutions were prepared at 700° a maximum solubility of 53% MnO in cadmium oxide was observed. Partial mutual solubility was found in the system MnO-MgO, the limiting solid solutions containing 31% MgO and 26% MnO, respectively. F. G. TRYHORN.

**Solid solutions, isomorphism, and symmorphisms among oxides of trivalent metals. Systems  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ ;  $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$ ;  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ .** L. PASSERINI (Gazzetta, 1930, 60, 544—558).—Solid solutions of the oxides of the above systems have been prepared by calcination at about 600° of the hydroxide mixtures obtained by the addition of an alkali hydroxide to mixed solutions of the chlorides or sulphates of the metals. An X-ray examination by the powder method has been made of preparations containing widely varying proportions of the constituents. The solid solutions, like the pure oxides, crystallise in the rhombohedral system. The pure oxides of aluminium, chromium, and iron prepared by calcination of the hydroxides were also examined, with the following results: chromium oxide, hexagonal cell,  $c/a$  1.374,  $a$   $4.950 \pm 0.005$ ,  $c$   $6.806 \pm 0.007$  Å.,  $v$   $143.4 \times 10^{-24}$  c.c.,  $d$  5.283; rhombohedral cell,  $a$   $5.38 \pm 0.005$  Å.,  $\alpha$   $54^\circ 50' \pm 5'$ ; ferric oxide, hexagonal cell,  $c/a$  1.366,  $a$   $5.020 \pm 0.005$ ,  $c$   $6.860 \pm 0.007$  Å.,  $v$   $148.6 \times 10^{-24}$  c.c.,  $d$  5.355; rhombohedral cell,  $a$   $5.43 \pm 0.005$  Å.,  $\alpha$   $55^\circ 6' \pm 5'$ ; aluminium oxide, hexagonal cell,  $c/a$  1.366,  $a$   $4.740 \pm 0.005$ ,  $c$   $6.478 \pm 0.007$  Å.,  $v$   $125.1 \times 10^{-24}$  c.c.,  $d$  4.075; rhombohedral cell,  $a$   $5.13 \pm 0.005$  Å.,  $\alpha$   $55^\circ 6' \pm 5'$ . Limited miscibility occurs in the systems  $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  at all the temperatures employed. An inverse relationship is found between the maximum amount of oxide held in solid solution in these systems and the difference between the diameters of the metallic

ions. The axial ratios of the cells of the solid solutions are intermediate between those of the pure oxides. Complete miscibility in the solid states was found in the system  $\text{Cr}_2\text{O}_3\text{-Fe}_2\text{O}_3$ , the axial ratios of the cells and the densities being, within experimental error, linear functions of the composition of the solid solutions. The results of these measurements indicate that solubility in the solid state among oxides of trivalent metals follows laws analogous to those found previously for oxides of bivalent metals (cf. A., 1928, 1316; 1929, 639). F. G. TRYHORN.

**Diffusion phenomena in solid molybdates and tungstates.** W. JANDER (Z. anorg. Chem., 1930, 191, 171—180).—A method has been developed for the detection and measurement of the diffusion of the metallic atoms and acid groups in the tungstates and molybdates of the alkaline earths and of zinc, cadmium, nickel, and manganese. In the alkaline-earth salts at 800—1000° the metallic atoms are firmly fixed in their positions in the lattice, whereas the acid radicals are relatively mobile. In the heavy metal salts the metals and the acid radicals share equally in the diffusion processes. H. F. GILLBE.

**Volatility of boric acid. I. Volatility in aqueous solution. II. Volatility in Roscoe's acids. III. Volatility of solid boric acid in steam.** G. BANCHI and M. GIANNOTTI (Annali Chim. Appl., 1930, 20, 271—285, 286—296, 296—301).—I. When aqueous boric acid solutions are distilled, the proportion of acid passing over in the distillate is proportional to the concentration of the original solution. If, however, the solution is heated under a reflux apparatus prior to the distillation, such proportionality is not observed, the quantity of boric acid then distilling remaining constant for different concentrations of the solution distilled. The results obtained on distillation of saturated boric acid solutions in presence of the solid phase are in good agreement with those of Nasini and Ageno (A., 1912, ii, 937). A distillate containing 3.86% of the acid may be obtained if the solution is heated in a bath maintained at a high constant temperature. That the volatility of boric acid from its solutions heated on a water-bath is not due to mechanical entrainment is confirmed. The discrepancies apparent in the published results are explainable by the influence of preliminary refluxing and of the rate of distillation (cf. Skirrow, B., 1901, 805).

II. The amounts of boric acid distilling from solutions in water and in azeotropic aqueous solutions of hydrochloric (b. p. 110°), nitric (b. p. 119.5°), and hydrobromic (b. p. 126°) acids under conditions otherwise similar increase as the b. p. of the solvent rises. From 10% solutions of boric acid in these solvents the proportions distilling are, respectively, 0.3638, 0.9054, 1.2230, and 1.3576 dg. per 1000 c.c. of distillate. Extrapolation indicates that no boric acid would distil at a temperature slightly below 100°. The amount of the acid distilling increases with the concentration of the solution and from a hydrobromic acid solution a distillate containing 0.24% of boric acid is obtainable, whilst if the heating bath is kept at 150°, the distillate contains about 1%. As was found with aqueous solutions (see above), the amounts

of boric acid distilling from the solutions in azeotropic hydrochloric and nitric acids are independent of the concentration of the boric acid if the solutions are first boiled in a reflux apparatus; the time of refluxing necessary to attain this constancy is, however, greater than with aqueous solutions. If the heating is effected on a water-bath, the amounts of boric acid evaporating from the aqueous, hydrochloric, and nitric acid solutions are equal.

III. The quantity of boric acid distilled from the solid in a current of steam subjected to different degrees of superheating increases as the temperature of the steam is raised. At 115° the curve connecting the concentration of boric acid in the distillate with the temperature of the steam changes its direction, the ratio between the acid distilling and rise of temperature suddenly increasing. This is probably due to transformation of orthoboric into the meta-acid, such change probably requiring a higher temperature in presence of steam than under ordinary conditions. The amounts of the acid distilling in steam are small compared with those distilling from aqueous or acid solutions, but do not differ greatly from the amounts found in boraciferous soffioni. T. H. POPE.

#### Solubility relations in gas-liquid systems.

III. Solubility of oxygen in benzene. J. L. R. MORGAN and H. R. PYNE (J. Physical Chem., 1930, 34, 2045—2048; cf. this vol., 1106).—The solubility of oxygen in benzene at 25° has been determined and compared with the results of Fischer and Pfeleiderer (A., 1922, ii, 841). The Ostwald solubility coefficient is  $0.2079 \pm 0.0007$ . L. S. THEOBALD.

Aniline and hydrogen sulphide. W. D. BANCROFT and B. C. BELDEN (J. Physical Chem., 1930, 34, 2123—2124).—Hydrogen sulphide dissolves in aniline in accordance with Henry's law. Up to pressures of 1200 mm. no evidence of the formation of a compound was obtained. The ratio of the mass of gas (in mg.) taken up by 1 c.c. of aniline to the pressure of the gas is 0.0273 at 22°.

L. S. THEOBALD.

Solubilities of the soluble electrolytes. IV. Salt volumes in solution and the contraction of solvent. A. F. SCOTT and E. J. DURHAM (J. Physical Chem., 1930, 34, 2035—2044; cf. A., 1929, 997; this vol., 1107).—The variation of the contraction of water molecules in saturated solution with temperature has been studied. The relationship  $\Delta V = V_s - \alpha N^2$  holds between 0° and 100° for the chlorides of potassium, rubidium, and caesium, for sodium and potassium bromides and iodides, and for sodium nitrate.  $\Delta V$  is the apparent volume of salt, of solubility  $N$  in a saturated solution,  $V_s$  is the hypothetical volume of an electrolyte in a saturated solution, and  $\alpha$  is a constant. The contraction,  $k$ , of each g.-mol. of solvent equals  $\alpha N$ ; its relation to other properties of saturated solutions is discussed.

L. S. THEOBALD.

Crystallisation of sodium bromide from supersaturated solutions. I. N. STRANSKI and Z. C. MUTAFTSCHIEV (Z. physikal. Chem., 1930, 150, 135—138; cf. A., 1929, 1133).—From a supersaturated solution of sodium bromide crystals of the anhydrous salt are deposited at about 50° on galena, which has

a lattice identical with that of the bromide. At a lower temperature (approximately 32°) crystals of the dihydrate are deposited. In the presence of pyrites, whether pure, or as impurity in galena, or sprinkled on the surface of pure galena, the anhydrous salt is not deposited, but the dihydrate forms at about 42°. Sphalerite and rutile give the same results as galena, whilst cuprite and marcasite behave like pyrites. The solubility of sodium bromide at 39° is  $53.6 \pm 0.05$  g. per 100 g. of solution. F. G. TRYHORN.

Experimental investigation into equilibrium relations between a plastic crystalline solid and its solution. B. LOCKSPEISER (Trans. Faraday Soc., 1930, 26, 605—623).—The thermodynamic reversibility of the physical transformations of plastic solids, e.g., dissolution and evaporation, which involve uncontrollable stress changes, has been investigated theoretically and experimentally. Study of the equilibrium of iodine in contact with its aqueous solution over closed temperature cycles between 91.2° and 24.2° shows the process of dissolution to be irreversible, since (1) the equilibrium at any temperature varies with the history of the system, (2) the curve showing the approach from a position of displaced equilibrium to equilibrium does not conform to reversibility of the equilibrium, and (3) the temperature coefficient of the molecular heat of dissolution, calculated on the assumption of reversibility, is inadmissible, viz., 60—80 g.-cal. per 1° for the range 21—66°. H. F. GILLBE.

Solubility of the halides of zirconium and hafnium. G. VON HEVESY and O. H. WAGNER (Z. anorg. Chem., 1930, 191, 194—200).—The solubilities of zirconium and hafnium oxybromides in dilute hydrogen bromide solutions at 25° are of the same order, that of the hafnium salt being somewhat the greater, but in concentrated solutions (13*N*) zirconium oxybromide is four to five times as soluble as hafnium oxybromide. The solubilities of the oxyfluorides in hydrogen fluoride solutions both exhibit a maximum, which for the zirconium salt occurs in about 6*N* solution and for the hafnium salt in about 8*N* solution. At all acid concentrations the zirconium salt is the more soluble, the difference being greatest in dilute and in concentrated (20*N*) solutions. The solubilities and densities of the solutions are tabulated.

H. F. GILLBE.

Molecular size and solubility in acetone of cadmium iodide, and mercuric chloride, bromide, and iodide. C. ZAPATA Y ZAPATA (Anal. Fis. Quím., 1930, 28, 603—610).—The solubilities in acetone at 25° (g./100 g.) of cadmium iodide and mercuric chloride, bromide, and iodide are 30.0, 54.9, 33.9, and 3.08, respectively. The high results reported by previous workers are ascribed to the use of acetone containing water. The degrees of association at various concentrations, determined by the b.-p. method, are: cadmium iodide, 2.5—19.9% solution, 0.9—1.68; mercuric chloride, 3.17—16.5%, 1.0—1.05; mercuric bromide, 3.4—8.9%, 1.26—1.43; the solubility of mercuric iodide in acetone is too small for the b.-p. elevation to be measured accurately.

H. F. GILLBE.



**Solubility curve of benzoic acid in toluene.** CHAPAS (Compt. rend., 1930, 191, 43—45).—For the solubility of benzoic acid in toluene from 0° to the m. p. of the acid the formula  $\log (\gamma/100) = a(1/T - 1/T_f)$ , where  $\gamma$  is the solubility in mols. per 100 mols. of solution,  $T$  the absolute temperature,  $T_f$  the m. p. of benzoic acid, and  $a$  is a constant = 1363, is valid to within 0.6%. Chipman's solubility curve is criticised, and his method has been modified to give considerably more consistent results.

H. F. GILLBE.

**Solubilities of succinchloroimide.** C. B. WOOD (J. Amer. Water Works Assoc., 1930, 22, 1266—1267).—The approximate solubility of succinchloroimide (m. p. 146—147°) has been determined in a variety of solvents at 20°.

H. INGLESON.

**Solubility of lactose in pyridine.** J. GILLIS (Natuurwetensch. Tijds., 1930, 12, 171—174).—The solubility of  $\beta$ -lactose in pure pyridine and in mixtures of water and pyridine containing, respectively, 50% and 90% of the latter by weight has been determined between 55° and 122° by the method of disappearance in sealed tubes. With 50% pyridine, the transition point  $\alpha_{aq.} \rightarrow \beta + H_2O$  is 94.5°. The solubility diminishes rapidly with increasing pyridine content of the solvent; at 122.1°, 100 g. of pure pyridine dissolve only 0.1144 g. of  $\beta$ -lactose.

S. I. LEVY.

**Solubility of water in solutions of acids in benzene.** R. P. BELL (Z. physikal. Chem., 1930, 150, 20—30; cf. Szyszkowski, A., 1928, 239).—The solubility of water in solutions of each of the three chloroacetic acids in benzene has been measured, with the object of ascertaining whether only the simple molecules undergo hydration. The solubility of water is directly proportional to the concentration of acid, whence it follows that the double as well as the single molecules are hydrated. The degree of hydration increases with the content of chlorine. Trichloroacetic acid with an equimolecular proportion of water is soluble in benzene, carbon tetrachloride, or hexane. Szyszkowski's values for the dissociation constants of double molecules of acids are inaccurate owing to his assumption that they are not hydrated.

F. L. USHER.

**Use of calcium hydride for the determination of solubility of water in benzene, carbon tetrachloride, and toluene.** C. K. ROSENBAUM and J. H. WALTON (J. Amer. Chem. Soc., 1930, 52, 3563—3573).—The saturated liquid under investigation is brought into contact with calcium hydride in a special apparatus. About 95% of the total hydrogen evolved is obtained in 10 hrs. and the method is applicable to liquids of low b. p. (cf. Notevarp, this vol., 560). Solubility data are recorded for temperatures between 10° and 60°, 0.1% of water being determined to within 0.001%. Moist benzene contains only 0.015% of water after distilling off 10—20% of the liquid.

J. G. A. GRIFFITHS.

**Solubility of water vapour in solid inorganic compounds at high temperatures.** E. W. R. STEACIE and G. B. GRAHAM (J. Physical Chem., 1930, 34, 2098—2102).—The solubility of water vapour in silica, alumina, potassium chloride, and sodium

sulphate at temperatures up to 900° has been investigated. Water vapour is not appreciably soluble in these compounds above the dissociation temperatures of their hydrates.

L. S. THEOBALD.

**Sextl's adsorption theory.** A. GANGULI (Z. Physik, 1930, 64, 81—83).—Mathematical. A formula derived by the author is shown to be the same as one obtained by Sextl.

A. J. MEE.

**Heats of adsorption and isotherms in the system platinum-hydrogen.** E. B. MAXTED (J.C.S., 1930, 2093—2100).—The heat of adsorption of hydrogen on platinum has been determined as a function of the quantity of gas adsorbed for specimens of platinum-black varying in age from 2 to 89 days. The integral heat of adsorption diminishes with increased age of the catalyst, and there is a well-defined maximum in the differential heat of adsorption curves, which, however, become flatter as the catalyst ages. The actual curve obtained with a given specimen of platinum-black depends on its history and on the degree of degassing to which it has previously been subjected. Isotherms of the adsorption process show that the quantity of gas adsorbed increases at first very rapidly with the pressure, but soon reaches a stage at which further increases of pressure have practically no effect; with increasing age of the catalyst the curves shift towards the pressure axis.

H. F. GILLBE.

**Adsorption of hydrogen and carbon monoxide on oxide catalysts.** W. E. GARNER and F. E. T. KINGMAN (Nature, 1930, 126, 352).—Hydrogen or carbon monoxide is adsorbed on oxide surfaces reversibly at the ordinary temperature, and irreversibly at higher temperatures. The gas adsorbed at the ordinary temperature on zinc oxide-chromic oxide catalysts at equilibrium pressures of  $10^{-3}$  to  $10^{-4}$  cm. is evolved at 100—120° and readsorbed within 20—30 min. to give a high vacuum; no further gas is evolved until 350°, when water vapour or carbon dioxide, respectively, is liberated. Mixtures of hydrogen and carbon monoxide behave in a similar manner; likewise hydrogen on copper oxide. The reduction of oxides by these gases occurs through the adsorption of the gas, chemical combination with the surface atoms, and desorption of the resultant gases.

L. S. THEOBALD.

**Heats of adsorption on catalytically active surfaces.** E. W. FLOSDORF and G. B. KISTIakovskiy (J. Physical Chem., 1930, 34, 1907—1918; cf. this vol., 552).—The heats of adsorption of hydrogen on reduced zinc-chromium oxide, on two samples of platinum-black supported on asbestos, and on unsupported platinum-black have been determined together with the heat of adsorption of oxygen and water vapour on the latter. On repeated heat treatments at 400° followed by degassing, the heat of adsorption and the adsorptive capacity show maximum values in the case of hydrogen and the zinc-chromium oxide. With the platinum-blacks, the supporting material greatly increases adsorption and prevents sintering of the metal; the heat of adsorption is not markedly changed. In the case of the unsupported material, comparison with the results

previously obtained (*loc. cit.*) shows that purity of material is as important as the method of preparation in determining the surface properties of a finely-dispersed metal. The values determined for the heat of adsorption of water vapour are in agreement with those calculated from the data for hydrogen and oxygen.

L. S. THEOBALD.

**Calorimetric determinations of heats of adsorption. Adsorption of sulphur dioxide by wood charcoal.** A. MAGNUS, H. GIEBENHAIN, and H. VELDE (*Z. physikal. Chem.*, 1930, **150**, 285—294).—The integral heats of adsorption of sulphur dioxide by coconut charcoal have been measured over a wide range of concentration (0.05—68 mg. of sulphur dioxide per g. of charcoal). With increase in the adsorbed amount there is a slow, regular fall of molar heat of adsorption. Differential heats of adsorption were measured by allowing about 0.12 mg. of gas per g. of adsorbent to be adsorbed on the already more or less charged charcoal. A marked discrepancy appears between the curves for integral and differential heats of adsorption, and this is explained by the slow establishment of equilibrium in the crevices on the surface of the adsorbent.

E. S. HEDGES.

**Determination of adsorbed gas layer on a metallic surface by a weighing method.** L. STROHHÄCKER (*Z. Physik*, 1930, **64**, 248—261).—The adsorption of a gaseous layer on metals has been proved for the first time by direct weighing, using a highly sensitive balance with equal arms. A thin sheet of the metal, previously outgassed, is weighed before and after it has adsorbed gas. With certain assumptions concerning the packing of the molecules on the surface it is possible to calculate the thickness of the adsorbed layer. Using gold, the layer was found to be unimolecular, and Langmuir's adsorption theory could thus be proved directly. The thickness of the foil used was  $5.6 \times 10^{-3}$  mm., and 762 sq. cm. of free surface was exposed. When this surface was kept for 40 hrs. in dry air under ordinary conditions of temperature and pressure the increase in weight was  $3.51 \times 10^{-5}$  g. On heating to redness for some time in a vacuum no gas appeared to be given up by the foil.

A. J. MEE.

**Adsorption of methyl alcohol films on rock-salt.** S. SILVERMAN (*Physical Rev.*, 1930, [ii], **36**, 311—318).—The isothermal adsorption of methyl alcohol films on rock salt was investigated for the pressure range  $10^{-5}$  mm. to 11 cm., using Frazer's modification of the optical method of Rayleigh and Drude (*cf. A.*, 1929, 503). Results indicate that a unimolecular layer is formed at  $10^{-5}$  to  $10^{-4}$  mm. pressure, with no further absorption below 2—3 cm., when a second layer begins to form, with completion at 9—10 cm. The thickness of the layers is calculated as approximately 4.5—5.0 Å. The effect of outgassing was examined, and the results indicate that with fall of temperature an underlying unimolecular layer of water vapour is formed, or that there is an increase in the natural ellipticity of the surface. The isothermal heat of adsorption is calculated from the experimental data.

N. M. Blich.

**Adsorption phenomena in solution. XXII. Orientation of the adsorption series and its dependence on the conditions of activation of sugar charcoal.** M. DUBININ (*Z. physikal. Chem.*, 1930, **150**, 145—160).—The adsorptive power of sugar charcoal, activated in air or carbon dioxide for varying periods at temperatures between 500° and 1000°, with reference to propionic, valeric, heptolic, hydrochloric, sulphuric, and phosphoric acids, iodine, and sodium hydroxide has been investigated. The degree and order in which these substances are adsorbed are discussed in relation to the physical nature of the charcoals. In general, the chief factors influencing the order of adsorption are the porosity, the temperature of activation, and the chemical nature of the surface film of oxide which forms on the charcoal during activation.

F. G. TRYHORN.

**Adsorption phenomena in solutions. XXI. Surface oxides of carbon.** N. SCHILOV, H. SCHATUNOVSKAJA, and K. TSCHMUTOV (*Z. physikal. Chem.*, 1930, **150**, 31—36; *cf. this vol.*, 991).—Further experiments on the adsorption of electrolytes by active carbon subjected to various treatments are described. The results are considered to support the authors' view that the effects observed are determined by the presence in the carbon surface of one or more of the oxides "A," "B," and "C."

F. L. USHER.

**Adsorption in solutions in relation to the dielectric properties of the solvent. I.** E. HEYMANN and E. BOYE (*Z. physikal. Chem.*, 1930, **150**, 219—256).—The relation to be expected between dielectric properties of solvents and the adsorption of solutes therefrom is discussed theoretically and has been investigated experimentally. Purified, almost ash-free wood charcoal was used as the adsorbent and it has been established that, in the adsorption of benzoic, acetic, formic, and butyric acids, and iodine (violet solutions only) from a number of solvents, weak adsorption occurs in strongly polar solvents and strong adsorption in weakly polar solvents. This antibatic relation between dipole moment and adsorption is not universal, however, and is probably influenced by the mutual affinities of the solute and solvent. This suggestion is supported by the observation that iodine is much more weakly adsorbed from brown solutions in alcohol, ether, and benzene, where it is solvated, than from violet solutions, where there is practically no solvation. A definite and constant relation between dielectric properties and adsorption occurs only in solvents which are closely related chemically, such as a homologous series of alcohols. The adsorption of benzoic or picric acid in alcoholic solution by charcoal falls with increasing molecular polarisation of the alcohol, *i.e.*, with increasing deformability of the molecule. A similar relation is found between adsorption and dipole moment in the adsorption of iodine from the series of chloromethanes. An investigation of adsorption in solvent mixtures was also made and a connexion was established between the adsorption curve (relating percentage adsorption to the composition of the mixture) and the molecular polarisation curve. In general, there are two types of behaviour. Linear

adsorption curves are obtained when both components of the solvent mixture are non-polar (benzene-carbon tetrachloride), or when one component is polar but when its specific polarisation is not altered appreciably by the presence of the non-polar solvent (mixtures of benzene with toluene, chloroform, or chlorobenzene). On the other hand, complicated curves, showing one or more minima, are obtained when the specific polarisation of the polar component is altered by admixture with the non-polar component (benzene with nitrobenzene or alcohol, carbon tetrachloride with alcohol or acetone), or when both components are polar. In such cases the maximum polarisation corresponds with the minimum of adsorption. Adsorption in solvent mixtures is further discussed in relation to vapour pressure and solubility.

E. S. HEDGES.

**Adsorption influence, activity, and solvation in salt solutions.** P. P. KOSAKEVITSCH and N. A. ISMAILOV (*Z. physikal. Chem.*, 1930, **150**, 295—309).—The adsorption by charcoal of phenol in aqueous solution and of benzoic acid in methyl- or ethyl-alcoholic solution is increased by the presence of the chlorides or bromides of lithium, sodium, or potassium. In aqueous solution the relative effects of the cations are in the order  $\text{Na} > \text{Li} > \text{K}$  and those of the anions  $\text{Cl} > \text{Br}$ . In methyl alcohol the same order is observed for the anions, but this order is reversed in ethyl alcohol. The salts raise the activity of the substance adsorbed, providing a means of calculating the relative activities of the latter from adsorption measurements. On the assumption that the neutral salt effect is due to solvation, values are obtained from adsorption measurements in good agreement with those calculated from the influence on solubility.

E. S. HEDGES.

**Precipitation and adsorption of traces of material on crystalline precipitates.** O. HAHN (*Z. angew. Chem.*, 1930, **43**, 871—875).—The simultaneous separation of small quantities of substances with crystalline precipitates may be classified in two groups, viz., precipitation and adsorption. The first type is independent of the conditions of precipitation and is caused by the formation of isomorphous or isodimorphous mixed crystals, but the adsorption type varies according to the conditions of precipitation and is not fully in accordance with the Fajans and Paneth adsorption laws. Study of the adsorption of thorium-*B* during the precipitation of calcium sulphate and of thorium-*C'* during the precipitation of silver bromide shows that the adsorption of the radioactive cation increases with increasing excess of the precipitating anion, and diminishes with increasing excess of the cation. The polar nature of the precipitate is also of importance; thorium-*B* is adsorbed to a much greater extent by silver bromide than by the weakly polar mercurous bromide, whilst in both cases reduction of the surface area of the precipitate by addition of acid to accelerate crystallisation causes a great diminution in the quantity adsorbed. The total adsorption is probably the result of a primary momentary adsorption, which is a function of the surface charge of the adsorbent and of the valency of the adsorbed ion, and of a secondary, slow adsorption, caused by a type of molecular com-

pound formation on the diminishing free surface of the adsorbent; this process may persist for a relatively long period, but if the adsorption compound formed has a high solubility this secondary adsorption becomes practically negligible.

H. F. GILLBE.

**Adsorption of soluble and sparingly soluble electrolytes on precipitates having a large surface.** L. LANGE (*Z. angew. Chem.*, 1930, **43**, 875—877).—The adsorption of lead and of actinium on the silver halides during precipitation is cited in support of the two-stage theory of adsorption by precipitates (cf. preceding abstract and A., 1929, 1377).

H. F. GILLBE.

**Dehydration of silicic acid by ignition.** B. NEUMANN (*Z. angew. Chem.*, 1930, **43**, 882—883).—The relation between the temperature of dehydration of a silica gel, the water content, and the adsorptive power from non-aqueous solutions has been determined between 200° and 1000°. The adsorption curve of indanthrene-bordeaux R from solution in xylene is almost identical in form with the dehydration curve, but the adsorption curve of gold from a gold-xylene sol is of a totally different form; the quantity adsorbed increases to a maximum at about 870° and thereafter diminishes. The transitions  $\alpha$ -quartz  $\rightarrow$   $\beta$ -quartz and  $\beta$ -quartz to  $\beta$ -tridymite are clearly indicated on both the dehydration and the adsorption curves.

H. F. GILLBE.

**Base exchange between dyes and soils.** W. L. HOFF and J. A. WILKINSON (*J. Physical Chem.*, 1930, **34**, 2092—2097).—The adsorption of methylene-blue and neutral-violet by six different Iowa soils has been investigated by the percolation method. From 80 to 90% of the adsorbed dye is taken up by base exchange with the metals of the soil. The equivalent weights of the metallic ions from the soil and of the chloride ions from the dye are equal. Neutral-violet replaces metals to a greater extent than does methylene-blue, but the ratio of the dye adsorbed to the base exchange is approximately the same for both dyes.

L. S. THEOBALD.

**Spreading of mercury globules on metallic surfaces.** G. TAMMANN and F. ARNTZ (*Z. anorg. Chem.*, 1930, **192**, 45—64).—When a drop of mercury is placed on a metal surface which it wets only slowly it assumes the form of a dome, from the edge of which a fringe sooner or later starts to spread. This behaviour points to the presence on the metal surface of an oxide film which is not wetted by the mercury. If the film is permeable to mercury vapour it is ultimately pierced immediately beneath the drop, which then commences to flatten out, rolling up the film before it. At the same time a fringe of mercury starts to creep under the film, this movement occurring, however, not on the metal surface but within it. Until the drop is quite flat the fringe expands at a rate which is constant and depends, not on the size of the drop, but only on the phase-boundary forces between the mercury and the metal at the periphery of the fringe and on the character of the film. Under solutions of substances, such as acids, which attack the film, spreading is more rapid than in air, whilst solutions of substances which tend to produce a film on a clean surface, e.g., hydrogen sulphide, have the

reverse effect. The rate of spreading on the surface of a "hard" metal either in air or under the surface of aqueous solutions is almost always greater than on the same metal in the "soft" state (cf. A., 1925, ii, 502). This effect is apparently not due to differences in orientation of the crystallites in the two states but to differences either in the boundary forces at the edge of the fringe or in the rate of wetting of the metal by mercury. The rate of spreading on mixed crystals of copper and nickel under 0.1N-sulphuric acid first falls very rapidly, then more slowly and in a linear manner with increase in the molar fraction of the nickel. R. CUTHILL.

**Coloured layers produced by sublimation.** A. MARCELIN and S. BOUDIN (Compt. rend., 1930, 191, 31—33; cf. this vol., 1111).—The sublimation of *p*-toluidine at temperatures just above the m. p. gives rise to films which exhibit interference colours, each coloured region being sharply differentiated from surrounding regions; the variations of thickness of the film are thus discontinuous, and correspond in all probability with the superposition of successive unimolecular layers. By observing the colour changes and the variations in the extent of the individual regions the mode of growth of the crystals may be studied; in general the crystal layer tends to become of uniform thickness. Comparatively few organic compounds give rise to these coloured films on sublimation, but the phenomenon appears to be independent of the chemical nature of the substance. H. F. GILLBE.

**Rate of evaporation of liquids from a heated metallic surface.** (MME.) H. BLASZKOWSKA-ZAKRZEWSKA (Bull. Acad. Polonaise, 1930, A, 188—190).—The temperature at which evaporation of a drop of liquid on a metal surface (aluminium bronze) takes place in minimum time is characteristic, and depends on the nature of the surface. It is a little below that at which the spheroidal state is assumed. After this minimum it increases to a maximum and then decreases again. Data for 12 liquids are given. C. A. SILBERRAD.

**Rate of evaporation of liquids from a heated platinum surface.** W. SWIENTOSLAWSKI and S. BAKOWSKI (Bull. Acad. Polonaise, 1930, A, 191—194; cf. preceding abstract).—A drop of liquid placed on a platinum-plated portion of a block of aluminium heated at a temperature a little above that corresponding with the minimum time of evaporation may, over a temperature interval of some 80°, show one of two periods, one approximating to the minimum, the other much longer, depending on whether the drop does or does not wet the surface. C. A. SILBERRAD.

**Antonov's rule and molecular orientation.** N. FUCHS (Kolloid-Z., 1930, 52, 262—269).—The angles of contact of a number of liquids having positive spreading coefficients have been measured and the experimental results are frequently in accordance with Antonov's rule; on the other hand, the rule is quite inapplicable in a number of cases. The deviation bears a relation to the molecular structure and probably depends on the degree of orientation of molecules in the saturated adsorption layer. E. S. HEDGES.

**Micellar and Donnan equilibria.** J. DUCLAUX and R. TITÉICA (Rev. gén. Colloid., 1930, 8, 251—259; cf. A., 1929, 1003).—Although Donnan's theory of membrane equilibria is generally accepted, it is suggested that the whole question should be reopened from the experimental point of view, since some of the hypotheses have no experimental justification and the existing experimental data are based on a small number of cases. Experiments on the ultrafiltration of a number of different types of sols showed that the intermicellar liquid has a constant composition, which is independent of the concentration of the sol and of the nature of the membrane. E. S. HEDGES.

**Ultrafiltration of petroleum.** A. ZAHARIA and E. LUCATU (Bul. Soc. Chim. România, 1930, 12, 90—94).—The question whether petroleum is a colloidal system is reviewed and the problem has been attacked by subjecting petroleum from various sources to ultrafiltration through a vulcanised rubber membrane. Paraffin and resins pass through the membrane, but both hard and soft asphalts are retained quantitatively. The asphalt is dispersed by benzene or cyclohexane and may again be removed from such solutions by ultrafiltration. After repetition of this treatment the ultrafilterable resins previously adsorbed are eliminated, and the pure, dry asphalt is found to redisperse in the ultrafiltrate of the petroleum. The asphalt-petroleum system is therefore to be regarded as a lyophilic colloid. E. S. HEDGES.

**Molecular motion in the light-image ultra-microscope.** H. SIEDENTOPF (Kolloid-Z., 1930, 52, 257—262).—A modified method of ultramicroscopical examination is described, in which the lower layer of the sol, about 1  $\mu$  in thickness, is illuminated by total reflexion. The method is specially suitable for the observation of the Brownian movement of very small particles and of ultramicroscopic gas bubbles. E. S. HEDGES.

**Determination of the number of free electric charges on air bubbles and oil droplets dispersed in water containing a small amount of cetyl-sulphonic acid.** J. W. MCBAIN and R. C. WILLIAMS (Coll. Symp. Ann., 1929, 7, 105—114).—Air bubbles had charges of  $2.4 \times 10^5$  and benzene bubbles  $5.9 \times 10^5$ , representing a surface covering of 0.0031—0.0017 and 0.0006, respectively. The classical treatment of electrokinetics on the basis of a double layer is invalid. CHEMICAL ABSTRACTS.

**Colloidal properties of systems soaps-o-cresol-water.** E. ANGELESCU and D. POPESCU (Bul. Soc. Chim. România, 1930, 12, 58—60).—Previous work (this vol., 692, 856) is summarised and the results are explained on the view that o-cresol causes a gradual diminution in the size of the colloidal soap particles and that there is a maximum viscosity at a medium degree of dispersion. E. S. HEDGES.

**Flow of colloids which show viscosity anomalies.** H. KROEPFELIN (Z. physikal. Chem., 1930, 149, 291—330).—Details are given of an apparatus and technique whereby the distribution of the velocity in the flow of colloidal solutions through tubes of circular cross-section, between parallel walls, and in the Couette apparatus may be studied. Gelatin solutions which do not show viscosity abnormalities

have a normal parabolic velocity distribution, but for those which do show such abnormalities the velocity distribution curve is a somewhat flattened parabola.

F. G. TRYHORN.

**Formation of paste from potato starch and some colloid-chemical properties of the product.** I. NOVOPOKROVSKI and N. TSCHEBOTAREVA (*Kolloid-Z.*, 1930, **52**, 302–304).—A summary of existing knowledge of the constitution and properties of starch paste.

E. S. HEDGES.

**Highly polymerised compounds. XLIII. Streaming double refraction of molecular colloids.** R. SIGNER (*Z. physikal. Chem.*, 1930, **150**, 257–277).—Solutions of many highly-polymerised compounds, including caoutchouc, cellulose derivatives, polystyrenes, etc., exhibit streaming double refraction and measurements of this property have been made at varying rates of shear. The streaming anisotropy increases with the concentration, but there is a specific double refraction given by  $(n_s - n_a)/G\eta$ , where  $G$  is the shearing velocity and  $\eta$  the viscosity, which is a characteristic constant for each substance and independent of the concentration. A relation between double refraction and viscosity exists in the sense that those solutions which obey the Hagen-Poiseuille law show a proportional rise of the double refraction with shearing gradient, whilst in solutions where the viscosity varies with the driving force the increase in streaming double refraction is slow. The optical phenomena indicate the presence of particles having a long axis, in agreement with the views on the molecular structure of highly polymerised compounds derived from other considerations. The specific double refraction varies with the solvent, having practically the same value in the non-polar liquids investigated and becoming smaller with increasing polarity of the solvent. This behaviour is probably due to an oriented adsorption of solvent molecules, partly compensating the effect due to the orientation of the particles. A relation between double refraction and chemical constitution is indicated. The variation of streaming double refraction with concentration and the change in a polymeric homologous series suggest that the dispersed particles are single molecules and not aggregates.

E. S. HEDGES.

**True and colloidal solubility; influence of interfacial tension.** E. HEYMANN (*Kolloid-Z.*, 1930, **52**, 269–280).—Recent research on pyrosols of metals in molten salts is reviewed and it is pointed out that with rising temperature the interfacial tension and the solubility vary in opposite senses; these systems appear to be true solutions. Measurements of the change of solubility and interfacial tension with temperature carried out with a number of liquid-liquid systems show that there is no definite quantitative relation between these properties, but that in all cases the properties vary qualitatively in opposite senses. In two-component mixtures of water with aniline, ethylene dibromide, benzene, hexane, olive oil, and carbon tetrachloride, respectively, and in the system isobutyl alcohol-glycerol the interfacial tension decreases and the solubility increases with rising temperature, whilst the reverse

behaviour is shown by two-component mixtures of water with amyl alcohol, heptane, heptaldehyde, and triethylamine, respectively. In the systems ethyl ether-water and octyl alcohol-water solubility increases in one phase and decreases in the other on raising the temperature. The theory of emulsification is discussed in the light of these experiments.

E. S. HEDGES.

**Influence of gases on lyophilic colloids. VIII. Mechanism of enzyme action.** J. WEICHNERZ, C. BODEA, and F. F. NORD (*Z. physikal. Chem.*, 1930, **150**, 1–19; cf. *A.*, 1929, 1200).—The surface tension of solutions of egg-albumin is raised by saturating them with ethylene or acetylene, and lowered by nitrous oxide. The same is true of sodium oleate solutions, although here the concentration relations are less simple. Nitrous oxide does not influence the interfacial tension of either substance against xylene, whereas ethylene or acetylene raises it. Measurements of the absorption of these three gases by sodium oleate, urease, egg-albumin, and gum arabic at different concentrations show that the absorption is chiefly or entirely a surface effect, except in the case of sodium oleate. No evidence was obtained of the coagulation of the above substances (with the exception of sodium oleate) by any of the gases. The results are discussed from the point of view of theories of narcosis.

F. L. USHER.

**Effect of ultra-violet light on colloids. II.** P. LAL and P. B. GANGULY (*J. Indian Chem. Soc.*, 1930, **7**, 513–520).—Hydrosols of silver iodide, arsenate, and thiocyanate, gold, silver, vanadium pentoxide, molybdenum-blue, thorium hydroxide, and arsenious sulphide are coagulated by exposure to ultra-violet light, whether the sols are positively or negatively charged. The hydrogen-ion concentration of the ultrafiltrate before and after exposure to the radiation has been determined and a detailed examination of the change has been made in the case of a silver sol stabilised by tannic acid and a thorium hydroxide sol prepared by dialysing thorium nitrate solution. It is shown that the coagulation of the silver sol is due to the photochemical decomposition of the tannic acid, which in the presence of a trace of potassium nitrate yields small amounts of ammonia. The coagulation of the thorium hydroxide sol and the accompanying change in hydrogen-ion concentration are explained by the photochemical decomposition of the stabilising nitric acid. The coagulation of colloidal solutions by light is considered to be due primarily to photochemical decomposition of the stabilising electrolytes.

E. S. HEDGES.

**Coagulation of clouds and mist.** E. FRANKENBERGER (*Physikal. Z.*, 1930, **31**, 835–840; cf. this vol., 540).—The formation of rain is treated as a coagulation of a colloidal system of water particles bearing similar electric charges, and the principles of colloid physics are applied to the process. A certain critical charge on the particles is necessary for the stability of a cloud and the influence of smaller electric charges on the velocity of coagulation is investigated mathematically. Under certain conditions, the rate of condensation of water vapour to cloud is equal to the rate of coagulation of the cloud

to rain drops, and the conditions leading to this "stationary state" of the cloud are formulated mathematically. E. S. HEDGES.

**Coagulation of quartz and bolus suspensions by gelatin, carrageen, and electrolytes.** F. DANNENBURG (*Kolloidchem. Beih.*, 1930, **31**, 447—467).—The coagulation of suspensions of quartz and of bolus by electrolytes is sensitised by gelatin in concentrations up to 0.01 g. per litre. The lower limit of sensitisation is about 0.00001 g. per litre for quartz and about 0.0001 g. per litre for bolus suspensions. The behaviour of the ions of potassium, barium, and aluminium is in accordance with the Schulze rule. The gelatin in these systems is probably in a hydrophobic state at the surface of the particles. At higher concentrations, 0.1—1.0 g. per litre, gelatin stabilises the suspensions, and is probably in a hydrophilic state at the surface of the particles. Carrageen sol does not coagulate suspensions of quartz or bolus in the absence of electrolytes, and the behaviour of added electrolytes is not in accordance with Schulze's rule. E. S. HEDGES.

**Ion antagonism in colloid models. IV. Double nature of Hofmeister's anion series and the factors of ion antagonism.** W. DOREMAN and D. ŠČERBAČEVA (*Kolloid-Z.*, 1930, **52**, 289—293; cf. this vol., 1116).—The stabilising effect of anions towards a sulphur sol against precipitation by electrolytes is in the following order: citrate > SO<sub>4</sub> > Cl > Br > NO<sub>3</sub> > I. This order is maintained whatever the cation of the salt, but marked quantitative differences between the members of the series are introduced with different cations. Whilst lithium salts show a high degree of antagonism varying considerably from the univalent to the tervalent end of the series, sodium and potassium salts are almost all equal in effect, and with magnesium salts the stabilising effect of the citrate and sulphate ions and the sensitising effect of the iodide ion are intensified. The Hofmeister series is considered to consist of two different groups, a valency group and a hydrophilic group. Both the charge and the hydrophilic properties of the ions have to be considered in ion-antagonism, and their effect on a given colloid also depends on the charge and degree of hydration of the colloid. E. S. HEDGES.

**Positive and negative acclimatisation phenomena in the coagulation of ferric hydroxide sol.** V. KRESTINSKAJA and O. MOLTSCHANOVA (*Kolloid-Z.*, 1930, **52**, 294—302).—Experiments on the coagulation of ferric hydroxide sols by various electrolytes indicate that in all the cases examined the phenomenon of acclimatisation can be traced to slow chemical changes produced by reaction of the colloid with the added electrolyte. With colloidal ferric hydroxide the added anion is the important factor and it may affect either the external, active part of the micelle or the kernel of the particle. In positive acclimatisation the added electrolyte forms a soluble salt with the substance of the kernel, with the result that the kernel diminishes and the active part of the micelle increases correspondingly, so that the stability of the sol is increased. This result is brought about by the slow addition of aluminium chloride and nitrate, ferric chloride,

and hydrochloric acid. Negative acclimatisation is observed in the addition of potassium hydroxide and arsenite, substances which react with the active part of the micelle and increase the kernel, thus decreasing the stability. The "apparent" negative acclimatisation observed with potassium and barium chlorides is traced to the slow coagulation caused by these electrolytes in low concentrations. In the case of arsenious sulphide sol the acclimatisation is due to chemical reactions between the added electrolyte and hydrolysis products of the sol. Ion antagonism is probably connected with acclimatisation and may be expected when one of the pair of added electrolytes alters the stability of the sol by chemical reaction. E. S. HEDGES.

**Transference of disperse phase from one dispersion medium to another by de-emulsification. I. The phenomenon and influence of the Hofmeister ion series.** A. JANEK and A. SCHMIDT (*Kolloid-Z.*, 1930, **52**, 280—288).—When a soluble alcohol and a water-insoluble organic liquid such as toluene, nitrobenzene, etc. are added to a gold hydrosol at a temperature such that the insoluble organic liquid goes into solution, the system on cooling separates at first into an emulsion and finally into two liquid layers. In general, one of three effects is observed: (a) the dispersed gold remains as a hydrosol and the second liquid layer consists mainly of the insoluble organic liquid, (b) the gold is removed from the aqueous layer and is found to be colloiddally dispersed in the organic liquid layer, (c) the gold is coagulated (or may collect in a concentrated but still colloiddally disperse form) at the boundary of the liquids. When the disperse phase is transferred from the aqueous phase to the organic liquid phase it often undergoes an increase in degree of dispersion, scarlet gold sols of considerable stability being obtained, whilst higher concentrations are possible. The conditions for this transference have been studied, and when the original gold sol is made by reduction with potassium citrate it is found that the amount of reducing agent used must lie between certain limits. The effects of the alcohol used, of the relative amount of insoluble organic liquid and the temperature of cooling and also the influence of various anions on the transference of the disperse phase have been examined. Potassium citrate, sulphate, chloride, and nitrate favour the transformation when present at low concentrations, but the effect is less pronounced with increasing concentration. In the presence of potassium iodide and thiocyanate no transference takes place. E. S. HEDGES.

**Liquid-liquid separation of sodium soaps of higher fatty acids by means of sodium sulphate and the relations of these systems to the phase rule.** W. OSTWALD and H. ERBRING (*Kolloidchem. Beih.*, 1930, **31**, 291—346).—Under suitable conditions, the addition of neutral salts to soap solutions causes a separation into two liquid layers. The sharpest surface of separation is produced by sodium sulphate, and examination of this system showed that separation begins at a certain critical concentration which falls with decreasing concentration of the soap solution. At higher concentrations



of both soap and sodium sulphate a solid coagulum is produced. The area enclosed by the separation curve increases as the temperature is lowered. The degree of hydrolysis may affect the extent of the separation region, for the area enclosed by the curve of separation is smallest when medium amounts of sodium hydroxide have been added. A detailed investigation of the systems sodium stearate, oleate, and palmitate with sodium sulphate has been conducted and has been further studied from the point of view of the phase rule. Such liquid-liquid systems behave somewhat similarly to mixtures of molecularly dispersed components, such as potassium carbonate-alcohol-water, but there are several important differences which appear on close examination. Chief of these is the observation that constancy of composition of one phase allows variability in the other phase. The systems have at least one degree of freedom more than is allowed for by application of the phase rule. The additional degrees of freedom possible in a colloid system are considered to be the degrees of dispersion and solvation, and for the systems under discussion the variable concerned is probably the degree of solvation.

E. S. HEDGES.

**Viscosities of dilute solutions of ash-free gelatin.** G. FUSEYA, K. SASAKI, and M. NAGANO (*J. Physical Chem.*, 1930, **34**, 2013—2027).—The viscosities and electrical conductivities of solutions of ash-free gelatin have been measured at 20° or 25°; the concentration-viscosity curve shows a sharp rise at a certain concentration which is near 0.1% of gelatin, but differs with the variety of gelatin used. The incidence of the rise is unaltered by 10<sup>-4</sup>*M*-sulphuric acid or *M*-copper sulphate, but is displaced to a higher concentration in 10<sup>-3</sup>*M*-nitric acid, whilst *M*-potassium chloride causes the step-like rise to change to a break in the curve. The electrical conductivity is at a minimum at a concentration slightly less than that corresponding with the step-like rise in the viscosity. The results are discussed with reference to the equilibrium between the sol and gel forms postulated by Smith (A., 1919, i, 179).

L. S. THEOBALD.

**Preparation and study of some hydroxide jellies.** S. PRAKASH and N. R. DHAR (*J. Indian Chem. Soc.*, 1930, **7**, 591—606; cf. A., 1928, 124).—Jellies of iron, chromium, and aluminium hydroxides are obtained in an acid medium by treating the metallic chlorides or nitrates with sodium acetate, ammonium sulphate, and ammonia in suitable concentrations; zirconium hydroxide jellies are obtained by using only sodium acetate with zirconium nitrate, and stannic hydroxide jellies by addition of sodium acetate and ammonium sulphate to stannic chloride solution. The production of these jellies is explained by assuming the initial formation of colloidal hydroxides stabilised by adsorption of metallic and hydrogen ions. The function of ammonia is to reduce the hydrogen ions to such an extent as to make the system liable to coagulation by ammonium sulphate, which reduces the positive charge of the colloidal particles, the system becoming more viscous and hydrated, and finally jellies are obtained. A comparative study of  $p_H$  values shows that the jellies of

different hydroxides cannot be obtained at the same hydrogen-ion concentration. J. R. I. HEPBURN.

**Phenomena in gels as properties of liquids showing viscosity anomalies.** D. DEUTSCH (*Z. physikal. Chem.*, 1930, **150**, 161—168).—The dependence of thixotropy on the dimensions of the containing vessel is only apparent, and its certain detection is based on the behaviour of the system under hydrostatic pressure. Liquids which possess fluid-elasticity behave as sols or gels according to the shape and volume occupied by a given mass. Such a liquid will not flow out of a narrow parallelepiped which is tilted so that the short side is vertical, but will do so if the long side is vertical. Gels which are not quite solid behave in a similar manner in the absence of a containing vessel (e.g., gelatin or ferric hydroxide gels). Air bubbles above a certain size rise in fluid-elastic liquids, but remain stationary if smaller. This property serves to differentiate such liquids from those which have normal viscosities. The very small, although finite, diffusion exhibited by markedly colloidal dyes, such as azo-blue, in gels is considerably reduced in fluid-elastic liquids. The occurrence of Brownian motion in gels as well as the greatly diminished rate of diffusion of larger particles may be considered as resulting from the fluid-elasticity of gels. The solvate-film theory is applied to the explanation of these properties. F. G. TRYHORN.

**Structure of jellies. II.** P. THOMAS and (MLLE.) M. SIBI (*Rev. gén. Colloid.*, 1930, **8**, 105—112; cf. this vol., 1117).—Measurements of the rates of diffusion of naphthol-yellow, cotton-blue, acid fuchsin, toluidine-blue, xyldine-ponceau, and benzopurpurin in jellies of sorbitol acetal, agar, gelatin, sodium nucleate, and eucupine acetate show that the diffusion velocity is almost independent of the gel, notwithstanding great variations in the concentration of the latter. The concentration of eucupine acetate used was only 0.025%. Benzopurpurin, Congo-red, and night-blue, which do not diffuse into the hydrogels mentioned, diffuse with the same velocity as the other dyes in alcogels of the same substances. The velocity of diffusion bears no relation to the amount of dry matter in the gel. Sorbitol acetate gel exhibits mutarotation and the viscosity of sols of sorbitol acetate increases with time. The existence of a minimum viscosity for gelatin at  $p_H$  4.6 has been confirmed and a similar effect has been observed with sorbitol acetal and benzoylcytine, the curves of which are almost identical, having a minimum between  $p_H$  5 and 6. On the other hand, agar and sodium nucleate have a maximum viscosity in the neighbourhood of neutrality. The gelation of apiine is strongly influenced by the hydrogen-ion concentration and under favourable conditions a gel having a concentration of only 0.07% can be obtained.

E. S. HEDGES.

**Surface tension-temperature curves of asphalt bitumen and allied products.** F. J. NELLENSTEYN and N. M. ROODENBURG (*Kolloidchem. Beih.*, 1930, **31**, 434—446).—The surface tension-temperature curves of several asphalt bitumens from different sources have been determined. For each material there is a characteristic temperature region over

which the relation is linear and there is also a sudden break in the curve. The position of this break is important in practice, for on it depends the temperature at which the substance can conveniently be mixed with other liquids. The results indicate that in general the temperature should not be lower than 150°.

E. S. HEDGES.

**Micelle structure of the wool fibre.** J. B. SPEAKMAN (*Nature*, 1930, 126, 565).—Determinations of the potential energy required to stretch fibres in various alcohols show the existence within the fibre of micelles which are relatively, if not entirely, impervious to molecules as small as those of water. The indicated thickness of the micelles is of the order of 200 Å., and the pore size in fibres swollen in water is of the order of 40 Å. Data for the adsorption of water after treatment of wool with sodium sulphide indicate that the probable shape of the micelles is lamellar, and that the disulphide linking in wool lies in a plane making an obtuse angle with the large faces of the micelles.

L. S. THEOBALD.

**Rhythmic formations.** D. N. GHOSH (*J. Indian Chem. Soc.*, 1930, 7, 509—512).—Periodic structures of a number of precipitates, including very sparingly soluble substances, such as silver chloride and barium sulphate (cf. Ostwald, A., 1925, ii, 530), have been obtained in the absence of a gel by placing drops of the reacting solutions on a glass plate, separating the drops by a fine paraffin line and finally covering with another glass plate, so that the two surfaces of the drops were caused to meet. The growth of the precipitate was followed by means of a microscope with a movable stage and it was observed that in the early stages of its formation the particles of precipitate were in every case in Brownian movement. When the drops of reacting solutions initially contained fine particles of the ultimate precipitate, periodic structures were still obtained, indicating that the supersaturation theory is not applicable. Previous investigations along similar lines have been carried out in the presence of a gel, where it is objected that the added nuclei cannot release supersaturation because they are coated with an adsorbed layer of the gel. The formation of Liesegang rings and allied periodic structures can be explained in terms of diffusion relations alone.

E. S. HEDGES.

**Application of triangular co-ordinates to the graphical representation of colloid states.** A. DUMANSKI (*Kolloidchem. Beih.*, 1930, 31, 418—433).—Colloids are treated as three-component systems, the components being (1) a salt, (2) a substance capable of forming a precipitate with the salt, and (3) a peptising agent. The first two components may produce the following series of changes: ion→complex ion→positively charged micelle→precipitate→negatively charged micelle→complex ion. These changes are represented on a triangular diagram, the co-ordinates of which represent the three components of the system. Published work on the formation of colloidal ferric hydroxide from ferric chloride and sodium hydroxide or ammonia in the presence of polyhydric alcohols, sugars, and hydroxy-acids is treated from this point of view and the triangular diagrams are applied to the phenomenon of peptis-

ation, sensitisation, stabilisation, hydrophobic and hydrophilic properties, emulsification, and foam formation.

E. S. HEDGES.

**Dissociation of hydrogen and its effect on the temperature of the acetylene welding flame.** SCHMOLKE (*Wärme*, 1930, 53, 97—99; *Chem. Zentr.*, 1930, i, 2622).—The difference between the calculated and observed values of the flame temperature is attributed to the inaccuracy of Langmuir's value for the heat of dissociation of hydrogen at constant pressure, and a new value is computed.

A. A. ELDRIDGE.

**Optical dissociation of mercuric bromide.** G. JUNG and W. ZIEGLER (*Z. physikal. Chem.*, 1930, B, 10, 86—88).—The absorption of light of wavelength 350—210  $\mu$  by mercuric bromide vapour apparently corresponds with dissociation into a normal mercurous bromide molecule and a normal bromine atom,  $\text{HgBr}_2 = \text{HgBr} + \text{Br}$ , the value 80 kcal. being deduced for the heat of dissociation. Terenin's value (A., 1927, 1009) is to be rejected.

R. CUTHILL.

**Spectroscopic determination of the equilibrium between nitric acid, nitric oxide, and nitrogen peroxide.** E. ABEL, H. SCHMID, and M. STEIN (*Z. Elektrochem.*, 1930, 36, 692—700).—The difficulty of measuring the nitrogen peroxide pressure renders it impossible to employ a dynamic method for the investigation of the equilibrium  $2\text{HNO}_3 + \text{NO} = 3\text{NO}_2 + \text{H}_2\text{O}$ , and a static method has therefore been developed wherein the absorption spectrum of the nitrogen peroxide in the equilibrium mixture is compared with that of a  $\text{NO}_2 + \text{N}_2\text{O}_4$  mixture of which the pressure is adjusted to give identical absorption. The equilibrium constant  $K = a^3_{\text{NO}_2} \cdot a_{\text{H}_2\text{O}} / a^2_{\text{HNO}_3} \cdot a_{\text{NO}}$ , where  $a$  is the appropriate activity, is, at 25°,  $4.4 \times 10^{-10}$ , whilst if the reaction be expressed in the form  $4\text{HNO}_3 + 2\text{NO} \rightleftharpoons 3\text{N}_2\text{O}_4 + 2\text{H}_2\text{O}$ , the equilibrium constant  $K = p^3_{\text{N}_2\text{O}_4} \cdot p^2_{\text{H}_2\text{O}} / p^4_{\text{HNO}_3} \cdot p^2_{\text{NO}}$ , where  $p$  is the partial pressure in atm., is  $1.4 \times 10^5$ .

H. F. GILBE.

**Study of electrolytic dissociation in nitric acid by the Raman effect.** I. R. RAO (*Proc. K. Akad. Wetensch. Amsterdam*, 1930, 33, 632—643; cf. this vol., 840).—The method previously described for determining the degree of dissociation in solutions of nitric acid by measuring the intensities of the Raman lines due to the undissociated molecules and to the ions has been considerably improved. The results show clearly that the dissociation of nitric acid increases with diminishing concentration, but the values of the degree of dissociation are much higher than those calculated from the viscosity-conductivity formula. It is considered that the Raman results give the true degree of dissociation.

O. J. WALKER.

**Electrolytic dissociation of nitric acid as revealed by its infra-red absorption spectrum.** E. L. KINSEY and J. W. ELLIS (*Physical Rev.*, 1930, [ii], 36, 603—604; cf. Rao, this vol., 840).—The absorption of nitric acid solutions of various concentrations and of the fuming acid was investigated, using the self-recording quartz spectrograph. The solutions showed only water bands, sharpened and

shifted slightly towards shorter wave-lengths. For the fuming acid new strong maxima appear, attributed to the undissociated  $\text{HNO}_3$  molecule. A set of three bands at 1.47, 1.01, and 0.78  $\mu$  fit an anharmonic formula and extrapolate to a fundamental at 2.85  $\mu$ . Two bands at 2.12 and 1.25  $\mu$  are interpreted as combinations between a fundamental in the Raman effect and bands of the anharmonic series. The vapour shows a group believed to be the same as for the liquid, but with each band shifted to shorter wave-lengths.

N. M. BLIGH.

**Dissociation theory of solutions.** (EARL OF) BERKELEY (Nature, 1930, 126, 313).—Two formulæ connecting osmotic pressure with the volumes, areas, and concentrations of aqueous solutions are given (cf. Bradford, this vol., 1120).

L. S. THEOBALD.

**Extent of dissociation of salts in water. II. Uni-bivalent salts.** E. C. RIGHELLATO and C. W. DAVIES (Trans. Faraday Soc., 1930, 26, 592–600).—The majority of uni-bivalent salts are not completely ionised in dilute solution. Satisfactory dissociation constants for the ionisation of the intermediate ion have been calculated for a number of such salts from conductivity data; the values of  $\log K$  vary from  $-2.0$  to  $-0.5$ , and are thus intermediate between those for uni-uni- and bi-bi-valent salts. The alkali metal sulphates show a decrease of ionisation with increase of atomic number as with the nitrates, and the same is true of the alkaline-earth nitrates; the chlorides, bromides, and iodides of the alkaline earths, like those of the alkalis, are much more strongly ionised than the nitrates. Thallous sulphate, lead chloride and nitrate, and cadmium chloride are but feebly ionised, but cadmium nitrate is relatively strongly ionised, probably on account of the absence of a tendency to complex formation. The dissociation constants obtained have been confirmed by comparison of calculated with experimental transport numbers.

H. F. GILLBE.

**Dissociation of calcium citrate.** W. J. WILEY (Biochem. J., 1930, 24, 856–859).—The dissociation of tricalcium citrate in aqueous solution at  $18^\circ$  has been studied and the values for the degree of dissociation are recorded.

S. S. ZILVA.

**Apparent dissociation constants, heat of dissolution, and apparent heat of ionisation of di-iodotyrosine.** J. B. DALTON, P. L. KIRK, and C. L. A. SCHMIDT (J. Biol. Chem., 1930, 88, 589–600).—The apparent acid and basic dissociation constants and the apparent heats of ionisation of di-iodotyrosine were calculated from solubility data for varying  $p_H$  at  $0^\circ$ ,  $25^\circ$ , and  $40^\circ$ . The heat of dissolution of di-iodotyrosine was calculated from solubility measurements of the isoelectric amino-acid at different temperatures over the range  $0$ – $47^\circ$ .

G. F. MARRIAN.

**Formation of complex cations of metal ions with glycine.** G. FUSEYA and K. MURATA (J. Physical Chem., 1930, 34, 2001–2012).—The formation of complexes of lead, iron, chromium, and copper salts with glycine has been detected by the spectrographic method; with zinc, nickel, and cobalt the evidence is less definite. The electrode potentials of zinc in a zinc sulphate solution, of lead in lead

nitrate, and of nickel in nickel sulphate solution are lowered by the addition of glycine, indicating complex formation. Migration experiments show that the complex ions are positively charged. Except in the case of ferric sulphate, the electrical conductivities of solutions of the metal sulphates are increased by the addition of glycine; those of silver and lead nitrates and of copper and nickel chlorides are decreased.

L. S. THEOBALD.

**Combination of sucrose with boric acid. Variation of acidity of boric acid in the presence of sugar.** J. VOICU and (MILE.) E. AXENTE (Bul. Soc. Chim. România, 1930, 12, 61–70).—The hydrogen-ion concentration of solutions of boric acid is increased when sucrose is added. The change takes place immediately and no further slow variation occurs. A similar effect is observed on the addition of dextrose or laevulose, the magnitude of the change increasing with increasing concentration of the boric acid. On the other hand, with sucrose the change in hydrogen-ion concentration is at a maximum in the presence of 1.03% of boric acid and is inappreciable at 4.13%. It seems probable that sucrose forms a compound with orthoboric acid, but not with the tetraboric acid present in the more concentrated solutions.

E. S. HEDGES.

**Titration constants of multivalent substances.** A. L. VON MURALT (J. Amer. Chem. Soc., 1930, 52, 3518–3523; cf. Simms, A., 1926, 681).—Mathematical. On the assumption of the validity of the "classical" mass law equations, it is shown that there is no difference between the titration curve of a polybasic acid and a suitably chosen mixture of monobasic acids.

J. G. A. GRIFFITHS.

**Physico-chemical studies of complex acids. III. Molybdic acid.** H. T. S. BRITTON and W. L. GERMAN (J.C.S., 1930, 2154–2166).—The potentiometric titration curve of sodium molybdate solutions with hydrochloric acid shows an inflexion at  $p_H$  4.8 corresponding with the formation of  $3\text{Na}_2\text{O}, 7\text{MoO}_3$  (or  $5\text{Na}_2\text{O}, 12\text{MoO}_3$ ). By boiling the solution or ageing prior to measuring the  $p_H$  a sharper inflexion, corresponding with  $\text{Na}_2\text{O}, 4\text{MoO}_3$ , is produced. In acidified solutions the sodium polymolybdate, which is first formed, gradually decomposes and yields a highly ionised polymolybdic acid, which causes the  $p_H$  of the solution to assume slightly lower values than would be produced by the hydrochloric acid. Further addition of acid causes the ionisation of the poly-acid to be thrown back until only non-ionised molybdenum trioxide remains in solution; only from relatively concentrated solutions is the trioxide precipitated on boiling. The changes of conductivity during the titration in general confirm the results obtained by the potentiometric method. Addition of a weak acid, such as acetic or phenylacetic, to a sodium molybdate solution causes the formation of a stable polymolybdate  $\text{Na}_2\text{O}, 3\text{MoO}_3$ , which is not further decomposed by the weak acid; in solutions containing monochloroacetic acid the salt formed has a composition between  $\text{Na}_2\text{O}, 3\text{MoO}_3$  and  $\text{Na}_2\text{O}, 5\text{MoO}_3$ . In solutions of molybdic acid there probably exists an equilibrium of the type  $\text{H}_2[\text{O}(\text{MoO}_3)_x] \rightleftharpoons 2\text{H}^+ + [\text{O}(\text{MoO}_3)_x]''$ , where  $x$  is about 4.

H. F. GILLBE.

**Simple electrochemical method for the simultaneous determination of the constitution and equilibrium constant of complex ions in solution. Application to complex silver ions.** F. K. V. KOCH (J.C.S., 1930, 2053—2063).—By consideration of the cell  $M|MS$  in solvent  $A|MS$  in solvent  $A+B|M$ , where  $M$  is a metal,  $MS$  a salt thereof, and  $A$  and  $B$  are solvents, a potentiometric method has been developed for the determination of the constitutions and equilibrium constants of the solvated ions  $MA_x^{n+}$  and  $MB_y^{n+}$ , especially for the case in which relatively stable complex ions are formed between the metal and one solvent only. The method is applicable only if the equilibrium constant is small. Measurements with the silver ion in ammonia-water, pyridine-water, pyridine-ethyl alcohol, and acetonitrile-water mixtures show that, except in the last-named solvent, there is a linear relationship between  $\log K_m/m^x$  and  $\log m$ , where  $K_m$  is the equilibrium constant,  $m$  the mol. fraction of the complex-forming solvent, and  $x$  is the number of molecules of solvent in each solvated ion;  $K_m$  and  $x$  may therefore be determined simultaneously. By this method the existence of  $Ag(NH_3)_2^+$  and of  $Ag(C_3H_5N)_2^+$  has been established, the equilibrium constants being  $6.3 \times 10^{-8}$ , and  $7.1 \times 10^{-5}$  and  $1.6 \times 10^{-4}$  for pyridine-water and pyridine-ethyl alcohol mixtures, respectively. The thermodynamic aspect of the equilibrium between solvated ions and the solvent molecules is discussed. A new concept termed the solvation activity coefficient of an ion in a given solvent  $S$  is introduced and is defined by the ratio  $P_r/P_s$ , where  $P_r$  and  $P_s$  are the solution tensions of the metal in water and in the solvent  $S$ , respectively.

H. F. GILLBE.

**The Debye-Hückel theory and its experimental testing.** H. VAN VELDHUIZEN (Chem. Weekblad, 1930, 27, 486—492).—The original Debye-Hückel theory is given in detail, including the derivations of the formulæ for the osmotic and activity coefficients, and the literature relating to the experimental investigation of the theory is reviewed.

H. F. GILLBE.

**Complexity of phosphorus pentoxide. II.** A. SMITS and H. W. DEINUM (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 619—631; cf. this vol., 1096).—Temperature-pressure-composition diagrams are given for the pseudo-system phosphorus pentoxide, which is assumed to be a binary system of two separate molecular species with a eutectic. By means of these diagrams the different behaviour of the stable form when heated very slowly and very rapidly, with the possibility of considerable superheating, and the peculiar position of the vapour-pressure curve of the unstable, more volatile form, can be explained. The complexity of phosphorus pentoxide is shown very clearly, because the inner transformations become noticeable only at about  $400^\circ$ , and therefore below this temperature the substance behaves as a mixture.

O. J. WALKER.

**Binary system iron-boron, and structure of iron boride,  $Fe_3B_2$ .** F. WEVER and A. MÜLLER (Z. anorg. Chem., 1930, 192, 317—336).—Thermal analysis of the above system for concentrations up to 16% of boron has shown the existence of the

compounds  $Fe_3B_2$  and  $FeB$ , the former melting incongruently. Boron depresses the A4 transition point and raises the A3 transition point, but does not affect the A2 transition point. Its solubility in  $\gamma$ -iron decreases slowly as the temperature falls. These results have been confirmed by microscopic and X-ray examination. Solutions of boron in  $\alpha$ -iron are shown by their X-ray diagram to be true solid solutions, the boron atoms replacing iron atoms in the  $\alpha$ -lattice. The compound  $Fe_3B_2$  has the tetragonal-scalenohedral space-grouping  $V_{II}^H$ , with 2  $Fe_3B_2$  molecules in the base; the iron atoms occupy an eight-fold point position with 2 degrees of freedom, and the boron atoms probably two-fold point positions with no degrees of freedom. The discrepancies between the above results and those recorded by other authors (cf. Hannesen, A., 1915, ii, 464) are attributed to the presence of impurities, particularly carbon, silicon, and aluminium, in the systems previously investigated.

R. CUTHILL.

**Binary systems of certain nitrotoluenes with benzoic acid.** H. D. CROCKFORD and A. E. HUGHES (J. Physical Chem., 1930, 34, 2117—2120).—The systems formed by benzoic acid with 2:4:6-trinitro-, 2:4-dinitro-, *o*- and *p*-nitro-toluene show no compound formation; the eutectics occur at  $64.5^\circ$ ,  $59.4^\circ$ ,  $-14.0^\circ$ , and  $44.1^\circ$ , respectively. The corresponding mol. fractions of benzoic acid are 75.00, 74.7, 94.7, and 77.33.

L. S. THEOBALD.

**Influence of particle size on the dissociation pressure of solids. Red mercuric oxide. Iceland spar.** J. KRUSTINSONS (Z. physikal. Chem., 1930, 150, 310—316).—Red mercuric oxide and powdered Iceland spar were separated into fractions of different grain size by means of graded sieves, and a difference between the dissociation temperatures of the finest and coarsest fractions was observed. On the assumption that the Thomson formula is valid for the equilibrium at the solid-gas boundary, the surface tensions of red mercuric oxide and Iceland spar are calculated to be 750,000 and 120,000 dynes/cm., respectively.

E. S. HEDGES.

**Oxide hydrates. XXVIII. System calcium oxide-water.** G. F. HÜTTIG and A. ARBES [with Z. HERRMANN and C. SLONIM] (Z. anorg. Chem., 1930, 191, 161—170).—The temperature-composition curve obtained by the desiccation of various specimens of hydrated calcium oxide at constant water vapour pressure (10 mm.) shows at about  $390^\circ$  the sharp vertical portion corresponding with the decomposition of  $CaO \cdot H_2O$ , until the substance contains about 0.1 mol. of water, and thereafter a gradual loss of water as the temperature is raised to about  $670^\circ$ . Debye diagrams of calcium oxide and calcium hydroxide prepared by different methods are given. The water retained in desiccation at the ordinary temperature of certain preparations of calcium hydroxide, although in some cases corresponding with the formula  $CaO \cdot 2H_2O$ , is nevertheless attached differently from the primary water molecule; calcium hydroxide prepared by addition of water to calcium oxide is almost completely converted into  $CaO \cdot H_2O$  by desiccation over sulphuric acid at the ordinary temperature.

H. F. GILLBE.

**Oxide hydrates. XXIX. Comparison and calculation of values of water vapour pressure of solid and liquid substances obtained by different methods.** G. F. HÜTTIG and K. TOISCHER (*Kolloidchem. Beih.*, 1930, **31**, 347—373).—A table of values of the water vapour pressure over various drying agents at different temperatures has been constructed. Methods of investigating the equilibrium between a solid body and a liquid phase are discussed, particularly in relation to the absorption of water by hydroxide gels, and experiments have been conducted with hydrated vanadium pentoxide in order to compare direct water vapour pressure measurements with those obtained by treating the gel with different dehydrating liquids and determining the loss of water. The effectiveness of the dehydrating agents used increases in the order acetone < ethyl alcohol < liquid ammonia. Similar measurements carried out with hydrated stannic oxide show that the ageing observed with this substance in an aqueous medium is enormously accelerated in a dehydrating liquid medium. E. S. HEDGES.

**Oxide hydrates. XXX. System  $\text{Ti}_2\text{O}_3\text{--H}_2\text{O}$ .** G. F. HÜTTIG and R. MYTYZEK (*Z. anorg. Chem.*, 1930, **192**, 187—192).—Desiccation at constant pressure of a specimen of thallium oxide of the approximate composition  $\text{Ti}_2\text{O}_3\cdot 1\cdot 47\text{H}_2\text{O}$ , prepared by the action of chlorine on a solution of thallous nitrate, shows that only about 0.8 mol. of water is attached more firmly than the remainder, and that this water is given off continuously as the temperature is raised to 330°, when the substance becomes anhydrous. The Debye diagram shows the hydrated oxide to have the same structure as that of the anhydrous material. H. F. GILLBE.

**Oxide hydrates. XXXI. System strontium oxide-water.** G. F. HÜTTIG and A. ARBES (*Z. anorg. Chem.*, 1930, **192**, 225—236).—Thermal decomposition diagrams of various specimens of hydrated strontium oxide at constant pressure (10 mm.) demonstrate the existence of the monohydrate, and although samples prepared in different ways vary in composition from  $\text{SrO}\cdot\text{H}_2\text{O}$  to  $\text{SrO}\cdot 1\cdot 2\text{H}_2\text{O}$ , the decomposition temperature is constant for all varieties at  $466^\circ \pm 2^\circ$ . Small quantities of water are retained in some cases at considerably higher temperatures, a phenomenon which has been observed with the hydrated oxides of most bivalent metals. De Forcrand's observation of  $375^\circ$  as the m. p. of strontium hydroxide appears to be erroneous. The decomposition isobars are reversible. Debye diagrams confirm the existence of  $\text{SrO}\cdot 9\text{H}_2\text{O}$ , but the ninth molecule of water appears to be attached in a manner different from that of the others. No definite compound exists having a composition between  $\text{SrO}\cdot 3\text{H}_2\text{O}$  and  $\text{SrO}\cdot 8\text{H}_2\text{O}$ , and the existence of the trihydrate is doubtful. The desiccation of  $\text{SrO}\cdot 2\text{H}_2\text{O}$  to  $\text{SrO}\cdot \text{H}_2\text{O}$  resembles qualitatively that of the analogous calcium compound, with the difference that  $\text{SrO}\cdot 2\text{H}_2\text{O}$  possesses a characteristic X-ray structure. Both the monohydrated and the anhydrous oxides yield characteristic Debye diagrams. H. F. GILLBE.

**System  $\text{NH}_4\text{NO}_3\text{--H}_2\text{O}$ .** E. JÄNECKE and E. RAHLFS (*Z. anorg. Chem.*, 1930, **192**, 237—244).—

The vapour pressure of dilute and of saturated ammonium nitrate solutions has been determined at temperatures up to the m. p. of the salt. The vapour pressure of the saturated solution is a maximum at  $128^\circ$ , and the curve is of the retrograde type found by Roozeboom in 1902 for silver nitrate solutions. A three-dimensional diagram has been constructed for the range  $-18^\circ$  to  $169\cdot 6^\circ$  and 0—1 atm. pressure.

H. F. GILLBE.

**Etherates of magnesium bromide.** W. V. EVANS and H. H. ROWLEY (*J. Amer. Chem. Soc.*, 1930, **52**, 3523—3534; cf. Meisenheimer and others, *A.*, 1925, i, 1252; 1928, 624).—If the two-phase liquid system resulting from the action of bromine on magnesium in dry ether is maintained below  $10^\circ$ , crystals of magnesium bromide trietherate are obtained. At the ordinary temperature, the product is the crystalline dietherate. Air and moisture must be excluded. Vapour-pressure data at temperatures between  $0^\circ$  and  $40^\circ$  show that the trietherate (vapour pressure, 187 mm. at  $0^\circ$ ) is stable below  $13^\circ \pm 0\cdot 5$ , at which temperature transition to the dietherate occurs. The latter (vapour pressure, 47 mm. at  $0^\circ$ ) is stable below  $28^\circ \pm 1\cdot 0$  and at higher temperatures yields the monoetherate (vapour pressure, 9 mm. at  $0^\circ$ ). The existence of these transition points is supported by visual observations. The slowness with which the system attains equilibrium probably accounts for the conflicting observations recorded in the literature.

J. G. A. GRIFFITHS.

**New fixed temperature points.** O. REDLICH and G. LOEFFLER (*Z. Elektrochem.*, 1930, **36**, 716—722).—The accurate measurement of temperature with the platinum resistance thermometer and the Kohlrausch-Jaeger method is described. The transition temperature of darapskite,  $\text{NaNO}_3\cdot\text{Na}_2\text{SO}_4\cdot\text{H}_2\text{O}$ , in presence of sodium nitrate and sodium sulphate decahydrate is  $13\cdot 145^\circ \pm 0\cdot 0011^\circ$ , and that of sodium sulphate in presence of sodium chloride is  $17\cdot 878^\circ \pm 0\cdot 012^\circ$ . The temperature of the potassium chloride-ice eutectic is  $-10\cdot 646^\circ \pm 0\cdot 0025^\circ$ . H. F. GILLBE.

**Theoretical phase-rule principles of the duralumin-like ageing effect in ternary systems.** E. SCHEIL (*Z. Metallk.*, 1930, **22**, 297—302).—The mechanism of the precipitation of one or both constituents of a doubly-supersaturated solid solution during ageing is discussed mathematically on considerations based on the phase rule, and it is shown that the determining factor in the precipitation is the shape of the unstable saturation surface in the space model of the ternary system. Three typical cases are described and the conditions under which dissolution of a crystal phase can occur are outlined. The application of the theory to the mechanism of the hardening of alloy steels is briefly discussed.

A. R. POWELL.

**System  $\text{H}_2\text{O--CO}_2\text{--NH}_3$ . II.** E. JÄNECKE [with E. RAHLFS] (*Z. Elektrochem.*, 1930, **36**, 645—654; cf. *A.*, 1929, 1388).—Thermal analysis of the system carbamide-ammonium hydrogen carbonate and carbamide-ammonium carbonate shows the existence of a eutectic in the first-named at  $84^\circ$  containing 60% of carbamide, and in the second at  $98^\circ$  containing 49% of carbamide, whilst by extrapolation a eutectic

between carbamide and dicyanodiamide has been discovered at 115°. Vapour-pressure measurements of the ammonia-carbamide system from -78° to 132° indicate the existence of the congruent melting compound  $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_3$ , which has m. p. 46° and of which the vapour pressure  $p$  is expressed by  $\log p = -7820/4.57T + 9.2$ , where  $T$  is the absolute temperature. The ammonia-dicyanodiamide system closely resembles the ammonia-carbamide system, a compound,  $(\text{CN}_2\text{H}_2)_2 \cdot \text{NH}_3$ , having the incongruent m. p. 49° being formed. The system carbamide-ammonium carbonate-ammonia is chiefly remarkable for the great increase of the solubility of ammonium carbonate in ammonia solutions in presence of carbamide. In the carbamide-dicyanodiamide-ammonia diagram the field of  $\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_3$  is, on account of its lower solubility, considerably larger than the  $(\text{CN}_2\text{H}_2)_2 \cdot \text{NH}_3$  field, whilst one of the three triple salt points is represented by the eutectic between ammonia and the two double salts. Vapour pressure-composition and solubility isotherms are given for the system carbamide-water-ammonia. The following new triple salt points have been identified:  $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{NH}_4 \cdot \text{NH}_4 \cdot \text{HCO}_3 \cdot \text{CO}(\text{NH}_2)_2$ , 95°;

$\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_2 \cdot \text{CO}_2 \cdot \text{NH}_4 \cdot \text{NH}_3$ , 40°;

$\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_2 \cdot \text{CO}_2 \cdot \text{NH}_4 \cdot \text{NH}_3$ , -78°;

$\text{CO}(\text{NH}_2)_2 \cdot \text{NH}_2 \cdot \text{CO}_2 \cdot \text{NH}_4 \cdot \text{NH}_3$ , 38°;

$\text{CO}(\text{NH}_2)_2 \cdot (\text{CH}_2\text{N}_2)_2 \cdot \text{NH}_3$ , 18°;

$\text{CO}(\text{NH}_2)_2 \cdot (\text{CH}_2\text{N}_2)_2 \cdot \text{NH}_3$ , -90°;

$\text{CO}(\text{NH}_2)_2 \cdot (\text{CH}_2\text{N}_2)_2 \cdot \text{NH}_4 \cdot \text{HCO}_3$ , 95°. The complete  $\text{CO}_2\text{-H}_2\text{O-NH}_3$  system is represented as a section of a three-dimensional tetrahedral model of the system C-H-O-N.

H. F. GILLBE.

**Polyiodides of caesium: system caesium iodide, iodine, and water at 25°.** T. R. BRIGGS, J. A. GREENWALD, and J. W. LEONARD (J. Physical Chem., 1930, 34, 1951—1960).—The ternary diagram for the system caesium iodide, iodine, and water at 25° has been completed. At 25°, two solid polyiodides, the tri-iodide of Wells and Penfield (A., 1892, 773) and a tetraiodide,  $\text{CsI}_4$ , exist; the penta-iodide of Wells and Wheeler (A., 1893, ii, 68) could not be prepared. Solutions saturated with two solid phases have the following compositions:  $\text{CsI}$  and  $\text{CsI}_3$ , 46.4% of  $\text{CsI}$  and 0.40% of iodine;  $\text{CsI}_3$  and  $\text{CsI}_4$ , 7.65% of  $\text{CsI}$  and 1.19% of iodine, and  $\text{CsI}_4$  and iodine, 2.39% of  $\text{CsI}$  and 1.23% of iodine. The solubility data of Foote and Chalker (A., 1908, ii, 586) have been confirmed and a method for preparing the pure polyiodides is described.

L. S. THEOBALD.

**Systems  $\text{Al}_2\text{O}_3\text{-Na}_2\text{O-H}_2\text{O}$  and  $\text{Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$ .** R. FRICKE and P. JUCATIS (Z. anorg. Chem., 1930, 191, 129—149).—The equilibria between aluminium hydroxide and sodium and potassium hydroxide solutions of concentrations from about 3 to 40% have been determined at 30° and 60° by shaking the solid and solution for from 1 to 6 weeks. In sodium hydroxide solutions up to about 22%, and potassium hydroxide solutions up to about 29%, at which points the solubility of aluminium hydroxide is a maximum, the equilibrium solid phase is insoluble in water, whilst at higher concentrations it is soluble. The solid phase in the case of the concentrated potassium

hydroxide solutions consists only of monopotassium aluminate, but with sodium hydroxide at concentrations up to about 38% the solid phase is monosodium aluminate, and at higher concentrations, probably trisodium aluminate; the equilibrium curve is, however, too flat to permit the transition point to be determined. The composition of the monosodium salt is represented by  $2\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and not, as reported by Goudriaan (A., 1920, ii, 759), by  $4\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ , whilst that of the trisodium salt approximates to  $3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 7\text{-}9\text{H}_2\text{O}$ . Goudriaan's results for the equilibria between aluminium hydroxide and sodium hydroxide solution could not be duplicated, but the cause of the discrepancy remains obscure.

H. F. GILLBE.

**Systems potassium sulphate, cadmium sulphate, and water, and ammonium sulphate, cadmium sulphate, and water at 25°.** K. L. MALHOTRA and H. D. SURI (J. Physical Chem., 1930, 34, 2103—2110).—Data and the ternary diagrams for these two systems are given. The solubility of potassium sulphate is increased by the addition of cadmium sulphate up to the triple point, indicating the formation of the double salt in solution. The solubility curve at 25° indicates a slight increase in the solubility of cadmium sulphate on addition of increasing amounts of potassium sulphate. The addition of potassium sulphate to a saturated solution of the compound  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  causes the separation of the salt  $\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4$ . The solubility of ammonium sulphate is decreased by the addition of cadmium sulphate, whilst that of cadmium sulphate is increased by the addition of ammonium sulphate. The existence of the double salt  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CdSO}_4 \cdot 6\text{H}_2\text{O}$  is confirmed.

L. S. THEOBALD.

**System  $\text{K}_2\text{O-CaO-SiO}_2$ .** G. W. MOREY, F. C. KRACEK, and N. L. BOWEN (J. Soc. Glass Tech., 1930, 14, 149—187).—The equilibrium relations in this system for all mixtures richer in silica than those on the line  $\text{K}_2\text{O} \cdot \text{SiO}_2\text{-K}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2\text{-CaO} \cdot \text{SiO}_2$  have been determined for the most part by the quenching method. The new compounds found and their properties are as follow:  $\text{K}_2\text{O} \cdot \text{CaO} \cdot \text{SiO}_2$ , m. p. 1630°, hexagonal bipyramids, optically +,  $n_D^{20}$  1.600;  $2\text{K}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2$ , m. p. 1005° (incongruent), octahedral, isotropic,  $\gamma = \beta = \alpha = 1.572$ ;  $\text{K}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ , decomposes at 960° to  $\text{K}_2\text{O} \cdot 2\text{CaO} \cdot 6\text{SiO}_2$  + glass, elongated needle prisms, parallel extinction, positive elongation, biaxial, negative,  $\gamma$  1.57,  $\gamma - \alpha$  0.010;  $4\text{K}_2\text{O} \cdot \text{CaO} \cdot 10\text{SiO}_2$ , m. p. 946° (congruent), uniaxial negative,  $n_D^{20}$  1.551,  $n_D^{25}$  1.539, usually flat plates with parallel extinction;  $2\text{K}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ , m. p. 959° (congruent), biaxial, negative,  $\gamma$  1.54, inclined extinction;  $\text{K}_2\text{O} \cdot 2\text{CaO} \cdot 6\text{SiO}_2$ , m. p. 1115° (incongruent), stout prisms, highly inclined extinction,  $\gamma$  1.59,  $\alpha$  1.575, biaxial, positive, large  $2V$ ;  $\text{K}_2\text{O} \cdot 2\text{CaO} \cdot 9\text{SiO}_2$ , m. p. 1050° (incongruent), biaxial, negative, large axial angle, slightly inclined extinction,  $\gamma$  1.535,  $\alpha$  1.515. Nineteen invariant points are recorded.

The data show that crystallisation in the  $\text{K}_2\text{O}$  system is uniformly more difficult than in the corresponding  $\text{Na}_2\text{O}$  system, the dominant factor being the higher viscosity in the first-named, whilst a second contributory cause is the number of compounds



formed in the  $K_2O$  system and their extreme dissociation. The use of potassium oxide in an  $Na_2O-CaO-SiO_2$  glass gives thermal stability to glasses with higher silica content.

M. PARKIN.

**Equilibria between iron, nickel, and their silicates in fused masses.** H. ZUR STRASSEN (Z. anorg. Chem., 1930, **191**, 209—245).—The equilibrium  $Fe + NiSiO_3 \rightleftharpoons Ni + FeSiO_3$  at 1480—1500° is readily established without mechanical agitation, and follows the mass action law, the equilibrium constant  $K$  being  $6.53 \times 10^{-3}$ ; the reaction must be conducted in an atmosphere of nitrogen in order to prevent excessive oxidation of the ferrous silicate. The composition of the silicate phase does not influence the equilibrium, and the introduction of impurities such as magnesium silicate or silica into the mass from, e.g., the crucible walls is without effect. The heat value of the reaction, calculated from determinations of  $K$  at 1480° and 1570°, is 7.6—9.5 kg.-cal. Neither ferrous nor nickelous metasilicate actually exists in the mass in accordance with Herty and Fitterer's thermal diagram. Iron and nickel are not appreciably soluble in the silicate layer. The equilibrium  $Fe + NiO \rightleftharpoons Ni + FeO$  could not be directly investigated owing to the difficulty of finding a suitable material for the crucible, but by consideration of the increasing displacement of the equilibrium produced by addition of aluminium oxide, silica, and titanium oxide, it appears that the equilibrium constant must be very small. The bearing of the experimental results on the equilibria in meteoric iron containing occluded silicates and on the equilibria relating to the metallic nucleus and silicate envelope of the earth is discussed. The apparent discrepancy between the latter and the experimentally determined equilibria is ascribed to the widely different conditions of temperature.

H. F. GILLBE.

**Equilibria between water and the nitrates, chlorides, and sulphates of sodium and potassium.** E. CORNEC, H. KROMBACH, and A. SPACK (Ann. Chim., 1930, [x], **13**, 525—623).—Study of the equilibria between water and the nitrates and sulphates of sodium and potassium (A., 1929, 267, 767, 1388) has been extended to the temperature range -2° to 50°; within this interval there are 14 series of solutions saturated with 3 salts and 5 series saturated with 4 salts. The results obtained at 25° do not confirm those of Hamid (A., 1926, 245). The equilibria between water and the nitrates, sulphates, and chlorides of sodium and potassium have been determined from 0° to 90°; there exist 24 series of solutions saturated with 4 salts and 6 series saturated with 5 salts. No solid phases exist other than those which are found also in systems of a lower order.

H. F. GILLBE.

**Calorimetric and X-ray investigations of dehydration process of hydrated alumina.** E. KLEVER (Trans. Ceram. Soc., 1930, **29**, 149—161).—The heats of dissolution of the dehydrated stages of hydrated alumina are compared with those of kaolin. Measurements were made at the ordinary temperature and at 52—54°, the latter in a new form of calorimeter which is described. The heat of dissolution of dehydrated alumina was found to be

92.5 g.-cal./mol. in 40% hydrofluoric acid at 18—20°. The same material was used for X-radiograms taken at different degrees of dehydration. These show that the diffraction pattern of bayerite persists up to 210°; between 210° and 900° a new pattern appears, namely, that of  $\gamma$ -alumina; between 900° and 1200° recrystallisation of the  $\gamma$ -alumina is completed; above 1200° the pattern of  $\alpha$ -corundum appears. Kaolin during dehydration does not dissociate between 500° and 900°, but the anhydride phase is probably present.

R. J. CARTLEDGE.

**Heats of dilution of uni- and multi-valent strong electrolytes at high dilutions.** E. LANGE [with J. MÖNHEIM] (Z. Elektrochem., 1930, **36**, 772—777).—The equation previously derived for the integral heat of dissolution (A., 1929, 1389; cf. this vol., 997, and previous abstracts) has been verified by measurements of the authors and other workers at moderate dilutions, but at the highest dilutions there are slight deviations, and at high concentrations considerable discrepancies, which have been only partly and qualitatively explained.

H. F. GILLBE.

**Rôle of impurities in the variation of the heat of dissolution of monomorphous salts.** K. P. MISCHTSCHENKO (Z. Elektrochem., 1930, **36**, 777—782).—The heat of dissolution of potassium chloride in water is -4195 g.-cal./mol., and is the same for various samples of the pure material of different origins. Traces of impurities produce marked variations of the heat of dissolution, but no evidence of the existence of metastable modifications could be obtained. Measurements made with potassium chloride containing 0.2—0.5% of calcium sulphate indicate that the influence of chemical impurities is purely additive. The necessity is emphasised of ensuring chemical purity, as well as physical homogeneity, of substances employed for the determination of physical constants.

H. F. GILLBE.

**Determination of transport numbers of solids.** W. JOST and H. SCHWEITZER (Z. physikal. Chem., 1930, **B**, **10**, 159—160).—A preliminary account is given of a method of determining the transport number for solid sodium chloride at high temperatures by observations of the change in the length of a cylinder of the salt resulting from the passage of a current.

R. CUTHILL.

**Galvanometric method of measuring electrolytic resistance.** J. A. C. TEEGAN (Nature, 1930, **126**, 504).—The telephone in the ordinary laboratory method is replaced by a galvanometer and a thermionic valve connected to act as a diode.

L. S. THEOBALD.

**Conductance of water irradiated with X-rays.** R. SCHNURMANN (Z. physikal. Chem., 1930, **150**, 110—114).—Irradiation of water by X-rays appears to cause a slight rise in conductance, but this rise is not permanent. The original conductance is regained a few hours after irradiation has ceased.

F. G. TRYHORN.

**High-frequency conductivity of strong electrolytes in aqueous sugar solution.** S. MIZUSHIMA and H. SACK (Physikal. Z., 1930, **31**, 811—815).—The conductivity of magnesium sulphate in aqueous

sugar solution has been measured at a frequency of  $4 \times 10^8$  Hertz. The experimental procedure is described. Measurements were made at different temperatures and it was found that the temperature effect is negligible. The effects of the dielectric constant, anomalous dispersion, and absorption are also discussed. Viscous solutions of magnesium sulphate conduct considerably better at high frequencies than at low frequencies. The results can be interpreted simply by means of Debye's theory of electrolytes. W. R. ANGUS.

**Heating of electrolytes in high-frequency fields.** J. C. McLENNAN and A. C. BURTON (Canad. J. Res., 1930, 3, 224—240).—The heating of solutions of certain chlorides and of sucrose by radiation of wave-length from 10 to 200 m. has been examined with reference to the influence of the concentration and wave-length. At very low concentrations (0–0.003*M*) the heat-concentration curves are linear, but at higher concentrations there is a sharp maximum, and the heating effect thereafter falls slowly. The maximum is independent of the composition of the solution, but is determined by the specific conductance, and is the more pronounced the higher is the radiation frequency; the conductivity at which the maximum occurs is proportional to the frequency. The heating effect is produced throughout the solution, skin effect being shown theoretically and experimentally to be negligible. The condition given by  $2C/\pi k = 1$ , where *C* is the specific conductance, *k* the dielectric constant, and  $\pi$  the radiation frequency, is applicable to solutions exhibiting the maximum heating effect. The possibility of selective heating of the components of a heterogeneous system is discussed, the variations of field strength with the dielectric constant and of the heating with the conductivity being considered. Experiments with blood indicate that most heat originates in the protein constituents, less in the corpuscles, and least in the electrolyte fluid of the plasma; the relative distribution of the heating varies with the wave-length, and the possibility of control by selection of wave-length, are discussed.

H. F. GILBE.

**Theory of electrodes.** E. NEWBERRY (Trans. Amer. Electrochem. Soc., 1930, 58, 19—42).—The author's views on the determination and significance of electrode potentials and electrolytic polarisation already put forward (cf. A., 1924, ii, 317; 1925, ii, 405; 1927, 210; 1928, 958; 1929, 768) are re-stated and discussed in relation to criticisms which have been advanced. It is claimed that the phenomena of overvoltage, transfer resistance, passivity, and valve action can be completely explained on the basis of compound formation between the electrode material and the discharged gas ions under the influence of very high pressures. Counter-criticisms of the conclusions of recent workers in this field are put forward, especially with regard to the work of Bowden and Rideal (A., 1928, 1088; 1929, 1391; this vol., 169), who maintain that transfer resistance is a secondary effect occurring only at high current densities (cf. Glasstone, A., 1924, ii, 600).

H. J. T. ELLINGHAM.

**Measurement of glass electrode potentials.** R. J. FOSBINDER and J. SCHOONOVER (J. Biol. Chem.,

1930, 88, 605—614).—The limitations of the glass electrode due to the difficulty of measuring the *E.M.F.* in a high-resistance system have been overcome by employing an improved form of vacuum-tube potentiometer (this vol., 883). By using a constant-temperature cell of new design the  $p_H$  of 0.05 c.c. of liquid may be determined with accuracy.

G. F. MARRIAN.

**Influence of solvent on *E.M.F.* of silver-silver halide cells.** A. S. AFANASIEV (J. Amer. Chem. Soc., 1930, 52, 3477—3483).—*E.M.F.* data are recorded for cells of the type  $\text{Ag}|\text{AgCl}, \text{KCl}(c_1)|\text{KBr}(c_2), \text{AgBr}|\text{Ag}$  in which the solvent media were respectively water, mixtures of ethyl alcohol and water, and mixtures of methyl alcohol and water (cf. A., 1929, 769). The observed *E.M.F.* accord well with the values calculated by means of Brodsky's formula (A., 1926, 688). Silver-silver halide electrodes made according to the method of Noyes and Ellis (A., 1918, ii, 27) are the most satisfactory. J. G. A. GRIFFITHS.

**Theory of local elements.** E. LIEBREICH (Korrosion u. Metallschutz, 1929, 5, 20—22; Chem. Zentr., 1930, i, 2307).—After the first impulse of the current, which depends on the cathodic current density, the polarisation of the cathode alone determines the current; this view is supported by experiments with the combinations  $\text{Pt}|\text{Zn}$ ,  $\text{Cl}|\text{Zn}$ ,  $\text{Cu}|\text{Zn}$ ,  $\text{Hg}|\text{Zn}$ ,  $\text{Fe}|\text{Zn}$ ,  $\text{Pb}|\text{Zn}$ ,  $\text{C}|\text{Fe}$ ,  $\text{Hg}|\text{Fe}$ , and  $\text{Hg}|\text{Cu}$ .

A. A. ELDRIDGE.

**Theory of hydrogen overvoltage.** T. ERDEY-GRÚZ and M. VOLMER (Z. physikal. Chem., 1930, 150, 203—213).—The experiments of Bowden and Rideal (A., 1928, 1088) are said to indicate that hydrogen overvoltage is due to accumulation, not of neutral hydrogen atoms, but of undischarged ions, which form an electric double layer. The theory leads to an evaluation of the constant *b* in Tafel's equation as 0.116 at 20°, in good agreement with the mean of experimental values. The variation of this constant with temperature and the rate of decay of overvoltage after breaking the circuit as deduced from the theory are also in good agreement with experiment. Metals like activated platinum are considered to have numerous cavities of atomic dimensions in their surface, and ions entering these recesses become more or less neutralised by the electrons of the surrounding platinum atoms, with which they form dipoles having a very small moment, thus producing the behaviour of discharged ions. E. S. HEDGES.

**Hydrogen overvoltages in glacial acetic acid.** S. SWANN, jun., and E. O. EDELMANN (Trans. Amer. Electrochem. Soc., 1930, 58, 75—81).—Using the chloranil electrode as reference electrode (cf. A., 1928, 129), measurements have been made of the potentials at which hydrogen is evolved from cathodes of various metals in the electrolysis of a 20% solution of sulphuric acid in glacial acetic acid at various current densities. At current densities above 2 amp./dm.<sup>2</sup> the hydrogen overvoltages so obtained are all greater than the corresponding values for aqueous solutions of sulphuric acid (Knobel, Caplan, and Eiseman, A., 1924, ii, 88) and increase much more rapidly with current density. Also the sequence of metals arranged according to the magnitude of the hydrogen over-

voltage is apparently quite different in the acetic acid solution; thus platinum has a high overvoltage coming between lead and zinc in the sequence.

H. J. T. ELLINGHAM.

**Theory of surface polarisation.** W. J. MÜLLER (Z. Elektrochem., 1930, 36, 679—686).—A discussion of passivity in terms of surface polarisation.

H. F. GILLBE.

**Electrolytic Peltier heats and their measurement by isothermal adiabatic differential calorimetry.** E. LANGE and J. MONHEIM (Z. physikal. Chem., 1930, 150, 177—202).—The electrolytic Peltier heats at reversible electrodes are discussed in relation to other thermodynamical quantities characteristic of the electrolytic cell. Earlier measurements are reviewed and an isothermal, adiabatic, differential calorimetric method is described and has been applied to the  $\text{Hg}|\text{Hg}_2^{++}$  electrode, using a mercury electrode in mercurous nitrate solution and the normal calomel electrode. The tabulated values show an increase in the positive direction with increasing metal-ion concentration, in agreement with theoretical prediction.

E. S. HEDGES.

**Physical processes in the so-called electrical gas purification.** II. R. LADENBURG and W. TIETZE (Ann. Physik, 1930, [v], 6, 581—621).—The mechanism of the process (this vol., 697) has been established. During the corona discharge individual glowing points are formed on the negative electrode whether it has a polished or a roughened surface; at these points positive and negative gas ions are formed, of which the former remain attached to the electrode, whilst the latter are driven with a velocity of several metres per sec. towards the walls of the vessel, and during their progress impart to the dust particles an electric charge. The velocity of the particles exceeds that calculated by Stokes' law from the field strength, on account of the existence of an electric wind of considerably higher velocity; under normal conditions of gas purification the gas currents which flow from each glowing point of the electrode to the anticathode, when practically the whole of the electric current is carried by the ions, have a velocity of 20—60 cm. per sec. In presence of large quantities of dust the whole of the electric current may be carried by the dust, and the high wind velocity is then developed only in the neighbourhood of the electrode. The time taken for the dust particles to wander to the anticathode under these conditions is considerably increased.

H. F. GILLBE.

**Quantum theory of kinetics of chemical reactions. Unimolecular reactions.** S. ROGIN-SKY and L. ROSENKRIVITSCH (Z. physikal. Chem., 1930, B, 10, 47—85).—The methods of wave-mechanics have been applied to the theory of unimolecular reactions by assuming that decomposition either is due to the field of force of the decomposing molecule (cf. this vol., 546) or is a phenomenon analogous to the Auger effect; the latter assumption is regarded as the more probable. A relationship between the constants  $A$  and  $B$  of Arrhenius' equation for the effect of temperature on reaction velocity is then deduced and found to agree well with the experimental data. The connexion between the order of a

reaction and the various energy changes involved has also been investigated, and the results have been used to elucidate the mechanism of various reactions, molecular oxidation by oxygen, for instance, being found to be explained most satisfactorily by the peroxide theory.

R. CUTHILL.

**Calculation of velocity coefficients. II.** G. SCHMID (Z. physikal. Chem., 1930, 149, 241—256; cf. A., 1926, 480).—The previous account of the author's method of calculating velocity coefficients, making use of the method of least squares, is amplified, and further possibilities of its application are discussed. The objections raised by Moesveld and de Meester (A., 1928, 599) to its use are examined and shown to be based on misconceptions.

F. G. TRYHORN.

**Graphical methods for the calculation of constants. I. Determination of the order of a reaction.** M. CRESPI (Anal. Fis. Quim., 1930, 28, 844—870).—When the initial concentrations,  $a$ , of the reactants are identical, the general kinetic equation  $dx/dt = K(a-x)^a(b-x)^b(c-x)^c \dots$  becomes  $dx/dt = K(a-x)^n$ , where  $n$  is the order of the reaction; by plotting  $t$  against  $x$  a hyperbolic curve is obtained and by making use of the properties of the tangents and normals to this type of curve the values of  $K$  and  $n$  may be determined graphically. The same method, with slight modifications, is applicable when the initial concentrations are not all identical.

H. F. GILLBE.

**Motion of flames in closed vessels.** C. W. STEPHENSON (Trans. Faraday Soc., 1930, 26, 577—587).—Ellis' experimentally derived conclusions (cf. B., 1929, 82) have been verified by mathematical analysis.

H. F. GILLBE.

**Kinetics of the thermal transition of parahydrogen.** A. FARKAS (Z. Elektrochem., 1930, 36, 782—784).—The thermal decomposition of parahydrogen at 700—900° is a homogeneous reaction, uninfluenced by the walls of the containing vessel. At 600—750° the course of the reaction is given by  $p_t - p_\infty = (p_0 - p_\infty) \times e^{-Kt}$ , where  $p_0$ ,  $p_t$ , and  $p_\infty$  are the parahydrogen concentrations at times 0,  $t$ , and  $\infty$ , respectively, and  $K$  is a constant. By assuming the reaction to be  $\text{H}_2 + \text{H} \rightarrow \text{OH} + \text{H}$ , the influence of pressure variation is given by  $(p_t - 0.25) = (p_0 - 0.25)e^{-Kt/\sqrt{p_h}}$ , where  $p_h$  is the total hydrogen concentration. This equation yields satisfactory values for the velocity coefficient, which at 600° and at pressures from 50 to 400 mm. has a mean value of  $1.245 \times 10^9$ . The heat of activation of the reaction is between 4000 and 11,000 g.-cal.

H. F. GILLBE.

**Effect of nitrogen peroxide on the explosion temperature of mixtures of oxygen and hydrogen.** H. J. SCHUMACHER (Z. physikal. Chem., 1930, B, 10, 7—8; cf. Thompson and Hinshelwood, A., 1929, 657).—It is suggested that the depression of the explosion temperature of a mixture of hydrogen and oxygen as a result of the addition of nitrogen peroxide is due to the peroxide molecules absorbing the energy of "hot" molecules formed by the reaction and dissociating in consequence,  $\text{NO}_2 = \text{NO} + \text{O}$ , the oxygen atoms then bringing about further reaction.

Since the frequency of the reaction  $O + NO_2 = NO + O_2$  is greater than that of the reaction  $H_2 + O = OH + H$  (cf. this vol., 1004), increase in the concentration of peroxide beyond a certain point will cause the former reaction to occur so rapidly that the latter reaction is negligible, i.e., the peroxide will cease to affect the explosion temperature.

R. CUTHILL.

**Influence of nitrogen dioxide on the ignition of hydrogen-oxygen mixtures.** L. FARKAS and P. HARTECK (Nature, 1930, 126, 351).—Schumacher's view (cf. this vol., 1127 and preceding abstract) is criticised.

L. S. THEOBALD.

**Heats of activation of bimolecular gas reactions; the reaction between chlorine and hydrogen.** J. FRANCK and E. RABINOVITSCH (Z. Elektrochem., 1930, 36, 794—799).—The relation of the heat of activation to the nuclear distances and impact radii of the reactants and resultants is discussed for the general reaction  $A + BC \rightarrow AB + C$ , and the conclusion deduced, viz., that the heat of activation must be greater the greater is the ratio nuclear distance/impact radius, is confirmed by reference to the reactions  $Cl + H_2 \rightarrow HCl + H$ ,  $H + Cl_2 \rightarrow HCl + Cl$ , and  $F + H_2 \rightarrow HF + H$ . The influence of iodine monochloride on the reaction between chlorine and hydrogen is discussed, and suggestions are made regarding the influence of water and of ultra-violet and visible radiation.

H. F. GILLBE.

**Reactions between the atoms and molecules of nitrogen and hydrogen.** W. STEINER (Z. Elektrochem., 1930, 36, 807—814).—No reaction takes place between nitrogen molecules and atomic hydrogen, but activated nitrogen combines with molecular hydrogen to form hydrazine if the concentrations of nitrogen atoms be sufficiently high; about three times the quantity of ammonia is simultaneously formed. The yield of ammonia from active nitrogen and active hydrogen increases at first with the time of contact, attains a maximum, and then decreases rapidly; the fall is attributable to decomposition of the ammonia formed by excess of active nitrogen. The after-glow of active nitrogen is markedly reduced by the presence of atomic hydrogen, and from a mixture containing 80—85% of active nitrogen and 15—20% of hydrogen a high yield of ammonia is produced; the active nitrogen molecules on collision with the hydrogen molecules are converted into the atomic state and then react with the hydrogen atoms present. The mechanisms of the reactions involved are discussed.

H. F. GILLBE.

**Rates of combustion of mixtures of gases.** G. TAMMANN and H. THIELE (Z. anorg. Chem., 1930, 192, 65—89).—The rate of combustion,  $v$ , of a mixture of air and carbon monoxide burning at a jet is increased by preheating the mixture, the effect being represented by the empirical equation  $v = ba^{T/2}$ , where  $T$  is the temperature at which the gas is preheated and  $a$  and  $b$  are constants, the former of which, but not the latter, is independent of the composition. The ratio of the value of  $v$  at  $700^\circ$  to that at  $18^\circ$  for the same mixture is the same for all mixtures, and the mixture having the maximum value of  $v$  is the same at both temperatures. Preheating a mixture of air and coal gas has a more pronounced

accelerating effect, but the relation of  $v$  to the composition and temperature of preheating is much less simple, the composition of the mixture with maximum  $v$  varying with the temperature. In explanation of Bone's surface combustion it is suggested that the absence of visible flame is due not so much to catalysis as to  $v$  being so high, as a result of the preheating of the combustible mixture in passing through the refractory diaphragm, that the flame retreats into the interstices. Similarly, the economy in fuel consumption achieved by using a hot blast in the blast furnace is probably to be attributed to the preheating causing an increase in  $v$  and therefore a diminution in the oxidising area in the vicinity of the tuyères (cf. Wüst, B., 1927, 816). If the rate of flow,  $c$ , of hydrogen sulphide burning at a jet in air is continuously increased, a critical rate,  $c_a$ , is ultimately reached at which the flame starts to leave the end of the jet, the value of  $c_a$  being related in a simple manner to  $v$ . It is found empirically that if  $V$  is the mean rate of flow through the surface of the inner cone of the flame at a gas pressure  $p$ , then  $c/pV^{3/2}$  is a constant, depending only on the gas and jet used, and at low values of  $c/V$  is equal to  $v$ . From experiments on these lines it is found that preheating the hydrogen sulphide causes  $c_a$  to increase, the  $c_a$ - $T$  graph being rectilinear up to about  $500^\circ$ , beyond which  $c_a$  begins to increase more rapidly. The rates of combustion of various organic substances burning in air have been compared by means of determinations of  $c_a$ .

R. CUTHILL.

**Oxide of iodine,  $I_2O_5$ . Intermediate compound [in the iodine-hydroxyl and hydriodic-iodic acid reactions].** W. C. BRAY (J. Amer. Chem. Soc., 1930, 52, 3580—3586).—The kinetics of the formation of iodate and iodide from iodine and hydroxyl (Skrabal, A., 1912, ii, 33) and of the reaction between hydriodic and iodic acids (Abel and Hilferding, A., 1928, 1194) are interpreted by reaction mechanisms which require the existence of the intermediate compounds  $H_2I_2O_3$  and  $I_2O_2$  in addition to the ion  $I_3O_2^+$ .

The corresponding reactions of bromine compounds are believed to proceed by way of analogous intermediate compounds.

J. G. A. GRIFFITHS.

**Velocity of the iodate-thiosulphate reaction.** R. RIEDER (J. Physical Chem., 1930, 34, 2111—2116).—The velocity of the reaction can be represented approximately by the equation  $-d[H^+]/dt = 3 \times 10^{10} \times [H^+]^2[IO_3^-][S_2O_3^{2-}]^2$ ;  $k^{34}/k^{24}$  is 1.3.

L. S. THEOBALD.

**Kinetics of alkaline solutions of iodine; the alkali borates.** O. LIEVIN and J. DECLERCK (Compt. rend., 1930, 191, 45—47).—The velocity of formation of iodate when iodine is dissolved in solutions of sodium and potassium metaborates has been determined. At the ordinary temperature the velocity in solutions containing iodine, potassium iodide, and sodium metaborate increases with increase of the borate concentration, but diminishes with increase of the iodide concentration; the influence of sodium iodide is similar to that of the potassium salt, but is less pronounced. Dilution of the solution increases the reaction velocity. Experiments with variation

of the potassium/boric acid ratio show that there is a maximum reaction velocity when there are present about 3 mols. of uncombined potassium hydroxide to one atom of iodine, a relationship which is valid also in absence of borate; further, this maximum velocity is of the same order as for simple solutions of potassium hydroxide. Thus metaborate solutions, in their behaviour towards iodine, resemble those of carbonates and tribasic phosphates, whilst solutions of borax resemble those of hydrogen carbonates and dibasic phosphates.

H. F. GILLBE.

**Kinetics of decomposition of hypochlorite solutions.** J. J. WEISS (Z. anorg. Chem., 1930, 192, 97—104).—Brönsted's theory of reaction velocity (A., 1925, ii, 681) has been applied to the decomposition of sodium hypochlorite in aqueous solution, the reaction determining the speed of formation of chlorate being taken to be  $\text{ClO}' + \text{Cl}_2\text{O} + \text{H}_2\text{O} = \text{ClO}_3' + 2\text{H}' + 2\text{Cl}'$ . Loss of active oxygen is ascribed to the reactions  $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HClO} \rightarrow 2\text{H}' + 2\text{Cl}' + 2\text{O}$ , and  $2\text{ClO}' = 2\text{Cl}' + 2\text{O}$ . These reactions are markedly catalysed by light and by metal ions, and the preservative action of colloids is probably due to their adsorbing the catalysing ions. The effect of electrolytes on the activity coefficient of hypochlorous acid over a wide range of concentrations agrees well with the requirements of Debye and McAulay's theory (*ibid.*, 171). A mechanism for the bleaching of fibres is suggested.

R. CUTHILL.

**Velocity of esterification in mixed solvents.** B. W. BHIDE (J. Indian Chem. Soc., 1930, 7, 575—576).—When an inert solvent like benzene is added to a solution of an organic acid in isoamyl alcohol with hydrogen chloride as catalyst the rate of esterification is greatly increased. Measurements of the velocity of esterification in the presence of different inert solvents showed that the solubility of the hydrogen chloride in the neutral solvent is the predominant factor.

E. S. HEDGES.

**Conductivity measurements of the comparative rates of hydrolysis of lactones derived from simple sugars.** S. R. CARTER, W. N. HAWORTH, and R. A. ROBINSON (J.C.S., 1930, 2125—2133).—The rate of hydrolysis may be used to distinguish between isomeric  $\gamma$ - and  $\delta$ -lactones derived from the same sugar. The lowest rate of hydrolysis among the  $\delta$ -lactones studied is several times as great as the highest rate among the  $\gamma$ -lactones.

C. W. GIBBY.

**Velocity of dissolution of oxygen in water.** II. S. MIYAMOTO, T. KAYA, and A. NAKATA (Bull. Chem. Soc. Japan, 1930, 5, 229—240).—A mixture of oxygen and air is passed under specified conditions into sodium sulphite solution and the velocity of oxidation of the latter determined by titration after measured time intervals. The velocities observed are independent of the concentration of the sulphite solution and are a linear function of the partial pressures of the oxygen. These results confirm the theoretical treatment of the subject (this vol., 866) and the values of the velocity coefficient agree with those derived theoretically, particularly at the higher partial pressures of oxygen.

H. I. DOWNES.

**Reaction kinetics of unimolecular adsorption layers.** H. DOHSE, W. KALBERER, and C. SCHUSTER (Z. Elektrochem., 1930, 36, 677—679).—A survey (cf. A., 1929, 1231; this vol., 431, 1003). H. F. GILLBE.

**Mechanism of the combustion of carbon at low pressures.** V. SIHVONEN (Z. Elektrochem., 1930, 36, 806—807).—The combination of carbon with oxygen at low pressures is a reaction of the first order. At temperatures from 800° to 1400° combustion in a current of oxygen results in the formation of a gaseous mixture of the constant composition  $\text{CO}_2 + 2\text{CO}$ . At temperatures between 1400° and 1500° the transition which takes place in the carbon surface causes a break in the reaction velocity curve. In the interval 800—1000° the carbon monoxide formed acts as an autocatalyst, but the presence of carbon dioxide hinders the reaction. Above the transition temperature the heat of formation of carbon monoxide is about 27 kg.-cal., and the presence of this gas accelerates its own formation, but hinders the production of carbon dioxide. From 1500° to 1800° the carbon dioxide heat effect in presence of the monoxide is —17 kg.-cal., which may be regarded as the approximate heat of evaporation of the carbon monoxide adsorbed by carbon at high temperatures. Traces of water vapour catalyse the formation of both oxides at 1600°. Unheated carbon dioxide reacts with carbon heated at 1500°, the process being inhibited by carbon monoxide; the effect may be observed at 1200° if the carbon dioxide be preheated.

H. F. GILLBE.

**Crystallisation velocity and number of nuclei of glycerol in relationship to the temperature.** G. TAMMANN and E. JENCKEL (Z. anorg. Chem., 1930, 193, 76—80).—The number of crystal nuclei which develop in glycerol when cooled to —40° to —70° and then kept for 10 min. at 0°, i.e., at approximately the temperature of maximum crystallisation velocity, shows at about —60° to —62° a sharp maximum which is independent of the actual number of nuclei formed. The crystallisation velocity at —50.2°, determined dilatometrically, is about 0.001 mm. per min., and at —61.3° is less than 0.000028 mm. per min.

H. F. GILLBE.

**Detonation of solid explosives.** W. E. GARNER (Trans. Faraday Soc., 1930, 26, 590—592).—An equation has been derived for the rate of decomposition of a solid material applicable to the stages between slow thermal decomposition and detonation.

H. F. GILLBE.

**Resistance of electrodeposits to corrosion, with special reference to cadmium and zinc.** W. S. PATTERSON.—See B., 1930, 912.

**New examples of homogeneous gas catalysis.** K. CLUSIUS and C. N. HINSHELWOOD (Z. Elektrochem., 1930, 36, 748—750).—A summary of work already published (this vol., 1130). The reactions concerned are attributable principally to the wandering of a hydrogen atom attached to a carbon atom which is adjacent to an oxygen atom.

H. F. GILLBE.

**Catalytic action of hydrogen on the carbon monoxide flame.** W. E. GARNER and D. A. HALL (J.C.S., 1930, 2037—2047).—Further experiments have

confirmed the existence of the "step" previously found (Garner and Johnson, A., 1928, 375; Garner and Roffey, A., 1929, 973) in the curves of radiation- $1/\log$  speed and radiation-concentration of added hydrogen. The step is at 0.03% hydrogen for gases initially at 1 atm. pressure, and at the step  $p_{H_2}, p_{CO+O_2}$  is constant. The decrease in the emission of radiation for hydrogen contents less than 0.03% is given by the equation  $R = R_0 k_1 / (k_1 + k_2 [H_2O])$ , where  $R_0$  is the radiation for the hydrogen-free mixture. The radiation-pressure curve for the hydrogen-free flame is linear; that of the flame containing hydrogen, and of the hydrogen flame itself, is concave to the radiation axis. An irregularity occurs in the radiation-pressure curves above the step, and moves to lower pressures with increasing hydrogen concentration.

C. W. GIBBY.

**Acid and salt effects in catalysed reactions. XXIV. Catalytic effects produced by acetic acid and acetate buffers under conditions of effectively constant ionic environment.** H. M. DAWSON and E. SPIVEY (J.C.S., 1930, 2180—2189).—Approximate constancy of ionic environment for the catalytic effects of acetic acid and acetate buffers on the acetone-iodine reaction has been secured by the presence of 0.75*N*-sodium chloride. The results confirm those previously obtained with pure water as solvent. The ion  $CH_3CO_2H, CH_3CO_2^-$  has been identified as a catalytic agent in acetate buffers for which the catalytic effects of the hydrogen and hydroxyl ions and of the water molecule are small. C. W. GIBBY.

**Reactions in basic solvents.** H. GOLDSCHMIDT (Z. Elektrochem., 1930, 36, 662—665).—A survey of work on basic solvents with special reference to the relationship between additive products and catalysis and to the catalytic influence of the undissociated molecules of electrolytes.

H. F. GILLBE.

**Catalysis by finely divided metals. V. Adsorption isotherm and condition of adsorbed hydrogen.** B. FORESTI (Gazzetta, 1930, 60, 516—519; cf. A., 1929, 874).—The results of Kistiakowsky, Flosdorf, and Taylor (A., 1927, 1021) are used to illustrate the author's contention that a quadratic adsorption equation does not necessarily imply adsorption in the atomic or ionic state. The existence of more than one type of active centre, with different activities and random distribution, may lead, at low pressures and with molecular adsorption, to an equation of the form  $v = K(p - m)^{1/2}$ , where  $m$  is a constant.

F. G. TRYHORN.

**Activation by admixture. Magneto-catalytic investigation of mixtures of manganese dioxide and hydrated cobaltic oxide.** F. MERCK and E. WEDEKIND (Z. anorg. Chem., 1930, 192, 113—122).—In continuance of the investigation of the catalysed combination of carbon monoxide with oxygen previously described (this vol., 430), the causes for the activation of the above catalysts when mixed together have been studied by means of measurements of the magnetic susceptibility. The results obtained point to the formation of some kind of compound between the two oxides at the phase boundaries as the probable explanation.

R. CUTHILL.

**Decomposition of nitrous oxide on heated platinum.** H. CASSEL and E. GLÜCKAUF (Z. physikal. Chem., 1930, B, 9, 427—436).—Measurements have been made of the rate of decomposition of nitrous oxide on a heated platinum wire at pressures of 0.1 mm. and at temperatures of 1000—1800° Abs. In this pressure region the addition of about an equal volume of nitrogen causes no change in the velocity of reaction, probably because, unlike the experimental conditions of Hinshelwood and Pritchard (A., 1925, ii, 310), diffusion may play no part in this pressure range. Addition of oxygen, however, diminishes the velocity of decomposition. This can be explained by the adsorption of atomic oxygen on the wire. The initial reaction on a clean platinum wire is formulated  $N_2O_{ads} = N_2 + O_{ads} + 38,000$  g.-cal., and the reaction on the oxygen-covered surface  $N_2O_{ads} + O_{ads} = N_2 + O_2 - 5000$  g.-cal. The latter reaction must be endothermic.

J. W. SMITH.

**Mixed catalysts.** A. MITTASCH (Z. Elektrochem., 1930, 36, 569—580).—A survey of the theory and application of mixed catalysts with special reference to the oxidation of ammonia in presence of ferric and bismuth oxides, the hydrogenation of hydrocarbons with the aid of nickel-alumina catalysts, and the reduction of carbon monoxide to methyl alcohol by hydrogen.

H. F. GILLBE.

**Catalytic oxidation of ammonia.** A. VON NAGEL (Z. Elektrochem., 1930, 36, 754—757).—The products of the catalytic oxidation of ammonia by air in presence of manganese dioxide have been determined for rates of flow ranging from 0.1 to 80 litres per hr. and at temperatures up to 800°. At high rates of flow a mixture containing 8% of ammonia yields as the main product at all temperatures nitric oxide, with 10—20% of nitrogen, but at medium rates nitrous oxide appears, and with a rate of flow of 5 litres per hr. at 350° corresponds with 70% of the ammonia used, no nitric oxide being formed; as the temperature is raised the nitrous oxide is replaced by nitric oxide. With very low gas velocities (0.1 litre per hr.) nitrous oxide is formed in relatively small quantities, the main product being nitrogen, which is derived partly from the decomposition of the nitrous oxide first formed. If air containing only 1% of ammonia be employed, nitrous oxide is produced in considerable quantity at all temperatures up to 400—500° and at all the gas velocities studied. Local overheating of the catalyst due to either too high an ammonia concentration or too high a velocity of flow causes decomposition of the nitrous oxide which is first formed at temperatures up to 500°. By employing as catalyst a mixture of manganese dioxide with ferric or bismuth oxide a 90% yield of nitrous oxide may be obtained at 300°. The primary reaction product is probably  $HNO$ , which at low temperatures decomposes according to the equation  $2HNO \rightarrow N_2O + H_2O$ , and at high temperatures is oxidised to nitric oxide and water. The precise nature of all the reactions which take place cannot yet be decided.

H. F. GILLBE.

**Nickel-molybdenum mixed catalyst in ammonia synthesis.** E. KEUNECKE [with MAYER, ASSMANN, and LEHRER] (Z. Elektrochem., 1930, 36,



690–692).—The activity of a nickel-molybdenum catalyst in the synthesis of ammonia from nitrogen and hydrogen at 550° and 200 atm. pressure is proportional to the percentage of molybdenum up to about 70% and thereafter diminishes. By increasing the period of contact the maximum activity occurs at about 80% of molybdenum, whilst for prolonged contact periods (3 weeks) catalysts containing less than 62% of molybdenum are entirely inactive, although the normal maximum occurs at 80%. In the early stages of the reaction the catalyst absorbs nitrogen in proportion to its molybdenum content up to the period in which it attains its maximum activity; for longer contact periods the nitrogen content diminishes and after three weeks the catalyst is again free from nitrogen. X-Ray analysis shows that during the reaction the compound  $\text{NiMo}$  and mixed crystals of nickel and molybdenum are formed, but both are catalytically inactive; the former appears at the beginning of the reaction only in catalysts containing more than 62% of molybdenum, and both are formed from nickel trimolybdate produced in the material during its preparation. The true catalyst appears to be molybdenum containing nitrogen, and it is activated by the compound  $\text{NiMo}$ . The formation of mixed crystals and of the compound is accelerated by heating the catalyst in a vacuum or in pure hydrogen, but is inhibited by ammonia.

H. F. GILLBE.

**Influence of foreign substances on the reactivity of crystals.** J. A. HEDVALL and W. ANDERSSON (*Z. anorg. Chem.*, 1930, **193**, 29–46).—The various ways in which a third substance can influence the nature of a reaction between two solid substances are described. At temperatures between 228° and 298° the equilibrium in the system  $\text{BaO} + \text{PbCl}_2 \rightarrow \text{BaCl}_2 + \text{PbO}$  is displaced to the right if 0.1% of barium chloride be added to the lead chloride, on account of a partial replacement of lead in the lead chloride lattice by barium, but to the left in presence of 1.0–5.0% of barium chloride; the increase in the reactivity is thus not due to partial fusion of the reactants. The reaction  $\text{BaO} + 2\text{CuCl} \rightarrow \text{BaCl}_2 + \text{Cu}_2\text{O}$  at 148–284° is facilitated by the addition to the cuprous chloride of 0.17 mol.-% of sodium chloride, due to exchange of sodium for copper in the cuprous chloride lattice; in presence of 8.18 mol.-% of sodium chloride at temperatures higher than 263° the reaction proceeds to a greatly increased extent on account of dissolution of sodium chloride in cuprous chloride. At higher sodium chloride contents, in the region wherein two solid solutions of the chlorides are formed, the cuprous chloride is protected by the sodium chloride from attack by the barium oxide. At the lower temperatures very little reaction takes place when the sodium chloride is present in the proportion necessary for the formation of  $\text{NaCl} \cdot 2\text{CuCl}$ , and  $2\text{NaCl} \cdot \text{CuCl}$ . Data are given also for the reaction at temperatures between 126° and 250° in presence of potassium chloride (0.98–4.21%), rubidium chloride (0.82–3.71%), and caesium chloride (0.59–2.88%). The  $\log K - 1/T$  curves, where  $K$  is the conductivity of the mixture and  $T$  the temperature, show the existence of the compound  $\text{CuCl} \cdot 2\text{KCl}$ , the eutectic between  $\text{CuCl} \cdot 2\text{RbCl}$  and  $3\text{CuCl} \cdot 2\text{RbCl}$  at about 150°,

and the eutectic between  $\text{CuCl}$  and  $2\text{CuCl} \cdot \text{CsCl}$ . The curves for mixtures containing caesium and rubidium both exhibit a sharp break at about 170°, and the significance of these and other inequalities in the curves are discussed. The increased extent of the reaction in presence of potassium, rubidium, and caesium chlorides is caused by partial fusion of the reactants.

H. F. GILLBE.

**Catalytic properties of rhenium.** H. TROPSCH and R. KASSLER (*Ber.*, 1930, **63**, [B], 2149–2151).—The catalyst is prepared by impregnating quartz sand with technical potassium perhenate, reduction in hydrogen at 600°, and removal of alkali by water. A copper-rhenium catalyst (1:1) is prepared by similar methods, but reduction is effected at 400°. The copper-free catalyst is about as effective as osmium in the reduction of carbon monoxide to methane; it rapidly loses its activity, but can be regenerated by contact with hydrogen at 400°. The copper-rhenium catalyst retained its activity after 20 hrs. At 470°, in the presence of the copper-rhenium catalyst, carbon monoxide is decomposed into carbon and carbon dioxide; reaction proceeds only to the formation of rhenium carbide. Hydrogenation of ethylene proceeds in the presence of rhenium at 300°.

H. WREN.

**Vapour-phase oxidation of organic compounds, using rare-earth oxides as catalysts.** I. METHYL and ETHYL ALCOHOLS. F. R. LOWDERMILK and A. R. DAY (*J. Amer. Chem. Soc.*, 1930, **52**, 3535–3545).—The oxidation of methyl and ethyl alcohols to the corresponding aldehydes by means of air and catalysts of pumice impregnated with copper oxide, samarium oxide, and copper oxide-samarium oxide (0.5–5%) mixture has been investigated. The catalytic activity of pure samarium oxide is very great, causing the decomposition of formaldehyde and charring in the case of ethyl alcohol. The mixed-oxide catalysts tended to make the oxidation proceed too far and gave smaller yields than the pure copper oxide catalyst, which gave better results than have been obtained previously with various forms of copper as catalyst. The attainment of optimal yields depended on the rate of flow of reactants, the length of the catalyst layer, and its temperature. When excess of catalyst was used the yield decreased markedly.

J. G. A. GRIFFITHS.

**Oxidation of apparently auto-oxidisable leucobases by molecular oxygen.** A. REID (*Ber.*, 1930, **63**, [B], 1920–1922).—The oxidation of leucothionine in a mixture of glacial acetic acid and ammonium acetate is accelerated by the addition of minute amounts of copper, but occurs also without such addition. This oxidation appears to be occasioned by metallic catalysis, since it is very greatly repressed by the presence of carbon monoxide. Similar observations are made with leucomethylene-blue.

H. WREN.

**Electrocrystallisation of metals.** I. **Structure of electrically deposited copper.** V. A. KISTIAKOVSKI, U. V. BAYMAKOV, and I. V. KROTOV (*Bull. Acad. Sci. U.S.S.R.*, 1929, **9**, 777–790).—An increase in the concentration of either the copper sulphate or the sulphuric acid, the latter above

2.5*N*, results in a finer deposit of copper, whilst the effect of an increase in current density is rather complex. The results support Kistiakovski's explanation of the process of electrocrystallisation taking place during the electrolysis of acid solutions of copper salts.

A. FREIMAN.

**Preparation of pure electrolytic nickel. II. Final elimination of copper and removal of cobalt and iron.** C. G. FINK and F. A. ROHRMAN (Trans. Amer. Electrochem. Soc., 1930, 58, 83—100; cf. B., 1930, 377).—A disc-shaped cathode capable of being rotated at speeds up to 6000 rev. per min. has been designed with a view to minimise concentration polarisation and thus effect sharp separations of metals by electrodeposition. The copper content of crystalline nickel sulphate was reduced from 0.02 to 0.001% by electrolysis of a *N*-solution of the salt ( $p_H$  5.0) at 20° with 0.35 amp./dm.<sup>2</sup> and rotating the cathode at 3000 rev. per min., the current efficiency of copper deposition being 98%. Also pure copper was deposited at a current efficiency of 23.5% on a cathode rotating at this speed from *N*-nickel sulphate containing only 1 part of copper in 100,000 parts of solution, using 0.3 amp. per dm.<sup>2</sup> at 25°. The higher is the current density, the higher is the minimum speed of rotation of the cathode needed to avoid any co-deposition of nickel. Copper was effectively removed at high current efficiency from waste liquors containing a considerable proportion of ferric iron by using the rotating cathode. The efficiency of removal of silver from copper nitrate and of gold from sodium chloride solutions was also examined. The possibility of separating iron and nickel or cobalt and nickel is discussed. On electrolysis *N*-nickel sulphate ( $p_H$  5.5) containing 1 part of cobalt per 100 parts of nickel at 20° with the cathode rotating at 1000 rev. per min., lowering the current density from 2.0 to 0.22 amp. per dm.<sup>2</sup> raised the cobalt content of the deposit from 27.2 to 43.2%, but at lower current densities the current efficiency of metal deposition soon falls to zero. Increasing the rate of rotation of the cathode also increases the percentage of cobalt in the deposit, but decreases the current efficiency. A sample of nickel which was spectroscopically pure except for very faint copper lines was prepared from Mond nickel by dissolving in hydrochloric acid, bringing the solution to  $p_H$  5, and electrodepositing the copper and some of the iron on a rotating cathode; then, after removing the rest of the iron by chemical means, the nickel was deposited on an aluminium cathode, keeping up the  $p_H$  of the solution by addition of sodium hydrogen carbonate. A laboratory apparatus for continuous circulation of liquids is described, and the possibility of employing rapidly rotating electrodes in technical practice is discussed.

H. J. T. ELLINGHAM.

**Electrolytic preparation of silver oxide.** M. R. NAYAR and P. S. MACMAHON (J. Indian Chem. Soc., 1930, 7, 589—590).—Pure silver electrodes are dipped in conductivity water in a silica beaker and an arc is struck for 1 or 2 min., when enough silver oxide is produced to make the water a fairly good conductor. The electrodes are then separated 2—3 mm. and ordinary electrolysis is continued. A dark brown

coating of silver oxide forms on the anode and may readily be scraped therefrom by means of a silica rod. No silver peroxide appears in the product, which, however, contains about 30% of metallic silver.

E. S. HEDGES.

**Electrodeposition of metals from liquid ammonia solutions of their salts.** L. F. AUDRIETH and L. F. YNTEMA (J. Physical Chem., 1930, 34, 1903—1906).—The deposits obtained by the electrolysis of solutions of the iodides, cyanides, or nitrates of copper, zinc, cadmium, tin, etc. in liquid ammonia are described. In general, the results closely resemble those obtained with aqueous solutions. In the case of the alkali metals, the free metal is discharged with the formation of the characteristic blue solution, which is stable for sodium salts but fugitive for caesium.

L. S. THEOBALD.

**Chemical reactions induced by the electrodeless discharge.** W. C. SCHUMB and H. HUNT (J. Physical Chem., 1930, 34, 1919—1923).—With the electrodeless discharge, sulphur, iodine, cupric chloride, potassium ferricyanide, sodium, calcium, and certain organic compounds are reduced in an atmosphere of a few mm. of hydrogen. Azoxybenzene is reduced in stages to aniline, and *p*-nitrotoluene is reduced to *p*-toluidine. Nitrogen mixed with 3 volumes of hydrogen gives a 30% yield of ammonia at the ordinary temperature with an initial pressure of 0.5—1 mm., whilst ammonia over the same range of pressure is decomposed to the extent of nearly 70%. In oxygen, nickelous and magnesium oxides are converted into higher oxides; in nitrogen, magnesium yields the nitride.

L. S. THEOBALD.

**Scientific principles of photochemistry.** M. BODENSTEIN (Z. angew. Chem., 1930, 43, 819—823).—A critical summary of modern theories of photochemical reactions is given.

J. LEWKOWITSCH.

**Elementary process in photochemical reactions.** H. SPÖNER (Z. angew. Chem., 1930, 43, 823—830).—A theoretical discussion is given of the relations between typical absorption spectra and activation processes of photochemical reactions (cf. preceding abstract).

J. LEWKOWITSCH.

**Photochemical reaction between oxygen and hydrogen chloride.** A. J. ALLMAND and R. G. FRANKLIN (J.C.S., 1930, 2073—2092).—Concentrated hydrochloric acid saturated with oxygen affords chlorine when exposed to the full radiation of tungsten or mercury arcs, but not when in the dark or in diffused light. In the presence of manganese chloride the reaction is retarded by about 20%. The production of chlorine is the greater the larger is the concentration of oxygen, and bears a similar relation to the acid concentration. Ultra-violet light can cause the formation of chlorine up to a limiting concentration, which is approached asymptotically, and is independent of light intensity and of moderate variations in oxygen concentration. The shorter wave-lengths are more effective than the longer. At the stationary state all wave-lengths are only slightly active. Chlorine solutions of concentration greater than that of the stationary state are decomposed by light of all wave-lengths between 254 and 436  $\mu$ . The increase in the extinction coefficients of chlorine

in the visible region caused by the addition of concentrated hydrochloric acid persists in the ultra-violet, and is very pronounced in the region of wave-lengths which cause the oxidation. The partial pressures of chlorine over aqueous solutions have been measured; the fugacity coefficient of the chlorine remains practically constant up to  $2.5 \times 10^{-3} N$  and then rises rapidly. The pale yellow colour of aqueous chlorine solutions decreases normally on dilution with sodium or potassium chloride solutions, but lithium chloride gives anomalous results. The stationary state produced in the oxidation of hydrochloric acid is a true one, corresponding with the equilibrium  $4HCl + O_2 \rightleftharpoons 2H_2O + Cl_2$ . The quantum efficiency is of the order of 0.2 at 260  $\mu$ , and diminishes at longer wave-lengths. In the absence of a liquid phase, even when the gases are partly dried, prolonged intense irradiation with light of wave-length greater than 300  $\mu$  leads to a state not far from the thermodynamic equilibrium, but in the presence of aqueous hydrochloric acid a complex stationary state is set up. A possible chain mechanism is discussed.

C. W. GIBBY.

**Photochemical reaction between hydrogen and carbon monoxide in presence of excited mercury atoms, and the optical detection of the reaction products.** W. FRANKENBURGER [with H. KLINKHARDT, C. STEIGERWALD, and W. ZIMMERMANN] (Z. Elektrochem., 1930, 36, 757—769).—At the ordinary temperature and pressure carbon monoxide and hydrogen unite in presence of mercury atoms excited by absorption of radiation of wave-length 2536 Å. with the formation of formaldehyde and glyoxal. The products are formed by the direct union of hydrogen atoms and CHO groups, there being no series of intermediate products as suggested by Marshall (A., 1926, 919). Traces of oxygen and of water vapour reduce the yield of aldehyde on account of the photochemical formation of hydrogen peroxide, but nitrogen and carbon dioxide are without influence. The yield increases in an approximately linear manner with the rate of flow of the gas mixture up to a limiting value, and decreases rapidly at constant rate of flow if either the hydrogen or carbon monoxide be present in excess, and also if the temperature be raised above 50°. Variation of the yield with the mercury vapour content of the gas mixture is ascribed to the production of disturbing side reactions. Under optimum conditions of temperature, rate of flow, and composition of the mixture, the quantum yield is about 1.0—1.5, and not, as found by Marshall, 3. The negative temperature coefficient of the reaction is consistent with the small heat of formation of the CHO group deduced from observations of the band spectra. The absorption spectrum of the gaseous mixture after the reaction shows the presence of formaldehyde and glyoxal, but there is no absorption which can be ascribed to the group CHO.

H. F. GILLBE.

**Halogen-sensitised oxidation of carbon monoxide.** R. LIVINGSTON (J. Physical Chem., 1930, 34, 2121—2122).—Bromine does not photosensitise the oxidation of carbon monoxide at the ordinary temperature and pressure.

L. S. THEOBALD.

**Influence of drying on the photolysis of carbon dioxide.** A. COEHN and T. SPITTA (Z. physikal. Chem., 1930, B, 9, 401—425).—Confirmation has been obtained of the observation of Coehn and Sieper (A., 1916, ii, 281) that moist or sulphuric acid-dried carbon dioxide at atmospheric pressure is dissociated only to the extent of about 1% in ultra-violet light, whereas when it is dried by slow streaming over phosphoric oxide it is about 20% dissociated. It is now shown, however, that still drier carbon dioxide, prepared by the action of ultra-violet light on a mixture of liquid air-dried carbon monoxide and oxygen and subsequent removal of the residual permanent gases, is less than 1% decomposed under similar conditions. Carbon dioxide dried for 4 months over phosphoric oxide shows an intermediate effect, as does the gas after slow passage over phosphoric oxide followed by liquid air fractionation. When liquid air-fractionated carbon dioxide is mixed with 0.01 of its volume of sulphuric acid-dried gas a considerable rise in the degree of dissociation is observed. This mixture is calculated to be equivalent to phosphoric oxide-dried carbon dioxide. It is therefore concluded that the effects observed are due to the moisture content and not to other impurity evolved from the phosphoric oxide. It is suggested that the water vapour acts in two different ways, viz., that its catalytic effect at low concentration is similar to its effect in other photochemical reactions, whilst at higher water-vapour concentrations the dissociation is retarded and the recombination of carbon monoxide and oxygen accelerated by collisions of water molecules and their dissociation products with activated carbon dioxide molecules and their dissociation products.

J. W. SMITH.

**Sensitised photosynthesis of carbon dioxide at low chlorine pressures.** G. K. ROLLEFSON (J. Amer. Chem. Soc., 1930, 52, 3562—3567).—The exponent 0.71 in the equation for the rate of the chlorine-sensitised oxidation of carbon monoxide to carbon dioxide (Schumacher, A., 1927, 1147) is probably due to two parallel reactions, one proportional to  $I_{abs}$ , predominating at low pressures of chlorine, and the other to  $I_{abs}^{1/2}$  predominating at high pressures. With excess of oxygen and pressures of chlorine between 2 and 13 mm. of mercury and with light of wave-lengths greater than 4050 Å., the rate of formation of carbon dioxide is given by  $d[CO_2]/dt = kI_0[Cl_2][CO]^{1/2}$ , and thus the suggestion regarding low pressures is verified. This result is more easily interpreted by the mechanism of Lenher and Rollefson (this vol., 433) than of Bodenstein and others (A., 1929, 894).

J. G. A. GRIFFITHS.

**Oxidation of sulphur dioxide in ultra-violet radiation.** G. KORNFELD and E. WEEGMANN (Z. Elektrochem., 1930, 36, 789—794).—The combination of sulphur dioxide with oxygen at pressures from 0.5 to 1 atm. under the influence of ultra-violet light at a number of wave-lengths between 3130 and 1860 Å. has been studied. No appreciable formation of sulphur trioxide takes place at wave-lengths greater than 2537 Å., and at lower wave-lengths the quantum yield is dependent only on the sulphur trioxide concentration and is independent of the ratio of sulphur

dioxide to oxygen. The initial quantum yield varies from 3.1 at 2070 Å. to 2.0 at 1860 Å., and decreases more rapidly with increase of the sulphur trioxide concentration at 1860 than at 2070 Å., in accordance with the greater absorption of the trioxide at the shorter wave-length; the stationary state at 2070 Å. corresponds with about 75% breakdown of the trioxide and at 1860 Å. with about 64%. Although at 1860 Å. the decomposition of the sulphur trioxide is proportional to a fractional power of the energy absorbed, at 2070 Å. the exponent is unity, in agreement with the observed independence of the yield on the energy density and on the area irradiated. Temperature variations between 18° and 65° are without influence on the reaction velocity, in contradiction to Coehn's and Becker's results. The mechanism of the reaction is discussed in relation to the absorption spectrum of sulphur dioxide, which exhibits two regions of active absorption, one with its maximum at about 2850 Å., and the other below 2200 Å. H. F. GILLBE.

**Heat of dissociation of oxygen [and photo-decomposition of nitrogen peroxide].** W. P. BAXTER (J. Amer. Chem. Soc., 1930, 52, 3468).—The quantum efficiency of the decomposition of nitrogen peroxide by light of wave-length 4047 Å. is not diminished by the addition of carbon dioxide and shows no decrease at pressures as low as 0.01 mm. Therefore the molecule dissociates into nitric oxide and an oxygen atom, and hence the heat of dissociation of oxygen may be as low as 115,000 g.-cal. (cf. Kondratév, this vol., 526; Mecke, *ibid.*, 668).

J. G. A. GRIFFITHS.

**Kinetics, temperature coefficients, and quantum yields of some photochemical reactions.** A. K. BHATTACHARYA and N. R. DHAR (Z. anorg. Chem., 1930, 192, 219–224).—The reaction in the dark between sodium malonate and iodine is bimolecular and has a temperature coefficient of the velocity of 2.22 between 20° and 30°. The temperature coefficient in the light varies from 1.85 at 4725 Å. to 2.08 at 8500 Å., and the quantum yield from 1.9 to 11.9. The temperature coefficients of the reaction between sodium oxalate and bromine at 20–30° are 5.6 (dark), 2.65 (4725 Å.), and 4.42 (8500 Å.). In the dark the reaction between potassium permanganate and citric acid is bimolecular and the temperature coefficient is 2.92 from 15° to 25°; in light the temperature coefficient is 2.23 at 4725 Å. and 2.56 at 8500 Å., and the quantum yield varies from 1.02 to 10.13. Between oxalic and iodic acids a unimolecular reaction takes place in light, the mean temperature coefficient being 1.7 at 15–25°, and the quantum yield 11.2–26.2. For all the reactions mentioned the quantum yield increases with rise of temperature, and with increase in the concentration of the reactants and in the frequency of the radiation; in each case there is measurable absorption at 7000 Å. which accelerates the reaction. The increase caused by absorption of radiation of the velocity of reactions in which halogens are reactants is probably due to the formation of active halogen molecules, and not of active atoms. H. F. GILLBE.

**Photochemical reactions between hydroxylamine hydrochloride and iodine and hydrazine**

**hydrochloride and iodine.** A. K. BHATTACHARYA and N. R. DHAR (Z. anorg. Chem., 1930, 192, 210–218).—In the dark the reaction between hydroxylamine and iodine in presence of hydrochloric acid is bimolecular, the temperature coefficient of the velocity being 2.54 from 20° to 30°. The temperature coefficients in the light at 4725, 5650, 7304, and 8500 Å. are 1.94, 2.1, 2.25, and 2.28, respectively, whilst the quantum yield varies from 2.35 to 17.4, according to the temperature and wave-length. The reaction between hydrazine and iodine in presence of hydrochloric acid is in the dark bimolecular, with a temperature coefficient from 25° to 35° of 2.6. At 4725, 5650, 7304, and 8500 Å. the temperature coefficients are 1.97, 2.08, 2.18, and 2.25, respectively, and the quantum yield varies from 2 to 14.6. Both these systems exhibit marked absorption at 7000 Å., which accelerates the reaction. The ratio of the intensity of the incident radiation to the reaction velocity varies from 0.25 to 1.5, and is dependent on the ratio of the velocities in the dark and in the light. H. F. GILLBE.

**Photochemical sensitisation in the ultra-violet.** L. FARKAS, F. HABER, and P. HARTECK (Z. Elektrochem., 1930, 36, 711–714).—See this vol., 554, 1260. H. F. GILLBE.

**Relationship between particle size and the sensitivity of photographic emulsions towards X-rays.** J. EGGERT (Z. Elektrochem., 1930, 36, 750–753).—Measurements of the darkening by X-radiation of photographic emulsions of identical composition but having mean particle masses  $\alpha$  ranging from 23.0 to  $0.53 \times 10^{-13}$  g. show the photographic effect of the radiation to be proportional to  $\alpha^{2.3}$ . The photographic effect of X-rays resembles that of visible radiation in that similar desensitisation of the emulsion is possible, and, further, the darkening curves and temperature variations of the sensitivity are of the same types. H. F. GILLBE.

**Influence of other ions on photochemical processes in alkali halides.** A. SMARULA (Nachr. Ges. Wiss. Göttingen, 1929, 110–115; Chem. Zentr., 1930, i, 2847).—The effect of lead, copper, thallium, and nitrate ions on the coloration by X-rays of sodium and potassium chloride was demonstrated.

A. A. ELDRIDGE.

**Influence of the developer on the properties of a photographic plate.** N. G. PERRAKIS (Compt. rend., 1930, 191, 562–564).—The density-wave-length curve of the Ilford "special rapid panchromatic" plate has well-marked maxima at 6430 and 4750 Å., the interval 6430–5950 Å. being the region of greatest sensitiveness. The chemical nature of the developer influences the value of the density, although the general shape of the curve is unaffected. The contrast factors for two developers were obtained from respective density-log. illumination isochromes, and plotted as functions of  $\lambda$  between 4000 and 7400 Å. The difference between the values for a particular value of  $\lambda$  is a measure of the influence of the developer. J. GRANT.

**Quantum theory of photographic exposure.** F. C. TOY (Phot. J., 1930, 70, 393).—Polemical against Silberstein and Trivelli (this vol., 717).

**Quantum theory of photographic exposure.** A. P. H. TRIVELLI (Phot. J., 1930, 70, 438).—A reply to Toy (preceding abstract). J. W. GLASSETT.

[Action of] mercuric chloride on the [photographic] plate. A. REYCHLER (Bull. Soc. chim. Belg., 1930, 39, 374—378; cf. B., 1929, 871).—Plates were treated by immersion in dilute mercuric chloride solution, touching with the fingers, and brief exposure to light, in varying order of application, and then developed. The finger-prints developed black on a grey ground, except in the two cases where the finger-marking occurred last. Explanations of the results are offered. Similar results were obtained by short contact of a plate with dry mercuric chloride (or coated paper), or by long contact with an object (e.g., a coin or a printed page), when plate or object had previously been in contact with mercuric chloride. Photographic papers behaved similarly.

J. LEWKOWITSCH.

**Herschel effect.** J. NARBUTT (Z. wiss. Phot., 1930, 28, 191—220).—An investigation of the Herschel effect in photographic papers has shown that the effect can probably be obtained with all such papers, provided that the experimental conditions are suitable. It appears that the effect is not observed unless the sensitivity in the red is fairly low, and that as the sensitivity is further diminished the effect becomes more and more intense. Potassium ions cause a slight diminution in the sensitivity of Satrox Universal paper, chromic and ferrous ions have a well-marked effect, cupric and ferric ions a still greater effect, and the vanadyl ion causes the greatest depression of all the ions. The desensitising action of the halogen ions falls in the order  $I'$ ,  $Br'$ ,  $Cl'$ ,  $F'$ , the effect of the fluoride ion being inappreciable. With plates there is a similar relationship between the sensitivity in the red and the Herschel effect; vanadyl nitrate in particular produces a well-marked effect, although it also has a destructive action on the latent image. Further, the latent image produced by exposure to light of practically any part of the spectrum can be bleached or even destroyed by exposure to light of the same or any other part of the spectrum, even the ultra-violet, provided that before the second exposure the emulsion is treated with a desensitiser in respect of the particular light to be used. The most satisfactory explanation of the above observations seems to be obtained by adopting the mechanism proposed by Trivelli for solarisation (Z. wiss. Phot., 1908, 6, 6), viz.,  $A \rightarrow B \rightarrow C$ , where  $A$  represents the silver halide,  $B$  the developable substance, and  $C$  the undevelopable substance of the solarised image. If the sensitivity is sufficiently high the process  $A \rightarrow B$  occurs so rapidly that the second stage has a negligible effect, whereas if the sensitivity is low the process  $B \rightarrow C$  is dominant, the result being the appearance of the Herschel effect.

R. CUTHILL.

**Formation of the latent photographic image.** M. SAVOSTIANOVA (Nature, 1930, 126, 399).—Optical investigations on the absorption spectra of exposed and unexposed silver bromide are recorded. The absorption band lies in the bluish-violet and the near ultra-violet regions. Illumination of the bromide with rays which it absorbs or with X-rays changes the

colour of the unexposed crystals from yellow to emerald-green; the absorption band of this phase lies in the red and infra-red. Heat and the action of red and infra-red radiations reverse the change. The analogy between these changes and the behaviour of rock-salt on irradiation by X-rays etc. is emphasised.

L. S. THEOBALD.

**Effect of photosensitised mercury vapour on the walls of silica vacuum tubes.** M. C. JOHNSON (Proc. Physical Soc., 1930, 42, 490—500).—In a severely outgassed tube of mercury and hydrogen, the initial pressure fall due to adsorption of the products of dissociation reaches a limit when a unimolecular layer having a quarter the surface density previously obtained by electrodeless discharges in glass tubes is completed. After the completion of this saturation, a liberation of gas from the silica begins. This liberation is shown to follow a law independent of the partial pressure of hydrogen, but dependent on that of mercury and on the adsorption of resonance radiation by the latter. This action on the solid surface is contrasted with the more usual experiments in which the final recipient of the energy of photosensitisation is solely gaseous.

W. E. DOWNEY.

**Decomposition and formation of hydrocarbons in discharge tubes by means of canal rays.** O. EISENHUT and R. CONRAD (Z. Elektrochem., 1930, 36, 654—662).—Experiments with methane, ethane, ethylene, and acetylene demonstrate that under the influence of canal rays in a discharge tube not only are all possible breakdown products formed, but simultaneously hydrocarbons which do not normally exist in the free state are capable of formation by recombination processes.

H. F. GILLBE.

**Photochemical formation of peroxide in ether.** C. BONZ (Süddeut. Apoth.-Ztg., 1930, 70, 128—129; Chem. Zentr., 1930, i, 2449).—The reaction is independent of the presence of atmospheric oxygen.

A. A. ELDRIDGE.

**Photo-oxidation of chloroform in tropical sunlight.** K. P. CHATTERJI and N. R. DHAR (Z. anorg. Chem., 1930, 191, 155—160).—Chloroform in an enclosed glass vessel exposed to tropical sunlight is oxidised to the extent of 2% in 2—3 hrs., the primary products being hydrogen chloride and carbonyl chloride, but the latter undergoes rapid thermal decomposition, carbon monoxide and chlorine being produced; the chlorine in turn reacts with chloroform and water to form hydrogen chloride, which is therefore the major product of the decomposition.

H. F. GILLBE.

**Effects of substituents on quantum efficiency in the quinone-alcohol reaction.** P. A. LEIGHTON and W. F. DRESLA (J. Amer. Chem. Soc., 1930, 52, 3556—3562).—In a continuation of previous work (Leighton and Forbes, this vol., 174) the effect of substituents on the photochemical decomposition of quinones has been investigated with monochromatic light of various wave-lengths between 2700 and 5770 Å. For each quinone the quantum efficiency ( $\gamma$ ) of the reaction increases with decreasing wave-length until a threshold region is reached beyond which  $\gamma$  is independent of wave-length, and in general,

substituents (chlorine or alkyl groups) which increase the oxidation potential of the quinone shift the threshold towards the red and *vice versa*. This effect is ascribed to changes produced by substitution on the energy of activation. As the mol. wt. is increased  $\gamma$  decreases, irrespective of the chemical nature of the substituents, and this is attributed to a "steric hindrance" affecting the probability of reaction of the activated molecule. J. G. A. GRIFFITHS.

**Photochemical and induced oxidation of glycerol by air.** C. C. PALIT and N. R. DHAR (Z. anorg. Chem., 1930, **191**, 150—154).—Under the action of light glycerol is oxidised by air primarily to carbon dioxide and not to an intermediate product, even in presence of an inductor. The influence of the three inductors investigated decreases in the order ferrous hydroxide, cerium hydroxide, sodium sulphite, and in each case the acidity of the solution increases during the reaction. H. F. GILLBE.

**Accuracy of the bubble-counting method for experiments on photosynthesis.** F. GÓRSKI (Bull. Acad. Polonaise, 1930, **B**, 1—37).—Precise eudiometric and analytical measurements have been made of the production of oxygen from the leaves and cut surface of stems of *Elodea canadensis* under water (partly saturated) at 20°, during assimilation under the influence of light. 40—80% of the oxygen appears as bubbles ( $V$  mm.<sup>3</sup> per hour) and the rest dissolves (total oxygen:  $O$  mm.<sup>3</sup> per hour). A linear relation exists between  $V$  and  $O/V$ ;  $O/V$  decreases with increased assimilation and increases with the size of the plant, and is very susceptible to the conditions of experiment; the average value found was 1.7. Results obtained by merely counting the number of bubbles are inaccurate and only relative. J. LEWKOWITSCH.

**Alkali pentaborates.** A. P. ROLLET and L. ANDRÉS (Compt. rend., 1930, **191**, 567—569).—The pentaborates of potassium, rubidium, and caesium,  $5B_2O_3 \cdot M_2O \cdot 8H_2O$ , form isomorphous (orthorhombic) crystals, the solubility in 100 g. of water at 18° being 3.66, 3.35, and 3.00 g., respectively. Dehydration occurs at 107—250° (in a current of nitrogen), but neither the dehydration curves between these temperatures nor the solubility curve (for  $5B_2O_3 \cdot Cs_2O$  between -0.36° and 101.6°) give a trustworthy indication of the existence of pentaborates containing  $2H_2O$  (cf. Rosenheim and Leyser, A., 1922, ii, 50). J. GRANT.

**Alkali fluoaluminates.** R. H. CARTER.—See B., 1930, 945.

**Products obtained by reducing action of metals on salts in liquid ammonia solution. III. Action of sodium on silver iodide and silver chloride.** W. M. BURGESS and E. H. SMOKER (J. Amer. Chem. Soc., 1930, **52**, 3573—3575; cf. A., 1929, 1154).—The reaction occurs in accordance with the equation  $Na + AgX = NaX + Ag$  (where  $X = I$  or  $Cl$ ), the end-point being sharply defined by the disappearance of the blue colour. J. G. A. GRIFFITHS.

**Hydrated sulphates containing three metals.** B. GOSSNER and T. BAUERLEIN (Ber., 1930, **63**, [B], 2151—2155).—The formula  $2KH_5(SO_4)_3 \cdot 3(FeAl)(OH)_3 \cdot 4FeSO_4 \cdot 4H_2O$  has been pro-

posed for voltaite, based on the ratios  $SO_3 : FeO : K_2O = 10 : 4 : 1$  and  $SO_3 : Fe_2O_3 = 10 : 1.5$ . Twelve analogously constituted sulphates have been prepared in which ferrous oxide is replaced by manganous, cobaltous, magnesium, zinc, or cadmium oxide and potassium oxide by ammonium, rubidium, and thallous oxides. The component  $Fe_2O_3$  remains unchanged. A portion of this (at most one third) is replaced by aluminium oxide. Only in one case has it been found possible to prepare a compound without alumina. The crystals are most readily prepared by heating suitable solutions of sulphates at 80°, avoiding evaporation as far as possible; the process may require days or weeks. The constitution of the "voltaites" is discussed. H. WREN.

**Silver borate.** A. P. ROLLET (Compt. rend., 1930, **191**, 488—490).—The precipitates obtained by the action of silver nitrate on concentrated solutions containing varying proportions of boric acid and sodium borate ( $2-17.1 B_2O_3 : 1Na_2O$ ) were filtered, washed with a little ice-water, dried in a vacuum over sulphuric acid in the dark, and analysed. The results indicate the production of the compound  $2B_2O_3 \cdot Ag_2O$  when the ratio  $B_2O_3 : Na_2O$  in the reactants exceeds 5. The diborate is white, slightly soluble in water, and fairly soluble in the presence of boric acid. It contains 2 mols. of water, which is evolved at 105—240°. J. GRANT.

**Formation of bleaching powder.** B. NEUMANN and C. KRÖGER (Z. anorg. Chem., 1930, **192**, 179—186).—The mechanism of the chlorination of calcium hydroxide (this vol., 176) is described; the small quantity of water necessary for the process serves first to bring about the formation of intermediate compounds and then to aid the diffusion of the chlorine through these substances. The actual chlorination takes place at the interface between the calcium hydroxide and the intermediate compounds. If less than 4% of water be present the reaction velocity diminishes rapidly. (Cf. A., 1925, ii, 488; B., 1926, 190.) H. F. GILLBE.

**Calcium aluminonitrate.** J. FORET (Compt. rend., 1930, **191**, 52—54).—By addition of a solution of calcium nitrate to one of calcium aluminate containing an excess of calcium hydroxide, the double salt  $3CaO \cdot Al_2O_3 \cdot Ca(NO_3)_2 \cdot 16H_2O$  separates as a white crystalline precipitate. The double salt is decomposed by water, and three distinct systems exist, according to the proportions of the components present; the solid phases in the three cases are: calcium hydroxide, tetracalcium aluminate, and double salt; tri- and tetra-calcium aluminates, and double salt; and aluminium hydroxide, tricalcium aluminate, and double salt. H. F. GILLBE.

**Reactions between zinc oxide and calcium chloride in presence of carbon dioxide.** L. CAMBI, G. BOZZA, and F. LA ROSA (Giorn. Chim. Ind. Appl., 1930, **12**, 387—394).—Höpfner's process for the conversion of zinc oxide into the chloride based on the reaction  $ZnO + CaCl_2 + CO_2 = ZnCl_2 + CaCO_3$  has been studied. The yield of zinc chloride is dependent on the temperature, the pressure of carbon dioxide, and the initial concentration of calcium chloride.



An increase in the last two factors increases the yield, which is reduced by rise in temperature. The maximum yield of zinc chloride under the most favourable conditions was equivalent to 27% of the initial amount of calcium chloride, so that the process does not appear to be practicable for the extraction of zinc from minerals. The intermediate formation of hydrogen carbonates is probable, *e.g.*,  $\text{ZnO} + \text{CO}_2 + n\text{H}_2\text{O} = \text{ZnCO}_3 \cdot n\text{H}_2\text{O}$ ;  $\text{ZnCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{HCO}_3)_2$ , the final complete equilibrium depending on the latter reaction together with the following separate equilibria:  $\text{Zn}(\text{HCO}_3)_2 + \text{CaCl}_2 \rightleftharpoons \text{ZnCl}_2 + \text{Ca}(\text{HCO}_3)_2$  and  $\text{Ca}(\text{HCO}_3)_2 \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ .

O. J. WALKER.

**Reaction of calcium cyanamide with carbon dioxide at high temperatures.** H. H. FRANCK and B. MEPPEN.—See B., 1930, 945.

**Reduction of metallic salts in solution by aluminium.** C. BOULANGER (Compt. rend., 1930, 191, 56—57).—If aluminium be employed in alkaline solution to reduce such metals as vanadium, molybdenum, manganese, and chromium from a high to a lower state of oxidation, the product adheres firmly to the aluminium surface. It is immaterial whether the sodium, potassium, or lithium salt be employed, but ammonium salts arrest the reduction. The majority of added salts are without influence, but some, which produce insoluble aluminium salts, *e.g.*, phosphates, cause irregular deposits to be formed, whilst others, such as tartrates and malates, cause partial dissolution of the metal; in all cases, however, the oxide film remains firmly adherent. Impurities in the aluminium are in general without influence, although some, such as magnesium, definitely facilitate the reduction. Reduction by zinc and certain of its alloys resembles that by aluminium.

H. F. GILLBE.

**[Separation of crystalline hydroxides of aluminium and chromium from solutions of their salts at high temperatures and under high pressures.]** V. IPATIEV (Ber., 1930, 63, [B], 2365).—The crystalline precipitate,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  (cf. A., 1927, 1043), has the lattice of böhmite.

H. WREN.

**Double sulphates of metals of the rare earths and of the alkali metals. XIII. Sulphates of praseodymium and ammonium.** F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1930, [vi], 11, 774—779; cf. A., 1929, 510).—The compounds  $\text{Pr}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  and  $\text{Pr}_2(\text{SO}_4)_3 \cdot 5(\text{NH}_4)_2\text{SO}_4$  are stable in contact with solutions of suitable composition at 25°. The crystalline and optical characteristics of these compounds are described.

F. G. TRYHORN.

**Products of the reactions between various types of carbon and fluorine. I. Carbon tetrafluoride.** O. RUFF and R. KEIM (Z. anorg. Chem., 1930, 192, 249—256).—Wood charcoal, freed from adsorbed gases, reacts spontaneously with fluorine at the ordinary temperature with the formation of a variety of carbon fluorides, from which carbon tetrafluoride may be isolated by fractional distillation at 100—200 mm. pressure. The tetrafluoride has m. p.  $-186^\circ$ , b. p.  $-130^\circ$ , and the density of the liquid

at  $-180^\circ$  is 1.96; the vapour pressure  $p$  from  $-180^\circ$  to the b. p. is expressed by  $\log p = 7.3067 - 632.31/T$ , where  $T$  is the absolute temperature. The chemical behaviour of the substance is described.

H. F. GILLBE.

**Formation of carbamide in the system carbon dioxide-ammonia, and its relationship to that in the system carbon oxysulphide-ammonia.** A. KLEMENC (Z. anorg. Chem., 1930, 191, 246—282).—The reaction  $\text{COS} + 2\text{NH}_3 = \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{S}$  affords a more suitable method for the manufacture of carbamide than the older process using ammonia and carbon dioxide; the theoretical yield is more than twice as high, the reaction velocity is much greater, and the product is of a high degree of purity, whilst the sulphur evolved as hydrogen sulphide may be recovered for further use. The free energy changes of the reactions involved have been calculated, and considerable experimental data obtained relative to the process and to the associated reaction  $\text{CO} + \text{S} = \text{COS}$ .

H. F. GILLBE.

**Carbon monosulphide.** A. KLEMENC [with E. HAYEK] (Z. Elektrochem., 1930, 36, 722—726).—Carbon disulphide vapour when subjected to the silent electric discharge becomes activated, but no other compound is formed. On freezing out the mixture of ordinary and active molecules on a glass surface with the aid of liquid air and then allowing the temperature to rise somewhat, the glass catalytically and explosively decomposes the active molecules, and carbon monosulphide and sulphur are formed. The content of sulphur in the deposit on the surface is, however, less than that required for either carbon di- or mono-sulphide, and it is therefore suggested that during the decomposition of the activated molecules active sulphur atoms are produced and combine with the excess of carbon disulphide, and are removed as carbon trisulphide during the distillation of the excess of disulphide. The decomposition process may involve also the reaction  $2\text{CS}_2 \rightarrow 2\text{C} + \text{S}_4$ .

H. F. GILLBE.

**Germanium. XXXV. Germanium monoxide. Germanium monosulphide.** L. M. DENNIS and R. E. HULSE (J. Amer. Chem. Soc., 1930, 52, 3553—3556; cf. Winkler, A., 1886, 985).—Germanium dioxide in 5*N*-potassium hydroxide is made 5*N* with respect to hydrochloric acid and is then reduced at 95° with hypophosphorous acid in an atmosphere of hydrogen. Subsequently ammonia is used to precipitate acid-soluble hydrated germanium monoxide, which in nitrogen at 650° is completely dehydrated to jet-black crystalline germanium monoxide (sublimes at 710°). The oxide is only slightly attacked by acids, fixed alkali hydroxides, and certain oxidising agents at the ordinary temperature. In dry air at 550°, oxidation begins, and in hydrogen chloride at 175° germanium chloroform and water are produced.

Amorphous germanium monosulphide ( $d_4^{20}$  3.31) is prepared by the action of hydrogen sulphide on aqueous germanous chloride. The sulphide is soluble in hydrochloric acid, alkali hydroxides and sulphides, and is rapidly attacked by oxidising agents. Slow oxidation occurs in air at 350°, and in nitrogen

at 450° the sulphide reverts to the form (sublimes 430°, m. p. 625°) described by Dennis and Joseph (A., 1928, 33).

J. G. A. GRIFFITHS.

**Metallic precipitation of zirconium.** H. S. GABLE (J. Amer. Chem. Soc., 1930, 52, 3741).—Zirconium metal is deposited on zinc when the latter is placed in a methyl-alcoholic solution of zirconium sulphate. If magnesium is substituted for zinc, a white substance, and not zirconium, is precipitated.

J. G. A. GRIFFITHS.

**Chemical and crystalline structure of some complex nitrites.** A. FERRARI and C. COLLA (Atti R. Accad. Lincei, 1930, [vi], 11, 755–760).—Potassium nitrite solution precipitates from mixed solutions of lead and copper acetates the compound  $K_2PbCu(NO_2)_6$  as a black crystalline powder, and from the mixed acetate solutions of nickel and lead the yellowish-brown compound  $K_2PbNi(NO_2)_6$ . The corresponding compound  $K_2PbCo(NO_2)_6$  is obtained as a dark brown precipitate by the addition of potassium nitrite to a mixed solution of lead and cobalt nitrates. X-Ray analysis indicates that these compounds are monometric and contain 4 mols. in the unit cell. The cell constants for the nickel, cobalt, and copper compounds are respectively 10.55, 10.49, and 10.52 Å., corresponding with the respective densities 3.50, 3.66, and 3.56. Potassium cobaltinitrite has a cubic lattice similar to the above compounds, with  $a$  10.32 Å. and  $d_{calc}$ , 2.73. The close analogies among these four compounds suggest that the 3 mols. of water associated with potassium cobaltinitrite are zeolitic in nature and entangled in the crystal lattice rather than bound in any sense to the principal molecule. Reasons are given for the assumption that these compounds contain ions of the type  $M(NO_2)_6^{4-}$ , where  $M$  is respectively Cu, Co, or Ni.

F. G. TRYHORN.

**Modes of reaction of phosphorus pentachloride.** C. HARNIST (Ber., 1930, 63, [B], 2307).—A historical comment on the communication of Bergmann and Bondi (this vol., 1030).

H. WREN.

**Reaction between iodic acid (alkali iodates) and hypophosphorous and phosphorous acids and their salts.** I. V. HOVORKA (Coll. Czech. Chem. Comm., 1930, 2, 559–570).—In the reaction between an acidified solution of a hypophosphite and potassium iodide the greater part of the former is oxidised in the first 15 min. and the remainder very slowly. Increasing the acidity accelerates the reaction. The oxidation of phosphites and of phosphorous acid proceeds more slowly.

C. W. GIBBY.

**Pyroarsenates.** A. ROSENHEIM (Z. anorg. Chem., 1930, 193, 73–75; cf. this vol., 558).—The formation of barium copper pyroarsenate at 180–200° in solutions containing 5–25% of arsenic acid has been studied; in all cases the complex is formed quantitatively and is of constant composition. In solutions containing lower concentrations of arsenic acid the precipitate consists mainly of copper orthoarsenate and barium arsenate, and traces only of the complex salt, and the same occurs if the more concentrated solutions are heated merely under a reflex condenser for long periods. By heating orthophosphoric acid with

copper carbonate, barium hydroxide, and water at 180–200°, the salt  $Ba[Cu(PO_4)_2]$  is formed, although not quantitatively, as deep blue crystals. The existence of Goguel's cadmium pyroarsenate,  $Cd_2As_2O_7$ , has now been established, but the lead, copper, and nickel salts could not be obtained.

H. F. GILLBE.

**Chloroantimonates.** L. I. SAUCIUO (Bul. Soc. Chim. România, 1930, 12, 36–43).—Sodium chloroantimonate,  $Na[SbCl_6] \cdot 3H_2O$ , was prepared by the action of chlorine on a cold solution containing the compound  $Na[SbCl_6] \cdot 3H_2O \cdot NaCl$ , antimony chloride, and hydrochloric acid. At high dilution the aqueous solution of this compound gives an intense violet coloration with aniline. The compounds  $Na[SbCl_6] \cdot C_5H_5N$ , and  $Na[SbCl_6] \cdot 3$  and  $5C_5H_5N$ ,  $[XCl(H_2O)_5][SbCl_6] \cdot 3H_2O$ , where  $X = Ca$  or  $Sr$ , and  $[CaCl_2 \cdot H_2N][SbCl_6] \cdot 3[SbCl_6] \cdot [ZnCl(H_2O)_2HCl][SbCl_6] \cdot H_2O$ ,  $2Cu[SbCl_6] \cdot 3H_2O$ ,  $[SbCl_6] \cdot H_2O$ , and  $3\{[Cu(H_2O)_4]2EtOH\}[SbCl_6] \cdot 13CuCl_2 \cdot 2H_2O$  are described.

E. S. HEDGES.

**Multimolecular antimony bromide compounds.** A. C. VOURNAZOS (Z. anorg. Chem., 1930, 192, 369–382).—By the action of an acetone solution of antimony tribromide on metallic bromides complex bromides of the following metals have been obtained in crystalline form: potassium,  $K_2Sb_3Br_{11}$ ; sodium,  $Na_2Sb_3Br_{11}$ ; lithium,  $Li_2Sb_3Br_{11}$ ; ammonium,  $(NH_4)_2SbBr_5 \cdot 2H_2O$ ; barium,  $BaSb_3Br_{11} \cdot 2H_2O$ , and cadmium,  $CdSb_3Br_{11}$ . By the action of hydrochloric acid on the potassium salt, or by the action of hydrobromic acid on an acetone solution of antimony bromide, an acid,  $H_2Sb_3Br_{11}$ , crystallising in yellow needles, has been obtained. By employing other metallic salts in place of the bromides, compounds of the following composition have been prepared:  $K_2Sb_3Br_9I_2$ ,  $K_2Sb_3Br_7F_2$ ,  $SrSb_3Br_9Cl_2 \cdot 6H_2O$ ,  $K_2Sb_3Br_9(SCN)_2$ ,  $K_2Sb_3Br_9(NO_3)_2$ , and  $NaSb_3Br_9N_3$ .

M. S. BURR.

**Gas reactions of atomic oxygen.** P. HARTECK and U. KOPSCH (Z. Elektrochem., 1930, 36, 714–716).—The reactions between oxygen containing about 20% of atomic oxygen and various other gases have been studied. No appreciable reaction takes place with hydrogen or water, on account of the small heat tones of the reactions  $H_2 + O \rightarrow HO + H$ , and  $H_2O + O \rightarrow 2OH$ , whilst carbon monoxide reacts to the extent of only about 5%. The hydrogen halides with the exception of hydrogen fluoride react with the formation of halogen and water, but the extent of the reaction is not proportional to the heat tone. Carbon disulphide and hydrogen sulphide are completely decomposed with emission of continuous radiation from the bluish-green to the near ultra-violet, a variety of products being formed. Chlorine is readily replaced by oxygen in molecules such as those of chloroform and mono- and di-chloromethanes; among the reaction products are carbonyl chloride, hydrogen chloride, water, and carbon monoxide and dioxide. Carbon tetrachloride yields carbonyl chloride and chlorine in equal quantities. Ammonia is decomposed with formation of an explosive substance of the possible composition  $HNO$ . Organic compounds in general react readily, especially if the

carbon content is high (cf. A., 1929, 1264). At very low temperatures ozone may be isolated from the gas, although it does not exist therein at the ordinary temperature.

H. F. GILLBE.

**Sulphur chlorides.** T. M. LOWRY (Z. Elektrochem., 1930, 36, 733—734).—A summary (cf. A., 1927, 505; 1929, 978; this vol., 666, 842).

H. F. GILLBE.

**Preparation of pure chromic anhydride.** V. V. POLYANSKI.—See B., 1930, 903.

**Behaviour of molybdenum pentachloride in organic solvents.** W. WARDLAW and H. W. WEBB (J.C.S., 1930, 2100—2106).—Molybdenum pentachloride reacts vigorously with dry methyl, ethyl, and benzyl alcohols, molybdenyl trichloride being formed, but there is no reaction with phenols. With dry ether the pentachloride forms a black hygroscopic complex,  $\text{MoCl}_5 \cdot 2\text{Et}_2\text{O}$ , which is decomposed by alcohol and yields ethyl chloride when heated at  $80^\circ$ . If moist ether be employed, a green oil, crystallising to green needles of the probable composition  $\text{MoOCl}_3 \cdot 2\text{Et}_2\text{O}$ , is formed; this substance is unstable and has not been prepared in a pure state. On saturation of the oil with hydrogen chloride a second compound, crystallising in green plates and of the approximate composition  $\text{MoOCl}_3 \cdot \text{Et}_2\text{O}$ , is produced. By a similar procedure the compound  $[\text{MoOCl}_5] \cdot 2\text{C}_5\text{H}_5\text{N}$  has been isolated. The reaction between pyridine and molybdenum pentachloride in a sealed vessel for 10 days yields pyridinium chloride and  $\text{MoCl}_4 \cdot 3\text{C}_5\text{H}_5\text{N}$ , a brown amorphous powder which is slowly decomposed by heating with water, dilute acids, or ammonia; the compound  $\text{MoCl}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$  may be isolated with difficulty from the mother-liquor. By boiling the tripyridinate with pyridine until dissolution is complete, and concentrating the solution over sulphuric acid,  $\text{MoCl}_4 \cdot 5\text{C}_5\text{H}_5\text{N}$  is formed; this substance readily loses pyridine in the air, and when kept over sulphuric acid in a vacuum gradually approaches the tripyridinate in composition, but the change is incomplete even after 3 months. The valency of the molybdenum in these compounds is 4, and the co-valency 7 or 8. The mechanism of their production probably involves the formation of an intermediate compound,  $\text{C}_5\text{H}_5\text{N}(\text{Cl}) \cdot \text{MoCl}_4$ , which decomposes into molybdenum tetrachloride and an additive compound of pyridine and chlorine; direct chlorination of pyridine probably does not occur.

H. F. GILLBE.

**Preparation of telluric acid.** J. MEYER and W. FRANKE (Z. anorg. Chem., 1930, 193, 191—192).—To 24 g. of barium chlorate dissolved in 100 c.c. of water a warm solution of 7.2 c.c. of sulphuric acid in 40 c.c. of water is added and after 5 hrs. the clear solution is removed. Finely-powdered tellurium (12.75 g.) is moistened with 5 c.c. of concentrated hydrochloric acid in a 500-c.c. flask, and 25% of the chloric acid solution is added; the liquid soon boils with the heat of the reaction, but should not be cooled. To the clear solution, maintained at the b. p., the remainder of the chloric acid is added in several portions, and after 30 min. the evolution of chlorine ceases. The solution is evaporated to about one third of its volume, and as soon as crystals begin to appear is

cooled to  $0^\circ$ . The mass of telluric acid crystals which separates is filtered through glass, washed with alcohol and ether, and dried in a vacuum. A further yield may be obtained by addition of alcohol to the mother-liquor. The yield is 90—95% of the theoretical.

H. F. GILLBE.

**iso- and Hetero-polyacids. XX. Paratungstates. [With J. E. KOCH and N. SIAO.] XXI. Heteropolytungstates.** A. ROSENHEIM and A. WOLFF (Z. anorg. Chem., 1930, 193, 47—63, 64—72).—XX. Boiling solutions of sodium paratungstate give a sharp end-point when titrated with hydrochloric acid in presence of phenolphthalein as indicator, and the results obtained, combined with determination of the residue on ignition, lead to the formula  $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$ ; the solubility of this salt has been determined from  $0^\circ$  to  $73^\circ$ , and no other hydrate exists within these limits. After heating, the solution shows a marked increase of specific conductivity, and since on isothermal dehydration of the salt at  $30^\circ$  over sulphuric acid 4 mols. of water are retained by the salt, it is suggested that the ordinary salt has the constitution  $\text{Na}_{10}\text{H}_4[\text{H}_4(\text{WO}_4)_6(\text{W}_2\text{O}_7)_3] \cdot 24\text{H}_2\text{O}$ , and that by heating in solution the binuclear anion decomposes into two completely hydrolysed single nuclear anions of the constitution  $[\text{H}_2(\text{WO}_4)_6]^\pm$ . This view is confirmed by the dehydration of zinc paratungstate, which when prepared by precipitation from a boiling solution of the sodium salt and dehydrated at  $100$ — $110^\circ$  retains 7 mols. of water; the salt thus has the formula  $\text{Zn}_5\text{H}_{10}[\text{H}_2(\text{WO}_4)_6]_2 \cdot 28\text{H}_2\text{O}$ . The barium and strontium salts when prepared in the same manner retain 7 and 4 mols. of water, respectively. The transition temperature of  $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 11\text{H}_2\text{O}$  to the heptahydrate, determined both dilatometrically and from solubility measurements from  $17^\circ$  to  $70^\circ$ , is  $50^\circ$ ; the heptahydrate is probably actually  $(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{WO}_4)_6]$ . Potentiometric titration of para- and meta-tungstate solutions with hydrochloric acid and with sodium hydroxide show that only tungstate and meta- and para-tungstate anions exist in the solution; the meta-ions are more stable than the para-, and their formation is a slow, complex reaction; they have probably the constitution  $[\text{H}_2(\text{W}_2\text{O}_7)_6]^\pm$ .

XXI. By addition of small quantities of arsenious oxide to a boiling sodium paratungstate solution until tungstic acid is no longer precipitated on acidification with hydrochloric acid, and concentration, a syrup is obtained which on treatment with potassium chloride yields gradually on cooling needle-shaped crystals of a very soluble salt,  $7\text{K}_2\text{O} \cdot \text{As}_2\text{O}_3 \cdot 18\text{WO}_3 \cdot 24\text{H}_2\text{O}$ ; if ammonium or guanidine chloride be employed, the salts  $3 \cdot 5(\text{NH}_4)_2\text{O} \cdot \text{As}_2\text{O}_3 \cdot 18\text{WO}_3 \cdot 45\text{H}_2\text{O}$  and  $5(\text{CH}_6\text{N}_3)_2\text{O} \cdot \text{As}_2\text{O}_3 \cdot 18\text{WO}_3 \cdot 41\text{H}_2\text{O}$  are formed, the latter as microscopic crystals, relatively sparingly soluble in water. By addition of antimony trioxide in the proportions  $1\text{Sb}_2\text{O}_3 : 9\text{WO}_3$  to a boiling sodium paratungstate solution and treatment with ammonium, potassium, or guanidine chloride, the colourless salts  $6(\text{NH}_4)_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 18\text{WO}_3 \cdot 38\text{H}_2\text{O}$ ,  $8\text{K}_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 19\text{WO}_3 \cdot 37\text{H}_2\text{O}$ , and  $6(\text{CH}_6\text{N}_3)_2\text{O} \cdot \text{Sb}_2\text{O}_3 \cdot 18\text{WO}_3 \cdot 31\text{H}_2\text{O}$  are obtained; the potassium and ammonium salts form very soluble

rhombic crystals, and the guanidine salt microscopic plates. If the sodium tungstate solution is saturated with antimony trioxide, deep yellow crystals are obtained of  $2.5(\text{NH}_4)_2\text{O} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 12\text{H}_2\text{O}$ ,  $3\text{K}_2\text{O} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , and  $2.5(\text{CH}_3\text{N}_3)_2\text{O} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 6\text{H}_2\text{O}$ , and of the barium salt,  $2.5\text{BaO} \cdot 2\text{Sb}_2\text{O}_3 \cdot 10\text{WO}_3 \cdot 18\text{H}_2\text{O}$ . By treatment of a boiling solution of normal sodium tungstate (6 mols.) with phosphorous acid (1 mol.) and hydrochloric acid (9–10 mols.) tungstic acid is precipitated, but redissolves on boiling the solution, and on cooling, yellowish-white crystals of  $4\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_3 \cdot 12\text{WO}_3 \cdot 33\text{H}_2\text{O}$  separate. By employment of potassium and ammonium tungstate solutions,  $4\text{K}_2\text{O} \cdot \text{P}_2\text{O}_3 \cdot 12\text{WO}_3 \cdot 34\text{H}_2\text{O}$  and  $2(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_3 \cdot 12\text{WO}_3 \cdot 33\text{H}_2\text{O}$  are obtained; the latter is sparingly soluble in water. All these complex salts react as metatungstates, and not as paratungstates. H. F. GILLBE.

**Iodine heptafluoride.** O. RUFF and R. KEIM (Z. anorg. Chem., 1930, **193**, 176–186).—An 83% yield of iodine heptafluoride may be obtained by heating a mixture of iodine pentachloride vapour and fluorine at 270–300°, condensing first the unchanged pentafluoride and then, at –100°, the heptafluoride; the reaction is reversible. The new compound forms a colourless mobile liquid, or white crystals of m. p. 5–6°, and its vapour pressure is expressed by  $\log p = 8.6604 - 1602.6/T$ , where  $T$  is the absolute temperature;  $p = 760$  mm. at 4.5°. The latent heat of evaporation is 7.33 kg.-cal., and Trouton's constant is 26.4; the substance is therefore probably polymerised in the liquid and vapour phases. The liquid has  $d_{20}^{20} = 2.75$ . The vapour is soluble in, and slowly decomposed by, water, and explodes when heated with hydrogen. The majority of organic compounds, including paraffins, benzene, and chlorinated hydrocarbons, cause decomposition with greater or less violence. Most metals are attacked, including chromium, iron, and cobalt, at a red heat; copper, silver, and mercury react but slightly, and platinum is inactive. The chemical properties in general, although more vigorous, resemble those of chlorine trifluoride; two of the fluorine atoms are readily removed. H. F. GILLBE.

**Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. X. Hydrolysis and aggregation products in aqueous ferric salt solutions.** G. JANDER and A. WINKEL (Z. anorg. Chem., 1930, **193**, 1–28).—Pure ferric perchlorate,  $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ , has been prepared by treating ferric chloride with perchloric acid. The rates of diffusion of the ferric ion in perchlorate solutions containing sodium perchlorate at various hydrogen-ion concentrations have been measured with a view to determine the change of aggregation with the  $p_{\text{H}}$  of the solution; they indicate a rapid increase in the aggregation as the  $p_{\text{H}}$  rises from 2 to 4, due probably to the formation of relatively stable molecules containing 10–12  $\text{FeO}(\text{ClO}_4)$  groups. Since the diffusion coefficients through various layers of solution are independent of the time, there must exist a whole series of intermediate products between ferric perchlorate and polymerised ferric hydroxide.

The absorption curves between 2200 and 6000 Å. of solutions of ferric perchlorate containing free perchloric acid and containing sodium hydroxide up to the quantity necessary completely to hydrolyse the ferric salt show that substances which are most highly aggregated possess the flattest absorption curves, and that for such substances the commencement of the absorption is displaced towards the region of longer wave-lengths; at the isoelectric point the absorption curve is flattest and is most displaced towards the red. The discontinuities in the absorption curves indicate that as the  $p_{\text{H}}$  of the solution is increased all possible complexes containing from 1 to 50 iron atoms are capable of existence and no one such substance is of outstanding stability. In any solution of given  $p_{\text{H}}$  the complex having the average mol. wt. is present in by far the greatest quantity. The chemical nature of the complexes is discussed; they consist of basic ferric perchlorates of which the mol. wt. increases with fall of the perchlorate content, and are probably composed of perchlorate groups attached to iron atoms which are linked into chains by alternate oxygen and iron atoms. This type of complex is characteristic only of the basic ferric perchlorates and nitrates, the complex basic chlorides being of a different structure. The velocity of aggregation is very rapid in the acid solutions, but diminishes as the hydroxyl content increases, the strongly hydrolysed compounds requiring several weeks for the establishment of equilibrium. The changes of structure of ferric hydroxide gels on ageing are discussed. H. F. GILLBE.

**Complex ammoniacal cobalt molybdates.** P. R. RAY and S. N. MAULIK (J. Indian Chem. Soc., 1930, **7**, 607–616).—A special method of preparation was employed, with the object of obtaining normal molybdates free from impurities in the form of di- and tri-molybdates, according to which a mixture of the cobalt salt and normal sodium molybdate or molybdic acid in presence of calculated quantities of ammonium salt and ammonia was oxidised by the passage of a vigorous current of air through the solution, followed by recrystallisation from an ammoniacal solution. The compounds prepared were: chloropentammine-, hydroxypentammine-, aquopentammine-, molybdatopentammine-, aquonitrotetrammine-, thiocyanatopentammine-, and nitratopentammine-cobaltic molybdates. J. R. I. HEPBURN.

**Theory of metal hydrate ions.** P. PFEIFFER, T. FLEITMANN, and T. INOUE (Z. anorg. Chem., 1930, **192**, 346–365).—The preparation of series of complex salts, of the typical compositions  $[\text{X}(\text{H}_2\text{O})_6](\text{O} \cdot \text{SO}_3 \cdot \text{R})_2$ ,  $[\text{X} \text{en}(\text{H}_2\text{O})_4](\text{O} \cdot \text{SO}_3 \cdot \text{R})_2$ ,  $[\text{X} \text{en}_2(\text{H}_2\text{O})_2](\text{O} \cdot \text{SO}_3 \cdot \text{R})_2$ ,  $[\text{X} \text{en}_3](\text{O} \cdot \text{SO}_3 \cdot \text{R})_2$ ,  $[\text{X}(\text{NH}_3)_6](\text{O} \cdot \text{SO}_3 \cdot \text{R})_2$ ,  $[\text{X}(\text{NH}_3)_5](\text{O} \cdot \text{SO}_3 \cdot \text{R})_2$ ,  $[\text{XCl}_6](\text{H}_2 \text{en})_2$ ,  $[\text{X}(\text{NH}_3)_4](\text{O} \cdot \text{SO}_3 \cdot \text{R})_2$ , of nickel, copper, zinc, and cadmium with naphthalene-1- and -2-sulphonic, benzenesulphonic, and *p*-toluenesulphonic acids is described. In the complex cation the co-ordination number of the metal atom is 6, and by gradually replacing ammonia or ethylenediamine by water molecules in the complex ion a definite gradation of colour is observed. This behaviour supports

Werner's theory of the hydration of ions, especially of cations. M. S. BURR.

**Supposed cases of co-ordination number 5; nickel thiosulphate ammines.** L. LE BOUCHER (Anal. Fis. Quim., 1930, 28, 895—904).—The complex  $\text{NiS}_2\text{O}_3 \cdot 5\text{NH}_3$ , described by Ephraïm, is not a pure substance. If the precipitate formed on addition of ammonia solution to a concentrated aqueous solution of nickel thiosulphate be maintained in a desiccator containing calcium oxide under an ammonia pressure of about 0.5 atm., equilibrium is established after about 6 days, and a homogeneous violet complex salt of the formula  $\text{NiS}_2\text{O}_3 \cdot 6\text{NH}_3$  and having  $d_4^{25}$  1.588 is obtained. The temperature/log. vapour pressure function is linear from 50° to 114°, and gives for the mol. heat of dissociation of the hexammine —12.1 kg.-cal. The vapour pressure of the hexammine at the ordinary temperature is 2—3 mm.; when kept in a desiccator over sulphuric acid or, more rapidly, when heated at 70° in a current of dry air, it affords a tetrammine,  $\text{NiS}_2\text{O}_3 \cdot 4\text{NH}_3$ , of a blue colour and having  $d_4^{25}$  1.884. An olive-green diammine,  $\text{NiS}_2\text{O}_3 \cdot 2\text{NH}_3$ , is produced by heating either the hex- or tetra-ammine at 95° in a current of dry air, and has  $d_4^{25}$  2.177; when exposed to the air the diammine absorbs 2 or 4 mols. of water, and becomes blue; it dissolves readily in ammonia solution with the evolution of considerable heat. The vapour pressure of the diammine at 105° is less than 1 mm., and by heating to 115° decomposition takes place leaving a residue of nickel sulphide and sulphur. H. F. GILLBE.

**Complex rhodium bromopyridinates.** P. POULENC (Compt. rend., 1930, 191, 54—56).—On addition of 2—3 mols. of pyridine to a solution of 1 mol. of rhodium bromide a brown amorphous precipitate of indefinite composition is slowly formed, but in presence of a sufficient quantity of alcohol there is produced an immediate precipitate of the brown compound  $[\text{Rh}_2(\text{C}_5\text{H}_5\text{N})_2(\text{H}_2\text{O})\text{Br}_6] \cdot 2\text{H}_2\text{O}$ . By increasing the quantity of pyridine to 6 mols. and warming the mixture, the orange compound,  $[\text{Rh}(\text{C}_5\text{H}_5\text{N})_3\text{Br}_3]$ , is formed, whilst with still more pyridine a mixture of the tripyridinate and the brown substance of indefinite composition is formed. The tripyridinate, after recrystallisation from a mixture of chloroform and alcohol, closely resembles the corresponding chlorine compound. Despite its non-ionic character it is decomposed by boiling concentrated hydrobromic acid, and the compound  $2\text{RhBr}_3 \cdot 3\text{C}_5\text{H}_5\text{N} \cdot 3\text{HBr}$  may be obtained by concentration of the solution. By the action of 5 mols. of pyridine on rhodium bromide solution there results the complex  $[\text{RhBr}_2(\text{C}_5\text{H}_5\text{N})_4]\text{Br} \cdot 6\text{H}_2\text{O}$ , which forms orange cubic crystals or golden plates; when heated in solution at 95° it readily loses pyridine and forms the tripyridinate. The analogous chlorine compound is considerably more stable under these conditions. By heating on the water-bath a mixture of 1 mol. of rhodium bromide, 2 mols. of pyridine, and 20 mols. of pyridine hydrobromide, the complex salt  $[\text{Rh}(\text{C}_5\text{H}_5\text{N})_2\text{Br}_4]\text{C}_5\text{H}_5\text{N}$  is deposited. H. F. GILLBE.

**Ternary rhodium compounds.** II. O. E. ZVJAGINSTSEV, E. A. VORONOVA, and S. I. KHORUN-  
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ZHENKOV (Ann. Inst. Platine, 1929, No. 7, 113—117).—Wilm's salt, hexagonal, has the formula  $(\text{NH}_4)_3[\text{RhCl}_5 \cdot \text{NH}_4\text{Cl}]\text{NO}_3$ . CHEMICAL ABSTRACTS.

**Nature of osmium tetroxide.** E. K. FRITZMAN (Ann. Inst. Platine, 1929, No. 7, 138—160).—A review of Tschugaev's work. CHEMICAL ABSTRACTS.

**Quantitative analysis of emission spectra in any percentage without standard curves.** G. SCHEIBE and O. SCHNETTLER (Naturwiss., 1930, 18, 753—754).—By photometric determination of the blackness of the spectral lines of a compound and a knowledge of the percentage relationships of the intensities of these lines to the intensities of known lines in the elements of which the compound is composed, it is possible to determine quantitatively the composition of the compound without reference to standard curves or photographic plates.

W. R. ANGUS.

**Indirect analysis.** O. LIESCHE (Z. anal. Chem., 1930, 81, 273—275).—A discussion of a paper by Fuchs (this vol., 441).

A. R. POWELL.

**Determination of gases in metals.** H. DIERGARTEN.—See B., 1930, 910.

**Standardisation of turbidity values in nephelometric determinations.** J. A. DE LOUREIRO (Biochem. Z., 1930, 224, 337—346).—The turbidity produced, under appropriate conditions, by suspensions of strychnine phosphomolybdate, made with 0.00002 and 0.00001M solutions of potassium dihydrogen phosphate in the instrument recommended by Kleinmann (A., 1926, 1068), is a convenient and satisfactory standard for nephelometry. Curves from which results can be obtained directly can be drawn, and the nephelometry of impure substances, or of substances for which suitable materials for comparison are not available, is greatly simplified. Nomograms can also be constructed. W. MCCARTNEY.

**Determination of hydrogen-ion concentration in presence of neutral salts.** L. WOLF (Z. Elektrochem., 1930, 36, 803—806).—The influence of *N*-sodium and -potassium chloride solutions on the apparent difference between the hydrogen-ion concentration of a phosphate buffer solution when determined potentiometrically with the hydrogen electrode and by means of various indicators has been measured. The difference is practically constant for indicators of the same type, e.g., for thymol-blue and bromothymol-blue, and for cresol-red and bromocresol-red. Investigation of the possibility of a reducing action of the hydrogen on the phosphate solution indicates that this does occur, although only in presence of platinum; it is not caused by dissolved hydrogen. The electro-metric method of  $p_H$  determination should, therefore, not be used as a standard for solutions containing neutral salts. H. F. GILLBE.

**Determination of total sulphur in combustible liquids.** L. BERMEJO.—See B., 1930, 976.

**Volumetric determination of hydrothiocyanic acid with permanganate.** B. REINITZER and H. POLLET (Z. anal. Chem., 1930, 81, 286—308).—In the direct titration of thiocyanate with permanganate a small proportion of the former escapes oxidation and

a small amount of dithionic acid is formed; this subsequently decomposes or is oxidised to more complex sulphur compounds by atmospheric oxygen or manganic oxide. Addition of bromide effects no improvement in the results. Correct figures are obtained by running the thiocyanate solution into a hot (60–70°) solution of permanganate acidified with an equal volume of 1 : 1 sulphuric acid until the colour fades to a pale pink. A. R. POWELL.

**Volumetric determination of hydrothiocyanic acid with permanganate.** K. SCHRÖDER (*Z. anal. Chem.*, 1930, **81**, 308–315; cf. preceding abstract).—Correct results are obtained by titrating at 15–20° in a current of carbon dioxide, removing the manganous salt formed in the titration by boiling with sodium carbonate, and again titrating the acidified filtrate. This suggests that the dithionic acid is a secondary product formed by the atmospheric oxidation of sulphurous acid. A. R. POWELL.

**Determination of ammonia in water.** M. W. E. EVERS.—See B., 1930, 967.

**Determination of silica in presence of silicon in ferrosilicon.** A. STADELER.—See B., 1930, 910.

**Micro-determination of carbon.** M. NICLOUX (*Compt. rend. Soc. Biol.*, 1929, **102**, 693–696; *Chem. Zentr.*, 1930, i, 2455).—The formation of carbon monoxide is avoided by oxidation of the substance, mixed with sodium sulphate, silver sulphate, and sulphuric acid, in two stages, using potassium iodate and then potassium dichromate.

A. A. ELDRIDGE.

**Determination of small quantities of carbon monoxide.** ANON.—See B., 1930, 945.

‡ **[Continuous] determination of carbon dioxide and oxygen in air.** W. F. HAMILTON.—See B., 1930, 930.

**Determination of cyanides by copper sulphate.** M. LORA Y TAMAYO (*Anal. Fis. Quim.*, 1930, **28**, 724–727).—The reaction previously studied (this vol., 444) has been applied to the determination of cyanides by titration with alkaline copper sulphate solutions containing tartrate; the results agree closely with those obtained by Denigès' method. Chlorides, iodides, bromides, and thiocyanates do not interfere, but ferrocyanides mask the end-point.

H. F. GILLBE.

**Bromo-iodometric investigations. I, II.** J. H. VAN DER MEULEN (*Chem. Weekblad*, 1930, **27**, 550–552, 558–560).—I. Whilst the oxidation of carbamide, ammonium salts, and formic acid by means of bromine is not complete in presence of alkali hydroxides, very accurate results are obtained in presence of sodium or potassium hydrogen carbonate or borate. In presence of potassium bromide, concentrated aqueous solutions of bromine may be prepared and kept without loss.

II. Excess of bromine water oxidises iodides rapidly and completely to iodates in presence of a hydrogen carbonate or borate of an alkali metal; the excess of bromine is readily destroyed by hydrogen peroxide, carbamide, formates, or oxalates. The iodate formed is treated in the usual way with potassium iodide in acid solution, and the liberated iodine titrated; the

four agents used to destroy excess of bromine do not reduce free iodine in acid solution, although formates in neutral solution are attacked. S. I. LEVY.

**Systematic qualitative separation and identification of inorganic anions.** F. E. RAURICH (*Anal. Fis. Quim.*, 1930, **28**, 749–770).—A new group of acid radicals, of which the barium salts are soluble but the zinc salts are insoluble, is recognised, and a system for the separation and identification of all the more usual inorganic anions is described and presented in tabular form. H. F. GILLBE.

**Determination of potassium as potassium per-rhenate.** H. TOLLERT (*Naturwiss.*, 1930, **18**, 849).—The solubility of potassium per-rhenate in alcohol at 18° is 0.180 g. per litre. The specific conductivity of a series of alcoholic solutions has been determined at 18°. A table is given showing the specific and molecular conductivities and molecular concentration of the solutions. The degree of dissociation of a saturated solution is 0.56. The determination of potassium as per-rhenate is analogous to the perchlorate method, but considerably less reagent is consumed, since per-rhenic acid does not evaporate. Rhenium can easily be recovered quantitatively by reduction in a stream of hydrogen.

W. R. ANGUS.

**Determination of alkali hydroxides in the presence of alkali carbonates or of ammonia, of iodides in the presence of chlorides and/or bromides and of mercuric salts.** O. SCHEWKET (*Biochem. Z.*, 1930, **224**, 325–327).—A standard solution of potassium iodide, mercuric chloride, and ammonium chloride is titrated with 0.1*N*-sodium hydroxide solution until a permanent yellow colour is produced. Another portion of the standard solution is then titrated with the alkali hydroxide solution (adjusted to contain about 0.5%) until the colour obtained is the same as that of the standard. For the determination of iodides, a 1.5% solution of the material to be investigated is titrated with a standard solution of mercuric and ammonium chlorides until a permanent yellow colour is produced. Mercuric salts in 0.5% solution (containing ammonium chloride) are determined by titration with a solution of potassium iodide made alkaline with sodium hydroxide until a permanent yellow colour of the same intensity as that obtained in an experiment with a known amount of mercuric chloride is produced. W. MCCARTNEY.

**Determination of silver by titration with thiocyanate.** W. HOLWECH (*Tidsskr. Kjemi*, 1930, **10**, 78–80).—The presence of copper affects the end-point of the Volhard titration method, and this metal is frequently present in silver alloys. It is consequently recommended that the thiocyanate solution should be standardised on a solution prepared from silver containing 20% of copper. In the analysis of an alloy, sufficient copper nitrate is added to the solution before titration to give a tint similar to the previous one. The end-point is best attained by titration to a reddish-yellow tint, followed by thorough shaking until the colour becomes constant. Standardised silver nitrate is then added from a micro-burette until the red colour disappears, and the solution is again cautiously titrated with the thiocyanate until the



first observable colour change is reached. The pure silver used in the standardisation is best prepared by Stas' method.

H. F. HARWOOD.

**Determination of silver ion.** F. G. GERMUTH (J. Franklin Inst., 1930, **210**, 345—351).—0.15*N*-Hydrochloric acid is most suitable as precipitant in the determination of silver, adsorption being minimal at this concentration. More dilute acid gives incomplete precipitation, whilst more concentrated acid causes adsorption of chloride ion by the precipitate.

J. R. I. HEPBURN.

**Identification of barytes, quartz, and silicates.** H. WAGNER.—See B., 1930, 903.

**Gravimetric determination of beryllium by means of hydrazine carbonate.** A. JÍLEK and J. KOŤA (Coll. Czech. Chem. Comm., 1930, **2**, 571—583).—A moderate excess of hydrazine carbonate is added to a slightly acid boiling solution of a beryllium salt containing a little ammonium nitrate. After 2 hrs. the precipitate is filtered and washed with boiling water or with a 0.5—1.0% solution of ammonium nitrate made neutral to methyl-red with ammonia. The precipitate is ignited and weighed as oxide. The mean error of 25 determinations was  $\pm 0.08\%$ , and quantities as small as 0.1 mg. may be determined.

C. W. GIBBY.

**Complete analysis of magnesium-aluminium alloys.** S. S. SINGER.—See B., 1930, 912.

**Determination of cadmium and copper in spelter and zinc ores by rapid internal electrolysis.** E. M. COLLIN.—See B., 1930, 951.

**Gravimetric determination of lead as sulphate and as chromate.** Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anal. Chem., 1930, **81**, 275—285).—Precipitation of lead as sulphate yields accurate results only when the solution of lead salt is free from chloride, bromide, ferric salts, and potassium salts. Precipitation of lead chromate by means of ammonium chromate from hot slightly acid solutions yields good results in the presence of moderate amounts of alkali nitrates, chlorides, bromides, or acetates.

A. R. POWELL.

**Analysis of red lead.** G. A. AMPT.—See B., 1930, 917.

**Chemistry and pharmacology of the thallium salt employed in dermatology.** J. M. CLAVERA and J. L. GUARDIOLA (Anal. Fis. Quim., 1930, **28**, 728—741).—The iodide and chloroplatinate methods are the most accurate for the determination of thallium. The thallium compound commonly employed as a depilatory is thallous acetate, which when pure has *m. p.* 126° (*lit.* 110°). The pure substance is extremely deliquescent and soluble in water, but it does not oxidise in the air and is unaltered by light. When administered internally satisfactory action is produced by doses of from 14 to 30 mg. per kg. of body-weight, but doses greater than 30 mg. per kg. may prove fatal.

H. F. GILLBE.

**Micro-determination of copper by means of urobilin.** A. EMMERIE (Chem. Weekblad, 1930, **27**, 552—554).—0.01—0.0001 Mg. of copper may be accurately determined colorimetrically in ammoniacal solution. A method of separating copper from organic

material, which involves electrolysis, is described. Gold and silver, even in large excess, do not interfere. Mercury salts give a similar coloration when present in quantity, but the effect can be suppressed by addition of potassium iodide. If mercury and silver are present together, the opalescence resulting from addition of the iodide is removed by addition of the necessary quantity of sodium thiosulphate, which has little effect on the colour reaction.

S. I. LEVY.

**Detection and determination of copper.** F. EPHRAIM (Ber., 1930, **63**, [B], 1928—1930).—The reagent is prepared by dissolving 1 g. of salicylaldoxime in 5 c.c. of cold alcohol and pouring the solution slowly into 95 c.c. of water at 80°. When the mixture has become clear, it is shaken and filtered. The copper solution is neutralised and then acidified with acetic acid. At a dilution of 1 in 100,000 a copious precipitate forms, whereas opalescence is distinct in presence of 1 part of copper in 1,000,000 parts of water. In the determination of the metal, the solution is treated with sodium hydroxide sufficient to give a slight permanent precipitate which is dissolved in acetic acid. The oxime solution is added in slight excess at the laboratory temperature. The precipitate,  $(C_5H_6O_2N)_2Cu$ , is collected, washed with water until the washings give no trace of colour with ferric chloride, dried at 100—105°, and weighed. The presence of zinc, nickel, cobalt, cadmium, ferric iron, silver, mercuric mercury, and tervalent arsenic is immaterial provided that the solution is acid.

H. WREN.

**Cæsium sulphate as confirmatory reagent in detection of aluminium.** H. YAGODA and H. M. PARTRIDGE (J. Amer. Chem. Soc., 1930, **52**, 3579—3580).—Aluminium at concentrations as low as 0.1 mg. per c.c. is easily detected by the addition of 0.5—1 c.c. of 0.25*M*-cæsium sulphate to 1—5 c.c. of a 3*M*-sulphuric acid solution of the aluminium. A white precipitate of cæsium alum develops within 3 min. Bismuth alone interferes.

J. G. A. GRIFFITHS.

**Indium. I. Detection and determination of indium by the arc spectrum.** J. PAPISH and D. A. HOLT (Z. anorg. Chem., 1930, **192**, 90—96).—The detection and determination of indium by means of the arc spectrum are described. For detection, the lines at 3256.1 and 3039.3 are the most sensitive.

R. CUTHILL.

**Colorimetric determination of small quantities of cobalt and potassium.** A. BLANCHETIÈRE and J. M. PIRLOT (Compt. rend. Soc. Biol., 1929, **101**, 858—860; Chem. Zentr., 1930, i, 2597).—The green colour produced by cobalt salts and hydrogen peroxide in presence of potassium or ammonium hydrogen carbonate is used to detect 0.004 g. of cobalt per litre; chlorine does not interfere. Potassium is precipitated as potassium sodium cobaltinitrite and the cobalt determined. Human blood contains 0.1—0.2% of potassium; the serum contains 0.03—0.05%.

A. A. ELDRIDGE.

**Colorimetric determination of small quantities of cobalt and potassium.** M. DELAVILLE (Compt. rend. Soc. Biol., 1929, **101**, 1082—1083; Chem. Zentr., 1930, i, 2927).—The potassium is precipitated

as cobaltinitrite and the cobalt determined colorimetrically.

A. A. ELDRIDGE.

**Determination of nickel, cobalt, and zinc by rapid electrolysis without mechanical agitation of the electrolyte.** B. TOUGARINOV (Bull. Soc. chim. Belg., 1930, 39, 331—348).—Satisfactory depositions and determinations have been made of nickel from ammonia-ammonium sulphate (or acetate) solutions, cobalt from ammonia-ammonium sulphate, and zinc from sodium hydroxide solutions. Platinum gauze electrodes of the Fischer type were used with high auxiliary electrolyte concentrations, the solutions being heated to boiling. Large currents were unnecessary. For the deposition of zinc the electrode was previously coated with nickel from acetic acid-sodium acetate solution, and a very homogeneous deposit was obtained. Only with cobalt was it necessary to keep the cathode potential constant.

J. LEWKOWITSCH.

**Evaluation of stibnite. II. Determination of antimony.** W. N. McNABB and E. C. WAGNER.—Sec B., 1930, 912.

**Analytical application of catalytic reactions. Identification of palladium in presence of other platinum metals.** F. FEIGL and P. KRUMHOLZ (Ber., 1930, 63, [B], 1917—1919).—For the detection of palladium, 1 c.c. of the faintly acid solution (acidity 0.1—0.5*N*) is boiled with 5 drops of 5% phosphomolybdic acid and treated with a rapid current of carbon monoxide. According to the amount of the metal a blue or green coloration is produced immediately or within a few minutes. The limit of the reaction is 0.025  $\gamma$  of palladium per c.c. Platinum, rhodium, iridium, osmium, and ruthenium do not show the change. Gold, mercury, and ferric salts diminish the sensitiveness of the reaction. Arsenic acid in concentrated solution and arsenious acid cause formation of the colour. Silver, lead, copper, cadmium, antimony, tin, nickel, cobalt, zinc, aluminium, calcium, magnesium, sodium, and potassium do not interfere in concentration less than 0.25—1%. Powerful oxidising or reducing agents may not be present.

H. WREN.

**Separation of elements in unweighable amounts.** O. ERBACHER and K. PHILIPP (Z. physikal. Chem., 1930, 150, 214—218; cf. A., 1929, 371).—Polonium may be separated from radium-*E* and -*D* by the following method. Silver is placed in the solution acidified with hydrochloric acid and, after deposition of the polonium (crude), the whole is dissolved in dilute nitric acid, an excess of hydrochloric acid is added, the solution decanted, the precipitated silver chloride washed with aqua regia, and the washings are added to the former solution, which contains the polonium. Repetition of the deposition on silver and subsequent dissolution four times effects a separation amounting to 1 in  $10^{-6}$ , even when the amounts of material involved are practically unweighable. The course of the separation was followed by measurement of  $\beta$ -particle activity. Similarly, radium-*E* can be separated from radium-*D* by deposition on nickel, which is immersed in the solution. The deposit is dissolved off the metal by means of 25% hydrochloric acid and is again deposited in the

presence of 0.1*N*-hydrochloric acid. Three repetitions of this process suffice to effect a separation in the ratio 1 :  $10^{-6}$ . The process of the adsorption of ions by metals is discussed.

E. S. HEDGES.

**Vacuum apparatus in industrial laboratories.** E. KUSS and G. RITTER (Chem. Fabr., 1930, 341—342, 355—357).—The vacuum apparatus in use at the Oppau research laboratory makes it possible to conduct practically all laboratory operations in a vacuum. Glass apparatus is as far as possible constructed in one piece and greased stopcocks are replaced by mercury valves. A simplified form of this installation is suitable for exact gas analyses, e.g., of hydrocarbon mixtures. A further simplification, which was worked out in connexion with an investigation of motor-car exhaust gases, is suitable for process laboratories. The gases were fractionally condensed and the middle fractions refracted under high vacuum. A similar apparatus is suitable for the determination of vapour densities of salt solutions. It has also been used in the investigation of the mechanism of the decomposition of ammonium ferrocyanide and of ammonia by metallic iron. It was shown that in the former case the supposed carbide  $\text{FeC}_2$  was not formed and that in the second iron nitride was the intermediate compound. A micro-apparatus for organic combustions in a vacuum in which the products of combustion are fractionally condensed by liquid air is also described.

C. IRWIN.

**Absolute amount of radiant heat emitted during gaseous explosions.** D. A. HALL and K. TAWADA (Trans. Faraday Soc., 1930, 26, 600—605).—During the explosion of a mixture of hydrogen and oxygen in a narrow cylindrical bomb 2.83% of the heat of combustion is lost by radiation through a quartz window, whilst 23.94% is lost through a fluorite window during the explosion of a dry mixture of carbon monoxide and oxygen. The high loss in the second case is probably due to chemiluminescence from the flame.

H. F. GILLBE.

**Rapid cooling device.** R. KOHLMANN (Chem. Ztg., 1930, 54, 764).—The liquid is fed through a funnel into the cooler, which consists of a water-jacketed glass spiral tube (4 mm. diam.) about 30 cm. long. The delivery tube is arranged in the form of a siphon in order to empty the cooler. 40 C.c. of wash liquor are sufficient to rinse out the last traces of the liquid; 0.5 litre can be cooled from 80° to 20° in 2.5 min.

E. LEWKOWITSCH.

**Sensitive thermoregulator.** J. WÜST (Biochem. Z., 1930, 224, 415—419).—The immersed portion of the regulator is shaped like a comb and contains chloroform or bromoform, the expansion of which is transmitted to a mercury contact-breaker through a column of water, concentrated salt solution, or ethyl alcohol. The apparatus, which can be adjusted to work between -50° and 140°, is sensitive to changes in temperature of  $\pm 0.01^\circ$ .

W. MCCARTNEY.

**Automatic cryostat.** A. I. SCHATTENSTEIN (Z. anorg. Chem., 1930, 193, 187—190).—A solid carbon dioxide-acetone cryostat is described. The temperature is controlled by a vessel containing solid carbon

dioxide of which the depth of immersion in the bath is regulated by a solenoid actuated by a thermostatically operated relay. Thick copper wire is employed to accelerate heat transference between the carbon dioxide container and the bath. The carbon dioxide consumption is small and the temperature remains constant to within  $0.01^\circ$ . H. F. GILLBE.

**Electrically heated water-bath for extraction apparatus.** A. BEHRE (Chem.-Ztg., 1930, 54, 763—764).—The water-bath, which is designed to eliminate the risk of fire, is suitable for ether extractions. Means for varying the temperature of the bath and for economising current when possible are provided. E. LEWKOWITTSCH.

**Electric-resistor furnace.** F. H. SCHOFIELD (J. Sci. Instr., 1930, 7, 287—289).—The heating element consists of single strips arranged longitudinally round a cylindrical furnace, and joined in parallel by metal rings at the two ends. C. W. GIBBY.

**Vacuum prebaking furnace.** L. R. HAFSTAD and O. DAHL (Rev. Sci. Instr., 1930, [ii], 1, 517—522).—The construction of two furnaces for outgassing metal parts is described in detail. They consist of quartz tubes with water-cooled caps and vacuum connexions inserted into cylindrical electrical heaters. C. W. GIBBY.

**Metallography at low temperatures.** W. ROSENHAIN and A. J. MURPHY (J. Roy. Microscop. Soc., 1930, [iii], 50, 316—318).—A brief account of experimental details already published (A., 1926, 996). C. W. GIBBY.

**Illumination of metallurgical specimens.** C. BECK (J. Roy. Microscop. Soc., 1930, [iii], 50, 319—322).—The various methods of securing vertical illumination are discussed. C. W. GIBBY.

**Physical measurements of short-lived intermediate products.** H. SCHMID (Z. Elektrochem., 1930, 36, 769—771).—The gases or liquids which on reaction produce the unstable substances are projected simultaneously and with a velocity high compared with the life of the intermediate product first on to a baffle which sets up a whirling motion and then through a tube. The mixture may be studied by electrochemical, thermochemical, or optical methods, since owing to the high velocity there is a constant supply of the intermediate product in the mixture flowing through the tube. Application of the method to the potentiometric study of the ferric thiosulphate complex which is the primary product of the reaction between a ferric salt and a thiosulphate in dilute solution shows this substance to be formed according to the equation  $\text{Fe}^{+++} + \text{S}_2\text{O}_3^{--} \rightarrow \text{FeS}_2\text{O}_3$ .

H. F. GILLBE.

**Action of the electron-counting tube of Geiger and Müller.** B. ROSSI (Atti R. Accad. Lincei, 1930, [vi], 11, 831—836; cf. A., 1929, 114, 1123).—Details are given of a modification of the method previously described by the author whereby a photographic record of the passage of electrons is obtained in place of audible signals. F. G. TRYHORN.

**Vacuum grating spectrograph.** F. SIMEON and C. F. SMITH (Rev. Sci. Instr., 1930, [ii], 1, 512—516).—An instrument based on that of Sawyer (A.,

1928, 209), but containing several additional features, is described. C. W. GIBBY.

**Electrical agitator for the laboratory.** M. L. DOMINGUEZ and J. PASCUAL (Anal. Fis. Quím., 1930, 28, 1003—1004).—An electrically driven stirring apparatus for laboratory use is described.

H. F. GILLBE.

**Determination of high temperatures, and application to platinum alloys.** O. FEUSSNER and L. MÜLLER (Heraeus Festschr., 1930, 1—17; Chem. Zentr., 1930, i, 2278).—The method employs a photoelectric cell which is calibrated against metals of known f. p.; it is applied in the range  $1500$ — $2300^\circ$ . The systems platinum-iridium and -rhodium form uninterrupted series of mixed crystals.

A. A. ELDRIDGE.

**Drying of gas streams.** L. L. BIRCHUMSHAW (J.C.S., 1930, 2213—2215).—The gas stream passes through a trap immersed in a mixture of ice and salt, and then through two more surrounded by acetone and solid carbon dioxide. The second and third traps are connected by a long piece of tubing exposed to the ordinary temperature, which has the effect of destroying the ice fog produced in the first trap, thus preventing it from being carried right through the system. C. W. GIBBY.

**Electromagnetic separator for mineral powders.** A. F. HALLEMOND (Min. Mag., 1930, 22, 377—381).—The sand or mineral powder is fed on to a revolving horizontal disc above which are three electromagnets of different strengths. By breaking the current as the disc revolves the attracted particles fall between gaps in the disc. The machine runs automatically and makes a clean separation of such minerals as ilmenite, garnet, monazite, etc. from a mixed sand. L. J. SPENCER.

**Density measurements at high temperatures.** X. Direct hydrometric method, and the density of molten metals, especially iron alloys, at temperatures up to  $1600^\circ$ . E. WIDAWSKI and F. SAUERWALD [with EISENREICH] (Z. anorg. Chem., 1930, 192, 145—160).—An apparatus employing a hydrometer of refractory material for determination of the density of liquids at high temperatures, and if necessary in a vacuum, is described. The mean error at temperatures in the neighbourhood of  $1600^\circ$  does not exceed  $0.4\%$ . For copper-tin alloys containing  $80\%$  of copper,  $dv/dT = 0.125 \times 10^{-4}$ , which is slightly higher than the value obtained by earlier observers. Volume isotherms of molten iron-carbon alloys containing up to  $5\%$  of carbon show the specific volume to be less than that calculated additively from the volumes of the components, thus demonstrating the existence of compounds in the liquid state. Addition of  $1\%$  of silicon to molten iron-carbon alloys increases the specific volume by about  $0.001 \text{ cm}^3 \text{ per g.}$

H. F. GILLBE.

**Spectrophotometric determination, in white light, of concentration of solutions of coloured substances.** E. KEVE (Biochem. Z., 1930, 224, 347—363).—In the spectrophotometric examination in white light of solutions of coloured crystalline substances the only portions of the spectra which

can be correctly used for the calculation of extinction coefficients are those at which the effects of altering the thickness of the layer of liquid examined are negligible.

W. MCCARTNEY.

**Removal of gases from liquids.** R. K. TAYLOR (J. Amer. Chem. Soc., 1930, **52**, 3576—3578; cf. A., 1929, 166).—A fractionating column fitted with special devices is employed for the removal of gases from volatile liquids, and an apparatus for the analysis of the evolved gases is described.

J. G. A. GRIFFITHS.

**Standardisation of a modified Ostwald viscosimeter.** H. M. CHADWELL and B. ASNES (J. Amer. Chem. Soc., 1930, **52**, 3493—3507).—The effect of varying the configuration of the ends of the capillaries from gradual trumpets to square fractures on the time of flow of water through otherwise similar viscosimeters of the Ostwald type, as modified by Washburn and Williams (A., 1913, ii, 557), has been investigated at temperatures between 15° and 30°. The coefficient,  $m$ , of the kinetic correction is negligible and the variation of the configuration of the ends of the capillaries is without effect. Viscosities calculated by the simple Poiseuille formula agree with the data of Bingham and Jackson (A., 1919, ii, 268).

The viscosities at 20° and 25° of 0—41.5% aqueous urethane solutions have been determined. These solutions are suitable for the standardisation of viscosimeters.

J. G. A. GRIFFITHS.

**Ruler for the interconversion of  $E.M.F.$  readings and  $p_H$  values in the electrometric measure-**

**ment of hydrogen-ion concentration.** J. GRANT (J.S.C.I., 1930, **49**, 302T).—A glass cursor, with rulings corresponding with the three calomel electrodes, is set at the  $E.M.F.$  reading on a scale on a rectangular ruler, and the corresponding  $p_H$  value read off at the intersection of the appropriate ruling with one of three oblique scales corresponding with the temperature of the experiment. The ruler may be used for the converse calculation, and provides for the hydrogen or quinhydrone electrode in combination with the 0.1*M*-, 1.0*M*-, or saturated calomel electrode at 18—30°. The error is normally 0.02  $p_H$  unit, but rises in certain cases to 0.06.

**Lecture experiment with liquid oxygen.** H. KEEFER (Physikal. Z., 1930, **31**, 742—743).—If a few c.c. of liquid oxygen are placed in a reaction tube connected to a water pump and the vapour of the oxygen is rapidly pumped off, the surrounding air is so completely cooled that it liquefies on the side of the tube. If the reaction tube, R, is placed inside a wider tube, M, which in turn dips in a Dewar flask containing liquid oxygen, then on pumping it is found that liquid air is deposited on the outer walls of R, whilst liquid oxygen is deposited on the outer walls of M.

W. R. ANGUS.

**Lecture demonstration of lattice planes in two dimensions.** R. W. LAWSON (Nature, 1930, **126**, 468—469).—An adaptation of a demonstration of optical diffraction patterns suitable for picturing lattice planes in X-ray crystallography is described.

L. S. THEOBALD.

## Geochemistry.

**Ozone and atomic oxygen in the upper atmosphere.** S. CHAPMAN (Phil. Mag., 1930, [vii], **10**, 369—383; cf. Mem. Roy. Meteor. Soc., 1930, iii, No. 26, 103).—The various modes of formation and destruction of ozone in the atmosphere are discussed. On the assumption that the production of atomic oxygen is effected chiefly by absorption of ultra-violet light in the band  $\lambda$  1300—1800 Å., and is antecedent to the formation of ozone by three-body collisions involving molecular oxygen, a number of equations are deduced from which the diurnal variation of the amount of ozone and of atomic oxygen at heights greater than 45 km. may be determined. Owing to the lack of precise numerical data the treatment is approximate and the conclusions reached are of a qualitative nature. It is probable that at high levels (about 80 km.) atomic oxygen predominates over molecular oxygen and nitrogen, and that the concentration of ozone decreases rapidly with height.

F. L. USHER.

**Hydrogen-ion concentration of rain and potable water.** M. C. POTTER (Nature, 1930, **126**, 434—435).—The  $p_H$  of rain water obtained in collecting vessels and from various plants varied between 5.5 and 7.6; the  $p_H$  values of the two samples were sometimes identical and sometimes not. The  $p_H$  values of potable water from different parts of England varied between 5.0 and 9.0.

L. S. THEOBALD.

**Structure of the chlorites.** L. PAULING (Proc. Nat. Acad. Sci., 1930, **16**, 578—582).—Oscillation and Laue photographs of penninite and clinocllore, of composition approximately  $Al_2Mg_5Si_3O_{16}(OH)_8$ , show the structure to be monoclinic, 2 mols. in the unit cell,  $a$  5.2—5.3,  $b$  9.2—9.3,  $c$  14.3—14.4;  $\beta$  96° 50'. The lattice is apparently end-centred on (001), space-group  $C_{2h}^2$ . The crystals normal to the cleavage plane consist of alternate layers of mica, of composition varying between  $[Mg_3AlSi_3O_{10}(OH)_2]^-$  and  $[Mg_2AlAl_2Si_2O_{10}(OH)_2]^-$  and brucite,  $[Mg_2Al(OH)_6]^-$  (cf. this vol., 732). This leads to the general formula  $X_mY_4O_{10}(OH)_8$ , where X and Y represent ions with co-ordination numbers 6 and 4, respectively, and  $m$  is  $\leq 4$  and  $\geq 6$ , but is usually 6 and probably never as low as 4, as this would give the composition of kaolinite which has a different structure.  $Y_4$  varies from  $Si_4Al$  (penninite and clinocllore) to  $Si_2Al_2$  (amesite), and  $X_6$  from  $Mg_3Al$  to  $Mg_4Al_2$  with  $Fe^{++}$  and  $Mn^{++}$  sometimes partly replacing  $Mg^{++}$ , and  $Fe^{+3}$  replacing  $Al^{+3}$ . The pseudohexagonal character is explained by the presence of hexagonal layers of tetrahedra and octahedra, whilst the presence of layers not held together by anion-cation contact explains the good cleavage on (001). Calculated and observed intensities accurately agree with this structure.

C. A. SILBERRAD.

**Nuclei containing vanadium, bleached spots, and bleached zones in the clay slates of the**

**Saxony Rotliegendes.** R. SCHREITER (Z. Deut. geol. Ges., 1930, 82, 41—47; Chem. Zentr., 1930, i, 2533).—The nuclei contain 14.93%  $V_2O_4$  and 1.42%  $V_2O_3$ . The formation of bleached spots is attributed to the reducing action of the lower oxide of vanadium. Small quantities of uranium are probably present.

A. A. ELDRIDGE.

**Volcanic rocks of eastern Algarve (Portugal).** P. DE SOUSA (Compt. rend., 1930, 191, 59—61).—Consideration of the nature of the volcanic rocks in the eastern Algarve region leads to the conclusion that the great Swiss upheaval was contemporaneous with the Lusitania-Spain-Morocco subsidence, and hence with the subsidence south of Arrabida and west of Algarve and Alemtejo.

H. F. GILLBE.

**Bianchite.** C. ANDREATTA (Atti R. Accad. Lincei, 1930, [vi], 11, 760—769).—The chemical and optical properties of a new white mineral, found at Raibl, are described. It occurs as minute incrustations on other minerals, and corresponds in composition with the formula  $FeSO_4 \cdot 2ZnSO_4 \cdot 18H_2O$ . Specimens vary somewhat in their water content, and from dehydration experiments evidence is found of the existence of a second hydrate.

$FeSO_4 \cdot 2ZnSO_4 \cdot 2H_2O$ . Over a considerable range dehydration is reversible. Dissolution and recrystallisation of bianchite under the microscope indicate a monoclinic habit for its crystals.

F. G. TRYHORN.

**Tungsten ores of Galicia. III. Wolframites from Juno, Monte Neme, Casayo, A. Veiga, and Vilacoba.** I. PARGA and A. ARANGO (Anal. Fis. Quím., 1930, 28, 905—909).—Further analyses of Galician tungsten ores are given; the tungstic oxide content varies from 74.94 to 75.98, the ferrous oxide from 7.97 to 23.58, and manganous oxide from 0.12 to 15.29%. The so-called tantalum-niobium residue is almost pure niobium pentoxide, free from tantalum, and containing traces only of titanium, tin, and tungsten.

H. F. GILLBE.

**Character and distribution of clays in Poland.** S. MALKOWSKI and M. KOWALSKI (Trans. Ceram. Soc., 1930, 29, 142—145).—The majority of the clays are similar in composition to the kaolins of continental Europe. The results of chemical and mechanical analysis and the m. p. of the clays are tabulated.

R. J. CARLIDGE.

**Identity of crystalline structure of cancrinite of Monte Somma with that of Mias (Urals).** F. ZAMBONINI and A. FERRARI (Atti R. Accad. Lincei, 1930, [vi], 11, 782—788).—An X-ray examination of a crystal of cancrinite from Monte Somma gave the values  $c/a$  0.401,  $a$  12.73 Å.,  $c$  5.10 Å.; identical results were obtained with a specimen from Mias. These results agree satisfactorily with previous goniometric values. The volume of the unit cell is  $715.7 \times 10^{-24}$  c.c. A comparison of the analyses of cancrinite from various sources, taking into consideration this value for the volume of the unit cell, leads to the formula  $3(Na_2, Ca)Al_2Si_2O_8 \cdot (Na_2, Ca)CO_3$  for this mineral. A slight excess of carbonates and a variable amount of water, however, are usually present.

F. G. TRYHORN.

**Miargyrite silver ore from the Randsburg district, California.** E. V. SHANNON (Proc. U.S.

Nat. Mus., 1929, 74, No. 21, 10 pp.).—Miargyrite, monoclinic,  $Ag_2S \cdot Sb_2S_3$ , is described; analytical and crystallographic data are recorded.

CHEMICAL ABSTRACTS.

**Mineralogy and geology of Cerro Mercado, Durango, Mexico.** W. F. FOSHAG (Proc. U.S. Nat. Mus., 1929, 74, No. 23, 7 pp.).

CHEMICAL ABSTRACTS.

**Tholeiitic phase of the quartz-dolerite magma of central Scotland.** F. WALKER (Min. Mag., 1930, 22, 368—376).—The Permo-Carboniferous quartz-dolerites of central Scotland are usually holocrystalline. Two intrusions are now described from Dalmeny in Linlithgowshire and Kinkell in Dumbartonshire in which the rock contains a fresh glassy base together with chlorophacite. Detailed petrographical descriptions with chemical analyses are given of these rocks. The residual glass is of acid composition, this being opposed to the conclusion of Fenner (A., 1929, 1162) on the crystallisation of a basaltic magma.

L. J. SPENCER.

**Moonstone from Ceylon and other areas; stability relations of the alkali-feldspars.** E. SPENCER (Min. Mag., 1930, 22, 291—367).—Fragments of moonstone of gem quality are abundant in a new china-clay pit in rotted pegmatite near Ambalangoda, south-west Ceylon. The schiller of the moonstone is due to a micropertthitic intergrowth with interlamination of soda-feldspar along a plane (13.0.2) in the potash-feldspar. One of several analyses of the moonstone gave:  $SiO_2$  65.42,  $Al_2O_3$  19.45,  $Fe_2O_3$  0.20,  $MgO$  0.12,  $CaO$  0.55,  $Na_2O$  4.61,  $K_2O$  9.80, ign. loss 0.20 = 100.35%,  $d$  2.579. Analyses are also given of schillerised feldspars and of their containing rocks from Kandy in Ceylon, Burma, and Colorado. The density and optical data of these feldspars show a regular variation with the chemical composition. The schiller colour and the micropertthitic structure are destroyed by heating the feldspar to about 1050°, and at the same time the density and optical constants undergo a change. The minute structure of the schillerised feldspar is brought out by heating the material in water and carbon dioxide under pressure; and in some natural specimens the albite lamellæ have been completely removed by selective decomposition. The equilibrium diagram of the potash-soda-feldspars is discussed, and a modification of that of Vogt and Warren is suggested.

L. J. SPENCER.

**Origin of the Württemberg bean-ores.** E. A. EHLMANN (Chem. Erde, 1930, 6, 117—142).—The pisolitic iron ores of the Swabian Alps occur in association with limestones, of which they are the residual products, representing "fossil laterites." Detailed analyses are given of the ores from several localities, and of the portions soluble in acids of various concentrations. They are clayey limonites, and the clay material is not simply kaolin. Analyses are also given of the limestones and of the residue left when they are dissolved in acid. The amounts of iodine in the ores and in the associated limestones give further indication of the origin of the ores. The White Jura limestone is richer in iodine (0.95 mg. per kg.) than the Muschelkalk (0.26 mg. per kg.), and the ores associated with the former are correspondingly richer

in iodine (0.32–0.47 mg. per kg.) than those (0.02–0.11 mg. per kg.) associated with the Muschelkalk.

L. J. SPENCER.

**Mineral constituents of the conglomerates of Diamantina, Minas Geraes, Brazil.** F. W. FREISE (Chem. Erde, 1930, 6, 66–71).—The diamond-bearing conglomerates, probably of Tertiary age, overlying Palaeozoic quartzites, itabirites, and phyllites, consist largely of magnetite (55%), with haematite, ilmenite, quartz (14%), etc., and are cemented by limonite with some silica. Gold occurs as original grains and as secondary cementing films. Other constituents are goethite, pyrite, pyrolusite, senaite ( $\text{TiO}_2$  49.91, FeO 25.44, MnO 11.88, PbO 12.01,  $\text{ZrO}_2$  0.68 = 99.92%), cassiterite, rutile, and chromite ( $\text{Cr}_2\text{O}_3$  37.66,  $\text{Al}_2\text{O}_3$  13.38, FeO 11.88, MnO 1.54, MgO 11.47, CaO 2.91,  $\text{SiO}_2$  20.15,  $\text{H}_2\text{O}$  0.89 = 99.98%). Only three diamonds have been found by the author actually in the conglomerate.

L. J. SPENCER.

**Manganese and iron enrichment in diluvial gravels of the Marchfeld.** (FRL.) G. SCHRECKENTHAL (Chem. Erde, 1930, 6, 51–59).—Certain beds are cemented with manganese oxide and others with iron oxide. These have been deposited from hydrogen carbonate solutions when the ground-water stood at a higher level.

L. J. SPENCER.

**Sorption of potassium in clayey sediments in relation to the formation of potash-mica by metamorphism.** W. NOLL (Chem. Erde, 1930, 6, 1–50).—Kaolin takes up very little potassium from a potassium carbonate solution, but with allophane clays the ratio  $\text{K}_2\text{O} : \text{Al}_2\text{O}_3$  may approach 1 : 3. A sediment which had taken up this amount of potassium would yield muscovite when subjected to metamorphism.

L. J. SPENCER.

**Spanish red-earths.** E. BLANCK and W. DÖRFELDT (Chem. Erde, 1930, 6, 60–65).—A red-earth overlying limestone in Valencia province is described. Bulk analyses and analyses of the acid extract and residue are given for the limestone and for the red-earth.

L. J. SPENCER.

**Organic matter, phosphorus, and vanadium contents of Black Sea deposits.** A. D. ARCHANGELSKI and E. V. KOPTSHEVA (Bull. Acad. Sci. U.S.S.R., 1930, 205–215).—The relationship between the organic matter content and the phosphorus and vanadium contents of the Black Sea deposits is discussed. The amount of phosphorus present varies inversely with the amount of organic matter present, but the relationship between the vanadium content and the organic matter content is much less clear. It is concluded that the origin of the vanadium present in sea-water is terrestrial, and not decaying animal organisms.

A. FREEMAN.

**Radioactivity of Estonian sulphide muds.** A. MICKWITZ (Z. anorg. Chem., 1930, 192, 105–112).—The radioactivity of dried curative mud from Arensburg and Hapsal has been found to be about half that of an equal weight of potassium chloride, and to be reduced by ignition.

R. CUTHILL.

**Red-earth-like soils on limestones in central Germany.** G. MAURMANN (Chem. Erde, 1930, 6, 77–116).—Bulk analyses and analyses of the acid

extracts are given of the Muschelkalk, of red and yellow weathering products in the crevices of the rock, and of the reddish and reddish-brown layer beneath the humus covering. These show a similarity in composition to the red-earth of southern Europe.

L. J. SPENCER.

**Relationship of climatic and geological factors to the composition of soil clay and the distribution of soil types.** E. A. CROWTHER (Proc. Roy. Soc., 1930, B, 107, 1–30).—Existing data for soil groups in the U.S.A. have been re-examined to trace the effects of rainfall, temperature, and geological grouping on soil formation. The ratio  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  in the clay fraction decreases with increase in rainfall, and increases with rise of temperature. The correlation between rainfall and temperature in the agricultural areas of the U.S.A. explains previous failures to demonstrate any influence of the latter. Lysimeter experiments at Rothamsted suggest that the effects of rainfall and temperature on clay formation are due to their influence on drainage through the soil. The ratio of silica to alumina is lowest for clays in sedentary soils from igneous rocks, and highest in young soils from sediments exposed to reworking in water. Weathering in dry regions in the presence of soluble silicates, or in wet regions where the parent material has been exposed to the dissolved silica in river water, leads to the formation of highly siliceous clays.

G. F. MARRIAN.

**Weathering and soil formation in tropical high altitudes.** M. W. SENSTIUS (Proc. Amer. Phil. Soc., 1930, 69, 45–97).—Podsolisation takes place in much the same way as in the lowlands of middle altitudes. The mechanism of the process is discussed.

CHEMICAL ABSTRACTS.

**Brown-earths as a transition stage of tropical red-earths and laterite.** R. ALBERT (Z. Pflanz. Düng., 1930, 18A, 1–5).—Analysis of certain brown Cameroon soils show these closely to resemble the brown earths of Ramann. Evidence is advanced that the transition of these soils to red-earths is merely a matter of time.

A. G. POLLARD.

**Mineralogical investigations of certain soils of the Akhmangansk plateau in Armenia.** Z. N. NEMOVA (Bull. Acad. Sci. U.S.S.R., 1930, 157–175).—A study of the mineralogical character of certain Armenian soils, which are all of the same nature. They consist mainly of hypersthene (up to 80%), with certain admixtures, the character of which is also constant.

A. FREEMAN.

**Orientation of kamacite in meteoric irons.** J. YOUNG (Min. Mag., 1930, 22, 382–385).—Three systems of kamacite are associated with each of the four triad axes of the octahedrite, giving in all a complex grouping of twelve systems of kamacite.

L. J. SPENCER.

**Origin of meteorites.** F. PANETH (Z. Elektrochem., 1930, 36, 727–732).—Study of the helium and radium contents of a number of meteorites, in conjunction with astrophysical considerations, leads to the conclusion that meteorites are derived from the mixture of elements in the sun, and that the oldest are of roughly the same age as the earth.

H. F. GILLBE.



**Isthilart meteorite.** E. II. DUCLOUX and F. PASTORE (Rev. fac. cienc. quim. La Plata, 1930, 6, 13—26).—The metallic portions contained Fe 87.69—87.97, Ni 8.59, S 2.18%, and smaller quantities of cobalt, manganese, chromium, titanium, and phosphorus. The non-metallic portion contained SiO<sub>2</sub> 44.25, FeO 13.37, MgO 24.39, Al<sub>2</sub>O<sub>3</sub> 4.21, CaO 2.42%, with smaller quantities of nickel, sodium,

sulphur, manganese, titanium, iron, cobalt, and phosphorus.

CHEMICAL ABSTRACTS.

**Rock-strata gases of the Cripple Creek district, Colo., and their effect on mining.** E. H. DENNY, K. L. MARSHALL, A. C. FIELDNER, A. H. EMERY, W. P. YANT, and W. A. SELVIG (U.S. Bur. Mines, Bull. 317, 1930, 66 pp.).

## Organic Chemistry.

**Decomposition of methane, ethane, and ethylene by an electric arc.** C. FUJIO (Bull. Chem. Soc. Japan, 1930, 5, 249—260).—The decomposition of these hydrocarbons in the electric arc was investigated with different spark voltages and a number of gas velocities. Carbon, hydrogen, acetylene, ethylene, and ethane are produced from methane, and the rate of decomposition is inversely proportional to the gas velocity; the production of acetylene remains constant, being about 30% of the decomposition products, whilst ethylene and ethane are produced in smaller amounts at higher spark voltages. Ethylene yields carbon, hydrogen, acetylene, and methane, the percentage amount of the latter increasing with the gas velocity, whilst that of hydrogen and methane decreases. Ethane yields the same products. Quantitative values of the decomposition mixtures are tabulated in each case and the significance of the results is discussed.

H. I. DOWNES.

**Electrosynthesis of hydrocarbons. II.** L. BERMEO and L. BLAS (Anal. Fis. Quim., 1930, 28, 706—708; cf. A., 1929, 775).—Butane is obtained pure and in good yield by the electrolysis of saturated zinc propionate solution with a mercury cathode and a platinum anode at a temperature not above 20° with a current density of 0.1 amp. per cm.<sup>2</sup> The side reactions which occur with alkali salts are completely avoided.

R. K. CALLOW.

**γ-Methylheptane.** (MLLE.) H. VAN RISSEGHEN (Bull. Soc. chim. Belg., 1930, 39, 369—373).—Methylethylbutylcarbinol (Konowalov, A., 1902, i, 336), obtained by interaction of methyl ethyl ketone with magnesium *n*-butyl bromide, is dehydrated by *p*-toluenesulphonic acid to a mixture of octenes which on hydrogenation in presence of platinum-black gives γ-methylheptane, b. p. 119°, *d*<sub>4</sub><sup>15</sup> 0.7095, *n*<sub>D</sub><sup>15</sup> 1.3990 (cf. Levene and Taylor, A., 1923, i, 81). The values of *n*<sub>D</sub><sup>15</sup> for other lines are given and a number of derived constants calculated.

H. A. PIGGOTT.

**Mechanism of thermal decomposition of normal olefines.** R. V. WHEELER and W. L. WOOD (J.C.S., 1930, 1819—1828).—The thermal decomposition of ethylene, propylene, and the two non-branched-chain butylenes has been effected at temperatures ranging from 650° to 900° with the gases both streaming and static in each case. Analyses of the products suggest that the principal primary reactions, common to all, are the formation of either the two-carbon or the four-carbon (or of both) atom members of the olefine series: 2C<sub>2</sub>H<sub>4</sub> → C<sub>2</sub>H<sub>2</sub> (I); 2C<sub>2</sub>H<sub>6</sub> → C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>8</sub> (II); C<sub>4</sub>H<sub>8</sub> → 2C<sub>2</sub>H<sub>4</sub> (III). Reaction

I is a true polymerisation, but the mechanisms of II and III are obscure.

Rapidly following the formation of butylene is the secondary decomposition (dehydrogenation) to butadiene (with butylene this is a primary mode of decomposition). In the presence of hydrogen (liberated during secondary reactions), the olefines decompose through the scission of the carbon chain at the last C-C linking, forming radicals which, by hydrogenation, produce methane and the next lower olefine: CH<sub>3</sub>·CH·CH<sub>2</sub> → CH<sub>3</sub>· + ·CH·CH<sub>2</sub>  $\xrightarrow{H-H}$  CH<sub>4</sub> + CH<sub>2</sub>·CH<sub>2</sub>; CH<sub>3</sub>·CH<sub>2</sub>·CH·CH<sub>2</sub> → CH<sub>3</sub>· + ·CH<sub>2</sub>·CH·CH<sub>2</sub>  $\xrightarrow{H-H}$  CH<sub>4</sub> + CH<sub>3</sub>·CH·CH<sub>2</sub>.

Butadiene and the lower olefines are always present in the early stages of decomposition. Ethylene and butylene combine in equimolecular proportions to produce cyclohexene; similarly, propylene and butylene combine with butadiene to form substituted hydroaromatic hydrocarbons. These lose hydrogen at higher temperatures, giving benzene and its homologues.

R. J. W. LE FÈVRE.

**Density of gaseous propylene.** W. R. ORMANDY and E. C. CRAVEN (J.S.C.I., 1930, 49, 374—376r).—Propylene prepared by the dehydration of isopropyl alcohol contains heavy impurities which can largely be removed by passing the gas through liquid hydrocarbons. The density of the propylene so purified, or as distilled from liquid propylene, was found to be 21.20 (O=16).

**Autocatalysis.** I. L. KONDAKOV (Chem. Listy, 1930, 24, 293—297, 317—320).—The polymerisation of butadienes is supposed to be catalysed by a hypothetical unstable dimeride, possessing numerous ethylenic linkings, the terminal atoms exhibiting a specific electronic arrangement. R. TRUSZKOWSKI.

**Attempted preparation of geometrical isomerides of *n*-Δ<sup>8</sup>-hexene by means of crotyl bromide.** (MLLE.) H. VAN RISSEGHEN (Bull. Soc. chim. Belg., 1930, 39, 349—368).—It was expected that the interaction of crotyl bromide with magnesium methyl bromide would yield the geometrical isomerides of *n*-Δ<sup>8</sup>-hexene. The product, however, differs from that of dehydration of *n*-hexan-β-ol (A., 1926, 1224) only in density, and this apparently due to insufficient purification. Its properties are not changed by the action of hydrochloric acid, or of bromine in sunlight, and the hydrocarbons prepared by the two methods do not interact. As by-products are obtained γ-methyl-Δ<sup>8</sup>-heptadiene, b. p. 113.5—115.5°, *d*<sub>4</sub><sup>15</sup> 0.7359, *n*<sub>D</sub><sup>15</sup> 1.4267, Δ<sup>8</sup>-octadiene, and γ-methyl-Δ<sup>8</sup>-pentene

(contained in a fraction, b. p. 51—55°,  $d_4^{25}$  0.6826); the first was identified by hydrogenation to  $\gamma$ -methylheptane and by oxidation to formic, acetic, and methylsuccinic acids; the second on hydrogenation gave *n*-octane.  $\gamma$ -Methyl- $\Delta^4$ -pentene was identified by hydrogenation to  $\gamma$ -methylpentane (A., 1921, i, 489) and by conversion of its dibromide, b. p. 191—195°, into an acetylenic hydrocarbon capable of forming a copper salt; it appears to be derived from methylvinylbromomethane contained in the crotyl bromide used (due to its preparation by the action of hydrogen bromide on aqueous methylvinylcarbinol).

H. A. PIGGOTT.

**Polymerisation and thermal decomposition of acetylene.** P. SCHLÄPFER and M. BRUNNER (Helv. Chim. Acta, 1930, 13, 1125—1151).—Polymerisation of acetylene begins at 300°, whilst the uncatalysed spontaneous decomposition occurs only above 500°. Polymerisation in glass vessels is accompanied by a fall in pressure which can be used as an approximate measure of the reaction velocity; at 420°, the pressure falls 110 mm. after 30 min. and 590 mm. after 5 hrs. The velocity increases rapidly with rise in temperature; at 550° it is so rapid that it could not be measured by the authors' procedure. Polymerisation proceeds in the homogeneous phase and the reaction is probably bimolecular (cf. Pease, this vol., 58). The fall in pressure is retarded greatly by the presence of iron powder or carbon (from acetylene).

The region of temperature and pressure in which the explosive spontaneous decomposition of acetylene occurs has been determined. Polymerisation occurs solely at 530° and pressures below 2.5 atm., but at higher temperatures deflagration takes place under much lower pressures (e.g., 700°/0.6 atm.). The addition of carbon and iron powder catalyses the relatively slow non-explosive decomposition, but retards the deflagration. Thus, in presence of the above substances no explosion occurs at 590° and 1960 and 2400 mm., respectively, whilst in their absence, deflagration takes place at 590°/1000 mm. Iron oxides act similarly. Impurities which are usually present in commercial acetylene have no noticeable effect on the spontaneous decomposition. The presence of small amounts of oxygen (or air) causes a large fall in the temperature at which deflagration occurs; with increasing oxygen content, the explosive decomposition diminishes in favour of the spontaneous ignition (oxidation). H. BURTON.

**Compounds of iodoform, bromoform, and chloroform with quaternary and ternary salts.** IV. W. STEINKOPF and H. TEICHMANN (J. pr. Chem., 1930, [ii], 127, 337—356).—The "triethylsulphonium hydroxide-iodoform" compound, m. p. 126°, of Bayer (G.P. 97,207) is readily formed in cold alcoholic solution, but is actually  $2\text{SEt}_3\text{I}\cdot 3\text{CHI}_3$ ; it may also be prepared from the sulphonium iodide and by recrystallisation of the 1:1 compound from alcohol. It is considered that compounds of the type base-iodoform are incapable of existence. The following new compounds are described:

$\text{NPh}(\text{CH}_2\text{Ph})\text{Et}_2\text{I}\cdot\text{CHI}_3$ , m. p. 120° [previously incorrectly described (A., 1926, 829) as the 2:3 compound];  $\text{NPh}(\text{CH}_2\text{Ph})\text{Et}_2\text{I}\cdot\text{CHBr}_3$ , m. p. 114—

116°;  $\text{NPh}(\text{CH}_2\text{Ph})\text{Et}_2\text{I}\cdot\text{CHCl}_3$ , m. p. 105°;  $\text{N}(\text{CH}_2\text{Ph})_3\text{Me}_2\text{I}\cdot\text{CHBr}_3$ , m. p. 108°;  $2\text{NH}(\text{CH}_2\text{Ph})_3\text{I}\cdot 3\text{CHBr}_3$ , m. p. 82° (sealed tube);  $\text{AsPh}(\text{CH}_2\text{Ph})\text{Et}_2\text{I}\cdot\text{CHI}_3$ , m. p. 122° (both from quaternary iodide and hydroxide);  $\text{AsPh}(\text{CH}_2\text{Ph})\text{Et}_2\text{I}\cdot\text{CHBr}_3$ , m. p. 113°;  $\text{AsPh}_2(\text{CH}_2\text{Ph})\text{EtI}\cdot\text{CHI}_3$ , m. p. 101—108° (partly decomposed by recrystallisation);  $\text{AsPh}_2(\text{CH}_2\text{Ph})\text{EtI}\cdot\text{CHBr}_3$ , decomp. 140—160° (sealed tube);  $\text{SEt}_3\text{I}\cdot\text{CHBr}_3$ , m. p. 98—100° (2:3 compound could not be obtained);  $\text{SMe}_3\text{I}\cdot 2\text{CHI}_3$ , m. p. 157° (decomp.);  $\text{SMe}_2\text{EtI}\cdot 2\text{CHI}_3$ , m. p. 136° (cf. Bayer, loc. cit.);  $\text{SMe}_2\text{EtI}\cdot\text{CHBr}_3$ , m. p. 35—40°;  $\text{NMe}_3(\text{CH}_2\text{CH}_2\text{OH})\text{I}\cdot 3\text{CHI}_3$ , m. p. 195° (from free base). Iodoform and betaine give trimethylaminoacetic acid hydriodide, m. p. 240—241° (decomp.), also obtainable from the base and hydriodic acid. The preparation of phenylbenzyl-diethylarsonium iodide, m. p. 149°, from phenyldiethylarsine, diphenylbenzylethylarsonium iodide, m. p. 178°, from diphenylethylarsine, and improvements in the preparation of phenylbenzyl-diethyl-, m. p. 120°, and dibenzyl-dimethyl-ammonium iodide, m. p. 193°, are recorded. The preparation of tribenzyl-*n*-propylammonium iodide from tribenzylamine (A., 1926, 829) could not be repeated; its existence and that of its iodoform compound are therefore doubtful.

H. A. PIGGOTT.

**Bivalency of carbon. IV. Halogen displacements from *s*-tetra-bromo- and -chloro-ethane and tri-bromo- and -chloro-ethylene.** A. M. WARD (J.C.S., 1930, 2143—2148; cf. this vol., 612).—Bromine is not displaced from tribromoethylene by ethyl alcohol alone; in presence of sodium hydroxide or ethoxide the reaction is bimolecular, the velocity coefficient being the same whether hydroxide or ethoxide is used, viz.,  $4.08 \times 10^{-5}$  at 15°, and  $184 \times 10^{-5}$  at 25°. Similarly, tetrabromoethane is stable in alcoholic solution, but in presence of sodium hydroxide or ethoxide one bromine atom is displaced instantaneously with the formation of tribromoethylene (cf. Gowing-Scopes, A., 1914, ii, 779), which then behaves as above, the values of  $k$  being slightly different, possibly on account of the production of the tribromoethylene in a purer form. Tetrachloroethane and trichloroethylene behave similarly but are less reactive. The bimolecular nature of the reaction necessitates some modification of the mechanism proposed by Lawrie, viz.:  $\text{CBr}_2\text{CHBr} \rightarrow \text{HBr} + \text{CBr}_2\text{C}$  (A., 1907, i, 3; cf. Nef, A., 1898, i, 102; 1900, i, 20); the necessity of postulating an intermediate stage renders the kinetic results valueless as a means of distinguishing between dibromoacetylidene and dibromoacetylene as the end-product.

H. A. PIGGOTT.

**Abnormal reactions of propylene dihalides and their interpretation by the synionic theory.** A. KIRRMANN and [in part] J. GRARD (Bull. Soc. chim., 1930, [iv], 47, 834—847).— $\alpha\gamma$ -Dibromopropene with magnesium phenyl bromide yields 50% of  $\gamma$ -bromoallylbenzene, b. p. 106—107°/12 mm.,  $d_4^{25}$  1.3418,  $n_D^{25}$  1.5629; with magnesium methyl bromide the reaction gives about 30% of ethane containing a little methane, about 5% of erythrene, a pentene (yielding a dibromo-

pentane, b. p. 62—63°/14 mm., 160—177°/760 mm.,  $d^{21}_4$  1.66,  $n^{21}_D$  1.5066), bromobutene, b. p. 92—94°,  $d^{17}_4$  1.23,  $n^{17}_D$  1.45, octadiene, b. p. 118—120°,  $d^{17}_4$  0.748,  $n^{17}_D$  1.4292, and a hydrocarbon,  $C_{10}H_{18}$  or  $C_{10}H_{16}$ , b. p. 70—80°/12 mm.,  $d^{20}_4$  0.808,  $n^{20}_D$  1.4618. With magnesium ethyl bromide, 30% of heptene, b. p. 94—96°,  $d^{15}_4$  0.701,  $n^{15}_D$  1.406, together with  $\alpha$ -bromo- $\Delta^2$ -pentene, b. p. 116—120°,  $d^{19}_4$  1.254,  $n^{19}_D$  1.4624, is obtained. Magnesium propyl bromide yields about 5% of hexane, b. p. 66—70°,  $n^{19}_D$  1.3825, 47% of  $\Delta^2$ -nonene, b. p. 144—146°,  $d^{18}_4$  0.732,  $n^{18}_D$  1.4212 (dibromide, b. p. 119—120°/12 mm.,  $d^{17}_4$  1.41,  $n^{17}_D$  1.4988), together with a hydrocarbon,  $C_{12}H_{22}$ , b. p. 83—88°/13 mm.,  $d^{18}_4$  0.778,  $n^{18}_D$  1.447 (tetrabromide, b. p. 170—180°/2 mm.), and a hydrocarbon, b. p. 125—135°/13 mm.,  $d^{17}_4$  0.803,  $n^{17}_D$  1.471). Similarly,  $\alpha\gamma$ -dibromo- $\beta$ -methylpropene and magnesium ethyl bromide yield about 30% of an octene, b. p. 118—121°,  $d^{20}_4$  0.733,  $n^{20}_D$  1.4182, a bromohexene, b. p. 39°/13 mm., 143°/760 mm.,  $d^{21}_4$  1.224,  $n^{21}_D$  1.4677, and a bromodecadiene, b. p. 96—100°/13 mm.,  $d^{18}_4$  1.119,  $n^{18}_D$  1.487.  $\alpha\alpha$ -Dichloro- $\Delta^2$ -propene with magnesium propyl bromide gives 25% of chlorohexene (this vol., 735) together with hexene,  $\Delta^2$ -nonene, and about 35% of dodecadiene. Epichlorohydrin yields the same products, but very little chlorohexene and more dodecadiene. Bromopropene, bromobutene, butylene oxide, and  $\alpha$ -bromo- $\Delta^2$ -heptene do not react with magnesium methyl iodide. Since therefore the linear vinyl bromides do not react with Grignard reagents, the formation of the linear hydrocarbon  $CHR:CH:CH_2R$  as principal product from  $C_3H_4X_2$  cannot be attributed to the consecutive reaction  $CH_2R:CH:CHX + RMgBr \rightarrow CH_2R:CH:CHR$ .

R. BRIGHTMAN.

#### $\beta$ -Dibromides and trimethylene hydrocarbons.

R. LESPIEAU (Bull. Soc. chim., 1930, [iv], 47, 847—857).— $\alpha$ -Bromo- $\Delta^2$ -pentene when repeatedly saturated with hydrogen bromide at  $-15^\circ$  and afterwards heated at 100° for 5 hrs. yields fractions, (A) b. p. 61—62°/15 mm., (B) b. p. 75—76.5°/12 mm., and (C) b. p. 68—72°/15 mm., in the proportion 10:10:1, together with 33% of unchanged bromide. Fraction A, b. p. 178°/750 mm., consists of  $\beta\gamma$ -dibromopentane with traces of  $\alpha\beta$ -dibromopentane, since the  $\Delta^2$ -pentinene obtained with alcoholic potassium hydroxide contains traces of the true acetylene. With zinc dust it yields a hydrocarbon,  $C_5H_{10}$ , b. p. 35.5—36.2°,  $d^{20}_4$  0.6504,  $n^{20}_D$  1.37965. Fraction (C) consists mainly of  $\alpha\beta$ -dibromopentane, and fraction (B) of  $\alpha\gamma$ -dibromopentane, which with zinc and alcohol yields ethyltrimethylene, b. p. 34.5°/743 mm.,  $d^{22}_4$  0.6738,  $n_D$  1.3785. After oxidation with potassium permanganate to eliminate pentenes the residual oil (three fifths of original) had b. p. 35—75°/765 mm.,  $d^{20}_4$  0.6764,  $n^{20}_D$  1.3789.

[With JOYAL].— $\Delta^2$ -Pentene- $\delta$ -ol with phosphorus tribromide yields a bromide,  $CHMe:CH:CHMeBr$ , b. p. 65—67°/125 mm.,  $d^{21}_4$  1.2312,  $n_D$  1.4752, converted by hydrogen bromide at  $-15^\circ$  and heating for 5 hrs. at 100° into a dibromide, b. p. 72—75°/22 mm.,  $d^{19}_4$  1.6654,  $n_D$  1.5032, which with zinc and alcohol yields 1:2-dimethyltrimethylene, b. p. 33.75—34.5°,  $d^{25}_4$  0.6635,  $n^{25}_D$  1.3771. After oxidation to remove pentenes the residual oil had b. p. 34—35°,  $d$  0.6683,

$n_D$  1.378. Examination of the Raman spectra indicates that about 40% of pentenes, probably  $\Delta^2$ -pentene, is present in the original sample.

When saturated with hydrogen bromide at  $-20^\circ$  and heated at 100° for 5 hrs., cinnamyl bromide yields  $\alpha\gamma$ -dibromo- $\alpha$ -phenylbutane, b. p. 142°/10 mm.,  $d^{23}_4$  1.632,  $n_D$  1.5935, converted by zinc and alcohol into an oil, b. p. 64—65°/16 mm.,  $d^{20}_4$  0.9328, from which phenyltrimethylene, b. p. 60—61°/13 mm., 170.5°/760 mm.,  $d^{24}_4$  0.9397,  $n^{20}_D$  1.5312, after oxidation of olefinic impurities with permanganate, is obtained. The crude oil contains a little allylbenzene, a crystalline product,  $C_{18}H_{26}Br_2$ , m. p. 145—146° [yielding with silver acetate in acetic acid an acetin, m. p. 86.5—88°, and on hydrolysis a glycol,  $C_{18}H_{26}(OH)_2$ , m. p. 178—180°], and a non-volatile residue. When heated with alcoholic potassium hydroxide at 100° for 8 hrs., at 120° for 4 hrs., and at 170° for 1 hr. allylbenzene is completely isomerised to propenylbenzene. In contrast to allylbenzene and propenylbenzene, phenyltrimethylene yields hydrogen bromide with bromine. When cooled in liquid air the three hydrocarbons congeal, giving products of approximate m. p.  $-40^\circ$ ,  $-20^\circ$ , and  $-31^\circ$ , respectively. In view of the different results obtained with cinnamyl bromide and  $\beta$ -bromo- $\Delta\gamma$ -pentene it is probable that the addition of hydrogen bromide is determined by the nature of the radicals linked to the  $\cdot CH:CH \cdot$  group.

R. BRIGHTMAN.

#### Reactivity of alkenyl halides of the types $CH_2:CH:CH_2 \cdot X$ and $CH_3:CH:CH:CH_2 \cdot X$ .

A. JUVALA (Ber., 1930, 63, [B], 1989—2009).—The rate of reaction of the halide with potassium iodide in acetone is measured at  $15^\circ$ ; the reaction mixture is poured into crushed ice, chloroform, and concentrated hydrochloric acid and titrated with 0.005*N*-potassium iodate until the chloroform becomes colourless. The addition of bromine is studied in carbon tetrachloride in the absence of light; the excess of bromine is determined by addition of potassium iodide and titration of the liberated iodine. The velocities of reaction of the halides  $CH_2:CH:CH_2 \cdot Br$ ,  $CH_2:CH:CH_2 \cdot Cl$ , and  $CH_3:CH:CH:CH_2 \cdot Br$  with potassium iodide follow the "saw-tooth" rule; the proportional maxima follow the odd and the corresponding minima the even values of  $n$ . Comparison of the velocities of reaction of the chlorides with those of the corresponding saturated chlorides shows that the former substances react the more rapidly and that the difference is most marked when  $n = 1$ . For the same values of  $n$ , the maxima for the rates of reaction of halides with potassium iodide correspond with the minima for the hydrolysis of esters.  $CH_2:CH:CH_2 \cdot O \cdot CO \cdot R$ , in acid solution. The rates of addition of bromine to the halides  $CH_2:CH:CH_2 \cdot Br$ ,  $CH_2:CH:CH_2 \cdot Cl$ , and  $CH_3:CH:CH:CH_2 \cdot Br$  increase as  $n$  increases and the maxima correspond with minima observed in the hydrolysis of esters  $CH_2:CH:CH_2 \cdot O \cdot CO \cdot R$  in alkaline solution. If in the halides  $CH_3:CH:CH:CH_2 \cdot Br$  the terminal group  $CH_3:CH:$  appears instead of the  $CH_2:$  group, the rate of reaction with potassium iodide is greater if  $n = 0$  but smaller when  $n = 1$ ; in the case of the addition of bromine, the change causes an increase in the rate whether  $n = 0$  or 1. The bromides

$\text{CH}_2\text{:CH}[\text{CH}_2]_n\text{Br}$  react more rapidly than the corresponding chlorides with potassium iodide or bromide.

The halides are prepared by the cautious addition of the alcohol (3 mols.) and pyridine (2/3 mol.) to phosphorus trihalide (1.2 mols.). The mixture is distilled. The crude distillate is neutralised with dilute potassium hydroxide, washed with water, dried over calcium chloride, and fractionally distilled. The following constants are recorded: vinyl bromide, b. p.  $16^\circ/758$  mm.,  $d_4^{20}$  1.5725; allyl bromide, b. p.  $70.5^\circ/757$  mm.,  $d_4^{20}$  1.4083; allyl chloride, b. p.  $44.8^\circ/754$  mm.,  $d_4^{20}$  0.9267,  $n_D^{20}$  1.40950;  $\Delta^2$ -buten- $\alpha$ -ol, b. p.  $112.5\text{--}113.5^\circ/748$  mm.,  $d_4^{20}$  0.8475,  $n_D^{20}$  1.42240, obtained by addition of ether and allyl bromide to magnesium turnings, trioxymethylene, and a trace of iodine;  $\Delta^2$ -butenyl bromide, b. p.  $98.5\text{--}99.0^\circ/758$  mm.,  $25^\circ/40.5$  mm.,  $d_4^{20}$  1.3230,  $n_D^{20}$  1.46215;  $\Delta^2$ -butenyl chloride, b. p.  $75^\circ/773$  mm.,  $d_4^{20}$  0.9211,  $n_D^{20}$  1.42330;  $\Delta^2$ -penten- $\alpha$ -ol, b. p.  $141.0\text{--}141.5^\circ/758$  mm.,  $d_4^{20}$  0.8457,  $n_D^{20}$  1.43085;  $\Delta^2$ -pentenyl bromide, b. p.  $126^\circ/763$  mm.,  $56^\circ/75$  mm.,  $d_4^{20}$  1.2581,  $n_D^{20}$  1.46397;  $\Delta^2$ -pentenyl chloride, b. p.  $103.5\text{--}104^\circ/773$  mm.,  $36.5^\circ/61$  mm.,  $d_4^{20}$  0.9125,  $n_D^{20}$  1.42973;  $\alpha$ -bromo- $\Delta^2$ -propene, b. p.  $59.0\text{--}61.0^\circ/752$  mm.,  $d_4^{20}$  1.4133,  $n_D^{20}$  1.45193;  $\alpha$ -bromo- $\Delta^2$ -butene, b. p.  $103\text{--}104^\circ/762$  mm.,  $d_4^{20}$  1.3331,  $n_D^{20}$  1.47638. H. WREN.

#### Highly polymerised compounds. XLIV.

**Polyvinyl bromide.** H. STAUDINGER, M. BRUNNER, and W. FEIST. **XLV. *as*-Polydichloroethylene.** H. STAUDINGER and W. FEIST (Helv. Chim. Acta, 1930, 13, 805—832, 832—842).—XLIV. Vinyl bromide polymerises much more readily in sunlight than in the dark; the product obtained is less soluble in benzene, tetrachloroethane, bromobenzene, dioxan, and tetrahydronaphthalene than are those similarly formed in presence of solvents such as ether or benzene. Polymerisation also occurs by ultra-violet irradiation (cf. Plotnikov, A., 1922, i, 419); this is retarded by pure oxygen. Polyvinyl bromide is not homogeneous, but consists of a mixture of products of varying degrees of polymerisation (cf. Ostromisslenski, A., 1916, i, 273; Flumiani, A., 1928, 836). Mol. wt. determinations are not possible owing to the sparing solubility of polyvinyl bromide in cold solvents and the ready decomposition which occurs in hot solvents; when the bromide is heated in absence of a solvent, elimination of hydrogen bromide takes place and the monomeric bromide is not produced. Treatment of polyvinyl bromide with zinc dimethyl in xylene at  $100\text{--}140^\circ$  affords a hydrocarbon,  $(\text{C}_5\text{H}_8)_x$ , which differs from caoutchouc in being less unsaturated. The hydrocarbon resembles cyclocaoutchouc (A., 1926, 840); when treated with ozone, laevulic or methylsuccinic acid is not produced. Zinc diethyl and polyvinyl bromide in xylene at  $50\text{--}160^\circ$  afford a hydrocarbon,  $(\text{C}_6\text{H}_{10})_x$ .

Reduction experiments indicate that the polymerised product is a mixture of long straight-chain compounds. Thus, reduction with zinc dust and acetic acid in presence of xylene at  $120\text{--}130^\circ$  in a current of hydrogen chloride gives an acetone-soluble hydrocarbon,  $\text{C}_{16}\text{H}_{26}$ , b. p.  $123\text{--}126^\circ/0.15$  mm.,  $d_4^{20}$  0.8771, which is saturated to bromine and is probably a benzenoid compound (cf. this vol., 889). Similar

reduction in dioxan solution affords only small amounts of high-boiling hydrocarbons. Reduction of polyvinyl bromide with red phosphorus and 70% hydriodic acid at  $170\text{--}180^\circ$ , dissolution of the product formed in a mixture of xylene and tetrahydronaphthalene, and precipitation with methyl alcohol give an impure hydrocarbon, m. p.  $114^\circ$ ,  $M$  1300—1530, which contains phosphorus. When this is distilled with soda-lime in a high vacuum, a mixture of hydrocarbons,  $\text{C}_{60}\text{H}_{122}$ , m. p.  $95^\circ$ , and  $\text{C}_{35}\text{H}_{72}$ , m. p.  $74\text{--}75^\circ$  (see below), is obtained. Fractionation of polyvinyl bromide by precipitating from a solution in tetrachloroethane with methyl alcohol gives benzene-soluble and -insoluble products. Reduction of these with red phosphorus and hydriodic acid gives impure hydrocarbons, m. p.  $114\text{--}116^\circ$ ,  $M$  about 1550, and m. p.  $121\text{--}122^\circ$ ,  $M$  about 2000, respectively. When polyvinyl bromide is heated with 10% alcoholic sodium hydroxide for 10 days, partial elimination of halogen occurs and the product formed is insoluble in organic solvents. Hydrogen bromide is eliminated when the bromide is heated with trimethylamine, but with triphenylphosphine in propyl alcohol an alcohol-soluble quaternary phosphonium salt is produced. This salt possesses properties similar to those of the analogous compounds from caoutchouc halides. When the bromide is heated with quinoline, a nitrogenous compound results.

Reduction of benzene-soluble and -insoluble polyvinyl chlorides with red phosphorus and hydriodic acid ( $d$  2.0) at  $160^\circ$  affords impure hydrocarbons, m. p.  $110\text{--}111^\circ$ ,  $M$  1340—1390, and m. p.  $116\text{--}117^\circ$ ,  $M$  about 1900, respectively. When the last-named compound is distilled with soda-lime in a high vacuum, a mixture of hydrocarbons,  $\text{C}_{40}\text{H}_{82}$ , m. p.  $70\text{--}75^\circ$ , and  $\text{C}_{55}\text{H}_{112}$ , m. p.  $88\text{--}94^\circ$ , results.

**XLV. *as*-Polydichloroethylene,**  $\cdots \text{CH}_2\text{CCl}_2[\text{CH}_2\text{CCl}_2]_x\text{CH}_2\text{CCl}_2\cdots$ ,  $x=50\text{--}100$ , is formed very readily when *as*-dichloroethylene polymerises in the light. The polymeric material is completely saturated, when heated above  $120^\circ$  chars and eliminates hydrogen chloride, and is fractionated by extraction with benzene. When reduced with red phosphorus and 70% hydriodic acid at  $170\text{--}180^\circ$ , a mixture of impure hydrocarbons, m. p. about  $111^\circ$ ,  $M$  1400—1500, and m. p.  $116\text{--}117^\circ$ ,  $M$  about 2400, is obtained. Distillation of the mixture with soda-lime in a high vacuum affords two hydrocarbons,  $\text{C}_{60}\text{H}_{122}$ , m. p. about  $95^\circ$ , and  $\text{C}_{36}\text{H}_{74}$ , m. p.  $74\text{--}75^\circ$  (vide supra). Similar reduction of tetrachloroethane-soluble and -insoluble *as*-polydichloroethylenes gives impure hydrocarbons,  $\text{C}_{100}\text{H}_{202}$ , m. p.  $112\text{--}113^\circ$ , and  $\text{C}_{160}\text{H}_{322}$ , m. p.  $119\text{--}120^\circ$ , respectively. Reduction of *as*-polydichloroethylene with zinc dust and acetic acid in a current of hydrogen chloride furnishes a product,  $(\text{C}_2\text{HCl})_x$ ; when heated with aniline for 14 days, almost complete elimination of halogen occurs and a benzene-soluble product  $(\text{CH}_2\text{:C:NPh})_x$  results. Chlorine-free substances are not obtained when *as*-polydichloroethylene is treated with sodium methoxide or ethoxide, trimethylamine, pyridine, or quinoline. H. BURTON.

**Dichloroacetylene.** E. OTT, W. OTTEMEYER, and K. PACKENDORFF (Ber., 1930, 63, [B], 1941—1944;

cf. Ottemeyer, Diss., Münster, 1926).—Dichloroacetylene, b. p. 29° (corr.)/743 mm., can be prepared in 65% yield without danger by passing trichloroethylene over granulated potassium hydroxide heated in an electric oven at 130°; local overheating tends to cause violent explosions. The hydroxide is previously heated in a silver dish until it becomes solid at 200°. Gaseous dichloroacetylene inflames spontaneously in contact with air. Dilute solutions in ether are only slowly oxidised by passage of oxygen, whereas change occurs rapidly with *s*-tetrachloroethane as solvent. The main products of auto-oxidation are carbonyl chloride, carbon monoxide and dioxide; oxalyl chloride cannot be detected with certainty. Dichloroacetylene is rapidly converted by bromine in carbon tetrachloride into dichlorodibromoethylene, b. p. 58.5—59.5°/13 mm., slowly by iodine in ether into dichlorodiiodoethylene, m. p. 70°.

H. WREN.

Interaction of etherates of magnesium halides and ethylene oxides. Magnesium bromide etherate and epichlorohydrin. L. RIBAS and E. TAPIA (Anal. Fis. Quím., 1930, 28, 636—644).—When zinc chloride is added to a solution of magnesium phenyl bromide and the resulting compound is allowed to react with epichlorohydrin the product of hydrolysis is found to contain glycerol dichlorohydrin, contaminated with the chlorobromohydrin, together with benzene and diphenyl. As epichlorohydrin is found not to react with magnesium chloride in aqueous solution, the first reaction is therefore probably with the etherate of zinc or magnesium chloride. Actually, zinc chloride or magnesium bromide (but not the chloride) in ethereal solution reacts vigorously with epichlorohydrin, and forms precipitates, for which the constitution  $(CH_2X)_2CH \cdot O \cdot MX$  is suggested, and dichloro- and chlorobromo-hydrins are obtained by hydrolysis.

R. K. CALLOW.

Glycols of high mol. wt. and their partial dehydration products. S. SABETAY and J. BLÉGER (Bull. Soc. chim., 1930, [iv], 47, 885—894).—To determine the constitutional factors responsible for the characteristic odour of linalol, formylisobutaldol has been condensed with magnesium isoamyl, isohexyl, and *n*-heptyl bromides, and the primary-secondary glycol converted through the acetin and bromoacetic into the unsaturated alcohol. Since  $\beta\beta$ -trimethyl- $\Delta^7$ -hepten- $\alpha$ -ol closely resembles linalol in odour, the characteristic linalolic odour is not due to the presence of a tertiary alcoholic group, but can also be obtained from a primary alcohol with a doubly-branched chain.

Formylisobutaldol, m. p. 94° (dimeride), obtained by Wessely's method at a lower temperature (A., 1900, i, 428), reacts as a monomeride with Grignard reagents, yielding with magnesium isoamyl bromide (2 mols.)  $\beta\beta$ -trimethylheptane- $\alpha$ -diol, b. p. 145—148°/20 mm.,  $n_D^{20}$  1.453 (diacetate, b. p. 154—155°/15 mm.,  $n_D^{20}$  1.4351), converted by hydrogen bromide in acetic acid into  $\gamma$ -bromo- $\alpha$ -acetoxy- $\beta\beta$ -trimethylheptane, b. p. 145—147°/16 mm.,  $n_D^{20}$  1.463, which with alcoholic potassium hydroxide yields  $\beta\beta$ -trimethyl- $\Delta^7$ -hepten- $\alpha$ -ol, b. p. 90—92°/17 mm.,  $d_4^{20}$  0.8373,  $n_D^{20}$  1.443. Dehydration of the glycol in presence of

iodine yields a similar fraction, b. p. 92—95°/14 mm.,  $n_D^{20}$  1.4415, with a linalolic odour, dehydration in presence of bromine yielding similarly a fraction, b. p. 88—92°/18 mm.,  $n_D^{20}$  1.4406. In presence of 5% sulphuric acid or 10% phosphoric acid the glycol is unchanged.  $\beta\beta$ -Trimethyloctane- $\alpha$ -diol, b. p. 155—156°/17 mm.,  $n_D^{20}$  1.4520 (diacetate, b. p. 155—157°/18 mm.,  $n_D^{20}$  1.4352; bromoacetic, b. p. 154—155°/15 mm.,  $n_D^{20}$  1.4645),  $\beta\beta$ -trimethyl- $\Delta^7$ -octen- $\alpha$ -ol, b. p. 102—103°/17 mm.,  $n_D^{20}$  1.449 (from the bromoacetic, together with a hydrocarbon, citron odour, b. p. 161—163°/756 mm.,  $n_D^{20}$  1.429),  $\beta\beta$ -dimethyldecane- $\alpha$ -diol (yield, 44%), b. p. 175—177°/22 mm.,  $n_D^{20}$  1.4545 (diacetate, b. p. 177—178°/17 mm.,  $n_D^{20}$  1.438; bromoacetic, b. p. 166.5—169°/14 mm.,  $n_D^{20}$  1.4628), and  $\beta\beta$ -dimethyl- $\Delta^7$ -decen- $\alpha$ -ol, b. p. 120—122°/18 mm.,  $n_D^{20}$  1.448 (from the bromoacetic, together with a hydrocarbon, b. p. 91°/21 mm.,  $n_D^{20}$  1.4311), are similarly obtained.

isoHexyl alcohol is obtained, together with formyl-diisohexylacetal, b. p. 117—120°/13 mm.,  $d_4^{20}$  0.8342,  $n_D^{20}$  1.4216, by the action of trioxymethylene on magnesium isoamyl bromide in presence of zinc chloride or by passing formaldehyde into the Grignard reagent. The alcohol is converted into the bromide by Kamm and Marvel's method (A., 1920, i, 282).

The monomeric form of formylisobutaldol, b. p. 69°/15 mm.,  $d_4^{20}$  0.976,  $n_D^{20}$  1.43744, is obtained [T. LIESCO] in 22% yield by condensation in cold ether in presence of potassium hydroxide granules; in slightly different conditions a dimeride, b. p. 78°/14 mm., insoluble in benzene is obtained, which does not reduce ammoniacal silver nitrate, and with Grignard reagents yields primary-tertiary glycols, reactions which indicate the ester-salt structure,  $OH \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot O \cdot CO \cdot CMe_2 \cdot CH_2 \cdot OH$ .

R. BRIGHTMAN.

Reaction between magnesium phenyl bromide and epichlorohydrin by the Grignard method. E. TAPIA and M. A. HERNÁNDEZ (Anal. Fis. Quím., 1930, 28, 691—693).—When magnesium phenyl bromide reacts with epichlorohydrin in ethereal solution and the reaction is completed by adding toluene and heating the mixture until the toluene begins to distil, the product, after hydrolysis, yields chlorobromohydrin and methylstyrene.

R. K. CALLOW.

Representative carbonates and carbethoxy-derivatives related to ethylene glycol. N. L. DRAKE and R. M. CARTER (J. Amer. Chem. Soc., 1930, 52, 3720—3724).—The following carbonates are prepared from  $\beta$ -alkoxyethyl alcohols (or their sodium derivatives) and carbonyl chloride: di- $\beta$ -methoxyethyl, b. p. 230.2—232.1°/760.4 mm.,  $d_4^{20}$  1.0936,  $n_D^{20}$  1.4193; di- $\beta$ -ethoxyethyl, b. p. 245.1—246.1°/758.8 mm.,  $d_4^{20}$  1.0635,  $n_D^{20}$  1.4239; di- $\beta$ -butoxyethyl, b. p. 297.2—298.2°/761.7 mm.,  $d_4^{20}$  0.9766,  $n_D^{20}$  1.4279; and di- $\beta$ -ethoxy- $\beta$ -ethoxyethyl, b. p. 231.9—234.9°/55 mm.,  $d_4^{20}$  1.0636,  $n_D^{20}$  1.4353. The following mixed carbonates are obtained similarly from ethyl chloroformate and the alkoxyethyl alcohol: ethyl- $\beta$ -methoxyethyl, b. p. 182.1—183.1°/760.4 mm.,  $d_4^{20}$  1.0424,  $n_D^{20}$  1.4036; ethyl- $\beta$ -ethoxyethyl, b. p. 194—194.9°/762.7 mm.,  $d_4^{20}$  1.0115,  $n_D^{20}$  1.5064; ethyl- $\beta$ -butoxyethyl, b. p. 223.9—224.4°/759 mm.,  $d_4^{20}$  0.9756,  $n_D^{20}$  1.4143, and

ethyl  $\beta'$ -ethoxy- $\beta$ -ethoxyethyl, b. p. 242.7—244.2°/764.4 mm.,  $d_{20}^{25}$  1.0485,  $n_D^{25}$  1.4203. The solvent actions of these esters on R.S. nitrocotton, A.S. nitrocotton, and cellulose acetate are given. H. BURTON.

**isoPropyl sulphate.** W. R. ORMANDY and E. C. CRAVEN (J.S.C.I., 1930, 49, 362t).—The preparation of isopropyl sulphate from propylene and sulphuric acid is described and its main physical and chemical properties are recorded.

**Organic oxidations by iodic acid.** T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, 52, 3647—3649).—Many phenols and amines are oxidised by iodic acid in presence of dilute acetic acid, forming dyes (various shades of brown on silk). Oxidations can also be carried out in presence of sodium hydroxide. Thus, mercaptans yield disulphides, *s*-diarylthiocarbamides give *s*-diarylcarbamides, arylthiocarbamides afford arylcyanamides, pyrogallol furnishes purpurogallin (92% yield), and benzoin yields benzoic acid. Tri- and tetra-substituted thiocarbamides, disulphides, sulphoxides, alcohols, most alkaloids, glucosides, and carbohydrates are not oxidised by iodic acid.

H. BURTON.

**Constitution of complex metallic salts.** F. G. MANN (J.C.S., 1930, 1745—1756).—Treatment of an aqueous-alcoholic solution of ammonium chloroplatinite with methyl ethyl sulphide at 50° gave dichlorobis(methyl ethyl sulphide)platinum, m. p. 125—126°, as the chief product; no potassium platino(methyl ethyl sulphide)trichloride was isolated.

*p*-Cyanobenzyl ethyl sulphide, b. p. 167—168°/16 mm. (from *p*-cyanobenzyl chloride and sodium ethyl sulphide suspended in benzene), yielded on hydrolysis *p*-carboxybenzyl ethyl sulphide, m. p. 124—125°, which co-ordinated with ammonium chloroplatinite in an aqueous-alcoholic medium at 100°, producing dichlorobis-(*p*-carboxybenzyl ethyl sulphide)platinum, m. p. 253—255° (decomp.). Isomeric with this deep orange form a nearly white form was obtained from the original filtrate after 24 hrs. with m. p. 254—255° (decomp.).

Diaminodiethyl sulphide dihydrochloride in *N*-hydrochloric acid solution and aqueous potassium chloroplatinite gave dichloro-( $\beta\beta'$ -diaminodiethyl sulphide monohydrochloride)platinum hemihydrate,  $[\text{Cl}_2\text{Pt}(\text{NH}_2\cdot\text{C}_2\text{H}_5)_2\text{S}\cdot\text{HCl}]\cdot 0.5\text{H}_2\text{O}$ , m. p. 105—107° (decomp.), which with aqueous oxalic acid or sodium picrate gave respectively dichloro-( $\beta\beta'$ -diaminodiethyl sulphide monohydrogen oxalate)platinum monohydrate, m. p. 198—199° (decomp.), or the corresponding picrate, an oil. Ammonium *d*-camphorsulphonate and the above monohydrochloride afforded the monocamphorsulphonate, m. p. 179—181° (decomp.),  $[\text{M}]_{\text{D}}^{25} + 59^\circ$ . Attempts to effect double decomposition of the aqueous hydrochloride with ammonium or sodium nitrocamphor furnished monochloro(diaminodiethyl sulphide)platinous monochloride,  $[\text{ClPt}(\text{NH}_2\cdot\text{C}_2\text{H}_5)_2\text{S}]\text{Cl}$ , m. p. indefinite.

Addition of hydrogen peroxide to dichloro(diaminodiethyl sulphide monohydrochloride)platinum hemihydrate in *N*-hydrochloric acid solution led to the formation of tetrachloro-( $\beta\beta'$ -diaminodiethyl sulphide monohydrochloride)platinum monohydrate, m. p. 190—

191° (decomp.), which, with excess of aqueous ammonium *d*-camphorsulphonate, afforded optically pure *d*-tetrachloro(diaminodiethyl sulphide mono-*d*-camphor- $\beta$ -sulphonate)platinum, m. p. 198—199° (decomp.),  $[\text{M}]_{\text{D}}^{25} + 1070^\circ$  (racemising in about 80 hrs.). Treatment of the last-named compound with ice-cold calcium chloride solution yielded the corresponding *d*-hydrochloride, m. p. 187—188° (decomp.),  $[\text{M}]_{\text{D}}^{25} + 926^\circ$ .

By boiling under reflux aqueous tetrachloro(diaminodiethyl sulphide monohydrochloride)platinum in the presence of dilute hydrochloric acid trichloro(diaminodiethyl sulphide)platinic monochloride, m. p. 220—222° (decomp.), was obtained, from which by treatment with silver camphorsulphonate the camphorsulphonate monohydrate, m. p. 216—217° (decomp.),  $[\text{M}]_{\text{D}}^{25} + 78^\circ$ , was formed. Treatment of the above monochloride with silver bromocamphorsulphonate or treatment of aqueous solutions of the monohydrochloride of the tetrachloro-compound with ammonium or silver bromocamphorsulphonate always led to trichloro(diaminodiethyl sulphide)platinic mono- $\alpha$ -bromocamphor- $\pi$ -sulphonate, m. p. 224—226° (decomp.),  $[\text{M}]_{\text{D}}^{25} + 367^\circ$ .

This work provides decisive evidence that in co-ordinated sulphides the three valencies of the sulphur atom possess a space direction similar to those of the sulphur atom in the asymmetric sulphoxides etc.

The following compounds are described incidentally: *p*-cyanobenzylethylsulphine-*p*-toluenesulphonylimine, m. p. 158—160°; dichlorobis-(1:4-thiazan)platinum dihydrate(?), m. p. 293—294° (decomp.); and diaminodiethyl sulphide chloroplatinate,  $(\text{NH}_2\cdot\text{C}_2\text{H}_5)_2\text{S}\cdot\text{H}_2\text{PtCl}_6$ , m. p. 217—218° (decomp.) (from aqueous solutions of the amine hydrochloride and platinic chloride). R. J. W. LE FÈVRE.

**Reactions of some mercaptans with alkaline sodium plumbite solutions.** E. OTT and E. E. REID (Ind. Eng. Chem., 1930, 22, 878—881).—The reactions between sodium plumbite solutions differing in concentration of alkali and in ratio of alkali to lead oxide, and *n*-butyl, *n*-hexyl, *n*-octyl, *sec*.-propyl, *sec*.-butyl, and *sec*.-octyl mercaptans, were studied quantitatively, and qualitative observations were also made with the complete secondary series from propyl to nonyl mercaptans. Both neutral and basic lead mercaptides were formed and marked differences were found between corresponding members of the secondary and normal series. The lead mercaptides studied behave like organic compounds and are mostly soluble in organic solvents. Both the neutral and basic lead derivatives of *n*-octyl mercaptan were isolated. The latter are more soluble and deeper in colour than the former. The decomposition of lead mercaptides accompanied by formation of lead sulphide is discussed. H. S. GARLICK.

**Auto-oxidation of lead mercaptides.** E. OTT and E. E. REID (Ind. Eng. Chem., 1930, 22, 882—884).—By the oxidation of lead mercaptides in the solid form and in benzene solution with atmospheric oxygen insoluble yellow substances possessing strong peroxide qualities are obtained. Such peroxides were obtained from the lead mercaptides of the *n*-mercaptans from ethyl to nonyl and the secondary



mercaptans from propyl to nonyl. No peroxide was obtained from the lead derivative of thiophenol; this is only slightly soluble in benzene, and benzyl mercaptan forms slowly from it. Pure compounds were not obtained except in the case of the *sec.*-butyl derivative. A case of inhibited peroxide formation was noticed. Peroxides of similar appearance and reaction may be prepared by direct action of hydrogen peroxide solution on lead mercaptide solutions.

H. S. GARLICK.

**Reactions of lead mercaptides with sulphur.** E. ORT and E. E. REID (Ind. Eng. Chem., 1930, 22, 884—886).—The addition of sulphur to a solution of a lead mercaptide leads to the formation of a dark-coloured insoluble product which is not simply lead sulphide, as generally assumed. Compounds corresponding with  $\text{RS}\cdot\text{Pb}\cdot\text{S}\cdot\text{Pb}\cdot\text{SR}$  in the case of *sec.*- and *n*-butyl compounds have been isolated as brown products. The basic lead mercaptides react similarly. From the basic lead derivative of *sec.*-butyl mercaptan two compounds,  $\text{Pb}_2(\text{OH})_2\text{S}_3$  and  $\text{Pb}_2(\text{OH})_2\text{S}_4$ , are formed. In one instance an orange product developed peroxide qualities. When sulphur is added to a solution of both neutral and basic lead mercaptides reddish-brown substances are formed which are mixtures of the reaction products of each component.

H. S. GARLICK.

**Isoprenesulphon.** E. EIGENBERGER (J. pr. Chem., 1930, [ii], 127, 307—336).—The crystalline unimolecular isoprenesulphon, m. p. 63—63.5° (cf. G.P. 236,386), can be prepared in a yield of 60% from isoprene and sulphur dioxide in ethereal solution at 100° for 5 hrs. It is decomposed into its components at 120°, but not by boiling 0.5*N*-alkali; concentrated alkali induces decomposition, and not fission into the sulphinic acid. Oxidation yields a disulphon,  $\text{C}_{10}\text{H}_{20}\text{O}_8\text{S}_2$ , m. p. 130°. Its constitution as  $\beta$ -methyl- $\Delta^2$ -butene- $\alpha\delta$ -sulphon,  $\begin{matrix} \text{CH}-\text{CH}_2 \\ | \quad \quad | \\ \text{CMe}-\text{CH}_2 \end{matrix} > \text{SO}_2$ , is proved by the conversion of its dibromide, m. p. 127° (decomposed by boiling water into  $\gamma$ -bromo- $\beta$ -methylbutan- $\beta$ -ol- $\alpha\delta$ -sulphon, m. p. 67—68° and hydrogen bromide), by hot methyl-alcoholic sodium hydroxide into  $\gamma$ -methoxy- $\beta$ -methyl- $\Delta^2$ -butene- $\alpha\delta$ -sulphon, m. p. 44—45° (dibromide, m. p. 151—152°), by loss of 1 mol. of hydrogen bromide, and replacement of the remaining bromine atom; this is hydrolysed by 2*N*-sulphuric acid to  $\beta$ -methylbutan- $\gamma$ -one- $\alpha\delta$ -sulphon,  $\begin{matrix} \text{CHMe}-\text{CH}_2 \\ | \quad \quad | \\ \text{CO}-\text{CH}_2 \end{matrix} > \text{SO}_2$ , m. p. 180° (phenylhydrazine, m. p. 167°), which, finally, is converted by aqueous alkali into  $\delta$ -hydroxy- $\beta$ -methylbutan- $\gamma$ -one- $\alpha$ -sulphinic acid,  $\text{SO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ , the relative positions of the hydroxyl and carbonyl groups in which are established by its isolation as the phenylhydrazine salt of the osazone.

By the use of less alkali in the cold, the main product from isoprenesulphon dibromide is a polymeride of  $\beta$ -methyl- $\Delta^2$ -butadiene- $\alpha\delta$ -sulphon, which, in presence of excess of methyl-alcoholic sodium methoxide, takes up methyl alcohol with formation of the methoxy-compound (m. p. 44—45°). Its constitution as an allene derivative is assumed on account of its ready oxidisability and generally un-

saturated nature, except towards bromine, and from its degradative oxidation by alkaline permanganate, by which means derivatives of  $\delta$ -aldehydo- $\gamma$ -keto- $\beta$ -hydroxy- $\beta$ -methylbutanesulphinic acid (phenylhydrazine and potassium salts of the osazone) and of  $\beta$ -keto- $\alpha$ -hydroxypropanesulphonic acid (phenylhydrazine salt of osazone) appear to have been obtained. On oxidation with nitric acid an amorphous substance,  $(\text{C}_5\text{H}_8\text{O}_4\text{S})_x$ , apparently a dihydroxy-derivative, is obtained.

H. A. PIGGOTT.

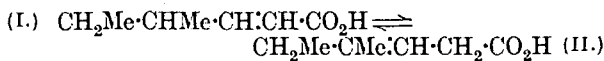
**Reaction for formic acid.** M. MASRIERA (Anal. Fis. Quím., 1930, 28, 916—931).—The substance to be tested is dissolved in a small quantity of ether or chloroform, and 2 vols. of light petroleum and a little aniline are added. The separation of white needles, m. p. 64°, indicates the presence of formic acid. The reaction cannot be employed quantitatively, since the aniline formate always contains an excess of aniline and on drying tends to become converted into formanilide, whilst titration of the precipitate with sodium hydroxide yields low results. The sensitivity of the reaction varies from 1:40 to 1:1000, according to the solvents used. The partition coefficients of formic and acetic acids between water and ether at 12° are 0.515 and 0.557, and between water and chloroform 0.120 and 0.128, respectively.

H. F. GILLBE.

**Products of the action of chlorosulphonic acid on butyryl chloride at the ordinary temperature.** M. KRAJČINOVIČ (Ber., 1930, 63, [B], 2276—2278; cf. A., 1929, 540).—Carbon monoxide and hydrogen chloride are continuously evolved from a mixture of butyryl chloride and chlorosulphonic acid at the ordinary temperature. The main isolable product is di-*n*-propyl ketone.  $\alpha$ -Sulphobutyric acid does not appear to be formed. With increasing length of hydrocarbon chain in the acyl chloride, the tendency towards condensation appears to diminish.

H. WREN.

**Olefinic acids. III. Homologues of tereaconic, terebic, and pyroterebic acids.** Further evidence of effect of two  $\gamma$ -alkyl groups on three-carbon tautomerism. R. P. LINSTAD and J. T. W. MANX (J.C.S., 1930, 2064—2073; cf. A., 1927, 1167).—The tautomeric change in alkaline solution between  $\gamma$ -methyl- $\Delta^4$ -hexenoic acid (the " $\alpha\beta$ -acid," I) and  $\gamma$ -methyl- $\Delta^5$ -hexenoic acid (the " $\beta\gamma$ -acid," II):



leads to an equilibrium mixture containing about 77% of  $\beta\gamma$ -acid, the mobility  $10(k_1+k_2)$  being 3.1(*t* hrs.); when derived from I it readily gives the ethyl ester of II on partial esterification (cf. Sudborough and Thomas, J.C.S., 1911, 99, 2307; Eccott and Linstead, A., 1929, 1271). Like pyroterebic acid, both isomerides tend to form additive products with hydrogen chloride, rendering difficult the preparation of derivatives through the acid chloride.

$\gamma$ -Methyl- $\gamma$ -ethylitaconic acid (III) and  $\gamma$ -methyl- $\gamma$ -ethylitaconic acid (IV) were obtained by an improvement of Stobbe's method (A., 1895, i, 142; 1902, i, 461). Both are converted into a mixture of

$\gamma$ -methyl- $\gamma$ -ethylisoparaconic acid, m. p. 128° (probably identical with Stobbe's acid, m. p. 125—126°), and  $\gamma$ -methyl- $\gamma$ -ethylparaconic acid (V), m. p. 146°, by heating with aqueous mineral acids; the former predominated in the case of III, and the latter in that of IV. Apparently III and IV are slowly interconvertible in the acid solution. These lactonic acids are difficult to separate, and Sircar's " $\gamma$ -methyl- $\gamma$ -ethylparaconic acid," m. p. 131—132° (A., 1927, 756), is probably a mixture. An alternative route to V is by hydrolysis of the fraction, b. p. 150—170°/15 mm., obtained in small yield by the interaction of ethyl acetosuccinate with magnesium ethyl iodide. When rapidly distilled by heating at 260° (cf. Goldberg and Linstead, A., 1928, 1214) V gives  $\gamma$ -methyl- $\Delta^{\beta}$ -hexenoic acid (II), b. p. 118°/12 mm.,  $d_4^{20}$  0.9644,  $n_D^{20}$  1.4512 (chloride, b. p. 64—68°/16 mm.; anilide, m. p. 91°), and  $\gamma$ -methyl- $\gamma$ -ethylbutyrolactone (Grignard, A., 1903, i, 141). The product of reduction of  $\gamma$ -methylsorbic acid, described as II by Auwers and Heyna (A., 1924, i, 8), is apparently a mixture.

$\alpha$ -Methylbutaldehyde (semicarbazone, m. p. 103°), from magnesium *sec*-butyl bromide and ethyl orthoformate, condenses with malonic acid in pyridine to  $\gamma$ -methyl- $\Delta^{\alpha}$ -hexenoic acid (I), b. p. 125°/13 mm.,  $d_4^{20}$  0.9441,  $n_D^{20}$  1.4526 (chloride, b. p. 65—66°/11 mm.; anilide, m. p. 110°; *p*-toluidide, m. p. 92°).

H. A. PIGGOTT.

**Conjugated double linkings. XIII. Synthesis of unsaturated, coloured, fatty acids.** R. KUHN and M. HOFFER (Ber., 1930, 63, [B], 2163—2174).—According to expectation (Kuhn and Winterstein, A., 1929, 1456) with regard to the influence of conjugated ethylenic linkings on the colour of compounds, octatrienoic acid is colourless, whereas decatrienoic acid is intensely yellow. Conversion of the acids into their salts causes a lightening of the colour.

A mixture of crude hexadienal and octatrienal is readily formed by the action of secondary amines, such as piperidine, on acetaldehyde or mixtures of acetaldehyde and crotonaldehyde; distillation of the mixture suffices to give fractions sufficiently pure for further work. Hexadienal is produced by condensation of crotonaldehyde with acetaldehyde and further converted by the last-named substance into octatrienal; formation of octatrienal from 2 mols. of crotonaldehyde does not occur under the experimental conditions adopted. From the hexadienal fraction the semicarbazone, m. p. 206° (decomp.) (cf. Baumgarten and Glatzel, A., 1927, 43), and the very characteristic azine,  $C_{12}H_{16}N_2$ , m. p. 173.2—173.5° (corr., slight decomp.), are readily produced. When heated with malonic acid and pyridine, hexadienal yields  $\Delta^{\gamma\gamma}$ -octatrienoic acid, m. p. 189—189.5° (corr., slight decomp.) (sodium, calcium, barium, copper, mercuric, and silver salts).  $\Delta^{\gamma\gamma}$ -Octatrienoyl chloride, from the acid and thionyl chloride, is transformed into methyl  $\Delta^{\gamma\gamma}$ -octatrienoate, m. p. 75.2—75.6° (corr.), and  $\Delta^{\gamma\gamma}$ -octatrienoamide, m. p. 196.7—197.7° (corr., decomp.). Catalytic reduction of the acid in presence of platinum oxide affords octoic acid [amide, m. p. 100—101.5° (corr.)]. From the octatrienal fraction are obtained octatrienalazine, decomp. 220—225° (corr.) when introduced into a bath preheated at 200°, octatrienal-

hydrazone, softening at 153—154° (corr.), octatrienaloxime, m. p. 186—187° (corr., decomp.), and a semicarbazone, decomp. about 250°. With pyridine and malonic acid the aldehyde affords  $\Delta^{\gamma\gamma}$ -decatetraenoic acid, m. p. (according to Berl) 210—211° (corr., decomp.), or m. p. up to 220° when more slowly heated; if heating is started at the ordinary temperature, the acid does not melt, but begins to carbonise at about 200°. The sodium, calcium, and barium salts are described. Methyl  $\Delta^{\gamma\gamma}$ -decatetraenoate, m. p. 135—136° (corr.), and  $\Delta^{\gamma\gamma}$ -decatetraenoamide, decomp. about 200°, are prepared from the chloride. Hydrogenation of the acid in presence of platinum oxide gives decoic acid (amide, m. p. 94—94.5°). The colour reactions of the azine and acids with concentrated sulphuric acid, formic acid, arsenic trichloride, and antimony trichloride are recorded.

H. WREN.

**Transformation of erucic into brassidic acid by means of sulphur.** G. RANKOFF (Ber., 1930, 63, [B], 2139—2142; cf. this vol., 65).—Treatment of erucic acid with flowers of sulphur and water at 180° or with saturated sodium hydrogen sulphite at 150° yields brassidic acid, m. p. 61.5° (corr.),  $n_D^{20}$  1.4347, after exhaustive purification by crystallisation and through the sodium salt. Simultaneously an acid containing sulphur is produced in minor amount which raises the m. p. of the product. The isomerising agent is sulphur, not sulphurous acid.

H. WREN.

**Preparation of  $\gamma$ -[butyrolactones.** W. L. NELSON and L. H. CRETCHER (J. Amer. Chem. Soc., 1930, 52, 3702—3704).—Hydrolysis of ethyl vinyloxyethylmalonate with concentrated aqueous potassium hydroxide, acidification of the mixture with hydrochloric acid (1:1), evaporation of the solution to dryness in a vacuum, extraction with ether, and thermal decomposition of the resultant acid affords  $\gamma$ -butyrolactone in 72% yield. *Brucine  $\gamma$ -hydroxybutyrate* has m. p. 147—148° after softening at 80°,  $[\alpha]_D^{20}$  -26.97° in water. Sodium  $\gamma$ -hydroxybutyrate is obtained from the lactone in 89% yield.  $\alpha$ -Ethyl-, b. p. 214—218°, and  $\alpha$ -propyl- $\gamma$ -butyrolactones, b. p. 230—235°,  $d_4^{20}$  1.008, are obtained similarly from ethyl ethyl- and propyl-vinyloxyethylmalonates, respectively.

H. BURTON.

**Reaction of bromine with aliphatic acids. IV. Succinic acid.** E. D. HUGHES and H. B. WATSON (J.C.S., 1930, 1733—1740).—Bromine and succinic acid do not react in open vessels; in sealed tubes, in the presence of absence of water, reaction is complete after 2—4 days at 100°, giving (from 2 mols. of bromine) a theoretical yield of dibromosuccinic acid or (from 1 mol. of bromine) dibromosuccinic acid and succinic acid. When large quantities of water are present the yield of dibromo-acid is decreased and brominated hydrocarbons are produced. *meso*-Dibromosuccinic acid is always alone produced. The introduction of the first bromine atom is probably preceded by enolisation, but the mechanism of further substitution is not deduced with certainty.

Interaction of succinic acid with 2 mols. of phosphorus pentabromide affords *succinyl bromide*, b. p. 105—106°/13 mm. Bromination of this leads, after

heating for 4 hrs. at 90°, to bromosuccinyl bromide, which, in turn, slowly yields a mixture of isomeric dibrominated bromides.

The bromination of succinic anhydride to produce the monobrominated anhydride, b. p. 130–133°/11 mm., is considered to proceed through the intermediate formation of an acid bromide. A mechanism for the bromination of succinic acid by the Hell-Volhard method is also given.

R. J. W. LE FÈVRE.

**Walden inversion.** III. H. N. K. RÖRDAM (J.C.S., 1930, 2017–2026).—A rigid mathematical discussion of the hypothesis put forward to explain this inversion (cf. A., 1928, 1215; 1929, 1041). By the application of the classical distribution law equations as applied to colliding reacting ions in solution a general equation is deduced relating the fraction of the product which retains its original configuration, and the concentration of the entering group. Further experimental results are given on the reaction between sodium *l*-bromosuccinate and potassium xanthate over a wide range of concentrations of components in the presence of neutral salts. By making certain assumptions, the results can be compared with the theoretical expectations over the wide range of concentration examined experimentally and the frequency of the postulated primary oscillation underlying the phenomenon of the inversion (*loc. cit.*) is calculated.

J. O. CUTTER.

**Direction of addition of hydrogen bromide to  $\alpha$ -methyleneglutaric acid.** J. W. BAKER (Proc. Leeds Phil. Soc., 1930, 2, 115–119).—Hydrolysis of  $\gamma$ -cyano- $\gamma$ -valerolactone, prepared by the method of Block, Kreckeler, and Tollens (Annalen, 1887, 238, 287), or of crude ethyl  $\gamma$ -cyano- $\gamma$ -hydroxyvalerate (Ulté, A., 1909, i, 293) with anhydrous alcoholic hydrogen bromide affords ethyl  $\alpha$ -hydroxy- $\alpha$ -methylglutarate, b. p. 115°/3 mm.,  $n_D^{20}$  1.4375, which is also obtained by the action of ethyl iodide on a boiling ethereal suspension of the corresponding silver salt (Block and others, *loc. cit.*). It is converted by phosphorus pentabromide in dry benzene into the crude bromo-ester, which, however, cannot be purified, since it readily passes on distillation even under reduced

pressure into the lactonic ester,  $\text{CH}_2\text{CH}_2\text{CO} > \text{O}$ , b. p. 99°/2.3 mm.,  $n_D^{20}$  1.4401 (Block, *loc. cit.*), with elimination of ethyl bromide. The same lactonic ester is obtained from ethyl  $\alpha$ -hydroxy- $\alpha$ -methylglutarate by distillation under atmospheric pressure or by treatment with phosphorus tribromide. Hydrolysis of ethyl  $\alpha$ -hydroxy- $\alpha$ -methylglutarate with boiling 20% sodium hydroxide affords an acid the equivalent of which (119.9) is intermediate between that of the hydroxy-dibasic acid (81) and the lactonic monobasic acid (144), and is converted into the pure lactonic acid, m. p. 73°, by distillation. Hydrolysis of crude ethyl  $\alpha$ -bromo- $\alpha$ -methylglutarate with hydrobromic acid affords a liquid acid product which could not be induced to crystallise even after seeding with a specimen of the bromo-acid, m. p. 112°, obtained by the addition of hydrogen bromide to  $\alpha$ -methyleneglutaric acid (von Pechmann and Röhm, A., 1901, i, 253), whilst hydrolysis with concentrated

hydrochloric acid gives, in small yield, an acid, m. p. 146–147°, not further investigated, the analytical data for which agree best with the structure of a dibromomethylglutaric anhydride. Although not conclusive, the evidence adduced suggests that the hitherto unoriented bromo-acid obtained by von Pechmann and Röhm is  $\alpha$ -(bromomethyl)glutaric acid ( $\delta$ -bromo- $\gamma$ -carboxyvaleric acid), addition of hydrogen bromide to  $\alpha$ -methyleneglutaric acid occurring in the direction anticipated from Burton and Ingold's theory (A., 1928, 634) of addition to conjugated compounds. Hydrolysis of the acid fraction, obtained in the addition of hydrogen cyanide to laevulic acid, with alcoholic hydrogen bromide yields (?) ethyl  $\alpha$ -ethoxy- $\alpha$ -methylglutarate, b. p. 200°/763 mm., 84.5–85°/3.5 mm., together with a smaller quantity of the corresponding hydroxy-ester.

J. W. BAKER.

**Complex acids of Japan wax.** Heneicosane- $\alpha$ -dicarboxylic acid,  $\text{C}_{23}\text{H}_{44}\text{O}_4$ . B. FLASCHENTRÄGER and F. HALLE (Z. physiol. Chem., 1930, 190, 120–140).—Repeated fractionation of the "japanese acid" fraction of Japan wax yielded eicosane- $\alpha$ -carboxylic acid,  $\text{C}_{21}\text{H}_{42}\text{O}_2$ , m. p. 74° (0.06% on the wax), and heneicosane- $\alpha$ -dicarboxylic acid,  $\text{C}_{23}\text{H}_{44}\text{O}_4$ , m. p. 127.5° (0.3% on the wax). The following esters of the latter were prepared: methyl, m. p. 70.8°; methyl hydrogen, m. p. 87°; ethyl, m. p. 61.5°; ethyl hydrogen, m. p. 83.3°. All m. p. are corr.

J. H. BIRKINSHAW.

**Synthesis of  $\alpha$ -methyl- $\alpha'$ -carboxyglutaric acid.** F. VOCKE (Z. physiol. Chem., 1930, 191, 83–85).—Treatment of  $\alpha$ -methylacrylic acid in methyl-alcoholic solution with hydrogen bromide yields methyl  $\beta$ -bromoisobutyrate, b. p. 65–67°/12 mm., which with ethyl malonate and sodium gives ethyl  $\beta$ -carbomethoxypropylmalonate, b. p. 240–250°/14 mm. On hydrolysis with 18% hydrochloric acid the ester loses carbon dioxide, yielding  $\alpha$ -methylglutaric acid, but *N*-alcoholic potassium hydroxide gives  $\alpha$ -methyl- $\alpha'$ -carboxyglutaric acid, m. p. 161° (decomp.).

J. H. BIRKINSHAW.

**Hydroxy-acids of the sugar group.** II. K. REHORST (Ber., 1930, 63, [B], 2279–2292; cf. A., 1928, 272).—Re-examination of *d*-gluconic acid shows that whereas its conversion into the lactone occurs in aqueous solution at the ordinary temperature, and the lactone separates from the moderately warm aqueous solution, the free acid is always exclusively formed when the solutions are immediately evaporated over boiling water. *l*-Arabonic acid is obtained crystalline by decomposing the barium salt with sulphuric acid and cautious evaporation of the aqueous solution after addition of ethyl and isobutyl alcohol. It has m. p. 118–119°,  $[\alpha]_D -10.02^\circ$  to  $-7.11^\circ$  to  $-41.6^\circ$  in water. Following Levene and Simms (A., 1925, i, 1380), the course of the change in the specific rotation is ascribed to a superposition of two actions, the rapid formation of the  $\delta$ -lactone and the slower but more persistent production of the  $\gamma$ -lactone. If the two lactones rotate in the same sense, which, according to Hudson's first rule, is the case when the hydroxyl groups attached to the  $\gamma$ - and  $\delta$ -carbon atoms are in the *cis*-position, an inflexion is scarcely

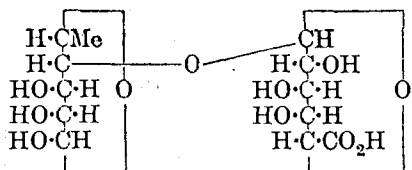
to be expected and has never been observed. If, however, the hydroxyl groups are in the *trans*-position, the lactones rotate in a different sense; the rotation of the acid initially tends towards that of the  $\delta$ -lactone and when the formation of this compound has been completed and the production of the  $\gamma$ -lactone slowly proceeds the rotation graph turns in the other direction. Such inflexions are observed in the cases of *d*-galactonic, *d*-gulonic, and *d*- $\alpha$ -glucoheptonic acids. If these considerations are applicable to the pentonic

acids, *l*-arabonic acid must have the configuration I and inflexions in the graphs of all eight pentonic acids are to be expected; this is the case with *d*-xylonic acid,  $[\alpha]_D^{20} -1.9^\circ$  to  $-3.6^\circ$  to  $+20.2^\circ$ .

(I.) Preparation of *l*-rhammonic acid from strontium *l*-rhamnonate by decomposition with sulphuric acid and treatment with water, ethyl and amyl alcohols could not be effected, since lactonisation is retarded only by the alcohols. Very rapid manipulation leads to a mixture of the free acid and its  $\delta$ -lactone in about equal proportions. Usually *l*-rhamnono- $\delta$ -lactone, m. p.  $171-179^\circ$  after softening at about  $150^\circ$ ,  $[\alpha]_D^{20} -97.14^\circ$  to  $-34.70^\circ$  in water, is obtained. It is converted by evaporation with 1% hydrochloric acid into *l*-rhamnono- $\gamma$ -lactone, m. p.  $148-150^\circ$ ,  $[\alpha]_D^{20} -38.54^\circ$  to  $-37.78^\circ$  in water. Sodium *l*-rhamnonate obtained from either lactone has  $[\alpha]_D^{20} +17.32^\circ$  in water. The acid from the sodium salt has  $[\alpha]_D^{20} +11.03^\circ$  to  $-28.13^\circ$  in water.

H. WREN.

**Composition of an aldobionic acid from flaxseed mucilage.** E. ANDERSON and J. A. CROWDER (J. Amer. Chem. Soc., 1930, 52, 3711-3715).—The air-dried mucilage is hydrolysed with 4% sulphuric acid at  $100^\circ$  (bath), the solution neutralised with calcium carbonate, concentrated in a vacuum, and the calcium aldobionate precipitated with alcohol; the barium salt is prepared similarly. Treatment of the calcium salt with bromine in 6% hydrobromic acid affords a mixture of mucic and rhammonic acids. *l*-Rhamnose is isolated from the hydrolysis product of the salts. The aldobionic acid is a compound of *l*-rhamnose and *d*-galacturonic acid; the last-named acid is identified by the method of Heidelberger and Goebel (A., 1927, 1114). The following structure is suggested for the aldobionic acid.



H. BURTON.

**Salts and esters of humic acids.** W. FUCHS and O. HORN (Brennstoff-Chem., 1930, 11, 372-375).—The potassium salts of three humic acids which were insoluble in aqueous potassium hydroxide, and of the corresponding nitrohumic acids, have been prepared by treating the acids with an alcoholic solution of potassium acetate, and also by the hydrolysis of the methylated acids with alcoholic potassium hydroxide.

The potassium content of the salts prepared by the latter method agreed well with the values calculated from the ester-methoxyl contents of the methylated acids. The salts prepared by the former method had in some cases a higher potassium content than corresponded with the carboxyl groups present, showing that the hydroxyl groups may also take part in the salt formation. The ratios of carboxyl to hydroxyl groups in the three humic acids were 1:1, 1:4, and 1:3, respectively, and in the corresponding nitrohumic acids 1:1, 1:1, and 1:2, respectively. The salts exhibited the phenomenon of base exchange shown by the raw brown coals; e.g., by treating them with a solution of ammonium chloride the potassium was completely replaced by ammonium.

A. B. MANNING.

**Fission of ethylenedisulphonylacetic acid in alkaline solution.** Sulphinoacetic acid and  $\beta$ -hydroxyethylsulphonylacetic acid. J. A. REUTERSKIÖLD (J. pr. Chem., 1930, [ii], 127, 269-276).—Ethylenedisulphonylacetic acid (Tiberg, A., 1916, i, 789) is hydrolysed by excess of alkali in accordance with the equation:  $\text{C}_2\text{H}_4(\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Na})_2 + \text{NaOH} \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Na} + \text{CH}_2(\text{CO}_2\text{Na})\cdot\text{SO}_2\text{Na}$ ; the reaction can be followed titrimetrically. From the neutral solution strontium chloride and acetone precipitate *strontium sulphinoacetate*, from which the *silver* salt is obtained. The sulphinoacetates are decomposed by dilute acids into sulphur dioxide and acetic acid; the strontium salt is oxidised by hydrogen peroxide to the sulphoacetate (cf. Stilleh, A., 1906, i, 552). The free acid cannot be isolated, but may be obtained in acetone solution, fairly stable at  $-70^\circ$ , by decomposition of the suspended silver salt by dry hydrogen chloride.

*Lead*  $\beta$ -hydroxyethylsulphonylacetate ( $+1\text{H}_2\text{O}$ ) may be precipitated from the mother-liquors after separation of strontium and chloride; incomplete precipitation occurs, however, in the presence of other salts, particularly sodium acetate. The free acid, m. p.  $87-89^\circ$ , is obtained by decomposition of the lead salt with hydrogen sulphide. Bromination of an aqueous solution of the sodium salt (containing chloride and acetate) gives  $\beta$ -(*dibromomethylsulphonyl*)-ethyl ether, m. p.  $126.5-127.5^\circ$ . An apparatus for the determination of sulphur dioxide by absorption in hydrogen peroxide is described. Carbon dioxide, if present, can subsequently be absorbed in a standard form of apparatus.

H. A. PIGGOTT.

**Morphology of substances of high mol. wt. I. Fibre formation with polyoxymethylenes.** H. W. KOHLSCHÜTTER (Annalen, 1930, 482, 75-104).—In connexion with the work of Staudinger on the constitution of polyoxymethylenes (cf. this vol., 579), the sublimation products of certain polyoxymethylene preparations are found to be composed of fibres which, formerly regarded as relatively simply built up, being oriented along the length of the molecule (cf. A., 1927, 647), are actually very diverse in nature; they are classified as complicated structural forms, the character of which depends on a fine gradation of chemical differences.

Polyoxymethylene when heated in the presence of a trace of sulphuric acid is dissociated into gaseous

formaldehyde and trioxymethylene; the latter accelerates the repolymerisation of formaldehyde. Moreover supercooled trioxymethylene (m. p. about 64°) dissolves formaldehyde, and when the solution crystallises the meanwhile polymerised product separates in a definitely oriented way, and an aggregate of more or less pronounced "fibre structure" results.

Trioxymethylene may also separate from the gaseous phase in needle crystals; the polyoxymethylene formed by condensation of formaldehyde on the surfaces will then also possess an orientation (as far as the sphere of activity of the crystal surface extends). In either case the trioxymethylene occupies the rôle of framework, a macroscopic fibre consisting of a pseudomorph of polyoxymethylene on a trioxymethylene crystal.

Trioxymethylene can itself undergo a kind of lattice conversion, by which it approximates in its properties to complex polyoxymethylenes, and then forms an integral part of the fibre structure. This change occurs under the influence of the polymerising formaldehyde even during crystal growth and leads to particularly stable polyoxymethylene fibres, of stable uniform inner structure.

By systematic variation of the sublimation conditions it has been possible to reproduce all shades of physical, chemical, and morphological difference. R. CHILD.

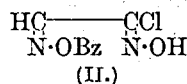
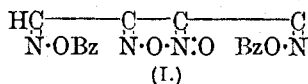
**Reaction between citronellal and organo-magnesium halides.** H. GILMAN and W. F. SCHULZ (J. Amer. Chem. Soc., 1930, 52, 3588—3590).—Treatment of the reaction product from citronellal and an excess of magnesium benzyl chloride with carbon dioxide affords phenylacetic acid as the only recognisable acidic product. It is concluded from this that, contrary to the statement of Rupe and Jäger (A., 1914, i, 131), addition of the Grignard reagent across the ethylenic linking does not occur. Similarly, addition does not take place with magnesium phenyl and *n*-butyl bromides. H. BURTON.

**Preparation of methylglyoxal solutions.** C. NEUBERG and E. HOFMANN (Biochem. Z., 1930, 224, 491—497).—When glyceraldehyde obtained by oxidation of glycerol with hydrogen peroxide in the presence of ferrous sulphate by a modification of the method of Witzemann (A., 1914, i, 1165) or dihydroxyacetone, from glycerol by the action of *Acetobacter suboxydans*, is distilled with 20% sulphuric acid according to the procedure of Neuberg and others (A., 1918, i, 91) solutions of methylglyoxal are obtained. W. MCCARTNEY.

**Volumetric determination of acetone.** A. MEYER and S. MATHIEY (Compt. rend., 1930, 191, 490—493).—Acetone is precipitated with mercuric sulphate and the residual mercury in the solution is titrated with potassium thiocyanate, using ferric ammonium sulphate as indicator. This method is applicable to industrial acetone liquors, methyl alcohol, and urines containing acetone. C. C. N. VASS.

**Dioximes.** LXIV. G. PONZIO and F. BALDRACCO. LXV. G. PONZIO. LXVI. G. PONZIO and F. DURIO (Gazzetta, 1930, 60, 415—429, 429—436, 436—448).—LXIV.  $\beta$ -Chloroglyoxime, m. p. 168° (decomp.), termed *anti*-chloroglyoxime by Hantzsch (A., 1892, i, 699), when heated with benzoyl

chloride (1 mol.) at 100° gives 2-benzoyl- $\beta$ -chloroglyoxime,  $\text{CH}(\text{N} \cdot \text{OBz}) \cdot \text{CCl} \cdot \text{N} \cdot \text{OH}$ , m. p. 165°, converted by agitation of its ethereal solution with 5% sodium carbonate, or by water at 100°, into the dibenzoyl derivative of  $\alpha$ -isocyanilic acid, m. p. 183—185° (Wieland, A., 1925, i, 1048; Steinkopf, A., 1910, i, 305). Adopting Wieland's configuration I for dibenzoyl- $\alpha$ -isocyanilic acid, 2-benzoyl- $\beta$ -chloroglyoxime should possess the structure II, wherefore  $\beta$ -chloroglyoxime must be an *amphi*-form.



With acetic anhydride and sodium acetate, 2-benzoyl- $\beta$ -chloroglyoxime yields 2-benzoyl-1-acetyl- $\beta$ -chloroglyoxime, m. p. 120°, whilst excess of benzoyl chloride at 100° gives dibenzoyl- $\beta$ -chloroglyoxime, m. p. 165° (III), also obtained directly from  $\beta$ -chloroglyoxime under the same conditions, and identical with the compound obtained by Wieland and Kitasato, (A., 1929, 1468) from metazonic acid,  $\text{CH}(\text{N} \cdot \text{OH}) \cdot \text{CH} \cdot \text{NO} \cdot \text{OH}$ , by treatment with benzoyl chloride in pyridine at low temperature. The *amphi*-configuration for the  $\beta$ -chloroglyoxime, which follows from the foregoing facts, is supported by the observation that contrary to the assertion of Hieber and Leutert (A., 1929, 1073)  $\beta$ -chloroglyoxime gives no nickel complex with nickel acetate in the presence of dilute acetic acid (cf. Atack, J.C.S., 1913, 103, 1318); neither in absence of acetic acid nor in alcoholic solution does complex formation occur.

$\alpha$ -Chloroglyoxime, termed *amphi*-chloroglyoxime by Hantzsch (*loc. cit.*), obtained as the monohydrate, m. p. 151° (decomp.), in 50% yield by a modification of Hantzsch's method, is converted quantitatively by ethereal hydrogen chloride into  $\beta$ -chloroglyoxime. Similarly, dibenzoyl- $\alpha$ -chloroglyoxime (IV), m. p. 165° (improved preparation described), by treatment with hydrogen chloride yields dibenzoyl- $\beta$ -chloroglyoxime. These results are discussed with reference to Brady's observations on the benzoylation of *syn*-aldoximes (J.C.S., 1922, 121, 2098; 1925, 127, 1357). The authors conclude that it is necessary to exchange the configurations hitherto adopted for the forms of chloroglyoxime.

The  $\alpha$ - and  $\beta$ -chloroglyoximes exhibit a large difference in the reactivity of the chlorine atom; thus  $\beta$ - (but not  $\alpha$ -)chloroglyoxime by treatment in alcoholic solution with gaseous ammonia gives aminoglyoxime,  $\text{CH}(\text{N} \cdot \text{OH}) \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{NH}_2$ , m. p. 152° [nickel derivative,  $(\text{C}_2\text{H}_4\text{O}_2\text{N}_3)_2\text{Ni}$  (cf. Steinkopf, *loc. cit.*)], also obtained from dibenzoyl- $\beta$ -chloroglyoxime in ethyl acetate solution with gaseous ammonia, and by agitation with sodium acetate in acetic acid solution affords hydroxyglyoxime, m. p. 135° (tribenzoyl derivative, m. p. 142—143°; cf. A., 1927, 135). Dibenzoyl- $\beta$ -chloroglyoxime by agitation with 6*N*-ammonia solution gives 2-benzoyl-1-aminoglyoxime,  $\text{CH}(\text{N} \cdot \text{OBz}) \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{NH}_2$ , m. p. 157—158°, also obtained from 2-benzoyl- $\beta$ -chloroglyoxime by the same method, giving a red colour with ferric chloride, and 2-benzoyl-1-acetyl-1-aminoglyoxime,  $\text{CH}(\text{N} \cdot \text{OBz}) \cdot \text{C}(\text{N} \cdot \text{OAc}) \cdot \text{NH}_2$ , m. p. 145—146°, with acetic anhydride.

The nickel dipotassium salt of  $\alpha$ -chloroglyoxime (Hieber and Leutert, *loc. cit.*) is prepared in the same way and has the same composition and properties as the complex salts of hydroxamic acids (Ley and Männchen, A., 1913, i, 346); also  $\alpha$ -chloroglyoxime resembles the hydroxamic acids by forming ammonium and aniline salts, whilst it exhibits none of the properties characteristic of the group  $-\text{CCl:N}\cdot\text{OH}$ . The structure  $\text{CH}(\text{N}\cdot\text{OH})\cdot\text{CCl}(\text{OH})\cdot\text{NH}\cdot\text{OH}$  is therefore suggested for the  $\alpha$ -chloroglyoxime hydrate, which by treatment with hydrogen chloride loses a molecule of water to give the true  $\beta$ -chloroglyoxime. (II, III, and IV, all of which have m. p.  $165^\circ$ , give m.-p. depressions).

LXV. The monoximes of  $\alpha$ -diketones (isonitroso-ketones) readily undergo the reaction ("disproportionation"):  $2\text{CR}(\text{N}\cdot\text{OH})\cdot\text{COR}' \rightarrow \text{R}\cdot\text{CO}\cdot\text{COR}' + \text{CR}(\text{N}\cdot\text{OH})\cdot\text{CR}'\text{N}\cdot\text{OH}$  (cf. Thilo, A., 1929, 681; Diels and Stern, A., 1907, i, 480). Thus oximino-methyl ethyl ketone by treatment with dilute hydrochloric and sulphuric acids at  $45$ – $50^\circ$  yields 25% and 10% of dimethylglyoxime, respectively.

The diacetylglyoximedioxime peroxide, m. p.  $145^\circ$  (Ponzio, A., 1924, i, 56), obtained from methylchloroglyoxime,  $\text{CMe}(\text{N}\cdot\text{OH})\cdot\text{CCl:N}\cdot\text{OH}$ , by treatment with sodium carbonate, is identical with the form of m. p.  $138$ – $139^\circ$  (Behrend and Tryller, A., 1895, i, 201), and gives a dibenzoyl derivative identical with the compound prepared by Avogadro and Vianello from 2-benzoylmethylchloroglyoxime. The isomerism underlying the forms of m. p.  $145^\circ$  and  $189$ – $190^\circ$  (Behrend and Schmitz, A., 1894, i, 108) is discussed.

Treatment of the diacetyl derivative, m. p.  $163^\circ$ , of dichloroglyoxime, m. p.  $201^\circ$  (decomp.) (Houben and Kauffmann, A., 1913, i, 1159), with gaseous ammonia in ethyl acetate solution gives diaminoglyoxime,  $\text{NH}_2\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NH}_2$ , m. p.  $196^\circ$  (decomp.), identical with the product of the action of cyanogen on hydroxylamine (Fischer, A., 1889, 1163; Houben and Kauffmann, *loc. cit.*). The anomalous behaviour of diaminoglyoxime toward acetic anhydride described by Houben and Kauffmann has been investigated, and precise directions are given for the preparation of the diacetyl derivative, m. p.  $184^\circ$ , and 5 : 5'-dimethylbisfuro-3 : 3'-diazolyl, m. p.  $165$ – $166^\circ$ .

Chlorobromoglyoxime, m. p.  $222$ – $223^\circ$  (diacetyl derivative, m. p.  $160$ – $161^\circ$ ), obtained from  $\beta$ -chloroglyoxime and bromine (1 mol.) in aqueous solution, gives diphenylaminoglyoxime, m. p.  $218^\circ$  (cf. lit.), with aqueous aniline.

LXVI. Aminoglyoxime,  $\text{CR}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NH}_2$  (I;  $\text{R}=\text{H}$ ) (monohydrate; oxalate, m. p.  $159^\circ$ ), which exists in one form only, furnishes an ON-diacetyl derivative, m. p.  $154^\circ$ , which gives no colour with ferric chloride (cf. Steinkopf, *loc. cit.*); by treatment with concentrated hydrochloric acid and potassium cyanate it affords carbamidoglyoxime,  $\text{CH}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $157^\circ$  (decomp.), which gives no nickel complex.

Arylamino-glyoximes (I;  $\text{R}=\text{aryl}$ ) exist in two forms (A., 1923, i, 855, 857; 1924, i, 294; 1928, 1030); the  $\alpha$ -forms are converted into  $\beta$ -forms by dilute acetic acid, give no nickel derivatives, and yield ON-diacetyl compounds with acetic anhydride; by dehydrogenation with bromine and dilute sulphuric

acid they give peroxides. The  $\beta$ -forms afford nickel salts, give OO-diacetyl compounds with acetic anhydride, and do not give peroxides; according to the Hantzsch-Werner theory the  $\beta$ -forms possess the anti-configuration (nickel salt formation).

Alkylaminoglyoximes (I;  $\text{R}=\text{alkyl}$ ) exist in a single form only (A., 1922, i, 627; 1923, i, 853; 1926, 295), which in the case  $\text{R}=\text{Me}$  has all the properties of a  $\beta$ -form. Aminoglyoxime thus has properties characteristic of both  $\alpha$ - and  $\beta$ -forms; it is therefore impossible to assign to it any one of the four configurations provided by the Hantzsch-Werner theory. The matter is complicated by the following results. Benzoylation of aminoglyoxime by the method of Jacobs and Heidelberger (A., 1917, i, 552) furnishes 1-benzoyl-1-aminoglyoxime,  $\text{CH}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OBz})\cdot\text{NH}_2$ , m. p.  $146$ – $147^\circ$  (monohydrate, m. p.  $134$ – $137^\circ$ ), converted by cold acetic anhydride into 1-benzoyl-2-acetyl-1-aminoglyoxime, m. p.  $166$ – $167^\circ$ , and in the hot into 3-cyano-5-phenylfurodiazole,  $\text{N}=\text{CPh}$   
 $\text{C}(\text{CN})\cdot\text{N} > \text{O}$  (II),

m. p.  $62^\circ$ . The diazole is obtained similarly from the 1-benzoyl-2-acetyl compound, and from OO-dibenzoyl-1-aminoglyoxime (III), m. p.  $186$ – $187^\circ$ , prepared by benzoylation of aminoglyoxime or of its 1- or 2-benzoyl derivative by the Schotten-Baumann method. From the formation of II, it appears that aminoglyoxime is an anti-form. The compound III is also obtained from  $\beta$ -chloroglyoxime :

$\text{CH}(\text{N}\cdot\text{OH})\cdot\text{CCl:N}\cdot\text{OH} \xrightarrow{\text{BzCl}} \text{CH}(\text{N}\cdot\text{OBz})\cdot\text{CCl:N}\cdot\text{OH}$   
 $(\text{IV}) \xrightarrow{\text{NH}_3} \text{CH}(\text{N}\cdot\text{OBz})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NH}_2 \xrightarrow{\text{BzCl}} \text{III}$ . Since IV is an *amphi*-form (preceding abstract), III and consequently aminoglyoxime appear to be *amphi*-forms. These apparent contradictions are discussed, and are considered by the authors to afford evidence of the insufficiency of the Hantzsch-Werner theory.

By treatment with alcoholic sodium ethoxide (1 mol.) at  $100^\circ$ , II gives sodium benzoylcyanamide and 3-carboxylamido-5-phenylfurodiazole, m. p.  $159$ – $160^\circ$ , also obtained from II and hydrochloric acid (*d* 1.19) at  $15^\circ$  for several days. Hydrogen sulphide in alcoholic solution at  $50$ – $60^\circ$  converts II into 3-thiocarboxylamido-5-phenylfurodiazole, m. p.  $171$ – $172^\circ$ . OO-Diacetylaminoglyoxime, m. p.  $82^\circ$  (cf. lit.), by partial hydrolysis with 20% sodium hydroxide gives N-acetylcyanofornamidoxime,  $\text{CN}\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{NHAc}$ , m. p.  $186^\circ$  (benzoyl derivative, m. p.  $149^\circ$ ). C. W. SHOPPEE.

Mechanism of carbohydrate oxidation. XII. Action of potassium hydroxide on L-arabinose and D-xylose. W. L. EVANS and R. F. CONAWAY (J. Amer. Chem. Soc., 1930, 52, 3680–3685).—The action of potassium hydroxide solution (1–6*N*) on L-arabinose and D-xylose has been studied by the methods previously described for other sugars (A., 1926, 149, 1228; 1928, 397, 741, 1222; this vol., 326) at  $25^\circ$ ,  $50^\circ$ , and  $75^\circ$ . The amount of lactic acid produced increases with rise in the normality of the alkali (2 : 3-enediol formation); the rate of formation of the acid is greater at  $50^\circ$  than at  $75^\circ$ . The effects of temperature and concentration of alkali on the amount of pyruvaldehyde formed are almost the same as those for trioses, certain hexoses, and maltose.



The maximum concentrations of formic and acetic acids correspond with the maximum quantity of pyruvaldehyde.

H. BURTON.

**Aldehyde-*l*-arabinose tetra-acetate.** M. L. WOLFROM and M. R. NEWLIN (J. Amer. Chem. Soc., 1930, 52, 3619—3623).—Treatment of *l*-arabinose ethyl mercaptal with acetic anhydride in pyridine affords the corresponding *tetra-acetate*, m. p. 79—80°,  $[\alpha]_D^{25}$  —29.9° in chloroform, converted by treatment with cadmium carbonate and mercuric chloride in aqueous acetone into *aldehyde-*l*-arabinose tetra-acetate*, m. p. 113—115° (corr.),  $[\alpha]_D^{25}$  —65.6° in chloroform [*semicarbazone*, m. p. 184—187° (corr.)]. The acetate exhibits mutarotation in methyl-alcoholic solution probably because of alcoholate formation.

H. BURTON.

**New isomerism in the sugar group.** E. BRAUN (Ber., 1930, 63, [B], 1972—1974).—A more detailed account of work already abstracted (this vol., 895).

H. WREN.

**Action of perbenzoic acid on substituted glucals.** P. A. LEVENE and A. L. RAYMOND (J. Biol. Chem., 1930, 88, 513—518).—3-Methylglucal when heated with perbenzoic acid in chloroform was converted into 3-methylglucose, m. p. 62—63°,  $[\alpha]_D^{25}$  +95.0° to +52.5° in water. Triacetylglucal treated in the same way yielded benzoyltriacetylglucose, m. p. 140—141°,  $[\alpha]_D^{25}$  +6.9° in chloroform. These results are in contrast to those of Bergmann (A., 1921, i, 649; 1924, i, 203) possibly owing to substitution in the 3-position of the glucal.

G. F. MARRIAN.

**Determination of dextrose in concentrated solutions.** E. E. MOORE (J. Amer. Pharm. Assoc., 1930, 19, 964—965).—In 35—48% solutions the concentration of dextrose is practically a linear function of either the sp. gr. or the optical rotation. The following equations are given: dextrose % (w/w) =  $0.633\alpha_D^{25} + 7.68 = 199.0d_D^{25} - 192.95$ ; dextrose % (w/v) =  $0.877\alpha_D^{25} + 2.13 = 265.3d_D^{25} - 276.58$ .

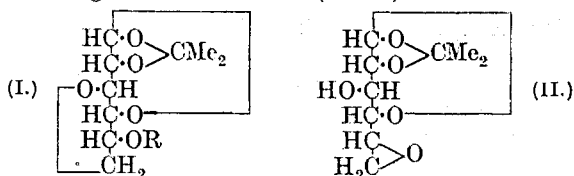
H. E. F. NOTTON.

**Isomerisation of hydroxy-aldehydes. III. Transformation of dextrose into a ketose (lævulose).** S. DANILOV, E. VENUS-DANILOVA, and P. SCHANTAROVITSCH (Ber., 1930, 63, [B], 2269—2274).—When heated with pyridine or, preferably, quinoline, dextrose is partly isomerised to lævulose, which is isolated in substance by repeated crystallisation of the product or as calcium fructosate and identified by its high lævulorotation, by the reaction of Sieben and Selivanov, by titration according to Willstätter and Schudel, as phenylmethylsazone, and as fructosecyanohydrin. Mannose does not appear to be formed. In aqueous pyridine or aqueous-alcoholic quinoline, mannose and 1—2% of organic acids are also produced.

H. WREN.

**Acetone [isopropylidene] sugars and other carbohydrate compounds. XXI. Anhydroglucose.** K. FREUDENBERG, H. TOEFFER, and S. H. ZAHEER (Ber., 1930, 63, [B] 1966—1969; cf. this vol., 1412).—Treatment of anhydroglucose (Fischer and Zach, A., 1912, i, 239, 678) with acetone in the presence of concentrated sulphuric acid affords anhydroglucose isopropylidene ether, m. p. 56°,  $[\alpha]_D^{25}$  +31.09° in water (*p*-toluenesulphonyl derivative,

m. p. 133°), identical with the product described by Ohle, von Vargha, and Erlbach (A., 1928, 871), thus confirming the constitution I (R=H). The structure

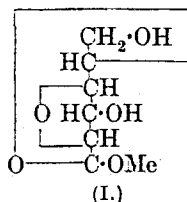


II therefore remains for the anhydroglucose isopropylidene ether, m. p. 133° (cf. Freudenberg and others, A., 1928, 1223; Ohle and von Vargha, A., 1929, 1279). Anhydroglucose isopropylidene ether, m. p. 133°, and acetobromoglucose are converted by silver carbonate in carbon tetrachloride and treatment of the product with pyridine and acetic anhydride into tetraglucosidomonoacetylglucose-6-bromohydrin isopropylidene ether, m. p. 169°,  $[\alpha]_D^{25}$  —59.75° in *s*-tetrachloroethane, identical with the substance derived from isopropylideneglucose-6-bromohydrin and acetobromoglucose and subsequent acetylation; the corresponding *iodohydrin*, m. p. 193°,  $[\alpha]_D^{25}$  —76.62° in *s*-tetrachloroethane, is described. The last-named substance is transformed by aqueous-alcoholic barium hydroxide into 5-glucosidoisopropylideneanhydroglucose, m. p. 130°,  $[\alpha]_D^{25}$  +20.16° in water.

The conversion of penta-acetylglucose into acetoiodoglucose, m. p. 109°, is described in detail.

H. WREN.

**Methylglucoside of a new anhydro-sugar; acyl migration with partly acylated dextrose.** B. HELFERICH and A. MÜLLER (Ber., 1930, 63, [B], 2142—2149; cf. A., 1927, 135).— $\beta$ -*D*-Glucose 1:2:3:4-tetra-acetate is conveniently converted into  $\beta$ -*D*-glucose 1:2:3:6-tetra-acetate,  $[\alpha]_D^{25}$  —32.18° in chloroform, by treatment with aqueous-alcoholic potassium hydroxide. With trichloroacetyl chloride in anhydrous pyridine the 1:2:3:6-derivative affords 1:2:3:6-tetra-acetyl-4-trichloroacetyl- $\beta$ -*D*-glucopyranose, m. p. 153°,  $[\alpha]_D^{25}$  —10.0° in chloroform, +11.3° in nitrobenzene. 1:2:3:6-Tetra-acetyl-4-toluenesulphonyl-*D*-glucopyranose is transformed by glacial acetic acid saturated with hydrogen bromide into  $\alpha$ -1-bromo-2:3:6-triacetyl-4-toluenesulphonyl-*D*-glucopyranose, m. p. 171° (corr., decomp.),  $[\alpha]_D^{25}$  +141° in chloroform, which, with silver carbonate and anhydrous methyl alcohol, yields 2:3:6-triacetyl-4-toluenesulphonyl- $\beta$ -methyl-*D*-glucopyranoside, m. p. 118° (corr.),  $[\alpha]_D^{25}$  —32.0° in pyridine, —37.8° in chloroform, identical with the product derived from  $\beta$ -methylglucoside. Treatment of the triacetyl-toluenesulphonylmethylglucopyranoside in chloroform with sodium in methyl alcohol leads to the formation of *anhydro- $\beta$ -methylglucoside* (? I), m. p. 158°,  $[\alpha]_D^{25}$  —118° in water, transformed by acetic anhydride and pyridine into the *diacetyl* derivative, m. p. 118°,  $[\alpha]_D^{25}$  —114.8° in chloroform; the corresponding *dibenzoyl* compound has m. p. 133°,  $[\alpha]_D^{25}$  —80.5° in chloroform.



Reply is made to Haworth, Hirst, and Teece (this

vol., 1023) and evidence against the migration of the 1-acetyl group is advanced.

H. WREN.

**Halogenoses of the  $\beta$ -series and their application to synthesis. V.  $\beta$ -Acetochlorogalactose and  $\beta$ -acetochloroxylose.** H. H. SCHLUBACH and R. GILBERT (Ber., 1930, 63, [B], 2292—2297; cf. A., 1929, 912).—Improvements in the technique of the preparation of  $\beta$ -acetochloroglucose have yielded a substance of constant  $[\alpha]_D^{25}$   $-18.6^\circ$  in carbon tetrachloride; the difference between the observed value and that calculated by Hudson's method therefore persists. A similar discrepancy is observed in the case of  $\beta$ -acetochlorogalactose, m. p.  $93-94^\circ$ ,  $[\alpha]_D^{25}$   $+5.8^\circ$  in carbon tetrachloride, prepared from acetobromogalactose,  $[\alpha]_D^{25}$   $+220.2^\circ$ ; the calculated value is  $[\alpha]_D^{25}$   $-39^\circ$ . Conversion of  $\beta$ -acetochloroglucose into tetra-acetyl- $\alpha$ -glucose is greatly improved by the addition of silver nitrate to the reaction mixture, whereby the change is considerably expedited.  $\beta$ -Acetochlorogalactose is similarly transformed into tetra-acetyl- $\alpha$ -galactose, m. p.  $133^\circ$ ,  $[\alpha]_D^{25}$   $+144.4^\circ$  in chloroform; addition of ammonia to the solution of the substance in alcohol causes an immediate fall to the constant equilibrium value,  $[\alpha]_D^{25}$   $+90.7^\circ$  ( $\pm 1.0^\circ$ ). The compound differs from that described by Skraup and Kremann (A., 1901, i, 507) and regarded by Hudson and Johnson (A., 1916, i, 546) as the  $\alpha$ -compound. The velocity of isomerisation of the  $\beta$ -halogenoses in anhydrous methyl alcohol or ether containing mercuric chloride is approximately the same for derivatives of dextrose and galactose.  $\alpha$ -Acetobromoxylose, when very rapidly manipulated, is similarly transformed into  $\beta$ -acetochloroxylose, m. p.  $112-113^\circ$ ,  $[\alpha]_D^{25}$   $-131.0^\circ$  in carbon tetrachloride (calc.  $[\alpha]_D^{25}$   $-99^\circ$ ). Since the compound is smoothly converted by silver chloride in ether into  $\alpha$ -acetochloroxylose and is transformed by silver carbonate in aqueous acetone into triacetyl- $\alpha$ -xylose it appears unlikely that any change in ring structure has been induced. The discrepancy between observed and calculated values for  $[\alpha]_D^{25}$  cannot therefore be ascribed to difference in the ring systems of the acetochloroxyloses.

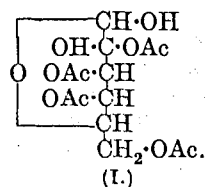
H. WREN.

**Halogenoses of the  $\beta$ -series and their application to syntheses. VI. Crystalline halogeno-acetyl derivative of *h*-galactose.** H. H. SCHLUBACH and V. PROCHOWNICK (Ber., 1930, 63, [B], 2298—2301).—The conversion of galactose into the mixture of isomeric  $\beta$ -penta-acetates and their subsequent separation is described in detail.  $\beta$ -Penta-acetyl-*h*-galactose is most conveniently transformed into  $\beta$ -acetochloro-*h*-galactose,  $[\alpha]_D^{25}$   $-77^\circ$  in chloroform, by the action of liquid hydrogen chloride; the method of Hudson and Johnson (A., 1916, i, 546) gives a crystalline product with difficulty and in poor yield. The half period for its mutarotation in chloroform (D.A.B. VI) and methyl alcohol is about 12 hrs. and less than 2 min., respectively, the corresponding periods for the isomeric *n*-compound being 23 hrs. and 5.3 min. Unexpectedly the action of liquid hydrogen bromide on  $\beta$ -penta-acetyl-*h*-galactose rapidly yields a  $\beta$ -acetodibromo-*h*-galactose, m. p.  $83-84.5^\circ$ ,  $[\alpha]_D^{25}$   $-116.2^\circ$  in carbon tetrachloride. Both bromine atoms are readily removed. One of them

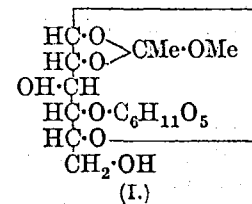
is doubtless attached to the 1-carbon atom, but the position of the other has not been established.

H. WREN.

**Unsaturated anhydro-sugars. IV. 2-Hydroxygalactal and preparation of kojic acid [5-hydroxy-2-hydroxymethyl-4-pyrone] from galactose.** K. MAURER and A. MÜLLER (Ber., 1930, 63, [B], 2069—2073).—2-Hydroxygalactal tetra-acetate (cf. A., 1927, 751) has m. p.  $111^\circ$ ,  $[\alpha]_D^{25}$   $+5.03^\circ$ ,  $+9.90^\circ$ ,  $-3.84^\circ$ , and  $-12.68^\circ$  in ethyl alcohol, methyl alcohol, chloroform, and *s*-tetrachloroethane, respectively. When treated with phenylhydrazine in 50% acetic acid it loses its acetyl groups and yields galactosazone, m. p.  $190^\circ$ . It is oxidised by potassium permanganate in aqueous alkaline solution to *potassium lyxonate*, m. p.  $166^\circ$ , transformed through the lead salt into lyxonolactone, m. p.  $110^\circ$ ,  $[\alpha]_D^{25}$   $+77.7^\circ$  in water. 2-Hydroxygalactal tetra-acetate is converted by chlorine in anhydrous ether followed by silver carbonate and water into tetra-acetylgalactosone hydrate (I), m. p.  $96^\circ$ ,  $[\alpha]_D^{25}$   $+45.68^\circ$  in chloroform, which in aqueous solution shows slow mutarotation accelerated by hydrogen or hydroxyl ions. It reduces Fehling's solution at the ordinary temperature, decolorises cold permanganate, and is hydrolysed by sodium hydroxide to galactosone. It is smoothly converted by a mixture of pyridine and acetic anhydride at  $0^\circ$  into diacetylkojic acid, hydrolysed by methyl-alcoholic ammonia to kojic acid, m. p.  $153^\circ$ .



**Acetone [isopropylidene] sugars and other carbohydrate compounds. XXII. Cyclic acetates in the sugar group.** K. FREUDENBERG and H. SCHOLZ (Ber., 1930, 63, [B] 1969—1972).—Re-examination of the hepta-acetylmethylmaltoside, m. p.  $163-164^\circ$  (cf. Freudenberg and others, A., 1928, 1222), shows that seven acetyl groups are removed by treatment with alcoholic toluenesulphonic acid. In the additional presence of potassium stearate only six acetyl groups are removed, so that one acetyl group in the compound is regarded as unique. The substance regarded previously as methylmaltoside (obtained from the hepta-acetate by means of ammonia) retains an acetyl group removable by toluenesulphonic acid and hence is *acetylmethylmaltoside* (I). The "superfluous isomerism" among the hepta-acetylchloromaltoses receives an explanation similar to that of the acetylmethylrhamnosides.



**Acetone [isopropylidene] sugars and other carbohydrate compounds. XX. Synthesis of methylated cellobiose. Crystalline methylcellobiose from cellulose. Gentibiose from amygdalin.** K. FREUDENBERG, C. C. ANDERSEN, Y. GO, K. FRIEDRICH, and N. W. RICHTMYER (Ber., 1930, 63 [B], 1961—1966; cf. A., 1929, 427).—2:3:6-Tri-methyl- $\beta$ -methylglucoside, m. p.  $58-59^\circ$ , prepared by the action of hydrogen chloride on 2:3:6-trimethylglucose in ether and treatment of the product

with silver carbonate and methyl alcohol, reacts with tetramethylglucose-1-chlorohydrin and silver carbonate in chloroform, giving a product from which heptamethyl- $\beta$ -methylcellobioside, m. p.  $86^\circ$ ,  $[\alpha]_{D}^{25} -16^\circ$  ( $\pm 1^\circ$ ), separates. The residual syrup appears to contain heptamethyl- $\beta$ -methylmaltoside or derivatives of trehalose or isotrehalose, which are also formed by the action of silver carbonate on the chlorohydrin alone.

Heptamethylbenzylcellobioside is converted by hydrogen in presence of spongy platinum and glacial acetic acid into heptamethylcellobiose.

Cotton wool is converted by acetic anhydride and glacial acetic acid containing sulphuric acid into cellobiose acetate and a mixture which is purified by successive treatment with water, ethyl and methyl alcohol. Methylation of the purified product with methyl sulphate gives heptamethyl- $\beta$ -methylcellobioside and decamethyl- $\beta$ -methylcellobioside, m. p.  $115^\circ$ , b. p.  $216-220^\circ/0.08$  mm.,  $[\alpha]_{D}^{25} -9.8^\circ$  ( $\pm 0.5^\circ$ ).

The conversion of amygdalin into gentiobiose is described in detail.

H. WREN.

**Glucomannan from "konjak."** K. NISHIDA and H. HASHIMA (J. Dept. Agric. Kyushu, 1930, 2, 277-360).—From "konjak powder" (powdered tubers of *Amorphophallus konjac*, C. Koch) glucomannan may be prepared by dispersion in water at  $120-125^\circ$  and precipitation as a copper complex by means of Fehling's solution. An identical product results from the digestion of konjak meal with pancreatin at  $35^\circ$  for 14 days in the presence of toluene. Examination of the products of acid hydrolysis confirms Ohtsuki's conclusion (A., 1928, 873) that this polysaccharide contains mannose and dextrose in the ratio 2 : 1. Acetylation with acetic anhydride containing a trace of sulphuryl chloride leads to a triacetate, m. p.  $180-187^\circ$ ,  $[\alpha]_{D}^{25} -21.5^\circ$  in chloroform,  $M$  2300 in bromoform. Acetolysis of glucomannan (1 g.) is best effected by treatment with acetic anhydride (5 g.), acetic acid (6 g.), and sulphuric acid (0.5 g.) at  $23^\circ$  for 15-20 days. From the products of acetolysis crystalline *glucomannotriose hendeca-acetate*, m. p.  $108-110^\circ$ ,  $[\alpha]_{D}^{25} +18^\circ$  in chloroform,  $+6^\circ$  in benzene,  $M$  924-1014 in benzene, has been isolated. De-acetylation with alcoholic ammonia at  $0^\circ$  affords *glucomannotriose*, m. p.  $216.5-217^\circ$  after softening at  $206^\circ$ ,  $[\alpha]_{D}^{25} -16.4^\circ$  in water,  $M$  504 in water, possibly identical with the amorphous "levidulin" of Mayeda (A., 1922, i, 694) and "lavidulinose" of Ohtsuki (*loc. cit.*), which yields 2 mols. of mannose and 1 mol. of dextrose on hydrolysis with acid. By de-acetylation of the mixture resulting from acetolysis two crystalline disaccharides have been isolated: *glucomannobiose*, m. p.  $150-160^\circ$ ,  $[\alpha]_{D}^{25} +10.5^\circ$  in water,  $M$  357-396 in water, yielding equal amounts of mannose and dextrose on hydrolysis, and *mannobiose*, m. p.  $125-140^\circ$ ,  $[\alpha]_{D}^{25} -7.9^\circ$ ,  $M$  324, which gives mannose alone on hydrolysis. Methylation of glucomannan with methyl sulphate and 30% sodium hydroxide affords a trimethyl derivative, which is hydrolysed by methylalcoholic hydrogen chloride to products appearing to consist essentially of 2 : 3 : 4-trimethylmethylglucoside and 2 : 3 : 6- and 2 : 3 : 4-trimethylmethylmann-

oside. Hydrolysis of the triose acetate with methylalcoholic hydrogen chloride, methylation of the product so obtained with methyl iodide and silver oxide, and de-acetylation with alcoholic ammonia yields a syrup and a small quantity of crystalline methylmannoside. The syrup may be separated by extraction with ether into two fractions, which appear to consist of 6-methylglucose,  $[\alpha]_{D}^{25} +75.8^\circ$  in water, and 6-methylmethylmannoside,  $[\alpha]_{D}^{25} +70^\circ$  to  $+54^\circ$  in alcohol,  $+61.5^\circ$  to  $+59.6^\circ$  in water.

T. H. MORTON.

**Digitalis glucosides. V. Oxidation and isomerisation of gitoxigenin.** W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1930, 88, 531-544).—Gitoxigenin on oxidation with chromic acid in acetic acid solution yielded  $\alpha$ -ketoisodigitoxigenone,  $C_{23}H_{30}O_5$ , m. p.  $204^\circ$ ,  $[\alpha]_{D}^{25} +88^\circ$  in acetone, which when treated with mineral acid or hydrolysed and subsequently acidified with acetic acid was converted into an isomeride  $\beta$ -ketoisodigitoxigenone, m. p.  $213^\circ$ ,  $[\alpha]_{D}^{25} +154^\circ$  in acetone. Either isomeride when treated with hot methyl alcohol gave the dimethyl acetal of  $\beta$ -ketoisodigitoxigenone,  $C_{25}H_{36}O_6$ , m. p.  $226-227^\circ$ . *isoGitoxigenone* treated in the same way yielded the corresponding dimethyl acetal,  $C_{25}H_{36}O_6$ , m. p.  $235^\circ$ .

Oxidation of dihydrodigitoxigenin with chromic acid in acetic acid solution yielded  $\alpha$ -ketodihydrodigitoxigenone,  $C_{23}H_{32}O_5$ , m. p.  $220-221^\circ$  (softening at  $200^\circ$ ),  $[\alpha]_{D}^{25} +89^\circ$  in acetone. Treatment of this compound with mineral acid yielded anhydro- $\beta$ -ketodihydrodigitoxigenone,  $C_{23}H_{30}O_4$ , m. p.  $240^\circ$ ,  $[\alpha]_{D}^{25} +154^\circ$  in acetone. By hydrolysis and subsequent acidification of this compound or of  $\alpha$ -ketodihydrodigitoxigenone, an isomeride of the former, m. p.  $220^\circ$ ,  $[\alpha]_{D}^{25} +173^\circ$  in acetone, was formed. Oxidation of dihydrodigitoxigenin also yielded a monocarboxylic acid,  $C_{23}H_{32}O_6$ , m. p.  $246^\circ$  (decomp.),  $[\alpha]_{D}^{25} -74^\circ$  in aqueous acetone (methyl ester, m. p.  $212^\circ$ ). The presence of a lactone group could not be demonstrated, nor was it possible to convert the acid into anhydroderivatives. Dihydrodigitoxigenone,  $C_{23}H_{34}O_4$ , m. p.  $160-162^\circ$ , prepared by the oxidation of dihydrodigitoxigenin, formed no anhydro-derivatives.

It is concluded that the second hydroxyl group in gitoxigenin (digitoxigenin and isogitoxigenin, one hydroxyl group) is not tertiary as originally supposed, and that it is probably attached to the carbon atom  $\delta$  to the  $\gamma$ -carbon atom of the lactone group.

G. F. MARRIAN.

**Strophanthin. XVIII. *alloCymarin* and *alloStrophanthidin*.** Enzymic isomerisation of cymarin and strophanthidin. W. A. JACOBS (J. Biol. Chem., 1930, 88, 519-529; cf. A., 1926, 618, 982).—Seeds of *Strophanthus kombe* were ground, defatted, and kept in contact with water for some days at  $25^\circ$ . A dilute alcoholic extract of the digested mixture, after purification with lead acetate and concentration, yielded in addition to cymarin an isomeric glucoside *allocymarin*,  $C_{30}H_{44}O_9$ , m. p.  $145^\circ$  (decomp.),  $[\alpha]_{D}^{25} +43^\circ$  in methyl alcohol. This substance was separated from the cymarin by reason of its low solubility in chloroform. It was pharmacologically inactive. On hydrolysis it yielded cymarose,  $C_7H_{14}O_4$ , m. p.  $93^\circ$ ,  $[\alpha]_{D}^{25}$  (final)  $+52^\circ$  in water, and *allostrophanthidin*,  $C_{23}H_{32}O_6$ , m. p.  $248-250^\circ$ ,  $[\alpha]_{D}^{25}$

+37° in 95% alcohol. Oximation of the latter yielded *allostrophanthidinoxime*,  $C_{23}H_{33}O_6N$ , decomp. 235°. Hydrogenation yielded successively *dihydroallostrophanthidin*,  $C_{23}H_{34}O_6$ , m. p. 230° after softening at 150°, and *dihydroallostrophanthidol*,  $C_{23}H_{36}O_6$ , m. p. 222°. The latter substance formed no oxime. Treatment of *allostrophanthidin* with alcoholic hydrochloric acid yielded the *ethyl semiacetal of oxidodihydroallostrophanthidin*,  $C_{25}H_{32}O_4$ , m. p. 191°. The preparation of these derivatives showed the presence of an aldehydic group, two tertiary groups, and one secondary hydroxyl group, as in *strophanthidin*. The isomerisation is due to an enzyme present in the seeds.

G. F. MARRIAN.

**Tigogenin, a digitalis sapogenin.** W. A. JACOBS and E. E. FLECK (J. Biol. Chem., 1930, **88**, 545—550).—The sapogenin prepared by the acid hydrolysis of crude gitonin when treated with light petroleum was separated into two fractions; the insoluble fraction consisted of gitogenin, whilst the soluble fraction contained a new sapogenin, designated *tigogenin*,  $C_{26}H_{42}O_3$ , m. p. 203—204°,  $[\alpha]_D^{25}$  —49° in pyridine. The following derivatives were prepared: *acetate*,  $C_{28}H_{44}O_4$ , m. p. 200—202°,  $[\alpha]_D^{25}$  —57° in pyridine; *benzoate*,  $C_{33}H_{46}O_4$ , m. p. 224—225°,  $[\alpha]_D^{25}$  —37° in pyridine; *tigogenone*,  $C_{26}H_{40}O_3$ , m. p. 206—207°,  $[\alpha]_D^{25}$  —35° in pyridine (*oxime*,  $C_{26}H_{41}O_3N$ , m. p. 256—258°). Reduction of *tigogenone* with zinc and hydrochloric acid yielded a *product*,  $C_{26}H_{42}O_2$ , m. p. 265—267°. A comparison of *sarsapogenin*, *sarsapogenone*, and *sarsapogenoneoxime* with *tigogenin* and its corresponding derivatives showed that these sapogenins were isomeric.

G. F. MARRIAN.

**Doubtful existence of the so-called "α-diamylose."** A. MIEKELEY (Ber., 1930, **63**, [B], 1957—1961).—Contrary to Pringsheim (A., 1926, 1128, and previous abstracts) treatment of α-tetra-amylose with acetic anhydride in presence of zinc chloride or pyridine yields only α-tetra-amylose acetate, from which the unchanged carbohydrate can be regenerated. The following constants are recorded: α-tetra-amylose (air-dried),  $[\alpha]_D^{25}$  +133.8° in water, (dried)  $[\alpha]_D^{25}$  +147.3° in water; α-tetra-amylose acetate, m. p. 153—154° (corr.),  $[\alpha]_D^{25}$  +103.8° in glacial acetic acid. α-Tetra-amylose forms crystals of the composition  $C_{24}H_{40}O_{20} \cdot 4H_2O$ , corresponding exactly with α-diamylose,  $C_{12}H_{20}O_{10} \cdot 2H_2O$ . The existence of "α-diamylose" appears doubtful.

H. WREN.

**Highly polymerised compounds. XL. Measurements of viscosity with polysaccharides and polysaccharide derivatives.** H. STAUDINGER and O. SCHWETZER (Ber., 1930, **63**, [B], 2317—2330).—The theoretical considerations are based on the following hypotheses: (1) Variation in the specific viscosity  $\eta_{sp}$  of a colloiddally dissolved substance with pressure is an indication of structure in the solution, which may be caused by the presence of macromolecules in such concentration that they are mutually impident. (2) With the macromolecular hydrocarbons the specific viscosity increases proportionally with the concentration in dilute sol solution but much more rapidly than the concen-

tration in concentrated sol solution and in the region of gel solution. (3) Approximate constancy in the specific viscosity of a solution over a considerable range of temperature is evidence of the presence of macromolecules in solution and against that of strongly solvatised micelles. (4) Measurements of viscosity in different solvents afford evidence of the influence of the medium on the macromolecules.

Observations on inulin dissolved in formamide show its behaviour to differ greatly from that of polystyrene or balata solutions. Since  $\eta_{sp}$  is much greater at lower than at higher temperatures, a change in the structure of the colloidal particles occurs which is attributed to alteration of the co-ordinative linkings of the molecules among themselves and with the solvent; these changes are reversible, since particles of the original size result when the solutions are cooled. Examination of solutions of lichenin in formamide shows the solute to be present in the molecular form at great dilution. In the more concentrated solutions, co-ordinative union exists between solvent and solute and between the molecules of solute; the latter linkings are resolved when the temperature is raised and for this reason a more pronounced fall in viscosity is observed than in more dilute solutions in which only the co-ordinative linkings between solute and solvent are ruptured. The mol. wt. of lichenin is markedly higher than that of inulin; the chain appears to contain about 300 unit molecules. Potato starch or soluble starch in formamide differs completely in its behaviour from polystyrenes and caoutchouc and markedly from lichenin. Since even dilute solutions do not obey the Hagen-Poiseuille law, deductions concerning mol. wt. from measurements of viscosity are inadmissible; freely mobile colloid molecules are not present. The specific viscosity diminishes with rise in temperature, but the starch is altered. Since the  $\eta_{sp}/c$  values in quite dilute solutions of differing concentration are not constant, irregular changes in the structure of the colloid particles appear to occur. It cannot therefore be determined whether macromolecules are present in a starch solution under definite conditions. It is assumed that the colloidal particles of starch are composed of associations of extremely unstable, readily cracked molecules and that the solution contains molecular aggregates (micelles) and not macromolecules.

Cellulose triacetate in *s*-tetrachloroethane and *m*-cresol appears to form associations of molecules in concentrated solution which become resolved when the temperature is raised. In dilute solution the change of the colloidal particles is uniform and attributable to a loosening of the co-ordinative linkings between the macromolecules and those of the solvent. Since with cellulose acetate, lichenin, and inulin, as with the highly complex hydrocarbons, the specific viscosity of the solutions is the same at different temperatures, the identity of the colloidal particles with the macromolecules is regarded as established. Dibenzylcellulose exhibits abnormal behaviour in *s*-tetrachloroethane, whilst methylcellulose (OMe=38%) shows still more marked divergence from the Hagen-Poiseuille law in the same solvent. With cellulose nitrate the measurements of viscosity

are particularly difficult to interpret, since mechanical treatment of the solution causes greater mobility.

H. WREN.

**Polysaccharides. XLIII. Processes taking place when polysaccharides are heated in glycerol.** P. KARRER and E. VON KRAUSS (Helv. Chim. Acta, 1930, 13, 1071—1073).—When acetylstarch (44.7% Ac) is heated in glycerol solution at 200—220°, elimination of acetyl groups occurs. Products containing 7—10% Ac, soluble in water, dialysing completely through a collodion membrane, and yielding maltose hepta-acetate on treatment with acetyl bromide, are obtained. The changes taking place are hydrolytic. *iso*Trihexosan (Pictet and Vogel, A., 1929, 914), dextrinose (idem, *ibid.*, 1167), and dextrinose are also converted into maltose hepta-acetate by treatment with acetyl bromide.

H. BURTON.

**Depolymerisation of inulin.** H. H. SCHLUBACH and H. ELSNER (Ber., 1930, 63, [B], 2302—2304).—Mainly a reply to Berner (this vol., 1025). Inulin which has been treated with glycerol and subsequently seven times with alcohol and ether can be freed completely from glycerol and alcohol by preservation in a high vacuum at 111° during 12 hrs. Berner's reliance entirely on cryoscopic determinations of mol. wt. as criteria of depolymerisation is considered to be unfortunate in view of the uncertain applicability of the method to carbohydrates. Measurements of the specific rotation permit the division of depolymerised products into two groups, (1) those obtained by Pringsheim, Reilly, and Donovan (A., 1929, 1282) and by Vogel (this vol., 198) which have the same specific rotation as the initial inulin into which they can be transformed, and (2) those prepared by Pictet and Vogel (A., 1928, 276), which have a specific rotation differing from that of the initial material and are not capable of spontaneous re-conversion. Inulin when treated with benzamide at 140°/vac. for 6 hrs. is converted into a mixture,  $[\alpha]_D + 29.6^\circ$ , separable into two portions having  $[\alpha]_D + 20^\circ$  and  $+75^\circ$ , respectively. The effect of addition of glycerol to the aqueous solution or of ethyl alcohol or glycerol to the solution in ethylene glycol on the optical activity of inulin has been examined.

The view is emphasised that a homogeneous inulin of definite mol. wt. does not exist. The material is a mixture of polymeric-homologous polyinulans the composition of which depends greatly on the botanical source, time of season, and mode of extraction and purification.

H. WREN.

**Existence of the cellobiose residue in cellulose.** W. N. HAWORTH, E. L. HIRST, and H. A. THOMAS (Nature, 1930, 126, 438).—The acetolysis of trimethyl-cellulose supports the view that cellobiose is pre-formed in cellulose. Under mild treatment at low temperatures, fully methylated cellulose undergoes cleavage to a diacetylhexamethylcellobiose, which readily gives crystalline heptamethyl- $\beta$ -methylcellobioside.

L. S. THEOBALD.

**Hydrolysis of cellulose.** J. CHALMERS and J. C. EARL (J. Proc. Roy. Soc. N.S. Wales, 1929, 63, 155—158).—Treatment of cellulose triacetate with a

boiling 5% methyl-alcoholic solution of hydrogen chloride results in the dissolution of a portion of the material in the formation of  $\alpha$ -methylglucoside. Re-acetylation of the insoluble fraction, which has suffered considerable de-acetylation, yields a triacetate,  $[\alpha]_D -10^\circ$ . Repetition of this process leads to a product,  $[\alpha]_D 0^\circ$ , indicating that the insoluble portion has suffered progressive and far-reaching hydrolytic degradation.

T. H. MORTON.

**Celluloses of some Australian plants.** W. G. ARNEMAN and J. C. EARL (J. Proc. Roy. Soc. N.S. Wales, 1929, 63, 44—46).—The celluloses were prepared by chlorination of the plants and subsequent extraction with alcohol. Pentosans were removed by a preliminary treatment with 2% sulphuric acid. The rotations ( $[\alpha]_D$ ) of the triacetates derived from these products by the method of Barnett (A., 1921, i, 164) are recorded: from the aquatic plants, *Posidonia*,  $-39.9^\circ$ , *Cymodocea* sp.,  $-22^\circ$ , *Polamogeton* sp.,  $0^\circ$ ; from the woods, *Doryphora sassafras*,  $-22.6^\circ$ , *Araucaria Cunninghamii*,  $-22.6^\circ$ ; and from the salt bush, *Atriplex vesicarium*,  $-20.1^\circ$ . It is suggested that the conclusion of Heuser (A., 1921, i, 708) that celluloses from all sources are identical is invalid.

T. H. MORTON.

**Highly polymerised compounds. XXXIX.**

**Cellulose.** H. STAUDINGER, K. FREY, R. SIGNER, W. STARCK, and G. WIDMER (Ber., 1930, 63, [B], 2308—2316).—The conflicting views with regard to the structure of cellulose are reviewed. The viscosity of more or less degraded triacetylcelluloses in chloroform has been determined. The products are dissolved in glacial acetic acid (in which according to Hess they are monomeric at great dilution), the solvent is largely removed in a vacuum, and the solute is precipitated by water. Since the viscosity of the products in chloroform is not affected by the treatment, it is considered that the cellulose acetates are different substances and that their difference does not depend on varying state of aggregation of one and the same molecule. Attempts were made to prepare polymeric-homologous series of cellulose derivatives. The acetates are unsuitable for this purpose. Fission of triacetylcellulose with hydrogen chloride leads to the production of degraded products of differing mean mol. wt. and varying chlorine content; solutions of the simpler products are less viscous than those of equally concentrated solutions of the more complex products. Allylation of cellulose proceeds more easily than methylation, but does not lead to fully alkylated products. Starch and cellulose react incompletely with sodamide in liquid ammonia and treatment of the products with methyl iodide affords only incompletely alkylated compounds.

Degradation of cellulose, starch, lichenin, etc. and their derivatives lead to series of polymeric-homologous products for which the following nomenclature is proposed. They are regarded as derivatives of polymeric glucans, mannans, or lævulans. The chains can be terminated by hydroxyl, methoxyl, acetyl, chlorine, etc. as with the polyoxymethylene and polyethylene oxide chains. The compounds  $OR-[C_6H_9O_5]_x-R'$  are thus polyglucan dihydrate ( $R=R'=H$ ), polyglucan diacetate ( $R=R'=Ac$ ), poly-

glucan dimethyl ether ( $R=R'=Me$ ). The position of the free hydroxyl groups is indicated by numerals, thus poly-(2:3:6-glucan) dihydrate. The degradation products of cellulose, starch, and lichenin are polycelloglucan, polyamyloglucan, and polylichenoglucan compounds. H. WREN.

**Action of hypiodite solution on cellulose preparations.** K. HESS, K. DZIENGEL, and H. MAASS (Ber., 1930, 63, [B], 1922—1927).—Examination of the action of hypiodite solution [according to the directions of Bergmann and Machemer (this vol., 457) on the biosan acetate of Hess and Friese (A., 1927, 44) shows that the "iodine value" increases greatly with increasing period of contact and that the carbohydrate residue is not stable towards renewed hypiodite. Further the "iodine value" of preparations which have been brought into colloidal solution by treatment with concentrated sodium hydroxide and subsequent dilution is greater than that of suspended preparations. The application of Bergmann and Machemer's method to the determination of the mean mol. wt. of cellulose preparations depends on the unfulfilled assumptions that the material is homogeneous in the sense that mixture of reducing sugars with non-reducing components is excluded, that uniform reaction occurs throughout the suspended or colloidal material, and that oxidation proceeds according to the scheme  $R\cdot CHO + O = R\cdot CO_2H$ . H. WREN.

**Highly polymerised compounds. XLI. Determinations of mol. wt. of cellulose acetates.** H. STAUDINGER and H. FREUDENBERGER (Ber., 1930, 63, [B], 2331—2343).—Cellulose is treated with acetic anhydride and zinc chloride at 60° and 80° respectively and, at definite intervals, portions of the solution are withdrawn, diluted with glacial acetic acid to a concentration of 0.25 or 0.29 mol., and subjected to viscosity measurements. With the series of poly-triacetylcelloglucan diacetates, the mol. wt. of the simpler members is determined by the method of Bergmann and Machemer, which is valid for degrees of polymerisation of 20—60. With more complex products the terminal groups form so insignificant a part of the molecule that their accurate determination is no longer possible. Viscosity measurements with these hemicolloids permit relationships to be established between viscosity and mol. wt. which can be applied to determination of the mol. wt. of the more complex products.

Initially, degradation of the cellulose molecule occurs very rapidly under the action of acetic anhydride and zinc chloride, but the simpler products are much more resistant. The initial, highly viscous solutions contain cellulose triacetates of mean degree of polymerisation 60—100; after 120 hrs. action the degree is reduced to 10. At the ordinary temperature reaction proceeds extremely slowly, giving products with degree of polymerisation 150. After 7 days at 30° the degree is 130 and after 10 days it is 100. Since native cellulose is more highly polymerised than the most complex of the acetates, its mol. wt. must be above 24,000; it appears probable that the cellulose molecule contains a chain of 500—

1000 glucose residues and thus has dimensions similar to those of the caoutchouc molecule.

The simpler cellulose acetates dissolve without swelling to mobile solutions the viscosity of which increases proportionally to the concentration over a large range. Slightly degraded cellulose acetates swell very markedly; their viscosity in solution increases far more rapidly than the concentration, so that very viscous solutions can be obtained at relatively great dilution. In them, the total region of the macromolecules is greater than the available volume in relatively dilute solution. In place of sol solutions in which the macromolecules have free movement, they represent gel solutions in which the macromolecules impede one another. A 10-triacetylcelloglucan diacetate behaves in solution like a simple substance and the gel condition is not reached until the concentration attains 22%. With a 150-triacetylcelloglucan diacetate the transition between sol and gel lies at 1.4%. H. WREN.

**Size of the cellulose molecule in copper-amine solution.** H. DOHSE (Z. physikal. Chem., 1930, 149, 279—283).—Cryoscopic measurements have been made with solutions of diethylenediamine-cupric hydroxide, with and without the addition of  $\alpha$ -cellulose. The f.p. depressions produced by diethylenediaminecupric hydroxide alone indicate that the compound is completely ionised. The dissolution of  $\alpha$ -cellulose caused a rise in f. p. which is regarded as evidence of the formation of long glucose chains in the ammine solution; the results are in sharp contradiction to the views of Hess on the constitution of such solutions. F. G. TRYHORN.

**Dissolution of cellulose in copper ethylenediamine solution.** K. HESS (Z. physikal. Chem., 1930, 149, 284—287).—Exception is taken to the hypothesis put forward by Dohse (preceding abstract) as to the constitution of solutions of cellulose in copper-amine solutions, on the ground that measurements of the increase in copper content of copper-amine solutions caused by the addition of cellulose fail to show stoichiometric relationships between the copper and the cellulose. It is pointed out that cryoscopic measurements must fail to give indications of the size of the cellulose molecules in solution if these tend to form colloidal aggregates.

F. G. TRYHORN.  
**Dissolution of cellulose in copper-ethylenediamine solution.** H. DOHSE (Z. physikal. Chem., 1930, 149, 288—290).—A reply to Hess (preceding abstract). F. G. TRYHORN.

**Process of dissolution of cellulose fibres in ammoniacal copper solution and the viscosity of the solutions.** I. SAKURADA (Ber., 1930, 63, [B], 2027—2042).—The solubility curves in ammoniacal copper solution are given for the following types of cellulose: (1) crude cotton wool extracted with boiling benzene and alcohol (1:1); (2) cotton wool purified by means of chlorine dioxide and sodium sulphite until constancy of chlorine dioxide titre; (3) cotton wool deprived of fat and repeatedly extracted with 2% sodium hydroxide at 95° in absence of air; (4) cotton wool, deprived of fat, treated successively with chlorine dioxide and sodium



sulphite and with sodium hydroxide; (5) technical, bleached cotton linters; (6) technical cellulose ( $\alpha$ -fibre); (7) technical, bleached ramie fibre; (8) crude ramie fibre treated with 2% sodium hydroxide; (9) ramie, mercerised with 17.5% sodium hydroxide; (10) cuprammonium, and (11) viscose silks. In general, more or less pronouncedly S-shaped curves are obtained, which, in relationship to the pre-treatment of the fibre, have different inclination of the tangents at the point of inflexion to the abscissa. The angle increases with intensity of purification of the fibres. The reagents do not attack cellulose under the conditions of experiment. Only with artificial silk is the curve rectilinear as expected from the observations of Hess and co-workers.

The copper content of the fibres with equal original concentration of copper and equal substrate relationship is practically identical in spite of the differing amounts of dissolved cellulose. It is probable therefore that the dissolution of natural cellulose fibres in ammoniacal copper solution depends on the structure and particularly on the integument material permeating the fibres in their natural state.

Determinations of the viscosity of the cellulose solutions show that slight purification of the fibre runs parallel with relatively high viscosity and great divergence from the Hagen-Poiseuille law. It appears that great caution is necessary in considering the properties of cellulose solutions in relation to the constitution of cellulose. It is not valid to assume that highly viscous cellulose solutions contain large cellulose molecules or micelles and that mobility of the solution is indicative of low mol. wt. of the solute. The X-ray spectra of cuprammonium silk and crude cotton wool show practically the same sharpness of interferences indicating the same dimensions of the crystallites.

H. WREN.

#### Kinetics of the "coppering" of cellulose fibres.

I. SAKURADA (Ber., 1930, 63, [B], 2043—2044).—The penetration of copper from ammoniacal copper solution into cellulose fibres takes place with a velocity consistent with the hypothesis that the reagent diffuses through an enclosing integument system and reacts within the fibre in accordance with the concentration of the solution to give copper-alkali-cellulose compounds. The simple expression for a bimolecular action appears to apply to the hydrolysis of the cellulose esters of the higher fatty acids. The mechanism of the reactions is not established.

H. WREN.

Copper oxide-ethylenediamine-cellulose. W. TRAUBE, G. GLAUBITT, and V. SCHENCK (Ber., 1930, 63, [B], 2083—2093).—If an ethylenediamine solution saturated with copper hydroxide is treated with oxalic acid in amount insufficient for neutralisation of the base, its capacity for dissolving copper hydroxide is not increased, whereas this effect is produced by polyhydroxy-compounds such as glycerol, tartaric acid, or cellulose, which afford opportunity for the production of an anion containing copper. The amount of cationic copper remains constant provided that sufficient copper hydroxide is present to maintain saturation. This increase in the amount of copper hydroxide is equal to that which has entered

into the anion of the compound. Ethylenediamine solution (3—15%), of which the maximal dissolution power for copper of hydroxide has been determined, is treated with sufficient copper hydroxide and a weighed quantity of cellulose. When the carbohydrate has completely dissolved, the copper content of the filtered solution is determined electrolytically. Since the possibility that cellulose passes into solution partly as simple salt or alkoxide is not excluded, the behaviour of dulcitol under similar conditions has been examined. In this case the crystalline compound,  $[\text{C}_6\text{H}_{10}\text{O}_6\text{Cu}][\text{Cu en}_2]$ , separates and the amounts of "new" copper hydroxide and dulcitol passing into solution are equimolecular, so that the carbohydrate is dissolved exclusively with formation of a bivalent anion containing copper. Further, if dulcitol is treated with a little water containing 2 mols. of potassium hydroxide and an excess of copper hydroxide, approximately molar amounts of the compounds are dissolved. If only 1 mol. of potassium hydroxide is present, dissolution of the dulcitol is partial, becoming quantitative when excess of copper hydroxide is used. Similar relationships are observed between potassium and copper hydroxides and biuret. The conclusion appears justified that cellulose when passing into solution becomes quantitatively converted into an anion containing copper. As a maximum a copper atom passes into the anion for each  $\text{C}_{12}\text{H}_{20}\text{O}_{10}$  group; this occurs only with at least 12—15% ethylenediamine solutions, used in considerable excess. It appears probable that the copper content of the cellulose anion is not greatly different when the carbohydrate dissolves in a saturated copper hydroxide-ethylenediamine solution in the absence of further metallic hydroxide. Addition of alcohol to the solution of cellulose causes precipitation of a compound containing 1.8 mols. of ethylenediamine and 1.9 atoms of copper for each  $\text{C}_{12}$  unit. The homogeneity of the material is not established, but its isolation removes all doubt with regard to the chemical nature of the reaction and the similarity in the behaviour of cellulose and simple polyhydroxy-compounds. The material swells in water without dissolving, but dissolution is complete in a copper hydroxide-ethylenediamine solution.

The behaviour of cellulose towards ammoniacal copper hydroxide appears more complicated.

Cellulose, copper hydroxide, and a large excess of guanidine yield the compound  $[\text{C}_{12}\text{H}_{16}\text{O}_{10}\text{Cu}](\text{CH}_3\text{N}_3)_2$ .

H. WREN.

Dissolution of cellulose in copper-ethylenediamine solution. C. TROGUS and I. SAKURADA (Ber., 1930, 63, [B], 2174—2179).—Equal weights of cellulose are brought into equal volumes of solution with increasing concentration of copper-ethylenediamine hydroxide in presence of an excess of copper hydroxide. After dissolution of the cellulose, the increase in the copper content of the solution is determined. This increase does not correspond with the expected relationship  $1\text{Cu}:1\text{C}_6$ , but is markedly displaced towards the cellulose. Either the anionic complex is markedly dissociated or the anion has a different composition, for example,  $[\text{Cu}(\text{C}_6)_2]$ . With increasing concentration of the copper base, the relationship of copper increase to dissolved cellulose

is displaced towards the copper and, in the most extreme case, attains the value  $0.55\text{Cu}:1\text{C}_6$ ; experimental conditions do not permit observations at higher concentrations. The "coppering" or dissolution of cellulose in copper-ammonium or copper-ethylenediamine solutions takes place in a similar manner in the sense that all the phenomena when ammonia is used are repeated at a considerably higher concentration in presence of ethylenediamine. The phenomena can be satisfactorily explained by the assumption that the stability of the  $[\text{Cu}(\text{en})_2]$  complex is considerably greater than that of the  $[\text{Cu}(\text{NH}_3)_4]$  complex and that the amount of the cellulose-copper anion is governed by the stability as well as by the concentration of the corresponding copper base.

H. WREN.

**Alkaline degradation of cellulose nitrate.** ANON. (Jahresber. VII Chem.-Tech. Reichsanst., 1928, 25—32; Chem. Zentr., 1930, i, 1924).—Decomposition of cellulose nitrate in methyl alcohol by means of sodium methoxide, followed by acidification of the filtrate, affords a substance which is probably an oxycellulose.

A. A. ELDRIDGE.

**Constitution of lignin. XIII. Separation of aldehydes and ketones by naphthylamine hydrochloride.** P. KLASON (Ber., 1930, 63, [B], 1981—1983).—Aldehydes react with  $\beta$ -naphthylamine hydrochloride in aqueous or alcoholic solution, frequently in the presence of added hydrochloric acid, at the laboratory or slightly higher temperature. Ketones do not possess this property, so that a convenient method of separating aldehydes and ketones appears to be indicated. Dextrose does not react to a marked extent with  $\beta$ -naphthylamine hydrochloride even in boiling solution; if hydrochloric acid is added, reaction does not occur at the ordinary temperature, but in hot solution the very stable "*anhydroglucosetri- $\beta$ -naphthylamine*,"  $\text{C}_6\text{H}_9\text{O}_3(\text{NH}\cdot\text{C}_{10}\text{H}_7)_3$ , is produced at a rate dependent on the concentration of the acid. The compound cannot be methylated or acetylated to a marked extent and is only incompletely hydrolysed by hot concentrated hydrochloric acid. *Anhydroarabinosetri- $\beta$ -naphthylamine* and *anhydroxylosedi- $\beta$ -naphthylamine* are described. The anhydrocarbohydratetri- $\beta$ -naphthylamines are converted by hot sugar solutions into di- $\beta$ -naphthylamine compounds.

H. WREN.

**Constitution of pine lignin. XIV.** P. KLASON (Ber., 1930, 63, [B], 1983—1985).—Reasons are advanced for the hypothesis that the alcoholysis of wood leads to the formation of semiacetals of trimeric coniferaldehyde thus:  $\text{C}_{30}\text{H}_{30}\text{O}_9\cdot\text{H}_2\text{O} + \text{EtOH} = \text{C}_{30}\text{H}_{32}\text{O}_9(\text{OH})\cdot\text{OEt}$ . The reaction between lignin and thiolacetic acid is analogously formulated,  $\text{C}_{40}\text{H}_{40}\text{O}_{12}\cdot\text{H}_2\text{O} + 2\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} = \text{C}_{40}\text{H}_{42}\text{O}_{12}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2 + \text{H}_2\text{O}$  and  $\text{C}_{40}\text{H}_{40}\text{O}_{12}\cdot 2\text{H}_2\text{O} + 4\text{SH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} = \text{C}_{40}\text{H}_{44}\text{O}_2(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_4 + 2\text{H}_2\text{O}$ . It appears more reasonable to halve the formula, thus  $\text{C}_{20}\text{H}_{22}\text{O}_6(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$ . If the acids are present in equimolecular proportion and the formula is halved, the formula  $\text{C}_{30}\text{H}_{32}\text{O}_9(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$  is derived, corresponding with the acid  $\text{C}_{30}\text{H}_{30}\text{O}_9\cdot\text{H}_2\text{SO}_3$ , which is the main product obtained by gentle treatment with sulphite. When, under the action of acids, the

native lignin is so hydrolysed that free aldehydic complexes are formed, these can react with alcohols, phenols, mercaptans, and sulphurous acid. In the last case, the loosely-combined sulphurous acid passes by a further reaction into a firmly united state.

H. WREN.

**Lignin and related compounds. IV. Nitration of glycol lignin.** H. HIBBERT and L. MARION (Canad. J. Res., 1930, 3, 130—139; cf. this vol., 1275).—Glycol lignin at  $-12^\circ$  dissolves completely in 10 parts of a mixture of acetic anhydride and fuming nitric acid (4:1). The product, obtained in 125% yield by allowing the mixture to rise to the ordinary temperature and pouring into water, is an acetylated and nitrated glycol lignin containing nitrogen also as nitrate, nitroso-groups, and another, unidentified form. It is an amorphous, yellow powder, soluble in organic solvents, and explodes when heated in oxygen. Further nitration at  $-12^\circ$  and  $80^\circ$  gives, after some initial oxidation, a slightly different product which is, in turn, practically unaltered by one, but appreciably altered by two further nitrations. Nitration of methylated glycol lignin takes a similar course, and oxidation and acetylation occur simultaneously. A different product is obtained by the methylation of nitrated glycol lignin, and the product has a methoxyl content more than double that of the original nitrated material. Nitrated glycol lignin can also be reduced and the product diazotised and coupled with  $\beta$ -naphtholdisulphonic acid. The soluble products of the nitration reaction contain an acidic component which has not been identified.

R. K. CALLOW.

**Local anæsthetics. Derivatives of amino-alcohols with a primary alcoholic group.** E. FOURNEAU, (Mlle.) G. BENOIT, and R. FIRMENICH (Bull. Soc. chim., 1930, [iv], 47, 858—885).—A series of amino-alcohols containing primary alcoholic groups has been obtained in yields of 40—60% by the action of methyl- or dimethyl-amine in benzene solution at  $140$ — $170^\circ$  on the bromoacetins, obtained by heating diprimary glycols with hydrogen bromide in acetic acid at  $100^\circ$  for 10—15 hrs. The benzoate hydrochlorides of the amino-alcohols are strong local anæsthetics characterised by a slow action, the anæsthetic power of the products I, II, and III (see below) on the cornea of rabbits being greater than that of stovaine; III is less toxic and I and II are more toxic to mice than is stovaine.

The following diprimary glycols are obtained in the yield indicated by heating hydratropaldehyde or other aldehydes for 12—18 hrs. with 3 mols. of 40% formaldehyde solution in presence of potassium carbonate:  $\beta$ -phenyl- $\beta$ -methylpropane- $\alpha\gamma$ -diol, m. p.  $87^\circ$ , b. p.  $180$ — $185^\circ/15$  mm. (yield 83%);  $\beta\beta$ -dimethylpropane- $\alpha\gamma$ -diol, m. p.  $127^\circ$ , b. p.  $135$ — $140^\circ/70$  mm. (60.2%);  $\beta$ -methyl- $\beta$ -ethylpropane- $\alpha\gamma$ -diol, b. p.  $115$ — $120^\circ/19$  mm., m. p.  $42^\circ$ , hygroscopic (yield 60.8%);  $\beta$ -methyl- $\beta$ -n-butylpropane- $\alpha\gamma$ -diol, b. p.  $130$ — $132^\circ/15$  mm., m. p.  $48^\circ$  (yield 82% from  $\beta$ -methylhexaldehyde, b. p.  $141^\circ/725$  mm.);  $\beta$ -methyl- $\beta$ -n-amylpropane- $\alpha\gamma$ -diol, b. p.  $142$ — $143^\circ/12$  mm., m. p.  $50^\circ$  (yield 86% from  $\beta$ -methylheptaldehyde, b. p.  $159$ — $161^\circ/725$  mm.);  $\beta$ -methyl- $\beta$ -isohexylpropane- $\alpha\gamma$ -diol,

b. p. 146—148°/13 mm., m. p. 53° (yield 87% from  $\beta$ -isohexylpropaldehyde, b. p. 54°/5 mm.);  $\beta$ -methyl- $\beta$ -heptylpropane- $\alpha$ - $\gamma$ -diol, m. p. 55°, b. p. 150—155°/14 mm. (yield 78% from  $\beta$ -methylnonaldehyde, b. p. 95—97°/11 mm.);  $\beta$ -methyl- $\beta$ -n-nonylpropane- $\alpha$ - $\gamma$ -diol, m. p. 62°, b. p. 185—187°/11 mm. (yield 82% from  $\beta$ -methyldecadecaldehyde, b. p. 119—122°/16 mm.), and  $\beta$ -methyl- $\beta$ - $\Delta^8$ -butenylpropane- $\alpha$ - $\gamma$ -diol, m. p. 29° (hygroscopic), b. p. 140—145°/18 mm. (yield 82.5%, from  $\beta$ -methyl- $\Delta^8$ -hexenal, b. p. 140°/725 mm.). Under the same conditions formaldehyde does not react with the corresponding ethylene oxides. With 1 mol. of formaldehyde, isobutaldehyde yields 50% of  $\beta$ - $\beta$ -dimethylpropane- $\gamma$ -ol- $\alpha$ -al, m. p. 89—90°, b. p. 80—90°/18 mm. (oxime, b. p. 90—95°/15 mm.), converted by 10% aqueous potassium hydroxide in presence of alcohol into  $\beta$ -dimethylpropane- $\alpha$ - $\gamma$ -diol and hydroxypivalic acid, m. p. 125°. Hydratropaldehyde is similarly converted into  $\beta$ -phenyl- $\beta$ -methylpropane- $\gamma$ -ol- $\alpha$ -al, b. p. 145—155°/17 mm. (oxime; sodium salt).

The following bromoacetins were obtained from the diprimary glycols by the method indicated above in the yields given (parentetical figures):  $\gamma$ -bromo- $\beta$ -phenyl- $\beta$ -methylpropyl acetate (65%), b. p. 165—168°/15 mm.;  $\gamma$ -bromo- $\beta$ - $\beta$ -dimethylpropyl acetate (84%), b. p. 90°/16 mm.;  $\gamma$ -bromo- $\beta$ -methyl- $\beta$ -ethylpropyl acetate (77.5%), b. p. 100—105°/15 mm.;  $\gamma$ -bromo- $\beta$ -methyl- $\beta$ -n-butylpropyl acetate (82%), b. p. 121—123°/14 mm.;  $\gamma$ -bromo- $\beta$ -methyl- $\beta$ -n-amylylpropyl acetate (78%), b. p. 134—138°/13 mm.;  $\gamma$ -bromo- $\beta$ -methyl- $\beta$ -isohexylpropyl acetate (84%), b. p. 138—140°/11 mm.; and  $\gamma$ -bromo- $\beta$ -methyl- $\beta$ -n-nonylpropyl acetate (80.5%), b. p. 178—182°/16 mm. With thionyl chloride in pyridine,  $\beta$ -phenyl- $\beta$ -methylpropane- $\alpha$ - $\gamma$ -diol yields an oil, b. p. 200°/2 mm., containing only traces of chlorine, and with phosphorus pentachloride a product, b. p. 110—112°/15 mm., which takes up bromine and contains little chlorine; the expected  $\gamma$ -chloro- $\beta$ -phenyl- $\beta$ -methylpropyl acetate was not obtained, and similarly with 66% hydrobromic acid for 8 hrs. at 100° the same oil, b. p. 200—210°/2 mm., was obtained.

The following amino-alcohols are described:  $\gamma$ -dimethylamino- $\beta$ -phenyl- $\beta$ -methylpropyl alcohol (yield 59%), b. p. 148—158°/17 mm. [hydrochloride, m. p. 137—138°; methiodide, m. p. 109—110°; benzoate hydrochloride, m. p. 182—183° (I)];  $\gamma$ -methylamino- $\beta$ -phenyl- $\beta$ -methylpropyl alcohol, b. p. 152—155°/16 mm. (hydrochloride, m. p. 119°);  $\gamma$ -dimethylamino- $\beta$ - $\beta$ -dimethylpropyl alcohol (yield 63.5%), b. p. 63°/15 mm., 164—166°/750 mm. [hydrochloride, m. p. 132°; methiodide, m. p. 224° (decomp.); benzoate hydrochloride, m. p. 152.5—153° (II)];  $\gamma$ -methylamino- $\beta$ - $\beta$ -dimethylpropyl alcohol (yield 56.5%), b. p. 69—71°/13 mm., m. p. 45—46° (hydrochloride, m. p. 172—173°);  $\gamma$ -dimethylamino- $\beta$ -methyl- $\beta$ -ethylpropyl alcohol, b. p. 76—78°/14 mm. (hydrochloride, m. p. 155°; methiodide, m. p. 70—75°?; methiodide, m. p. 155°);  $m$ -nitrobenzoate hydrochloride, m. p. 151—152°);  $\gamma$ -dimethylamino- $\beta$ -methyl- $\beta$ -n-butylpropyl alcohol, b. p. 102—103°/13 mm. (hydrochloride, very hygroscopic; methiodide, m. p. 129°);  $\gamma$ -dimethylamino- $\beta$ -methyl- $\beta$ -n-amylylpropyl alcohol, b. p. 113—116°/13 mm. (hydrochloride, m. p. 97—98°; methiodide, m. p. 124°; benzoate hydrochloride, m. p. 111°);  $\gamma$ -dimethylamino-

$\beta$ -methyl- $\beta$ -isohexylpropyl alcohol, b. p. 119—122°/12 mm. (hydrochloride, m. p. 125°; methiodide, m. p. 148°);  $\gamma$ -dimethylamino- $\beta$ -methyl- $\beta$ -n-nonylpropyl alcohol, b. p. 165—170°/15 mm. (hydrochloride, m. p. 99—103°; methiodide, m. p. 157.5°;  $m$ -nitrobenzoate hydrochloride, m. p. 109°); and  $\gamma$ -methylamino- $\beta$ -methyl- $\beta$ -n-nonylpropyl alcohol, b. p. 170°/16 mm. (hydrochloride, m. p. 105—108°).  $\gamma$ -Dimethylamino- $\gamma$ -phenylpropyl alcohol, b. p. 155—160°/25 mm. [hydrochloride, m. p. 182° (decomp.); methiodide, m. p. 158°; benzoate hydrochloride, m. p. 146° (III)], is obtained in 42% yield by the action of dimethylamine in 33% benzene solution on  $\gamma$ -chloro- $\gamma$ -phenylpropyl alcohol. No crystalline benzoyl derivatives could be obtained in the case of  $\gamma$ -dimethylamino- $\beta$ -methyl- $\beta$ -butylpropyl alcohol or of  $\gamma$ -dimethylamino- $\beta$ -methyl- $\beta$ -isohexylpropyl alcohol.  $\beta$ -Methyl- $\beta$ - $\Delta^8$ -butenylpropane- $\alpha$ - $\gamma$ -diol yielded no bromoacetin but a product, b. p. 100—105°/16 mm., containing only 20.2% of bromine.  $\beta$ -Methylbutaldehyde, b. p. 85—90°/645 mm., is obtained in about 60% yield by heating  $\alpha$ -methyl- $\alpha$ -ethylethylene oxide with copper powder for 3 hrs. at 210°. The ethylene oxide is obtained in 63% yield by heating the chlorhydrin with sodium hydroxide at 40—50° for 2 hrs.

R. BRIGHTMAN.

**Polysaccharides. XLIV. Chitin.** P. KARRER and S. M. WHITE (Helv. Chim. Acta, 1930, 13, 1105—1113).—The formyl, propionyl, butyryl, and benzoyl derivatives of chitosan are not affected by snail-chitinase (cf. A., 1929, 915, 1430); the enzyme appears to be specific for chitin and acetylated chitosan. The benzenesulphonyl and 1-naphthalenesulphonyl derivatives of chitosan are also described; the former of these is soluble in dilute alkali hydroxide. Methylation of chitosan with methyl iodide at 100° affords a monomethylchitosan,  $C_{14}H_{24}Me_2O_{10}N_2$  (dihydriodide; benzenesulphonyl derivative, insoluble in alkali hydroxide), which could not be methylated further. These results appear to show that chitosan is not a primary amine, although the total nitrogen is present as amino-nitrogen (Van Slyke). The acetyl groups (about 12%) present in chitosan are not attached to nitrogen. The chemical behaviour of chitosan resembles that of glucosaminemethylglucoside (Irvine and others, J.C.S., 1911, 99, 250; 1912, 101, 1128).

H. BURTON.

**Reaction of glycine and some other acyclic amino-acids.** V. ARREGUINE (Semana méd., 1930, 37, 1074).—The reagent is prepared by heating uric acid (0.1 g.) with water (0.1 c.c.) and nitric acid (0.1 c.c.) until interaction is complete, and diluting to 5 c.c. Glycine, after neutralisation with sodium carbonate, gives a deep red colour when heated with the reagent; alanine, leucine, glutaric [glutamic?] acid, and ammonium salts behave similarly.

CHEMICAL ABSTRACTS.

$\alpha$ - and  $\epsilon$ -Monomethyl-lysine. R. ENGER and H. STEIB (Z. physiol. Chem., 1930, 191, 97—102).— $\epsilon$ -Benzamido- $\alpha$ -bromo- $n$ -hexoic acid, obtained from the lactam of  $\epsilon$ -aminohexoic acid, when treated with alcoholic methanol yields  $\epsilon$ -benzoyl- $\alpha$ -methyl-lysine, m. p. 234° (decomp.). The latter by hydrolysis with 20% hydrochloric acid yields dl- $\alpha$ -methyl-lysine

(picrolonate, m. p. 243.5°). Similarly  $\epsilon$ -benzomethyl-amidoheptic acid, m. p. 79–80°, after bromination and treatment with ammonia furnishes  $\epsilon$ -benzoyl- $\epsilon$ -methyl-lysine, m. p. 232°, and the latter with 20% hydrochloric acid forms dl- $\epsilon$ -methyl-lysine (picrate, decomp. 227°; picrolonate, decomp. 228°).

J. H. BIRKINSHAW.

**Monobetaines of lysine.** R. ENGER and F. HALLE (Z. physiol. Chem., 1930, 191, 103–111).— $\alpha$ -Bromo- $\epsilon$ -benzamido-*n*-hexoic acid when heated with alcoholic trimethylamine yields  $\epsilon$ -benzoyl- $\alpha$ -trimethyl-lysine (chloroaurate,  $C_{18}H_{25}O_3N_2AuCl_4$ , m. p. 181°). Hydrolysis of the betaine derivative with 20% hydrochloric acid gives  $\alpha$ -trimethyl-lysine [chloroaurate,  $C_{18}H_{23}O_3N_4Au_3Cl_{12}$ , m. p. 207–208° (decomp.)]. Hydrolysis of dl-lysine with 0.2% barium hydroxide furnishes a mixture of 86% of  $\alpha$ -benzoyl-lysine, m. p. 235° (corr.) [monohydrate, m. p. 230° (corr.)], and 6% of  $\epsilon$ -benzoyl-lysine, m. p. 254° (corr.). The  $\alpha$ -product with toluenesulphonyl chloride forms  $\epsilon$ -p-toluenesulphonyl- $\alpha$ -benzoyl-lysine, m. p. 140° (corr.), and the  $\epsilon$ -product  $\alpha$ -p-toluenesulphonyl- $\epsilon$ -benzoyl-lysine, m. p. 199° (corr.).  $\alpha$ -Bromo- $\epsilon$ -benzamido-*n*-hexoic acid with alcoholic methylamine yields  $\epsilon$ -benzoyl- $\alpha$ -methyl-lysine, m. p. 234° (decomp.); the latter with toluenesulphonyl chloride gives  $\alpha$ -p-toluenesulphonyl- $\epsilon$ -benzoyl- $\alpha$ -methyl-lysine, m. p. 180° (corr.). The same product is obtained by the methylation of  $\epsilon$ -benzoyl- $\alpha$ -p-toluenesulphonyl-lysine with methyl sulphate.  $\epsilon$ -p-Toluenesulphonyl- $\alpha$ -benzoyl-lysine with methyl sulphate yields  $\epsilon$ -p-toluenesulphonyl- $\alpha$ -benzoyl- $\alpha$ -methyl-lysine, m. p. 148° (corr.).  $\alpha$ -Benzoyl-lysine after methylation with methyl sulphate and hydrolysis with 20% hydrochloric acid yields  $\epsilon$ -trimethyl-lysine (chloroaurate,  $C_9H_{23}O_2N_2Au_3Cl_3$ , m. p. 187–189°), identical with the product from methylated caseinogen.

J. H. BIRKINSHAW.

**Isolation of the  $\epsilon$ -monobetaine of lysine from methylated caseinogen.** J. KAPFHAMMER (Z. physiol. Chem., 1930, 191, 112–116).—After feeding the hydrolysis products of methylated caseinogen to a dog, the  $\epsilon$ -monobetaine of lysine was isolated from the urine and identified as the chloroaurate.

J. H. BIRKINSHAW.

**$\epsilon$ -Glycyl-dl-lysine.** R. ENGER (Z. physiol. Chem., 1930, 191, 117–122).—Toluenesulphonation of the  $\alpha$ -amino-group of  $\epsilon$ -benzoyl-lysine and removal of the  $\epsilon$ -benzoyl group followed by coupling with toluenesulphonylglycine in sodium carbonate solution gives  $\epsilon$ -toluenesulphonylglycyl- $\alpha$ -toluenesulphonyl-lysine, m. p. 132°. (If sodium hydroxide is used in place of the carbonate the diketopiperazine of toluenesulphonylglycine, m. p. 275°, is obtained.) Removal of the toluenesulphonyl groups as tolyl mercaptan by reduction gives  $\epsilon$ -glycyl-lysine (picrolonate, decomp. 238–240°). No hydrolysis was observed with trypsin or erepsin.

J. H. BIRKINSHAW.

**Physico-chemical behaviour of polypeptides obtained from glycine.** E. ABDERHALDEN and J. HEUMANN (Ber., 1930, 63, [B], 1945–1950).—Polypeptides of relatively low mol. wt. (474, 531, 588) composed exclusively of glycyl units can exist in the colloidal state in circumstances in which polypeptides containing other components do not exhibit this

phenomenon. The polypeptide particles are positively charged corresponding with the feebly acidic character of the hydrosol. Determination of the mol. wt. of polyglycyl polypeptides in melting resorcinol in absence of air generally gives very low values. Extension of the observations to other polypeptides shows that satisfactory values are obtained with materials which are rapidly soluble in resorcinol, but that more or less pronounced alteration of the substrate occurs when protracted warming is requisite to produce dissolution. Even readily soluble peptides containing the glycyl residue are liable to give low results. Attempts to use benzoic acid as cryoscopic solvent are described; the f. p. of the solution becomes constant only after repeated melting and solidification. Slightly low values are observed for dl-leucyl-dl-aminoheptic acid, di-dl-alanylcystine, and dl-leucyl-dl-norleucine, and very low values for glycyl-dl-aminobutyryl-dl-aminobutyric acid. H. WREN.

**Colorimetric determination of cystine by means of the uric acid reagent.** C. RIMINGTON (Biochem. J., 1930, 24, 1114–1118).—The influence of the quantity of sodium carbonate and of *N*-sodium hydroxide on the colour intensity and the conditions necessary to suppress the turbidity in Folin and Marenzi's modification (A., 1929, 1093) of Folin and Looney's colorimetric method for the determination of cystine are described. S. S. ZILVA.

**Sensitive reaction for cysteine.** R. FLEMING (Biochem. J., 1930, 24, 965–966).—Cysteine hydrochloride reacts readily with dimethyl-*p*-phenylenediamine hydrochloride when heated in presence of a small quantity of ferric chloride, giving a deep blue colour which is stable. The test is sensitive with 0.05 mg. of cysteine hydrochloride. Sulphides,  $\alpha$ -thiolpropionic or thiolacetic acid, and oxidised or reduced glutathione do not give the colour under conditions in which cysteine does. S. S. ZILVA.

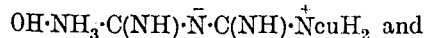
**Purification of acetamide.** E. C. WAGNER (J. Chem. Educ., 1930, 7, 1135–1137).—Acetamide is dissolved in 0.5 part of hot methyl alcohol, the solution filtered, and diluted to 1 : 0.8 part. It is then treated with ether (8–10 c.c. per g. of acetamide).

CHEMICAL ABSTRACTS.

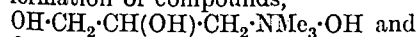
**Synthesis of the *r*-hydroxyasparagines.** A. C. CHIBNALL. Their dissociation constants. R. K. CANNAN (Biochem. J., 1930, 24, 945–953).—*r*-para-Hydroxyaspartic acid diethyl ester was obtained from *r*-hydroxyaspartic acid (Dakin, A., 1922, i, 143) and on treatment with ammonia it yielded *r*-para-hydroxy-aspartdiamide, m. p. 174° (decomp.), which by partial hydrolysis with barium hydroxide was converted into a mixture of the  $\alpha$ - and  $\beta$ -isomerides of *r*-para-hydroxyasparagine. The former was obtained from the mixture by crystallisation from hot water and the latter from the mother-liquor. The synthesis of the *r*-anti-hydroxyasparagines was similar to that of the *para*-compounds. The  $\alpha$ - and  $\beta$ -isomerides are differentiated by means of their crystalline form, water of crystallisation, and copper salts. The  $\alpha$ -forms contain 1 mol. of water and take two equivalents of the metal, whilst the  $\beta$ -forms contain no water of crystallisation and take one equivalent of

the metal. The two isomerides exhibit different dissociation constants. S. S. ZILVA.

**Theory of alkaline copper solutions and the biuret reaction.** W. TRAUBE and G. GLAUBITT (Ber., 1930, **63**, [B], 2094—2098).—Review of the literature on the behaviour of dulcitol, biuret, and similar compounds towards copper hydroxide in the presence of alkali shows that the acidic properties of these compounds are increased by the introduction of copper in complex union into the anion. The carbohydates all behave as very weak acids and contain at least one hydrogen atom replaceable by metal. In a solution containing much hydroxyl ion they become partly dissolved as anion which, in contrast to the undissociated compound, has the power of giving complex compounds with copper. Guanylearbamide and diguanide dissolve copper hydroxide in the absence of alkali hydroxide. It is probable that they behave in solution as ammonium hydroxides and that the central imino-hydrogen atom retains to some extent the acidic character exhibited by it in biuret. Consequently, there exists a tendency towards the formation of internal salts which is strengthened by the entry of copper into the molecule and the consequent increase in the acidic properties of the hydrogen atom. Following Pfeiffer, the following structures may be assigned to the compounds,  $\text{OH}\cdot\text{NH}_3\cdot\text{C}(\text{NH})\cdot\text{N}\cdot\text{C}(\text{NH})\cdot\text{NcuH}_2$  or

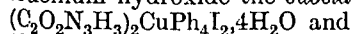


$\text{NH}_2\cdot\text{CO}\cdot\text{N}\cdot\text{C}(\text{NH})\cdot\text{NcuH}_2$  ( $\text{cu}=\text{Cu}/2$ ), which explains the conversion by the introduction of copper of diguanide into a monoacid base and of guanylearbamide into a non-basic substance. Introduction of basic groups into glycerol and mannitol leads to the formation of compounds,



$\text{OH}\cdot\text{NMe}_3\cdot\text{C}_6\text{H}_8(\text{OH})_4\cdot\text{NMe}_3\cdot\text{OH}$ , which dissolve copper hydroxide directly.

From thallium hydroxide, biuret, and the requisite metallic salt the compounds  $(\text{C}_2\text{O}_2\text{N}_3\text{H}_3)_2\text{CuTl}_2$  and  $(\text{C}_2\text{O}_2\text{N}_3\text{H}_3)_2\text{NiTl}_2$  are derived, whilst with diphenyliodonium hydroxide the substances



$(\text{C}_2\text{O}_2\text{N}_3\text{H}_3)_2\text{NiPh}_4\text{I}_2\cdot 4\text{H}_2\text{O}$  are obtained. H. WREN.

**Hydrogen cyanide. II. Compounds formed by action of hydrogen halides on hydrogen cyanide.** L. E. HINKEL and R. T. DUNN (J.C.S., 1930, 1834—1839).—Hydrogen chloride combined with liquid hydrogen cyanide either in the pure state or in presence of solvents after a latent period giving the sesquichloride,  $2\text{HCN}\cdot 3\text{HCl}$ . No such compound as  $\text{HCN}\cdot\text{HCl}$  was observed. The sesquichloride when heated alone, or with liquid hydrogen cyanide, or when kept in a vacuum over sodium hydroxide, yielded *chloromethyleneformamidine*,  $\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{CHCl}$ , a hygroscopic solid, which with aniline gave diphenylformamidine, m. p.  $142^\circ$ , and with dimethylaniline at  $100^\circ$  yielded hexamethyltriaminotriphenylmethane, m. p.  $177^\circ$ .

Heating chloromethylene formamidine with quinoline led to bimolecular hydrogen cyanide—evidently *imidoformylcarbylamine*,  $\text{NH}\cdot\text{CH}\cdot\text{N}\cdot\text{C}$ , m. p.  $85^\circ$ , since

with magnesium phenyl bromide etc. benzaldehyde was obtained and with hydrogen chloride and bromide in ether *chloro-* and *bromo-methyleneformamidines*, respectively, were formed.

Hydrogen bromide and iodide combined with anhydrous hydrogen cyanide at  $-10^\circ$  forming the corresponding *sesquihalides*,  $2\text{HCN}\cdot 3\text{HBr}$ , m. p.  $240^\circ$  (decomp.), and  $2\text{HCN}\cdot 3\text{HI}$ , m. p.  $158-160^\circ$  (decomp.).

R. J. W. LE FEVRE.

**Auto-complex formation as probable cause of the unique position of thallium alkyl compounds.** E. KRAUSE and P. DITTMAR (Ber., 1930, **63**, [B], 1953—1957).—The thallium alkyl compounds with simple alkyl groups are not suitable for mol. wt. determinations by reason of their insolubility. Examination of thallium di-*n*-hexyl, diisooamyl, and diisobutyl fluorides in freezing benzene shows that they have not the simple molecular structure. The suitability of the method is demonstrated with tin triisooamyl fluoride, tin triphenyl chloride, and lead triphenyl chloride. *Thallium di-n-hexyl chloride*, decomp.  $198^\circ$  when brought into a bath pre-heated at  $190^\circ$ , is prepared from thallium chloride and magnesium *n*-hexyl chloride in ether; the corresponding *fluoride*, incipient decomp.  $185^\circ$  when slowly heated, *bromide*, decomp.  $216^\circ$  after incipient melting at  $205^\circ$ , *iodide*, gradual decomp. above  $190^\circ$ , and *nitrate*, decomp.  $270-271^\circ$ , are described.

H. WREN.

**Mercuration of compounds containing the reactive methylene group.** K. G. NAIK and C. C. SHAH (J. Indian Chem. Soc., 1930, **7**, 655—662).—The following *di(chloromercuri)malonalkylamides* are prepared by mercurating the requisite amide by Neogi and Chatterji's method (A., 1928, 783): *di(chloromercuri)malon-amide*, m. p.  $220^\circ$  (decomp.) after shrinking at  $191-192^\circ$  (converted by bromine water into dibromomalonamide); *-methylanide*, m. p.  $241^\circ$  (decomp.); *-ethylanide*, decomp.  $191^\circ$ ; *-propylanide*, m. p.  $173-175^\circ$  after changing colour at  $162^\circ$ ; *-butylanide*, m. p.  $90^\circ$ ; *-isobutylanide*, m. p.  $108-109^\circ$ ; *-amylanide*, m. p.  $143^\circ$  (decomp.); *-isoamylanide*, m. p.  $105^\circ$ , and *-heptylanide*, m. p.  $117^\circ$  (converted by treatment with hydrochloric acid or alcoholic potassium iodide into malonheptylamide). *Malon-amylamide*, m. p.  $126^\circ$ , and *-isoamylanide*, m. p.  $55^\circ$ , are prepared from ethyl malonate and the requisite amine at  $120^\circ$  and  $200^\circ$ , respectively.

Similar mercuration of ethyl malonate gives ethyl *di(chloromercuri)malonate*, not melted at  $300^\circ$ , which when treated with alcoholic hydrochloric acid affords *ethyl chloromercurimalonate*, turns grey at  $192-195^\circ$ . The last-named compound is also formed by the action of cold aqueous potassium iodide solution on the dimercurated ester; when hot solutions are used, both mercury atoms are eliminated. Treatment of the dimercurated ester with hydrogen sulphide in alcohol gives an immediate precipitate of mercuric sulphide; with sodium thiosulphate a small amount of a red substance is produced.

H. BURTON.

**Organic antimonial compounds. II.** W. J. C. DYKE and W. J. JONES (J.C.S., 1930, 1921—1927).—Tri-*n*-propylstibine reacts energetically with air, *tri-n-propylstibinic metantimonite*, unchanged at  $220^\circ$ ,

being at once formed; when shaken in absolute-alcoholic solution with red mercuric oxide, *tri-n-propylstibinic oxide*, a gelatinous mass, is obtained. Refluxing of a mixture of tripropylstibine, powdered rhombic sulphur, and water yields *tri-n-propylstibinic metathioantimonite*, blackens at 180°, m. p. above 200°. Treatment of an absolute-alcoholic solution of *tri-n-propylstibinic oxide* with dry hydrogen sulphide leads to *tri-n-propylstibinic sulphide*, m. p. 88°. The halogens combine directly with the stibine (in suitable solvents), producing *tri-n-propylstibinic chloride*, *bromide*, and *iodide*; methyl iodide similarly gives *methyltri-n-propylstibonium iodide*, m. p. 140°, which, with fresh moist silver oxide, yields the corresponding *hydroxide* [*sulphate*; *chloroplatinate*, m. p. 142° (decomp.)].

*Ethyltri-n-propylstibonium iodide*, m. p. 185° (decomp.), and *chloroplatinate*, m. p. 141° (decomp.), are also described.

Butyl- and amyl-stibines behaved similarly to the propyl analogue, producing *tri-n-butylstibine oxides*,  $(C_4H_9)_3SbO_3$  (by aerial oxidation),  $(C_4H_9)_3SbO$  (by mercuric oxide oxidation); *tri-n-butylstibinic chloride*, *bromide*, and *iodide*; *methyltri-n-butylstibonium hydroxide* [corresponding *chloroplatinate*, m. p. 134° (decomp.)]; *tri-n-amylstibinic oxide*, *metantimonite*, *chloride*, *bromide*, *iodide*; and *methyltri-n-amylstibonium chloroplatinate*, m. p. 127° (decomp.).

A decreased affinity of antimony for the higher alkyl radicals, causing certain experimental precautions to be adopted during the preparation of antimonials, is noted. R. J. W. LE FÈVRE.

**Carbon rings. XV. Preparation and physical data of various carbon rings containing up to 32 carbon atoms.** L. RUZICKA, M. STOLL, H. W. HUYSER, and H. A. BOEKENOOGEN (Helv. Chim. Acta, 1930, 13, 1152—1185).—The following hydrocarbons are prepared by the Clemmensen reduction of the corresponding monoketones ( $C_{12}$ – $C_{16}$  and  $C_{20}$ ) and diketones ( $C_{22}$ – $C_{30}$ ): *cyclododecane*, b. p. 118°/18 mm., m. p. 60–61°,  $d_4^{25}$  0.8223; *cyclotridecane*, b. p. 112–113°/9 mm., m. p. 17–18°,  $d_4^{25}$  0.8636; *cyclotetradecane*, b. p. 143°/16 mm., m. p. 52–53°,  $d_4^{25}$  0.8259; *cyclohexadecane*, b. p. 170–171°/20 mm., m. p. 56–57°,  $d_4^{25}$  0.819; *cyclodocosane*, b. p. 212°/16 mm., m. p. 45–46°,  $d_4^{25}$  0.8174 (obtained together with *cyclodocosanone*, m. p. 30–32°); *cyclotetracosane*, m. p. 46–47° (accompanied by *cyclotetracosanone*, m. p. 35–36°); *cyclohexacosane*, b. p. 218–219°/0.5 mm., m. p. 41–42°,  $d_4^{25}$  0.812 (formed together with *cyclohexacosanone*, m. p. 41–42°); *cyclooctacosane*, b. p. 213–214°/0.25 mm., m. p. 47–48°,  $d_4^{25}$  0.8103 (accompanied by *cyclooctacosanone*, b. p. 210°/0.25 mm., m. p. 44–45°); *cyclononacosane*, b. p. 215°/1.1 mm., m. p. 46–47°,  $d_4^{25}$  0.8308; *cyclotriacontane*, m. p. 55–56° (lit. 53–54°). Further details are given for the preparation of various cyclic ketones by the action of heat on yttrium polymethylenedicarboxylates. In accordance with previous observations (A., 1928, 642, 887), the ketones  $[CH_2]_n > CO$ , are accompanied by the diketones  $[CH_2]_n < \begin{smallmatrix} CO \\ CO \end{smallmatrix} [CH_2]_n$  when the dicarboxylate  $[CH_2]_n(CO_2)_2M$  is decomposed. The following are described: *cyclotetracosane-1:13-dione*, b. p.

216°/0.25 mm., m. p. 64–65°,  $d_4^{25}$  0.8930; *cyclohexacosane-1:14-dione*, b. p. 235°/0.3 mm., m. p. 68–69°,  $d_4^{25}$  0.878; *cyclooctacosane-1:15-dione*, b. p. 238–241°/0.2 mm., m. p. 72–73°,  $d_4^{25}$  0.8629; *cyclodotriacontane-1:17-dione*, b. p. 258–262°/0.16 mm., m. p. 77–78°,  $d_4^{25}$  0.8446. *cycloOctanone*, regenerated from its semicarbazone, has m. p. 40–41° (lit. 32–33°),  $d_4^{25}$  (supercooled) 0.9477. Crystallographic data are given for *cyclohexacosane-1:11-dione* (A., 1928, 887). The m. p. of the hydrocarbons and ketones generally oscillates up to about  $C_{14}$ , reaches a maximum at  $C_{18-19}$ , then decreases to about  $C_{22}$ , and finally rises again. The densities, molecular refractions, and molecular volumes of the compounds are discussed. [With H. SCHINZ.]—*cyclopentadecanol*, b. p. 145°/0.3 mm., m. p. 80–81°, is prepared by reduction of exaltone with sodium and alcohol. H. BURTON.

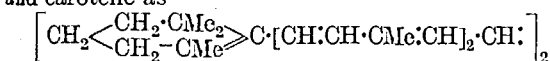
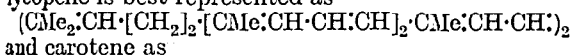
**Auto-oxidation of cyclohexene by oxygen.** N. D. ZELINSKI and P. P. BORISOV (Ber., 1930, 63, [B], 2362–2365).—Consideration based on the octet theory lead the authors to the hypothesis that auto-oxidation of a substance like *cyclohexene* would proceed without aid to the peroxide stage, whereas the presence of a catalyst would be required for rupture of the molecule. *cycloHexene* is found to absorb only half the expected quantity of oxygen, yielding the peroxide,  $\begin{smallmatrix} CH_2 \cdot CH_2 \cdot CH \\ CH_2 \cdot CH_2 \cdot CH \end{smallmatrix} > O_2$ , the remainder of the hydrocarbon appearing to be unchanged.

H. WREN.

**Plant colouring matters. XXV. Constitution of lycopene and carotene.** P. KARRER, A. HELFENSTEIN, H. WEHRLI, and A. WETTSTEIN (Helv. Chim. Acta, 1930, 13, 1084–1099).—Oxidation of a benzene solution of carotene with alkaline potassium permanganate solution, first at the ordinary temperature and then at the b. p., affords  $\alpha$ -dimethylsuccinic and -glutaric acids (cf. this vol., 76). Similar oxidation of an auto-oxidised specimen of carotene, freed from a small amount of oil by distillation with steam, gives the above acids and a trace of dimethylmalonic acid. Treatment of carotene in acetic acid suspension with ozone, dilution of the resulting solution with water, and further oxidation of this with hydrogen peroxide affords small amounts of  $\alpha$ -dimethylglutaric and geronic [ $\delta$ -acetyl- $\alpha$ -dimethyl-*n*-valeric] acids; these acids are also obtained by similar treatment of  $\beta$ -ionone. The isolation of the above acids confirms the presence of the trimethylcyclohexene ring in carotene which gives rise to  $\beta$ -ionone (cf. *loc. cit.*). Determinations of the number of mols. of acetic acid produced by permanganate oxidation of  $\alpha$ - and  $\beta$ -ionones, carotene, and lycopene (1 mol.) give values of 1.43, 1.25, 4.34, and 4.2–4.6, respectively, whilst chromic acid oxidation affords 2, 1.7, 5.7, and 5.92 mols., respectively. These differences are ascribed to the presence of  $\cdot CH_2 \cdot CH_2 \cdot CMe \cdot$  groupings. In view of these oxidation experiments and the observations that no butane- $\beta\beta\delta$ - or pentane- $\beta\beta\epsilon$ -tricarboxylic acids have been isolated, it appears improbable that the second ring in carotene is formed by cyclisation of the  $\cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CHMe$  group, which occurs in the formula previously proposed for lycopene (A., 1929, 569). It is shown that butane- $\beta\beta\delta$ -tricarboxylic



acid is readily isolated by oxidation of  $\alpha$ -acetyl- $\alpha$ -methylglutaric acid (a possible intermediate) with potassium permanganate at the ordinary temperature. The failure to isolate either of the above tricarboxylic acids, the deficit of acetic acid formed on oxidation, and the absence of optical activity suggest that lycopene is best represented as



These formulæ explain the observed oxidative degradation products. The suggestion is made that lycopene can originate from 2 mols. of phytolaldehyde by a benzoin-like condensation followed by dehydrogenation.

Treatment of zeaxanthin with ozone in carbon tetrachloride, decomposition of the resulting ozonide with water, and subsequent oxidation of the non-volatile (in steam) products with potassium permanganate affords  $\alpha\alpha$ -dimethylsuccinic acid.

Squalene is probably related to lycopene and it is suggested that the former hydrocarbon can be represented as  $(\text{CMe}_2\cdot[\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}]_2\cdot\text{CH}\cdot\text{CH}_2)_2$  (cf. Heilbron and others, A., 1929, 789, 790). This structure readily explains the formation of methyl isohexyl ketone, hexahydro- $\psi$ -ionone,  $\gamma$ -methylvaleric acid, 3,6-dimethylnonoic acid, and the ketone  $\text{C}_{15}\text{H}_{30}\text{O}$  (*loc. cit.*) by oxidation of hydrogenated squalene. The last-named ketone would be  $\beta\zeta\kappa$ -trimethylhexadecan- $\alpha$ -one and not the  $\gamma\eta\lambda$ -trimethyl derivative as stated by Heilbron. The  $\beta\zeta\kappa$ -trimethyl derivative is synthesised (no details given) as follows. The ether obtained from magnesium hexahydrofarnesyl bromide and methyl chloromethyl ether is converted by hydrobromic acid into 3,6- $\mu$ -trimethyltridecyl bromide, convertible by the acetoacetic ester method into the above ketone; the m. p. (73–74°) of the semicarbazone is not depressed by admixture with the semicarbazone obtained by Heilbron (*loc. cit.*).

H. BURTON.

**Sorption of hydrogen sulphide by potassium benzenesulphonate and a thiohydrate of this salt.** I. W. LANGE and G. LEWIN (Ber., 1930, 63, [B], 2156–2163).—Potassium benzenesulphonate forms a *hemihydrate*, stable in air but readily dehydrated in presence of desiccating agents. Examination of hydration isotherm at 15° discloses the existence of a second *hydrate*,  $4\text{Ph}\cdot\text{SO}_3\text{K}\cdot\text{H}_2\text{O}$ . At –60.6°, anhydrous potassium benzenesulphonate and hydrogen sulphide afford the *compound*  $4\text{Ph}\cdot\text{SO}_3\text{K}\cdot\text{H}_2\text{S}$ . At 0° in presence of hydrogen sulphide at differing pressures the amount of gas absorbed approaches asymptotically 0.25 mol., and true equilibria,  $4\text{Ph}\cdot\text{SO}_3\text{K} + \text{H}_2\text{S} \rightleftharpoons (\text{Ph}\cdot\text{SO}_3\text{K})_4\cdot\text{H}_2\text{S}$ , are observed. At a constant pressure of 760 mm., a gradual approach to the limiting value  $(\text{Ph}\cdot\text{SO}_3\text{K})_4\cdot\text{H}_2\text{S}$  is observed with falling temperature; the limit is reached shortly before liquefaction of the gas. The possibility that the effect is due essentially to adsorption is excluded by the observation that the same reactions are obtained with a sample of potassium benzenesulphonate which has been melted and allowed to cool. At 0° and 760 mm., ethylene is absorbed by potassium benzenesulphonate in the molar ratio

0.290 : 1. Its double linking is thereby weakened to such an extent that ethyl mercaptan is immediately formed in the presence of hydrogen sulphide.

H. WREN.

**Stereoisomerism of disulphoxides and related substances. VI. Co-ordination compounds of some disulphides and diamines.** G. M. BENNETT, A. N. MOSSES, and F. S. STATHAM (J.C.S., 1930, 1668–1676).—The preparation is described of chelate complexes of the general formulæ  $[\text{C}_2\text{H}_4 \begin{array}{c} \text{SR} \\ \text{SR} \end{array} \text{MX}_2]$

and  $[\text{C}_2\text{H}_4 \begin{array}{c} \text{NRR}' \\ \text{NRR}' \end{array} \text{MX}_2]$ ; in no case was any trace of a second isomeride detected by crystallisation etc. Thus dimethyl- and diethyl-thioethanepalladous chlorides, m. p. 234° and 174° (corresponding mercuric iodide derivative, m. p. 103°), respectively; diphenylthioethanepalladous chloride, m. p. 280°; di-*p*-tolylthioethanepalladous chloride, m. p. 234° (decomp.) (acetone compound; chloroform compound); di-*p*-tolylthioethanemercuric iodide, m. p. 110° (decomp.); dibenzylthioethaneplatinous chloride, decomp. without melting; the corresponding mercuric iodide, m. p. 111–113° (decomp.), and palladous chloride, m. p. 181° (decomp.), bisdibenzylthioethanenickel thiocyanate, ethylenediphenyldiamineplatinous chloride, and palladous chloride, both without m. p., ethylenediphenyldimethylthioethanepalladous chloride, and ethylenedi-*p*-methoxyphenyldiaminepalladous chloride, were all found to be homogeneous substances.

*p*-Anisidine and ethylene dibromide yielded ethylenedi-*p*-methoxyphenyldiamine, m. p. 105° (dihydrochloride, m. p. 238°; di-*p*-toluenesulphonyl derivative, m. p. 188°; diacetyl derivative, m. p. 164°), which, when boiled with commercial methyl alcohol, was converted into di-*p*-anisyltetrahydroglyoxaline, m. p. 134°; from this, by the action of acids and acyl halides, derivatives of the parent base were formed with elimination of formaldehyde.

Alcoholic solutions of the first (m. p. 105°) base with aqueous formaldehyde yielded a *base*, m. p. 226°, to which the formula  $\text{CH}_2\cdot\text{CH}_2\cdot\text{NH} \cdot \text{OMe}\cdot\text{C}_6\text{H}_3\cdot\text{N}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\cdot\text{OMe}$  is ascribed. R. J. W. LE FÈVRE.

**Synthesis of propenylbenzene.** L. BERT and M. RAYNAUD (Compt. rend., 1930, 191, 454–455).—Addition of  $\gamma$ -chloroallylbenzene to powdered sodium in toluene at 110° (bath) affords a mixture of propenylbenzene ( $\alpha$ -phenyl- $\Delta^a$ -propene), unsaturated substances, b. p. above 200°, and undistillable products, instead of the expected mixture of allylbenzene and benzylacetylene. The above method of preparation of propenylbenzene is better than that previously described (A., 1929, 1433). H. BURTON.

**New reaction of the aliphatic double linking.** Z. FÖLDI (Ber., 1930, 63, [B], 2257–2269).—Examples are cited of the addition of halogenated amines to aliphatic double linkings,  $\text{:C:C:} + \text{:NBr} \rightarrow \text{:CBr}\cdot\text{C(N):}$ .

$\alpha$ -Phenyl- $\Delta^a$ -propene is converted by  $\text{NN}'$ -dibromo- $\text{NN}'$ -dimethyloxamide followed by treatment of the product with 3*N*-hydrochloric acid into *r*- $\psi$ -ephedrine, m. p. 118°, which is also formed from *N*-bromo-*N*-methylurethane and  $\alpha$ -phenyl- $\Delta^a$ -propene. Benzene-

sulphonmethylbromoamide is prepared in 85% yield by the gradual addition of 5*N*-sodium hydroxide to a mixture of bromine and benzenesulphonmethylamide. Addition of it to  $\alpha$ -phenyl- $\Delta^a$ -propene affords a mixture of products from which  $\alpha$ -bromo- $\beta$ -benzenesulphonmethylamido- $\alpha$ -phenylpropane,  $\text{CHPhBr}\cdot\text{CHMe}\cdot\text{NMe}\cdot\text{SO}_2\text{Ph}$ , m. p. 105–106°, is isolated. It is converted by sodium acetate in glacial acetic acid into the corresponding non-crystalline  $\alpha$ -acetoxy-compound, which is hydrolysed to  $\beta$ -benzenesulphonmethylamido- $\alpha$ -hydroxy- $\alpha$ -phenylpropane, m. p. 105°, identical with *N*-benzenesulphonylephedrine; the compound derived from *r*-ephedrine is smoothly converted by phosphorus pentabromide into  $\alpha$ -bromo- $\beta$ -benzenesulphonmethylamido- $\alpha$ -phenylpropane. The constitution of the additive compound is therefore established, but its configuration is not decided. For this reason, *l*-ephedrine hydrochloride is converted by benzenesulphonyl chloride in presence of chloroform and 33% sodium hydroxide solution into 1-*N*-benzenesulphonylephedrine, m. p. 99°,  $[\alpha]_D^{25} -44.59^\circ$  in ethyl alcohol, and *l*- $\psi$ -ephedrine into 1-benzenesulphonyl- $\psi$ -ephedrine, m. p. 70°,  $[\alpha]_D^{25} -27.86^\circ$ ; both reactions occur without change of sign of rotation. With phosphorus pentabromide the ephedrine derivative affords 1-bromo-*N*-benzenesulphonylephedrine, m. p. 88°,  $[\alpha]_D^{25} -111.02^\circ$  in ethyl alcohol, whereas the  $\psi$ -ephedrine derivative suffers inversion and gives *d*-bromo-*N*-benzenesulphonylephedrine, m. p. 88°,  $[\alpha]_D^{25} +109.60^\circ$  in ethyl alcohol (also prepared from *d*-bromoephedrine hydrobromide and benzenesulphonyl chloride). If equal quantities of the antipodes are mixed, *r*-bromo-*N*-benzenesulphonylephedrine, m. p. 105–106°, is obtained (also prepared from *N*-benzenesulphonyl-ephedrine or  $\psi$ -ephedrine and phosphorus pentabromide). Alteration of the sequence of the reactions does not lead to the production of the  $\psi$ -derivative, since *l*- $\psi$ -ephedrine gives *d*-bromoephedrine hydrobromide, m. p. 174.5°, which subsequently affords *d*-bromo-*N*-benzenesulphonylephedrine. *r*-Ephedrine hydrochloride, however, yields a difficultly separable mixture of *r*-bromoephedrine and *r*-bromo- $\psi$ -ephedrine hydrobromides, converted by benzenesulphonyl chloride into the corresponding derivatives, from which *r*-bromo-*N*-benzenesulphonyl- $\psi$ -ephedrine, m. p. 120°, is readily isolated.

$\alpha$ -Phenyl- $\Delta^a$ -propene reacts in a more complicated manner with the sodium derivative of benzenesulphonchloroamide; dichlorophenylpropane and  $\alpha$ -chloro- $\beta$ -benzenesulphonamido- $\alpha$ -phenylpropane, m. p. about 123°, are isolated.

Cinnamyl alcohol and benzenesulphonmethylbromoamide afford  $\alpha\beta\gamma$ -tribromo- $\alpha$ -phenylpropane, m. p. about 125°, in 50% yield. With allyl bromide, reaction occurs mainly in accordance with the scheme,  $2\text{CH}_2\text{CH}\cdot\text{CH}_2\text{Br} + 2\text{Ph}\cdot\text{SO}_2\cdot\text{NMeBr} \rightarrow \text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br} + \text{CH}_2\text{Br}\cdot\text{CH}(\text{NMe}\cdot\text{SO}_2\text{Ph})\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{SO}_2\text{Ph}$ ;  $\alpha\beta\gamma$ -tribromopropane is isolated in 80% yield. Allyl alcohol appears to yield di- $\beta$ -bromoallyl ether mixed with a little dibromopropyl alcohol. H. WREN.

**Electrolytic reduction of ketones. II. Formation of hydrocarbons.** G. SHIMA. See this vol., 1291.

**Action of metallic sodium on trichloro-diphenyl- and -ditolyl-ethanes.** E. E. HARRIS (J. Amer. Chem. Soc., 1930, 52, 3633–3636).— $\beta\beta\beta$ -Trichloro- $\alpha\alpha$ -di-*p*-tolylethane and sodium react in boiling toluene, forming about 50% of 4 : 4'-dimethylstilbene and 45% of 4 : 4'-dimethyltolane. Similarly,  $\beta\beta\beta$ -trichloro- $\alpha\alpha$ -diphenylethane affords a mixture of stilbene, isostilbene, and tolane. The following mechanism is suggested:  $\text{CHR}_2\cdot\text{CCl}_3 \xrightarrow{3\text{Na}} \text{CHR}_2\cdot\text{C}\cdot \rightarrow \text{CHR}\cdot\text{CR}; 2\text{CHR}\cdot\text{CR} \rightarrow \text{CHR}\cdot\text{CHR} + \text{CR}\cdot\text{CR}$ . H. BURTON.

**1-Chloronaphthalene. V. Chlorination of naphthalene in solution.** P. FERRERO and J. CORBAZ (Helv. Chim. Acta, 1930, 13, 1009–1025; cf. A., 1929, 1054).—Chlorination of naphthalene dissolved in benzene, chlorobenzene, *o*- and *p*-dichlorobenzenes, nitrobenzene, toluene, decahydronaphthalene, alcohol, acetic acid, ethyl acetate, ether, tetra- and penta-chloroethanes, and carbon tetrachloride has been studied using naphthalene (2 g.-mols.), solvent (500 g.), and chlorine delivered at 35 g./hr. in absence and presence of 0.5% of iodine or 0.5% of ferric chloride. With aromatic and hydroaromatic solvents the results are in agreement with those previously described (*loc. cit.*). Acetic acid gives results almost as good as those obtained with chlorobenzene; optimum yields of 1-chloronaphthalene (80–90% on naphthalene consumed) are obtained at 115° in presence of iodine; the acetic acid is not attacked. With the other solvents used, reaction is usually slow and, in most cases, relatively large amounts of polychloro-derivatives are produced.

H. BURTON.

**Isomerisations of brominated naphthalenes by aluminium chloride.** H. LOHFERT (Ber., 1930, 63, [B], 1939–1941).—1 : 2-Dibromonaphthalene is converted by acetyl chloride and aluminium chloride in presence of carbon disulphide into 1 : 4-dibromonaphthalene, m. p. 83°, and acetyl-1 : 2-dibromonaphthalene, m. p. 146°; under somewhat different conditions it affords unchanged material and 1 : 5-dibromonaphthalene, m. p. 131°. Isomerisation appears to be due to the hydrogen chloride liberated from the acetyl chloride, since the 1 : 2-dibromoderivative is transformed by hydrogen chloride in presence of carbon disulphide and aluminium chloride into 2 : 6-dibromonaphthalene, m. p. 158°, or, in some instances, into 1 : 5-dibromonaphthalene.

H. WREN.

**Fluorene series.** C. COURTOT (Ann. Chim., 1930, [x], 14, 5–146).—Mainly an account of work previously reviewed (A., 1924, i, 956; 1925, i, 926; 1927, 234, 348, 654). The following appears to be new. Treatment of fluorene with sulphur trioxide in chloroform below 20° (cf. B., 1929, 707) gives the same 2-sulphonic acid (sodium; potassium; barium + 0.5H<sub>2</sub>O, and cadmium + 6H<sub>2</sub>O, salts) as is produced when sulphonation is effected by chlorosulphonic acid (A., 1924, i, 956). Oxidation of the above potassium salt with aqueous potassium permanganate at 25° affords the potassium salt (oxime) of fluorenone-2-sulphonic acid (sulphonyl chloride, m. p. 192°), which when fused with potassium hydroxide yields 70% of 4'-hydroxydiphenyl-2-carboxylic acid (cf. A., 1925, i, 926). Similar fusion of fluorene

furnishes 6% of diphenyl-2-carboxylic acid. Treatment of fluorenone-2-sulphonic acid with phosphorus pentachloride at 170° affords a small amount of 2-chlorofluorenone, whilst fluorenone-2:7-disulphonic acid [potassium salt (oxime); disulphonyl chloride, m. p. (block) 221°] gives 2:7:9:9-tetrachlorofluorene. This tetrachloro-compound is also produced from 2:7-dinitrofluorenone and phosphorus pentachloride at 180°. Potassium hydroxide fusion of the above disulphonic acid yields 4:4'-dihydroxydiphenyl-2-carboxylic acid (cf. *loc. cit.*). Treatment of fluorene first with sulphuric acid monohydrate at 80° and then with fuming sulphuric acid (92.8% SO<sub>3</sub>) at 90° affords a fluorenetrisulphonic acid [barium and potassium salts; trisulphonyl chloride, m. p. (block) 214°], oxidised by potassium permanganate to a fluorenetrisulphonic acid, m. p. 95° (potassium salt). Alkaline fusion of this gives carbonaceous products. 2-Iodofluorene, prepared by the usual method from 2-aminofluorene, is oxidised by sodium dichromate and acetic acid to 2-iodofluorenone, m. p. 152° (lit. 142—143°). 4-Nitrofluorenone, obtained by way of 4-nitrophenanthraquinone and the nitrodiphenyleneglycollic acid, is reduced by ammonium sulphide to 4-aminofluorenone, m. p. 135—136°, and by zinc dust and ammonia to 4-aminofluorenol, m. p. 183—184° (corr.). The introduction of an amino-group into the fluorenone molecule causes a considerable increase in the colour.

The dinitrofluorene, m. p. 207°, obtained in 23% yield together with 60% of 2:7-dinitrofluorene, m. p. 334° (lit. 269°), when fluorene is nitrated with nitric and acetic acids is shown to be the 2:5-derivative by a method identical with that of Morgan and Thomason (A., 1926, 1239). Reduction of 2:7-dinitrofluorenone with ammonium sulphide gives the 2:7-diamino-derivative; with zinc dust and aqueous-alcoholic ammonia 2:7-diaminofluorenol, m. p. 216° (corr.), results. 2:5-Diaminofluorenone, m. p. 260—261° (corr.) (dihydrochloride), and 2:5-diaminofluorenol, m. p. 201° (corr.), are prepared similarly. 2:7-Diaminofluorenone is much more intensely coloured than the 2:5-isomeride. The compound obtained when the diazo-solution from 2:7-diaminofluorenone is heated is a nitroso-2:7-dihydroxyfluorenone, C<sub>13</sub>H<sub>9</sub>O<sub>4</sub>N, m. p. (block) 304—305°, and not 2:7-dihydroxyfluorenone, m. p. (block) 338° (obtained when 4:4'-dihydroxydiphenyl-2-carboxylic acid is heated with zinc chloride), as stated by Schmidt, Retzlaff, and Haid (A., 1912, i, 695). The nitroso-derivative is also produced when the dihydroxyfluorenone is treated with nitrous acid.

Treatment of 2-nitrofluorene with sulphuric acid monohydrate at 20° affords 2-nitrofluorene-7-sulphonic acid (sodium, potassium, and calcium salts; sulphonyl chloride, m. p. 239°). This is reduced by stannous chloride and hydrochloric acid to 2-aminofluorene-7-sulphonic acid, not melted at 330° (sodium and potassium salts), prepared also by sulphonating 2-aminofluorene, which gives a stable diazonium sulphate, decomp. 160°. Treatment of the diazonium chloride with alcohol and copper sulphate furnishes fluorene-2-sulphonic acid, which is nitrated by a mixture of nitric and sulphuric acids at 50—60° to the above nitrosulphonic acid. 2-Nitrofluorenone-

7-sulphonic acid [potassium salt; sulphonyl chloride, m. p. (block) 240°] is converted by phosphorus pentachloride at 180° into 2:7:9:9-tetrachlorofluorene. 2-Aminofluorenone-7-sulphonic acid is also described. Nitration of fluorene-2:7-disulphonic acid with nitric and sulphuric acids at 30—50° gives a nitro-derivative (potassium salt), the barium salt of which is reduced by stannous chloride and hydrochloric acid or iron and acetic acid to barium aminofluorene-2:7-disulphonate, (C<sub>13</sub>H<sub>10</sub>O<sub>6</sub>NS<sub>2</sub>)<sub>2</sub>Ba.

2:7-Dibromofluorene is nitrated by nitric (d 1.5) and acetic acids at the ordinary temperature to a nitro-derivative, m. p. 196° (corr.) [corresponding amino-compound, m. p. 190° (corr.)], oxidised by chromic oxide in acetic acid to a 2:7-dibromonitrofluorenone, m. p. 192° (corr.). This could not be oxidised further by potassium permanganate; when heated with ammonia and cuprous chloride, profound decomposition usually occurs. 2:7-Dibromoaminofluorenone, m. p. 255° (corr.) (hydrochloride), and 2:7-dibromoaminofluorenol, m. p. 199° (corr.), are obtained from the above fluorenone by reduction with ammonium sulphide and zinc dust and alcoholic ammonia, respectively. Reduction of 2:7-dibromofluorenone to the fluorenol and treatment of this with hydrochloric acid affords 9-chloro-2:7-dibromofluorene, m. p. 154—155°.

When 2-bromofluorenone is heated with sodium hydroxide at 135—145° a small amount of 4-bromodiphenyl-2-carboxylic acid, m. p. 165° (corr.), is obtained. With sodamide in presence of various hydrocarbons at the b. p. (110—240°) no reaction occurs, whilst fusion with sodamide causes profound decomposition; similar results are obtained with 2-nitro-, 2-bromo-7-nitro-, and 2:7-dibromo-fluorenes. 2:7-Dibromofluorenone and potassium hydroxide at 145—155° give 20—25% of 4:4'-dibromodiphenyl-2-carboxylic acid, m. p. 212—213°, prepared but not analysed by Holm (A., 1883, 921).

The results show that whilst the 9-hydrogen atom of fluorene is replaced by treatment with sodamide or organomagnesium compounds, halogenation, nitration, and sulphonation cause substitution first in the 2- and then in the 7-position. H. BURTON.

**Berginisation of anthracene.** N. A. ORLOV and N. D. LICHATSCHEV (Ber., 1930, 63, [B], 2179—2185).—Anthracene is heated at 460—470° with hydrogen (initial pressure 100 atm.) in presence of 3% of metallic sodium and the product is fractionally distilled. The most volatile portion consists of benzenoid hydrocarbons apparently containing a small quantity of naphthenes. The less volatile fraction yields naphthalene and 2-methylnaphthalene, but polyalkylnaphthalenes do not appear to be present. Dehydrogenation of the portion of this fraction which does not unite with picric acid proceeds slowly in presence of selenium, energetically but with formation of much asphalt-like material in presence of sulphur. Some 2-methylnaphthalene is formed. The anomalous dehydrogenation suggests the presence of five-membered rings. Berginisation of 1:2:3:4-tetrahydronaphthalene leads to the production of a mixture of methylhydrindenes. Berginisation of anthracene appears to follow the

course: anthracene  $\rightarrow$  1:2:3:4-tetrahydroanthracene  $\rightarrow$  naphthalene  $\rightarrow$  1:2:3:4-tetrahydronaphthalene  $\rightarrow$  benzene. H. WREN.

**Interaction of iodine monochloride with substances containing the reactive methylene group.** K. G. NAIK and C. C. SHAH (J. Indian Chem. Soc., 1930, 7, 633—635).—Treatment of the following malonamides with iodine monochloride in chloroform first at 30° and then at 100° (bath) affords dichloromalonamides: malon-amide, -propylamide, -heptylamide, -benzylamide, -*o*- and -*p*-toluidides, and malon-*p*-toluidic acid. Malonanilide affords malon-chloroanilide (Naik and Trivedi, this vol., 938), whilst malon- $\alpha$ -naphthylamide gives dichloromalon-chloro- $\alpha$ -naphthylamide, m. p. 191°. Malonanilic acid furnishes chloromalonchloroanilic acid, m. p. 152°; methylmalon-anilide and -*o*-toluidide yield  $\alpha$ -chloro- $\alpha$ -methylmalon-chloroanilide, m. p. 164°, and -chloro-*o*-toluidide, m. p. 184°, respectively; malonmethyl-anilide affords chloromalonmethyl-anilide.

H. BURTON.

**Condensation of ethyl acetoacetate with aromatic amines.** I. G. V. JADHAV (J. Indian Chem. Soc., 1930, 7, 669—676).—Ethyl acetoacetate reacts with anilines, usually at the b. p., forming acetoacetanilides, ethyl  $\beta$ -anilinoacetonates, and  $\beta$ -anilinoacetonanilides. Thus, ethyl acetoacetate and *m*-nitroaniline give acetoacet-*m*-nitroanilide, m. p. 120—121°, which when heated with *m*-nitroaniline at 140—150° affords  $\beta$ -*m*-nitroanilinocroton-*m*-nitroanilide, m. p. 152—153°. Hydrolysis of this with hydrochloric acid in the cold furnishes the former anilide, which when heated with ammonia yields  $\beta$ -aminocroton-*m*-nitroanilide, m. p. 129—130°. Ethyl acetoacetate and *p*-nitroaniline give a mixture of ethyl  $\beta$ -*p*-nitroanilinocrotonate, m. p. 122—123°, and  $\beta$ -*p*-nitroanilinocroton-*p*-nitroanilide, m. p. above 250°. The last-named compound is hydrolysed by cold hydrochloric acid to acetoacet-*p*-nitroanilide, m. p. 122—123°, convertible as above into  $\beta$ -aminocroton-*p*-nitroanilide, m. p. 189—190°. The following are prepared similarly: acetoucel-*p*-aniside, m. p. 117—118°, -*m*-chloroanilide, m. p. 105—106°, -*p*-chloroanilide, m. p. 132—133°, and -*o*-chloroanilide, m. p. 107—108°;  $\beta$ -aminocroton-*p*-aniside, m. p. 109—110°, -*o*- and -*p*-chloroanilides, m. p. 96—97° and 110°, respectively;  $\beta$ -*p*-anisidinocroton-*p*-aniside, m. p. 235—236°; ethyl  $\beta$ -*p*-phenetidinocrotonate, m. p. 60—61°;  $\beta$ -*p*-phenetidinocroton-*p*-phenetide, m. p. 230—231°;  $\beta$ -*p*-xylydinocroton-*p*-xylylide, m. p. above 275°;  $\beta$ -*m*-4-xylydinocroton-*m*-4-xylylide, m. p. above 275°;  $\beta$ -*m*-chloroanilinocroton-*m*-chloroanilide, m. p. 240—241°; ethyl  $\beta$ -*p*-chloroanilinocrotonate, m. p. 55°;  $\beta$ -*p*-chloroanilinocroton-*p*-chloroanilide, m. p. above 275°, and  $\beta$ -*o*-chloroanilinocroton-*o*-chloroanilide, m. p. 236°. *o*-Nitroaniline could not be condensed with ethyl acetoacetate.

H. BURTON.

**Action of mixed organomagnesium compounds on *N*-substituted crotonanilides.** N. MAXIM and N. IOANID (Bul. Soc. Chim. România, 1930, 12, 28—32).—By the action of magnesium ethyl or phenyl bromide on the methyl-anilide, b. p. 158°/16 mm., and ethylanilide, m. p. 46° (Bischoff, A., 1901, i, 526) (prepared by the action of the alkylaniline on the acid

chloride in benzene), of crotonic acid are obtained 50—60% yields of the corresponding saturated anilides  $\text{CHMeR} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NR} \cdot \text{Ph}$  (cf. A., 1928, 1004) together with a by-product, of higher b. p., probably formed by condensation between the original unsaturated and the saturated anilides. Thus are obtained  $\beta$ -methyl-*n*-valermethylanilide, b. p. 170°/18 mm. (together with a substance, b. p. 170—210°/18 mm.);  $\beta$ -phenyl-*n*-butyrmethylanilide, b. p. 205—210°/18 mm. (together with diphenyl and a compound, b. p. 210—270°/18 mm.); and  $\beta$ -methyl-*n*-valerethylanilide, b. p. 160°/14 mm. (together with a compound, b. p. 160—270°/10 mm.). Hydrolysis of these anilides with 40% hydrobromic acid affords the corresponding saturated acids.

J. W. BAKER.

**Constitution of some dibromophenetidines.** G. BARGELLINI (Gazzetta, 1930, 60, 559—572).—The work of Staedel (A., 1883, 662) has been repeated, and the conclusion of Jackson and Fiske (A., 1902, i, 362) that the substance, m. p. 107—108°, described as 2:6-dibromo-4-nitrophenetole by Staedel, is actually 2:6-dibromophenetidine (I) is confirmed; 2:6-dibromo-4-nitrophenetole has m. p. 59°. A new synthesis of I has been effected as follows: 2:6-dibromo-4-nitrophenol, m. p. 143°, obtained by bromination of *p*-nitrophenol in acetic acid, by reduction with sodium hyposulphite in alkaline solution gives 2:6-dibromo-4-aminophenol, m. p. 191—193° (N-2:4-dinitrophenyl derivative, m. p. 213—215°), which condenses with piperonaldehyde and benzaldehyde at 100° in an atmosphere of carbon dioxide to give respectively 2:6-dibromo-4-piperonylidene-aminophenol, m. p. 150—152°, and 2:6-dibromo-4-benzylidene-aminophenol, m. p. 94—95°; the latter by ethylation and hydrolysis affords I, m. p. 108°. A specimen of I prepared by Staedel's method, when acetylated with acetyl chloride in benzene solution, yields 2:6-dibromophenacetin, m. p. 198° (cf. Fuchs, A., 1918, i, 64). The preparation of 3:5-dibromophenetidine, m. p. 79° (Fuchs, A., 1915, i, 520; *loc. cit.*), has been repeated: condensation products with 2:4-dinitrochlorobenzene and benzaldehyde could not be obtained. Treatment with benzoyl chloride (1 mol.) in benzene solution affords 3:5-dibromo-*N*-benzoylphenetidine, m. p. 186—188°; acetyl chloride (1 mol.) similarly yields 3:5-dibromophenacetin, m. p. 144° after softening at 130° (cf. Fuchs, *loc. cit.*); by treatment with excess of boiling acetic anhydride, 3:5-dibromophenetidine gives a diacetyl derivative, m. p. 91—92°, partly hydrolysed by ammonia solution or potassium hydroxide to 3:5-dibromophenacetin. Bromination of phenacetin in acetic acid gives 2:5-dibromophenacetin, m. p. 170—171° (benzoyl derivative, m. p. 145—147°; piperonylidene derivative, m. p. 143—145°; N-2:4-dinitrophenyl derivative, melting and decomposing from 145° to 165°), converted by boiling acetic and hydrochloric acids into 2:5-dibromophenetidine hydrochloride, m. p. 225—226°, from which 2:5-dibromophenetidine, m. p. 55—56°, is obtained by treatment with ammonia; 2:5-dibromophenacetin may also be prepared from phenacetin by treatment with a concentrated solution of sodium bromide and bromate in the presence of hydrochloric acid, and its constitution is proved by

de-ethylation with hydriodic acid (*d* 1.7) to 2:5-dibromo-4-aminophenol, m. p. 195—197°, which by oxidation with cold potassium dichromate and dilute sulphuric acid affords 2:5-dibromo-*p*-benzoquinone, m. p. 185—186° (cf. lit.). C. W. SHOPPEE.

**Derivatives of diphenylcarbonyl chloride.** T. W. EVANS and W. M. DEHN (J. Amer. Chem. Soc., 1930, 52, 3645—3647).—Treatment of sodioacetanilide with an equivalent of diphenylcarbonyl chloride in warm toluene affords a soluble additive compound, indicating that the sodio-derivative contains the  $\cdot\text{ONa}$  grouping. The additive compound decomposes when heated to sodium chloride and acetyltriphenylcarbamide, m. p. 144°. Evidence of additive compound formation is also obtained with the chloride and sodioacet-*p*-phenetidine;  $\alpha$ -acetyl- $\gamma$ -diphenyl- $\alpha$ -*p*-phenethylcarbamide, m. p. 131°, is eventually produced. The following compounds are prepared from the chloride and the requisite base (or its metallic derivative) either alone or in toluene:  $\alpha$ -acetyl- $\gamma$ -diphenyl- $\alpha$ -*p*-bromophenylcarbamide, m. p. 137°; pyrrole-1-carboxydiphenylamide, m. p. 117°; piperidine-1-carboxydiphenylamide, m. p. 110°;  $\alpha$ -diphenyl- $\gamma$ -*o*-, -*m*-, and -*p*-chlorophenylcarbamides, m. p. 115°, 129°, and 169°, respectively. Oxaldiphenylamide, m. p. 187°, is obtained from the above chloride and sodium. The following diphenylthiocarbamates ( $\text{NPh}_2\text{CO}\cdot\text{SR}$ ) are prepared from the chloride and the sodium derivative of the requisite mercaptan: ethyl ( $\text{R}=\text{Et}$ ), m. p. 108°; benzyl, m. p. 125°, and *p*-tolyl, m. p. 180—182°. H. BURTON.

**Fluorene series.** K. NAKAMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 184—188; cf. this vol., 466).—The local anæsthetic action of the salts of 9-aminofluorene extends to the hydrogenated derivatives. R. CHILD.

**Aryl amides.** S. WEIL, J. SLIFERSKI, F. BOMBERG, C. WIERZBICKA, and Z. WYSZOGROD (XV Spraw. prac. Państw. Inst. Farm., 1926, 10 pp. Chem. Zentr., 1930, i, 2551—2552).—See A., 1927, 240.

**Production of amines from organic acids and their anhydrides.** KNOLL A.-G. CHEM. FABR., and K. F. SCHMIDT.—See B., 1930, 939.

**Manufacture of arylaminesulphonyl chlorides.** I. G. FARBERIND. A.-G.—See B., 1930, 941.

**Azo-dyes and their intermediates. II. Reductive fission of eriochrome-black and 1:6-diamino- $\beta$ -naphthol-4-sulphonic acid.** P. RUGGLI, A. ZIMMERMANN, and F. KNAPP. **III. 6-Amino- $\beta$ -naphthol-4-sulphonic acid as a dye component.** P. RUGGLI and A. ZIMMERMANN. **IV. Acetyl-1:5-naphthylenediamine and its coupling.** P. RUGGLI and F. KNAPP (Helv. Chim. Acta, 1930, 13, 748—756, 756—763, 763—768).—II. Reduction of eriochrome-black T (sodium 6-nitro-1-*l*'-hydroxy-2'-naphthaleneazo- $\beta$ -naphthol-4-sulphonate) with stannous chloride and hydrochloric acid gives 2-amino- $\alpha$ -naphthol and 1:6-diamino- $\beta$ -naphthol-4-sulphonic acid (monohydrochloride  $+\text{H}_2\text{O}$ ); the acid oxidises readily in alkaline solution. The acid imparts only a slight colour to wool; after-chroming gives a deep black dye. Desulphonation of the acid does not

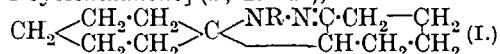
occur on treatment with sodium amalgam and dilute acid at 50°, indicating an internal salt or betaine structure. Treatment of the solution obtained from the acid and sodium amalgam in alkaline solution at 35° in a current of carbon dioxide with benzoyl chloride affords a mixture of 1:6-dibenzamido- $\beta$ -naphthyl benzoate, m. p. 267—269°, and its 4-sulpho-derivative [pyridine salt, m. p. 276° (not sharp)], also formed when the acid is benzoylated in pyridine solution]. Treatment of the diamino-acid first with acetic anhydride and then with cold sodium hydroxide solution yields an acetyl derivative, desulphonated by sodium amalgam and hydrochloric acid below 80° to 1:6-diacetamido- $\beta$ -naphthol, m. p. about 235°. This is acetylated further to 1:6-diacetamido- $\beta$ -naphthyl acetate, m. p. 203°, also prepared by acetylation of 1:6-diamino- $\beta$ -naphthol (Loewe, A., 1890, 1424). Desulphonation of the diamino-acid takes place when it is heated with aniline and a small amount of aniline hydrochloride at 160°; a tetra-anilinonaphthalene is probably produced. Treatment of the diamino-acid with phenylcarbimide and pyridine furnishes pyridine 1:6-di(phenylcarbamido)- $\beta$ -naphthol-4-sulphonate, m. p. 221°.

**III. 6-Nitro- $\beta$ -naphthol-4-sulphonic acid** (this vol., 205) couples with diazotised sulphanilic acid and *p*-nitroaniline in presence of sodium acetate at 0—30°, forming 6-nitro-1-benzeneazo- $\beta$ -naphthol-4:4'-disulphonic acid, red (orange-red; all shades given in parentheses are shades on wool), and 6-nitro-1-*p*-nitrobenzeneazo- $\beta$ -naphthol-4-sulphonic acid, red (bright orange-red). Coupling of 6-amino- $\beta$ -naphthol-4-sulphonic acid (*loc. cit.*) with diazotised aniline and *p*-nitroaniline in presence of sodium carbonate yields 6-amino-1-benzeneazo-, violet-black (bordeaux), and 6-amino-1-*p*-nitrobenzeneazo- $\beta$ -naphthol-4-sulphonic acid (dark brown), respectively. Dyes are also prepared from the amino-acid and diazotised dehydrothio-*p*-toluidinesulphonic acid (greyish-green), diazotised aminoazobenzenesulphonic acid (olive-green; poor shade), and tetrazotised benzidine (acid coupling brown; alkaline coupling bluish-grey). Alkaline  $\beta$ -naphthol and diazotised 6-amino- $\beta$ -naphthol-4-sulphonic acid give sodium 6-2'-hydroxy-1-1'-naphthaleneazo- $\beta$ -naphthol-4-sulphonate (garnet-red).

**IV. Reduction of 1:5-dinitronaphthalene with phenylhydrazine in xylene at 130—160° gives 5-nitro- $\alpha$ -naphthylamine** (best prepared by Nietzki and Zübelen's method; A., 1889, 513), the acetyl derivative, m. p. 218°, of which is reduced by iron powder and 50% alcohol containing a small amount of acetic acid to acetyl-1:5-naphthylenediamine, m. p. 164°. This couples with diazotised sulphanilic acid, forming 5-acetamido-2-benzeneazo- $\alpha$ -naphthylamine-4'-sulphonic acid, reduced by stannous chloride and hydrochloric acid to 5-acetamido-1:2-naphthylenediamine (dihydrochloride, decomp. 175°; diphenylquinoxaline derivative, m. p. 248—250°). The acetamido-group prevents coupling in the 4-position (cf. Finzi, A., 1925, i, 701). H. BURTON.

**Anhydro-[(1'-hydrazino-1'-cyclohexyl)-1-cyclohexan-2-one].** R. STOLLÉ and F. HANUSCH (Ber., 1930, 63, [B], 2211—2215).—cycloHexanoneazine, m. p. 35°, is converted by anhydrous oxalic, maleic,

or succinic acid into *anhydro*-[(1'-hydrazino-1'-cyclohexyl)-1-cyclohexanone] (I; R=H),



b. p. 165°/17 mm., m. p. about 64°, which gives a *methiodide*, m. p. 186°, in poor yield, a *phenylcarbamide* derivative (I; R=CO·NHPh), m. p. 124°, a *phenylthiocarbamide* compound (I; R=CS·NHPh), m. p. 168°, and a *carbamide* derivative (I; R=CO·NH<sub>2</sub>), m. p. 161°. *s*-Dicyclohexylhydrazine is transformed by phenylcarbimide in ether into 4-phenyl-1:2-dicyclohexylsemicarbazide, NHC<sub>6</sub>H<sub>11</sub>·N(C<sub>6</sub>H<sub>11</sub>)·CO·NHPh, m. p. 124°, also prepared from the product of the reduction of cyclohexanoneazine by sodium and alcohol, which is therefore regarded as *s*-dicyclohexylhydrazine and not as the unsymmetrical product as stated by Kishner and Bjelov (J. Russ. Phys. Chem. Soc., 43, 577). 1:2-Dicyclohexyl-4-phenylthiosemicarbazide has m. p. 129°.

H. WREN.

**Mechanism of the formation of formazyl compounds.** II. M. BUSCH and R. SCHMIDT (Ber., 1930, 63, [B], 1950—1952).—The supposed production of a formazyl compound,

NPhMe·N:CPh·N:N·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, from *p*-nitroisodiazo-benzene hydroxide and benzaldehydephenylmethylhydrazone is at variance with the author's theory of the production of formazyl compounds (cf. A., 1926, 831). Since the compound yields benzaldehyde when hydrolysed by dilute sulphuric acid and is reduced to *p*-phenylenediamine and a primary aromatic amine it must be regarded as the *azo*-compound, NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·N:N·C<sub>6</sub>H<sub>4</sub>·NMe·N:CHPh. Benzaldehydephenylmethylhydrazone behaves analogously to the methyl compound, whereas benzaldehyde-*as*-dibenzylhydrazone does not afford a trace of *azo*-derivative.

H. WREN.

**Constitution and reactions of the isomeric diazo-hydrates (diazo-hydroxides).** A. ANGELI (Ber., 1930, 63, [B], 1977—1980; cf. this vol., 906).—In reply to Hantzsch (this vol., 1032), numerous examples are cited showing that normal diazo-hydroxides act generally as oxidising agent, whereas *isodiazo*hydroxides have not this power. Hantzsch's admission that a compound, Ph·NO·NH, exists which has the same composition as the diazo-hydroxides and gives the coupling reactions characteristic of normal derivatives is emphasised.

H. WREN.

**cis-trans-Isomerism and steric hindrance.** XII. 2-Butylcyclohexanols. G. VAYON and A. GUÉDON (Bull. Soc. chim., 1930, [iv], 47, 901—910).—*cis*-2-Butylcyclohexanol, b. p. 112—113°/18 mm., *d*<sub>4</sub><sup>20</sup> 0.9115, *n*<sub>D</sub><sup>20</sup> 1.4672 (3:5-dinitrobenzoate, m. p. 76°; *hydrogen phthalate*, m. p. 58—59°; *phenylurethane*, m. p. 64—65°), is obtained by hydrogenating 2-butylcyclohexanone, b. p. 90—91°/10 mm., *d*<sub>4</sub><sup>20</sup> 0.914, *n*<sub>D</sub><sup>20</sup> 1.4603 (*semicarbazone*, m. p. 143—144°, converted when hydrogenated with platinum-black in aqueous alcohol in presence of hydrochloric acid into the *semicarbazide*, m. p. 96—97°; *oxime*, m. p. 43—44°), in presence of platinum-black in acetic and hydrochloric acids. *trans*-2-Butylcyclohexanol, b. p. 111—112°/16 mm., *d*<sub>4</sub><sup>20</sup> 0.9046, *n*<sub>D</sub><sup>20</sup> 1.4654 (3:5-dinitrobenzoate, m. p. 72—73°; *hydrogen phthalate*, m. p.

71°; *phenylurethane*, m. p. 68°), is similarly obtained by hydrogenation with sodium and alcohol, the crude mixture, b. p. 107—110°/12 mm., rich in *trans*-isomeride being obtained in 87% yield. In both cases the isomerides are purified through their dinitrobenzoates. In accordance with Auwers' rule, the *trans*-isomeride has a slightly lower density and refractive index and a higher molecular refraction than the *cis*-isomeride. At 100° the velocities of esterification of the alcohols by acetic acid in the absence of a catalyst are approximately equal; at 39° and in presence of 2% of sulphuric acid the *trans*-isomeride is esterified about 1.6 times as rapidly as the *cis*-isomeride. Similarly, the *trans*-hydrogen phthalate is hydrolysed by alkali more rapidly than the *cis*-isomeride. At 39° in 0.1*N*-aqueous solution the ratio of the velocity coefficients is 3.6 and in 75% alcohol 2.5. The difference is less marked at 69°, the ratio in 75% alcohol being 1.09. Contrary to the cases of ethyl *isovalerate* or *benzoate*, hydrolysis is more rapid in alcohol than in water, the differences between the isomerides being more marked in water in consequence.

2-Butylcyclohexanone is obtained in 60% yield by hydrogenation of *o*-butylphenol, b. p. 115—118°/13 mm., *d*<sub>4</sub><sup>20</sup> 0.987, *n*<sub>D</sub><sup>20</sup> 1.522 (*p*-nitrobenzoate, m. p. 38—39°; *dinitrobenzoate*, m. p. 81—82°), with platinum-black in acetic acid, or in 20% yield by condensation of butaldehyde with cyclohexanone in presence of 5% sodium hydroxide, dehydration of the fraction, b. p. 130—145°/15 mm., by distillation in presence of 2% of oxalic acid at 30—40 mm., and hydrogenation of the fraction, b. p. 105—120°/20 mm., in presence of platinum-black. *o*-Butylphenol is obtained in 45% yield by diazotisation of *o*-butylaniline and decomposition in presence of sulphuric acid. *o*-Butylaniline, b. p. 124—126°/15 mm. (acetyl derivative, m. p. 100°), is obtained in 86% yield by catalytic reduction in presence of platinum-black in acetic acid of *o*-nitrobutylbenzene, b. p. 124—127°/10 mm. Butylbenzene, obtained by dehydrating phenylpropylcarbinol in presence of potassium hydrogen sulphate and hydrogenating in presence of platinum-black, when nitrated at 0° with nitric acid, *d* 1.49, in acetic anhydride yields 85% of a mixture of mononitro-compounds containing 3 parts of *ortho*- and 5 parts of *para*-derivative. Condensation of 2-chlorocyclohexanone with magnesium butyl bromide also affords 2-butylcyclohexanone together with some butyl cyclopentyl ketone, b. p. 104—106°/25 mm., *d*<sub>4</sub><sup>20</sup> 0.893, *n*<sub>D</sub><sup>20</sup> 1.4479 (*semicarbazone*, m. p. 122°, yielding on hydrogenation in presence of platinum-black a *semicarbazide*, m. p. 68°), the constitution of which has been verified by its synthesis [with M. BARBIER] from cyclopentanaldehyde (from magnesium ethyl bromide and chlorocyclohexanol) and magnesium butyl chloride, and oxidation with chromic acid of the cyclopentylbutylcarbinol, b. p. 110°/16 mm., *d*<sub>4</sub><sup>20</sup> 0.902, *n*<sub>D</sub><sup>20</sup> 1.4628, obtained in 60% yield.

R. BRIGHTMAN.

**Catalytic hydrogenation of simple and cyclic ethers.** S. KOMATSU and M. MASUMOTO (Bull. Chem. Soc. Japan, 1930, 5, 241—248).—Phenyl ether, hydrogenated with a nickel catalyst under 60 atm. and not higher than 250°, yields a mixture of cyclo-



hexane, cyclohexanol, and cyclohexyl ether. Similar hydrogenation of furfuraldehyde at 160°/100 atm. yields furan, methylfuran, and furfuryl alcohol, the last-named being the main product. By similar hydrogenation of furfuryl alcohol under different conditions of temperature and pressure dihydro- and tetrahydro-furfuryl alcohol, tetrahydrofuran, methyltetrahydrofuran, and *n*-butyl alcohol are obtained. The course of the chemical changes in these hydrogenations is suggested in the light of these results.

H. I. DOWNES.

**Methylation of phenols.** A suggested mechanism. H. H. HODGSON and J. NIXON (J.C.S., 1930, 2166—2168).—The percentage yields of methylation products of the following phenols by methyl sulphate in xylene solution in the presence of anhydrous potassium carbonate (method B) and by methyl sulphate and 10% aqueous sodium hydroxide (method A) under standard conditions were obtained: phenol, 0 and 65; *o*-, 0 and 71.4, *m*-, 0 and 82.0, and *p*-cresol, 0 and 71.3; *o*-, 71.5 and 47.0, *m*-, 65.0 and 65.0, and *p*-nitrophenol, 79.6 and 55.5; *o*-, 14.0 and 72.5, *m*-, 28.0 and 81.0, and *p*-chlorophenol, 9.0 and 81.0; 6-chloro-2-nitrophenol, 75.0 and 19.5; 2-chloro-4-nitrophenol, 86.0 and 8.0; 4-chloro-2-nitrophenol, 75.0 and 0; 5-nitro-*o*-cresol, 0 and 0; 2-nitro-*p*-cresol, 73 and 9; 6-nitro-*o*-cresol, 41.5 and 18; 4-fluoro-2:6-di-iodo-, 9.7 and 40.0, 4-fluoro-2:6-dibromo-, 53.0 and 53.0, and 4-fluoro-2:6-dichloro-phenol, 60.0 and 10.0. The results, except for *m*-nitro-*o*-cresol, which is unaffected, are in accord with the view that reaction A proceeds by the initial attachment of methyl sulphate at the anionoid oxygen of the ionised phenol, so that if the charge is not sufficiently localised very little reaction occurs, and that in method B, where ionisation is reduced to a minimum, reaction occurs between methyl sulphate and an almost non-ionised potassium salt at an incipient dipole, the formation of which will be enhanced by nitro- and halogeno-substituents, but repressed by methyl groups.

A. I. VOGEL.

**Dinitration of monosulphonated *m*-chloro-phenol and sulphonation and subsequent further nitration of 3-chloro-2- and -6-nitrophenols.** H. H. HODGSON and A. KERSHAW (J.C.S., 1930, 2169—2171).—*m*-Chlorophenol when dissolved in 100% sulphuric acid and treated with oleum (25% SO<sub>3</sub>) below 15°, and then dinitrated with nitric acid (*d* 1.5) in oleum (25% SO<sub>3</sub>), and the product hydrolysed with steam, yields a mixture of 3-chloro-2:4- and -2:6-dinitrophenols, separated by dissolution of the isomerides in dilute acetic acid (6:1), the 3-chloro-2:4-compound separating on cooling and the ammonium salt of the isomeride being precipitated from the filtrate with excess of ammonia. Sulphonation at 100° and subsequent dinitration and hydrolysis yielded a similar mixture, but with a larger proportion of 3-chloro-2:6-dinitrophenol.

3-Chloro-2-nitrophenol when treated with oleum (30% SO<sub>3</sub>) below 20° and subsequently with potassium carbonate gives potassium 3-chloro-2-nitrophenol-4-sulphonate dihydrate, converted by nitration and subsequent hydrolysis into 3-chloro-2:6-dinitrophenol. Similar sulphonation of 3-chloro-2-nitrophenol,

followed by nitration below 20° with nitric acid (97%) and oleum (30% SO<sub>3</sub>), and then addition of potassium carbonate, gives potassium 3-chloro-2:6-dinitrophenol-4-sulphonate and potassium 3-chloro-2:4-dinitrophenol-6-sulphonate, separated by fractional crystallisation.

By treatment with oleum (30% SO<sub>3</sub>) and then with potassium carbonate 3-chloro-6-nitrophenol yields potassium 3-chloro-6-nitrophenol-4-sulphonate dihydrate (dinitration and hydrolysis gave 3-chloro-2:6-dinitrophenol); nitration of the sulphonation mixture gives potassium 3-chloro-2:6-dinitrophenol-4-sulphonate.

A. I. VOGEL.

**Process of nitration.** III. Nitration of *o*- and *m*-cresol. S. VEIBEL (Ber., 1930, 63, [B], 2074—2082).—The methods described previously are applied to *o*- and *m*-cresol (cf. this vol., 1033). Nitration of *o*-cresol leads to the production of 3- and 5-nitro-*o*-cresol in approximately equal amount. Changes in the initial concentration of nitrous acid have little influence on this ratio, which appears to increase slightly with the concentration of nitric acid. During the nitration of *m*-cresol, 4-nitro- (sum of 4- and 2-nitro-) and 6-nitro-*m*-cresol are produced in the ratio 2:3. Changes in the concentration of nitrous and nitric acids have no effect.

H. WREN.

**Action of sulphur monochloride on mercaptans.** II. Formation of organic trisulphides and hexasulphides. P. P. PATEL, I. SENGUPTA, and G. C. CHAKRAVARTY (J. Indian Inst. Sci., 1930, 13A, 73—84).—Sulphur monochloride reacts with *p*-tolyl mercaptan in anhydrous benzene solution to give di-*p*-tolyl trisulphide, m. p. 82—83°, and di-*p*-tolyl hexasulphide. When copper *p*-tolyl sulphide is boiled with sulphur (2 atoms) in dry benzene for 9—10 hrs., di-*p*-tolyl trisulphide is obtained in good yield: this is a general method for the preparation of trisulphides. The following compounds were similarly prepared: *pp'*-dibromodiphenyl trisulphide, m. p. 69°, and hexasulphide; *pp'*-di-iododiphenyl trisulphide, m. p. 91°; dibenzyl tri-, m. p. 47—48°, and hexa-sulphide;  $\beta\beta$ -dinaphthyl tri-, m. p. 107—108°, and tetra-sulphide, m. p. 99°; diethyl tri- and hexa-sulphide; dipropyl and di-*n*-butyl trisulphide.

A. I. VOGEL.

**Valency problem of the quinquivalent electronegative phosphorus atom.** I. L. ANSCHÜTZ and F. WENGER (Annalen, 1930, 482, 25—35).—To throw light on the orientation and nature of the valencies of the quinquivalent electronegative phosphorus atom (i.e., as in compounds derived from phosphorus oxyacids with a quinquivalent central atom) an attempt has been made to resolve the compound [C<sub>6</sub>H<sub>5</sub>Me<O>P<O>C<sub>6</sub>H<sub>5</sub>Me]Cl (I), which should exist in two enantiomorphous forms if four of the valencies are disposed tetrahedrally.

Homocatechol (details are given of preparation from protocatechualdehyde by Clemmensen's method) is converted by means of phosphorus pentachloride in dry ether into bishomocatechyl phosphorus chloride (I), a crystalline solid very sensitive to moisture. With *l*-menthol in ether I affords 1-bis-

4-methyl-1:2-phenylene menthyl orthophosphate, m. p. 65–70°, readily soluble in alcohol. Attempts to resolve the latter by fractional extraction were unsuccessful. Preliminary experiments with other substituted catechols have so far also been fruitless.

Phosphoryl chloride in ether converts homocatechol into homocatechyl phosphorus chloride,  $\text{Me}\cdot\text{C}_6\text{H}_3\text{O}_2\cdot\text{PCl}$ , m. p. 22–24°, b. p. 102°/11 mm. (4-methyl-1:2-phenylene phosphite, b. p. 265°/11 mm., is a by-product). Chlorination of the latter yields the corresponding trichloride, b. p. 158°/11 mm. (not obtained directly from homocatechol and phosphorus pentachloride; see above, and cf. phosphorus catechyl trichloride, A., 1927, 146), and heating at 190° with sulphur gives homocatechyl phosphorus chlorosulphide,  $\text{Me}\cdot\text{C}_6\text{H}_3\text{O}_2\cdot\text{PClS}$ , b. p. 142–143°/11 mm.

The results are discussed in connexion with the work of Gall and Schuppen (this vol., 461), Bergmann and Bondi (*ibid.*, 1050), and others (cf. also A., 1927, 663). R. CHILD.

**Manufacture of [nuclear] alkylated phenols.** SCHERING-KAHLBAUM A.-G.—See B., 1930, 940.

**Manufacture of aminophenol derivatives [ $\alpha$ -methylaminophenol].** H. T. CLARKE, ASSR. TO EASTMAN KODAK CO.—See B., 1930, 940.

**Manufacture of vinyl ethers.** I. G. FARBENIND. A.-G.—See B., 1930, 981.

**Action of monochlorodimethyl ether on magnesium benzyl chloride.** A. C. BOTTOMLEY, A. LAPWORTH, and A. WALTON (J.C.S., 1930, 2215–2216).—Contrary to G.P. 154,658 (1903), magnesium benzyl chloride reacts with chlorodimethyl ether in dry ethereal solution at 0° to give a mixture, separated into two fractions, b. p. 175–205° and 205–270°. The former consisted chiefly of  $\alpha$ -phenylethyl methyl ether, together with small quantities of  $\omega$ -methoxy- $\alpha$ - and - $p$ -xylene, since oxidation with alkaline potassium permanganate at 100° yielded chiefly benzoic acid accompanied by a little phthalic and terephthalic acids.

Magnesium benzyl chloride condenses with both acetone and acetaldehyde to products which gave only benzoic acid on oxidation. A. I. VOGEL.

**Synthesis of an isomeride and a homologue of ephedrine.** E. FOURNEAU, (MLE.) E. BENOIT, and R. FIRMINICH (Bull. Soc. chim., 1930, [iv], 47, 894–900).—Condensation of paraformaldehyde with styrene at 25° in presence of glacial acetic and concentrated sulphuric acid gives a methylene ether, b. p. 120–140°/15 mm., and a 47·8% yield of the diacetate of  $\alpha$ -phenylpropane- $\alpha\gamma$ -diol, b. p. 150–155°/15 mm., from which the glycol, b. p. 175–185°/18 mm., m. p. 45° (dibenzoate, m. p. 51°), is obtained (yield 74·5%) on hydrolysis with 15% alcoholic potassium hydroxide.  $\beta$ -Phenylpropane- $\alpha\gamma$ -diol was not obtained. With hydrogen chloride at 31°  $\alpha$ -phenylpropane- $\alpha\gamma$ -diol is converted into  $\alpha$ -chloro- $\alpha$ -phenylpropane- $\gamma$ -ol, b. p. 130–180°/19 mm., which could not be purified. The diacetate is similarly converted in 14 hrs. at 100° into  $\gamma$ -chloro- $\gamma$ -phenylpropyl acetate, b. p. 155–172°/22 mm., yielding on distillation two fractions, b. p. 145–155°/17 mm., and b. p. 155–162°/17 mm. Methylamine in benzene or aqueous

solution at 125° converts the chlorohydrin into  $\gamma$ -methylamino- $\gamma$ -phenylpropyl alcohol, b. p. 160–163°/21 mm., m. p. 59–60° (hydrochloride, m. p. 95–96°, without sympathomimetic action).  $\gamma$ -Dimethylamino- $\gamma$ -phenylpropyl alcohol is an oil (hydrochloride, m. p. 182°; methiodide, m. p. 158°; benzoate hydrochloride, m. p. 146°).

$\beta$ -Bromo- $\gamma$ -methylamino- $\alpha$ -phenylpropyl acetate with methylamine in benzene at 150° for 24 hrs. similarly gives (yield 48%)  $\gamma$ -methylamino- $\beta$ -phenyl- $\beta$ -methylpropyl alcohol, b. p. 142–148°/12 mm. (hydrochloride, m. p. 119°). The hydrochloride produces definite hypertension in canine arteries and appears to have a more pronounced action than ephedrine on muscular tissues. R. BRIGHTMAN.

**Mobile anion tautomerism. V.  $\gamma$ -Phenyl- $\alpha$ - $p$ -dimethylaminophenylallyl alcohol.** H. BURTON (Proc. Leeds Phil. Soc., 1930, 2, 61–63).—Attempts to prepare  $\gamma$ -phenyl- $\alpha$ - $p$ -dimethylaminophenyl- and  $\gamma$ -phenyl- $\alpha$ - $p$ -methoxyphenyl-allyl alcohols have been made, since these alcohols should show greater anionotropic mobility ( $\text{OH}\cdot\text{CHR}\cdot\text{CH}\cdot\text{CHR}'\rightarrow\text{CHR}\cdot\text{CH}\cdot\text{CHR}'\cdot\text{OH}$ ) than the corresponding  $\alpha$ - $p$ -chlorophenyl derivative (A., 1928, 634). The product from magnesium styryl bromide and  $p$ -dimethylaminobenzaldehyde could not be characterised, but with hydrochloric acid it gives an intense crimson coloration. The colour is ascribed to the formation of the quinonoid ammonium salt,

$\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\text{Cl}$ . A similar formulation is given to the dark red perchlorate of  $\gamma$ -phenyl- $\alpha$ -di- $p$ -methoxyphenylallyl alcohol (Ziegler and Ochs, A., 1922, i, 151), and the red compound produced (but not isolated) when the reaction product from magnesium  $p$ -anisyl bromide and cinnamaldehyde is treated with sulphuric and acetic acids.

H. BURTON.

**Synthesis of phenylpropargyl alcohol and its nuclear-substituted homologues.** L. BERT (Compt. rend., 1930, 191, 493–495).—Phenylpropargyl alcohol is prepared by treatment of dibromocinnamyl acetate (cf. Bert and Dorier, this vol., 1286, 1290) with sufficient alcoholic potassium hydroxide at 66° to remove two molecules of hydrogen bromide and simultaneously the acetyl radical. C. C. N. VASS.

**Naphthalene-green V.** F. FRISCH (Helv. Chim. Acta, 1930, 13, 768–785).—Sulphonation of  $\alpha$ -naphthylamine-7-sulphonic acid with fuming sulphuric acid (25%  $\text{SO}_3$ ) at 50–60°, subsequent addition of fuming acid (66%  $\text{SO}_3$ ), and continuation of the reaction at 85–90°, affords  $\alpha$ -naphthylamine-2:4:7-trisulphonic acid ( $+2\text{H}_2\text{O}$ ) [disodium hydrogen ( $+1\cdot5\text{H}_2\text{O}$ ); dipotassium hydrogen ( $+1\cdot5\text{H}_2\text{O}$ ); barium hydrogen ( $+3\text{H}_2\text{O}$ ); calcium hydrogen ( $+1\cdot5\text{H}_2\text{O}$ ), and magnesium hydrogen ( $+1\cdot5\text{H}_2\text{O}$ ), salts]. When the above calcium salt is heated with  $pp'$ -tetramethyldiaminobenzhydrol, 10% sulphuric acid, 50% acetic acid, and water at 100° (bath), an almost theoretical yield of  $pp'$ -tetramethyldiaminodiphenyl-1:4-amino-naphthylmethane-3:6-disulphonic acid (I), is obtained. This is oxidised by lead peroxide to the corresponding carbinol [fast acid-blue B (cf. G.P. 76,073)]. Similar oxidation of the acetyl and phthalamic acid derivatives

of I affords the corresponding *carbinols*, which dye wool with green and bluish-green shades, respectively. Replacement of the amino-group in I by chlorine and subsequent oxidation give the corresponding *carbinol* (bluish-green on wool). When I is diazotised, then treated with sulphur dioxide in presence of copper powder, the resulting sulphinic acid oxidised by atmospheric oxygen to *pp'*-tetramethyl-diaminodiphenyl-1-naphthylmethane-3 : 4 : 6-trisulphonic acid, and this oxidised by lead peroxide, the *carbinol* obtained dyes wool with a green shade. The fastness of the above dyes to ammonia, sodium hydroxide and carbonate, and light is given.

$\alpha$ -Naphthylamine-2 : 4 : 7-trisulphonic acid reacts with *pp'*-tetraethyl-diaminobenzhydrol in presence of 50% sulphuric and acetic acids and sufficient water to effect solution at 100° (bath), forming *pp'*-tetraethyl-diaminodiphenyl-1-4-aminonaphthylmethane-3 : 6-disulphonic acid. Elimination of the amino-group from this by the usual method and subsequent oxidation with lead peroxide affords *pp'*-tetraethyl-diaminodiphenyl-1-naphthylcarbinol-3 : 6-disulphonic acid, identical with naphthalene-green V. The structure recorded for this dye in the literature (G.P. 108,129, 110,086, 169,929) is incorrect. H. BURTON.

Montignie's isomeride of cholesterol, and the effect of heat on cholesterol. Y. KAISHIO and J. A. GARDNER (Biochem. J., 1930, 24, 1047—1050; cf. Montignie, A., 1929, 1292).—The alleged isomeride is an impure cholesterol containing cinnamic acid and cholesteryl cinnamate. Pure specimens of cholesterol, whether distilled in a high vacuum or heated at 185° in a vacuum for many hours, after recrystallisation from alcohol (m. p. 148—148.5°) gave no colour with Rosenheim's reagent even on prolonged keeping. Specimens heated in open test-tubes at various temperatures from 160° to 200° after recrystallisation from alcohol gave a copper sulphate-blue colour with the reagent. The absorption spectrum was characterised by a well-marked band at 6600 Å. and in some cases a fainter band at about 6068 Å.; the specific rotatory power was slightly depressed. A profound change was obtained when cholesterol was heated at about 180° in a slow current of oxygen for 20 hrs. or more. S. S. ZILVA.

Isomerisation of ergosterol with fuller's earth. F. G. McDONALD and C. E. BILLS (J. Biol. Chem., 1930, 88, 601—604).—Ergosterol was boiled in benzene solution with fuller's earth and the benzene extract after evaporation extracted with hot alcohol. The residue obtained by evaporation of the alcohol was crystallised ten times, and finally yielded a substance, m. p. 142°,  $[\alpha]_{D}^{25}$  —37.3°, showing an absorption band at 248 m $\mu$ . These data agree with those given for *isoergosterols* prepared by the action of hydrochloric and hydrobromic acids on ergosterol. Iodine value determinations showed that the substance has the same number of double linkings as ergosterol. Since the Rosenheim test was positive, one of these is probably in the  $\Delta^{1:2}$  (or  $\Delta^{1:3}$ ) position. An acetate, m. p. 149°,  $[\alpha]_{D}^{25}$  —52.4°, saponification value 129.3, was also prepared. G. F. MARRIAN.

Aldehyde reactions with irradiated ergosterol and a colloid-chemical aldehyde test. A. STEIG-

MANN (Kolloid-Z., 1930, 52, 349—350).—After irradiation ergosterol gives tests for aldehydes. A new aldehyde test has been devised. To 5% sodium thio-sulphate solution are added 5 c.c. of 2*N*-sulphuric acid; in the presence of even traces of aldehydes the appearance of colloidal sulphur is strongly retarded or completely inhibited. Ketones do not produce this effect.

E. S. HEDGES.

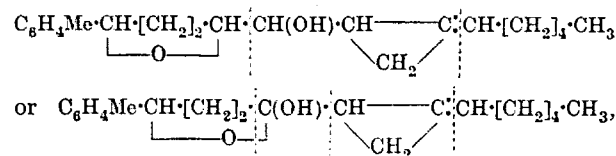
Stigmasterol and its empirical formula. H. SANDQVIST and J. GORTON (Ber., 1930, 63, [B], 1935—1938).—Recorded analyses of stigmasterol and its derivatives fail to discriminate between the empirical formulae,  $C_{30}H_{50}O$  and  $C_{29}H_{48}O$ . Determination of the mol. wt. in camphor gives very variable results. Titration of the dicarboxylic acid derived from stigmasterol indicates the composition  $C_{29}H_{48}O$  for the parent substance; this formula is confirmed by quantitative hydrolysis of stigmasteryl acetate. The following constants are recorded: stigmasteryl acetate tetrabromide, m. p. 202—203° (corr., decomp.),  $[\alpha]_D$  —40° in chloroform; stigmasteryl acetate, m. p. 144.0—144.6° after softening at 143.2°,  $[\alpha]_D$  —55.0°; stigmasterol, m. p. 169—170° after softening at 168°,  $[\alpha]_D^{25}$  —51.0°. H. WREN.

Sterols from yeast. II. H. WIELAND and G. A. C. GOUGH (Annalen, 1930, 482, 36—49; cf. A., 1929, 1200).—Yeast sterol residues (from the technical preparation of ergosterol) of m. p. above 120° still contain ergosterol; zymosterol is present in larger amount in residues of m. p. below 120°. From the latter have been isolated the following new sterols: *episterol* (I),  $C_{27}H_{43}OH$  (+1H<sub>2</sub>O when air-dried), m. p. 135—136°,  $[\alpha]_D^{25}$  +6.2°, separated as its *benzoate*, m. p. 161—163°,  $[\alpha]_D^{25}$  +11.8°; *anasterol* (II),  $C_{27}H_{43}OH$ , m. p. 157—159°,  $[\alpha]_D^{25}$  —8.1°, also isolated as *benzoate*, m. p. 180—182°,  $[\alpha]_D^{25}$  —13.8°; and *hyposterol* (III),  $C_{27}H_{41}OH$  (+1H<sub>2</sub>O), m. p. 100—102°,  $[\alpha]_D^{25}$  +12.5°, separated from a starting material of m. p. about 105° as the *p*-nitrobenzoate, m. p. 154—155° to a turbid liquid clearing at 180°,  $[\alpha]_D^{25}$  +26.7° (*benzoate*, m. p. 119—121° to a turbid liquid clearing at 138°,  $[\alpha]_D^{25}$  +19.1°). The last-named is unstable and is not therefore obtained from residues which have been kept; the instability and low rotation of samples of zymosterol not specially purified (*loc. cit.*; cf. Reindel and Weickmann, A., 1929, 1443) are ascribed to the presence of III. From the same starting material as III has been isolated a *sterol* (IV),  $C_{27}H_{43}OH$ , m. p. 144—146°,  $[\alpha]_D^{25}$  —33.8° (*benzoate*, m. p. 158—160°,  $[\alpha]_D^{25}$  —4.4°), of doubtful homogeneity. Diagrams are given of the ultra-violet spectra of I—IV and of the sterols previously described; the close resemblance of the spectra of neosterol and ergosterol is significant, and that of IV indicates the presence of ergosterol in the latter. A table is also given of colour reactions, comparing I—IV with ergosterol and zymosterol. R. CHILD.

Constitution of cannabinol, the active principle of hashish. I. F. BERGEL [in part with R. WAGNER] (Annalen, 1930, 482, 55—74).—The residue from the extraction with alcohol or light petroleum of African hemp (*Cannabis africana*) after removal of acids and the hydrocarbon "cannabene" (Fraenkel, Arch. exp. Path. Pharm., 1903, 49, 266) is distilled in

a high vacuum. The pharmacologically active fraction ("cannabinol," I) has b. p.  $156^{\circ}/0.05$  mm. (cf. Wood and others, J.C.S., 1896, 69, 539; 1899, 75, 20; Czerkis, A., 1907, i, 331),  $[\alpha]_D^{25}$   $-108.5^{\circ}$ ,  $n_D^{25}$  1.547,  $d_4^{25}$  1.0311 (cf. the constants given by Casparis, Pharm. Acta Helv., 1926, 1, 210; 1927, 2, 1). Neither acetylcannabinol (II), b. p.  $180^{\circ}/0.05$  mm.,  $n_D^{25}$  1.529 (contrary to the statement of Wood, *loc. cit.*), nor benzoylcannabinol, b. p.  $170-180^{\circ}/0.6$  mm., could be crystallised. Dihydrocannabinol (III) (by catalytic hydrogenation) (cf. Casparis, *loc. cit.*), b. p.  $176-177^{\circ}/0.35$  mm.,  $n_D^{25}$  1.54, closely resembles the parent substance; the acetyl derivative (IV) (also obtained by reduction of acetylcannabinol), b. p.  $162-164^{\circ}/0.15$  mm.,  $n_D^{25}$  1.5171, is pharmacologically active. Cannabinol takes up three molecules, dihydrocannabinol two molecules, of bromine, in each case with formation of two molecules of hydrogen bromide. Perhydrocannabinol (V) (by hydrogenation under pressure), b. p.  $145-155^{\circ}/0.6$  mm., contains eight hydrogen atoms more and one oxygen atom less than cannabinol (see below), and is stable in the cold to oxidising agents. With Millon's reagent I and III give positive, II, IV, and V negative reactions. From the products of oxidation of I by means of permanganate have been isolated *n*-hexoic acid (identified as the anilide) and isophthalic acid; oxidation of II also affords *n*-hexoic acid. Oxidation of III by means of permanganate gives besides *n*-hexoic acid, an acid,  $C_{11}H_{10}O_4$ , m. p.  $202-203^{\circ}$  (ethyl ester, m. p.  $103-104^{\circ}$ ), possibly cannabinolactonic acid (Wood, *loc. cit.*), and a neutral substance of mol. wt. above 900, empirical formula  $C_{20}H_{30}O_2$ ; whilst the use of permanganate in acetone solution affords an acid (isolated as the anilide, m. p.  $148.5^{\circ}$ ,  $C_{10}H_{17}O \cdot NHPh$ ), for which the structure  $CH_3 \cdot [CH_2]_5 \cdot CH < \begin{smallmatrix} CH_2 \\ CH \cdot CO_2H \end{smallmatrix}$  is tentatively suggested on the ground that failure to hydrogenate the anilide indicates the absence of double linkings.

Analyses indicate the formula  $C_{20}H_{30}O_2$  for I (the other derivatives, II to V above, follow), but  $C_{21}H_{30}O_2$  is not excluded. Attempts to account for the oxidation products described lead to the following provisional structures for I, when one of Wood's suggested formulations of cannabinolactone is adopted (cf., however, Cahn, this vol., 913):



points of fission being indicated by the dotted lines.

The oxidation of I by means of nitric acid in acetic acid solution yields *n*-hexoic acid and nitrocannabinolactone (Wood, *loc. cit.*), obtained also from II and III; aminocannabinolactone and nitrocannabinolactonic acid from the latter have properties agreeing with earlier descriptions (Wood, *loc. cit.*; Cahn, *loc. cit.*). Alkali fusion of the last-named affords an acid, sinters above  $300^{\circ}$ , probably 2-nitroisophthalic acid.

$\gamma$ -*p*-Tolylbutyrolactone, m. p.  $69^{\circ}$ , is obtained by reduction of  $\beta$ -*p*-toluoylpropionic acid (Katzenellenbogen, A., 1902, i, 121). Nitration of the latter gives

a nitrotoluyolpropionic acid, m. p.  $149^{\circ}$ , reduced to an amino-*p*-tolylbutyrolactone, m. p.  $105^{\circ}$ , not identical with aminocannabinolactone. R. CHILD.

**Halogenation. IV. Bromination and iodination of aromatic acids.** P. S. VARMA and P. B. PANICKER (J. Indian Chem. Soc., 1930, 7, 503-504).—Benzoic acid and some derivatives may be brominated and iodinated by action of the halogen in an inert solvent (e.g., carbon tetrachloride or glacial acetic acid) or in the absence of a solvent, and in presence of (1) nitric and nitrosulphonic acids, or (2) sodium nitrite and fuming sulphuric acid. Benzoic acid gives *m*-bromo- and *m*-iodo-benzoic acids by both methods, the yield by the former being excellent. By method 2, *p*-toluic acid gives 2-bromo-(or iodo)-*p*-toluic acid, *o*-toluic acid gives 4-bromo-(or iodo)-*o*-toluic acid, and anisic acid gives 3-bromo-(or iodo)-anisic acid. *m*-Toluic, the three phthalic, and negatively substituted (e.g., nitro- and chloro-)benzoic acids are unaffected. H. A. PIGGOTT.

**Organo-antimony compounds. IV. Stibinic acids derived from local anaesthetics.** S. C. NIXON (J. Indian Chem. Soc., 1930, 7, 577-587).—Benzyl *o*-nitrobenzoate, m. p.  $54-55^{\circ}$ , and *m*-nitrobenzoate, m. p.  $48-49^{\circ}$ , are prepared from the appropriate acid chloride and benzyl alcohol in pyridine. Benzyl *p*-nitrobenzoate (cf. Bamberger and Renauld, A., 1898, i, 20) also results from the interaction of the acid and alcohol at  $160-180^{\circ}$ ; this method occasionally succeeds with *o*-nitrobenzoic acid, but does not give consistent results. Interaction of *o*- and *m*-nitrobenzoyl chlorides with benzyl alcohol in presence of excess of aqueous alkali gives, not the esters, but *o*-nitrobenzoic anhydride, m. p.  $128-129^{\circ}$ , and *m*-nitrobenzoic anhydride, m. p.  $162-163^{\circ}$ , respectively. *o*-Nitrobenzyl benzoate, m. p.  $101-102^{\circ}$ , is obtained from *o*-nitrobenzyl alcohol and benzoyl chloride in pyridine. The interaction of *o*-nitrobenzyl chloride and sodium benzoate in aqueous solution (Gomberg and Buchler, A., 1920, i, 839) gives an impure product, but the method readily yields *m*-nitrobenzyl benzoate, m. p.  $71-72^{\circ}$ , and *p*-nitrobenzyl benzoate, m. p.  $94-95^{\circ}$ . Benzyl *p*-aminobenzoate, m. p.  $90-91^{\circ}$ , and *m*-aminobenzoate hydrochloride, m. p.  $199-200^{\circ}$ , are obtained by reduction of the nitro-compounds with alcoholic ammonium sulphide, whilst for benzyl *o*-aminobenzoate hydrochloride, m. p.  $162-163^{\circ}$ , *o*-aminobenzyloxy benzoate (Paal and Bodewig, A., 1893, i, 20), and *m*-aminobenzyloxy benzoate hydrochloride, m. p.  $198-199^{\circ}$ , the aluminium-mercury couple in moist ether is used. No definite product was isolated by reduction of *p*-nitrobenzyl benzoate. By application of the Bart-Schmidt reaction to these amino-derivatives, sodium benzylbenzoate-4-stibinate, -3-stibinate, -2-stibinate, and -5-stibinate are prepared.

H. A. PIGGOTT.

**Nitration. IV. Nitration by means of a mixture of nitrosulphonic and fuming nitric acids.** P. S. VARMA and S. SHARMA (J. Indian Chem. Soc., 1930, 7, 629-631; cf. A., 1925, i, 238).—Nitration of *p*-nitrophenol, *p*-dibromobenzene, *p*-chlorophenol, cinnamic acid, and 1-nitronaphthalene with a mixture of nitrosulphonic and fuming nitric

acids, usually in presence of chloroform or carbon tetrachloride, gives varying amounts of mono-nitrated derivatives (or mixtures). When the inert solvent is not used reaction is usually violent. Similar treatment of sulphanilic acid affords a mixture of *p*-nitro-, 2:4-dinitro-, and 2:4:6-trinitro-phenols; *o*-amino-benzoic acid furnishes salicylic acid, whilst *m*- and *p*-aminobenzoic acids give 4-nitro-3- and 3-nitro-4-hydroxybenzoic acids, respectively. Benzoin is oxidised to benzil, whilst quinol yields a mixture of quinhydrone and *p*-benzoquinone. H. BURTON.

**Hydrogenation of amino-acids.** F. LIEBEN and E. VON PAPHAZY (Biochem. Z., 1930, 225, 227—237).

—Tyrosine, tryptophan, and histidine are not reduced by sodium amalgam. The reduction of cystine is, however, quantitative in pure solution, but is inhibited in protein hydrolysates. Reduction may then be rendered complete by addition of zinc chloride during hydrolysis. Catalytic reduction of tyrosine, phenylalanine, tryptophan, dihydroxyphenylalanine, and adrenaline succeeds with platinum on carbon. The Millon reaction with tyrosine is still quantitatively obtained after addition of 1 molecule, decreases to half after addition of 2, and disappears after addition of 3 molecules of hydrogen. Cystine is reduced by platinum-black, but tyrosine, phenylalanine, and histidine are not reduced. Catalytic hydrogenation of protein with platinum was not successful.

P. W. CLUTTERBUCK.

**Dynamic stereochemistry. I, II.** H. ERLÉNMEYER (Helv. Chim. Acta, 1930, 13, 731—747).—I. Theoretical. Differences in stereochemical form are discussed mainly from observations recorded in the literature.

II. When *d*-cinchotine cinnamate is treated with bromine in chloroform solution at 0° or 20° and the resulting product freed from base by treatment with dilute hydrochloric acid, an optically active specimen of  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid is obtained; this contains 57.8—58.3% of the *d*-acid. Bromination of the salt in the solid phase gives an acid containing 51.3—51.9% of the optically active form. Similar results are obtained when *d*-glucosamine cinnamate is treated with bromine in the solid state and in aqueous solution in presence of charcoal. In the last case the salt is adsorbed by the charcoal and bromination of the adsorbed molecules occurs. It is concluded that the transference of asymmetry from the optically active base to the synthesised asymmetric carbon atom occurs more readily in the amorphous molecule (i.e., in solution) than in the crystal molecule. These molecules are, therefore, not identical, but possess differing stereochemical form. Treatment of *d*- $\alpha$ -pipercoline cinnamate with bromine, either in the solid state or in chloroform solution, gives an optically inactive  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid.

H. BURTON.

**Stability of unsaturated compounds in presence of catalysts.** M. N. GOSWAMI (J. Indian Chem. Soc., 1930, 7, 647—650).—When styrene, phenylacetylene, stilbene, or ethyl cinnamate is passed over reduced nickel at 350°, no decomposition occurs; eugenol is partly transformed into isoeugenol. The phenyl and carboxy-groups stabilise the unsaturated linking.

Similar treatment of cinnamic acid affords a mixture of benzene, phenylacetylene, stilbene, and styrene (main product). Cinnamyl alcohol and cinnamaldehyde also furnish styrene, whilst coumarin is converted into coumarone.

H. BURTON.

**Mechanism of the action of organo-magnesium compounds on *N*-disubstituted amides of  $\alpha\beta$ -unsaturated acids.** C. D. NENITZESCU (Bul. Soc. Chim. România, 1930, 12, 48—57).—The “unsaturated esters” A, B, and C, obtained by Maxim and Ioanid (A., 1928, 1004; 1929, 442) by the action of acetyl chloride on the product obtained by the addition of magnesium phenyl bromide to the methylanilide, ethylanilide, and diphenylamide, respectively, of cinnamic acid, are actually the ketones obtained in accordance with the scheme  $\text{CHPh:CH}\cdot\text{CO}\cdot\text{NEtPh} \xrightarrow{\text{MgPhBr}}$

$\text{CHPh}_2\cdot\text{CH}\cdot\text{C(OMgBr)}\cdot\text{NEtPh} \xrightarrow{\text{AcCl}}$   
 $\text{CHPh}_2\cdot\text{CHAc}\cdot\text{CO}\cdot\text{NEtPh}$ , since the compound B is identical with the ethylanilide, m. p. 138°, of  $\alpha$ -benz-hydrilacetoacetic acid, prepared by heating the ethyl ester of this acid (Henderson and Parker, J.C.S., 1897, 71, 676) with ethylaniline at 150° and finally at 220—230°, which, moreover, forms an identical phenylhydrazone, m. p. 178°. The by-product  $\text{C}_{33}\text{H}_{31}\text{O}_2\text{N}_2$ , obtained by Maxim (this vol., 594) by the action of magnesium methyl iodide on crotondiphenylamide, is actually the di(diphenylamide) of  $\beta$ -methyl- $\alpha$ -isopropylglutaric acid, m. p. 116—117°, since it yields this acid on complete hydrolysis with either 49% hydrobromic acid or alcoholic potassium hydroxide. The hydrolysis carried out by Maxim was incomplete, since no trace of a substance, m. p. 133°, could be detected, whilst the substance, m. p. 156°, is obtained only by incomplete hydrolysis and is probably a mixture of the original diamide with the product obtained by hydrolysis of one of the carboxylamide groups, since it yields the glutaric acid on further hydrolysis. These results vitiate the arguments concerning the mechanism of the original Grignard reaction deduced by the earlier author, the  $\text{C}_{33}$  compound being formed in accordance with the scheme:  $\text{CHMe:CH}\cdot\text{CO}\cdot\text{NPh}_2 \xrightarrow{\text{MgMeI}} \text{CHPr}^i\text{:C(OMgI)}\cdot\text{NPh}_2 \xrightarrow{\text{CHMe:CH}\cdot\text{CO}\cdot\text{NPh}_2}$

$\text{NPh}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CPr}^i\text{:C(OMgI)}\cdot\text{NPh}_2$ , the initial stage suggested by Kohler and Heritage (A., 1905, i, 207, 208) being followed by an ordinary Michael additive reaction.

J. W. BAKER.

**Isomeric  $\alpha\beta$ -diphenyl- $\delta$ -ketonic acids.** I. S. AVERY and G. C. JORGENSEN (J. Amer. Chem. Soc., 1930, 52, 3628—3633).—Phenylacetone nitrile reacts with styryl *tert*-butyl ketone in presence of methyl-alcoholic sodium methoxide, forming  $\gamma$ -trimethylacetyl- $\alpha\beta$ -diphenylbutyronitrile, m. p. 86° (corr.), hydrolysed by a mixture of acetic and 50% sulphuric acids to  $\gamma$ -trimethylacetyl- $\alpha\beta$ -diphenylbutyric acid, m. p. 236°. The methyl ester, m. p. 175°, of this is formed together with a small amount of an ester, m. p. 110—115°, from methyl phenylacetate and the above ketone. When the more fusible ester is hydrolysed (acid) a  $\gamma$ -trimethylacetyl- $\alpha\beta$ -diphenylbutyric acid (or a mixture), m. p. 189—190°, is formed. This acid is also produced as one of the products of the acid hydrolysis of an impure specimen of the above nitrile or by alkaline hydrolysis of the ester of m. p. 175°. Phenylacet-

aldehyde and the above ketone condense in presence of sodium methoxide, forming a stable compound,  $C_{22}H_{24}O_2$ , m. p. 158°.

Phenyl styryl ketone and phenylacetoneitrile afford  $\gamma$ -benzoyl- $\alpha\beta$ -diphenylbutyronitrile, m. p. 118°, which on acid hydrolysis gives  $\gamma$ -benzoyl- $\alpha\beta$ -diphenylbutyric acid, m. p. 260—261° (cf. Meerwein, A., 1919, i, 21; Kohler and Allen, A., 1924, i, 855). Phenyl styryl ketone and methyl phenylacetate furnish a mixture of methyl esters which on acid hydrolysis yields the acid of m. p. 260—261° and an isomeric acid, m. p. 186—187° (ethyl ester, m. p. 100.5°) (cf. Meerwein, *loc. cit.*). Treatment of the acids of m. p. 186—187° and 260—261° with acetyl chloride gives lactones, m. p. 136° and 220—222°, respectively, which on acid hydrolysis regenerate the respective keto-acids. When the pure esters of either acid are hydrolysed with alcoholic sodium or potassium hydroxide, mixtures of the acids result; various discrepancies in the literature are thus explained. H. BURTON.

Minjak pelandjau, the exudation from the wood of *Pentaspadon molleyi*, Hook f. II. P. VAN ROMBURGH, A. G. VAN VEEN, and A. J. H. SMIT (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 589—594).—The acid,  $C_{24}H_{36}O_3$ , described previously (A., 1929, 1204) is termed pelandjaic acid (cf. Jones and Smith, Proc. Roy. Soc. Queensland, 1929, 41, 73, who name the compound pentaspadonic acid). Tetrahydropelandjaic acid has m. p. 93—94° (cf. Jones and Smith, *loc. cit.*). Methyl methylpelandjauate, b. p. 223—225°/0.4 mm.,  $d_4^{25}$  0.9697,  $n_D^{25}$  1.5067, is reduced by hydrogen in presence of platinum-black and ethyl acetate to the tetrahydro-derivative, m. p. 45—46°, which is oxidised by chromic oxide in acetic acid to stearic acid. Catalytic reduction in presence of platinum oxide gives methyl methyldecahydropelandjauate, m. p. 49—51°. When pelandjaic acid is heated at 200—220° in a current of nitrogen, 1 mol. of carbon dioxide is eliminated and a phenol,  $C_{24}H_{38}O$ , b. p. 210—215°/0.5 mm., results. This is reduced catalytically (platinum-black) in ethyl acetate to a decahydro-derivative,  $C_{24}H_{48}O$ , m. p. 35°. In one experiment elimination of oxygen occurred and a hydrocarbon,  $C_{24}H_{48}$ , m. p. 34°, was obtained; this is not identical with octadecylcyclohexane, m. p. 35°, prepared by the action of magnesium on a mixture of cyclohexyl and octadecyl bromides. Methylation of the above phenol with methyl sulphate and sodium hydroxide solution affords a methyl ether,  $C_{24}H_{37}OMe$ , b. p. 200—205°/0.2 mm.,  $d_4^{25}$  0.9146,  $n_D^{25}$  1.5052, reduced catalytically (platinum-black) to a tetrahydro-derivative, m. p. 38° (oxidised by chromic and acetic acids to stearic acid); with platinum oxide as the catalyst, a decahydro-derivative, m. p. 25° (?), results. Dehydration of the corresponding decahydrophenol (not described) with zinc chloride at 180—190° furnishes a hydrocarbon,  $C_{24}H_{46}$ , b. p. 175—180°/0.3 mm., m. p. 25°,  $d_4^{25}$  0.838,  $n_D^{25}$  1.4664, which when treated with ozone in carbon tetrachloride gives a keto-acid (silver salt; methyl ester,  $C_{24}H_{48}O_3$ , b. p. 220—222°/0.3 mm., m. p. 48—50°) together with small amounts of acidic and neutral products. Pelandjaic acid is probably 3-hydroxy-2- $\Delta^8$ -heptadecadienyl-p-toluic acid (cf. Jones and Smith, *loc. cit.*). H. BURTON.

Polyhydric alcohol-polybasic acid reaction. II. Ethylene glycol-phthalic anhydride. R. H. KIENLE and A. G. HONEY (J. Amer. Chem. Soc., 1930, 52, 3636—3645).—The reaction between ethylene glycol and phthalic anhydride at 190—230° is similar to that with glycerol (B., 1929, 293). Resinous esters and water are the sole products of the reaction; intermediate aldehyde formation does not occur. Reaction proceeds rapidly at first (50% complete during the first minute) with evolution of heat and a corresponding rapid decrease in acid value; the flow point increases gradually as reaction proceeds. The resinous product formed is completely volatilised at 400°. The reaction differs from that with glycerol in so far as gelation does not occur at any stage. The kinetic data of the two reactions give similar curves.

H. BURTON.

Action of hydrazine acetate on 3-nitrophthalic anhydride. M. MIHAILESCU and (MME.) L. PROTOPESCU (Bul. Soc. Chim. România, 1930, 12, 95—102; cf. A., 1924, i, 1070).—In part polemical against Radulescu and Georgescu (A., 1925, i, 1185). 3-Nitrophthalic anhydride reacts with hydrazine sulphate in boiling glacial acetic acid in the presence of sodium acetate to yield 3-nitro-N-aminophthalimide (I), not melting at 300° (monoacetyl, m. p. 230°, and benzoyl, m. p. 260°, derivatives; diacetyl derivative could not be obtained), which is soluble in alkalis and carbonates (contrary to Radulescu and Georgescu it is not reprecipitated by carbon dioxide) with the formation of the potassium salt of 3-nitro-N-aminophthalamic acid (barium and silver salts). The aminophthalimide is converted by methyl sulphate at 120° into its N-methyl derivative, m. p. 265°, and condenses with anisaldehyde in the presence of fused sodium acetate to give anisylidene-3-nitro-N-aminophthalimide, m. p. 280°. On the basis of these results and from its general properties the original product (I) is assigned the structure

$NO_2 \cdot C_6H_3 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} N \cdot NH_2$ , and not that of the hydrazide,  $NO_2 \cdot C_6H_3 \begin{smallmatrix} \diagup CO-NH \\ \diagdown CO-NH \end{smallmatrix}$ , as suggested by the other authors.

J. W. BAKER.

Diaryl sulphides. III. Synthesis of thiothyronine. G. H. LAW and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 3623—3627).—Sodium p-ethoxythiophenoxide and p-chloronitrobenzene in alcohol afford 4-nitro-4'-ethoxydiphenyl sulphide, m. p. 96°, reduced by stannous chloride and alcoholic hydrochloric acid to 4-amino-4'-ethoxydiphenyl sulphide, m. p. 53° (hydrochloride, m. p. 184—185°). This is converted by the usual method into the 4-cyano-derivative, m. p. 95—96°, and thence by Stephen's method (A., 1925, i, 1131) into 4-aldehydo-4'-ethoxydiphenyl sulphide, m. p. 83° (phenylhydrazone, m. p. 126—127°). Condensation of this with hydantoin in presence of acetic acid, acetic anhydride, and sodium acetate gives p-4'-ethoxyphenylthiolbenzylidenehydantoin, m. p. 254° (decomp.), reduced by 2.5% sodium amalgam and alcohol to p-4'-ethoxyphenylthiolbenzylhydantoin, m. p. 184—185°. Hydrolysis of this with barium hydroxide solution at 100° yields  $\alpha$ -amino- $\beta$ -p-4'-ethoxyphenylthiolphenylpropionic acid, m. p. 208—210° (decomp.) [hydrochloride, m. p. 218—220° (de-



comp.], which is de-ethylated by a mixture of 48% hydrobromic acid and acetic anhydride at 90° to  $\alpha$ -amino- $\beta$ -p-4'-hydroxyphenylthiolphenylpropionic acid (thiothyronine), m. p. 240–242° (decomp.) after darkening at 230°.

$\alpha$ -Amino- $\beta$ -p-4'-methylphenylthiolphenylpropionic acid, m. p. 198–200° (decomp.) [hydrochloride, m. p. 205–207° (decomp.)], is prepared similarly by way of p-4'-methylphenylthiolbenzyl-, m. p. 187–189°, and p-4'-methylphenylthiolbenzylidene-hydantoins, m. p. 239–240°. 4-Nitro-, m. p. 81.5°; 4-amino-, m. p. 73.5° (hydrochloride, m. p. 183–184°); 4-cyano-, m. p. 102–103°, and 4-aldehydo-4'-methylphenyl sulphides, m. p. 69° (phenylhydrazones, m. p. 149–150°), are described. 4-Ethoxy- and 4-methyl-4'-carboxydiphenyl sulphide have m. p. 201–202° and 197–198°, respectively.

H. BURTON.

**Syntheses of cyclic compounds. VII. Stereoisomeric  $\beta$ - $\gamma$ -diphenyladipic acids.** M. P. OOMMEN and A. I. VOGEL (J.C.S., 1930, 2148–2154).—Reduction of methyl cinnamate with moist aluminium amalgam in ether (Vogel, A., 1927, 449) yielded a product from which methyl *meso*- $\beta$ - $\gamma$ -diphenyladipate (I), m. p. 175°, separated first; methyl  $\beta$ -phenylpropionate was separated from the filtrate by distillation, and the residue consisted chiefly of methyl *r*- $\beta$ - $\gamma$ -diphenyladipate (II), m. p. 73–74°. Hydrolysis of I and II with alcoholic potassium hydroxide afforded *meso*-, m. p. 270–271° (acid chloride, m. p. 181°), and *r*- $\beta$ - $\gamma$ -diphenyladipic acids, m. p. 185–186°, respectively (cf. Henle, A., 1906, i, 669, m. p. about 270° and 169–170°, respectively). When the former acid is heated with excess of acetic anhydride at 140°, a substance,  $C_{18}H_{16}O_3 \cdot C_4H_6O_3$ , m. p. 109–110°, solidifying and remelting at 235–245° (cf. Henle, *loc. cit.*), is formed; the latter acid under similar conditions yielded an oil.

*r*- $\beta$ - $\gamma$ -Diphenyladipic acid, m. p. 185–186°, was resolved with brucine in aqueous solution yielding d-, m. p. 200–201°,  $[\alpha]_D^{20}$  14.4° in absolute alcohol, and l- $\beta$ - $\gamma$ -diphenyladipic acid, m. p. 200–201°,  $[\alpha]_D^{20}$  –14.3° in absolute alcohol, respectively. The acid, m. p. 270–271°, could not be resolved with brucine in aqueous solution or with strychnine and quinine in alcoholic solution.

Ethyl  $\beta$ - $\gamma$ -diphenylbutane- $\alpha\alpha\delta\delta$ -tetracarboxylate, m. p. 88° (Vogel, A., 1928, 640), on hydrolysis with alcoholic potassium hydroxide, followed by heating at 200°, yields the acid, m. p. 270–271°, and hence this ester together with ethyl  $\alpha\delta$ -dibromo- $\beta$ - $\gamma$ -diphenylbutane- $\alpha\alpha\delta\delta$ -tetracarboxylate, m. p. 180°, are now considered to be *meso*-compounds. A. I. VOGEL.

**Additive power of cholic acid.** S. MINOVICI and M. VANGHELOVICI (Bul. Soc. Chim. România, 1930, 12, 5–13).—By heating cholic acid (A) with the following reactive organic compounds (B) with rigid exclusion of moisture, cooling, and washing the separated crystals with toluene and light petroleum, the following unstable additive compounds of the type AB are obtained: nitrobenzene, m. p. 159–160°; aniline, m. p. 140°; amyl alcohol, m. p. 180–182°; benzaldehyde, m. p. 137°; *m*-toluidine, m. p. 130°; benzyl alcohol, m. p. 126°; glyceryl trioleate, m. p. 146°; and oleic acid, m. p. 130°, the last-named

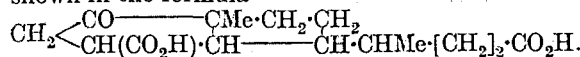
being very unstable and not obtained in the pure state. These compounds, unlike those obtained with deoxycholic acid (Wieland and Sorge, A., 1916, i, 710), are unstable in air and are decomposed by water, alcohol, and dilute sodium hydroxide. It is suggested that the function of cholic acid in the bile is to form similar complexes with fats and nutrient materials usually insoluble in water, thus rendering them soluble in the intestine for transportation in the blood-stream, where, in a medium of different  $p_H$  value, they are decomposed, the liberated cholic acid being returned to the bile through the liver.

J. W. BAKER.

**Bile acids. XXVIII. M. SCHENCK and H. KIRCHHOFF** (Z. physiol. Chem., 1930, 191, 89–96; cf. this vol., 915).—The nitrohydroxamic acid,  $C_{24}H_{34}O_9N_2$ , on oxidation with alkaline permanganate yields bilianic acid,  $C_{24}H_{34}O_8$ , and a dibasic acid,  $C_{24}H_{33}O_8N$ , decomp. 260–270°, which is converted into bilianic acid by boiling with alkali. A third product may be biliobanic acid. Treatment of the nitroamino-acid,  $C_{24}H_{36}O_{10}N_2$ , with 90% sulphuric acid yields an *isomeride*, decomp. 205°.

J. H. BIRKINSHAW.

**Bile acids. XXX. Constitution of the tetracarboxylic acid,  $C_{16}H_{24}O_8$ .** H. WIELAND and F. VOCKE (Z. physiol. Chem., 1930, 191, 69–82; cf. this vol., 473).—The tetracarboxylic acid,  $C_{16}H_{24}O_8$  (A., 1924, i, 857), when distilled in a high vacuum from a bath at 305–310° gives the ketodicarboxylic acid,  $C_{15}H_{22}O_5$ , in improved yield. The latter by reduction with amalgamated zinc in hydrochloric acid forms a *dicarboxylic acid*,  $C_{15}H_{24}O_4$ , m. p. 145° (methyl ester, m. p. 70–71°). By means of the Grignard reaction (bromobenzene) the dicarboxylic acid methyl ester forms an acid diphenylcarbinol, which with chromic anhydride in acetic acid yields an acid,  $C_{14}H_{22}O_4$ , m. p. 238°, indicating that one of the carboxyl groups of the  $C_{15}$  acid is linked to a  $CH_2$  group. This is confirmed by the oxidation of a neutral tetraphenylcarbinol produced in the Grignard reaction, which gives a *diphenylcarbinolcarboxylic acid*,  $C_{26}H_{32}O_3$ , m. p. 183°. The methyl ester of the latter by a repetition of the Grignard reaction and oxidation yields a *diphenylcarbinolcarboxylic acid*,  $C_{25}H_{30}O_3$ , m. p. 185°. This was also obtained from the acid  $C_{14}H_{22}O_4$ ; it indicates the loss of a further  $CH_2$  group. The ketodicarboxylic acid when treated with bromine in potassium hydroxide solution furnishes a *dibromotricarboxylic acid*,  $C_{15}H_{22}O_5Br_2$ , m. p. 204°, which when warmed with potassium hydroxide solution gives an unsaturated *bromodicarboxylic acid*,  $C_{14}H_{21}O_4Br$ , m. p. 153°. The latter by oxidation with alkaline permanganate yields the tricarboxylic acid,  $C_{13}H_{20}O_6$ , m. p. 187°, previously obtained by nitric acid oxidation of the ketodicarboxylic acid. By treatment with sodium amalgam the dibromotricarboxylic acid forms a *tricarboxylic acid*,  $C_{16}H_{24}O_6$ , m. p. 208°. The ketodicarboxylic acid with bromine in acetic acid gives a *dibromoketodicarboxylic acid*,  $C_{15}H_{20}O_5Br_2$ , m. p. 214°. These reactions agree with the constitution for the ketodicarboxylic acid shown in the formula



J. H. BIRKINSHAW.

**Mellitic acid and its derivatives.** H. MEYER and H. RAUDNITZ (Ber., 1930, 63, [B], 2010—2018; cf. A., 1914, i, 841, 963).—Mellitic acid is prepared in the yield indicated in parentheses from finely-ground graphite (10), yellow graphitic acid (50), Staudenmayer's pyrographitic acid (35), ordinary pyrographitic acid (35), finely-divided beech charcoal (8), animal charcoal (6), and sugar charcoal (26%). Trustworthy results are obtained by treating carboraffin with nitric acid (*d* 1.5—1.52) at the ordinary temperature and subsequently on the water-bath. After addition of a little vanadic acid, the mixture is boiled with further addition of nitric acid (or sulphuric acid if necessary); the crude mellitic acid is purified through the ammonium and copper salts. Mellitic acid and phenol are converted by stannic chloride at 115—120° into *phenolmellitein*,  $C_{48}H_{36}O_{16}$ , which gives a blood-red solution in alkalis, but is not superior as an indicator to phenolphthalein. With pyrogallol at 160°, mellitic acid yields *pyrogallolmellitein*, converted by methyl sulphate and alkali hydroxide into the *methyl ether*,  $C_{60}H_{48}O_{22}$ , and by sulphuric acid at 190° into *mellitcoerulein*. When heated with acetyl chloride at 120°, mellitic acid passes into the trianhydride  $C_{12}O_9$ , also prepared by boiling the acid with acetic anhydride for 3 hrs. With thionyl chloride even under extreme conditions or with acetic anhydride for a short period mellitic dianhydride is formed from the acid, and yields the trianhydride when further treated with acetic anhydride. Under the action of benzene in presence of aluminium chloride, mellitic trianhydride smoothly yields *tribenzoylbenzenetricarboxylic acid* converted by thionyl chloride into the *ψ-chloride*, m. p. 239°, and by phosphorus pentachloride into the non-crystalline, true *chloride*. *Methyl tribenzoylbenzenetricarboxylate* is amorphous. With quinol in presence of sodium and aluminium chloride, the trianhydride yields *hexahydroxyanthraquinone* (non-crystalline *acetyl derivative*).

Pyromellitic anhydride, phenol, and stannic chloride at 115—120° afford *phenolpyromellitein*,  $C_{34}H_{22}O_8$ , decomp. above 180°, transformed by acetic anhydride and sodium acetate into the corresponding *tetraacetyl derivative* and by methyl sulphate into the *tetramethyl ether*, m. p. below 100°. With bromine in boiling alcohol and glacial acetic acid phenolpyromellitein affords the *octabromo-derivative*,  $C_{34}H_{14}O_8Br_8$ , whilst with excess of the halogen more highly brominated compounds are obtained. Mellitic trianhydride or the dianhydride, unless used in a solvent of high b. p., give colour reactions with a large number of organic compounds (table given). Additive compounds (1 : 1) of mellitic anhydride with naphthalene, anthracene, phenanthrene, and veratrole are described.

H. WREN.

**Manufacture of arylacetic acids and substitution products thereof.** I. G. FARBENIND. A.-G.—See B., 1930, 895.

**Manufacture of β-naphthylaminoaryloxy-fatty acids.** I. G. FARBENIND. A.-G.—See B., 1930, 940.

**Production of cyclohexenealdehydes and cyclohexenecarboxylic acids which contain at least**

one dialkylated ring-carbon atom. Soc. ANON. M. NAEF ET CIE.—See B., 1930, 981.

**p-Phenylphenacyl bromide, a reagent for identifying organic acids.** N. L. DRAKE and J. BRONITSKY (J. Amer. Chem. Soc., 1930, 52, 3715—3720).—Diphenyl and acetic anhydride react in presence of aluminium chloride and carbon disulphide, forming *p*-phenylacetophenone, brominated in acetic acid below 45° to *p*-phenylphenacyl bromide, m. p. 125.5°. *p*-Phenylphenacyl esters of the following acids are prepared from the bromide and sodium or methylamine salts in aqueous alcohol: formic, m. p. 74°; acetic, m. p. 111°; propionic, m. p. 102°; butyric, m. p. 97°; *n*-valeric, m. p. 63.5°; isovaleric, m. p. 76°; hexoic, m. p. 65°; αα-dimethylbutyric, m. p. 86.5°; heptonic, m. p. 62°; octoic, m. p. 67°; dodecoic, m. p. 84°; stearic, m. p. 91°; oleic, m. p. 60.5°; chloroacetic, m. p. 116°; maleic, m. p. 168°; oxalic, m. p. 165.5° (decomp.); succinic, m. p. 208°; lactic, m. p. 145°; mucic, m. p. 149.5° (decomp.); citric, m. p. 146°; benzoic, m. p. 167°; *o*-, *m*-, and *p*-toluic, m. p. 94.5°, 136.5°, and 165°, respectively; cinnamic, m. p. 182.5°, and hippuric, m. p. 163°. The m. p. of these esters are compared (where possible) with those of the corresponding phenacyl and *p*-halogenophenacyl esters.

H. BURTON.

**Action of bases on αβ-dibromoketones and related substances.** E. P. KOHLER and C. R. ADDINALL (J. Amer. Chem. Soc., 1930, 52, 3728—3736).—Aryl αβ-dibromo-β-arylethyl ketones react with sodium alkoxide forming two types of acetals:  $CR(Oalk)_2 \cdot CH_2 \cdot CO \cdot R'$  (II)  $\leftarrow$   $CHRBr \cdot CHBr \cdot CO \cdot R'$  (I)  $\rightarrow$   $CHR(Oalk) \cdot CH(OH) \cdot CR'(Oalk)_2$  (III). When II is formed as the sole product of the reaction, the β-hydrogen atom of the dibromoketone is active as in the aryl αβ-dibromo-β-*p*-nitrophenylethyl ketones; reaction proceeds:  $I \rightarrow CHR \cdot CBr \cdot CO \cdot R' \rightarrow CHR(Oalk) \cdot CHBr \cdot CO \cdot R' \rightarrow CR(Oalk) \cdot CH \cdot CO \cdot R' \rightarrow II$ . In all other cases the reactions taking place are:  $CHR(Oalk) \cdot CHBr \cdot CO \cdot R' \rightarrow$

$CHR(Oalk) \cdot CHBr \cdot CR'(Oalk) \cdot ONa \rightarrow$   
 $CHR(Oalk) \cdot CH \cdot O \cdot CR' \cdot Oalk \rightarrow III$ . A mechanism

involving the intermediate formation of a piperidinoethylene oxide derivative is postulated to explain the production of α-diketones from similar dibromoketones and piperidine (cf. Dufraisse and Moureu, A., 1927, 571).

Treatment of *p*-bromophenyl αβ-dibromo-β-phenylethyl ketone, m. p. 187° (lit. 184°), or *p*-bromophenyl α-bromostyryl ketone, b. p. 230°/3 mm. (cf. Weygand and others, A., 1928, 291), with an excess of methylalcoholic sodium methoxide at the ordinary temperature affords two stereoisomeric *p*-bromophenyl α-hydroxy-β-methoxy-β-phenylethyl ketone dimethylacetals, m. p. 77° and 90°, together with an oil which is hydrolysed to *p*-bromodibenzoylmethane. Hydrolysis of the acetals with dilute acetic acid gives the corresponding ketones, m. p. 96° and 89°, respectively, which with magnesium phenyl bromide furnish two βγ-dihydroxy-α-methoxy-xy-diphenyl-γ-*p*-bromophenylpropanes, an oil and m. p. 119—120°, respectively. Both glycols are oxidised by chromic and acetic acids to

*p*-bromobenzophenone and methyl benzoate. The above dibromoketone and alcoholic sodium ethoxide give a mixture of *p*-bromophenyl  $\beta$ -ethoxystyryl ketone, m. p. 112°, and the diethylacetal, m. p. 99°, of *p*-bromophenyl  $\alpha$ -hydroxy- $\beta$ -ethoxy- $\beta$ -phenylethyl ketone, m. p. 72°. When *p*-bromophenyl styryl ketone is treated with mercuric acetate in methyl alcohol a compound,  $C_{16}H_{17}O_4BrHg$ , m. p. 140°, results. This is converted by bromine in methyl alcohol into *p*-bromophenyl  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -phenylethyl ketone.

Treatment of phenyl  $\alpha\beta$ -dibromo- $\beta$ -*p*-nitrophenylethyl ketone (Weygand, *loc. cit.*) with potassium acetate in acetone and methyl alcohol yields two phenyl  $\alpha$ -bromo-*p*-nitrostyryl ketones, m. p. 62° and 130°; the ketone, m. p. 106°, described by Weygand is probably a mixture. Phenyl *p*-nitrostyryl ketone is converted by successive treatment with mercuric acetate and bromine in methyl alcohol into phenyl  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -*p*-nitrophenylethyl ketone, m. p. 131°. The above nitro-compounds are all converted by sodium methoxide into a product which is almost completely hydrolysed by acetic acid to *p*-nitrodibenzoylmethane. Similar treatment of phenyl  $\alpha\beta$ -dibromo- $\beta$ -*m*-nitrophenylethyl ketone and phenyl  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -*m*-nitrophenylethyl ketone, m. p. 132°, affords a mixture of phenyl  $\alpha$ -hydroxy- $\beta$ -methoxy- $\beta$ -*m*-nitrophenylethyl ketone, m. p. 110°, and *m*-nitrodibenzoylmethane.

*p*-Methoxyphenyl  $\alpha$ -bromo- $\beta$ -methoxy- $\beta$ -phenylethyl ketone, m. p. 126°, is obtained from the corresponding  $\alpha\beta$ -dibromo-derivative and sodium methoxide, from *p*-methoxyphenyl  $\alpha$ -bromostyryl ketone and methyl alcohol in presence of a small amount of sodium methoxide, or by successive treatment of *p*-methoxyphenyl styryl ketone with mercuric acetate and bromine. When treated with sodium methoxide it furnishes a product which is hydrolysed by dilute acetic acid to *p*-methoxydibenzoylmethane.

H. BURTON.

#### Degradation of quaternary ammonium salts.

II. T. S. STEVENS (J.C.S., 2107—2119; cf. A., 1929, 180).—The reaction of the type  $Ph \cdot CO \cdot CH_2 \cdot N(CH_2Ph) \cdot Me_2X$  (I)  $\rightarrow$   $Ph \cdot CO \cdot CH(CH_2Ph) \cdot NMe_2$  (II), occurring only in an alkaline medium, has been studied with the benzyl radical replaced by *m*-bromo- and *p*-methoxy-benzyl,  $\alpha$ -phenylethyl, benzhydryl, or 9-fluorenyl, the phenacyl group by *p*-bromo-phenacyl, and the dimethylammonium system by piperidinium, and is shown to be a general one; the benzhydryl and the fluorenyl radicals wander so readily that no quaternary ammonium salts could be isolated. In each case the assigned structure has been confirmed by degradation to, or synthesis from, the related chalkone or hydrochalkone, which defined the carbon skeletons of the products. The reaction is an intramolecular one, since a mixture of phenacyl-*m*-bromobenzyl- and *p*-bromophenacylbenzyl-dimethylammonium bromides when treated with 0.1*N*-sodium ethoxide solution yielded only  $\omega$ -dimethylamino- $\omega$ -benzyl-*p*-bromoacetophenone and dimethylamino-*m*-bromobenzylacetophenone, and the rates of transformation separately, under similar conditions, are of the same order of magnitude. An electronic interpretation is given, but velocity measurements

of the relative migratory tendencies of substituted benzyl groups in absolute-alcoholic sodium ethoxide solution, whilst showing that the reaction was unimolecular, were irreconcilable with the mechanism. An alternative mechanism involving the detachment of the benzyl radical as an anion, similar to the reversed Michael reaction, is proposed.

Rearrangement was attained by heating for 30 min. with excess of 2*N*-sodium hydroxide solution; the yields were nearly quantitative.

The following are described (in methylations by the Eschweiler method, the hydrochloride of the initial base was heated for 3 hrs. with excess of 40% "formalin" and the product separated from non-basic material): phenacyl-*m*-bromobenzyl-dimethylammonium bromide, m. p. 140—143°, from bromoacetophenone and *m*-bromobenzyl-dimethylamine (*picrate*, m. p. 139—141°) in cold benzene solution;  $\omega$ -dimethylamino- $\omega$ -*m*-bromobenzylacetophenone (methosulphate when boiled with alkali gave phenyl *m*-bromostyryl ketone, m. p. 84—85°, also formed from *m*-bromobenzaldehyde and acetophenone in warm methyl alcohol in the presence of a little potassium hydroxide solution); phenacyl-*p*-methoxybenzyl-dimethylammonium bromide, m. p. 133—136° (*picrate*, m. p. 112—113°), from *p*-methoxybenzyl-dimethylamine [obtained by the Eschweiler methylation of *p*-methoxybenzylamine; hydrochloride, m. p. 237—239° (lit., m. p. 231°)] (*picrate*, m. p. 103—105°), and bromoacetophenone in cold ether;  $\omega$ -dimethylamino- $\omega$ -*p*-methoxybenzylacetophenone, m. p. 52—54° (*picrate*, m. p. 143—145°; methosulphate yielded phenyl *p*-methoxystyryl ketone with aqueous sodium hydroxide solution); phenacyl- $\alpha$ -phenylethyl-dimethylammonium bromide, m. p. 155—157° (decomp.), from bromoacetophenone and  $\alpha$ -phenylethyl-dimethylamine (*picrate*, m. p. 134—137°) in cold benzene, which on rearrangement gave two stereoisomeric  $\omega$ -dimethylamino- $\omega$ - $\alpha$ -phenylethylacetophenones,  $\alpha$ -, m. p. 111—112° (*picrate*, m. p. 186—187°), and  $\beta$ -, m. p. 111—113° (*picrate*, m. p. 174—176°; dimorphous), separated by crystallisation from dilute acetic acid for the  $\alpha$ -form, or from acetone and light petroleum for the  $\beta$ -form; the  $\beta$ -form was synthesised from  $\omega$ - $\alpha$ -phenylethylacetophenone, through  $\omega$ -bromo- $\omega$ - $\alpha$ -phenylethylacetophenone, m. p. 76° (with bromine in carbon tetrachloride), followed by treatment with 2 mols. of dimethylamine for 12 hrs. at the ordinary temperature and 2 hrs. at 100°;  $\omega$ -dimethylamino- $\omega$ -benzhydrylacetophenone, m. p. 167°, from benzhydryl-dimethylamine, m. p. 68—69° (*picrate*, m. p. 196—198°; hydrobromide, m. p. 215°), and bromoacetophenone in benzene;  $\omega$ -dimethylamino- $\omega$ -fluorenylacetophenone, m. p. 145—148° (decomp.) (methosulphate yielded  $\omega$ -fluorenylacetophenone with zinc and sulphuric acid), from 9-fluorenyldimethylamine (*hydrobromide*, m. p. 204—206°) (prepared from fluorenoneoxime through 9-fluorenylamine hydrochlorides, and subsequent Eschweiler reaction) and bromoacetophenone in cold benzene solution; in hot benzene the principal product was  $\omega$ -fluorenylideneacetophenone, m. p. 137—140°, also prepared by conversion of fluorenylacetophenone with bromine in warm chloroform into the bromo-ketone, m. p. 111—113°, followed by treatment with dimethylamine in ether; *p*-bromophenacylbenzyl-dimethylammonium

bromide, m. p. 188—191° (bromide; nitrate), from *p*-bromophenacyl bromide and benzyldimethylamine in cold benzene; *p*-bromo- $\omega$ -dimethylamino- $\omega$ -benzylacetophenone, m. p. 106—107° [hydrochloride, m. p. 235—238° (decomp.); methosulphate yielded *p*-bromophenyl styryl ketone, m. p. 104—105° (lit. m. p. 100—101°), with aqueous sodium hydroxide]; phenacylbenzylpiperidinium bromide, m. p. 135—138° (decomp.), from 1-benzylpiperidine and bromoacetophenone in cold benzene;  $\omega$ -piperidino- $\omega$ -benzylacetophenone, m. p. 80—81° [picrate, m. p. 185—187° (decomp.)].  
A. I. VOGEL.

**Syntheses in the phenanthrene series. I. Acetylphenanthrenes.** E. MOSETTIG and J. VAN DE KAMP (J. Amer. Chem. Soc., 1930, 52, 3704—3710).—Treatment of phenanthrene with acetyl chloride in presence of aluminium chloride and nitrobenzene at the ordinary temperature affords a mixture of 15% of 2-acetylphenanthrene, m. p. 143° (corr.) [semicarbazone, m. p. 260° (decomp.), resolidifying with m. p. 297—299° (decomp.); phenylhydrazone, m. p. (vac.) 187—188° (corr.) with darkening; 9:10-quinone, m. p. (vac.) 223—224° (corr.)], 63.5% of 3-acetylphenanthrene, m. p. 72° [semicarbazone, m. p. 228—230° (corr.); phenylhydrazone, m. p. (vac.) 192.5—194° (corr.); oxime, m. p. 143.5—144° (corr.); picrate, m. p. 125—125.5° (corr.); 9:10-quinone, m. p. (vac.) 217—218.5° (corr.) after sintering at 214°], and a small amount of a compound, m. p. 279—280°. When the reaction is carried out in presence of carbon disulphide as the solvent, a small amount of crystalline material and much oil are produced (cf. Willgerodt and Albert, A., 1911, i, 882). Oxidation of 2-acetylphenanthrene with aqueous sodium hypochlorite gives phenanthrene-2-carboxylic acid, m. p. 258.5—260° [methyl ester, m. p. 96—96.5° (corr.); ethyl ester, m. p. 73—73.5°; amide, m. p. 242—243° (corr.)], also obtained by hydrolysis of the nitrile formed when barium phenanthrene-2-sulphonate is dry distilled with potassium ferrocyanide. Phenanthrene-3-carboxylic acid, m. p. 270° [methyl ester, m. p. 94.5—95° (corr.); ethyl ester, m. p. 56—57° (corr.); amide, m. p. 233—234° (corr.) (lit. 228°)], is prepared similarly.

Methyl phenanthrene-9-carboxylate, m. p. 116° (corr.), and phenanthrene-9-carboxylamide, m. p. 232—233° (corr.), are also described.  
H. BURTON.

**Effect of substituents on the rearrangement of benzopinacol.** J. C. BAILAR, jun. (J. Amer. Chem. Soc., 1930, 52, 3596—3603).—The following *s*-substituted benzopinacols are prepared, generally by the method of Gomberg and Bachmann (A., 1927, 245): 2:2'-dimethyl-, m. p. 156°; 3:3'-dimethyl-, m. p. 147—148°; 4:4'-diethyl-, m. p. 162—163°; 4:4'-diisopropyl-, m. p. 161—162°; 2:2'-dimethoxy-, m. p. 168—169°; 3:3'-dimethoxy-, m. p. 139—141°; 4:4'-dimethyl-4'':4'''-diethyl-, m. p. 155—156°; 4:4'-diphenyl-4'':4'''-dimethyl-, m. p. 175—176°.  $\alpha\beta$ -Dihydroxy- $\alpha\beta$ -di-*p*-anisyl- $\alpha\beta$ -di-1-naphthylethane, m. p. 143—144°, is prepared from anisil and magnesium 1-naphthyl bromide.  $\alpha\beta$ -Dihydroxy- $\alpha\beta$ -di-*p*-tolyl- $\alpha\beta$ -di-1-naphthylethane has m. p. 150°. 3-Methoxybenzophenone is obtained from magnesium phenyl bromide and *m*-methoxybenzonitrile, b. p. 140°/34 mm.; *m*-methoxybenzamide has m. p. 130°. The Friedel-

Crafts reaction with benzoyl chloride and isopropylbenzene gives 4-isopropylbenzophenone, b. p. 197°/10 mm., whilst *p*-toluoyl chloride and ethylbenzene afford 4-methyl-4'-ethylbenzophenone, b. p. 215°/10 mm.

The mixtures of pinacolins produced when the above glycols are heated with acetic acid and a small amount of iodine are decomposed with alcoholic potassium hydroxide into mixtures of triphenylmethane derivatives and substituted benzoic acids. The original composition of the pinacolic mixture is deduced from the equivalent of the mixed acids. From the results now obtained and those recorded in the literature the migratory tendencies of various aryl groups are: *p*-anisyl, about 40;  $\alpha$ -naphthyl, about 18; *p*-tolyl, 12—15; *p*-diphenyl, 12.5; *p*-isopropylphenyl, 9; *p*-ethylphenyl, 5; *p*-fluorophenyl, 1.86; *p*-iodophenyl, 1; phenyl, 1 (standard); *p*-bromophenyl, 0.75; *p*-chlorophenyl, 0.66; *m*-tolyl, 0.6; *m*-anisyl, 0.2. The migratory tendencies of the *o*- and *m*-chloro- and -bromo-phenyl, *p*-tolyl, and *o*-anisyl groups are very small.

Phenyl 4:4'-diisopropyltriphenylmethyl ketone, m. p. 140°, when treated with alcoholic potassium hydroxide gives a quantitative yield of 4:4'-diisopropyltriphenylmethane.  
H. BURTON.

**cycloAcetals of benzoin and their transformation.** M. BERGMANN and G. WEIL (Ber., 1930, 63, [B], 1911—1917).—Re-examination of the action of 30% methyl-alcoholic hydrogen chloride on benzoin at 20° shows that the compound  $C_{30}H_{28}O_4$ , m. p. 296° (corr.) (cf. Irvine and Weir, J.C.S., 1907, 94, 1384; Irvine and McNicoll, *ibid.*, 1908, 93, 950, 1601), is to be regarded as 2:5-dimethoxy-2:3:5:6-tetraphenyldioxan,  $OMe \cdot CPh \langle \begin{smallmatrix} O \cdot CHPh \\ CHPh \cdot O \end{smallmatrix} \rangle CPh \cdot OMe$ ,

since it is rapidly and almost quantitatively converted by *N*-hydrochloric acid in presence of phenol (as solvent) into benzoin and transformed by saturated methyl-alcoholic hydrogen chloride into benzoin methyl ether. The compound  $C_{29}H_{24}O_3$ , m. p. 188—189° (corr.) (*loc. cit.*), is considered to be 2-methoxy-2:3:5:6-

tetraphenyl- $\Delta^5$ -dioxen,  $CPh \langle \begin{smallmatrix} O \cdot CHPh \\ CPh \cdot O \end{smallmatrix} \rangle CPh \cdot OMe$ . It is transformed by saturated methyl-alcoholic hydrogen chloride into benzoin methyl ether and by ozone into benzoylbenzoin and benzoic acid. With bromine in moist chloroform it affords benzoin and benzil in approximately equal proportions. It is catalytically hydrogenated in presence of spongy palladium to  $\alpha\beta$ -diphenylethane; this compound is also obtained under similar conditions, but in smaller yield, from benzoin or benzoin methyl ether. Hydrolysis of the unsaturated cycloacetal with hot *N*-hydrochloric acid in presence of phenol gives deoxybenzoin and benzil.

H. WREN.

**Anthraquinhydrone and anthraquinone-carboxylic acids.** R. SCHOLL and O. BÖTTGER (Ber., 1930, 63, [B], 2120—2126).—When amorphous anthraquinone is mixed with sodium amalgam and alcohol, a green solution which becomes decolorised by atmospheric oxidation is formed independently of the presence of water. In an atmosphere of hydrogen the green solution rapidly becomes red when agitated, but becomes green again after addition of a suitable

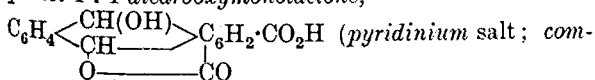
oxidising agent. In the absence of alcohol the green colour can be obtained in the presence of highly concentrated potassium hydroxide. The green compound,  $2C_{14}H_8O_2 \cdot C_{14}H_8O_2Na_2 \cdot EtOH \cdot EtONa$ , is isolated by treating anthraquinone with 2.5% sodium amalgam in a little 99% alcohol, filtration, and treatment of the red filtrate with a little amyl nitrite.

The reduction of anthraquinonecarboxylic acids by alkaline hyposulphite or sodium amalgam in alcohol in absence of air to anthraquinolcarboxylic acids and re-conversion of the latter by air into anthraquinonecarboxylic acids does not appear to proceed directly, since the solutions pass through an olive-green stage. Such solutions are also obtained by mixing the almost colourless solutions of anthraquinonecarboxylic acids with the red alkaline anthraquinolcarboxylic acids. Obviously salts of anthraquinhydronecarboxylic acids are present. The colour is observed only in alkali hydroxide solutions; in presence of sodium carbonate or ammonia the solutions are red. The free anthraquinhydronecarboxylic acids are obtained by precipitation of very dilute solutions of their salts with hydrochloric acid. H. WREN.

**Anthraquinoneazine and anthraquinoneaz-hydrin.** R. SCHOLL and H. LAMPRECHT (Ber., 1930, 63, [B], 2126—2128; cf. Scholl and Berblinger, A., 1904, i, 110; 1907, i, 257).—Anthraquinoneazine is reduced and benzoylated by boiling benzoyl chloride, giving unchanged material and dibenzoylindanthrone. Re-examination of the behaviour of anthraquinoneazine towards concentrated hydrochloric acid (*loc. cit.*) gives no certain evidence of the existence of anthraquinoneazhydrin; it appears probable that the material previously examined was a mixture of anthraquinoneazine with more or less indanthrene.

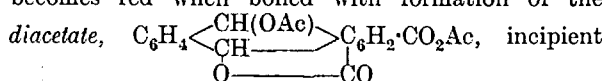
H. WREN.

**Carboxylated, blue anthraquinol- $\alpha$ -carboxylactones.** R. SCHOLL and O. BÖTTGER [with A. KELLER and H. K. MEYER] (Ber., 1930, 63, [B], 2128—2138).—1:4-Diaminoanthraquinone is transformed into 4-aminoanthraquinone-1-carboxylic acid and thence through the *diazonium sulphate* into 4-cyanoanthraquinone-1-carboxylic acid, hydrolysed by sulphuric acid to anthraquinone-1:4-dicarboxylic acid. Alternatively, *o*-2:5-dimethylbenzoylbenzoic acid, prepared from phthalic anhydride and *p*-xylene in presence of aluminium chloride and tetrachloroethane, is converted into 1:4-dimethylantraquinone, which is oxidised to anthraquinone-1:4-dicarboxylic acid by precipitated manganese dioxide and sulphuric acid or by nitric acid (*d* 1.1) at 180—190°. When treated with sodium hyposulphite in cold alkaline solution and subsequently acidified, anthraquinone-1:4-dicarboxylic acid yields *anthraquinol-1:4-dicarboxylic acid* as a brown or brownish-red precipitate. When boiled, the strongly acid solution becomes dark violet-blue owing to the formation of *anthraquinol-1:4-dicarboxymonolactone*,



pound with 1 mol. of acetone), which forms blue solutions in ammonia, sodium carbonate, or very dilute sodium hydroxide, but red solutions sensitive

to air with the warm hydroxide. Warm acetic anhydride dissolves it to a violet solution, which becomes red when boiled with formation of the



m. p. 193°, transformed by boiling glacial acetic acid into *mesoacetylanthraquinol-1:4-dicarboxymonolactone*, m. p. 239—240°. Lactonisation of the dicarboxylic acid is most conveniently induced by treatment with sodium hyposulphite and glacial acetic acid; a dilactone could not be prepared. The possibility that the blue lactone is a radical is excluded by the observation that it reacts with two equivalents of oxygen when titrated to yellow with sodium hypochlorite after hydrolysis with sodium hydroxide in an atmosphere of hydrogen. Examination of the absorption spectra of the red anthraquinol-1-carboxylactone and the blue anthraquinol-1:4-dicarboxymonolactone in ethyl acetate establishes the similarity of their constitutions. The introduction of a carboxyl group in position 4 into anthraquinol-1-carboxylactone has therefore a marked bathochromic effect. It has a similar action when introduced into anthraquinol, which gives yellow solutions in indifferent media, whereas its carboxylic acid gives red solutions.

H. WREN.

**Anthraquinone series. Synthesis of anthraquinones related to morindone and emodin.** P. C. MITTER and A. K. SARKAR (J. Indian Chem. Soc., 1930, 7, 619—628).—3-Nitrophthalic anhydride reacts with toluene in presence of anhydrous aluminium chloride at 40—50°, forming 3-nitro-2-*p*-toluoylbenzoic acid, m. p. 218—219° (cf. Lawrance, A., 1922, i, 340), reduced by ferrous sulphate and ammonia to 3-amino-2-*p*-toluoylbenzoic acid, m. p. 165°. This is converted by the usual method into 3-hydroxy-2-*p*-toluoylbenzoic acid, m. p. 225—226°, and thence by treatment with a mixture of boric anhydride, sulphuric acid (*d* 1.84), and fuming sulphuric acid (20%  $SO_3$ ) at 100° (bath) into 1-hydroxy-6-methylantraquinone, m. p. 147° (*acetyl* derivative, m. p. 172°). Nitration of this with potassium nitrate and sulphuric acid affords a 2:4:5(?)-trinitro-derivative, m. p. 285—286°. 4-Nitro-2-*p*-toluoylbenzoic acid, m. p. 171° (cf. Lawrance, *loc. cit.*), is obtained only when partly hydrated aluminium chloride is used in the Friedel-Crafts reaction between 4-nitrophthalic anhydride and toluene. The acid is converted as above by way of the corresponding *amino*-, m. p. 175°, and *hydroxy*-derivatives, m. p. 182—183°, into 2-hydroxy-6-methylantraquinone, m. p. 278° (*acetyl* derivative, m. p. 145—147°), which when heated with 50% potassium hydroxide solution and sodium arsenate at 185—195° gives 1:2-dihydroxy-6-methylantraquinone [6-methylalazarin] (cf. A., 1929, 319). The 1-hydroxy-isomeride could not be converted into the alazarin by alkaline fusion. Methylation of the 2-hydroxy-derivative with methyl sulphate and sodium hydroxide affords 2-methoxy-6-methylantraquinone, m. p. 177°, nitrated by potassium nitrate and sulphuric acid at 100° (bath) to a *dinitro*-2-methoxy-6-methylantraquinone, m. p. 260—262°. Treatment of this with methyl-alcoholic potassium methoxide furnishes a *trimethoxy*-6-methylantraquinone, m. p. 230—233°,

demethylated by aluminium chloride at 230° to the corresponding *trihydroxy*-compound, m. p. 240—245°.

H. BURTON.

**Hydrazides. IV. Condensation of diarylaminoguanidines with phenanthraquinone and derivatives.** S. C. DE and D. N. DUTT (J. Indian Chem. Soc., 1930, 7, 537—544).—The monoximes of phenanthraquinone and its substitution products readily condense with diarylaminoguanidines in alcoholic solution to yield normal products of hydrazone type. In glacial acetic acid, however, a compound, most probably of type I, is produced by loss of a molecule of hydroxylamine and of nitrogen. The same result is obtained by heating the primary condensation products (from alcohol) with acetic acid. With phenanthraquinone the final product appears to be of type II, nitrogen and arylhydroxylamine being eliminated.



The following are described (corresponding derivatives of 2-nitro- and 2:7-dinitro-phenanthraquinone being given in parentheses following the parent compound): *phenanthraquinonediphenylaminoguanidine*, m. p. 240° (2-nitro-, m. p. 238°; 2:7-dinitro-derivative, m. p. 235°); *compound* (II, R=Ph), (2-nitro- and 2:7-dinitro-derivatives); *phenanthraquinonemonoximediphenylaminoguanidine*, m. p. 158° (2-nitro-, m. p. 233°; 2:7-dinitro-derivative, m. p. 245°); *compound* (I, R=Ph), m. p. 180° (decomp.) (2-nitro-, m. p. 193°; 2:7-dinitro-derivative, m. p. 202°); *phenanthraquinonedi-p-tolylaminoguanidine*, m. p. 236° (2-nitro-, m. p. 228°; 2:7-dinitro-derivative, m. p. 263°); *compound* [II, R=C<sub>7</sub>H<sub>7</sub> (p)], (2-nitro- and 2:7-dinitro-derivatives); *phenanthraquinonemonoximedi-p-tolylaminoguanidine*, m. p. 227° (2-nitro-, m. p. 228°; 2:7-dinitro-derivative); *compound* [I, R=C<sub>7</sub>H<sub>7</sub> (p)], m. p. 156° (2-nitro-, m. p. 190°; 2:7-dinitro-derivative, m. p. 223°); *phenanthraquinonedi-β-naphthylaminoguanidine*, m. p. 240° (2-nitro-, m. p. 200°; 2:7-dinitro-derivative, m. p. 270°); *compound* [II, R=C<sub>10</sub>H<sub>7</sub> (β)], (2-nitro-, m. p. 276°; 2:7-dinitro-derivative); *phenanthraquinonemonoximedi-β-naphthylaminoguanidine*, m. p. 235°; *compound* [I, R=C<sub>10</sub>H<sub>7</sub> (β)], m. p. 245°. Where no m. p. is given, it is "above 300°."

H. A. PIGGOTT.

**Plant colouring matters. XXIII. Xanthophyll from dandelion flowers.** P. KARRER and H. SALOMAN (Helv. Chim. Acta, 1930, 13, 1063—1067).—Extraction of 6 kg. of the dry flowers of *Taraxacum officinale* with light petroleum (b. p. 30—50°), and hydrolysis of the extracted material with an excess of 1.5*N*-methyl-alcoholic potassium hydroxide in an atmosphere of nitrogen gives the unsaponifiable matter, separated into sterols, a substance, m. p. 247—248° (4 g.), and a *xanthophyll*, C<sub>40</sub>H<sub>56</sub>O<sub>2</sub>, m. p. 175—176°, [α]<sub>D</sub><sup>20</sup> +167.2° in chloroform (0.2 g.). H. BURTON.

**Plant colouring matters. XXVI. Esters of xanthophyll.** P. KARRER and S. ISHIKAWA. **XXVII. Methylation of xanthophyll.** P. KARRER and B. JIRGENSONS (Helv. Chim. Acta, 1930, 13, 1099—1102, 1102—1103).—XXVI. The following esters are prepared from xanthophyll, m. p. 188°, and

the requisite acyl chloride in pyridine in an atmosphere of nitrogen: *dipropionate*, m. p. 138°; *di-n-butyrate*, m. p. 156°; *di-n-valerate*, m. p. 128°; *di-n-hexate*, m. p. 117°; *di-n-heptate*, m. p. 111°; *di-n-octate*, m. p. 108°, and *dipalmitate*, m. p. 89°. With the exception of the dipropionate, the m. p. of the esters decrease with increasing number of carbon atoms.

**XXVII. Xanthophyll monomethyl ether**, C<sub>41</sub>H<sub>56</sub>O<sub>2</sub>, m. p. 150°, is prepared by the action of methyl iodide on potassium xanthophyll in toluene; the potassium derivative is prepared from potassium *tert*-amyloxide and xanthophyll. H. BURTON.

**Saponin of *Camellia sasanqua*, Thunb. S.** AOYAMA (J. Pharm. Soc. Japan, 1930, 50, 454—461).—The seeds yielded *sasanguasaponin*, C<sub>73</sub>H<sub>118</sub>O<sub>33</sub>·3H<sub>2</sub>O, decomp. 222°, [α]<sub>D</sub><sup>20</sup> +30.54° in 80% alcohol, hydrolysed to a *prosapogenin*, C<sub>50</sub>H<sub>80</sub>O<sub>14</sub>, decomp. 208°, a pentose, and galactose. Hydrolysis of the *prosapogenin* affords an *endosapogenin*, decomp. 201°, which has lactic acid properties. CHEMICAL ABSTRACTS.

**Rotenone. VII. Structure of tubanol and tubaic acid.** H. L. HALLER and F. B. LAForge (J. Amer. Chem. Soc., 1930, 52, 3207—3212).—Improved methods of preparation of tubaic and rotenenic acids from rotenone and isorotenone, respectively, are given. Alternative structural formulæ, based on observations in the literature, are suggested for tubanol, "rotenol" (derived from rotenenic acid by loss of carbon dioxide), tubaic acid, and rotenenic acid.

H. BURTON.

**Rotenone. VIII. Isomeric hydroxy-acids and their relation to dehydrorotenone.** F. B. LAForge and L. E. SMITH (J. Amer. Chem. Soc., 1930, 52, 3603—3609).—Treatment of dehydrodihydro-rotenonic acid (this vol., 781) with zinc dust and alcoholic potassium hydroxide affords *β-dihydrohydroxyrotenonic acid*, C<sub>23</sub>H<sub>26</sub>O<sub>7</sub>, m. p. 198° after darkening at 192°, oxidised by alkaline hydrogen peroxide to derric acid. During the treatment with alkali, addition of a molecule of water occurs. The *β*-acid is not dehydrated by treatment with alcoholic sulphuric acid; esterification takes place. Catalytic reduction (Adams) of acetylrotenolone (*loc. cit.*) in ethyl acetate gives a mixture of acetyldihydro-rotenolone and *acetyl-α-dihydrorotenolonic (acetyl-α-dihydrohydroxyrotenonic) acid*, C<sub>25</sub>H<sub>28</sub>O<sub>8</sub>, m. p. 210—214° (decomp.). The last-named compound is hydrolysed to *α-dihydrorotenolonic (α-dihydrohydroxyrotenonic) acid* (I), also formed in small amount together with dihydrorotenolone by hydrogenating rotenolone. Oxidation of rotenonic acid with warm alkaline hydrogen peroxide affords a mixture of *dehydrorotenonic acid*, C<sub>23</sub>H<sub>22</sub>O<sub>6</sub>, m. p. 225°, and a *hydroxyrotenonic acid*, C<sub>23</sub>H<sub>24</sub>O<sub>7</sub>, m. p. 137°. Catalytic reduction of the last-named acid furnishes a *α-dihydrohydroxyrotenonic acid*, m. p. 132° after previous sintering, isomeric with I. Both the above *α*-acids are dehydrated to dehydrodihydrorotenonic acid by treatment with alcoholic sulphuric acid. Catalytic reduction of dehydrorotenonic acid (also formed when hydroxyrotenonic acid is dehydrated with alcoholic sulphuric acid) also affords dehydrodihydrorotenonic acid, which is oxidised by alkaline hydrogen peroxide to a *compound*, C<sub>11</sub>H<sub>12</sub>O<sub>7</sub>, m. p. 262° (decomp.).



This compound is also produced by oxidising derric acid. When dehydrodihydrotrotenonic acid is heated with acetic acid lactonisation probably occurs with the formation of dihydrotrotenonone (*loc. cit.*). Oxidation of dihydrodihydroxytrotenononic acid (*loc. cit.*) with alkaline hydrogen peroxide yields dihydrotubaic acid. Attempts to resolve derric acid by means of brucine were unsuccessful.

H. BURTON.

**Energy value of the ozonide linking formed during the ozonisation of  $\alpha$ -terpineol.** E. BRINER, M. MOTTIER, and H. PAILLARD (Helv. Chim. Acta, 1930, 13, 1030—1035).—The heats of combustion of  $\alpha$ -terpineol and its ozonide, prepared in presence of hexane, are 1501 and 1445 kg.-cal./g.-mol., respectively. The heat of formation of the ozonide is calculated to be 90 kg.-cal.;  $C_{10}H_{18}O + O_3 = C_{10}H_{18}O_4 + 90$  kg.-cal.

H. BURTON.

**Action of semicarbazide on pulegone.** S. A. BUSSE and H. L. GUREWITSCH (Ber., 1930, 63, [B], 2209—2211).—*Pulegonepyrazoline*,

$CHMe \cdot CH_2 \cdot \overset{\text{N}}{\parallel} \cdot NR$  (I; R=H), b. p. 113.7—114°/11—12 mm., prepared in 97% yield by the action of hydrazine hydrate on pulegone in methyl alcohol, is converted by potassium cyanate and glacial acetic acid into *carbamylpyrazolylpulegone* (I; R=CO·NH<sub>2</sub>), m. p. 156—157°. The last-named compound also results from the action of semicarbazide on pulegone.

H. WREN.

**Plöchl's reaction. Aminocamphor and formaldehyde.** H. RUPE, F. BUXTORF, and W. FLATT (Helv. Chim. Acta, 1930, 13, 1026—1030).—In an attempt to prepare dimethylaminocamphor by Plöchl's methylation process (A., 1888, 1051), aminocamphor hydrochloride was heated with aqueous formaldehyde at 140—150°; camphorquinone was isolated in 87% yield. Only a trace of the expected base was isolated, but tetramethylethylenediamine, (CH<sub>2</sub>·NMe<sub>2</sub>)<sub>2</sub>, was also formed; ammonia could not be detected. Aminocamphor hydrochloride and water alone do not give the quinone, and this is formed only in very small amount from dimethylaminocamphor hydrochloride and water at 160°. Dimethylaminocamphor hydrochloride and aqueous formaldehyde at 170° afford camphorquinone and probably trimethylamine, but not tetramethylethylenediamine. The last-named base is not formed from ammonium chloride and formaldehyde. A probable mechanism for the initial reaction is given.

H. BURTON.

**Oxidising action of ozone on hemicyclic double linking.** J. PALMÉN (Finska Kemistsamf. Med., 1930, 38, 124—128; Chem. Zentr., 1930, i, 2086).—The ozonisation of hydroxymethylencamphor yields the camphorquinone with camphoric anhydride as the chief product.

L. S. THEOBALD.

**Dependence of optical rotatory power on chemical constitution. VIII. Stereoisomeric *d*-, *l*-, *dl*-*p*-phenylene-, 1 : 4-naphthylene-, *pp'*-diphenylamine-, and *pp'*-diphenylmethane-bis-aminocamphors; *p*-phenylene-, *pp'*-diphenylmethanebisaminocamphors; *p*-diphenylamine-aminocamphors and *p*-diphenylamine-amino-**

**camphors, and their derivatives.** B. K. SINGH and B. BHADURI (J. Indian Chem. Soc., 1930, 7, 545—574).—A study of the optical properties of a number of new derivatives of camphorquinone and aromatic diamines. With the exception of the 1 : 4-naphthylene and *pp'*-diphenylamine compounds the iminocamphor derivatives have been reduced to the corresponding amino-compounds, which are colourless and have considerably lower rotatory powers. The imino-compound is shaken in benzene solution with 10% aqueous potassium hydroxide and zinc dust until the benzene layer is colourless, and the (di-)hydrochloride of the amino-compound is then precipitated from the dried solution in benzene by hydrogen chloride. The following are described: *l*-*p*-phenylenebisiminocamphor, m. p. 259—260°,  $M[\alpha]_D^{25} = -6387^\circ$  in benzene,  $-5078^\circ$  in methyl alcohol; the *dl*-derivative appears to be a mixture, and not a true racemic compound; *d*- and *l*-*p*-phenylenebisaminocamphors, m. p. 204°,  $M[\alpha]_D^{25} \pm 469^\circ$  in chloroform,  $\pm 240^\circ$  in pyridine (dihydrochloride, m. p. 217—225°; monoacetyl derivative, m. p. 253—254°,  $M[\alpha]_D^{25} \pm 125^\circ$  in chloroform,  $\pm 103^\circ$  in pyridine); *dl*-*p*-phenylenebisaminocamphor, m. p. 220° (monoacetyl derivative, m. p. 192—193°); *l*- and *dl*-1 : 4-naphthylenebisiminocamphors, m. p. 220—222°,  $M[\alpha]_D^{25} -13320^\circ$  in pyridine,  $-8215^\circ$  in chloroform, and m. p. 213—214°, respectively (cf. Singh and Singh, J.C.S., 1920, 117, 1601); *l*- and *dl*-*pp'*-diphenylaminebisiminocamphors, m. p. 212—213°,  $M[\alpha]_D^{25} -13080^\circ$  in ethyl alcohol,  $-11690^\circ$  in chloroform, and m. p. 144—145° (cf. Singh, Singh, and Lal, J.C.S., 1921, 119, 1975), (*d*- and *l*-acetyl-*pp'*-diphenylaminebisiminocamphors, m. p. 227°,  $M[\alpha]_D^{25} \pm 4520^\circ$  in benzene,  $\pm 3443^\circ$  in methyl alcohol); *d*- and *l*-*p*-iminocamphordiphenylamines, m. p. 134—135°,  $M[\alpha]_D^{25} \pm 7059^\circ$  in ethyl alcohol,  $\pm 5308^\circ$  in benzene (acetyl derivatives, m. p. 163—164°,  $M[\alpha]_D^{25} \pm 2368^\circ$  in benzene,  $\pm 1869^\circ$  in methyl alcohol; also of the *dl*-compound, m. p. 153—154°); *d*- and *l*-*p*-aminocamphordiphenylamines, m. p. 121—122°,  $M[\alpha]_D^{25} \pm 250^\circ$  in benzene,  $\pm 136^\circ$  in pyridine (diacetyl derivatives, m. p. 190—191°,  $M[\alpha]_D^{25} \pm 284^\circ$  in benzene,  $\pm 125^\circ$  in pyridine), *dl*-compound, m. p. 93—94° (monoacetyl derivative, m. p. 175—176°); *d*- and *l*-*pp'*-diphenylmethanebisiminocamphors, m. p. 203—204°,  $M[\alpha]_D^{25} \pm 4530^\circ$  in pyridine,  $\pm 3966^\circ$  in methyl alcohol, *dl*-compound, m. p. 200—201°; *d*- and *l*-*pp'*-diphenylmethanebisaminocamphors, m. p. 182°,  $M[\alpha]_D^{25} \pm 490^\circ$  in benzene,  $\pm 250^\circ$  in pyridine, *dl*-compound, m. p. 164—165°. Observations of the molecular rotations are also made for the yellow and green mercury lines, where possible in chloroform, benzene, acetone, pyridine, and ethyl and methyl alcohols. (The highest and lowest mean values for the sodium *D* line are quoted above.) Within the limits of experimental error they are equal and opposite for the optical isomerides, no discrepancy being observed even in the highest values. They are not parallel to the dielectric constant of the solvent, and there is no constancy of behaviour in this respect from case to case. No connexion exists between the number of  $\alpha$ -carbon atoms and the type of rotatory dispersion exhibited, but the values of the molecular rotation are closely related to the length and compactness of the conjugated system.

H. A. PRIGGOTT.

**Higher terpene compounds. XLI. Constitution of santonin.** L. RUZICKA and E. EICHENBERGER (Helv. Chim. Acta, 1930, **13**, 1117—1124).—Catalytic reduction (platinum oxide) of santonin in presence of acetic acid affords *hexahydrosantonin*, m. p. 210—211°, dehydrogenated by selenium at 240—320° to 1-methyl-7-ethylnaphthalene. The formation of this supports the formula proposed for santonin by Clemo, Haworth, and Walton (this vol., 919). Oxidation experiments, details of which are to be published (cf. Angeli and Marino, A., 1907, i, 321; 1908, i, 543; Bargellini and Gialdini, A., 1908, i, 345), also support the above-mentioned formula.

[With H. RAMONDT and A. WICK.]—The following synthesis of 1:4-dimethyl-6-ethylnaphthalene, a possible dehydrogenation product from santonin assuming that older structures are correct, is described. *p*-Ethylacetophenone is converted by the Reformatsky reaction into ethyl  $\beta$ -methyl-*p*-ethylcinnamate, b. p. about 160°/12 mm., which is reduced by the Bouveault method to  $\gamma$ -*p*-ethylphenylbutyl alcohol, b. p. about 140°/12 mm. The chloride, b. p. 110—115°/0.5 mm., of  $\gamma$ -*p*-ethylphenylvaleric acid, b. p. 175—180°/12 mm. (obtained from the above alcohol by way of the bromide and cyanide), is converted by treatment with aluminium chloride into 4-keto-1-methyl-6-ethyl-1:2:3:4-tetrahydronaphthalene, b. p. 130—135°/0.7 mm. This is treated with magnesium methyl iodide, water is eliminated from the carbinol by distillation, and the resulting dihydronaphthalene dehydrogenated by selenium at 280—300° to 1:4-dimethyl-6-ethylnaphthalene, b. p. about 155°/0.5 mm. (*picrate*, m. p. 85°; unstable *styphnate*, m. p. about 175° after sintering at 74° and becoming colourless at 120°).

H. BURTON.

**Action of organomagnesium compounds on furfurylideneacetophenone. New furan ketones.** N. N. MAXIM (Bul. Soc. Chim. România, 1930, **12**, 24—27).—Phenyl  $\beta$ -furylvinyl ketone,  $C_6H_5O\cdot CH:CHBz$ , b. p. 180°/12 mm., m. p. 46° (Kostanecki and Podrajanski, A., 1896, i, 688), reacts with the appropriate Grignard reagent to form saturated ketones of the type  $C_4H_3O\cdot CHR\cdot CH_2Bz$ , and thus are obtained: *phenyl  $\beta$ -furyl-*n*-propyl ketone*, b. p. 178°/30 mm. (*semicarbazone*, m. p. 140—141°); *phenyl  $\beta$ -furyl-*n*-butyl ketone*, b. p. 173°/12 mm. (*semicarbazone*, m. p. 119—120°), and *phenyl  $\beta$ -phenyl- $\beta$ -furyl-*n*-propyl ketone*, b. p. 219°/12 mm., m. p. 70° (*oxime*, m. p. 90°).

J. W. BAKER.

**Preparation of ketones containing the furan nucleus.** N. N. MAXIM (Bul. Soc. Chim. România, 1930, **12**, 33—35).—The *diethylamide*, b. p. 140°/20 mm., m. p. 23° (prepared by the action of diethylamine on the acid chloride in benzene), of pyromucic acid, reacts with the appropriate magnesium alkyl halide to give furyl ethyl ketone (*semicarbazone*, m. p. 190°) and furyl *n*-propyl ketone (*semicarbazone*, m. p. 189°) identical with specimens prepared by the method of Asahina and Murayama (A., 1915, i, 429).

J. W. BAKER.

**Constitution of hydrangenol and phyllostulcin. III. Synthesis of hydrangenol.** Y. ASAHINA and J. ASANO (Ber., 1930, **63**, [B], 2059—2063).—3-Nitrophthalic acid is converted into 3-hydroxy-

phthalic acid, which with methyl iodide and silver oxide in anhydrous ether affords methyl 3-methoxyphthalate. Hydrolysis of the ester yields 3-methoxyphthalic acid, from which the anhydride, m. p. 160°, is obtained by means of acetyl chloride and acetic anhydride. 3-Methoxyphthalic anhydride and *p*-methoxyphenylacetic acid in presence of anhydrous sodium acetate afford 7:4'-*dimethoxybenzylidene-phthalide*, m. p. 183°, in small yield, reduced by sodium amalgam to 7:4'-*dimethoxybenzylphthalide*, m. p. 108°. If the last-named substance is dissolved in hot methyl-alcoholic potassium hydroxide, the solution evaporated to dryness, and the residue heated at 200° in a vacuum, methyl and water are lost with formation of 3-hydroxy-4'-methoxystilbene-2-carboxylic acid, m. p. about 150°, identical with hydrangeic acid monomethyl ether and transformed by diazomethane into the dimethyl ether, m. p. 108°. The acid passes at 180° into hydrangenol methyl ether [8-hydroxy-4'-methoxy-3-phenyl-3:4-dihydroisocoumarin], m. p. 123°. Treatment of hydrangeic acid monomethyl ether with potassium hydroxide in a vacuum at 220—230° gives a mixture of unchanged material and hydrangeic acid [3:4'-dihydroxystilbene-2-carboxylic acid], which is transformed at 180° into hydrangenol [8:4'-dihydroxy-3-phenyl-3:4-dihydroisocoumarin], m. p. 181°.

H. WREN.

**Anthocyan and anthocyanidin. III. Methylation product of malvin.** K. KONDO (J. Pharm. Soc. Japan, 1930, **50**, 452—454).—Methylation of malvin, isolated as the compound  $C_{27}H_{29}O_{15}Cl(OMe)_2$ , with methyl sulphate afforded the compound  $C_{27}H_{23}O_9Cl(OMe)_8$ , which on hydrolysis gave methyl-malvidin,  $C_{15}H_{15}OCl(OH)_2(OMe)_4$ , corresponding with the methylanthocyanidin obtained by the methylation of althæin.

CHEMICAL ABSTRACTS.

**Plant colouring matters. XXIV. Colouring matter of wild and cultivated blackberry.** P. KARRER and B. PIEPER (Helv. Chim. Acta, 1930, **13**, 1067—1070).—The colouring matter of both fruits is a cyanidin monoglucoside. The anthocyanin is identical (or isomeric) with chrysanthemin (Robinson and Willstätter, A., 1929, 192) in all properties except the crystalline form. Details are given for the extraction of the colouring matter with 2% methyl-alcoholic hydrochloric acid, whereby the *chloride*,  $C_{21}H_{21}O_{11}Cl$ , is obtained; purification is effected through the *picrate*.

H. BURTON.

**Fluoran from copper phthalate.** J. B. EKELEY and I. H. MATTISON (J. Amer. Chem. Soc., 1930, **52**, 3003—3004).—Careful dry distillation of copper phthalate at temperatures between 300° and a dull red heat (cf. A., 1917, i, 338) yields up to 91.5% of the theoretical yield of fluoran. Copper tetrachlorophthalate gives a similar distillate, which does not, however, yield satisfactory analytical figures for a dodecachlorofluoran.

H. E. F. NOTTON.

**Pyrrolenitriles and their transformations.** H. FISCHER and P. ROTHMUND (Ber., 1930, **63**, [B], 2249—2257).—Ethyl 3-cyano-2:4-dimethylpyrrole-5-carboxylate is hydrolysed by aqueous sodium hydroxide to 3-cyano-2:4-dimethylpyrrole-5-carboxylic acid, m. p. 250°, which passes into 3-cyano-2:4-dimethyl-

pyrrole, m. p. 107°, when heated in a vacuum at 150°. Ethyl acetoacetate in glacial acetic acid is treated with sodium nitrite, and to the product acetoacetamide and zinc dust are added, thus yielding ethyl 3-carbamyl-2:4-dimethylpyrrole-5-carboxylate, m. p. 173°, transformed by acetic anhydride and anhydrous sodium acetate into ethyl 3-cyano-2:4-dimethylpyrrole-5-carboxylate, m. p. 173°. 3-Cyano-2:4-dimethylpyrrole is converted by formaldehyde and a little concentrated hydrochloric acid into 4:4'-dicyano-3:3':5:5'-tetramethylpyrromethane. With hydrobromic acid (*d* 1.49) and formic acid it gives 4:4'-dicyano-3:3':5:5'-tetramethylpyrromethene hydrobromide, m. p. 242° (decomp.); the corresponding hydrochloride, m. p. 225° (decomp.), is analogously prepared. 4:4'-Dicyano-3:3':5:5'-tetramethylpyrromethene, m. p. 280° (decomp.), gives the copper salt,  $C_{30}H_{28}N_8Cu$ , cobalt salt,  $C_{30}H_{28}N_8Co$ , and zinc salt,  $2C_{30}H_{28}N_8Zn \cdot Zn(OAc)_2 \cdot H_2O$ .

Ethyl 3-cyano-2:4-dimethylpyrrole-5-carboxylate is transformed by sulphuryl chloride in ether and treatment of the product with boiling water into ethyl 3-cyano-4-methyl-2-hydroxymethylpyrrole-5-carboxylate, m. p. about 195–196° after softening and darkening at 145°. Under different conditions, ethyl 3-cyano-2:4-ditrichloromethylpyrrole-5-carboxylate, m. p. (indef.) 98°, is produced. Ethyl 3-cyano-2-tribromomethyl-3-hydroxymethylpyrrole-5-carboxylate, m. p. 183°, is described.

3-Cyano-2:4-dimethylpyrrole is transformed by hydrogen cyanide and hydrogen chloride through the imine hydrochloride into 3-cyano-2:4-dimethylpyrrole-3-aldehyde, m. p. 223° (oxime, m. p. 206°; semicarbazone, gradually decomposing above 250° without melting; phenylhydrazone, m. p. 175°). It is converted by boiling acetic anhydride and anhydrous potassium acetate into 3:5-dicyano-2:4-dimethylpyrrole, m. p. 209°. Boiling 10% hydrochloric acid transforms the aldehyde into 4:4'-dicyano-3:3':5:5'-tetramethylpyrromethene hydrochloride, m. p. 222° (decomp.) (see above), whereas reduction according to Wolff-Kishner gives 2:4:5-trimethylpyrrole and 3-cyano-2:4:5-trimethylpyrrole, m. p. 140°.

3-Cyano-2:4-dimethylpyrrole is transformed by bromine in glacial acetic acid into 5-bromo-5-cyano-2:4-dimethylpyrrole, darkening, without melting, at 130°.

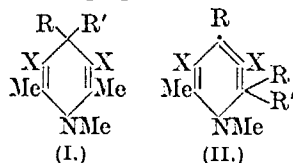
3-Cyano-2:4-dimethylpyrrole-5-aldehyde and 2:3:4-trimethylpyrrole are converted by alcohol containing hydrobromic acid into 4-cyano-3:5:3':4':5'-pentamethylpyrromethene hydrobromide, decomp. 230°. 4-Cyano-3:5:3':5'-tetramethyl-4'-ethylpyrromethene hydrobromide, m. p. 241° after darkening at 190°, is derived from cryptopyrrole-aldehyde and 3-cyano-2:4-dimethylpyrrole or from 3-cyano-2:4-dimethylpyrrole-5-aldehyde and cryptopyrrole. The cyanoaldehyde and cryptopyrrole-carboxylic acid afford 4-cyano-3:5:3':5'-tetramethylpyrromethene-4'-propionic acid hydrobromide, m. p. 240° (decomp.).

3-Cyano-2:4-dimethylpyrrole is not reduced by sodium and alcohol.

H. WREN.

**Dihydropyridine derivatives and pyridones.** K. VON AUWERS (Ber., 1930, 63, [B], 2111–2119).—

Observations of the dihydropyridine derivatives (I and II) prepared by Mumm (A., 1924, i, 83; 1925,



(R and R' = H, Alk, or Aryl; X = CO<sub>2</sub>Et)

i, 965) show that these compounds exhibit very marked exaltations due to the action of the residual valency of nitrogen on the conjugated system and that the two types are spectroscopically distinct. The formulae assigned by Mumm to the individual compounds are confirmed and two doubtful substances are shown to be ethyl 1:2:4:4:6-pentamethyl-1:4-dihydropyridine-3:5-dicarboxylate and ethyl 4-phenyl-1:2:4:6-tetramethyl-1:4-dihydropyridine-3:5-dicarboxylate. Examination of ethyl 2-keto-3-acetyl-1:4:6-trimethyl-1:4-dihydropyridine-5-carboxylate and ethyl 2-keto-3-acetyl-1:6-dimethyl-1:2-dihydropyridine-5-carboxylate gives surprisingly small exaltations. Simple pyridones and their derivatives have therefore been examined. The spectrochemical constants of several O-ethers and of 3-hydroxypyridine are in accordance with expectations, whereas those of the N-alkylpyridones do not harmonise with the carbonyl or betaine structure. They are explicable on the hypothesis that a partial neutralisation of residual affinity takes place between the doubly-linked oxygen and the nitrogen, but that this is not equal in value to an ordinary linking. The compounds are in a state intermediate between those expressed by the pyridone and betaine structures. This applies to free 2-pyridone, for which an equilibrium between the phenolic and other forms is also possible; in this case spectrochemical evidence excludes only an exclusively phenolic structure.

The spectrochemical data for the pyrones do not create any necessity for modifying the usual structural formulae.

The following constants, *inter alia*, are recorded: ethyl *s*-N-methyldihydrocollidinedicarboxylate,  $d_{400}^{25}$  1.0214,  $n_{D}^{25}$  1.50060; ethyl *s*-1-methyl-4-isobutyldihydro-2:6-lutidinedicarboxylate,  $d_{400}^{25}$  0.9844,  $n_{D}^{25}$  1.48816; ethyl *as*-N-methyldihydrocollidinedicarboxylate,  $d_{400}^{25}$  1.0977,  $n_{D}^{25}$  1.55249; ethyl *as*-1-methyl-4-ethylidihydro-2:6-lutidinedicarboxylate,  $d_{400}^{25}$  1.0403,  $n_{D}^{25}$  1.52922; ethyl *as*-1-methyl-4-isobutyldihydro-2:6-lutidinedicarboxylate,  $d_{400}^{25}$  1.0483,  $n_{D}^{25}$  1.53593; ethyl *s*-1:2:4:4:6-pentamethyldihydropyridine-3:5-dicarboxylate,  $d_{400}^{25}$  1.0618,  $n_{D}^{25}$  1.51121; ethyl 4-phenyl-1:2:4:6-tetramethyldihydropyridine-3:5-dicarboxylate,  $d_{400}^{25}$  1.0784,  $n_{D}^{25}$  1.54143; ethyl 2-keto-3-acetyl-1:4:6-trimethyl-1:2-dihydropyridine-5-carboxylate,  $d_{400}^{25}$  1.1127,  $n_{D}^{25}$  1.51716; ethyl 2-keto-3-acetyl-1:6-dimethyl-4-isobutyl-1:2-dihydropyridine-5-carboxylate,  $d_{400}^{25}$  1.0514,  $n_{D}^{25}$  1.50009; 2-ethoxypyridine,  $d_{400}^{25}$  1.0088,  $n_{D}^{25}$  1.49240; 3-ethoxypyridine,  $d_{400}^{25}$  1.0855,  $n_{D}^{25}$  1.61034; 4-methoxypyridine,  $d_{400}^{25}$  1.0802,  $n_{D}^{25}$  1.51780; 4-phenoxy-pyridine,  $d_{400}^{25}$  1.0932,  $n_{D}^{25}$  1.56457; 1-ethyl-2-pyridone,  $d_{400}^{25}$  1.0861,  $n_{D}^{25}$  1.55056.

H. WREN.

**β-Diketones in ring formation.** I. U. BASU (J. Indian Chem. Soc., 1930, 7, 481–494).—Benzoyl-

*O*-ethylacetone and *O*-methylbenzoylacetone condense with alcoholic sodiocyanoacetamide, or with cyanoacetamide under the influence of diethylamine, with formation of 3-cyano-6-phenyl-4-methyl-2-pyridone, m. p. 310°, and 3-cyano-6-methyl-4-phenyl-2-pyridone, m. p. 275—276°, respectively (cf. Issoglio, A., 1905, i, 609, who, however, describes the latter in an impure form, m. p. 263—264°). Cyanoacetamide, although a ketonic reagent, must therefore react primarily with these *O*-ethers according to the Michael reaction, for an aldol condensation would lead to a reversal of the products. Benzoylacetone itself gives a mixture of the two (cf. Bardhan, A., 1929, 1462). Confirmation of this view is afforded by the condensation of the ketonic and enolic forms of  $\alpha\alpha$ -dibenzoylthane (Dieckmann, A., 1922, i, 1020) with cyanoacetamide, both of these yielding 3-cyano-4 : 6-diphenyl-5-methyl-2-pyridone, m. p. 304—305°, hydrolysed by 80% sulphuric acid into 4 : 6-diphenyl-5-methyl-2-pyridone, m. p. 263—264°. Dibenzoylmethane itself gives 3-cyano-4 : 6-diphenyl-2-pyridone, m. p. 318—320°, hydrolysed by 80% sulphuric acid to 4 : 6-diphenyl-2-pyridone. The condensation of cyanoacetamide with acetylacetone could not be effected under acid conditions, but condensation under the usual variety of conditions gives 3-cyano-4 : 6-dimethyl-2-pyridone. The sodium salt of this compound, the initial product when the reaction is carried out with sodiocyanoacetamide in benzene suspension, gives with methyl iodide and methyl alcohol 3-cyano-1 : 4 : 6-trimethyl-2-pyridone, m. p. 203—204°; this also results from the condensation of cyanoacetmethylamide, m. p. 104° (prepared from ethyl cyanoacetate and methylamine), under the influence of piperidine or sodium ethoxide; the sodium is therefore attached direct to nitrogen. The sodium compound from acetylacetone and sodiocyanoacetmethylamide in benzene gives on methylation 3-cyano-1 : 4 : 5 : 6-tetramethyl-2-pyridone, m. p. 180°, also obtained from  $\alpha\alpha$ -diacetylene and cyanoacetmethylamide; in this case, therefore, the sodium must be attached to the carbon atom in the 5-position.  $\alpha\alpha$ -Diacetylene with cyanoacetamide gives the known 3-cyano-4 : 5 : 6-trimethyl-2-pyridone, m. p. 305—306°. Ethyl acetylpyruvate condenses with sodiocyanoacetamide in suspension in benzene to give the yellow sodium salt of ethyl 3-cyano-6-methyl-2-pyridone-4-carboxylate (cf. Bardhan, loc. cit.); from the free ester 6-methyl-2-pyridone-4-carboxylic acid, m. p. above 325°, (+1H<sub>2</sub>O), m. p. 225—226° (very rapidly heated). The condensation of ethyl cyclohexanone-2-oxalate with cyanoacetamide gives a compound which by analogy with the previous condensation is regarded as ethyl 3-cyano-5 : 6 : 7 : 8-tetrahydro-2-quinolone-4-carboxylate, m. p. 214—215°, hydrolysed by fuming hydrochloric acid at 170—180° to 5 : 6 : 7 : 8-tetrahydro-2-quinolone-4-carboxylic acid, m. p. 308°. H. A. PIGGOTT.

**Catalytic reduction of  $\alpha$ -picoline to pipercoline.** P. BORISSOV (Ber., 1930, 63, [B], 2278).—The reduction takes place readily and almost quantitatively in presence of 29% palladised asbestos at 160°. H. WREN.

**Dealkylation of tertiary amines by organic acids.** II. Nicotine. J. VON BRAUN and K.

WEISSBACH (Ber., 1930, 63, [B], 2018—2026; cf. this vol., 458).—Nicotine is attacked with some difficulty by boiling benzoic acid yielding partly racemised, original material and a non-separable mixture of benzoylnornicotine and benzoylmetan nicotine; the last-named substance has b. p. 208—210°/0.1 mm. Nicotine and boiling  $\beta$ -phenylpropionic acid afford the  $\beta$ -phenylpropionyl derivatives of nornicotine and metan nicotine, 3- $\beta$ -propionylmethylamino- $\alpha$ -hydroxy-*n*-butylpyridine, C<sub>5</sub>H<sub>4</sub>N·CH(OH)·[CH<sub>2</sub>]<sub>3</sub>·NMe·CO·Et, b. p. 160—162°/0.2 mm. (*picrate*, m. p. 127—128°), methyl  $\beta$ -phenylpropionate,  $\beta$ -phenylpropionmethylamide, components of high b. p., and, apparently, free meta- and nor-nicotine. The fraction of the product mainly composed of the  $\beta$ -phenylpropionyl derivatives of nor- and meta-nicotine is treated with fuming hydrobromic acid at 150—160°, whereby metan nicotine is converted into the unstable 3- $\beta$ -bromo- $\delta$ -methylamino-*n*-butylpyridine (the corresponding chloro-compound is more stable), whereas nornicotine remains unaffected. The product is treated with hot water followed by ether into which the nornicotine passes, leaving an undissolved mixture of hydrobromides formed by intra- and extra-molecular loss of hydrogen bromide from the bromo-compound described above. Nornicotine has b. p. 266—267°/atmos. pressure, 139—140°/12 mm.,  $d_4^{20}$  1.044,  $[\alpha]_D^{20}$  about -5.5° (the product is partly racemised during the reaction). Contrary to M. and M. Polonovski (A., 1927, 785) it does not become brown or resinify when exposed to air. The *picrate*, m. p. 188—190°, *picrolonate*, m. p. 239—240°, not crystalline *hydrochloride*, *chloroplatinate*, decomp. 295° after darkening at 270°, and *chloroaurate*, m. p. 217°, are described. *Nitrosornicotine*, b. p. 190—192°/0.5 mm., gives a non-crystalline *picrate*, *hydrochloride*, and *chloroaurate*, a *chloroplatinate*, m. p. 190°, and a *methiodide*, m. p. 144°; it is converted by concentrated hydrochloric acid into nornicotine. Acetylnornicotine has b. p. 212—214°/12 mm.,  $[\alpha]_D^{20}$  -3.24° in benzene; it yields a *picrate*, m. p. 151°, non-crystalline *chloroaurate*, *chloroplatinate*, decomp. 245° after darkening at 200°, and *methiodide*, m. p. 201°. *Nornicotylcarbamide*, m. p. 164—166°, from nornicotine hydrochloride and potassium cyanate, gives a *chloroplatinate*, decomp. 270° after darkening at 250°, and a non-crystalline *picrate*. *Phenylnornicotylthiocarbamide* has m. p. 171°. Nornicotine and ethyl iodide afford a quaternary iodide and *N*-ethylnornicotine, b. p. 127—128°/12 mm. (very hygroscopic *hydrochloride*; *chloroaurate*, decomp. 203°; *picrate*, m. p. 174—176°). *N*-Allylnornicotine, b. p. 136—137°/12 mm., affords a *picrate*, m. p. 180—182°, *chloroaurate*, decomp. 145—148°, and *chloroplatinate*, decomp. 255° after darkening at 230°. H. WREN.

**Syntheses in the indole group. VII. Nitration and bromination of indole-3-carboxylic ester and a new synthesis of the dye of ancient purple.** R. MAJIMA and M. KOTAKE (Ber., 1930, 63, [B], 2237—2245; cf. A., 1925, i, 1450).—According to the conditions, the action of ethyl chloroformate on magnesium indolyl iodide yields ethyl indole-1 : 3-dicarboxylate, m. p. 102—103°, or ethyl indole-3-carboxylate. Treatment of the last-named compound with nitric acid

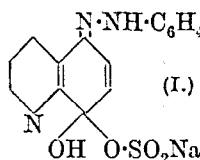
(d 1.4) in glacial acetic acid yields *ethyl 6-nitroindole-3-carboxylate*, m. p. 198—199°, accompanied by small and varying amounts of two substances, m. p. 273—275° and 157—158°, respectively. 6-Nitroindole-3-carboxylic acid, decomp. about 275—278° after softening at 227°, obtained by hydrolysis of the ester, is oxidised by alkaline potassium permanganate to 4-nitro-2-aminobenzoic acid, m. p. 262—264°. *Ethyl 6-aminoindole-3-carboxylate*, m. p. 149—150° (*hydrochloride*; *chloroplatinate*), is obtained by reduction of the nitro-ester with stannous chloride and hydrogen chloride in glacial acetic acid. 6-Nitroindole-3-carboxylic acid is decarboxylated in quinoline at 140—145° to 6-nitroindole, m. p. 139—140.5°, reduced to the very unstable 6-aminoindole, which yields a readily decomposed *hydrochloride*, *chloroplatinate*, and *picrate*. Indole-3-aldehyde and nitric acid (d 1.4) in glacial acetic acid at the ordinary temperature give an additive compound,  $C_8H_7ON.HNO_3$ , decomp. 94°; with excess of nitric acid a vigorous change occurs at 65—70°, leading to the formation of a *nitroindole-3-aldehyde*, m. p. about 290° (decomp.). According to conditions, bromination of *ethyl indole-3-carboxylate* in glacial acetic acid affords *ethyl 6-bromoindole-3-carboxylate*, m. p. 134—137° (corresponding acid, m. p. 212°), or *ethyl 5:6-dibromoindole-3-carboxylate*, m. p. 223—225° (5:6-dibromoindole-3-carboxylic acid, m. p. 255—257°; 5:6-dibromoindole, m. p. 154°). Oxidation of the dibromoindolecarboxylic acid with chromium trioxide in glacial acetic acid gives 5:6-dibromoisatin, m. p. 290°, transformed by further oxidation into 4:5-dibromo-2-aminobenzoic acid, m. p. 227—228° (decomp.), and by distillation with solid potassium hydroxide into 3:4-dibromoaniline. 6-Bromoindole-3-carboxylic acid, when similarly oxidised, is converted into 6-bromoisatin, m. p. 256—258°. When treated with ozone in alkaline solution, the acid affords 6:6'-dibromoindigotin (antique purple). 5:5':6:6'-Tetrabromoindigotin is prepared similarly. H. WREN.

**Syntheses in the indole group. VIII. Harman and harmin.** S. AKABORI and K. SAITO (Ber., 1930, 63, [B], 2245—2248).—3- $\beta$ -Aminoethylindole is converted by acetaldehyde in presence of dilute sulphuric acid into tetrahydroharman, m. p. 179—180° (*chloroplatinate*), transformed by maleic acid and palladium-black in boiling water into harman, m. p. 235—236°. Magnesium 6-methoxyindolyl iodide and chloroacetonitrile yield 6-methoxy-3-cyanomethylindole, m. p. 113—114°, reduced by sodium in boiling ethyl alcohol to 6-methoxy-3- $\beta$ -aminoethylindole, m. p. 142.5—143.5°. Treatment of the amine with acetaldehyde gives tetrahydroharmin, m. p. 196—196.5°, dehydrogenated to harmin, m. p. 259—259.5°. H. WREN.

**Modification of the Skraup synthesis of quinoline.** E. W. COHN (J. Amer. Chem. Soc., 1930, 52, 3685—3688).—The violence of the reaction of the ferrous sulphate modification (Clarke and Davis, "Organic Syntheses," 1922, 2, 79) of the Skraup reaction is diminished by the addition of boric acid and the yield of quinoline is improved. H. BURTON.

**Action of sulphurous acid and its salts on quinoline derivatives.** N. N. VOROSHOV and

J. M. KOGAN (Ber., 1930, 63, [B], 2354—2362).—A mixture of quinoline and water is saturated with sulphur dioxide and gently warmed until the oily layer disappears. Yellow crystals,  $C_9H_7N.SO_2$ , m. p. 80—81°, separate from the cold solution which are decomposed by hot water, dilute acids, or alkalis. The compound is also obtained by use of sodium hydrogen sulphite solution. Analogous treatments of 8-hydroxyquinoline afford the compound  $C_9H_7O_3NS$ , m. p. 127—129°. Benzeneazo-8-hydroxyquinoline yields an apparently analogous, orange compound. *p*-Sulphonylbenzeneazo-8-hydroxy-



quinoline and aqueous sodium hydrogen sulphite yield the substance I, which decomposes into its components in aqueous solution in a degree which increases with dilution, is decomposed by sodium hydrogen carbonate to a rapidly increasing extent with increasing concentration of the hydrogen carbonate, and is stabilised by the addition of traces of hydrochloric acid. It thus appears completely analogous with the additive product from sodium hydrogen sulphite and *p*-sulphonylbenzeneazo- $\alpha$ -naphthol. H. WREN.

**2:4-Dihydroxydimethoxyquinoline.** Y. ASAHINA and S. NAKANISHI (Ber., 1930, 63, [B], 2057—2059).—6-Nitro-3:4-dimethoxybenzoyl chloride, ethyl malonate, and sodium ethoxide afford *ethyl 6-nitro-3:4-dimethoxybenzoylmalonate*, converted by tin and hydrochloric acid in alcohol into 2:4-dihydroxy-6:7-dimethoxyquinoline, not molten below 320° [*nitroso-derivative*, m. p. about 266° (decomp.)]. Similarly, *ethyl 2-nitro-3:4-dimethoxybenzoylmalonate*, m. p. 108—110°, affords 2:4-dihydroxy-7:8-dimethoxyquinoline, m. p. 250° (*nitroso-derivative*, decomp. 248°), identical with the product derived from skimmianic acid (this vol., 1454). H. WREN.

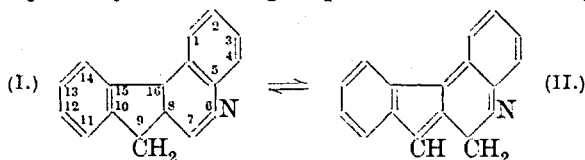
**Quinoline compounds. I.** U. N. BRAHMACHARI and T. BHATTACHARJEE (J. Indian Chem. Soc., 1930, 7, 527—530).—The following were prepared by condensation of the appropriate quinaldine derivative with *p*-dimethylaminobenzaldehyde: 2-*p*-dimethylaminostyrylquinoline, m. p. 175° (cf. Noelting and Witte, A., 1906, i, 886); 6-methyl-, m. p. 199°, 6-hydroxy-, m. p. above 240°, 6-ethoxy-, m. p. 212°, and 6-methoxy-2-*p*-dimethylaminostyrylquinoline, m. p. 202°. Quinoline-6-aminoacetamide, m. p. 197°; quinoline-8-aminoacetamide, m. p. 183°, 6-ethoxyquinoline-8-aminoacetamide, m. p. 235°, and 6-methoxyquinoline-8-aminoacetamide, m. p. 226°, were obtained by interaction of the appropriate aminoquinoline and chloroacetamide. H. A. PIGGOTT.

**Indoquinoline derivatives.** G. SINGH and J. N. RAY (J. Indian Chem. Soc., 1930, 7, 637—645).—*o*-Nitrobenzaldehyde condenses with  $\alpha$ -hydrindone in presence of acetic anhydride, forming 2-*o*-nitrobenzylidene-1-hydrindone, m. p. 167°, reduced by zinc dust and acetic acid to indoquinoline (*hydrochloride*, m. p. 170—175°) (cf. Armit and Robinson, J.C.S., 1922, 121, 828; A., 1925, i, 1170). 2-6'-Nitro-3':4'-methylenedioxybenzylidene-1-hydrindone, m. p.

178° (lit. 182°), is reduced similarly in an atmosphere of hydrogen to 7:8-methylenedioxyindoquinoline [hydrochloride, m. p. 197° (decomp.) after shrinking at 194°]. 2-6'-Nitro-3':4'-dimethoxybenzylidene-1-hydrindone, m. p. 210°, is described. The o-nitrobenzylidene, m. p. 212°, 6-nitro-3:4-methylenedioxybenzylidene, m. p. 232°, and 6-nitro-3:4-dimethoxybenzylidene, m. p. 250°, derivatives of 4:5-methylenedioxy-1-hydrindone (?) are reduced similarly to 3:4-methylenedioxy-, m. p. 202° after shrinking at 195°, 3:4:7:8-dimethylenedioxy-, m. p. 283°, and 7:8-dimethoxy-3:4-methylenedioxy-indoquinolines [hydrochloride, m. p. 257° (decomp.) after shrinking at 255°], respectively. Similarly, o-nitrobenzylidene-, m. p. 188°, 6-nitro-3:4-methylenedioxybenzylidene-, m. p. 232°, and 6-nitro-3:4-dimethoxybenzylidene-, m. p. 237°, 4:5-dimethoxy-1-hydrindone (?) give 3:4-dimethoxy- [hydrochloride, m. p. 232° (decomp.)], 3:4-dimethoxy-7:8-methylenedioxy- [hydrochloride, m. p. 270° (decomp.)], and 3:4:7:8-tetramethoxy-indoquinolines [hydrochloride, m. p. 235° (decomp.)]. When the above reductions are carried out in presence of air, fluorescent solutions are often formed as intermediates; the fluorescence is ascribed to oxidation (dehydrogenation) of the methylene group in the indoquinoline.

Deoxybenzoin and o-nitrobenzaldehyde condense in presence of alcoholic potassium hydroxide solution, forming a mixture of a compound, m. p. 110°, and o-nitrobenzylidenedeoxybenzoin, m. p. 210°; the latter could not be reduced. H. BURTON.

**Synthesis of isoindenoquinolines.** I. G. R. CLEMO and H. J. JOHNSON (J.C.S., 1930, 2133—2138).—The synthesis of 12:13-dimethoxyisoindenoquinoline leads to two forms, light yellow and brownish-red, respectively, both having m. p. 193—194°, and being



deposited together from benzene solution; hence, as the ring system is stable and uniplanar, they are considered to be the isomerides I and II.

4-Keto-1:2:3:4-tetrahydroquinoline (Clemo and Perkin, A., 1924, i, 1103) (N-acetyl derivative, m. p. 94°), when condensed with veratraldehyde under the influence of hydrogen chloride in acetic acid, gives 4-keto-3-veratrylidene-1:2:3:4-tetrahydroquinoline, red, m. p. 177—178°, readily converted by alcoholic sodium hydroxide into the isomeric 4-hydroxy-3-homoveratrylquinoline, m. p. 225°, the product of the original condensation when carried out in alcoholic alkaline solution. The N-acetyl derivative (above) interacts similarly to give 4-keto-1-acetyl-3-homoveratrylidene-1:2:3:4-tetrahydroquinoline, m. p. 164°, reduced by hydrogen and palladised charcoal in acetic acid to 4-keto-1-acetyl-3-homoveratryl-1:2:3:4-tetrahydroquinoline, m. p. 89° (oxime, m. p. 208°) (cf. Perkin, Ray, and Robinson, A., 1926, 732). When heated with 80% sulphuric acid at 100° this undergoes ring closure with elimination of water and formation of the isoindenoquinolines (I and II).

4-Hydroxy-3-homoveratrylquinoline yields with bromine in acetic acid the 6'-bromo-derivative, m. p. 233°, with concentrated sulphuric acid the 6'-sulphonic acid, m. p. 308° (decomp.), and with phosphoryl chloride 4-chloro-3-homoveratrylquinoline, m. p. 96° [methiodide, m. p. 208° (decomp.)]; 6'-bromo-derivative, m. p. 112°; dibromo-derivative, m. p. 220° (decomp.)]. The action of aluminium chloride on 4-chloro-3-homoveratrylquinoline and of copper by Ullmann's method on its 6'-bromo-derivative failed to effect ring closure. H. A. PIGGOTT.

**Hydantoins. XLIX. New rearrangement leading to the formation of 4-aminoglyoxaline derivatives.** R. M. HERBST and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 3676—3680).—Benzyl methyl ketone, dry hydrogen cyanide, and methylamine in alcohol afford α-methylamino-α-benzylpropionitrile, the hydrochloride, m. p. 106—108° (decomp.) after sintering at 102°, of which reacts with potassium cyanate in acetic acid, forming α-cyano-β-phenyl-α-methylethylmethylcarbamide, NH<sub>2</sub>·CO·NMe·CMe(CN)·CH<sub>2</sub>Ph, m. p. 130—131°. The carbamide is hydrolysed by warm 20% hydrochloric acid to 5-benzyl-1:5-dimethylhydantoin, m. p. 134—135°, and converted by boiling with water for a short time into 4-amino-2-keto-5-benzyl-1:5-dimethyl-2:5-dihydroglyoxaline, m. p. 267—268° (decomp.) [hydrochloride, m. p. 218—223° (decomp.)]; picrate, m. p. 226—227° (decomp.)]. Both these derivatives are probably formed through the intermediate 4-imino-compound, which is either hydrolysed or tautomerises according to the acidity of the reaction mixture. All m. p. are corr. H. BURTON.

**Action of glyoxal on carbamide; new methods of formation of hydantoins.** H. PAULY and H. SAUTER (Ber., 1930, 63, [B], 2063—2069).—Paracet-aldehyde is converted by aqueous nitric acid containing nitrous fumes into glyoxal, which after repeated evaporation with water under diminished pressure to remove as much acid as possible is concentrated to a syrup and mixed with carbamide at the ordinary temperature. Carbamide nitrate and a little glyoxal-diureine are precipitated; the main product is glyoxalmonoureine [2-keto-4:5-dihydroxytetrahydroiminazole], m. p. 146° (disodium compound). Interaction of glyoxal and carbamide in the presence of hydrochloric acid (d 1.14) affords glyoxaldiureine and a compound, C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>N<sub>4</sub>·3H<sub>2</sub>O, m. p. 95—97° (disodium derivative), to which the constitution CH(OH)·NH·CO·NH  
CH—O—CH is assigned; they are conveniently separated from one another by means of 27% hydrochloric acid. Re-examination of the work of Behrend, Meyer, and Rusche (A., 1905, i, 419) shows that the product obtained was a very impure mixture of the compound C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>N<sub>4</sub>·3H<sub>2</sub>O with glyoxaldiureine and hydantoin; their compounds C<sub>11</sub>H<sub>18</sub>O<sub>10</sub>N<sub>6</sub> and C<sub>20</sub>H<sub>36</sub>O<sub>19</sub>N<sub>12</sub> should be deleted from the literature. Glyoxalmonoureine and the compound C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>N<sub>4</sub>·3H<sub>2</sub>O are transformed by boiling hydrochloric acid into hydantoin. Glyoxal or its sulphate is converted by urethane in presence of dilute hydrochloric acid into glyoxaldicarboethoxymide,



$[\text{CH}_2\text{N} \cdot \text{CO}_2\text{Et}]_2$ , which does not melt when heated and by thiocarbamide into *glyoxaldithioureine*,  
 $\text{CS} \begin{array}{c} \text{NH} \cdot \text{CH} \cdot \text{NH} \\ \text{NH} \cdot \text{CH} \cdot \text{NH} \end{array} \text{CS}.$  H. WREN.

**Pyrazolone series. Action of semi- and thio-semi-carbazides on ketonic esters.** III. S. C. DE and D. N. DUTT (J. Indian Chem. Soc., 1930, 7, 473—480).—The interaction of semicarbazide and thiosemicarbazide with the alkylacetoacetic esters generally leads to the pyrazolone from which the carbamyl or thiocarbamyl group has been eliminated. With ethyl methylacetoacetate only is there evidence of the formation of a semicarbazone or thiosemicarbazone. These cyclise when gently heated; in other cases external heating is needed for combination. The following are described: *ethyl methylacetoacetate-thiosemicarbazone*, m. p. 192°; *3:4-dimethylpyrazolone*, m. p. 262° [identical with the product "m. p. 249°," prepared by Rothenburg (A., 1895, i, 686) from ethyl methylacetoacetate and hydrazine hydrate; that from methyl iodide and 3-methylpyrazolone, m. p. 249° (*loc. cit.*), is different, and is probably 1:3-dimethylpyrazolone]; *3:4:4-trimethylpyrazolone*, m. p. 262—263°; *3-methyl-4-ethylpyrazolone* (Rothenburg, *loc. cit.*), and *3-methyl-4-ethylpyrazolone-1-carboxylamide*, m. p. 258°.

Ethyl oxalacetate with semicarbazide gives *ethyl pyrazolone-3-carboxylate*, m. p. 178°, and 3-(5'-*keto-1':2':4'-triazolyl*)pyrazolone,  $\text{CO} \cdot \text{CH}_2 \cdot \text{N} \cdot \text{CO} \begin{array}{c} \text{NH} \cdot \text{N} \\ \text{NH} \cdot \text{N} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{CO} \\ \text{NH} \cdot \text{NH} \end{array}$  m. p. 265°, ethyl benzoyl-acetoacetate gives *ethyl 3-phenyl-5-methylpyrazole-4-carboxylate*, m. p. 232° (also with thiosemicarbazide), but ethyl acetylacetoacetate yields 3-methylpyrazolone and *ethyl 3:5-dimethylpyrazole-4-carboxylate*, m. p. 96°, and in addition with thiosemicarbazide 3-methylpyrazolone-1-thiocarboxylamide. From ethyl acetosuccinate and semicarbazide are produced *ethyl 2-keto-3-methyltetrahydropyridazine-4-carboxylate*, m. p. 220° [this structure being assumed on account of its non-identity with ethyl 3-methylpyrazolone-4-acetate (Curtius, A., 1895, i, 246)], and a substance, m. p. 258° (decomp.), of unknown constitution. H. A. PIGGOTT.

**Reduction potential of alloxantins; preparation of alloxans and alloxantins.** E. BILMANN and N. BERG (Ber., 1930, 63, [B], 2188—2204).—In aqueous solution, alloxantin is very considerably dissociated into dialuric acid and alloxan, which must necessarily be present in equivalent proportion in solutions of the pure substance if no account is taken of the probable formation of alloxan anhydride in small amount. The required potential is the reversible reaction,  $\text{alloxan} + \text{H}_2 \rightleftharpoons \text{dialuric acid} + \text{H}_2\text{O}$ , which depends on the pressure of the hydrogen and on the logarithm of the ratio of the concentration of alloxan to dialuric acid in the solutions and not on the absolute values of these concentrations. Measurements are recorded for the chain, Pt-quinhydrone, 0.1*N*-sulphuric acid, alloxantin|Pt- at 18° and 25°. Data are recorded for alloxantin, dimethyl-, tetramethyl-, dimethyldiethyl-, dimethyldipropyl-, diethyl-, and tetraethyl-alloxantin. The values are

very little affected by the presence of substituents, the difference between the maximum and minimum figures being only 0.0069 volt. Consideration of the reduction potentials shows that it is impossible to predict the course of the reaction when attempts are made to prepare "mixed alloxantins."

Dimethyldiethylalloxantin is most conveniently prepared from theobromine, which is converted into ethyltheobromine, m. p. 163°, in 64% yield when treated with ethyl sulphate and sodium hydroxide at 80—90°. Gradual addition of potassium chlorate is made to a solution of ethyltheobromine in hydrochloric acid at 50—55°. Excess of chlorine is removed by sulphur dioxide, after which the solution is treated with hydrogen sulphide. The dimethyldiethylalloxantin thus produced is separated from admixed sulphur by treatment with boiling water in an atmosphere of carbon dioxide, filtered, and the alloxantin is crystallised from the filtrate.

Alloxans are readily prepared by oxidation of the requisite benzylidenobarbituric acids with chromic acid in acetic acid containing a little water. In some cases the alloxan separates directly from the reaction mixture. When this is not the case, the dissolved alloxan is immediately subjected to partial reduction by stannous chloride after addition of water and hydrochloric acid; the substituted dialuric acid thus produced unites with unchanged substituted alloxan to give the required substituted alloxantin. The following examples are cited: benzylidenobarbituric acid to alloxan monohydrate in 80% yield; 5-benzylidene-1-methylbarbituric acid, m. p. 220.5—222.5°, to 1-methylalloxan monohydrate; 5-benzylidene-1:3-dimethylbarbituric acid, m. p. 164—165°, to tetramethylalloxantin; 5-benzylidene-1:3-diethylbarbituric acid, m. p. 100—100.6°, to tetraethylalloxantin.

H. WREN.

**Preparation and reduction potential of diethyl-alloxantin.** E. BILMANN and A. KLIT (Ber., 1930, 63, [B], 2205—2208).—Ethylcarbamide, m. p. 90—92°, prepared in 90% yield by the interaction of ethylamine and nitrocarbamide in water, is converted into ethylbarbituric acid, which affords 5-benzylidene-1-ethylbarbituric acid, m. p. 189—191°, when treated with benzaldehyde in alcohol. Oxidation of the acid with chromium trioxide in glacial acetic acid followed by partial reduction of the product by stannous chloride leads to the production of 1:3-diethylalloxantin (the use of calcium chloride in the desiccation of alloxantins should be avoided on account of a possible ammonia content). The reduction potential of diethylalloxantin is 0.3652 and 0.3627 volt at 18° and 25°, respectively. H. WREN.

**Pyrimidines. CXVI. Improved technique for the syntheses of *N*-alkyl derivatives of thymine.** T. B. JOHNSON (Ber., 1930, 63, [B], 1974—1976).—In certain cases, pyrimidines containing alkoxy-groups are readily converted by heat or alkyl halides into isomerides in which the alkyl group is attached to nitrogen. Thus the compound  $\text{OMe} \cdot \text{C} \begin{array}{c} \text{N} \cdot \text{C}(\text{OMe}) \\ \text{N} \end{array} \text{CH} \cdot \text{CMe}$  passes at 200° smoothly into 1:3-dimethylthymine.

The work of Bachstesz (this vol., 781) is criticised.

H. WREN.

**Hydrolysis of diacetyl-*o*-diamines.** M. A. PHILLIPS (J.C.S., 1930, 1409—1419).—The view that *o*-diamines occur as intermediates in the formation of benziminazoles by hydrolysis of diacetyl-*o*-diamines (A., 1928, 1381) is only partly correct. Quantitative investigation indicates that acid hydrolysis follows the courses:  $R \cdot C_6H_3(NHAc)_2$  (I)  $\xrightarrow{AcOH}$   $R \cdot C_6H_3(NH_2) \cdot NHAc$  (II)  $\xrightarrow{AcOH}$   $R \cdot C_6H_3(NH_2)_2$  (III)  $\xrightarrow{AcOH}$   $R \cdot C_6H_3 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} CMe$  (IV), and II  $\rightarrow$  IV. The stage I  $\rightarrow$  II could not be proved by isolation of II in the hydrolysis of 4-nitro-1:2-diacetamidobenzene, but is inferred since 4- and 5-nitro-2-aminoacetanilides (II) behave with hot hydrochloric acid in the same way. When methyl-alcoholic hydrogen chloride is used (removal of acetic acid as methyl acetate) IV arises directly from I or II, and since benziminazoles (IV) are stable to hot concentrated hydrochloric acid, III is also formed from I or II. With diacetyl-*o*-phenylenediamine and hot hydrochloric acid IV only was found, even with limited hydrolysis; using methyl-alcoholic hydrogen chloride at 160°, *NN'*-dimethyl-*o*-phenylenediamine, m. p. 34°, was obtained without detectable amounts of IV.

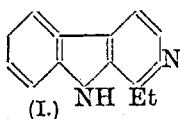
Alkaline hydrolysis of nitrodiacetyl-*o*-diamines follows the above scheme; with diacetyl-*o*-phenylenediamine and 25% sodium hydroxide IV only could be detected. Reduction of 2:4-dinitroacetanilide with 6% ammonium sulphide gives 4-nitro-2-aminoacetanilide, m. p. 205°, and 5-nitro-2-methylbenziminazole, m. p. 221°, also obtained together with 5-nitro-2-aminoacetanilide, m. p. 195°, from 4-nitro-1:2-diaminobenzene by mono-acetylation in acetic acid. Since the solution is alkaline in the former and acid in the latter case, the cyclic product appears to arise directly from the initial material. Similarly, by treatment with methyl-alcoholic hydrogen chloride 4-nitro-2-acetamidomethylaniline gives 5-nitro-1:2-dimethylbenziminazole and 4-nitro-2-aminomethylaniline, both formed independently from the initial material.

When nitrated with potassium nitrate and sulphuric acid at 0—5°, 5(or 6)-acetamido-2-methylbenziminazole gives 5(or 6)-nitro-6(or 5)-acetamido-2-methylbenziminazole, m. p. 235°, in 70% yield, reduced by iron and acetic acid to 5(or 6)-amino-6(or 5)-acetamido-2-methylbenziminazole, m. p. above 300° [*dihydrochloride*; *triazole*, m. p. above 300°; acetyl derivative, m. p. above 300° (cf. lit.)]. 1:2:4-Triacetamidobenzene similarly gives 65% of 5-nitro-1:2:4-triacetamidobenzene, m. p. 261°, hydrolysed to 5-nitro-1:2:4-triaminobenzene, m. p. 210°, together with 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole, m. p. 292°, also obtained by hydrolysis of its acetyl derivative, from 5-nitro-1:2:4-triacetamidobenzene and hydrochloric acid, and from 5-nitro-1:2:4-triaminobenzene with acetic anhydride and hot mineral acid; the *hydrochloride* by reduction with tin and 5*N*-hydrochloric acid gives 70% of 5:6-diamino-2-methylbenziminazole *dihydrochloride*; the corresponding *triazole* melts above 300°. By treatment with boiling alcohol, diazotised 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole affords 70% of 5(or 6)-nitro-2-methylbenziminazole, and by the Bart reaction gives 5(or 6)-nitro-2-methylbenziminazole-6(or 5)-

arsinic acid, m. p. above 300° (calcium, magnesium, and barium salts), reduced by ferrous hydroxide at 60° to give 65% of 5(or 6)-amino-2-methylbenziminazole-6(or 5)-arsinic acid (acetyl derivative). With tin and 5*N*-hydrochloric acid 5-nitro-1:2:4-triaminobenzene is reduced to 1:2:4:5-tetra-amino-benzene tetrahydrochloride (Nietzki and Hagenbach, A., 1887, i, 476), converted by formic and hydrochloric acids, followed by ammonia, into  $\alpha$ -benzibenziminazole, m. p. above 300°. With hot dilute acids 5(or 6)-amino-6(or 5)-acetamido- and 5:6-diacetamido-2-methylbenziminazole rapidly give  $\alpha$ -2:2'-dimethylbenzibenziminazole (cf. Nietzki and Hagenbach, loc. cit.), also obtained from 1:2:4:5-tetra-amino-benzene or 5:6-diamino-2-methylbenziminazole (Kym and Ratner, A., 1913, i, 102) by treatment with acetic and hydrochloric acids. 4-Nitro-2-acetamidomethylaniline has m. p. 185°. C. W. SHOPPEE.

**Quinazolines. I. Interaction of 2:4-dichloroquinazoline with sodium alkoxides and phenoxides with the replacement of one halogen to form halogen-oxygen ethers.** N. A. LANGE, W. E. ROUSH, and H. J. ASBECK (J. Amer. Chem. Soc., 1930, 52, 3696—3702).—Treatment of 2:4-dichloroquinazoline with sodium methoxide and ethoxide solution affords 2:4-dimethoxy- and 2:4-diethoxyquinazoline, m. p. 55° (lit. 51°), respectively. When the reaction is carried out in presence of phenol, 2-chloro-4-methoxy-, m. p. 99—100°, and 2-chloro-4-ethoxyquinazoline (I), m. p. 92°, are produced. If a relatively large amount of phenol is used, 2-chloro-4-phenoxyquinazoline, m. p. 121°, is also formed in addition to the alkoxy-derivative. The phenoxy-derivative is also produced from the dichloroquinazoline, phenol, and sodium phenoxide, whilst with sodium ethoxide and resorcinol a mixture of I and 2-chloro-4-m-hydroxyphenoxyquinazoline, m. p. 171—172°, results. Reduction of I with zinc dust and alcoholic acetic acid or sodium and methyl alcohol in ether furnishes 4-ethoxyquinazoline. Hydrolysis of I or the chloromethoxy-compound with water at 100° (bath) gives 2:4-diketo-1:2:3:4-tetrahydroquinazoline. All m. p. are corr. H. BURTON.

**Syntheses of 4-carbolines.** E. SPÄTH and E. LEDERER (Ber., 1930, 63, [B], 2102—2111; cf. this vol., 353).—Tryptamine is converted by propionic acid at 150° into the corresponding propionyl compound, which suffers ring closure when gradually treated with phosphoric oxide in boiling xylene, giving 3-ethyl-5:6-dihydro-4-carboline, m. p. 172—173° [*picrate*, m. p. 226° (decomp.)], transformed by spongy palladium at 170° into 3-ethyl-4-carboline (I), m. p. 194—195°. 3-*n*-Propyl-5:6-dihydro-4-carboline, m. p. 182—183° [*picrate*, m. p. 231° (decomp.)], 3-*n*-propyl-4-carboline, m. p. 211—212° (*hydrochloride*), 3-isopropyl-5:6-dihydro-4-carboline, m. p. 178—179° [*picrate*, m. p. 232—235° (decomp.)], 3-isopropyl-4-carboline, m. p. 162—163°, 3-phenyl-5:6-dihydro-4-carboline, m. p. 221—222° [*picrate*, m. p. 240° (decomp.)], and 3-phenyl-4-carboline, m. p. 246—247°, are analogously prepared.  $\gamma$ -Amino-*n*-butaldehyde diethylacetal is transformed by *as*-phenylmethyl-



hydrazine in presence of zinc chloride at 180° into the non-crystalline 1-methyltryptamine (*picrate*, m. p. 180—181°; *carbonate*), transformed by successive treatment with acetic anhydride and phosphoric oxide into 1-methylharmalan, m. p. 91—92° [*picrate*, m. p. 245° (decomp.)], converted into 1-methylharmalan. The non-crystalline 1-methyl-3-ethyl-5:6-dihydro-4-carboline [*picrate*, m. p. 195° (decomp.)], and 1-methyl-3-ethyl-4-carboline, m. p. 124—125°, are described. From *p*-methoxyphenylhydrazine and  $\gamma$ -amino-*n*-butaldehyde diethylacetal by a similar change is obtained 5-methoxytryptamine, m. p. 120—121° [*picrate*, m. p. 214—215° (decomp.)], which yields 10-methoxyharmalan, m. p. 208—209° [*picrate*, m. p. 258° (decomp.)], and 10-methoxyharmalan, m. p. 273—274°. From *o*-methoxyphenylhydrazine are derived 7-methoxytryptamine, m. p. 135—136° [*picrate*, m. p. 218° (decomp.)], 12-methoxyharmalan, m. p. 182—183°, and 12-methoxyharmalan, m. p. 239—240°. Formyltryptamine does not afford 5:6-dihydro-4-carboline when heated with phosphoric oxide in xylene, whereas traces of it are formed in boiling tetrahydronaphthalene. Tryptamine is transformed by formaldehyde in presence of dilute sulphuric acid, extraction of the basified solution with ether, and treatment of the residue from the ethereal solution with boiling dilute sulphuric acid into 3:4:5:6-tetrahydro-4-carboline, m. p. 207—208° (identical with the product of the reduction of 4-carboline with sodium and amyl alcohol), smoothly dehydrogenated by palladium sponge to 4-carboline, m. p. 197—198°. From 1-methyltryptamine are prepared 1-methyl-3:4:5:6-tetrahydro-4-carboline and 1-methyl-4-carboline, m. p. 108—109° [*picrate*, m. p. 258° (decomp.)], 10-methoxy-3:4:5:6-tetrahydro-4-carboline, m. p. 223—224°, and 12-methoxy-3:4:5:6-tetrahydro-4-carboline, m. p. 217—218° [*picrate*, m. p. 227—229° (decomp.)], are described.

H. WREN.

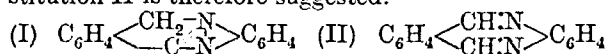
**1-Chlorophenazine.** F. WREDE and O. MÜHLROTH (Ber., 1930, 63, [B], 1931—1935; cf. Wrede and Strack, A., 1929, 1314).—3-Chloro-1:2-dihydroxybenzene (modified method of preparation given) is oxidised by silver oxide in anhydrous ether to 3-chloro-*o*-benzoquinone, which condenses with *o*-phenylenediamine in presence of glacial acetic acid with production of 1-chlorophenazine, m. p. 122—123° [*chloroaurate*, m. p. about 232° (decomp.); *chloroplatinate*, not molten below 295°; *perchlorate*]. The compound, could not be caused to react with alkali bromide or iodide or ammonia. With sodamide in xylene it yields phenazine. Compounds almost free from halogen are obtained by the action of potassium sulphide or disulphide.

H. WREN.

**Colour of complex diazoles. IV. Constitution of Thiele's supposed *o*-benzylene-1:3-benziminazole.** M. V. BETRABET and G. C. CHAKRAVARTY (J. Indian Chem. Soc., 1930, 7, 495—502).—The fusion of phthalide with *o*-phenylenediamine yields, instead of the expected *o*-benzylene-1:3-benziminazole, benziminazole-2-benzyl-*o*-phenylenediamine, m. p. above 300°. In boiling alcoholic solution the interaction gives *o*-aminophenylamino-methyl-*o*'-aminobenzanilide, m. p. 162° (acetyl derivative, m. p. 135—136°), which on fusion gives the benzimin-

azole derivative. *o*-Phenylenediamine, when condensed with *o*-hydroxymethylbenzoic acid in the presence of 4*N*-hydrochloric acid (cf. Phillips, A., 1928, 1381), gives benziminazole-2-benzyl-*o*-phenylenediamine and benziminazole-2-hydroxymethylbenzene, m. p. 237—239°. In cold alcoholic solution the product is an additive compound (*o*'-aminophenylammonium *o*-hydroxymethylbenzoate?), m. p. 103—104°, which when boiled with alcohol gives *o*-hydroxymethyl-*o*'-aminobenzanilide, m. p. 152°, also obtained from phthalide and *o*-phenylenediamine in cold alcoholic solution. *o*-Hydroxymethyl-*o*'-aminobenzanilide, when heated at 180—190° for a few minutes, gives benziminazole-2-benzyl-*o*-phenylenediamine and *o*-benzylene-1:3-benziminazole (I), m. p. 185°, also obtained by carrying out the dehydration in acetic anhydride. The last is oxidised by acid permanganate in benzene-water to *o*-benzoylene-1:3-benziminazole.

The product, m. p. 210°, obtained by Thiele and Falk (A., 1906, i, 750) from *o*-phthalaldehyde and *o*-phenylenediamine cannot therefore be I, in spite of its oxidation to *o*-benzoylene-1:3-benziminazole (I, CO in place of CH<sub>2</sub>), and the alternative constitution II is therefore suggested.



The interaction of phthalide and ethylenediamine in cold alcoholic solution leads to *o*-hydroxymethyl- $\beta$ -aminoethylbenzamide, m. p. 179—180°, and in boiling alcohol to dihydroiminazole-2-hydroxymethylbenzene, m. p. 210—211°, which when heated with acetic anhydride gives *o*-benzylenedihydroiminazole, m. p. 152—153°. Like I, this is oxidised by acid permanganate to *o*-benzoylenedihydroiminazole, m. p. 229—230°, the preparation of which from phthalic anhydride and ethylenediamine is reported. H. A. PIGGOTT.

**$\gamma$ -Triazines: synthesis of phenylamino-hydroxytriazine.** A. OSTROGOVICH (Atti R. Accad. Lincei, 1930, [vi], 11, 843—847).—2-Amino-4-hydroxy-6-phenyl-1:3:5-triazine,  $\text{N} \begin{array}{c} \text{CPh} \\ \diagup \quad \diagdown \\ \text{C(NH}_2\text{)-N} \end{array} \text{C-OH}$ , m. p. 334—335° (corr.), first prepared by Elzanowski (Diss., Fribourg, 1898) by the action of nascent nitrous acid on benzoguanamine (diaminophenyltriazine) in acetic acid solution and termed benzoguanide, may be readily obtained by the interaction of benzamidine hydrochloride and guanylecarbamide acetate. This reaction, which gives rise also to small amounts of benzonitrile, acetamide, and benzamide, is probably applicable to the synthesis of other amino-hydroxytriazines. Whether prepared by this method or by that of Elzanowski, aminohydroxyphenyltriazine crystallises with 1H<sub>2</sub>O, and forms a silver salt and a *picrate*, m. p. 296—297° (decomp.). The conversion of diaminophenyltriazine into the corresponding monohydroxy-derivative may be effected by boiling it with aqueous potassium hydroxide and a little alcohol until it is dissolved and then at once precipitating with acetic acid. If the action of the alkali is continued, dihydroxyphenyltriazine is obtained.

T. H. POPE.

**Porphyrin syntheses. XXX. Synthesis of some porphyrins of the  $\alpha$ etio porphyrin III type**

and of a tetramethyltripropionic acid porphrin. H. FISCHER and E. JORDAN (*Z. physiol. Chem.*, 1930, **191**, 36—64; cf. this vol., 932).—As starting point, 3 : 4 : 3'-trimethyl-4-ethyl-5 : 5'-dibromomethylpyrromethene hydrobromide, darkens at 195°, m. p. not below 294°, was prepared by bromination of 3 : 4 : 5 : 3' : 5'-pentamethyl-4'-ethylpyrromethene hydrobromide (from trimethylpyrrole and cryptopyrrolealdehyde), m. p. 285° (free base, m. p. 134°). The brominated methene hydrobromide fused with succinic acid condenses with 4 : 4'-dimethyl-5 : 5'-dibromo-3 : 3'-dipropionic acid-pyrromethene hydrobromide (from cryptoic acid), yielding 1 : 2 : 3 : 5 : 8-pentamethyl-4-ethyl-6 : 7-dipropionic acid porphrin, m. p. 283° (copper salt, m. p. 364—366°; iron complex salt gives a dimethyl ester, m. p. 197°). The dimethyl ester, m. p. 255°, furnishes a copper salt, m. p. 214°, an iron complex salt, decomp. 273°, and a silver complex salt, m. p. 233°. The silver salts of both ester and free acid contain 1 atom of silver to 4 pyrrole nuclei.

Hæmopyrrole and trimethylpyrrolealdehyde with hydrobromic acid yield 4 : 5 : 3' : 4' : 5'-pentamethyl-3-ethylpyrromethene hydrobromide, decomp. 255—258°, which on bromination forms 3' : 4 : 4'-trimethyl-3-ethyl-5 : 5'-dibromomethylpyrromethene hydrobromide. The latter when condensed with the methene from brominated cryptoic acid in fused succinic acid forms 1 : 3 : 4 : 5 : 8-pentamethyl-2-ethyl-6 : 7-dipropionic acid porphrin, m. p. 385° (copper complex salt, m. p. 382°). The dimethyl ester, m. p. 290°, forms a copper complex salt, m. p. 266°, an iron complex salt, m. p. 277°, and a silver complex salt, m. p. 272°.

3 : 3' : 4 : 4' : 5 : 5'-Hexamethylpyrromethene hydrobromide was brominated to the 5 : 5'-dibromomethyl compound and the latter condensed with the cryptoic acid methene in fused succinic acid, forming 1 : 2 : 3 : 4 : 5 : 8-hexamethyl-6 : 7-dipropionic acid porphrin (hydrochloride, m. p. 387°; iron complex salt, not decomp. below 360°). The dimethyl ester, m. p. 318—320°, yields a copper complex salt, m. p. 297°, and an iron complex salt, m. p. 316°.

5 : 5'-Dibromo-3 : 3' : 4 : 4'-tetramethylpyrromethene hydrobromide and 4 : 3' : 5 : 5'-tetramethylpyrromethene hydrobromide (or preferably its dibromoderivative) condensed in fused succinic acid yield 1 : 3 : 5 : 6 : 7 : 8-hexamethylporphrin, m. p. 415—420°. The latter can be separated from ætioporphyrin by means of 0.7% hydrochloric acid. With excess of bromine in chloroform and acetic acid it gives an octabromo-derivative, m. p. 410°, from which six bromine atoms can be removed by acetone.

5 : 5'-Dibromo-4 : 4'-dimethylpyrromethene-3 : 3'-dipropionic acid hydrobromide and 3 : 3' : 5 : 5'-tetramethylpyrromethene-4'-propionic acid hydrobromide in fused succinic acid give 2 : 3 : 5 : 8-tetramethyl-4 : 6 : 7-tripropionic acid porphrin. The trimethyl ester, m. p. 215°, forms a copper complex salt, m. p. 233°. When heated with potassium ethoxide the tripropionic acid was completely resistant under conditions which yield phyllo- and pyrro-porphyrin from chlorophyll. J. H. BIRKINSHAW.

**Synthesis of porphyrins.** A. KIRRMANN (*Bull. Soc. chim.*, 1930, [iv], **47**, 913—932).—A lecture.

**Chlorophyll. XIII. Mesochlorin and oxy-mesoporphyrins.** H. FISCHER, H. GEBHART, and A. ROTHHAAS (*Annalen*, 1930, **482**, 1—24).—Reduction of mesohæmin or of the complex iron salt of tetramethylhæmatoporphyrin (but not of mesoporphyrin, its dimethyl ester, or copper salt) by means of sodium and amyl alcohol (cf. A., 1929, 941) in an atmosphere of hydrogen affords, besides by-products (which include mesohæmin diamyl ester,  $C_{44}H_{56}O_4N_4FeCl$ ), a perhydrochlorin (not purified), oxidised by ferric chloride to mesochlorin (I),  $C_{34}H_{40(42)}O_4N_4$ , m. p. above 300° (spectrographic data given) [dimethyl ester,  $C_{36}H_{44}O_4N_4$ , m. p. 190—191° (depresses the m. p. of meso-ester IX)]. In acid or ammoniacal solution I is stable to air, but is converted in boiling methyl-alcoholic alkali solution into mesoporphyrin IX (identified as the dimethyl ester); the complex iron and copper salts of I are very sensitive to oxidation, and on removal of the metal, mesoporphyrin remains. Sodium amalgam converts I into a leuco-compound, oxidised to the original substance and a trace of porphyrin (cf. acid VII, A., 1929, 941); hydriodic acid causes breakdown of the molecule. Oleum (cf. A., 1928, 1383) converts I, according to the experimental conditions, into mesorhodin or anhydromesochlorin, m. p. above 280°,  $C_{34}H_{28}O_3N_4$  (spectroscopically similar to phytochlorin e).

Study of the oxidation of ætioporphyrin (A., 1927, 469) has been extended to mesoporphyrin. The last-named with potassium persulphate in 75—80% sulphuric acid affords in small yield dioxymesoporphyrin (II),  $C_{34}H_{38(40)}O_6N_4$ , m. p. above 275° (spectroscopically similar to the chlorins) (iron complex salt; dimethyl ester, from II and methyl-alcoholic hydrogen chloride, m. p. 181—182°); in 50% sulphuric acid the reaction is more complex, and three products isolated have been only characterised spectroscopically. Reduction of II with sodium amalgam followed by reoxidation, or treatment with hydriodic or hydrobromic acid in acetic acid, yields only a trace of porphyrin, and none is obtained by the use of methyl-alcoholic potassium hydroxide or of formic acid. The latter reagent causes elimination of an oxygen atom from II, with formation of monooxymesoporphyrin (III),  $C_{34}H_{38}O_5N_4$  (spectroscopically identical with II); the same change is effected also in the following ways: esterification of II by means of diazomethane gives the dimethyl ester of III, m. p. 188° (copper derivative, m. p. 203°) (mixture with dimethyl ester of II, 210—212°); II with copper acetate affords the complex copper salt of III, m. p. 278.5° (the above iron salt of II gives unchanged II on decomposition); II and its ester with hydroxylamine give the corresponding derivatives of III,  $C_{34}H_{39}O_5N_5$  and  $C_{36}H_{43}O_5N_5$ , m. p. 224—225°, respectively. II contains 1.4 atoms of active hydrogen (Tschugaev); decomposition of the magnesium compounds from the determination yields two substances differing in spectra from II (one of these possibly corresponding with a by-product of the preparation of II in 50% sulphuric acid; see above); the ester of III gives an active hydrogen value of 1, and decomposition of the magnesium compound in this case gives yet a further spectroscopically distinct substance. Sodium ethoxide (sealed tube) converts

both II and III into I; the presence of oxygen in the molecule thus has an activating effect on the porphyrin complex such as iron has on the hæmins. Oxidation of I by hydrogen peroxide gives not II, but a porphyrin and a chlorin-like substance.

The dioxyporphyrin,  $C_{32}H_{38}O_2N_4$  (from ætioporphyrin I and hydrogen peroxide in sulphuric acid), is spectroscopically identical with II. Porphyrin is reduced by the method of Busch (Z. angew. Chem., 1926, 38, 521) to mesoporphyrin.

R. CHILD.

**Oxidation. III. Behaviour of formyl-, acetyl-, and benzoyl-thiosemicarbazide towards lead oxide.** S. C. DE (J. Indian Chem. Soc., 1930, 7, 651—654).—Oxidation of acylthiosemicarbazides,  $OH\cdot CR:N\cdot N\cdot C(NH_2)\cdot SH$ , with lead oxide in alcohol furnishes 2-amino-5-alkyl(or aryl)-1:3:4-oxdiazoles,  $CR:N\cdot N\cdot C\cdot NH_2$  (I). Thus, formylthiosemicarbazide

—O— gives 2-amino-1:3:4-oxdiazole (I, R=H), m. p. 155°, acetylthiosemicarbazide affords 2-amino-5-methyl-1:3:4-oxdiazole (I, R=Me), m. p. 183° (acetyl derivative, m. p. 180°), and benzoylthiosemicarbazide yields 2-amino-5-phenyl-1:3:4-oxdiazole (I, R=Ph), m. p. 245° (decomp.) (hydrochloride, decomp. 175—176°; acetyl derivative, m. p. 223°; benzoyl derivative, m. p. 203°). Treatment of the last-named amine with nitrous acid gives a nitrosoamine, blackens at 103°, reduced by zinc dust and dilute acetic acid to 2-hydrazino-5-phenyl-1:3:4-oxdiazole. This could be isolated only as the benzylidene derivative, m. p. 243° (decomp.), which on hydrolysis with dilute hydrochloric acid affords an unidentified base, m. p. 152° (hydrochloride, m. p. 208°). Oxidation of 2-amino-5-phenyl-1:3:4-oxdiazole with aqueous-alcoholic calcium hypochlorite gives the corresponding azo-derivative, m. p. 329—330°, reduced by alcoholic ammonium sulphide to the hydrazo-compound, m. p. 233°.

H. BURTON.

**Dyes derived from 2-aminothiazole-4:5-dicarboxylic acid.** S. C. DE (J. Indian Chem. Soc., 1930, 7, 617—618).—Condensation products, all with m. p. above 298—300°, are obtained from 2-aminothiazole-4:5-dicarboxylic acid and the following phenols at 170—200° in absence or presence of sulphuric acid or zinc chloride: pyrocatechol, phloroglucinol, orcinol, *m*-aminophenol, and *m*-dimethylaminophenol. The fluorescein, m. p. 246° (tetrabromo-derivative, m. p. 210°), from resorcinol and the above acid is accompanied by a small amount of a non-fluorescent material. The colours of alkaline solutions of the above dyes are recorded; these and their fluorescences are similar to the analogous compounds from citraconic acid (Dhar and Dutt, A., 1927, 969).

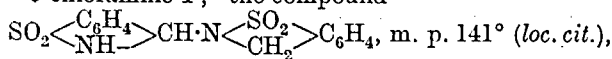
H. BURTON.

**Synthesis of thiazole amines possessing pharmacological interest. IV. W. S. HINE-GARDNER and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 3724—3727).—2-Phenyl-4-chloromethylthiazole, b. p. 155—156°/4 mm., m. p. 31°, prepared from *s*-dichloroacetone and thiobenzamide, and ethyl sodiomalonate afford a mixture of ethyl 2-phenyl-4-thiazolylmethylmalonate, b. p. 218—222°/4—5 mm., m. p. 30—31° (free acid, m. p. 141—142°), and ethyl**

**di-2-phenyl-4-thiazolylmethylmalonate, m. p. 116° (free acid, m. p. 156—157°).** Thermal decomposition of the above acids gives  $\beta$ -2-phenyl-4-thiazolylpropionic acid, m. p. 83—84° (ethyl ester, b. p. 170—171°/3—4 mm., m. p. 42—43°; hydrazide, m. p. 142—143°; azide, m. p. 72°), and di-2-phenyl-4-thiazolylacetic acid, m. p. 127—128° [ethyl ester, b. p. 272°/2—3 mm., m. p. 61·5—62° (hydrochloride, m. p. 91—92°); hydrazide hydrochloride, m. p. 235—238°; azide, m. p. 80°], respectively. The above azides are converted into *s*-di- $\beta$ -2-phenyl-4-thiazolylethylcarbamide, m. p. 176—177°, and *s*-di-( $\alpha$ -di-2-phenyl-4-thiazolylisopropyl)-carbamide, m. p. 182—183°, respectively, and thence by fusion with phthalic anhydride into  $\beta$ -2-phenyl-4-thiazolylethylphthalimide, m. p. 113—114°, and  $\alpha$ -di-2-phenyl-4-thiazolylisopropylphthalimide, m. p. 158—159°, respectively. These phthalimides are converted by treatment with hydrazine (cf. Ing and Manske, A., 1926, 1132) into  $\beta$ -2-phenyl-4-thiazolylethylamine, b. p. 146—147°/2—3 mm. (hydrochloride, m. p. 171—172°; dihydrochloride, m. p. 206—209°), and  $\alpha$ -di-2-phenyl-4-thiazolylisopropylamine (hydrochloride, m. p. 235—238°), respectively. These amines are physiologically active. H. BURTON.

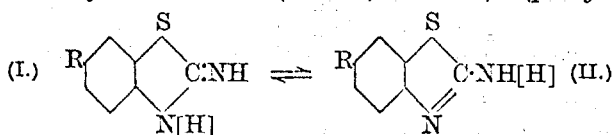
**Oxidising power of chloroamines.** J. KOETSCHET, P. KOETSCHET, and P. VIAUD (Helv. Chim. Acta, 1930, 13, 587—619; cf. A., 1929, 942).—“Chloramine-B” and “halazone” (*p*-dichloroamidodisulphobenzoic acid) are more convenient than “chloramine-T” as oxidising agents, since they do not undergo autooxidation. The characteristic action of chloroamines is the oxidation of a terminal methyl group to aldehyde. Oxidation of *o*-nitro-*p*-toluenesulphonamide gives *o*-nitrobenzaldehyde-*p*-sulphonamide, m. p. 149—151°, in poor yield (the benzylidene-aniline has m. p. 171—171·5°, phenylhydrazone, m. p. 238—239°). *p*-Nitro-*o*-toluenesulphonamide gives  $\psi$ -*p*-nitrobenzaldehyde-*o*-sulphonamide (phenylhydrazone, m. p. 228°), and toluene-2:4-disulphonamide gives benzaldehyde-2:4-disulphonamide (phenylhydrazone, m. p. 242°). Toluene and *o*-nitrotoluene yield the corresponding aldehydes; *m*- and *p*-xylene give *m*- and *p*-tolualdehydes. “Chloramine-B” and “halazone” give approximately equal yields when used for these reactions under the same conditions. The following compounds have been prepared from the products of hydrolysis of “chloramine-T”: dimethyl-*p*-sulphonamidobenzylidene-*p*-tolylhydrazone, m. p. 160°, and -phenylmethylhydrazone, m. p. 134—136°; dimethyl-*p*-sulphonamidobenzyl alcohol, m. p. 247—248°. Derivatives of the autooxidation products of “*o*-chloramine-T” (A., 1929, 943) are described, viz.: 1-*S*-dioxo-2-acetyl-, m. p. 108—109°; -2-benzoyl-, m. p. 117—117·5°; -2-phenylsulphonyl-, m. p. 174—175°; and -2- $\beta$ -naphthylsulphonyl-2:3-dihydro- $\alpha\beta$ -benzoisothiazole, m. p. 214°, prepared from 1-*S*-dioxo-2:3-dihydro- $\alpha\beta$ -benzoisothiazole by the action of sodium hydroxide and boiling acetic anhydride or the corresponding acid chloride, respectively. The phenylmethylhydrazone, m. p. 165°, and the *p*-tolylhydrazone, m. p. 207—209°, of  $\psi$ -benzaldehyde-*o*-sulphonamide are described. The instability of this  $\psi$ -aldehyde is due to the occurrence of internal dehydration with formation of 1-*S*-dioxo- $\alpha\beta$ -benzoiso-

thiazole, m. p. 257°, on evaporation. Condensation of the  $\psi$ -aldehyde with aniline and with dimethylaniline occurs on warming the reactants in the presence of zinc chloride, yielding 1-*S*-dioxo-2:3-dihydro-3-*p*-aminophenyl- $\alpha\beta$ -benzothiazole, m. p. 236—237°, and 1-*S*-dioxo-2:3-dihydro-3-*p*-dimethylamino-phenyl- $\alpha\beta$ -benzothiazole, m. p. 153—154°, respectively. The principal product of the hydrolysis of "o-chloramine-T," the compound



has been synthesised by condensation of benzaldehyde-*o*-sulphonamide with the anhydro-alcohol. These may be recovered in nearly theoretical yield by the action of hot or cold sodium sulphite on the product, which is not attacked by cold sodium hydroxide or milk of lime. An acetyl derivative, m. p. 250—254°, has been prepared. A structural formula for the compound is proposed. Conditions under which saccharin may be methylated by means of dimethylaniline are described. F. L. USHER.

Unsaturation and tautomeric mobility of heterocyclic compounds. III. Effect of substituents on mobility of the aminobenzthiazole system and bromination of *s*-diarylthiocarbamides. Ultra-violet absorption of mobile and static semicyclic amidines of the benzthiazole group. R. F. HUNTER and J. W. T. JONES (J.C.S., 1930, 2190—2213; cf. this vol., 483, 934).—1-Amino-5-methylbenzthiazole (I  $\rightleftharpoons$  II, R=Me) (phenyl-



thiocarbimide derivative, m. p. about 310°) is the product of hydrolysis both of 1-imino-2-acetyl-5-methyl-1:2-dihydrobenzthiazole (I, R=Me, Ac in place of [H]), m. p. 192°, and also of 1-acetamido-5-methylbenzthiazole (II, R=Me, Ac in place of [H]), m. p. 216° [hydrotribromide, m. p. 149° (decomp.)], the constitutions of which are fixed by their preparation by reduction of the bromo-additive products of *as*- and *s*-acetyl-*p*-tolylthiocarbamides, respectively. Nevertheless, on methylation by a variety of methods, only one methyl derivative is produced, viz., 2:5-dimethyl-1:2-dihydrobenzthiazole (I, R=Me, Me in place of [H]), [sulphate, m. p. 160°; hydride, m. p. 290° (decomp.)]; acetyl derivative, m. p. 168°, the identity of which is proved by synthesis of its acetyl derivative from *as*-*p*-tolylmethylthiocarbamide, m. p. 109° (from methyl-*p*-toluidine hydrochloride and potassium thiocyanate), and of the isomeric 1-methylamino-5-methylbenzthiazole, m. p. 152° [acetyl derivative, m. p. 162°; hydrotetrabromide, m. p. 90° (decomp.)], from *s*-*p*-tolylmethylthiocarbamide, m. p. 126° (formed by interaction of *p*-tolylthiocarbimide with methylamine in absolute alcohol). 1-Imino-2-acetyl-5-ethoxy-1:2-dihydrobenzthiazole, m. p. 147° [hydrotetrabromide, m. p. 139° (decomp.)], gives on hydrolysis 1-amino-5-ethoxybenzthiazole, converted by acetylation into 1-acetamido-5-ethoxybenzthiazole; the constitution of the acetyl derivatives is derived by synthesis from the appropriate thiocarbamides. Methylation is similar

to the above and yields 1-imino-5-ethoxy-2-methyl-1:2-dihydrobenzthiazole, m. p. 147°, alone; this may be synthesised from *s*-*p*-ethoxyphenylmethylthiocarbamide, m. p. 129° (from *p*-ethoxyphenylthiocarbimide and methylamine).

1-Methylamino-5-ethoxybenzthiazole has m. p. 145°. Rational syntheses of 5-bromo- and 5-chloro-1-aminobenzthiazoles were not achieved, but both give a single methyl derivative of the above type, *as*, m. p. 157°, and *s*-Acetyl-*p*-bromophenylthiocarbamide, m. p. 205°, are prepared by short and long contact, respectively, of *p*-bromophenylthiocarbamide with acetic anhydride at 80°; the latter gives a substance, m. p. 234°, on bromination or on oxidation with perhydrol. *as*, m. p. 157°, and *s*-Acetyl-*p*-chlorophenylthiocarbamide, m. p. 186°, and a substance, m. p. 227°, from the latter and hydrolysable to yield *p*-chloroaniline, are described; also 5-chloro-1-acetamido-2-methyl-1:2-dihydrobenzthiazole, m. p. 197° (by methylation followed by acetylation of 5-chloro-1-aminobenzthiazole; *s*-*p*-chloromethylthiocarbamide, m. p. 147°, and 5-chloro-1-methylaminobenzthiazole, m. p. 214° (acetyl derivative, m. p. 175°)). 5-Nitro-1-aminobenzthiazole, m. p. 243°, is obtained either by direct nitration of 1-aminobenzthiazole or from *p*-nitrophenylthiocarbamide. Methylation gives 5-nitro-1-imino-2-methyl-1:2-dihydrobenzthiazole, m. p. 167°, obtained in a pure condition by nitration of 1-imino-2-methyl-1:2-dihydrobenzthiazole; 5-nitro-1-methylaminobenzthiazole, m. p. 272° (acetyl derivative, m. p. 241°), is also produced by direct nitration, but is not present in the methylation product.

In contrast to the above, 1-anilinobenzthiazole reacts on methylation in both forms, 1-phenylmethylaminobenzthiazole (as picrate, m. p. 185°) and 1-phenylimino-2-methyl-1:2-dihydrobenzthiazole [as picrate, m. p. 112° (decomp.)] being produced. 1-Aminobenzthiazole can be diazotised and then undergoes the Sandmeyer reaction: the 1-chlorobenzthiazole, more readily produced by this method than by that of Hofmann (A., 1879, 805), reacts with methylaniline to produce 1-phenylmethylaminobenzthiazole. 4'-Bromo-1-anilinobenzthiazole is methylated to 4'-bromo-1-phenylmethylaminobenzthiazole (picrate, m. p. 242°) alone; this is also produced from 1-chlorobenzthiazole and *p*-bromomethylaniline. In this case the apparent stability of the isomeric forms is completely reversed.

The following thiocarbamides are obtained by condensation of phenylthiocarbimide or substitution products with the appropriate amine, and are converted by bromination and reduction into substituted aminobenzthiazoles, the constitution of which is determined by synthesis from 1-chlorobenzthiazole or a substituted derivative and an amine: *p*-ethoxy-*s*-diphenylthiocarbamide, m. p. 148°; 4'-ethoxy-1-anilinobenzthiazole, m. p. 166°; *p*-nitro-*s*-diphenylthiocarbamide, m. p. 141°; 4'-nitro-1-anilinobenzthiazole, m. p. 212° (acetyl derivative, m. p. 180°); *s*-*p*-ethoxyphenyl-*p*-tolylthiocarbamide, m. p. 137°; 1-anilino-4'-ethoxy-5-methylbenzthiazole, m. p. 171° (3-bromo-derivative, m. p. 156°); *s*-*p*-bromophenyl-*p*-tolylthiocarbamide, m. p. 187°; 4'-bromo-1-anilino-5-methylbenzthiazole, m. p. 209° [picrate, m. p. 250° (decomp.)]; *s*-*p*-nitrophenyl-*p*-tolylthiocarbamide, m. p. 175°; 4'-nitro-



1-anilino-5-methylbenzthiazole, m. p. 265°; s-p-bromo-p'-ethoxydiphenylthiocarbamide, m. p. 169°; 4'-bromo-1-anilino-5-ethoxybenzthiazole, m. p. 198° (3-bromo-derivative, m. p. 226°), was prepared from the thiocarbamide only, and was not identical with 5-bromo-1-anilino-4'-ethoxybenzthiazole, m. p. 199° (from 1-chloro-5-bromobenzthiazole and *p*-phenetidine): s-p-chloro-p'-bromodiphenylthiocarbamide, m. p. 187°; 4'-chloro-5-bromo-1-anilinobenzthiazole, m. p. 218°; s-p-bromo-p'-nitrodiphenylthiocarbamide, m. p. 186°; 5-bromo-4'-nitro-1-anilinobenzthiazole, m. p. 258°. *s*-Phenyl-*p*-tolylthiocarbamide gives an indefinite mixture in which neither 1-anilino-5-methylbenzthiazole, m. p. 158°, nor 1-anilino-4'-methylbenzthiazole, m. p. 177° (both prepared by the chlorobenzthiazole synthesis), can be recognised. 1-Chloro-5-methylbenzthiazole, b. p. 148—152°/15 mm., is prepared either by the action of phosphorus pentachloride on *p*-tolylthiocarbimide at 170°, or, better, from 1-amino-5-methylbenzthiazole by the Sandmeyer reaction.

1-Methylamino-5-methylbenzthiazole hydrotetramide is converted by heating in alcoholic solution into 3-bromo-1-methylamino-5-methylbenzthiazole, m. p. 165° [hydrotribromide, m. p. 137° (decomp.): by bromination of 1-methylamino-5-methylbenzthiazole in chloroform], identified by the following synthesis: s-di-m-bromo-*p*-tolylthiocarbamide, m. p. 163°, prepared from *m*-bromo-*p*-toluidine, carbon disulphide, and sulphur, is converted by hot acetic anhydride into *m*-bromo-*p*-tolylthiocarbimide, m. p. 53°; s-m-bromo-*p*-tolylmethylthiocarbamide, m. p. 162°, gives the above thiazole in the usual way.

s-*p*-Bromophenylthiocarbamide yields an *S*-methyl derivative, m. p. 78°, unaffected by methyl iodide, but converted by the sulphate into *S*-methyl-*s*-phenyl-methyl-*p*-bromophenylthiocarbamide, m. p. 93°, also obtained by methylation of s-phenylmethyl-*p*-bromophenylthiocarbamide, m. p. 156°: the *S*-methyl derivative is therefore considered to react in the form  $\text{NPh}_2\text{C}(\text{SMe})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$ . A *perbromide* of Claus' bromothiocarbamide of m. p. 191° (decomp.) (Claus, A., 1876, i, 572, gives 176°), is described. The ultraviolet absorption spectra of 1-amino-5-methyl-, 1-acetmethylamido-5-methyl-, 1-acetimidido-2:5-dimethyl-1:2-dihydro-, and 1-anilino-benzthiazoles are figured.

H. A. PIGGOTT.

Action of sulphur monochloride on mercaptans. III. Oxidation of unsymmetrically substituted hydrazodithiodicarbonamides to thiodiazoles. P. P. PATEL and G. C. CHAKRAVARTI (J. Indian Inst. Sci., 1930, 13A, 85—92).—4-Phenylthiosemicarbazide reacts in the presence of alcoholic potassium hydroxide with sulphur monochloride in benzene at the ordinary temperature to give s-diphenylhydrazodithiocarbonamide (I), m. p. 184°, and 2:5-diphenyldi-imino-2:3:4:5-tetrahydro-1:3:4-thiodiazole (II), m. p. 247° (diacetyl derivative, m. p. 225°), separated by fractional crystallisation; at 0° II is the sole product, and at 27° only I is formed, the latter being converted into the former by boiling pyridine. 4-*p*-Tolylthiosemicarbazide, m. p. 139—140°, similarly yields s-di-*p*-tolylhydrazodithiocarbonamide, m. p. 198°, and 2:5-tolyl-di-imino-2:3:4:5-tetrahydro-1:3:4-thiodiazole,

m. p. 248° (diacetyl derivative, m. p. 172°; Guha, A., 1923, i, 608, gives m. p. 235°), whilst 4-*o*-tolylthiosemicarbazide gives s-di-*o*-tolylhydrazodithiocarbonamide, m. p. 175°, and 2:5-di-*o*-tolyl-di-imino-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 222° (diacetyl derivative, m. p. 222°). Interaction of 4-phenylthiosemicarbazide and sulphur monochloride in dry chloroform at the ordinary temperature yielded 4-phenylthiosemicarbazide hydrochloride and I.

1-Phenyl-6-*o*-tolylhydrazodithiocarbonamide, m. p. 179°, yields 2-phenyl-5-*o*-tolyl-di-imino-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 200° (diacetyl derivative, m. p. 227°), on oxidation with alcoholic iodine solution. 2-Phenyl-5-*m*-tolyl-, m. p. 216° (diacetyl derivative, m. p. 177°), 2-*o*-tolyl-5-*m*-tolyl-, m. p. 190° (diacetyl derivative, m. p. 231°), *m*-tolyl-2:5-*m*-xylyl-, m. p. 190° (diacetyl derivative, m. p. 263°), *m*-xylyl-2:5-*o*-tolyl-, m. p. 205° (diacetyl derivative, m. p. 224°), and 2-phenyl-5-*m*-xylyl-di-imino-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 189° (diacetyl derivative, m. p. 120°), were similarly prepared.

A. I. VOGEL.

Thiodiazines. VI. P. K. BOSE and B. K. NANDI (J. Indian Chem. Soc., 1930, 7, 733—739).—Interaction of *p*-methylphenacyl bromide and 4-substituted thiosemicarbazides yields thiodiazines (III), whilst with thiosemicarbazide itself a thiazole derivative (I) results. The two types of product are not formed simultaneously as in some previous cases (cf. A., 1925, i, 167, 1465). 2-Keto-4-*p*-tolyl-2:3-dihydro-1:3-thiazolehydrazone  $\text{C}_7\text{H}_7\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \text{CH-S} \end{smallmatrix}\text{C}\cdot\text{N}\cdot\text{NH}_2$  (I) has m. p. 178° [hydrochloride, m. p. 133°; benzylidene, m. p. 205°; isopropylidene, m. p. 230°; benzoyl (also prepared from benzylidenethiosemicarbazide), m. p. 201°, and acetyl (also from acetylthiosemicarbazide), m. p. 195°, derivatives]. Thiocyanic acid and I afford 2-keto-4-*p*-tolyl-2:3-dihydro-1:3-thiazole-thiosemicarbazone,  $\text{C}_7\text{H}_7\cdot\text{C}\begin{smallmatrix} \text{NH} \\ \text{CH-S} \end{smallmatrix}\text{C}\cdot\text{N}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$  (II), m. p. 218°, which condenses readily with a further molecule of *p*-methylphenacyl bromide to give bis-(2-keto-4-*p*-tolyl-2:3-dihydro-1:3-thiazole)-azine, m. p. 120°. Similarly, I with the corresponding thiocarbimides yields 2-keto-4-*p*-tolyl-2:3-dihydro-1:3-thiazole-4-methyl-, m. p. 146°, -phenyl-, m. p. 191°, -*o*-tolyl-, m. p. 174°, and -*p*-tolyl-, m. p. 166°, -thiosemicarbazones.

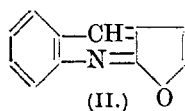
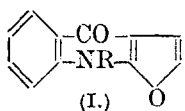
2-Methyl-, m. p. 249° (hydrochloride, m. p. 195°), 2-isobutyl-, m. p. 159° (hydrochloride, m. p. 125°; acetyl derivative, m. p. 167°), 2-phenyl-, m. p. 198° (hydrochloride, m. p. 135°; acetyl derivative, m. p. 170°), 2-*o*-tolyl-, m. p. 179° (hydrochloride, m. p. 171°; acetyl compound, m. p. 199°), and 2-*p*-tolyl-, m. p. 187° (hydrochloride, m. p. 199°; acetyl derivative, m. p. 154°), -amino-5-*p*-tolyl-1:3:4-thiodiazines,

$\text{C}_7\text{H}_7\cdot\text{C}\begin{smallmatrix} \text{NH}\cdot\text{N} \\ \text{CH-S} \end{smallmatrix}\text{C}\cdot\text{NHR}$  (III), result when *p*-methylphenacyl bromide is condensed with the appropriate 4-substituted thiosemicarbazide.

4-isoButylthiosemicarbazide, from hydrazine hydrate and isobutylthiocarbimide, has m. p. 79° (benzylidene, m. p. 125°, and isopropylidene, m. p. 112°, derivatives).

R. CHILDS.

**Alkaloid of *Skimmia repens*, Nakai.** Y. ASAHINA, T. OHTA, and M. INUBUSE (Ber., 1930, 63, [B], 2045—2051).—The leaves are treated with 10% sodium carbonate solution followed by light petroleum. The combined petroleum extracts are treated with 5% hydrochloric acid, which is extracted with ether and subsequently with chloroform after basification with sodium carbonate. The ethereal solution contains a nitrogen-free compound, m. p. 120°. From the chloroform solution, dictamnine, m. p. 132—133°,  $[\alpha]_D^{20} \pm 0^\circ$ , is isolated, identical with the alkaloid obtained by Thoms (A., 1923, i, 639) from *Dictamnus* root and to which the composition  $C_{12}H_9O_2N$  is now ascribed. It contains one methoxyl group. The *picrate*, m. p. 163°, and *hydrochloride*, m. p. about 170° (decomp.), are described. The base cannot be acetylated and does not yield an oxime. It is not affected by alkyl iodides in open vessels, but is transformed by methyl iodide at 80° into isodictamnine (I, R=Me), m. p. 188°, which does not contain a methoxyl group, and by ethyl iodide at 100° into homoisodictamnine (*tri*hydrate, m. p. about 80°; *semi*hydrate, m. p. 143°; anhydrous, m. p. about 150°). When heated with benzoyl chloride and benzoic anhydride, dictamnine evolves methyl chloride and forms N-benzoyl-nordictamnine (I, R=Bz), m. p. 165°, hydrolysed by alcoholic potassium hydroxide to nordictamnine (I, R=H), m. p. 249°, also obtained from dictamnine and hydrogen bromide in glacial acetic acid. Oxidation of the alkaloid in acetone by permanganate yields dictamnol,  $C_{10}H_6O_3N \cdot OMe$ , m. p. 259—260° (*phenylhydrazone*, m. p. 228°), and dictamnamic acid,  $C_{10}H_6O_3N \cdot OMe$ , m. p. 260° (decomp.). Treatment of the acid with hydrochloric or hydrobromic acid affords 2:4-dihydroxyquinoline, identified by conversion into nitroso-2:4-dihydroxyquinoline and 2:4-dichloroquinoline. Since 4-hydroxy-2-methoxyquinoline-3-carboxylic acid, m. p. 225°, prepared by the action of hydrogen chloride, alcohol, and granulated zinc on methyl o-nitrobenzoylmalonate, is quite distinct from dictamnamic acid, the last-named substance must be regarded as 2-hydroxy-4-methoxyquinoline-3-carboxylic acid. To dictamnine the constitution II is therefore ascribed.

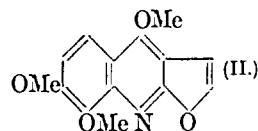
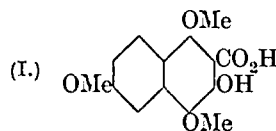


therefore ascribed.

H. WREN.

**Skimmianine.** Y. ASAHINA and M. INUBUSE (Ber., 1930, 63, [B], 2052—2056).—The leaves of *Skimmia japonica*, Thunb., are macerated with alcohol, the extract is evaporated, and the residue treated with 5% hydrochloric acid. The solution is basified with sodium carbonate and extracted with chloroform, into which the alkaloid passes. The extract, which is insoluble in hydrochloric acid, yields umbelliferone to ether and contains palmitic acid. Skimmianine, obtained as described above or by the method used in isolating dictamnine whereby also the nitrogen-free compound, m. p. 120°, is obtained (preceding abstract), has m. p. 176° and is identical with the substance obtained by Honda (A., 1905, i, 152). Its composition is  $C_{14}H_{13}O_4N$ . The *picrate*, m. p. 195—197° (decomp.), is described. It contains three methoxyl groups. Its

close relationship to dictamnine is proved by the great similarity of the absorption spectra. It does not give an acetyl derivative, oxime, or semicarbazone. With methyl iodide at 100° it affords isoskimmianine, m. p. 185°, which contains two methoxyl groups and is de-methylated to a dihydroxy-compound,  $C_{12}H_9O_4N$ , m. p. 218° (*diacetate*, m. p. 183°), reacting with ferric chloride in a manner which suggests that the hydroxyl groups are vicinal in the benzene nucleus. Oxidation of skimmianine by permanganate in acetone affords skimmianal,  $C_{11}H_4O_2N(OMe)_3$ , m. p. 238° (*phenylhydrazone*, m. p. 210°), and skimmianic acid,  $C_{10}H_4O_3N(OMe)_3$ , m. p. 248°. Since the acid is transformed by concentrated hydrochloric acid into 2:4-dihydroxy-7:8-dimethoxyquinoline, m. p. 250° [nitroso-derivative, m. p. 247° (decomp.)] (cf. this vol.,



1447), the constitutions I and II are assigned to it and to skimmianine, respectively.

H. WREN.

**Lupinine.** P. KARRER and A. VOGT (Helv. Chim. Acta, 1930, 13, 1073—1077).—Treatment of lupinine with thionyl chloride affords chlorolupinane, b. p. 124—125°,  $[\alpha]_D^{20} -32.9^\circ$  in alcohol, which with 33% alcoholic trimethylamine at 130—135°, gives lupinanyltrimethylammonium chloride,  $[\alpha]_D^{20} -17.9^\circ$  in alcohol. Thermal decomposition of the hydroxide from this furnishes trimethylamine and anhydrolupinine, b. p. 86—88°/15 mm.,  $d_4^{20} 0.929$ ,  $[\alpha]_D^{20} -49.8^\circ$ . Catalytic reduction (platinum oxide) of this in dilute hydrochloric acid (sufficient to give a neutral solution) affords lupinane, b. p. 80—81°/14 mm.,  $d_4^{20} 0.930$ ,  $[\alpha]_D^{20} -0.65^\circ$ . When chlorolupinane is treated with sodium and alcohol, a small amount of lupinane, b. p. 84—86°/15 mm.,  $[\alpha] -9.4^\circ$  in methyl alcohol, is obtained together with high-boiling products. The existence of the optically active anhydrolupinine is new evidence for the existence of two asymmetric centres in the lupinine molecule (cf. A., 1929, 200).

H. BURTON.

**Constitution of hydroxylupanine.** I. M. UENO (J. Pharm. Soc. Japan, 1930, 50, 435—442).—Hydroxylupanine,  $C_{15}H_{24}O_2N_2$ , m. p. 173—174° (benzoyl derivative, m. p. 199—199.5°), from the seeds of *Lupinus albus*, L., affords two methiodides,  $\alpha$ -, decomp. 238—239°, and  $\alpha'$ -, m. p. 236—239°. Hydroxylupaninaldehyde (gold salt, decomp. 167—171°; semicarbazone, m. p. 221—223°; oxime, m. p. 217—218°), has m. p. 93—95°.

CHEMICAL ABSTRACTS.

**Phytochemically interesting synthesis of di-tetrahydropapaverine.** E. SPÄTH and F. BERGER (Ber., 1930, 63, [B], 2098—2102).—3:4-Dimethoxyphenylacetaldehyde, obtained by ozonisation of eugenol methyl ether, is isolated as the sodium hydrogen sulphite compound, which is decomposed by sodium carbonate and immediately extracted with ether. It condenses with 3:4-dimethoxyphenylethylamine to yield the corresponding Schiff's base, transformed by hot 19% hydrochloric acid into

*dl*-tetrahydropapaverine in small yield; the picrate, m. p. 157—159°, and *hydrogen oxalate*, m. p. 204—205°, are described. The poverty of the yield is due to the instability of the Schiff's base towards acid and the ready resinification of the aldehyde liberated by its decomposition. H. WREN.

**1:2-Dihydropapaverine and modified syntheses of papaverine and papaveraldine (xanthaline).** J. S. BUCK (J. Amer. Chem. Soc., 1930, 52, 3610—3614).—The *N*-homoveratroyl derivative of  $\omega$ -aminoacetoveratrone is converted by treatment with phosphoryl chloride in boiling toluene into 4-*keto*-6:7:3':4'-*tetramethoxy*-3:4-*dihydroproto-papaverine*, m. p. 116—117° [methiodide, m. p. 202° (decomp.)]. Reduction of this in presence of acetic and hydrochloric acids, platinic chloride, platinum oxide, and colloidal platinum gives 4-*hydroxy*-6:7:3':4'-*tetramethoxy*-1:2:3:4-*tetrahydroproto-papaverine*, m. p. 123°, converted by treatment with phosphorus pentachloride in chloroform into 1:2-*dihydropapaverine*, m. p. 97—98° (picrate, m. p. 151°; perchlorate, m. p. 238° with blackening after previous sintering). This is reduced catalytically to tetrahydropapaverine, dehydrogenated by heating with palladium-black at 170—180° in an inert atmosphere to papaverine, and oxidised by atmospheric oxygen or hydrogen peroxide in acetic acid to 9-*keto*-6:7:3':4'-*tetramethoxy*-1:2-*dihydrotopapaverine*, m. p. 187°. The last-named compound is also produced when the above hydroxy-derivative is dehydrated with phosphoric oxide or phosphoryl chloride; when it is heated with methyl-alcoholic potassium hydroxide papaveraldine (xanthaline) results. H. BURTON.

**Optical rotatory power and constitution of certain bases of the type of tetrahydroberberine.** W. LEITHE (Ber., 1930, 63, [B], 2343—2347; cf. this vol., 1049).—1-Benzyltetrahydroisoquinoline is transformed into tetrahydroprotoberberine in more than 50% yield by modifying the synthesis of Chakravarti, Haworth, and Perkin (A., 1927, 1096) in that ring closure is effected by phosphoric oxide in boiling tetrahydronaphthalene instead of by phosphoryl chloride. Resolution of the base is effected by means of *d*- and *l*-tartaric acid. *d*-Tetrahydroprotoberberine has m. p. 88.5—89°,  $[\alpha]_D^{20} + 463^\circ$  in benzene (*hydrochloride*, m. p. 240° in an evacuated tube; *hydrogen d-tartrate*, m. p. 78—80°  $[\alpha]_D^{20} + 202^\circ$  in ethyl alcohol). 1-Tetrahydroprotoberberine has m. p. 88.5—89°,  $[\alpha]_D^{20} - 462^\circ$  in benzene. Values for  $[M]_D$  in carbon disulphide, pyridine, chloroform, and ethyl and methyl alcohols are recorded. Base and salt rotate in the same direction. The influence of solvent and salt formation lies in the same sense as with other similarly rotating bases with analogous centres of asymmetry, for example, *l*-protolaudanosine. The configurative relationship of these compounds is thereby established. Direct transition from active *l*-benzyltetrahydroisoquinoline to active tetrahydroprotoberberine is impossible by reason of complete racemisation during ring closure. The specific rotations of *l*-canadine and *d*-tetrahydropalmatine have been determined in various solvents and their hydrochlorides examined. *l*-Canadine is found to be related to *l*-tetrahydro-

protoberberine and *d*-tetrahydropalmatine to *d*-tetrahydroprotoberberine. The former alkaloid belongs therefore to the series of natural laudanosine, the latter to that of laudanidine.

Alkaloids of the type of corydaline contain a second asymmetric carbon atom in addition to the 1-*iso*-quinoline carbon atom. This second atom, on account of its distance from nitrogen and by reason of the value of  $[M]_D \pm 663^\circ$  for *mesocorydaline*, is considered to have only a subsidiary effect on the total rotation. *d*-Corydaline, corybulbine, and *isocorybulbine* are therefore configuratively related to the dextrorotatory alkaloids of the protoberberine type. H. WREN.

**Degradation experiments on dihydrobrucine.** H. WIELAND and W. GUMELICH (Annalen, 1930, 482, 50—55).—The lactam ring in dihydrostrychnine (Oxford and others, A., 1927, 1208) and in dihydrobrucine is not opened by alcoholic alkali to yield the corresponding imino-acid; that of dihydrovomine (A., 1929, 708) is opened similarly to that of strychnine and brucine.

Degradation products of dihydrobrucine have been examined to see whether the difference in this reaction from the parent brucine extends to these.

Dihydrobrucine (cf. Achmatowicz and others, this vol., 1300) is oxidised by aqueous nitric acid (1:1) at 50° to *dihydrocacotheline*, which is converted by bromine according to the method of Leuchs (A., 1922, i, 1052) into the dihydro-Hanssen acid,  $C_{19}H_{24}O_6N_2$ , isolated as the *hydrobromide*, and converted through the silver salt into the *acid*, colourless prisms,  $[\alpha]_D^{20} - 2.9^\circ$ . The *tetrahydro-acid*,  $C_{19}H_{26}O_6N_2$ ,  $[\alpha]_D^{20} + 17.7^\circ$ , is obtained by hydrogenation of the foregoing or of Hanssen's acid. The lactam ring of dihydrocacotheline is opened by alkali, and the two reduced acids show no great difference from Hanssen's acid.

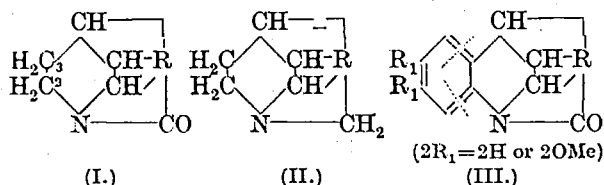
Careful fusion of dihydrobrucine with alcoholic potassium hydroxide affords a *base*, decomp. 240°,  $[\alpha]_D^{20} - 183.7^\circ$ ,  $C_{23}H_{30}O_6N_2$  [*sulphate*; *hydrochloride* (+H<sub>2</sub>O)], which is insoluble in alkali and does not yield a nitrosoamine; it is not therefore an imino-acid and is provisionally termed *dihydrobrucine hydrate*. The *methiodide*, m. p. above 290°, gives with silver oxide a strong base, decomp. about 240°.

*Dihydrobrucine methiodide* (+1H<sub>2</sub>O not lost at 110°) has m. p. 290° (decomp.) (cf. Achmatowicz and others, loc. cit.); no simple product could be obtained by thermal decomposition of the corresponding quaternary base or by the Emde degradation of the methochloride.

It is noticed that the two above-mentioned quaternary bases are not, like that from brucine methiodide, rapidly converted into betaines. R. CHILD.

**Strychnos alkaloids. LVI. Transformations of 2:3-diketonicucidine, 2:3-diketonic acid hydrate, and carboxyaponucine.** H. LEUCHS and W. WEGENER (Ber., 1930, 63, [B], 2215—2226).—It is proposed to designate the alkaloids and acids obtained in common from strychnine and brucine by particular names. These are based on two substances which stand to one another in the same relationship as strychnine and strychnidine and are termed *nucine* (I) (from *Strychnos nux vomica*) and *nucidine* (II). The

four aromatic carbon atoms which are not further united are separated according to III.



Strychnine is electrolytically reduced in sulphuric acid solution, whereby strychnidine and tetrahydrostrychnine are produced in 70% and 20% yield, respectively. Oxidation of strychnidine with chromic acid yields an acid,  $C_{21}H_{22}O_4N_2$ , not molten below  $320^\circ$  (nitrate; hydrobromide; hydriodide; perchlorate; sulphate). 2:3-Diketonnucidine is converted by acetic anhydride into the compound  $C_{17}H_{20}O_3N_2 \cdot AcOH$ , m. p. 269—274° (decomp.) after softening at  $230^\circ$ . Reduction of 2:3-diketonnucidine by amalgamated zinc and hydrochloric acid unexpectedly affords 2-keto-3-hydroxynucidine, m. p. 252—254° after softening at  $240^\circ$  (perchlorate), also obtained by treatment of the base with sodium amalgam. 2-Keto-3-acetoxynucidine,  $C_{19}H_{24}O_4N_2 \cdot AcOH \cdot H_2O$ , m. p. 121—122° after softening at  $117^\circ$ , the corresponding free base, m. p. 143—144°, and its perchlorate are described; the base affords a methiodide,  $C_{17}H_{22}O_3N_2 \cdot MeI$ , not molten below  $290^\circ$ . 2-Keto-3-hydroxynucidine is oxidised by bromine water to 2-keto-3-hydroxynucidaldehyde, isolated as the perchlorate,  $C_{17}H_{22}O_5N_2 \cdot HClO_4$ , and monohydrated hydrobromide,  $[\alpha]_D^{20} + 106.0^\circ/d$  in water; the newly-formed carbonyl group is identified by the formation of a semicarbazone perchlorate,  $C_{18}H_{25}O_5N_5 \cdot HClO_4$ , and oxime hydrobromide,  $C_{17}H_{23}O_5N_3 \cdot HBr$ . The aldehyde hydrobromide or perchlorate is oxidised by yellow mercuric oxide to 2-keto-3-hydroxynucidic acid,  $C_{17}H_{22}O_6N_2$ , which darkens at about  $300^\circ$  and has  $[\alpha]_D^{20} + 119.7^\circ/d$  (perchlorate). Diketonnucidine is degraded by hydrogen peroxide in presence of barium hydroxide to the amino-acid, carboxyapponucidine, isolated as the perchlorate,  $C_{16}H_{22}O_3N_2 \cdot 2HClO_4 \cdot 2H_2O$ ,  $[\alpha]_D^{20} - 59.7^\circ$  in water, which is accompanied by an amine oxide, isolated as the salt,  $C_{17}H_{20}O_4N_2 \cdot HClO_4 \cdot H_2O$ ,  $[\alpha]_D^{20} + 36.4^\circ$ . (The acid is considered to be derived from apponucidine,  $C_{15}H_{22}ON_2$ , the compound from which all the six carbon atoms of the strychnidine benzene nucleus have been removed.) Oxidation of carboxyapponucidine with bromine gives the corresponding aldehyde, obtained as the dihydrobromide,  $C_{16}H_{22}O_5N_2 \cdot 2HBr$ ,  $[\alpha]_D^{20} + 11.1^\circ/d$  in water, and the triperchlorate; the corresponding semicarbazone dihydrobromide,  $C_{17}H_{25}O_5N_5 \cdot 2HBr$ ,  $[\alpha]_D^{20} - 16^\circ/d$  in water, and oxime dihydrobromide,  $[\alpha]_D^{20} - 8.5^\circ/d$  in water, are described. Treatment of the aldehyde dihydrobromide with yellow mercuric oxide yields carboxyapponucidic acid, analysed as the hydrobromide,  $C_{16}H_{22}O_6N_2 \cdot HBr$ ,  $[\alpha]_D^{20} - 3.6^\circ/d$  in water; the corresponding nitrate, hydriodide, and perchlorate are described. Attempts to esterify the acid hydrobromide with ethyl-alcoholic hydrogen chloride yield the acid hydrochloride,  $C_{16}H_{22}O_6N_2 \cdot 2HCl$ , m. p.  $266^\circ$  (decomp.).

2-Keto-3-hydroxynucic acid hydrate is trans-

formed by boiling 8.8*N*-hydrobromic acid into 2-keto- $\Delta^3$ -nucenic acid hydrate,  $C_{17}H_{20}O_7N_2$ , decomp. about  $270^\circ$  after softening at  $255^\circ$ .

Distillation of carboxyapponucine with zinc dust in a vacuum at  $330$ — $400^\circ$  affords a resinous product from which the perchlorate,  $C_{15}H_{20}ON_2 \cdot 2HClO_4$ ,  $[\alpha]_D^{20} + 209^\circ/d$ , is isolated in small amount. H. WREN.

**Strychnine; sensitivity of chemical and physiological tests.** J. C. WARD and J. C. MUNCH (J. Amer. Pharm. Assoc., 1930, 19, 954—957).—The minimum amount of strychnine which gives a complete sequence of colours with potassium dichromate in sulphuric acid is  $1.0 \mu g.$  ( $10^{-6} g.$ ). With lead dioxide, potassium permanganate, manganese dioxide, and Mandelin's reagent  $1.7 \mu g.$ , with potassium iodate  $5.0 \mu g.$ , and with Malaquin's reagent  $6.7 \mu g.$  are required. The average limit of perceptibility of strychnine base, hydrochloride, or sulphate in distilled water is  $5.0 \mu g.$  The apparent bitterness is diminished by both sodium chloride and sucrose, the limit of perceptibility being  $7$ — $9 \mu g.$  in  $0.9\%$  salt solution and  $14$ — $17 \mu g.$  in  $10\%$  sucrose. Differences in reaction time, place of detection on the tongue, and sensitivity have been detected with different observers, but the results with one person usually agree within  $5\%$ . H. E. F. NORTON.

**Diastereoisomerism. VI. Configurations of morphine alkaloids.** H. EMDE (Helv. Chim. Acta, 1930, 13, 1035—1058).—It is deduced, mainly from observations recorded in the literature, that the optical configurations of the five asymmetric carbon atoms in morphine are  $C_6(-)$ ,  $C_5(-)$ ,  $C_{13}(+)$ ,  $C_{14}(+)$ ,  $C_9(-)$ ; the numbering is that used by Gulland and Robinson (J.C.S., 1923, 123, 980). Thebaine (Schöpf, A., 1927, 472) has  $C_5(-)$ ,  $C_{13}(+)$ , and  $C_9(-)$ . When a model is constructed for morphine using planar rings, it is found that the quaternary asymmetric carbon atom ( $C_{13}$ ) prevents all the five rings from being in the same plane; ring III (or V) is inclined against the plane of the other four rings. When  $C_{13}$  is not asymmetric, as in apomorphine or morphothebaine, then all five rings are in the same plane.

The following molecular rotations (in water unless stated otherwise) are recorded for the *D* line: morphine hydrochloride ( $+3H_2O$ ),  $-370^\circ$ ; codeine hydrochloride ( $+2H_2O$ ),  $-402^\circ$ ; thebaine hydrochloride ( $+H_2O$ ),  $-574^\circ$ ; apomorphine hydrochloride,  $-149^\circ$ ; morphothebaine hydrochloride,  $-146^\circ$ ; codeine methiodide,  $-362^\circ$ ;  $\alpha$ -6-acetylmorphine hydrochloride,  $-593^\circ$ ; diacetylmorphine hydrochloride,  $-619^\circ$ ; dipropionylmorphine, m. p.  $107^\circ$ ,  $-685^\circ$  in alcohol [hydrochloride, anhydrous and  $+1.5H_2O$ , m. p.  $210^\circ$  (not sharp) with reddening,  $-613^\circ$ ]; dihydrocodeine,  $-459^\circ$  (hydrogen tartrate,  $-588^\circ$ ); dihydrothebaine,  $-623^\circ$  in dilute hydrochloric acid. H. BURTON.

**Aromatic arsenic compounds containing sulphur groups attached to the nucleus. I. Sulphonic acids and their derivatives.** H. J. BARBER (J.C.S., 1930, 2047—2053).—3-Sulphophenylarsinic acid is obtained in poor yield by the action of potassium ethyl xanthate on 3-aminophenylarsinic acid (cf. Hewitt and others, A., 1926, 851). The product obtained by Krishna and Krishna (A., 1929, 1320) from benzenesulphonic acid by Béchamp's method appears

to have different properties, and in view of the failure of this method when applied to phenol-*p*-sulphonic acid, is of doubtful identity. 3-Sulpho-4-hydroxyphenylarsinic and 5-sulpho-2:4-dihydroxyphenylarsinic acids are obtained by direct sulphonation, which is assumed to occur in the same position as nitration. 4-Amino-, 4-acetamido-, 3-hydroxy-4-acetamido-, and 4-chloro-phenylarsinic acids could not be sulphonated under the most drastic conditions. 4-Aminophenylmethylsulphone is converted by the Bart reaction into 4-methylsulphonylphenylarsinic acid. Sodium 2-iodophenylarsinate reacts with sodium sulphite in presence of a trace of copper acetate to give 2-sulphophenylarsinic acid (barium salt), converted by action of phosphorus tri- and penta-chlorides, followed by decomposition with ice into an oil, probably 2-chlorosulphonylphenylchlorohydroxyarsine, which is hydrolysed further by cold water to 2-chlorosulphonylphenylarsenious oxide [2-sulphonanilidophenylarsenious oxide gives with hydriodic acid the di-iodoarsine, and with thiolacetamide di(carbamidomethyl)-2-sulphonanilidophenylthioarsinite]. 2-Chlorosulphonylphenylarsinic acid [2-sulphonamido- (thiolacetamide derivative, m. p. 171—173°) and 2-sulphonanilidophenylarsinic acid are described; the latter is also obtained by oxidation of the corresponding arsenious oxide] results from oxidation of the arsenious oxide (above). It is reduced by sodium sulphite to 2-sulphophenylarsenious oxide, the silver salt of which gives with methyl iodide a product that may be oxidised to 2-methylsulphonylphenylarsinic acid. 2-Iodo-5-aminophenylarsinic acid, prepared by reduction of the corresponding nitro-compound with ferrous hydroxide, is converted by sodium sulphite into 2-sulpho-5-aminophenylarsinic acid. Attempted preparations of 2-iodo-4-hydroxy- and 4-acetamido-phenylarsinic acids by application of the Sandmeyer reaction to the appropriate amino-compound failed.

H. A. PIGGOTT.

The  $p_H$  of neosalvarsan and sulpharsphenamine in relation to differences in structure. A. E. JURIST and W. G. CHRISTIANSEN (J. Amer. Pharm. Assoc., 1930, 19, 951—953).—The  $p_H$  of 10% solutions of commercial and experimental samples of sulpharsphenamine which varies between 2.4 and 4.4 and their ultimate analysis indicate that they contain varying quantities of the free acid, 3:3'-disulphon-methylamido-4:4'-dihydroxyarsenobenzene ( $p_H$  2.15). Sulpharsphenamine is less stable at the  $p_H$  range of neosalvarsan (5.8—8.7), whilst the latter decomposes in acid solution. The stability of the free acid from sulpharsphenamine may be due to anhydride formation between the sulphonic acid radicals and the phenolic groups.

H. E. F. NOTTON.

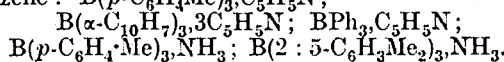
Boron-carbon linking. I. Oxidation and nitration of phenylboric acid. A. D. AINLEY and F. CHALLENGER (J.C.S., 1930, 2171—2180).—Phenylboric acid is decomposed by water at 140—150°, or by concentrated alkali or hydrochloric acid, into benzene and boric acid. Cadmium and zinc halides also produce benzene in aqueous solution, whilst copper sulphate gives in addition phenol and diphenyl. This effect is not produced by the lower members of group II, and is ascribed, not to hydro-

lytically produced acid, but to intermediate formation of an organometallic compound. Halogenobenzenes are produced by direct action of the halogens or, better, hypohalites, and in excellent yield by the action of cupric halides. The last reaction, as also the action of mercuric bromide, which gives mercury phenyl bromide, is a direct replacement, and of use in orientation. Thus *p*-tolylboric acid gives with mercuric chloride mercury *p*-tolyl chloride, and with cupric bromide *p*-bromotoluene; similarly, *p*-borobenzoic acid gives *p*-chlorobenzoic with cupric chloride. Phenylboric acid is readily oxidised to phenol by cold hydrogen peroxide.

Nitration in concentrated sulphuric acid at about -20° gives *m*-nitrophenylboric acid, m. p. 273° (decomp.), identified by conversion by cupric chloride into *m*-chloronitrobenzene, by mercuric chloride into mercury *m*-nitrophenyl chloride (Kharasch and Chalkley, A., 1921, i, 377), by bromine water into *m*-bromonitrobenzene, and by oxidation with hydrogen peroxide to *m*-nitrophenol. The crude nitration product, when converted into the bromonitrobenzenes and analysed by the method of Francis and Hill (A., 1925, ii, 163), gives figures corresponding with a yield of 71.9% of *m*-isomeride; a fraction of the bromonitrobenzenes can be nitrated to 2:4-dinitro-bromobenzene, indicating the presence of an *o*- or a *p*-isomeride. Phenylboric acid does not react with hydroferriehloric acid (cf. Robinson, A., 1925, ii, 606); consequently salt formation is unlikely to be the cause of *m*-nitration, explanations of which, based on the presence of an incomplete octet, are advanced.

H. A. PIGGOTT.

Valency problem of boron. V. Mol. wt. of the boron triaryls and certain of their additive compounds. E. KRAUSE and P. DITTMAR (Ber., 1930, 63, [B], 2347—2353).—The marked tendency of boron aryls to form additive compounds by employment of subsidiary valencies does not appear to find its counterpart in a tendency towards polymerisation. Determination of mol. wt. in freezing or boiling benzene usually gives normal values. With certain compounds, notably boron tricyclohexyl, polymerisation appears to occur with age after solidification of the molten material. The following compounds have been used: boron triphenyl, tri-*p*-tolyl, tri-cyclohexyl, tri- $\alpha$ -naphthyl and its compound with 2 mols. of benzene, and bismuth triphenyl. The following complex compounds of boron aryls with nitrogenous base usually exhibit simple mol. wt. and are not decomposed at the temperature of boiling benzene:  $B(p-C_6H_4Me)_3 \cdot C_5H_5N$ ;



H. WREN.

Organic compounds of bismuth. F. FARRY-KANT (XVII Spraw. państw. inst. farm., 1927, 13 pp.; Chem. Zentr., 1930, i, 2548).—Small quantities of bismuth  $\omega$ -tristyrene were obtained from  $\beta$ -bromostyrene by interaction of the organomagnesium compound with bismuth trichloride; diphenylbutadiene was also produced.

A. A. ELDRIDGE.

Organic germanium compounds. III. Diphenylgermanium dihalides and diphenylger-

**Germanium imine.** C. A. KRAUS and C. L. BROWN (J. Amer. Chem. Soc., 1930, 52, 3690—3696).—Germanium tetraphenyl (A., 1927, 268) is treated with bromine in carbon tetrachloride, the resulting mixture of bromides converted into oxides, and thence by treatment with hydrochloric acid into chlorides. Fractionation of this mixture gives *diphenylgermanium dichloride*, b. p. 100°/0.005 mm., m. p. 9°, which is hydrolysed to the oxide. This is shown by extraction with benzene and alcohol to be a mixture of complex oxides. *Diphenylgermanium dibromide*, b. p. 120°/0.007 mm., and *disulfuride*, b. p. 100°/0.007 mm., are prepared from the oxide and the requisite halogen acid. Treatment of the dichloride with liquid ammonia affords *diphenylgermaniumimine*,  $\text{NHGePh}_2$ , which is a viscous liquid at the ordinary temperature. The imine is readily hydrolysed with water to diphenylgermanium oxide and ammonia.

H. BURTON.

**Mercuration of phthaleins in neutral solution with mercuric chloride.** F. R. GREENBAUM (Amer. J. Pharm., 1930, 102, 535—544).—Even when all four *ortho*-positions of the phenolic rings are occupied, phthaleins give well-defined mono- or dimercury compounds when mercuration is effected with mercuric chloride in perfectly neutral solution according to G.P. 308,335 and U.S.P. 1,455,495. The following are described: monomercury compounds of tetraiodophenolphthalein, tetraiodo-, and tetrabromo-fluorescein, *monochloromercuridinitrophenolphthalein*, *monochloromercurimononitro-m-cresolphthalein*, *dichloromercurigallein*, and a mixture of mono- and di-chloromercuridinitrofluorescein. E. H. SHARPLES.

**Formation of a closed, heterocyclic ring containing mercury atoms.** L. VECCHIOTTI (Ber., 1930, 63, [B], 2275—2276).—*o*-Dibromobenzene is converted by 2% sodium amalgam in petroleum at 120° into the compound  $\text{C}_6\text{H}_4\langle\text{Hg}\rangle\text{C}_6\text{H}_4$ , which does not melt below 300°. Its constitution is established by its decomposition with boiling glacial acetic acid into benzene and *o*-diacetoxymercuribenzene,  $\text{C}_6\text{H}_4(\text{Hg}\cdot\text{OAc})_2$ , not molten below 300°, which is transformed by iodine in potassium iodide into *o*-di-iodobenzene, m. p. 270°. H. WREN.

**"Machine" for analysis with Grignard reagents.** E. P. KOHLER and N. K. RICHTMYER (J. Amer. Chem. Soc., 1930, 52, 3736—3738).—An improved form of the apparatus previously used (A., 1928, 160) for determining the quantity of gas evolved and the amount of reagent consumed in reactions with magnesium methyl iodide is described.

H. BURTON.

**Structure of gelatin.** E. ABDERHALDEN and A. SCHMITZ (Z. physiol. Chem., 1930, 190, 101—119).—Gelatin contains at least three types of group reacting with benzoyl chloride, since one portion of the benzoylated product (type A, 2.5% Bz) is hydrolysed by 0.1*N*-sodium hydroxide, another portion (type B, 1.7% Bz) by 2*N*-sodium hydroxide in the cold, and a third portion (type C, 2.3% Bz) only by 2*N*-sodium hydroxide on heating. A similar effect is noted with the *dl*- $\alpha$ -bromoisohexoyl derivative, but A and B are not differentiated.

Methylation with methyl sulphate yields a methoxy-derivative corresponding with the total cold saponifiable fraction (A+B); diazomethane yields a methoxy-derivative with B only. Type B probably corresponds with aromatic and A with aliphatic hydroxyl groups. The determination of amino-methylation shows that the free amino-groups to which the benzoyl radicals are relatively firmly attached (type C) are trebly methylated by methyl sulphate and doubly by diazomethane. Oxyproline and oxyglutamic acid could not be benzoylated at the hydroxyl group; *dl*-leucyl-*dl*-oxyglutamic acid yielded only the *amino-benzoylated* derivative. Pepsin-hydrochloric acid, which attacks free gelatin, does not hydrolyse the benzoylated or methylated products; both these are hydrolysed by trypsin-kinase. Erepsin has no action on gelatin or the derivatives. J. H. BIRKINSHAW.

**Chemical change in gelatin resulting from the method of storage.** K. V. THIMANN and A. B. PAGE (Biochem. J., 1930, 24, 1058—1060).—Gelatin purified by flocculation in the electric field and stored in a moist condition yields less diamino-acid precipitate when hydrolysed than the normal dry-stored product. S. S. ZILVA.

**Zwitter ions. I. Proof of the zwitter-ion constitution of the amino-acid molecule.** L. J. HARRIS. II. **Amino-acids, polypeptides, etc. and proteins as zwitter ions, with instances of non-zwitter-ion ampholytes.** T. W. BIRCH and L. J. HARRIS (Biochem. J., 1930, 24, 1080—1097).—Hydrogen chloride and sodium hydroxide titration curves of glycine determined in the presence of increasing concentrations of formaldehyde show that the weakening of the basicity of the amino-group caused by the formation of the methylene derivative displaces the sodium hydroxide curve and not the hydrochloric acid curve, which suggests that "replacement" (back-titration) of the carboxyl and amino-groups of the amino-acid by a stronger acid and a stronger base takes place. This evidence is a direct proof of the validity of the zwitter-ion theory. Similar investigations with free bases and ammonium salts etc. and with other amino-acids and ampholytes show that the shift due to the lowered basicity is characteristic of a basic curve. Titration curves for histidine, lysine, arginine, aspartic acid, glutamic acid, tyrosine, and cysteine have been obtained. New formulæ are given for the monohydrochloride and the free amino-acid in the case of the mono-acid-dibasic ampholytes, the dihydrochloride and sodium salt retaining the old constitution. With glutamic and aspartic acids the monosodium salt and free ampholyte are given new constitutions, the other salts remaining unchanged. With tyrosine and cysteine only the free amino-acid is changed and both the sodium salts are unaltered. The apparent acid constant of taurine is related to the basic group. *p*-Aminophenol and *p*-aminobenzoic acid are not zwitter ions, whilst polypeptides and gelatin are.

S. S. ZILVA.

**Separation of the products of protein hydrolysis.** M. A. B. BRAZIER (Biochem. J., 1930, 24, 1188—1198).—The separation is based on the different solubilities of the copper salts of the amino-acids in



various solvents. Details of a complete analysis of zein by this method are given. S. S. ZILVA.

**Arginine and prearginine groups in edestin.** H. S. SMITHS (J. Gen. Physiol., 1930, 14, 87—97).—A larger quantity of arginine is found in edestin hydrolysates than would account for the contribution of arginine to the titration curve. Titration data indicate that a basic group with an index of 3.8—4.6 is present in the original protein, to which the name *prearginine* is given. P. G. MARSHALL.

**Combination of edestin with hydrochloric acid.** D. I. HITCHCOCK (J. Gen. Physiol., 1930, 14, 99—103).—*E.M.F.* measurements of cells without liquid junction indicate that 1.0 g. of edestin in 0.1*N*-hydrochloric acid has a combining capacity of  $13.4 \times 10^{-4}$  equivalent of  $H^+$  and  $3.9 \times 10^{-4}$  equivalent of  $Cl^-$ . P. G. MARSHALL.

**Fractionation of gliadin.** G. HAUGAARD and A. H. JOHNSON (Compt. rend. Trav. Lab. Carlsberg, 1930, 18, No. 2, 1—138).—Two experiments relating to an attempt to fractionate wheat gliadin by fractional cooling to 0° and -11° of its solution in 52 wt.-% alcohol (60 vol.-%) using as the starting material, in the first case, gluten freed as far as possible from starch, and, in the second, a purified sample of gliadin prepared by Dill and Alsberg's method (A., 1925, i, 1478) are described in detail, the two fractionations giving essentially the same results. Differentiation of the fractions was established by a study of their composition, optical rotations, precipitation temperatures (the temperature at which turbidity first appears when a solution of gliadin in 52% alcohol is cooled), hydrogen-ion activities ( $p_{aH}$  values), viscosities in alcoholic solution, solubility, osmotic pressure, acid- and base-binding capacities, and of the products obtained by acid and enzymic hydrolysis of the fractions; the effect of the alteration of conditions on these properties was also investigated. Only the following broad conclusions admit of summarisation. The moisture content of the air-dried fractions varied between 1.07 and 2.10%, and the ash contents between 0.04 and 0.09% in the first, and between 0.14 and 0.17% (as sulphates) in the second experiment. The nitrogen content of all fractions was approximately constant at 17.65% (on water- and ash-free samples). The precipitation temperature of a gliadin solution is largely affected by the presence of lithium chloride (used in the purification processes), small concentrations of this salt (up to 0.002 mol.) causing an increase, followed, at higher salt concentrations, by a rapid fall. The presence of small quantities of lithium chloride in the gliadin fractions accounts for the variation of precipitation temperature with the gliadin concentration, since, in agreement with Dill and Alsberg's results (*loc. cit.*), in the presence of 0.2*N*-lithium chloride it is independent of the gliadin concentration within wide limits, but is dependent in a high degree on the alcohol concentration and on the  $p_{aH}$  value, being a maximum at  $p_{aH}$  7.5, at which point it is independent of the gliadin content. In the presence of 0.2*N*-lithium chloride and under the same conditions, the various gliadin fractions had widely different precipitation temperatures. The solubility of gliadin in 52% alcohol

at 0° and at approximately the isoelectric point ( $p_{aH}$  7.1) is, in distinction to the precipitation temperature, dependent on the gliadin concentration, increasing with the quantity of gliadin used to a point characteristic for each fraction (maximum solubility), after which the solubility appears to be constant. This maximum solubility in 52% alcohol at 0° varies for the fractions from the first fractionation experiment from 0.7 to 11.5, and for those from the second experiment from 1.8 to 25.8 mg. gliadin-nitrogen per c.c., and this property is considered to be an important one for the characterisation of the fractions. The solubility is also considerably affected by the lithium chloride concentration and the  $p_{aH}$  value, minimum solubility being observed with a salt concentration of 0.001*N* and at  $p_{aH}$  7.3. The precipitation temperatures of the fractions are the higher the lower is the maximum solubilities. Whilst the fractions from the first fractionation showed only small differences in optical rotation, those from the second experiment showed a significant interdependence between this property and the maximum solubility, the least readily soluble fractions exhibiting the highest rotation and *vice versa*. The rotation is dependent both on the lithium chloride concentration and the hydrogen-ion activity, being a minimum at  $p_{aH}$  7.1—7.2 (isoelectric point), but is independent of the gliadin concentration and the age of the solution. Gliadin solutions exhibit simple rotatory dispersion. The viscosities of gliadin solutions in 40, 50, 60, and 70 vol.-% alcohol lie essentially on the same curve up to concentrations of 15 mg. of gliadin-nitrogen per c.c., but at higher concentrations the solution in 70% alcohol has a much higher viscosity. The viscosity is almost independent of the  $p_{aH}$  value and of lithium chloride up to moderately high concentrations of this salt. A marked correlation exists between the viscosity and the maximum solubility of the gliadin fractions. Under identical conditions the viscosity is the greater the lower is the maximum solubility of the gliadin fraction. The acid- and base-binding capacity (with hydrochloric acid and lithium hydroxide, respectively) of three fractions from the second experiment gave the same curve after the introduction of a small correction for the unequal content of lithium and chlorine in the samples, this common characteristic curve of all gliadin fractions showing an isoelectric reaction in 52% alcohol at about  $p_{aH}$  7.1, in good agreement with Hoffman and Gortner's value of 5.76 in water (A., 1925, i, 1479). The osmotic pressures of the same three fractions were determined, the most sparingly soluble fraction having the lowest osmotic pressure. One of the fractions from the first fractionation was again separated into nine fractions by similar fractional cooling. Under comparable conditions the precipitation temperatures of these nine fractions varied between -0.5° and 21°, but a sample obtained by mixing aliquot parts of these fractions had the same precipitation temperature (6°) as the original sample, thus showing that the fractionation is reversible (denaturation not having occurred) and that it is not complete in the first experiment. Moreover, when two fractions with different precipitation temperatures were mixed, both fractions had marked effects

on the precipitation temperature of the mixture. The various fractions obtained in the original experiment were each subjected to hydrolysis with 20% hydrochloric acid and the humin, ammonia, arginine, acid and basic groups, tyrosine and tryptophan determined in the hydrolysate of each. The most readily soluble gliadin fraction had the highest content of acid-insoluble humin, tryptophan, non-amino-nitrogen, and proline, and the lowest content of acid-soluble humin, ammonia-nitrogen, tyrosine, and amino-nitrogen, the least readily soluble fraction behaving in the opposite manner. Whilst the fractions from the second experiment behaved identically on hydrolysis with trypsin-kinase, with pepsin the velocity was the same for the first 10 hrs., but thereafter hydrolysis proceeded most rapidly with the most readily soluble fraction. On the basis of these results it is considered that gliadin must be regarded as Sørensen suggests (Compt. rend. Lab. Carlsberg, 1926, 16, No. 8; cf. Linderström-Lang, A., 1929, 1093) as a reversible, co-precipitation system, the original gliadin complex,  $A_pB_qC_r$ , splitting into one complex of higher and one of lower solubility than the original, the process  $A_pB_qC_r \rightleftharpoons A_{p-p}B_{q-q}C_{r-r} + A_pB_qC_r$ , representing only the first stage in the ultimate dissociation. Finally the equilibrium between gliadin, alcohol, and water at 0° was investigated and a specific gravity method for the accurate determination of alcohol concentration in gliadin solutions is worked out. Under essentially equal conditions the most readily soluble gliadin preparation is precipitated at 0° with relatively more water and less alcohol than is a less readily soluble preparation. The alcohol concentration of solutions which afforded precipitates at 0° with the same alcohol content as the decantate and as the original solution were, for the least readily and most readily soluble fractions, 27 and 38 wt.-%, respectively. The whole equilibrium is represented on a ternary diagram on the assumption that the precipitated phase is homogeneous.

J. W. BAKER.

**Spectrophotometric researches on the aldehyde fixation of the proteins and their hydrolysis products, also on the enolisation of the peptide linkings.** J. GRÓH and M. HANÁK (Z. physiol. Chem., 1930, 190, 169—183).—The absorption spectra of certain amino-acids alone and in presence of alkali and of formaldehyde were studied. The absorption of caseinogen agrees well with the theoretical absorption curve calculated from the tryptophan and tyrosine content. The same holds for egg-albumin. It is concluded that in these two proteins the only chromophoric groups present are those of tryptophan and tyrosine. When the two proteins are partly hydrolysed in alkaline solution a considerable displacement of the curves occurs (greater absorption). This is attributed to enolisation of the peptide linkings.

J. H. BIRKINSHAW.

**Mol. wt. of lactalbumin.** B. SJÖGREN and T. SVEDBERG (J. Amer. Chem. Soc., 1930, 52, 3650—3654).—The partial specific volume of lactalbumin is 0.75 at 20°, its isoelectric point is approximately  $p_H$  5.2, and its ultra-violet absorption curve shows a maximum at 279  $\mu\mu$  and a minimum at 255  $\mu\mu$ . Deter-

minations of the mol. wt. of crystallised lactalbumin (cf. Wichmann, A., 1899, i, 838) by the ultracentrifugal method give values of 12,000—25,000, showing that the product is not homogeneous. It is shown by centrifugal methods that the lactalbumin in milk differs from the "purified" product, since the original substance has a mol. wt. not exceeding 1000. During the "purification" aggregation is caused by the action of ammonium sulphate.

H. BURTON.

**Detection of carbon, hydrogen, and sulphur in organic compounds.** O. SCHEWKET (Biochem. Z., 1930, 224, 328—330).—Organic compounds (including those which do not char when heated alone) char when ignited with sodium sulphite or thiosulphate and in some cases carbonate is also formed. If hydrogen is present hydrogen sulphide is evolved. Sulphur in organic compounds is detected by heating them with a substance rich in hydrogen (dextrase, starch); hydrogen sulphide is produced, and can be recognised by the usual tests.

W. MCCARTNEY.

**Determination of halogens in organic compounds.** K. V. ALEKSEVSKI and Y. S. PIKAZIN (J. Appl. Chem., Russia, 1930, 3, 273—284).—Ter Meulen and Hesling's method is favoured, but cyclic compounds are not always completely decomposed. Air may be substituted for hydrogen. Stepanov's method may be used for cyclic compounds. In the application of catalytic hydrogenation copper or silver may be employed, but cerium is quickly poisoned.

CHEMICAL ABSTRACTS.

**Colour reaction of ephedrine.** J. SIVADJIAN (J. Pharm. Chim., 1930, [viii], 12, 266—269).—Ephedrine and other derivatives containing a hydroxyl group in the  $\alpha$ - and a methylamino-group in the  $\beta$ -position to the benzene nucleus give with hydrogen peroxide containing 4% of sodium chloride in warm, slightly alkaline solution a red coloration becoming violet-red on cooling. In the absence of sodium chloride the ephedrine is oxidised to benzaldehyde. The substances obtained by etherification of the alcoholic group, by oxidation to the ketone, or by methylation or demethylation of the amino-group all fail to give the reaction.  $\beta$ -Methylamino- $\alpha$ -phenylbutan- $\gamma$ -ol gives a yellow colour and ethyl  $p$ - $\beta$ -hydroxy- $n$ -propylaminobenzoate a faint yellow colour.  $\psi$ -Ephedrine,  $\psi$ -methylephedrine, and norephedrine give orange-yellow colours. Pyramidone (cf. Charonnat and Delaby, this vol., 223) gives a transient blue colour.

H. E. F. NOTTON.

**Reactions of thiophen.** L. EKKERT (Pharm. Zentr., 1930, 71, 625—626).—One drop of an alcoholic solution of thiophen of the concentration given in parentheses gives the following colour reactions in concentrated sulphuric acid: with alloxan deep blue, becoming violet or red in presence of water (1%); with formaldehyde ruby-red (0.1%); with  $p$ -dimethylaminobenzaldehyde violet to red with a green fluorescence (1%), rose-pink (0.1%); and with nitroso- $\beta$ -naphthol intense green (1%). In the first two reactions the colours may also be obtained by superposing an aqueous or alcoholic solution of the reagents on sulphuric acid.

H. E. F. NOTTON.

**Microchemical detection of barbituric acid derivatives.** L. VAN ITALLIE and A. J. STEEN-

HAUER (Pharm. Weekblad, 1930, 67, 977—985).—The nature of the precipitates obtained by addition to a solution of the derivative in potassium hydroxide of acetic acid, ammonium phosphate, thallium acetate, silver nitrate, ammoniacal cupric hydroxide, bromine water, or baryta water, and the conditions favourable to precipitation in each case, are described. It is claimed that suitable combinations of the reactions are sufficient to identify any of the common derivatives.

S. I. LEVY.

**Reactions of homatropine and novatropine.** L. EKKERT (Pharm. Zentr., 1930, 71, 641).—To about 0.01 g. of substance are added an equal amount of chloroamine and 10 drops of fuming hydrochloric acid (36%) and the mixture is evaporated to dryness; the yellow or dirty brown residue is dissolved in 0.5 c.c. of sulphuric acid and 0.01 g. of codeine added. A characteristic bright colour is developed on carefully warming the solution—blood-red to carmine with homatropine, carmine to purplish-red with novatropine. Atropine, hyoscyamine, hyoscyne, and scopolamine do not give characteristic colours and may be tested by the furfuraldehyde reaction previously described (A., 1926, 533).

R. CHILD.

**Titrimetric determination of primary arsinic acids.** H. KING and G. V. RUTTERFORD (J.C.S.,

1930, 2138—2143).—Primary arsinic acids may be determined volumetrically by titration in a solution saturated with sodium chloride using thymol-blue (thymolsulphonaphthalein) as indicator, or, more accurately, in a solution half saturated with sodium chloride in presence of thymolphthalein. Thymol-blue is the less satisfactory indicator, having a less striking colour change, and being itself affected by certain arsinic acids. The method is not satisfactory in presence of amino-, hydroxyl, sulphonamido-, carbamido-, or similar groups capable of conferring basic or additional acidic properties. The following procedure is recommended. About 0.1 g. of the acid, accurately weighed, is heated with two drops of 0.1% alcoholic thymolphthalein and titrated with 0.1N-sodium hydroxide (free from carbonate) until a blue colour appears. An approximately equal volume of saturated sodium chloride, neutral to thymolphthalein, is then added, and the titration continued until a blue colour is again produced, which then corresponds with the formation of the disodium salt of the acid.

H. A. PIGGOTT.

**Toxicological determination of morphine.** A. C. PEREIRA (Rev. Chim. pur. appl., 1929, 4, 1—5; Chem. Zentr., 1930, i, 2457).—Alcoholic (10%) chloroform is employed for the extraction.

A. A. ELDRIDGE.

## Biochemistry.

**Adrenaline as a disturbing factor in the determination of blood-gases.** T. VACEK (Pflüger's Archiv, 1930, 224, 144—149; Chem. Zentr., 1930, i, 2131).—When adrenaline is added to the blood as well as potassium ferricyanide the quantity of expelled gas is considerably increased and is larger than the total amount of so-called free oxygen. Potassium ferricyanide alone liberates only a small amount of gas from blood-serum; with the addition of adrenaline 200 volumes more gas are liberated.

L. S. THEOBALD.

**Specific detection of human blood by Ganasini's reaction.** D. GANASSINI (Arch. Ist. Biochim. Ital., 1930, 2, 401—410).—An extract of the suspected human blood-stain is prepared containing the same concentration of pigment as a control solution of human blood. Exact equality is attained after comparing the pigment content in equal portions of the two solutions colorimetrically, either directly, after conversion into methæmoglobin, or by comparison of the iron content. The two solutions are then treated simultaneously with eosin-blue in alcoholic potassium hydroxide solution and dilute hydrogen peroxide, and the rates of colour change observed. With animal bloods the change takes two or three times as long as with human blood.

R. K. CALLOW.

**Detection of blood by means of benzidine hydrochloride.** S. L. LEIBOFF (J. Lab. Clin. Med., 1929, 14, 1187—1191).—The preparation of the pure reagent and its use in the examination of urine and faeces are described.

CHEMICAL ABSTRACTS.

**Determination of hæmoglobin.** M. KARSHAN and R. G. FREEMAN, jun. (J. Lab. Clin. Med., 1929, 15, 74—78).—The methods of Wong and of Cohen and Smith give results in accord with those obtained by Van Slyke and Neill's method.

CHEMICAL ABSTRACTS.

**Reactions of cyanide with globin-hæmochromogen.** M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1930, 14, 43—54).—Cyanide is capable of forming mono- and di-cyano-compounds with reduced hæm, whilst only one (probably mono-) globinhæmochromogen exists. Differing amounts of cyanide are added to reduced hæm in the presence of varying concentrations of globin and the spectra of the resulting solutions indicate whether the cyanide is competing with the globin in its attachment to the hæm molecule. Cyanide is found to react with globin-hæmochromogen in two ways: first, in which it forms a *cyanoglobin-hæmochromogen*, and, secondly, in which it displaces the globin, forming a dicyanohæmochromogen.

P. G. MARSHALL.

**Elementary composition of crystallised oxy-hæmocyanin from *Helix pomatia*.** F. HERNLER and E. PHILIPPI (Z. physiol. Chem., 1930, 191, 23—27).—The composition of air-dried crystalline oxy-hæmocyanin from *Helix pomatia* is C 48.59, H 7.04, N 14.26, S 0.71, Cu 0.232% (mean values).

J. H. BIRKINSHAW.

**Action of papain on hæmocyanin from *Helix pomatia*.** E. PHILIPPI and F. HERNLER (Z. physiol. Chem., 1930, 191, 28—35).—Filtered snail's blood

containing 2—3% of sodium fluoride when treated with 2% of papain deposits crystals on keeping (Dhéré and Baumeler, *Compt. rend. Soc. Biol.*, 1929, **101**, 1071). The composition and absorption spectrum of the crystals agree best with the assumption that they are oxyhaemocyanin. J. H. BIRKINSHAW.

**Determination of the  $p_H$  of serum and plasma by the quinhydrone electrode.** E. P. LAUG (*J. Biol. Chem.*, 1930, **88**, 551—573).—By application of a predetermined correction factor to the usual equation, the quinhydrone electrode may be used for the determination of slightly alkaline  $p_H$ . At 38°, a progressive drift of the electrode in the direction of a more acid  $p_H$  was observed in determinations on serum or plasma. By extrapolation to zero time, an approximation to the true initial  $p_H$  was obtained. At 20° this drift was less marked. The quinhydrone electrode at 20° or 38° gave results on dog serum or plasma averaging 0.03  $p_H$  more acid than parallel determinations with a hydrogen electrode. Confirmation of Havard and Kerridge's results (*A.*, 1929, 1189) on the first acid change of shed blood has been obtained, using both the quinhydrone and hydrogen electrodes. G. F. MARRIAN.

**Erythrocyte and plasma catalase.** I, II. H. KUROKAWA (*Tohoku J. Exp. Med.*, 1930, **14**, 520—538).—Although the amount of catalase is decreased in post-hæmorrhagic anæmia it is not parallel to the blood-hæmoglobin. Catalase free from hæmoglobin is obtained by shaking a hæmoglobin solution with toluene or chloroform. Avian, amphibian, and mammalian blood-catalases differ in their effect on hydrogen peroxide. Plasma-catalase is unaffected by hunger, bleeding, intraperitoneal injection of blood, or ingestion of phosphorus; it is increased by intravascular hæmolysis or by chloroform or carbon tetrachloride poisoning. CHEMICAL ABSTRACTS.

**Influence of formaldehyde on the precipitation of serum-proteins.** M. MASCRÉ and M. HERBAIN (*Bull. Soc. Chim. biol.*, 1930, **12**, 978—993).—Sera of man, horse, bull, and heifer were treated with various deproteinising agents, viz., trichloroacetic acid, sodium sulphate, magnesium sulphate, acetone, and alcohol in the presence and in the absence of formaldehyde, the degree of deproteinisation being determined by measuring the quantity of nitrogen not precipitated. With all reagents the effect of the presence of formaldehyde is to decrease the quantity of unprecipitated nitrogen, the effect being least marked in the case of alcohol and negligible when boiling alcohol is used. W. O. KERMACK.

**Determination of blood-non-protein-nitrogen.** S. L. LEIBOFF (*J. Lab. Clin. Med.*, 1929, **15**, 155—157).—In the Koch-McMeekin method digestion is effected in flat-bottomed flasks on a sand-bath, and a correction is made for the nitrogen content of the hydrogen peroxide solution. CHEMICAL ABSTRACTS.

**Amino-nitrogen of human blood.** I—III. E. MILHEIRO (*Rev. Chim. pur. appl.*, 1928, **3**, 85—101, 164—181; 1929, **4**, 27—47; *Chem. Zentr.*, 1930, **i**, 2457, 2438).—Sources of error in the determination are discussed. In the absence of external influences the blood-amino-nitrogen is substantially constant for an

individual. The value, which is 42—70 mg. per litre in hunger, falls after meals, and is markedly diminished when the diet is low in nitrogen. The excretion of amino-nitrogen is unaffected by the quantity present in the blood. If the diet contains a sufficient quantity of protein the urinary amino-nitrogen increases during gastric digestion and diminishes during intestinal digestion; it increases during periods of activity. Corresponding, but reciprocal, variations in the urinary ammonia are observed. Apparently the blood-amino-nitrogen is the precursor of urinary ammonia. A. A. ELDRIDGE.

**Alleged presence of bile salts in normal blood.** E. WALKER (*Biochem. J.*, 1930, **24**, 1489—1492).—The positive Pettenkofer reaction obtained with alcoholic extracts of blood is due to cholesteryl oleate. The presence of bile salts in normal blood (ox and sheep) cannot be demonstrated. Cholesteryl oleate is present in human blood. S. S. ZILVA.

**Detection of bile acids in blood.** M. JENKE and F. STEINBERG (*Arch. exp. Path. Pharm.*, 1930, **153**, 244—256).—The application of the Pettenkofer reaction in the detection and determination of bile salts in blood was examined and the limits of its applicability were determined. In healthy men bile salts were not found in a concentration greater than 0.025 mg. per 100 c.c., but in certain icteric patients the concentration of bile salts may reach 2—8 mg. per 100 c.c. Bile acids can also be detected in the blood of dogs after injection of cholic acid. W. O. KERMACK.

**Effect of diet on the bile pigment of the blood.** H. JACOBY (*Klin. Woch.*, 1930, **9**, 307—308; *Chem. Zentr.*, 1930, **i**, 2439).—Egg-yolk markedly increases the blood-bilirubin. A. A. ELDRIDGE.

**Serum-cholesterol.** L. BUGNARD (*Compt. rend. Soc. Biol.*, 1929, **102**, 291—293; *Chem. Zentr.*, 1930, **i**, 2578).—The serum-cholesterol of dog's blood collected and clotted in absence of air is greater than that of the corresponding plasma by 0.42 mg. per 100 c.c., whilst the difference with preparations made in presence of air is 0.30 mg. Corresponding values for human blood were 0.40 and 0.30. A. A. ELDRIDGE.

**State of solution of cholesterol in blood-serum.** I. Artificial mixtures of lipin and protein. II. Extractability of cholesterol from blood-serum by alcohol and a method of determination of free and esterified cholesterol. III. Relations between cholesterol and proteins. S. M. NEUSCHLOSZ (*Biochem. Z.*, 1930, **225**, 115—122, 123—129; 130—140).—I. The solubility of cholesterol in aqueous solutions of albumin and lecithin increases with increasing concentration of both substances, but the influence of the albumin is somewhat decreased by the presence of lecithin and inversely. The extractability of lecithin from the aqueous mixture with ether decreases with increasing concentration of albumin and increases with increasing concentration of lecithin. The adsorbability of cholesterol on animal charcoal depends only on the albumin concentration, increasing as this decreases, and is unaffected by the lecithin concentration.

II. By precipitation of a given amount of serum

with at least nineteen times its volume of alcohol, the filtrate contains practically all the cholesterol, the deviations from that present in the serum being not greater than 5%. A colorimetric method of determining cholesterol, based on this fact, is described and modified to give separate determinations of free and esterified cholesterol.

III. The protein-cholesterol complex of Troensegaard and Kondahl (A., 1926, 634, 1166) cannot be detected when the serum is precipitated with alcohol, but only when deproteinisation is effected by a reagent in which the lipin is insoluble. Fixation of cholesterol occurs when an artificial mixture of albumin and cholesterol is precipitated by saturated ammonium sulphate solution.

P. W. CLUTTERBUCK.

**Determination of cholesterol in blood.** J. ALLARDYCE (Canad. J. Res., 1930, 3, 115—119).—Consistent and satisfactory results are obtained by combining the method of Myers and Wardell (A., 1918, ii, 461) of drying the blood on plaster of Paris with the extraction procedure of Ling (A., 1928, 437) and colorimetric determination by the Liebermann-Burchard reaction.

R. K. CALLOW.

**Micro-determination of the total fat and lipin content of blood.** I. R. IWATSURA, M. MORIMOTO, and M. TAMURA (Biochem. Z., 1930, 224, 437—447).—The fat and lipin content of 20—40 mg. of blood is determined (as triolein) by extraction with alcohol and ether, oxidation with sulphuric and chromic acids, and iodometric determination of the excess of the latter (cf. Bang, A., 1919, ii, 85; Bloor, A., 1914, ii, 392). In calculating results allowance must be made for the presence in blood of oxidisable material other than fats and lipins.

W. MCCARTNEY.

**[Blood-]protein sugar.** H. BIERRY (Compt. rend. Soc. Biol., 1930, 101, 1066—1068; Chem. Zentr., 1930, i, 2440).—Plasma-protein affords, in addition to dextrose and *d*-mannose, a sugar which appears to be galactose.

A. A. ELDRIDGE.

**Factors which may influence the sugar content of the blood and urine.** E. M. WATSON (J. Lab. Clin. Med., 1929, 15, 234—238).—Increased alkalinity of morning urine is associated with an increase of urinary and blood-sugar.

CHEMICAL ABSTRACTS.

**"Unfermentable matter" in blood.** E. J. BIGWOOD and A. WUILLOT (Compt. rend. Soc. Biol., 1930, 103, 43—45; Chem. Zentr., 1930, i, 2752).—The value is unaffected by the quantity of yeast employed.

A. A. ELDRIDGE.

**Determination of reducing substances in blood with potassium ferricyanide.** H. L. BRYANT (J. Lab. Clin. Med., 1929, 14, 1082—1086).—The protein-free filtrate, obtained by Folin and Wu's method, is treated with a solution of potassium ferricyanide containing sodium carbonate, the excess of the former being determined iodometrically after precipitation of ferrocyanide with zinc sulphate.

CHEMICAL ABSTRACTS.

**Folin's micro-method for the determination of blood-sugar.** S. L. LEBOFF and D. KOPPEL (J. Lab. Clin. Med., 1929, 15, 151—154).—The method is slightly less accurate than Folin and Wu's macro-

method. A method for the purification of the gum arabic employed is described.

CHEMICAL ABSTRACTS.

**Micro-determination of blood-sugar.** R. J. PICKARD and L. F. PIERCE (J. Amer. Med. Assoc., 1930, 94, 1134).—In a micro-modification of the method of Folin and Wu 0.1—0.05 c.c. of blood is used; for 75—150 mg. of dextrose per 100 c.c. the average error is less than 2%.

CHEMICAL ABSTRACTS.

**Guinea-pig's blood.** B. TEICH (Compt. rend. Soc. Biol., 1929, 102, 151—153; Chem. Zentr., 1930, i, 2752).—The blood contained Ca 0.06—0.13, K 0.53—0.99, P 0.22—0.43 g. per litre; plasma alkali reserve 19.33—30.35 (young animals 33—65.2) vol.-% CO<sub>2</sub>; *p<sub>H</sub>* 7.36—7.39 (7.23—7.30); dry matter 14.09—22.61 g., and ash 1.22—1.95 g. per 100 c.c. of blood.

A. A. ELDRIDGE.

**Blood normals for cattle; some pathological values.** J. ALLARDYCE, R. H. FLEMING, and R. H. CLARK (Canad. J. Res., 1930, 3, 120—124).—The range of normal content of cholesterol, sugar, non-protein-, urea-, and amino-acid-nitrogen, creatine, creatinine, calcium, phosphate, and chloride in the blood of cattle is similar to that of man. A variation of cholesterol content with diet is observed. Cattle in various pathological conditions, in particular hæmaturia vesicalis ("red water"), gave, in general, normal values.

R. K. CALLOW.

**Determination of blood-chloride.** E. FÖLDES and H. TAUBER (J. Lab. Clin. Med., 1929, 15, 59—61).—The chloride content of deproteinised blood is determined by titration with silver nitrate.

CHEMICAL ABSTRACTS.

**Micro-determination of iodine in blood.** R. G. TURNER (J. Biol. Chem., 1930, 88, 497—511).—The blood (10 c.c.) is dried with potassium carbonate solution, and ashed in an atmosphere of oxygen, the residue is extracted with water, and to the extract are added saturated potassium sulphate and 10% barium chloride solutions. The supernatant fluid, after centrifuging the precipitate of barium sulphate, is decanted and evaporated to dryness and the residue extracted with absolute alcohol. The alcoholic extract is evaporated and ignited, and the residue extracted with 2 c.c. of water. The iodide in this solution is oxidised to iodate by bromine in the presence of sulphuric acid, and the blue colour produced by the addition of potassium iodide in the presence of starch is matched against a standard containing a known amount of iodine. It is claimed that quantities of iodine from 0.0005 to 0.005 mg. may be determined with an error of 10—15%.

G. F. MARRIAN.

**Determination of iodine in blood.** H. A. A. AITKEN (Biochem. J., 1930, 24, 1456—1459).—The titrimetric method is modified so that the titration is performed in a volume of about 0.2 c.c.—a concentration which ensures a deep blue colour with starch iodide and a definite end-point. The experimental error is about  $\pm 1\%$ .

S. S. ZILVA.

**Use of sodium citrate as anticoagulant in the chemical examination of blood.** S. L. LEBOFF and I. S. WITCHELL (J. Lab. Clin. Med., 1929, 14,

1094—1096).—The use of sodium citrate is admissible in determinations of non-protein-nitrogen, urea-nitrogen, uric acid (for which it is preferred to potassium oxalate), creatinine, and sugar.

#### CHEMICAL ABSTRACTS.

**Glycogen of mammalian muscle and its behaviour after death.** I. A. ANDERSON and J. J. R. MACLEOD (Biochem. J., 1930, 24, 1408—1420).—In rabbits killed by chloroform or in decapitated cats corresponding muscles of opposite sides do not necessarily contain equal percentages of glycogen, although the averages of three corresponding muscles on each side usually agree. In rats killed by spinal transection with a cleaver the two hind-limbs contain equal percentages of glycogen. The glycogen of intact mammalian muscle does not appreciably diminish when the muscle is kept for 1 hr. at the ordinary temperature after death. Lactic acid accumulates under the foregoing conditions. When the muscle is killed a reaction leading to the disappearance of glycogen is stimulated and the *post-mortem* increase of lactic acid is usually out of proportion to any decrease in glycogen. S. S. ZILVA.

**Effect of freezing in a concentrated solution of sodium chloride on the colour of red muscle.** J. BROOKS (Biochem. J., 1930, 24, 1379—1383).—In brine-freezing the sodium chloride penetrates the tissue and influences the oxidation of hæmoglobin to methæmoglobin by increasing the rate of oxidation and by increasing the depth of the superficial layer of tissue in which oxidation is possible. S. S. ZILVA.

**Frozen state in mammalian muscle.** T. MORAN (Proc. Roy. Soc., 1930, B, 107, 182—187).—Dilatometric measurements of the amount of ice present in mammalian muscle when frozen to equilibrium between  $-1.5^{\circ}$  and  $-20^{\circ}$  indicate that there is not more than 6% of "bound water" in the muscle. C. C. N. VASS.

**Glutathione content of muscles and other organs and tissues, especially of rabbits.** T. MATSUMORI and M. OKUDA (J. Biochem. Japan, 1930, 11, 407—414).—The glutathione content of red muscle is greater than that of white skeletal muscle. Of other organs the adrenals contain most, and blood least, glutathione.

#### CHEMICAL ABSTRACTS.

**Distribution of nitrogen in the muscles of various species of animals. II. Rays and sharks.** R. KAPPELLER-ADLER and J. KRAEL (Biochem. Z., 1930, 224, 364—377; cf. this vol., 1056).—The muscle of sea fish contains considerably more betaine than does that of fresh-water fish. Trimethylamine oxide is probably one of the most important end-products of the metabolism of sea fish, in the urine of which it may be the chief constituent (cf. Grollman, A., 1929, 464). Methylamine is also present in appreciable amounts in the muscle of sea fish. Since rapid changes occur in dead fish, results obtained immediately after death may differ greatly from those obtained later (cf. Hoppe-Seyler and Schmidt, A., 1928, 195). W. MCCARTNEY.

**Amino-acids of tissues. IV. Diamino-acid content of muscle tissue of different classes of animals.** J. L. ROSEDALE and J. P. MORRIS. V.

**Monoamino-acids of the horse mackerel (*Caranx rotti*).** J. L. ROSEDALE and C. J. OLIVEIRO (Biochem. J., 1930, 24, 1294—1296, 1297—1300).—IV. Tissues of the crocodile, cockroach, mosquito larvæ (*A. ludlowi*), oysters, and sponge (Monaxonids) have been analysed by Van Slyke's method. An increase in the amount of histidine-nitrogen and a decrease of lysine-nitrogen is found in the lower organisms.

V. Tyrosine, glutamic acid, aspartic acid, leucine, and proline were isolated. S. S. ZILVA.

**Determination of carbamide in *Selachii*.** B. KISCH (Biochem. Z., 1930, 225, 197—207).—The carbamide contents of the blood, urine, cerebrospinal fluid, the fluids of the auditory organ, the aqueous humour, pericardial and perivisceral fluids, bile, heart-muscle, body-muscle, electric organ, and spleen of a number of *Selachii* are determined.

P. W. CLUTTERBUCK.

**Detection of phosphagen in the electric organ of *Torpedo*.** B. KISCH (Biochem. Z., 1930, 225, 183—192).—The electric organ of *Torpedo* contains about the same amount of creatine as the musculature. With the fresh unstimulated organ, 77% of the phosphorus of the acid extract is present as phosphagen. During activity of the organ and during asphyxiation the amount of phosphagen rapidly diminishes, resynthesis occurring during rest in presence of oxygen. The organ contains a second phosphorus compound which is determined colorimetrically as phosphagen.

P. W. CLUTTERBUCK.

**Tryptophan content of the adrenals.** P. GRETSCHEV (Russ. J. Physiol., 1930, 12, 321—329).—Extracts of fresh adrenals contain 2.9 mg. of tryptophan per 100 g. of fresh tissue. W. O. KERMACK.

**Acetylcholine and choline from animal organs. I. Preparation from ox-blood.** J. KAPFHAMMER and C. BISCHOFF (Z. physiol. Chem., 1930, 191, 179—182).—With the aid of Reinecke acid as precipitant, acetylcholine was isolated from ox-blood in a yield of 28.8 mg. per litre. On conversion into the gold salt some decomposition to free choline occurred.

J. H. BIRKINSHAW.

**Nuclein metabolism. XXV. Specificity of Dische's colour reactions with diphenylamine and carbazole on the purine- and pyrimidine-nucleosides of thymus-nucleic acid.** M. ANGERMANN and F. BIELSCHOVSKY (Z. physiol. Chem., 1930, 191, 123—125; cf. this vol., 1218).—The difference in the colour reactions shown by purine- and pyrimidine-nucleosides is due to the fact that the pyrimidine linking is much more stable than that of the purine bases. There is no evidence of a difference in the combined carbohydrate; the value of the reaction lies in its power of distinguishing between yeast- and thymus-nucleic acids and their degradation products.

J. H. BIRKINSHAW.

**Nature and origin of ovarian lipins.** E. PREISSECKER (Zentr. Gynäkol., 1928, 2740—2743; Chem. Zentr., 1930, i, 2435).—The lipins (in rats) appear unconnected with the hormones; they do not take part in fat metabolism. A. A. ELDRIDGE.



**Fatty acids in the liver of the sheep.** K. TURNER (Biochem. J., 1930, 24, 1327—1336).—Oxidation of the ethyl esters of the fatty acids by Armstrong and Hilditch's method (A., 1925, i, 355) yielded a mixture of nonoic and hexoic acids. Oxidation of the mixed fatty acids with hydrogen peroxide (cf. Hilditch, A., 1926, 938) gave rise to dihydroxystearic acid, but not to tetrahydroxystearic acid. Dilute alkaline permanganate, however, produces a mixture of both these acids. The oleic acid present is the  $\Delta^4$ -modification. Linoleic acid and arachidonic acid are also present, but linolenic acid was not found.

S. S. ZILVA.

**Value of Smith's method [of staining] with Nile-blue sulphate in differentiation of neutral fats from the corresponding fatty acids and soaps.** F. LEINATI (Arch. Ist. Biochim. Ital., 1930, 2, 447—456).—Sections of tissue in which traumatic liponecrosis has occurred show, when stained by Smith's method, foci round which gradations of colour from the rose-red given by healthy tissue through lilac and violet to blue are observed. The changes in appearance with duration of the necrosis are concordant with the assumption that the gradation of colour is parallel with the disintegration of the original neutral fat into fatty acids and soaps. Fixation in dilute alcohol or formaldehyde does not seem to influence the coloration.

R. K. CALLOW.

**Plasmalogen. II. Preparation of plasmal; hydrolysis of plasmalthiosemicarbazone.** M. BEHRENS (Z. physiol. Chem., 1930, 191, 183—186; cf. A., 1929, 342).—The plasmalogen is hydrolysed by acid and the plasmal converted into thiosemicarbazone after neutralisation. The water is removed under reduced pressure, the residue dissolved in a mixture of alcohol and ether, and the thiosemicarbazone precipitated with alcoholic silver nitrate. The silver compounds are purified by dissolution in ether and reprecipitation with alcohol, decomposed by hydrogen sulphide, and the thiosemicarbazone is recrystallised from xylene and alcohol. Free plasmal is obtained by dissolving the thiosemicarbazone in alcohol and adding the solution in small portions to boiling dilute sulphuric acid through which a current of steam passes to carry off the plasmal.

J. H. BIRKINSHAW.

**Chemical constitution of aqueous humour of the dog.** A. C. KRAUSE and A. M. YUDKIN (J. Biol. Chem., 1930, 88, 471—477).—Analyses of the aqueous humour under cocaine local anaesthesia gave the following average results:  $n$  1.33504,  $CO_2$  60.2 vol.-%, NaCl 617, inorganic sulphate as S 0.35, inorganic phosphate as  $P_2O_5$  1.1, total nitrogen 40, non-protein-nitrogen 24, urea-nitrogen 12, amino-acid-nitrogen 9, and creatinine 1.7 mg. per 100 c.c. Amytal or ether anaesthesia caused no change in refractive index, creatinine, sodium chloride, total nitrogen, or non-protein-nitrogen. Ether anaesthesia greatly increased the dextrose content. High refractive indices and low dextrose values were shown by aqueous humour obtained from dogs that had died some hours before. A comparison of aqueous humour with cerebrospinal fluid and venous blood from dogs under amytil anaesthesia showed that the two former have nearly

the same composition. Cerebrospinal fluid contained less sodium chloride than aqueous humour or venous blood, and the last-named contained less non-protein-nitrogen than the first two.

G. F. MARRIAN.

**Microchemical studies on the nervous system.**

**III. Water and phosphorus compounds of the nerve during degeneration.** R. MAY (Bull. Soc. Chim. biol., 1930, 12, 934—953).—During the first month of degeneration the water content increases until it reaches 14% above normal, then it decreases slowly until it reaches about 64—67% of its normal value. The total phosphorus decreases during the first two months until it reaches one third of its normal value; the phosphatide fraction showing the greatest decrease reaches one sixth of its normal value in 100 days, whilst the alcohol-soluble fraction ultimately falls to one third of its normal value. The protein-nitrogen rises during the first few days and then falls to one third of its normal value. The water-soluble phosphorus shows an increase of 25% during the first few days and of 35% in 6 months.

W. O. KERMACK.

**Block staining of nervous tissue with silver.**

H. A. DAVENPORT (Stain Tech., 1930, 5, 139—147).—Cat's spinal chord was stained by Cajal's technique with variations made to determine the optimum concentration of ammonia in alcohol for fixing, and the value of mixtures of alcohol and chloroform or alcohol and pyridine.

*Post-mortem* autolysis of 5 hrs.' duration caused no change in the staining of fibres.

H. W. DUDLEY.

**Frozen section technique.** E. G. MILLER (J. Roy. Micros. Soc., 1930, [iii], 50, 302—306).—Details of methods of cutting, mounting, and staining frozen sections are given.

C. W. GIBBY.

**Copper content of infant livers.** D. B. MORRISON and T. P. NASH (J. Biol. Chem., 1930, 88, 479—483).—The average copper content of the livers from 25 children up to the age of 2 years was 24.0 mg. per kg. of fresh tissue. The average for 7 white children was 17.3 mg., and for 17 negro children, 26.6 mg. The average copper content of 7 adult negroes was 4.0 mg. per kg. Two of the lowest individual values (one child and one adult) were associated with severe anaemia.

G. F. MARRIAN.

**Detection of fluorine in bones.** J. CASARES and R. CASARES (Anal. Fis. Quím., 1930, 28, 910—915).—Traces of fluorine in substances such as bone may be detected by treating the calcined material with sulphuric acid and powdered glass and a small quantity of silver sulphate in a porcelain basin covered with a watch-glass supporting a drop of barium acetate solution acidified with acetic acid. A film of hydrated silica or crystalline barium fluosilicate is formed if traces of fluorine are evolved. Examination by this method of various specimens of bone indicates that fluorine does not exist either in the teeth or bones of young animals, but is present in increasing quantity as the animal grows older. Considerable quantities exist in marine products such as coral.

H. F. GILLBE.

**Determination of small amounts of silicon and calcium in the lungs.** A. G. KROESE and F. J.

NIEUWENHUYZEN (Biochem. Z., 1930, 225, 208—211).—A method for the determination of calcium and silicon in large amounts of organic substances is described, the material being ashed in a nickel flask in a stream of oxygen at 300—350°.

P. W. CLUTTERBUCK.

**Mineral metabolism in infancy. I. Mineral constituents of human milk and cow's milk.** S. V. TELFER (Glasgow Med. J., 1930, 113, 246—256).—Values, respectively, are: CaO 0.045, 0.16; MgO 0.006, 0.018; P<sub>2</sub>O<sub>5</sub> 0.048, 0.21; Fe 0.0001, 0.00008%. The milk of under-nourished women is low in iron and phosphorus.

CHEMICAL ABSTRACTS.

**Utilisation of pentoses by the animal organism. Effect of intravenous injection of pentoses on the secretion of lactose. I. I. NITZESCU and M. BENETATO** (Compt. rend. Soc. Biol., 1930, 102, 1119—1122; Chem. Zentr., 1930, i, 2757).—Injection of dextrose, but not of sucrose, into ewes increased the lactose content of the milk; the same effect was produced, but less markedly, by xylose, rhamnose, and arabinose.

A. A. ELDRIDGE.

**Influence of formaldehyde on the precipitation of the proteins of milk.** M. MASCRÉ and E. BOUCHARA (Bull. Soc. Chim. biol., 1930, 12, 994—1000).—The effect of various concentrations of formaldehyde on the precipitation of milk-proteins by acetic acid and trichloroacetic acid has been studied, the extent of precipitation being determined by measuring the non-precipitated nitrogen. The general effect of the formaldehyde is to render the precipitation of the proteins more complete and less reversible. The precipitation by trichloroacetic acid is more complete than by acetic acid, but the difference tends to decrease with increase in concentration of formaldehyde.

W. O. KERMACK.

**Effect of milk feeding on secretion of gastric juice.** G. N. POKROVSKI (Russ. J. Physiol., 1930, 12, 331—347).—From experiments on dogs with a stomach pouch it is concluded that milk contains a substance stimulating the secretory activity of the gastric glands. The substance is thermostabile, and is soluble in 96% alcohol, water, and ether, but not in absolute alcohol.

W. O. KERMACK.

**Micro-determination of pepsin in gastric juice.** S. M. DIONESOV (Russ. J. Physiol., 1930, 13, 547—555).—A micro-modification of Volhard's method (Münch. med. Woch., 1903, No. 49) is sufficiently accurate for dilutions of 1:8500, and the formulæ deduced by him still hold for small quantities of juice.

P. G. MARSHALL.

**Pigment of cocoon silk of silkworm. I. Xanthophyll.** M. OKU (J. Agric. Chem. Soc. Japan, 1930, 6, 40—49).—Xanthophyll was extracted with difficulty; physico-chemical combination with sericin is postulated.

CHEMICAL ABSTRACTS.

**Poisons of the Japanese toad. IV.** H. WIELAND and F. VOCKE (Annalen, 1930, 481, 215—232; cf. Wieland and Alles, A., 1922, i, 784).—Concentration of the cold methylated spirit extract of the skins of the Japanese toad yields first cholesterol, and then a small quantity of *bufothionine*, C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>N<sub>2</sub>S,

m. p. 250° (decomp.; darkens at 240°), which is a weak base and is unchanged by catalytic reduction or by heating with *N*-sodium hydroxide. Hydrolysis with *N*-hydrochloric acid, however, causes fission of the sulphur as sulphuric acid and yields the *hydrochloride*, m. p. 242° (decomp.), of a strong base, C<sub>12</sub>H<sub>14</sub>ON<sub>2</sub> (*hydrogen sulphate*, m. p. 209°), which is auto-oxidisable in the air and forms a *nitrosoamine*, and hence one of the nitrogen atoms is secondary. From the petroleum extract of the residual resin from the original alcoholic extract is isolated, in small yield, *gamabufogenin*, C<sub>24</sub>H<sub>34</sub>O<sub>5</sub>, m. p. 254—255° (decomp.). When heated with acetic anhydride and sodium acetate at 100° this yields a *diacetyl* derivative, m. p. 251—252°, which is isomeric, but not identical, with acetylbufotalin (*loc. cit.*). Whilst the action of concentrated hydrochloric acid on bufotalin removes 1 mol. of acetic acid and 1 mol. of water, with gamabufogenin only 1 mol. of water is eliminated, forming *anhydrogamabufogenin*, m. p. about 260° (not sharp). Catalytic reduction of this using palladium-black in alcohol yields *anhydrotetrahydrogamabufogenin*, + EtOH, m. p. 130°, similar reduction of gamabufogenin itself giving *tetrahydrogamabufogenin* + EtOH, m. p. indef. about 138°. From the chloroform-insoluble portion from which gamabufogenin has been isolated is obtained the poison *gamabufotoxin*, C<sub>38</sub>H<sub>60</sub>O<sub>10</sub>N<sub>4</sub>, m. p. 210° (decomp.) (microscopic examination by STEINMETZ). This is hydrolysed by *N*-aqueous-alcoholic hydrogen chloride to anhydrogamabufogenin and suberylarginine, isolated as suberic acid and arginine after further hydrolysis. Shorter hydrolysis with 0.5*N*-aqueous-alcoholic hydrogen chloride affords another form + EtOH and solvent-free, m. p. 204°, of anhydrogamabufogenin, converted into the form of m. p. 260° by concentrated hydrochloric acid. The close similarity between gamabufotoxin (I) and bufotoxin (II) (which yields bufotalin on hydrolysis) is thus indicated: C<sub>38</sub>H<sub>60</sub>O<sub>10</sub>N<sub>4</sub>(I) → C<sub>24</sub>H<sub>32</sub>O<sub>4</sub> + C<sub>6</sub>H<sub>14</sub>O<sub>4</sub> (suberic acid) + C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub> (arginine), C<sub>40</sub>H<sub>62</sub>O<sub>11</sub>N<sub>4</sub>(II) → C<sub>24</sub>H<sub>30</sub>O<sub>3</sub> + AcOH + C<sub>6</sub>H<sub>14</sub>O<sub>4</sub> + C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>, and suggests the constitutions RO·CO·[CH<sub>2</sub>]<sub>6</sub>·CO·NH·CH(CO<sub>2</sub>H)·[CH<sub>2</sub>]<sub>3</sub>·NH·C:(NH)·NH<sub>2</sub> (I, R = C<sub>24</sub>H<sub>35</sub>O<sub>5</sub>; II, R = C<sub>26</sub>H<sub>37</sub>O<sub>6</sub>), the C<sub>26</sub> residue in R being an acetyl derivative of a similar but not identical C<sub>24</sub> residue in I. Similarly, comparison of bufotalin and gamabufogenin indicates that both are doubly unsaturated trihydroxylactones derived from one tetracyclic skeleton with 24 carbon atoms, but in bufotalin one hydroxyl group is acetylated, and the positions of the hydroxyl groups, and possibly also of the double linkings, are different in the two compounds.

J. W. BAKER.

**Xanthhydrol method of determination of carbamide in animal fluids.** B. KISCH (Biochem. Z., 1930, 225, 193—196).—Carbamide (0.5 mg.) added to perivisceral fluid (1 c.c.) is determined with an accuracy of 97—98%.

P. W. CLUTTERBUCK.

**Additive power of cholic acid.** S. MINOVICI and M. VANGHELOVICI.—See this vol., 1435.

**Bile pigments in relation to the van den Bergh reaction.** W. J. GRIFFITHS and G. KAYE (Biochem. J., 1930, 24, 1400—1407).—By extracting bile desiccated in a vacuum with chloroform, a pigment

can be obtained in the residue which yields a prompt direct van den Bergh reaction. This pigment is not bilirubin or one of its ordinary salts. Pure bilirubin when suspended in blood-serum does not give the direct reaction, although serum containing bilirubin gives the indirect reaction. The above pigment ("direct action" pigment) is present in those icteric sera which give a direct van den Bergh reaction.

S. S. ZILVA.

**Determination of the bile-acid content of urine.** G. A. SAMARIN and A. L. MYASNIKOV (Terap. Arch., 1929, 7, 799—810).—The fluorescence method is specific, and may be applied to a 24-hr. specimen.

#### CHEMICAL ABSTRACTS.

**Determination of uric acid [in urine].** O. SCHEWCKET (Biochem. Z., 1930, 224, 322—324).—Two methods are described. Urine containing more than 0.1% of protein must first have the protein removed and urine from which urates have been deposited must be heated until these dissolve and used while hot. In the first method magnesia mixture is added to the urine, the precipitate is collected, and ammoniacal silver nitrate solution is added to the filtrate. Purine bases are removed from the precipitate formed with sulphuric acid and the residue is boiled with sulphuric acid and titrated at once with 0.05*N*-potassium permanganate solution. According to the second method the urine is mixed with an equal volume of mercuric acetate solution. The precipitate is washed successively with dilute sulphuric acid, dilute potassium hydroxide solution, and water, and is either dissolved in concentrated sulphuric acid and titrated with potassium permanganate solution or is boiled with sodium sulphide solution, acidified with dilute sulphuric acid, and again filtered. The precipitate separated thus is washed, heated with concentrated sulphuric acid until hydrogen sulphide ceases to be evolved, cooled, and titrated as before. The second method gives the more accurate results.

W. MCCARTNEY.

**Urocarmine reaction.** W. R. FEARON and A. G. THOMPSON (Biochem. J., 1930, 24, 1371—1378).—*o*-Cresol indogenide (*o*-cresol urocarmine) was prepared by treating *o*-cresol with indoxyl and oxidising the resulting leuco-base with hydrogen peroxide. *Resorcinol indogenide* was prepared by a similar method; two isomerides were obtained, a stable carmine pigment and an unstable violet pigment. The urocarmine reaction accounts for many of the pigments obtained from urine which are insoluble in chloroform.

S. S. ZILVA.

**Pigment of urine. III. Extraction. IV. Properties.** D. L. DRABKIN (J. Biol. Chem., 1930, 88, 433—442, 443—448).—III. *iso*- and *n*-Butyl alcohols and *isobutylaldehyde* were found to be the most satisfactory solvents for the direct extraction of urochrome from urine. Extraction was complete at  $p_H$  4.3—3.9. At  $p_H$  above 4.5 the pigment was not extracted. Urochrome could be transferred to aqueous solution by extraction of the butyl-alcoholic solution with water at  $p_H$  above 7.5. The following method was adopted. Urine was acidified with acetic acid and shaken with *n*-butyl alcohol, the alcoholic extract was washed with water, concentrated, and then extracted successively with chloroform, benzene, and

ether to remove other pigments. By concentration of the butyl-alcoholic extract or by addition of anhydrous ether or alcohol, the pigment was obtained as a dry brown powder.

IV. Urochrome as prepared above was usually semi-crystalline. It was very soluble in hot or cold water, less soluble in dilute ethyl alcohol, and insoluble in absolute alcohol, ether, chloroform, benzene, or acetone. In ether-alcohol or alcohol-chloroform mixtures it was slightly soluble. After keeping in a vacuum desiccator for one year over concentrated sulphuric acid its solubility in cold water was lost. Urea and uric acid could not be detected, whilst spectroscopic examination gave no indication of the presence of carotene, bile pigments, urobilin, or hæmatoporphyrin. "Chromatographic analyses" (Tswett, Ber. deut. bot. Ges., 1906, 24, 316) indicated that the pigment was not a mixture. Urochrome gave negative biuret, negative nitroprusside, positive Millon, and faintly positive Adamkiewicz reactions. From aqueous solution at  $p_H$  9 it was precipitated by copper, iron, mercury, zinc, and silver salts. All except the silver precipitate were soluble in hydrochloric acid. The silver and copper salts were soluble in ammonia solution. At  $p_H$  3.8 it was precipitated by phosphotungstic or silicotungstic acid as a crystalline compound. Reduction with zinc dust and hydrochloric acid caused complete decolorisation. Partial decolorisation resulted from treatment with sodium hyposulphite, whilst hydrogen in the presence of a platinum catalyst had no effect. A colour of not quite the same tint was restored to decolorised solutions by keeping in air or by hydrogen peroxide. It is calculated that an adult man excretes about 73 mg. of the pigment per 24 hrs.

G. F. MARRIAN.

**Spectrophotometric determination of hæmatoporphyrin in urine.** C. SHEARD, A. E. OSTERBERG, and W. H. GOECKERMANN (J. Lab. Clin. Med., 1929, 15, 162—169).—The maximal absorption of alcoholic solutions of acetic acid precipitates of hæmatoporphyrin from urine occurs at 5550 Å. A method for the calculation of the amount of hæmatoporphyrin in urine in terms of the equivalent amount of blood is described.

#### CHEMICAL ABSTRACTS.

**Determination of total fatty acids in fæces.** E. GLASER and O. KÄHLER (Z. physiol. Chem., 1930, 191, 187—192).—The fæces ( $\frac{1}{3}$ —1 g. as dry material) are boiled with 5 c.c. of 20% aqueous potassium hydroxide solution for  $\frac{1}{2}$  hr., filtered after the addition of 15 c.c. of alcohol, the residue is washed with alcohol, and the filtrate evaporated. The evaporation residue is dissolved in water and the solution (10.5 c.c.) placed in a butyrometer tube and bleached by the addition of 10.5 c.c. of sulphuric acid and 0.05 g. of potassium chlorate. After shaking, 1 c.c. of amyl alcohol coloured with Sudan-red is added and the mixture centrifuged. The volume of total fatty acids is then read off.

J. H. BIRKINSHAW.

**Determination of small quantities of urobilinogen and urobilin in fæces.** O. FÜRTH and K. SINGER (Z. ges. exp. Med., 1929, 69, 152—158; Chem. Zentr., 1930, i, 2598).—The fæces (5 g.) are ground with water (50 c.c.) and treated with 50 c.c. of freshly prepared 16% ferric ammonium sulphate

solution followed, slowly, by 50 c.c. of 12% sodium hydroxide solution; the mixture is kept in a closed vessel in absence of air and light for at least 6 hrs. The filtrate (50 c.c.) is treated with acetic acid (20–30 c.c.) and then vigorously extracted with ether (20 c.c.) purified with sodium hydroxide. After repeated extraction with water the ethereal solution is treated with a little *p*-dimethylaminobenzaldehyde and 10 drops of 20% hydrochloric acid. After addition of 3 c.c. of concentrated sodium acetate solution a colorimetric comparison is made with freshly prepared alkaline phenolphthalein solution (1 c.c. of 0.05% alcoholic phenolphthalein and 5 c.c. of cold saturated sodium carbonate solution diluted to 100 c.c., corresponding with 0.4 mg. of urobilinogen per 100 c.c.).  
A. A. ELDRIDGE.

**Iron metabolism in pernicious and in secondary anæmia.** H. H. RIECKER and M. E. WINTERS (Arch. Int. Med., 1930, 46, 458–469).—The mean value of the iron content of blood-serum (from 40 normal individuals) is found to be  $1.1 \pm 0.022$  mg. per 100 c.c. Non-hæmoglobin-iron is increased in pernicious anæmia; in most of the cases examined, a return to normal levels follows liver-extract therapy and is accompanied by an increase in excretion over the intake of iron. In pernicious anæmia, hæmolysis of immature erythrocytes is suggested as the source of serum-iron in excess of normal. F. O. HOWITT.

**Composition of urinary calculi.** C. NEWCOMB (Indian J. Med. Res., 1930, 17, 1037–1054).—Vesical calculi usually consist of a mixture, of variable composition, of calcium oxalate, calcium and magnesium ammonium oxalate, protein, uric acid, and other substances. Kidney stones usually consist of oxalates.

CHEMICAL ABSTRACTS.

**Composition of urinary calculi in rats.** C. NEWCOMB and S. RANGANATHAN (Indian J. Med. Res., 1930, 17, 1055–1059).—Vesical calculi in rats consist almost entirely of magnesium ammonium phosphate, and very little calcium or oxalate.

CHEMICAL ABSTRACTS.

**Lactic acid and carcinoma of the stomach.** E. C. DODDS and J. D. ROBERTSON (Lancet, 1930, 218, 171–174).—Lactic acid occurs in non-malignant as well as in malignant diseases of the stomach. In seven cases, the acid has been isolated as the zinc salt and is inactive; it is produced by fermentation. The stomach mucosa and the carcinoma both appear to be incapable of producing the acid. Pyloric obstruction favours the production of lactic acid in all cases. The presence of this acid is of no diagnostic value in cases of carcinoma.  
L. S. THEOBALD.

**Reaction of the fluid of rat sarcoma 10.** L. C. MAXWELL and F. BISCHOFF (J. Pharm. Exp. Ther., 1930, 40, 1–5).—The acidity generally increases with the age of the tumour, but cannot be correlated with the rate of growth.  
F. O. HOWITT.

**Parathyroid tumour and changes of the bones.** I. SNAPPER (Arch. Int. Med., 1930, 46, 506–523).—In a case of pseudo-osteomalacia extreme decalcification of the bones and a high calcium content of the serum were associated with an adenoma of a parathyroid gland. Extirpation of the tumour re-

sulted in a rapid disappearance of the hypercalcaemia and eventual clinical recovery.  
F. O. HOWITT.

**Metabolism of normal and tumour tissue. II. Respiratory quotient and the relationship of respiration to glycolysis.** F. DICKENS and F. ŠIMER (Biochem. J., 1930, 24, 1301–1326).—In all cases the normal foodstuffs are consumed in the process of respiration without appreciable interconversion of one form into another. Only highly glycolysing normal tissues such as brain, retina, chorion, and embryo have a carbohydrate quotient. Normal tissues with low glycolytic power consume largely noncarbohydrate material, presumably fat. Submaxillary, spleen, and testes form an intermediate group both in glycolysis and value of respiratory quotient. All the tumours had a respiratory quotient definitely below the carbohydrate level in spite of their very marked ability to convert dextrose into lactic acid. Tumour tissue does not utilise added lactic acid and differs in this respect from normal tissue having a similar value of respiratory quotient. Tumour tissues and normal tissues can utilise pyruvic acid freely in their oxidative metabolism. Fluoride inhibits oxidative as well as glycolytic decomposition of carbohydrate. Fluoride does not affect the respiratory quotient or respiration of normal tissues (rat testis) in the presence of an adequate supply of lactate.  
S. S. ZILVA.

**Avitaminosis-B in relation to tumour growth.** E. GILROY (Biochem. J., 1930, 24, 1384–1389).—The growth of a transplantable tumour in mice on a diet deficient in vitamin-B is affected only if the general health of the animals is impaired. The arginine content of caseinogen is not reduced by the process employed in the destruction of the vitamin-B complex. Arginine may exert a toxic effect in mice on a vitamin-B-deficient diet. If wheat germ and yeast are added to such a diet the effect of arginine injections is detrimental only in the case of males.  
S. S. ZILVA.

**Experimental yellow fever in *Macacus rhesus*. II. Nitrogen metabolism.** A. M. WAKEMAN and C. A. MORRELL (Arch. Int. Med., 1930, 46, 382–401).—The changes in the non-protein-nitrogen of the blood and urine are followed. The uricolytic function is not seriously altered and creatinine excretion is remarkably constant. Blood-creatinine, -uric acid, and -ammonia experience little change, whilst the urinary ammonia increases at the expense of urea-nitrogen coincidentally with larger excretions of organic acids and phosphorus in the urine. These changes, which take place only during the terminal stages of the disease, are interpreted as resulting from loss of liver function.  
F. O. HOWITT.

**Urinary urobilinogen.** G. F. SHTYKALEVA (Kazan. Med. J., 1930, 26, 137–143).—In infectious disease the urinary urobilinogen is high. Women give higher values than men, and adults than children.

CHEMICAL ABSTRACTS.

**Congestive heart failure. II. Respiratory exchange during and after exercise.** T. R. HARRISON and C. PILCHER. **III. Buffering power of blood and tissues.** C. PILCHER, G. CLARK, and T. R. HARRISON. **IV. Potassium content of**

**skeletal and cardiac muscle.** T. R. HARRISON, C. PILCHER, and G. EWING (J. Clin. Invest., 1930, 8, 291—315, 317—323, 325—335).—Only in severe heart failure are the  $p_{H}$  and carbon dioxide content of the blood abnormal. The potassium content of skeletal and cardiac muscle is low before death with oedema.

CHEMICAL ABSTRACTS.

**Increase in blood-uric acid in patients with cardiac decompensation.** J. L. WILLIAMS (J. Lab. Clin. Med., 1929, 15, 13—17).—Cardiac decompensation without nephritis may be associated with a rise in blood-uric acid, -urea, and -non-protein nitrogen.

CHEMICAL ABSTRACTS.

**Retention nephritis.** J. R. NAKADA (J. Lab. Clin. Med., 1929, 14, 1077—1081).—Renal damage is usually indicated by more than 5 mg. P and 50 mg. of non-protein-nitrogen per 100 c.c. of blood.

CHEMICAL ABSTRACTS.

**Relationship between the density and protein content of the plasma and oedema in nephritis.** N. S. MOORE and D. D. VAN SLYKE (J. Clin. Invest., 1930, 8, 337—355).—A linear relationship exists between the density and protein content of the plasma in normal and nephritic blood. Exceptions to the relation between plasma-protein deficit and oedema are recorded.

CHEMICAL ABSTRACTS.

**Lactic acid metabolism in the muscles in cases of kidney damage.** K. KIMURA (Tôhoku J. Exp. Med., 1930, 15, 153—176).—After nephrectomy there is a marked change in muscle activity. In the resting state the blood-lactic acid is higher, and there is less difference than normally between arterial and venous blood. In activity there is a less marked increase in the blood-lactic acid and in oxygen consumption; the muscle-sugar decreases only slightly. Similar retardation of the resynthesis of lactic acid is occasioned by tying the ureters or by poisoning the kidneys with cantharidin.

CHEMICAL ABSTRACTS.

**Phosphorus content of the cerebrum and cerebellum in parathyroid- and thyroparathyroid-ectomised dogs.** C. I. PARHON and G. WERNER (Compt. rend. Soc. Biol., 1930, 103, 455—456; Chem. Zentr., 1930 i, 2577).—Values (%) for normal and deficient dogs were, respectively: brain, 0.24—0.3, 0.11—0.18; cerebellum, 0.145—0.215, 0.13—0.312.

A. A. ELDRIDGE.

**Urinary pentose in chronic pentosuria.** P. HÁRI (Biochem. Z., 1930, 224, 474—480; cf. Levene and La Forge, A., 1914, i, 1027).—The sugar obtained from the urine of five persons suffering from chronic pentosuria probably belonged to the xylose group.

W. MCCARTNEY.

(a) **Alkali-reserve in psychoneurotic children.**  
(b) **Relationship between ammonia content and free acidity of the urine of psychoneurotic children.** G. D. OBRASOV (Russ. J. Physiol., 1930, 13, 570—575, 576—584).—(a) The alkali reserve is raised and there appears to be some relationship between it and the blood-calcium.

(b) Hasselbalch's observations on the relationship between  $p_{H}$  and ammonia content of urine are not confirmed. There is a disturbance of liver function which is manifested in the regulation of the acid-base

equilibrium at the expense of the nitrogen metabolism.

P. G. MARSHALL.

(a) **Magnesium in the blood of psychoneurotic children.** (b) **Potassium and calcium in the blood of psychoneurotic children.** M. P. KALLI-NIKOVA (Russ. J. Physiol., 1930, 13, 602—605, 606—611).—(a) The blood-magnesium falls within normal limits and there is an increase in the calcium : magnesium ratio.

(b) The blood-potassium of psychoneurotic children is lower than in normal individuals and is subject to greater fluctuations in common with the blood-calcium.

P. G. MARSHALL.

**Experimental rickets. I. Influence of ultra-violet rays on mineral metabolism and composition of bone.** F. ROGOZIŃSKI and M. STARZEWSKA (Bull. Acad. Polonaise, 1930, B, 157—178).—Irradiation of the animals increases the retention of both calcium and phosphorus by rats on a rachitogenic diet. Excretion of both calcium and phosphorus in the faeces is diminished, but excretion of calcium in the urine is increased. The magnesium balance is unaffected. The ash content of the bone is increased by irradiation. The proportion of calcium in the ash is the same for rachitic and normal rats, but the proportion of phosphorus is less in the case of rachitic rats, as found by Chick *et al.* (A., 1927, 176).

R. K. CALLOW.

**Chemical study of sclerema neonatorum.** T. CHEN (Nat. Med. J. China, 1930, 16, 360—364).—The fat extracted from the skin of babies dying of sclerema shows no significant deviation from that of normal infantile cadavers in m. p., or in iodine, acetyl, and saponification values. The calcium and phosphorus contents of the fat-free tissues of the normal and sclerema infants are also without significant differences.

F. O. HOWITT.

**Distribution of iron in the organism after splenectomy.** E. CHANTEL (Arch. Ist. Biochim. Ital., 1930, 2, 457—466).—In splenectomised dogs there is a diminution of the iron content of the blood and an increase of that of the liver and kidneys, but the values return to normal after 3—4 months. Other definite effects are a decrease in the erythrocyte count and an increase in the leucocyte count, both of which return to normal after a short time.

R. K. CALLOW.

**Tetany. III. Blood serum-calcium and -phosphorus in hyperventilation tetany with adrenaline or ergotamine.** G. POPOVICIU and H. POPESCU (Z. ges. exp. Med., 1929, 69, 1—13; Chem. Zentr., 1930, i, 2436).

**Blood chemistry in trypanosome infection.** R. W. LINTON (J. Exp. Med., 1930, 52, 103—111).—Infection with *T. equiperdum* causes acidosis which reduces the carbon dioxide capacity of the blood; there is also terminal kidney degeneration resulting in increase of the non-protein-nitrogen and uric acid of the blood.

E. BOYLAND.

**Modifications of the acid-base equilibrium and of ionised calcium in the blood in tuberculosis.** B. V. FUENTES, P. RECARTE, and J. ESCULIES (Rev. Asoc. med. Argentina, 1929, 42, 645—659).—In

pulmonary or cutaneous tuberculosis the  $p_H$  remains normal; the carbon dioxide content varies between 51.3 and 65.3 vol.-%. The serum-total calcium, -ionised calcium, and -inorganic phosphorus are unchanged.

CHEMICAL ABSTRACTS.

**Distribution of total non-protein-nitrogen in experimental uræmia.** B. V. FUENTES, J. DUOMARCO, and A. MUNILLA (Rev. Asoc. med. Argentina, 1929, **42**, 423—431).—In uræmia produced in dogs by bilateral nephrectomy or by ligation of both ureters the creatinine and uric acid progressively increased, whilst in that produced by intravenous injection of urea such increases were not observed. The amino-nitrogen did not increase in experimental or clinical uræmia.

CHEMICAL ABSTRACTS.

**Excretion of oxalic acid in pathological conditions.** G. GARRY and M. PUFFELES (Biochem. Z., 1930, **224**, 331—336).—The urine of diseased persons often contains much more oxalic acid than that of healthy persons. Increase in the amount of oxalic acid excreted also occurs in healthy persons following vigorous muscular activity. Possible causes of the increases are considered.

W. MCCARTNEY.

**Behaviour of bound sugar in the incubated hen's egg.** J. SAGARA (J. Biochem. Japan, 1930, **11**, 433—436).—The bound sugar decreases continuously, and the free sugar up to the 20th day. At the 7th and 10th days the bound sugar of the white increases, whilst that of the yolk decreases.

CHEMICAL ABSTRACTS.

**Action of gymnastic exercises on the gas exchange, heart, vascular system, and blood.** V. A. VOLSCHINSKI, G. S. GAHN, and A. N. KRESTOVNIKOV (Russ. J. Physiol., 1930, **13**, 352—373).—The exercises increase the gas exchange, pulse, vascular activity as measured by the blood-pressure, and amount of hæmoglobin and leucocytes, and effect changes in the nature of the formed elements of the blood. The increase in the gas exchange is directly proportional to the musculature employed in each exercise. The further increased respiratory coefficient after cessation of exercise suggests a definite after-effect.

C. C. N. VASS.

**Modification of the dextrose tolerance test as an index of metabolic activity of the liver.** T. L. ALTHAUSEN, L. GUNTHER, J. B. LAGEN, and W. J. KERR (Arch. Int. Med., 1930, **46**, 482—493).—As a functional test of hepatic efficiency insulin (20 units) is administered to the fasting patient followed 20 min. later by 50 g. of dextrose in 500 c.c. of water and 1000 c.c. of water by mouth. A terminal hypoglycæmia indicated by the blood-sugar-time curve is interpreted as indicating hepatic insufficiency. The influence of various diseases on the response to the test, its limitations, and the physiological basis of the method are discussed.

F. O. HOWITT.

**Liver-chemistry during inanition.** L. VAUDIN, and M. JAVILLIER [with H. ALLAIRE and M. SCHIRMER] (Bull. Soc. Chim. biol., 1930, **12**, 894—902).—Analyses have been made of the livers of two dogs the weight of which was originally approximately equal, after the one had been starved for 18 days, whilst the other was on a normal diet. The liver of

the starved animal was deficient chiefly in carbohydrate, inorganic salts, and in the true fats. Lecithin and cholesterol are less depleted, protein and nucleoprotein still less, whilst unsaponifiable compounds other than cholesterol are relatively little changed.

W. O. KERMAK.

**Rôle of the liver reticuloendothelium in the resynthesis of lactic acid.** E. O. GAESSLER (Z. ges. exp. Med., 1929, **69**, 105—112; Chem. Zentr., 1930, i, 2444).—If the liver reticuloendothelium is blocked the fall in blood-lactic acid, following the rise after intravenous injection of the acid, is slower than normally.

A. A. ELDRIDGE.

**Metabolism of animals on a carbohydrate-free diet. I. Distribution of glycogen and fat in the liver.** A. HYND and D. L. ROTTER (Biochem. J., 1930, **24**, 1390—1399).—In rats on a carbohydrate-free diet the blood-sugar tends to be high, there is practically no change in the muscle-glycogen but a large increase in the liver-fat content, and the liver-glycogen is reduced to half that on a carbohydrate diet. Mice yield similar results. With kittens only slight differences are detected on the two types of diet. The fasting of rats for a period of 12—24 hrs. causes a very rapid disappearance of the excess of fat from the liver, a slow fall in both muscle- and liver-glycogen, and a fall in blood-sugar to the normal fasting level of 0.11—0.12%.

S. S. ZILVA.

**Quantitative conversion of uric acid into allantoin in the horse's liver.** R. FOSSE, A. BRUNEL, and P. DE GRAEVE (Compt. rend. Soc. Biol., 1930, **103**, 67—70; Chem. Zentr., 1930, i, 2583).—Theoretical conversion ( $\pm 1\%$ ) was observed.

A. A. ELDRIDGE.

**Formation of ornithuric acid in the rabbit.** J. J. SAGARA (J. Biochem. Japan, 1930, **11**, 427—431).—The rabbit cannot synthesise ornithuric acid from benzoic acid or ornithine, but injected ornithuric acid is decomposed to a small extent by the liver and kidney.

CHEMICAL ABSTRACTS.

**Specific dynamic action of alanine.** E. AUBEL (Biochem. Z., 1930, **225**, 81—93).—The view that the specific dynamic action of alanine may be explained in terms of its conversion into dextrose is supported by a series of heat and respiratory measurements on frogs which, after reduction to a constant respiratory exchange by starvation, received known amounts of alanine, sodium pyruvate, and lactate.

P. W. CLUTTERBUCK.

**I. Cystine deficiency of the proteins of peas and potatoes. II. Relationship between deficiency and growth of hair.** J. R. BEADLES, W. W. BRAMAN, and H. H. MITCHELL (J. Biol. Chem., 1930, **88**, 615—622, 623—627).—I. Feeding experiments on rats showed that the proteins of fresh garden peas and potatoes are deficient in cystine.

II. The rats used in these experiments which were receiving added cystine grew a greater weight of hair per unit body-surface than the controls on the cystine-deficient diets.

G. F. MARRIAN.

**Digestion. Efficiency with various foods and under various conditions.** J. H. CHILDREY, W. C. ALVAREZ, and F. C. MANN (Arch. Int. Med., 1930, **46**,



361—374).—The amount of faecal residue after digestion of various foods is studied in the colectomised dog. Meat, rice, dextrose, and fat in small amounts are best digested, raw meat being better digested than cooked meat. The combination of certain foods results in an improved digestion of both substances. Purgatives, sodium hydrogen carbonate, and barium sulphate interfere with digestion, whilst morphine retards the progress of material through the bowel.

F. O. HOWITT.

**Influence of a diet rich in cystine on the glutathione content of the tissue.** L. MÉLON (Compt. rend. Soc. Biol., 1929, 101, 1166—1167; Chem. Zentr., 1929, i, 2580).—In experiments with rats the muscle-, testicular, and lung-glutathione content was scarcely altered, whilst the liver-glutathione (normally 197—263 mg. per 100 g.) was markedly increased. Cystine was not found in the tissue.

A. A. ELDRIDGE.

**Variations in the urinary C : N ratio of men on similar diets.** A. BICKEL (Z. ges. exp. Med., 1929, 67, 420—424; Chem. Zentr., 1930, i, 2268).—Little variation in the average C : N ratio for a period is normally observed.

A. A. ELDRIDGE.

**Metabolism of the phosphatides. II. Influence of growth on phosphatide and cholesterol content of the rat.** R. G. SINCLAIR (J. Biol. Chem., 1930, 88, 575—587).—The total phosphatide content in the bodies of albino rats, on the basis of fresh tissue weight, shows a maximum at about 3 weeks of age. Calculated on the basis of dry tissue weight, however, a continued decrease is observed. The most rapid decrease in phosphatide coincides with the period of most rapid growth of the animal. The ratio of phosphatide to unsaponifiable material was found to be constant.

G. F. MARRIAN.

**Absorption of fats and lipins in the plaice (*P. platessa*, L.).** B. DAWES (J. Marine Biol. Assoc., 1930, 17, 75—102).—Microscopical examination of stained sections of the superficial epithelium of the alimentary tract shows that the stomach is the effective organ of fat absorption. Resynthesis of cleavage products of fats does not seem to occur in the areolar tissue layer. Data of rates of digestion are given.

R. K. CALLOW.

**Biochemistry of aluminium. I. Excretion and absorption of aluminium in the pig.** K. MACKENZIE (Biochem. J., 1930, 24, 1433—1441).—The intake and excretion (which is confined to the faeces) of aluminium are equal. The absorption of aluminium from normal diets containing moderate amounts of available aluminium, as determined by the analysis of the organs, is small. No diversion of phosphates from the urine to the faeces occurs on such diets. The feeding of comparatively large amounts of aluminium has no harmful effect on general growth and metabolism.

S. S. ZILVA.

**Calcium. II. Urinary output of calcium in normal individuals after oral administration of calcium lactate and calcium gluconate.** A. L. LIEBERMAN (J. Pharm. Exp. Ther., 1930, 40, 71—76).—Both salts cause a definite diuretic effect and are

absorbed to approximately the same degree, but the lactate is less tolerated than the gluconate.

F. O. HOWITT.

**Water intoxication.** M. YOSHIDA (Japan. Med. World, 1929, 9, 335—338).—The effect on the characteristics of the blood of rabbits is recorded.

CHEMICAL ABSTRACTS.

**Chemical stimulation by alcohols in the barnacle, the frog, and *Planaria*.** W. H. COLE and J. B. ALLISON (J. Gen. Physiol., 1930, 14, 71—86).—In *Balanus tintinabulum* the criterion for stimulating effect is a change in the rhythmic movements of the cirri, and in the frog and *Planaria*, the reappearance of spontaneous movements following a period of quiescence. Normal and decerebrate frogs do not differ in their reactions to alcohols. The concentrations of successive homologous alcohols required to produce a definite stimulation vary according to the series:  $1 : a^{-1} : a^{-2} : a^{-3} : a^{-4} \dots$ , where the value of  $a$  is about 3 for the barnacle and *Planaria*, but about 2.9 for the frog. The stimulating effect is considered to be due to the non-polar group in the alcohols.

P. G. MARSHALL.

**Synergism of local anaesthetics.** T. H. RIDER (J. Pharm. Exp. Ther., 1930, 40, 7—22).—The synergism curve of various mixtures of 1% cocaine and 1% potassium chloride solutions shows potentiation for all values, whilst that for 1% cocaine and 0.5% potassium chloride solution fails in this respect over part of the curve. Both curves, however, have a maximum and two minima and two of these are determined by the absolute concentration of potassium chloride present and not by the relative cocaine : salt concentration. Ammonium and magnesium chlorides give smooth potentiation curves. "Butyn" shows a well-marked synergising action with cocaine hydrochloride, due to the chloride ion. The theory of local anaesthesia is discussed.

F. O. HOWITT.

**Rôle of surface tension in the activity of cinchona alkaloids.** R. N. CHOPRA, B. B. DIKSHIT, and K. V. PILLAI (Indian J. Med. Res., 1929, 17, 360—366).—The greater efficacy of quinine when ingested together with alkali may be due to the more efficient adsorption at the intestinal cells resulting from the diminished surface tension.

CHEMICAL ABSTRACTS.

**Physiological assay of belladonna extracts and other drugs with atropine-like action.** L. JENDRASSIK and G. WILL (Arch. exp. Path. Pharm., 1930, 153, 94—108).—The inhibitory effect on a section of isolated rabbit's intestine immersed in a solution containing pilocarpine of the substance to be assayed is compared with that of a standard solution. Application of this method to fresh belladonna extracts gives almost the same results as those obtained by chemical methods. With old belladonna and hyoscyamine extracts the results are much less than are to be expected from the total alkaloid content.

W. O. KERMACK.

**Chemical and biological methods of ergot assay.** M. I. SMITH and E. F. STOHLMAN (J. Pharm. Exp. Ther., 1930, 40, 77—96).—The isolated rabbit uterus method of Broom and Clark (*ibid.*, 1923, 22, 59) was compared with the colorimetric method

previously described by one of the authors (Pub. Health Rep., 1930, 45, 1466) and with the cock's-comb (U.S.P.) method for the evaluation of fluid extracts of ergot. Satisfactory agreement within the limits of experimental error was generally obtained.

F. O. HOWITT.

**Distribution between erythrocytes and plasma of certain chemical substances used in therapeutics.** R. FABRE (Bull. Soc. Chim. biol., 1930, 12, 954—964).—A dog into which 1 g. of veronal was injected contained 6 mg. in its corpuscles and 3 mg. in its plasma per 100 g. of blood 1 hr. after administration. The corresponding figures with isopropylallylbarbituric acid were 28 mg. in the corpuscles and 5 in the plasma, the dog weighing 16 kg. Likewise quinine and hydrastine are partly taken up by the corpuscles after intravenous administration to a dog.

W. O. KERMACK.

**Comparative actions of sympathomimetic compounds.** (A) "Synephrine" isomerides and ketone. M. L. TAINTER and M. A. SEIDENFELD. (B) Pyrocatechol derivatives. M. L. TAINTER (J. Pharm. Exp. Ther., 1930, 40, 23—42, 43—64).—(A) The median pressor dose of "l-synephrine" (l-p-hydroxyphenylmethylaminoethanol) is 0.05 mg. per kg. intravenously in the anaesthetised atropinised cat, whilst the dl- and d-compounds possess only one half and one sixtieth of this activity, respectively. The l-isomeride, whilst being chemically more stable than adrenaline, has only about one sixtieth of its activity. Adrenalectomy does not modify the pressor action, which is one of direct stimulation of the vascular muscle.

(B) The pressor activities of l-, dl-, and d-adrenaline on urethanised atropinised cats are in the approximate ratio of 20 : 2 : 1. Their action on ergotaminised and cocaineised animals indicates stimulation of the vasoconstrictor mechanism. Epinine and adrenalone behave similarly but to a smaller degree. Pyrocatechol gives inconstant pressor effects which are irregularly sensitised by cocaine and reversed by ergotamine. The relation between chemical structure and pharmacological action of these compounds is discussed.

F. O. HOWITT.

**Significance of chemical configuration for the pharmacological action of adrenaline-like compounds.** B. HASAMA (Arch. exp. Path. Pharm., 1930, 153, 161—186).—The lethal doses of the following compounds have been determined and also their actions on the blood-pressure, the blood-vessels, and on bronchial spasm.  $\beta$ -Phenylethylamine,  $\beta$ -hydroxy- $\beta$ -phenylethylamine,  $\beta$ -hydroxy- $\alpha$ -phenylethylamine, tyramine, 3 : 4-dihydroxyphenylalanine, ephedrine,  $\beta$ -hydroxy- $\beta$ -phenyl- $\alpha$ -methylethylamine (mydriatin), adrenalone,  $\beta$ -hydroxy- $\alpha$ - $\beta$ -diphenylethylamine, and  $\beta$ -phenoxyethylamine. The presence of a hydroxyl group either in the para-position of the benzene ring or in the  $\beta$ -position of the side-chain increases the comparatively small sympathomimetic activity of  $\beta$ -phenylethylamine.  $\beta$ -Hydroxy- $\alpha$ -phenylethylamine has practically no sympathomimetic action. The introduction of an  $\alpha$ -methyl group reduces the activity of  $\beta$ -hydroxy- $\beta$ -phenylethylamine, whilst the introduction of a phenyl

group in the  $\alpha$ -position destroys the action on the nerve, but brings about a stimulating action on the muscles.  $\beta$ -Phenoxyethylamine has no action on the sympathetic, but paralyses smooth muscle.

W. O. KERMACK.

**Action of ultra-violet rays on venoms.** J. VELLARD and J. PENTEADO (Compt. rend., 1930, 191, 458—460).—Exposure of 0.1% solutions of the venoms from *Lachesis atrox* and *jararaca*, *Crotalus terrificus*, *Naja tripudians*, and *Bufo marinus* in saline to ultra-violet rays causes various changes in the physico-chemical and physiological properties. The viscosities of all the solutions increase and gelation tends to occur at the surface. The heat-stability is increased, all the solutions become more acid, and in some cases precipitation of material occurs. The physiological action (e.g., power of coagulation) is diminished considerably, the more so the longer is the irradiation. Irradiated solutions of the venoms from *L. atrox* and *C. terrificus* still retain antigenic properties, since immunisation of guinea-pigs and goats is possible by injection of large amounts of the irradiated material.

H. BURTON.

**Formation of a histamine-like substance from histidine under ultra-violet irradiation.** F. ELLINGER (Arch. exp. Path. Pharm., 1930, 153, 120—127).—The conversion of histidine hydrochloride by ultra-violet irradiation into a histamine-like substance lowering the blood-pressure and stimulating the guinea-pig's isolated intestine occurs when histidine is irradiated in solid form as well as in aqueous solution. Ultra-violet light inactivates dilute solutions of histamine hydrochloride, but this is prevented by the presence in the solution of irradiated histidine hydrochloride.

W. O. KERMACK.

**Effect of colloids on the action of histamine.** A. BERNFELD (Biochem. Z., 1930, 224, 487—490).—The action of histamine on the isolated surviving small intestine of the guinea-pig suspended in physiological salt solution is strengthened by the addition of small amounts of kaolin or talc or of aqueous muscle extracts and diminished by addition of larger amounts.

W. MCCARTNEY.

**Changes in composition of blood after injection of radioactive substances into animals.** Ionium nitrate. Y. POURBAIX (Compt. rend. Soc. Biol., 1930, 103, 536—538; Chem. Zentr., 1930, i, 2752).—During the period of apparent health the (rabbits') blood-sugar rose, and the blood-cholesterol rose from 0.122 to 0.454. With the onset of anaemia the albumin : globulin ratio rose from 0.78—2.8 to 4.4.

A. A. ELDRIDGE.

**Variation of the physiological action of Ringer's solution after filtration.** S. N. MILOVANOV (Russ. J. Physiol., 1930, 13, 313—315).—Filtration of Ringer's solution (NaCl 0.6, KCl 0.01, CaCl<sub>2</sub> 0.01, NaHCO<sub>3</sub> 0.01%) through certain filter-papers causes a variation in its physiological action on the isolated frog's heart which is avoided if the amount of calcium chloride is increased.

C. C. N. VASS.

**Antitoxic action of calcium with respect to manganese in *Bombinator igneus*.** A. ROUYERON (Compt. rend. Soc. Biol., 1930, 103, 396—397;

Chem. Zentr., 1930, i, 2120).—The subcutaneous injection of 1 c.c. of 1% manganese chloride solution in the toad brings about paralysis and finally death. The addition of 2% of calcium chloride either prevents this or delays the action. Equivalent doses of manganese lactate or calcium formate or lactate produce the same effects.

L. S. THEOBALD.

**Toxicity of strontium. Comparison with other cations employed in therapeutics.** D. LOESER and A. L. KONWISER (J. Lab. Clin. Med., 1929, 15, 35—41).—The minimum lethal dose of strontium for rats is 123 mg. per kg. when administered intravenously as the chloride, bromide, or iodide. The following cations are in order of increasing toxicity: sodium, strontium, calcium, potassium, magnesium, barium.

CHEMICAL ABSTRACTS.

**Effect of mercury and sodium oxalate on blood-calcium.** F. D. MCCREA (J. Lab. Clin. Med., 1929, 14, 1161—1164).—The blood-calcium is decreased by administration to animals of mercuric succinate or sodium oxalate.

CHEMICAL ABSTRACTS.

**Effect of intravenous injection of sodium oxalate and citrate on the concentration of plasma-calcium and inorganic phosphorus.** C. TSAI and F. Y. HSU (Chinese J. Physiol., 1930, 4, 273—287).—The administration of sodium oxalate to normal dogs causes a fall in the plasma-calcium followed by a rapid rise to normal. The plasma-inorganic phosphorus also falls slightly and then rises, the ratio of the rise of inorganic phosphorus to that of calcium being greater than that of the two elements in the bone. In thyroparathyroidectomised dogs similar results are obtained, but the rise in calcium and inorganic phosphorus is slower and less marked. Analogous results are obtained by the administration of calcium citrate, but the fall of plasma-calcium is smaller, although larger quantities of citrate solution than of oxalate are used.

W. O. KERMACK.

**Index of trypanocidal activity of certain aryl derivatives of arsine acid.** L. LAUNOY and (MILLE) ENGLER (Bull. Soc. Chim. biol., 1930, 12, 886—893).—A new chemotherapeutic index is proposed in which the numerator represents the dose of the substance required to cure an animal injected with *T. Brucei*, *T. equiperdum*, or *T. Evansi*, whilst the denominator is the dose tolerated in 50—60% of the animals. This index has been determined in the case of atoxyl, tryparsamide, or arsamine (sodium *p*-acetamido-*o*-hydroxybenzenearsinate).

W. O. KERMACK.

**Acute action of neosalvarsan on the circulation.** II. Cause of action. O. KRAYER (Arch. exp. Path. Pharm., 1930, 153, 50—66).—The occasional action of neosalvarsan solutions on the circulation is apparently brought about by oxidation of the compound with subsequent increase of the size of the dissolved particles and an increased acidity of the solution. The viscosity of the blood containing the drug is thereby increased and an action also takes place on the walls of the vessels resulting in increased resistance.

W. O. KERMACK.

**Pharmacology of "salyrgan." IV. Chemistry of "salyrgan."** K. O. MÖLLER (Arch. exp. Path.

Pharm., 1930, 153, 109—119).—A solution of "salyrgan,"  $\text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{HgOH}$ , contains practically no mercuric ions. Treatment of the solution with 1 mol. of acid yields a flocculent precipitate of salyrganic acid, probably

$\text{C}_6\text{H}_4\cdot\begin{matrix} \text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{OMe} \\ \text{O}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2 \end{matrix}$ , relatively insoluble in water, but moderately soluble in 25—50% sulphuric acid. Salyrganic acid and therefore salyrgan are dissociated in acid solutions and the mercury is precipitated by hydrogen sulphide. The dissociation of the mercuric ions increases with increase in the hydrogen-ion concentration. The solubility of salyrganic acid rapidly increases with increase in the sodium chloride content of the medium, the increase in solubility being more than proportional to the sodium chloride content. The mercuric-ion concentration decreases as the sodium chloride concentration increases. Similarly, salyrganic acid is also easily soluble in solutions of potassium chloride, ammonium chloride, calcium chloride, magnesium chloride, sodium iodide, sodium bromide, and barium chloride, but is sparingly soluble in sodium sulphate, sodium nitrate, zinc chloride, ferric chloride, and mercuric chloride solutions and in dilute hydrochloric and other acids. In alkaline urine salyrgan is excreted unchanged, but in acid urine it is converted into salyrganic acid.

W. O. KERMACK.

**Catalase of milk. I. Determination of milk catalase by potassium permanganate titration.** J. ZAYKOVSKY and P. ALEXEEV (Fermentforsch., 1930, 12, 55—66).—The special forms of apparatus used for determination of the catalase of milk give results varying within wide limits. The permanganate titration method is accurate. To 2 c.c. of fresh milk 98 c.c. of water and 5 c.c. of 0.3% hydrogen peroxide are added, the mixture is kept for 30 min. at 17—18°, treated with 5 c.c. of 10% sulphuric acid, and titrated with 0.1N-potassium permanganate. A similar determination is carried out with boiled (i.e., catalase-free) milk. The difference in titration corresponds with the catalase content. J. H. BIRKINSHAW.

**Specificity of the dehydrogenase of succinic acid and glycerophosphoric acid.** N. ALWALL (Skand. Arch. Physiol., 1929, 58, 65—76; Chem. Zentr., 1930, i, 2432).—Except in the optic lens, which contains only the latter dehydrogenase, both were present with varying activity in all the tissues examined. The results support the view that the enzymes differ.

A. A. ELDRIDGE.

**Iodometric determination of oxidase activity.** J. D. GUTHRIE (J. Amer. Chem. Soc., 1930, 52, 3614—3618).—A mixture of dextrose and *N*-sodium hydroxide is heated at 80°, neutralised with phosphoric acid, treated with active charcoal, and diluted, and the resulting solution is used as substrate for the determination of the oxidase activity of potato juice. A mixture of the substrate and juice is aerated in presence of paraffin oil, the mixture treated with iodine in trichloroacetic acid solution, and the excess of iodine determined. The difference in the amount of iodine used in this and in a blank with the substrate alone is a fairly accurate measure of the oxidase

activity of the juice. The determinations are carried out at  $p_H$  6.5. The oxidase activity is approximately constant at  $p_H$  6—7, and is a linear function of the enzyme concentration. Applications of the method to other juices are quoted.

H. BURTON.

**Mode of action of tyrosinase.** C. E. M. PUGH (Biochem. J., 1930, 24, 1442—1455).—Tyrosinase could not be separated into two enzymes able to act respectively on monohydric and on *o*-dihydric phenols. Attempts to find a coenzyme also failed. Moderate heating or storage of certain tyrosinase preparations increases their activity on monohydric relatively to *o*-dihydric phenols. Cyanide or sulphite has the contrary effect. The action of tyrosinase on monohydric phenols is hastened by water containing homoquinone and by hydrogen peroxide in small concentration. There is also slight initial activation of action on *o*-dihydric phenol in the latter case. Tyrosinase alone in the presence of molecular oxygen is not able to oxidise monohydric phenols. The initial acceleration of the action of tyrosinase on monohydric phenols by traces of *o*-dihydric phenols appears to be due to peroxide formation (hydrogen peroxide or both hydrogen peroxide and *o*-benzoquinone).

S. S. ZILVA.

**Laccase of Japanese lacquer.** K. SUMINOKURA (Biochem. Z., 1930, 224, 292—321).—The influence of heat, reaction, hydrogen peroxide, hydrogen cyanide, sodium chloride, the gases of the atmosphere, carbon monoxide, inorganic manganese salts, salts of organic acids, and irradiation on laccase from Japanese lacquer has been studied. The results show that laccase is a genuine oxidase but not a peroxidase. Its activity can be determined by the method of Willstätter and Stoll (A., 1918, i, 555).

W. MCCARTNEY.

**The invertase-accelerator of serum and other enzyme-accelerators reported in serum.** J. FINE (Biochem. J., 1930, 24, 1282—1293).—Intraperitoneal injections of invertase but not of sucrose give rise to serum-invertase. Sera of man, sheep, cow, guinea-pig, and rat contain an invertase accelerator which acts on dilute invertase solution. It is not destroyed by heating at 70° for 30 min. and its action is not diminished by shaking the serum with chloroform. The extent of acceleration varies with the concentration of serum. The relationship is linear for low concentrations of serum and the acceleration is at a maximum at 20%, diminishing at higher concentrations of serum. In the case of both sheep and guinea-pig there is no influence on invertase action at  $p_H$  5 in sheep serum; by using less dilute invertase, acceleration is obtained only at  $p_H$  3, whilst at  $p_H$  4 and above  $p_H$  5 there is invertase inhibition. In guinea-pig serum invertase inhibition occurs only at  $p_H$  6, whilst acceleration is obtained at  $p_H$  3—5 and 7—8 when very weak invertase is used. Increasing the concentration of invertase widens the  $p_H$  band of inhibition.

S. S. ZILVA.

**Lecture experiment to illustrate the occurrence of the methylglyoxal and pyruvic acid stage during the alcoholic fission of sugars.** C. NEUBERG and M. KOBEL (Ber., 1930, 63, [B], 1986—1989).—Magnesium hexosediphosphate solution (8%,

30 c.c.) is treated with 0.5 g. of fresh baker's yeast and 1—2 c.c. of toluene. After thorough agitation, the mixture is preserved at 37° for 1—2 days. It is then treated with trichloroacetic acid and filtered. Methylglyoxal in the filtrate is precipitated by addition of 2 : 4-dinitrophenylhydrazine. The precipitate is washed with 25% sodium carbonate solution and water and then treated with about 0.5% alcoholic potassium hydroxide, which gives a dark bluish-violet colour. To demonstrate the production of pyruvic acid a similar mixture, except that 3 g. of baker's yeast are added, is kept at 37° with frequent agitation and aeration for 1—2 days. Pyruvic acid is precipitated in the filtrate from the mixture as the 2 : 4-dinitrophenylhydrazone, which is purified by dissolution in sodium carbonate solution and re-precipitation. It gives a red to brownish colour in 0.5% alcoholic potassium hydroxide. Toluene may be replaced by bromobenzene.

H. WREN.

**Dismutation of methylglyoxalylacetic acid to *d*- $\alpha$ -hydroxyglutaric acid.** C. NEUBERG and H. COLLATZ (Biochem. Z., 1930, 225, 242—246).—Details are given for carrying out the asymmetric dismutation of methylglyoxalylacetic ( $\gamma$ -diketo-valeric) acid, the yield of *d*- $\alpha$ -hydroxyglutaric acid being 86.5% of theoretical (sodium salt,  $[\alpha]_D^{25} + 7.48^\circ$ ).

P. W. CLUTTERBUCK.

**Photochemical and phytochemical formation of acyloins. (Carboligatic action.)** C. NEUBERG (Biochem. Z., 1930, 225, 238—241).—The literature on the mechanism of the formation of acetoin is critically reviewed.

P. W. CLUTTERBUCK.

**Hydrolysis by emulsin of two glucosides considered non-hydrolysable by this method: asebotin and phloridzin.** M. BRIDEL (Bull. Soc. Chim. biol., 1930, 12, 921—930).—Contrary to accepted views, asebotin and phloridzin are hydrolysable by emulsin and are therefore  $\beta$ -glucosides.

W. O. KERMACK.

**Reduction in the activity of the  $\beta$ -glucosidase of almond emulsin during successive syntheses of  $\beta$ -methylglucoside.** M. BRIDEL and N. IOANID (Bull. Soc. Chim. biol., 1930, 12, 931—933).—A suspension of almond meal was shaken with 70% methyl alcohol containing 30% of dextrose and the course of the formation of  $\beta$ -methylglucoside followed by polarimetric observations. The almond suspension was then separated and again shaken with methyl alcohol containing dextrose until equilibrium was reached and this process repeated several times. The results indicated loss of the synthetic activity as the result of the action of the enzyme.

W. O. KERMACK.

**Enzymic synthesis of raffinose.** A. V. BLAGOVESHCHENSKI (Biochem. J., 1930, 24, 1337—1339).—The positive rotation of incubated mixtures of sucrose, galactose, and emulsin in acetone increased after 2—3 months. On incubating the mixture with emulsin, after removing the acetone, for 3 months the rotation decreased. Crystals having  $[\alpha]_D + 95.66^\circ$  were obtained from the incubated mixture containing acetone which when treated with emulsin in aqueous solution had  $[\alpha]_D + 2.34^\circ$  in ten days. Raffinose had

thus been synthesised by the enzyme in the presence of acetone. S. S. ZILVA.

**Lipase and its action.** I. **Synthetic action of pancreatic lipase in the system oleic acid-glycerol-water-dissolved lipase.** E. A. SYM (Biochem. J., 1930, 24, 1265—1281).—The adsorption of lipase on the oil-glycerol interface, which is partly reversible, takes place in two ways. The lipase is at first adsorbed in a few minutes, the velocity being independent of temperature, and then a membrane is formed at the phase interface. The second process proceeds five times as rapidly at 38° as at 18°. The whole of the lipase remaining in solution after the completion of the first process is concentrated in this membrane after a few days. The synthesis of olein appears to follow the law of mass action and the reaction is bimolecular. Where the quantity of the aqueous phase is varied, keeping the contact-surface, the amount of oleic acid, and the concentration of lipase constant, the initial velocity of reaction increases for the whole system with the amount of aqueous phase taken. The number of millimols. of combined oleic acid per g. of aqueous phase falls, however, with increase in volume of the latter phase. Increase in the concentration of glycerol in the aqueous phase accelerates the reaction and shifts the equilibrium point in the direction of synthesis. The initial velocity of reaction, but not the equilibrium constant, is directly proportional to the concentration of enzyme in the aqueous phase. S. S. ZILVA.

**Concentration of pepsin and chemistry of its action.** I. A. SMORODINCEV and A. N. ADOVA (Biochem. Z., 1930, 224, 471—473; cf. A., 1928, 1282).—Lustig's results (this vol., 112) agree with those of the authors if the ratio  $\text{NH}_2/\text{CO}_2\text{H}$  is calculated from equivalent values instead of from percentage values. W. McCARTNEY.

**Specificity of peptidases.** M. BERGMANN and H. SCHLEICH (Naturwiss., 1930, 18, 832).—Glycyldehydrophenylalanine,  $\text{CHPh}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2$ , is hydrolysed by commercial pancreatin preparations, but not by the trypsin fraction of the extract and scarcely at all by the erepsin fraction. Glycerol extracts of the commercial pancreatin act well. Dipeptidase from yeast or from pig's pancreas, polypeptidase from yeast or from pig's intestinal mucous membrane, and trypsin from pancreatin were without action on the dehydrogenated peptide. The active principle in the commercial pancreatin is therefore probably a new and specific enzyme. W. O. KERMACK.

**Stereochemical specificity and homogeneity of erepsin.** P. RONA and T. MARSSON (Biochem. Z., 1930, 224, 384—414).—*d*-Glycyl-leucine is only very slowly or not at all attacked by erepsin from pig intestine, pig pancreas, or ox intestine, and the *l*-component only of the *r*-acid is attacked by the enzyme. The hydrolysis of this component by the enzyme from pancreas or intestine proceeds more slowly than that of the isolated *l*-acid. Since the hydrolysis of the *l*-acid is restricted by additions of the *d*-acid, it is concluded that the enzyme forms a compound with the latter. Attempts to show that erepsin contains more than one constituent are

unsuccessful, although in solutions the enzyme can be stabilised by addition of glycerol or glycol. These substances, which seem to act more by virtue of their physical than their chemical properties, also protect the enzyme from the effects of the impurities which accompany it. W. McCARTNEY.

**Behaviour of polypeptides containing proline towards the erepsin and trypsin-kinase complex.** E. ABDERHALDEN and O. ZUMSTEIN (Fermentforsch., 1930, 12, 1—19).—The following compounds were prepared: *chloroacetyl-l-proline*, m. p. 112—113°; *glycyl-l-prolineamide*, m. p. about 90°; *glycyl-l-proline*,  $[\alpha]_D^{25}$ —86.21°; *dl- $\alpha$ -bromopropionyl-l-proline*, m. p. 137—138°; *dl- $\alpha$ -hydroxypropionyl-l-prolineamide*, m. p. 109—110°; *dl-alanyl-dl-proline*, m. p. 280°; *dl-alanyl-l-proline*,  $[\alpha]_D^{25}$ +92.68°; *dl-alanyl-l-proline methyl ester*, m. p. 89—93°; *dl-alanyl-l-proline anhydride*, m. p. 114—115°; *dl- $\alpha$ -bromo-n-butyryl-l-proline*, m. p. 120—123°; *dl- $\alpha$ -hydroxy-n-butyryl-l-prolineamide*, m. p. 76—78°; *dl- $\alpha$ -amino-n-butyryl-l-proline*,  $[\alpha]_D^{25}$ —45.4°; inactive  *$\alpha$ -amino-n-butyrylprolineamide*, m. p. above 300°; *dl- $\alpha$ -bromo-n-valeryl-l-proline*, m. p. 85—87°; *dl- $\alpha$ -hydroxy-n-valeryl-l-prolineamide*, m. p. about 60°; inactive *norvalylproline*, m. p. 258—259°; *dl-norvalyl-l-proline*,  $[\alpha]_D^{25}$ —56.25°; *dl- $\alpha$ -bromoisovaleryl-l-proline*; *dl- $\alpha$ -hydroxyisovaleryl-l-prolineamide*; inactive *valylproline*, m. p. 275°; *dl-valyl-l-proline*,  $[\alpha]_D^{25}$ —36.66°; *dl- $\alpha$ -bromo-n-hexoyl-l-proline*, m. p. 69—70°; *dl-norleucyl-l-proline*, m. p. 225—226°; *dl- $\alpha$ -bromoisohexoyl-l-proline*; *dl-leucyl-l-proline*, m. p. 211—212°; *dl- $\alpha$ -hydroxyisohexoyl-l-prolineamide*, m. p. 124°; *dl-leucyl-l-proline methyl ester*. Of the dipeptides erepsin hydrolysed only glycylproline, trypsin-kinase none. The latter hydrolysed *dl- $\alpha$ -bromoisohexoyl-l-proline*, but not *dl- $\alpha$ -bromopropionyl-l-proline*. Neither enzyme attacked *dl- $\alpha$ -hydroxyhexoyl-l-prolineamide*. J. H. BIRKINSHAW.

**Action of N-alkali, erepsin, and trypsin-kinase on polypeptide-like compounds containing  $\beta$ -aminoisovaleric acid.** E. ABDERHALDEN and F. REICH (Fermentforsch., 1930, 12, 20—41).—The following polypeptides and precursors were prepared: *glycyl- $\beta$ -aminoisovaleric acid*, m. p. 210° (decomp.), from *chloroacetyl- $\beta$ -aminoisovaleric acid*; *dl-leucyl- $\beta$ -aminoisovaleric acid*, m. p. 195—198° (decomp.), from *dl- $\alpha$ -bromoisohexoyl- $\beta$ -aminoisovaleric acid*, m. p. 104—105°; *glycyl-dl-leucyl- $\beta$ -aminoisovaleric acid*, m. p. 200° (becomes brown), from *chloroacetyl-dl-leucyl- $\beta$ -aminoisovaleric acid*, m. p. 125—130°; *dl-leucylglycyl- $\beta$ -aminoisovaleric acid*, decomp. 225°, from *dl- $\alpha$ -bromoisohexoylglycyl- $\beta$ -aminoisovaleric acid*; *glycyl-dl-leucylglycyl- $\beta$ -aminoisovaleric acid*, decomp. 175°, from *chloroacetyl-dl-leucylglycyl- $\beta$ -aminoisovaleric acid*, m. p. 170°; *dl-valylglycyl-dl-leucylglycyl- $\beta$ -aminoisovaleric acid*, m. p. 193—198° (decomp.), from *dl- $\alpha$ -bromoisovalerylglycyl-dl-leucylglycyl- $\beta$ -aminoisovaleric acid*;  *$\beta$ -bromoisovaleryl chloride*, b. p. 60—62°/20 mm.;  *$\beta$ -aminoisovaleryl-dl-leucylglycine*, m. p. about 125°, from  *$\beta$ -bromoisovaleryl-dl-leucylglycine*, m. p. about 120°;  *$\beta$ -aminoisovaleryl-dl-leucylglycyl-dl-leucine*, m. p. 125—130° (decomp.), from  *$\beta$ -bromoisovaleryl-dl-leucylglycyl-dl-leucine*, m. p. about 145°;  *$\beta$ -aminoisovalerylglycyl-dl-leucylglycyl- $\beta$ -aminoisovaleric acid*.

valeric acid, m. p. 185° (decomp.), from  $\beta$ -bromoiso-valerylglycyl-dl-leucylglycyl- $\beta$ -aminoisovaleric acid, m. p. 112—114°; dl-leucyl- $\beta$ -aminoisovaleryl-dl-leucylglycine, m. p. 245° (decomp.), from dl- $\alpha$ -bromoiso-hexoyl- $\beta$ -aminoisovaleryl-dl-leucylglycine.

Of the polypeptides, erepsin attacked glycyl-dl-leucyl- $\beta$ -aminoisovaleric acid most strongly but also hydrolysed dl-leucylglycyl- and glycyl-dl-leucylglycyl- $\beta$ -aminoisovaleric acid. Trypsin-kinase hydrolysed only  $\beta$ -aminoisovaleryl-dl-leucylglycyl-dl-leucine and dl-leucyl- $\beta$ -aminoisovaleryl-dl-leucylglycine. Thus  $\beta$ -aminoisovaleric acid hindered the action of amino- or carboxy-polypeptidase whenever it provided the amino- or carboxyl group of the polypeptide chain. All the polypeptides with the exception of dl-leucyl- $\beta$ -aminoisovaleric acid were readily hydrolysed by N-sodium hydroxide. J. H. BIRKINSHAW.

**Action of N-sodium hydroxide, erepsin, and trypsin-kinase on polypeptides containing glycine.** E. ABDERHALDEN and J. HEUMANN (Fermentforsch., 1930, 12, 42—54).—The polypeptides built up of glycine units were obtained by successive coupling with chloroacetyl chloride. The following were prepared: hexaglycylglycine, sinters and becomes yellow above 230°, from chloroacetyl-pentaglycylglycine, sinters and turns yellow at about 225°; heptaglycylglycine, from chloroacetyl-hexaglycylglycine, sinters above 225° (yellow and decomp.); octaglycylglycine, from chloroacetyl-heptaglycylglycine; nonaglycylglycine, from chloroacetyl-octaglycylglycine; 2-naphthalenesulphonyl-hexaglycylglycine. Erepsin at  $p_H$  7.8 hydrolysed tri- and tetra-glycylglycine, but left the higher molecular polypeptides unattacked; at  $p_H$  8.4 the hydrolysis was greater and the pentaglycylglycine was attacked. Trypsin-kinase at  $p_H$  7.8 hydrolysed all the halogenoacyl compounds but none of the polypeptides. At  $p_H$  8.4 none of the halogenoacyl compounds was hydrolysed; of the polypeptides only hexaglycylglycine was attacked. Hexa- to nona-glycylglycine were hydrolysed by sodium hydroxide.

J. H. BIRKINSHAW.

**Hydrolysis of peptones and polypeptides by the enzymes of the pancreas.** R. SCHÖNFELD-REINER (Fermentforsch., 1930, 12, 67—127).—The enzymic fission of a variety of peptones, dipeptides, and a tripeptide by enzymes prepared by various methods from the pancreas was studied. The acid-coagulation method of Fodor and the separation of the dried preparation into a soluble and an insoluble portion were employed to separate the enzymes. The acid coagulum and the insoluble portion respectively proved to be the carriers of dipeptidase; the filtrate from the acid coagulum and the soluble portion attacked the tripeptide and peptones. On autolysis the soluble portion begins to hydrolyse the dipeptides. Fresh preparations (macerates) show a linear course for the hydrolysis of peptone, older preparations and acid filtrates a parabolic course. The soluble portion has an optimum  $p_H$  of 7.58, the insoluble portion 7.96 for dipeptide and 8.00 for peptone hydrolysis. The autolytic degradation products of macerates which are also formed by digestion of the substrates accelerate peptone and inhibit dipeptide hydrolysis. Dialysis reverses this effect.

Pre-treatment with glycine has a varying effect on both types of hydrolysis, according to the conditions. The two types of hydrolysis are attributed to different enzyme carriers rather than to different specific enzymes. J. H. BIRKINSHAW.

**Uricase. II. Bacterial nature of the action of uricolytic extracts and dialysates. III. Comparison with activated charcoal. Contact nature of the action of uricase. IV. Preparation and properties of ox-kidney uricase.** R. TRUSZKOWSKI (Biochem. J., 1930, 24, 1340—1348, 1349—1358, 1359—1370).—II. Soluble uricase preparations such as extracts and dialysates contain *B. proteus vulgaris*, *B. mesentericus*, *B. faecalis alkaligenes*, and *B. fluorensens liquefaciens*. These bacteria multiply between  $p_H$  6 and 9 (optimum 7.4—8.4) at the ordinary temperature in the presence of thymol or of 6% methyl alcohol and destroy uric acid. Their growth and action are completely inhibited by chloroform and by toluene. Bacteria killed by the addition of toluene have no uricolytic action. Dog's liver and kidney removed and minced under aseptic conditions do not decompose uric acid appreciably at 16° unless bacterial growth takes place. On the other hand, at 38° they decompose uric acid, more so when shaken even in the presence of toluene or of chloroform. Glycerol and glycerol-chloroform suspensions of kidney tissue are active in sterile systems.

III. The velocity of oxidation of uric acid in the presence of ox-kidney uricase is greatest at  $p_H$  8. The action of Warburg and Brefeld's active charcoal on uric acid, which it does not adsorb, is approximately constant up to  $p_H$  7.5, above which value the velocity increases rapidly to a maximum at about  $p_H$  9. isoPropyl and *n*-butyl alcohols and potassium cyanide inhibit the uricolytic action of charcoal partly, whilst sodium pyrophosphate does not inhibit it at all. The activity of extracts (suspensions) is most probably associated with the presence of macroscopic fragments of cell debris.

IV. The  $p_H$ -activity curves of different uricase preparations are of the same general type. Two maxima exist, one at  $p_H$  about 7.5 and the other at 9.4. The curves approach zero between  $p_H$  11 and 12 because of the irreversible dissolution of the particles in suspension. The residue obtained by centrifuging uricolytic extracts is more active than the whole extract. The suspended particles are evidently inhibited, at least partly, by the viscosity of the system due to dissolved proteins and to the glycerol. The addition of glycerol to suspensions of uricase in water increases the action of the suspension up to 2—3%; at higher concentrations the activity falls in direct proportion to the glycerol content until in 50% glycerol 80% inactivation is attained. In shaken systems no activation is achieved by the addition of glycerol. The uricolytic action of kidney tissue is a function of the degree of division of the tissue. Uricase does not pass into solution either under the influence of surface-active substances such as *n*-butyl alcohol or at any  $p_H$  between 6 and 12. S. S. ZILVA.

**Abderhalden reaction in urine.** E. ABDERHALDEN (Fermentforsch., 1930, 12, 128).—Kafka's priority is recognised. J. H. BIRKINSHAW.



**Dependence of the reducing action of fermenting yeast on the source of nitrogen.** K. PIRSCHLE and H. MENGDEHL (Biochem. Z., 1930, 225, 151—176).—Apart from a number of organic dyes such as safranine and fuchsin which show no visible effect, the substances investigated may be divided into those which are reduced most readily in presence of ammonium-nitrogen (e.g., methylene-blue, Lauth's violet, molybdate, chromate, thiosulphate, ferro- and ferricyanide) and those in presence of nitrate-nitrogen (e.g., sulphur, nitrobenzene, valeraldehyde). Potassium, sodium, and calcium nitrates on the one hand and ammonium sulphate and chloride on the other behave similarly. The action of the ammonium-nitrogen in ammonium nitrate predominates. Amino-nitrogen (asparagine and peptone) acts like ammonium-nitrogen, whilst carbamide acts in some cases, e.g., with methylene-blue, like ammonium- and in others, e.g., with molybdate and sulphur, like nitrate-nitrogen. Velocities of reductions with and without added nitrogen are compared. Relatively strong reduction with ammonium- or nitrate-nitrogen occurs when the reaction is acid (lactic) or alkaline (lime). Lime accelerates the reduction of methylene-blue and lactic acid that of thiosulphate, whereas both lime and lactic acid inhibit the reduction of sulphur. Small amounts of nitrite (1—20 mg.  $N_2O_3$  per litre) in ammonium salt cultures accelerate the formation of hydrogen sulphide from sulphur, and of aniline from nitrobenzene. *Torula utilis* and acetone-dried yeast show the same behaviour as the ordinary pressed yeast. P. W. CLUTTERBUCK.

**Effect of low pressures on cell oxidation.** S. F. COOK (J. Gen. Physiol., 1930, 14, 55—70).—The uptake of oxygen by the yeast cell is diminished to a greater extent by reduced pressure than by reduced partial pressure of oxygen, whilst anaërobic respiration is unaffected. P. G. MARSHALL.

**Behaviour of glutathione in yeast.** N. U. MELDRUM (Biochem. J., 1930, 24, 1421—1427).—The respiration of yeast may be reduced by 60—90% by narcotics and by cyanide without the amount of reduced glutathione being affected; the latter is not affected by cooling. Glutathione does not reduce cytochrome in yeast. Dehydrogenases do not reduce glutathione with simultaneous oxidation of their substrates. Yeast may be starved until its rate of respiration falls to about 5% of that in dextrose solution without affecting the thiol content. Glutathione is not directly concerned in carbohydrate oxidation of yeast. S. S. ZILVA.

**Liquefaction of starch by the enzyme in yeast autolysate.** S. NISHIMURA (Bull. Agric. Chem. Soc. Japan, 1928, 4, 126).—The autolysate contained an enzyme, amylpectinase, which liquefies starch paste and is similar to maltase.

#### CHEMICAL ABSTRACTS.

**Physiology of some Synievski dextrins.** A. JOSZT and M. KUNINSKI (Z. physiol. Chem., 1930, 191, 65—68).—*Spirogyra nitida* cultivated in the dark on sugar or dextrin media with the addition of sodium chromate to prevent bacterial infection converted dextrose, maltose, sucrose, and two erythro-

dextrins, one from amylopectin and the other from unreduced "limit" dextrin I, into starch.

J. H. BIRKINSHAW.

**Phytase of *Aspergillus* species.** T. KAWAHARA (Bull. Agric. Chem. Soc. Japan, 1929, 5, 7—8).—Phytase was present in 12 species examined; the optimum conditions for phytase activity are 50° and  $p_H$  4.67. The action of phytase on phytin proceeds in several stages.

#### CHEMICAL ABSTRACTS.

**Formation of kojic acid by *Aspergillus oryzae*.** I. H. KATAGIRI and K. KITAHARA (Bull. Agric. Chem. Soc. Japan, 1929, 5, 38—47).—The optimal conditions were established by a 5% dextrose solution containing 0.05% of ammonium sulphate at  $p_H$  2.4; at  $p_H$  5.0 the growth of the mould is greatest. Kojic acid was formed from dextrose, maltose, sucrose, inulin, laevulose, and xylose (10—40%), mannose, arabinose, galactose (1—6%), sorbitol, dulcitol, glycerol, glycerol- $\beta$ -phosphate, inositol, and gluconic acid.

#### CHEMICAL ABSTRACTS.

**Fermentation products of moulds.** IV. *Aspergillus glaucus*. I. Y. SUMIKI (Bull. Agric. Chem. Soc. Japan, 1929, 5, 10—13).—Fumaric, citric, succinic, oxalic, tartaric, malic, and 2-hydroxymethylfuran-5-carboxylic acids, and an unidentified substance, were produced. The composition of the medium was: dextrose or sucrose 10, inorganic and organic nitrogen compounds 0.08—2.0, potassium mono- and di-hydrogen phosphates each 0.015, magnesium sulphate 0.01, calcium chloride 0.01% with traces of ferric and sodium chlorides and (if necessary) calcium carbonate.

#### CHEMICAL ABSTRACTS.

**Dissimilation of salts of fatty acids and of carbohydrates by thermophilic bacteria.** II. **Starch and sugars.** C. COOLHAAS (Zentr. Bakt. Par., 1928, II, 75, 344—360; Chem. Zentr., 1930, i, 2434).—Two varieties of *B. thermoamylolyticus* converted starch (80%) into maltose, no gas, and only small amounts of acid, being formed. In presence of sugar a thermophilic organism (*B. thermobutylicus*), which caused vigorous fermentation, was isolated; dextrose, sucrose, and starch afforded carbon dioxide, hydrogen, and a mixture of butyric, acetic, and lactic acids with a small amount of propionic acid. Calcium pyruvate cannot be regarded as an intermediate product in the thermophilic butyric acid fermentation.

A. A. ELDRIDGE.

**Actions of acetic bacteria.** E. SIMON (Biochem. Z., 1930, 224, 253—291).—Large numbers of experiments with *B. pasteurianum*, *B. suboxidans*, and *Acetobacter suboxidans* show that the bacteria contain carboxylase, keto-aldehyde-mutase, phosphatase, and glycolase, that they can act anaërobically, and that they form a complete system for fermentation including true alcoholic fermentation. W. MCCARTNEY.

**Formation of lactic acid by *Bacterium xylinum*.** Lactic acid fermentation by kombucha. H. HAEHN and M. ENGEL (Zentr. Bakt. Par., 1929, II, 79, 182—185; Chem. Zentr., 1930, i, 1812—1813).—The existence of a reserve enzyme is indicated by the fact that small quantities of lactic and formic acids are formed in addition to gluconic acid. The produc-

tion of lactic acid by "Teepilz" is due to the presence of *B. xylinum*. A. A. ELDRIDGE.

[A] Effect of small and large amounts of humus on the fixation of nitrogen by *Azotobacter chroococcum*, in presence of various glucosides, mannitol, and calcium malate. [B] Influence of humus on nitrogen-fixing organisms. *A. chroococcum* and *Clostridium pastorianum* in impure mixtures. Biochemical action of humus. J. VOICU and E. LUNGULESCU (Bul. Soc. Chim. România, 1930, 12, 71—81, 82—89).—[A] Humus affects *A. chroococcum* in two ways: it influences the utilisation of energy foods and the rate and degree of nitrogen fixation. Under the same conditions these effects are controlled by the nature of the energy food available. In doses of 5 mg. per 100 c.c. of culture medium, humus accelerates the utilisation of sucrose, but retards that of dextrose. In doses of 100 mg. per 100 c.c. humus gives positive but variable effects throughout. So far it has not been possible to correlate acceleration of fixation with total yields of fixation products.

[B] The effect of adding humus to cultures of *C. pastorianum* and *A. chroococcum* may be compared with that of lowering the oxygen pressure in the culture, with a corresponding reduction of the rate of oxidation. The difficulty of oxidising humus in the soil, and the slow rate with which its nitrogen becomes available, are considered valuable factors in soil plant-food economy. E. HOLMES.

Composition of the gum produced by root nodule bacteria. E. W. HOPKINS, W. H. PETERSON, and E. B. FRED (J. Amer. Chem. Soc., 1930, 52, 3659—3668).—Cultures of *Rhizobium meliloti* 100 (alfalfa), *R. trifolii* 201 and 205 (clover), and *R. leguminosarum* 311 (pea) were grown usually on culture media containing mannitol, agar, and various salts. The gums produced contain varying amounts of ash and uronic acid, and on hydrolysis give dextrose. Bacterial fermentation tests indicate the absence of pentoses in the hydrolysis product. The results suggest that the gums are complexes of dextrose and a uronic acid (probably glycuronic acid).

H. BURTON.

Pigment of *B. prodigiosus*. W. MOYCHO (Compt. rend., 1930, 191, 497—499).—The pigment is formed on the autolysis of the bacteria in the presence of oxygen; it is rose-coloured from  $p_{\text{H}}$  4.0 to 8.0 and yellow from  $p_{\text{H}}$  8.0 to 9.0. C. C. N. VASS.

Chemistry of tubercle bacillus. I. Analysis of bacilli. II. Analysis of media. F. B. COOPER (J. Biol. Chem., 1930, 88, 485—491, 493—496).—I. A culture of *B. tuberculosis* (B. C. G.) was separated into virulent S and avirulent R types. Each type after cultivation on Sauton's medium was filtered, washed, dried, and extracted with a series of solvents. The R type contained a higher proportion of ether-soluble material, whilst the S type contained more glycogen, substances soluble in 0.5% sodium chloride, and substances soluble in 0.5% sodium hydroxide. Differences in the physical properties of the two types were also observed.

II. Similar fractionations on the media employed in these experiments showed that more glycogen,

carbohydrate, and substances soluble in 0.5% sodium hydroxide are elaborated by the S type than by the R type. G. F. MARRIAN.

Lipins of the tubercle bacillus. XVI. Composition of the total extractable fat. XVII. Occurrence of an unsaturated hexacosic acid in the fat. R. J. ANDERSON and E. CHARGAFF. XVIII. Polysaccharide from the lipins. E. CHARGAFF and R. J. ANDERSON (Z. physiol. Chem., 1930, 191, 157—165, 166—171, 172—178; cf. this vol., 819).—XVI. The fatty acid fraction of the toluene-soluble lipins was examined. The aqueous solution after saponification contained glycerol and probably butyric acid. The fatty acids consisted of saturated solid, saturated liquid, and unsaturated liquid acids. The last are completely hydrogenated with difficulty. The saturated liquid acid fraction contained tuberculostearic acid ( $\text{C}_{18}\text{H}_{36}\text{O}_2$ ) and phthioic acid ( $\text{C}_{26}\text{H}_{52}\text{O}_2$ ) and small amounts of a further acid,  $[\alpha]_{\text{D}}^{25} + 8.0^\circ$ , mol. wt. 592—600, corresponding with about  $\text{C}_{40}\text{H}_{80}\text{O}_2$ .

XVII. The unsaturated fatty acids which were reduced with difficulty were catalytically hydrogenated and the methyl esters distilled in a high vacuum. The esters of palmitic, stearic, and of a third acid,  $\text{C}_{26}\text{H}_{52}\text{O}_2$ , m. p. 82—82.5°, were obtained. This hexacosic acid probably has a branched chain, since it differs from the normal acid, m. p. 88—89°.

XVIII. From the lipins a carbohydrate complex,  $[\alpha]_{\text{D}}^{25} + 42.28^\circ$ , was obtained, probably containing a mixture of polysaccharides. The hydrolysis products contained *d*-arabinose, mannose, galactose, and inositol. J. H. BIRKINSHAW.

Natural and chemically defined media. A. BERTHELOT (Bull. Soc. Chim. biol., 1930, 12, 1025—1028).—Various media suitable for the growth of *B. tuberculosis* are discussed. A high content of arginine is favourable, and use may be made of products derived by proteolysis from naturally occurring substances. W. O. KERMACK.

Composition of peptone from ground-nut meal and its application to the culture of pathogenic bacteria. A. BERTHELOT, G. AMOUREUX, and D. PETIT (Bull. Soc. Chim. biol., 1930, 12, 1029—1030).—Analyses are given of two commercial samples of peptone prepared from ground-nut meal by peptic and tryptic hydrolysis, respectively. The differences account for the different results which may be obtained when these preparations are employed in media for the growth of bacteria. W. O. KERMACK.

Cell structure and cell activity. M. PENROSE and J. H. QUASTEL (Proc. Roy. Soc., 1930, B, 107, 168—181).—Lysis of *Micrococcus lysodeikticus* by dilute solutions of egg-white or saliva causes an increased activity of the catalase, fumarase, urease, and oxidase of *p*-phenylenediamine, which is attributed to the increased facility of access of the reagents to the enzymes on disintegration of the cell. No apparent change in the peroxidase activity is observable. The activities of the dehydrogenases of dextrose, laevulose, glutamic acid, and glycerophosphoric acid are completely destroyed and those of lactic acid and succinic acid greatly diminished, whilst the activity

of the aerobic oxidation of hydrogen donors is almost eliminated when *M. lysodeikticus* is disintegrated.  
C. C. N. VASS.

Oxidation-reduction studies in relation to bacterial growth. III. Positive limit of oxidation-reduction potential required for germination of *B. tetani* spores *in vitro*. B. C. J. G. KNIGHT and P. FILDES (Biochem. J., 1924, 24, 1496—1502).—Germination is completely inhibited at potentials more positive than  $E_h + 0.11$  volt.  
S. S. ZILVA.

Influence of hydrogen-ion concentration on the sporulation of *B. welchii*. J. C. TORREY, M. C. KAHN, and M. H. SALINGER (J. Bact., 1930, 20, 85—98).—Sporulation of *B. welchii* does not occur in media more acid than  $p_H$  6.6, the optimum range being  $p_H$  7.4—8.0. Neither mannitol nor raffinose favours sporulation.  
A. G. POLLARD.

Improved technique for the Voges-Proskauer test. C. H. WERKMAN (J. Bact., 1930, 20, 121—125).—The coloration produced in the Voges-Proskauer reaction is made more permanent by the addition of ferric chloride which accelerates the oxidation of acetylmethylcarbinol to diacetyl. Two drops of 2% ferric chloride solution are added to 5 c.c. of the culture solution, followed by 5—10 c.c. of 10% sodium hydroxide solution. The deep copper colour produced in a positive test remains for several days.  
A. G. POLLARD.

Comparative cryptotoxic power of the sodium salts of the fatty acids. H. VINCENT (Compt. rend., 1930, 191, 463—465). The toxins of tetanus and diphtheria were treated with varying concentrations of the sodium salts for 4 days at 38° and the resultant toxicity was tested against the guinea-pig. The first member of the series to possess cryptotoxic power was sodium butyrate; of the higher acids the palmitate alone was active. No correlation between the concentration of the salt or the physical properties of the solutions and the cryptotoxic power was observed.  
C. C. N. VASS.

Bactericidal action of ultra-violet light. III. Absorption of ultra-violet light by bacteria. F. L. GATES (J. Gen. Physiol., 1930, 14, 31—42).—The incident energy required to effect 50% destruction of *Staphylococcus aureus* varies with the wave-length employed, from 3150 ergs per  $mm^2$  at 302  $m\mu$  to 88 ergs at 266  $m\mu$ . Films of bacteria between quartz plates, of thickness 5—15  $\mu$ , are used for irradiation. The curves of incident energy indicate a maximum bactericidal action for *S. aureus* and *B. coli* of light with a wave-length of 260—270  $m\mu$ .  
P. G. MARSHALL.

The question of the identity of a bacterial growth-promoting factor with vitamin- $B_1$ . J. G. DAVIS and J. GOLDING (Biochem. J., 1930, 24, 1503—1506).—Vitamin- $B_1$  concentrates of the same order of potency for rat protection have widely different effects on the growth of a lactobacillus; some have no effect at all. Commercial peptones contain negligible amounts of vitamin- $B_1$ . The bacterial growth-stimulating substance (Davis and Mattick, J. Dairy Res., 1929, 1, 50; 1930, 1, 136) is not identical with vitamin- $B_1$ .  
S. S. ZILVA.

Pituitrin and blood-sugar. X. CHAHOVITCH (Compt. rend. Soc. Biol., 1930, 103, 332—334; Chem. Zentr., 1930, i, 2748).—Subcutaneous or intracardial injection of pituitrin produces hyperglycæmia in rabbits, due partly to liberation of protein-sugar.  
A. A. ELDRIDGE.

Rôle of the adrenals in synthalin hyperglycæmia. X. CHAHOVITCH (Compt. rend. Soc. Biol., 1930, 103, 328—330; Chem. Zentr., 1930, i, 2748).—Primary hyperglycæmia is not observed after injection of synthalin into adrenalectomised rabbits.  
A. A. ELDRIDGE.

Stimulating action of adrenaline on muscle oxidation. U. VON EULER (Compt. rend. Soc. Biol., 1930, 103, 445—446; Chem. Zentr., 1930, i, 2115).—Adrenaline increases muscle metabolism by about 25%.  
L. S. THEOBALD.

Hormone control of the colloid-osmotic pressure of the blood. S. TADA and F. NAKAZAWA (Tohoku J. Exp. Med., 1930, 15, 119—134).—The osmotic pressure of blood colloids is increased by injection of "thyroglandol"; pituitrin decreases the pressure, whilst insulin and adrenaline cause an increase followed by a decrease. The change is ascribed to a qualitative change in the blood-protein.  
CHEMICAL ABSTRACTS.

Glycogen content of the animal liver after injection of parathyroid extract. C. I. PARHON and M. CAHANE (Compt. rend. Soc. Biol., 1929, 101, 1179—1180; Chem. Zentr., 1930, i, 2577).—No significant change was observed with guinea-pigs.  
A. A. ELDRIDGE.

Plasma-calcium and -inorganic phosphorus following intravenous injection of parathyroid extract. The source of mobilised calcium. C. TSAI and F. Y. HSU (Chinese J. Physiol., 1930, 4, 265—272).—Dogs to which "parathormone" is administered show rises in the plasma-calcium and -inorganic phosphorus in the ratio 2 : 1, approximately the same as that of the calcium to phosphorus in bone. This result supports the conclusion of Greenwald and Gross (cf. A., 1926, 206) that the bone is the source of calcium appearing in the blood as the result of the action of "parathormone." The rise in the plasma-calcium precedes that of the plasma-phosphorus by about 2 hrs., but the phosphorus falls less quickly, due apparently to less efficient excretion.  
W. O. KERMACK.

Action of the parathyroid hormone on the bone-calcium of the growing animal. G. BISCHOFF (Z. ges. exp. Med., 1929, 68, 772—784; Chem. Zentr., 1930, i, 1320—1321).—A dog on a rachitic diet suffered more than similar dogs receiving also injections of parathyroid extract; the bones of the former contained 14% less calcium than those of the latter.  
A. A. ELDRIDGE.

Mechanism of the action of insulin. A. A. SCHMIDT (Arch. exp. Path. Pharm., 1930, 153, 79—93).—The sugar contents have been determined in samples of blood drawn from the femoral vein and artery and hepatic and portal veins of dogs before and after the administration of insulin. It is concluded that insulin markedly increases the uptake of sugar by the muscles and probably causes an increase in the liberation of sugar by the liver. W. O. KERMACK.

**Distribution of insulin in the organism after injection of insulin. I. II. Dependence on diet and blood-sugar content.** H. HORSTERS (Arch. exp. Path. Pharm., 1930, **153**, 214—230, 231—243).—Insulin is assayed in the blood or organs of an animal by elution with warm Tyrode solution and injecting the extract into white mice in order to determine its hypoglycaemic action (cf. Brugsch and Horsters, Z. exp. Med., 1929, **65**, 569). After the intravenous injection of insulin into rabbits it gradually disappears from the blood, about 10% remaining there after 50 min. and appears in the liver and slowly in the muscles, in which it gradually accumulates, about 50% being found there after 210 min. After subcutaneous administration of insulin the largest amount of storage is observed in about 60 min., after which time the amount which can be extracted from the organs gradually decreases.

II. Hyperglycaemia brought about by administration of dextrose or adrenaline approximately doubles the amount of insulin which can be eluted from the liver and muscles. After the administration of insulin the amount of insulin capable of being extracted from the muscles 60 min. after the injection of insulin may, in the case of animals in a hyperglycaemic condition as the result of carbohydrate feeding or administration of adrenaline, amount to more than double that injected.

W. O. KERMACK.

**Initial changes in the liver- and muscle-glycogen in fasting dogs under the influence of insulin. II. Initial changes in the liver- and muscle-glycogen in pancreatectomised dogs.** F. RATHERY, R. KURILSKY, and S. GIBERT (Compt. rend. Soc. Biol., 1930, **103**, 376—378, 378—380; Chem. Zentr., 1930, i, 2116—2117).—I. Liver and muscle retain considerable quantities of glycogen even after 31 days' fasting. With respect to the glycogen reserve, insulin acts on starving animals in the same way as on normal animals.

II. After removal of the pancreas glycogen disappears to a fixed extent both in muscle and liver. The latter often shows complete disappearance and the first injection of insulin removes the last traces, but in muscle only a slight further diminution occurs.

L. S. THEOBALD.

**Activation of insulin. Crystallised insulin.** H. JENSEN and A. M. DE LAUDER (Biochem. Z., 1930, **225**, 141—150).—In experiments with crystallised insulin, activation by means of serum, enterokinase, and yeast juice could not be confirmed.

P. W. CLUTTERBUCK.

**Pancreas and blood-sugar regulation.** B. A. HOUSSAY, J. T. LEWIS, and V. G. FOGLIA (Rev. soc. Argentina biol., 1929, **5**, 1—14).—The fall in blood-sugar after intravenous injection of insulin into dogs was the same whether the animals were normal, pancreatectomised, or pancreatectomised with a pancreas grafted between the carotid artery and jugular vein.

CHEMICAL ABSTRACTS.

**Effect of liver diet on blood-sugar.** E. LOMBARDI (Réf. Med., 1930, **46**, 7—14).—Liver pulp appears to contain a hypoglycaemic substance.

CHEMICAL ABSTRACTS.

**Secretin and blood-sugar.** E. ZUNZ (Compt. rend. Soc. Biol., 1929, **102**, 339—340; Chem. Zentr., 1930, i, 2577).—Preparations of secretin, when free from substances which diminish the blood-pressure, do not affect the blood-sugar. A. A. ELDRIDGE.

**Female sexual hormone. IV. Preparation of pure follicular hormone from urine of pregnancy. V. Physical and chemical properties of crystalline follicular hormone.** A. BUTENANDT (Z. physiol. Chem., 1930, **191**, 127—139, 140—156; cf. this vol., 646).—IV. The crystalline hormone may be obtained from "crude hormone oil" from urine of pregnancy (a) by partition of the crude oil between 50% alcohol and light petroleum of high b. p., the hormone remaining in the alcohol; (b) by partition of the partly purified product between 60% aqueous alcohol and benzene; (c) by extracting the ethereal solution of the crude oil with alkali hydroxide and shaking out the acidified extract with ether. The highly-purified oil may be distilled in high vacuum (0.02—0.03 mm.). The greater portion sublimes at 150°. The crystals are recrystallised from ethyl acetate and light petroleum of high b. p.

V. The crystalline hormone,  $C_{18}H_{22}O_2$ , m. p. 250—251° (corr.),  $[\alpha]_D^{25} +156^\circ$ , absorption maximum at 283—285 m $\mu$ , has an activity of  $8-40 \times 10^6$  units per g. It yields an oxime, decomp. 230° (uncorr.), an acetyl derivative, m. p. 111—112° (probably contains water), 126° (anhydrous), and a benzoyl derivative, m. p. 211—212° (decomp.). Hydrogenation gives a compound,  $C_{18}H_{30}O$ , softens at 95°, m. p. 104° (uncorr.). The hormone thus appears to contain a hydroxyl and a keto-group and three double linkings, and is different from Marrian's product (this vol., 1320).

J. H. BIRKINSHAW.

**Non-identity of the active substance of the placenta with the pituitary hormone.** M. KLEIN (Compt. rend. Soc. Biol., 1930, **102**, 1070—1071; Chem. Zentr., 1930, i, 2748).—Although placenta and anterior pituitary extract have a similar action on the ovary, the former does not act like the latter on the thyroid. Hence the placental hormone is distinct from the anterior pituitary hormone.

A. A. ELDRIDGE.

**Relation of carotene to vitamin-A.** E. M. HUME and I. SMEDLEY-MACLEAN (Lancet, 1930, **218**, 290—292).—The effect of administering purified carotene as the only source of vitamin-A to rats fed on diets containing fat or fat-free has been investigated. The presence or absence of fat in the diet has no significance, but the solvent employed is an important factor. The relationship between carotene and the substance responsible for the biological activity in vitamin-A of liver extracts is still uncertain.

L. S. THEOBALD.

**So-called vitamin-A.** W. CORNELI (Z. physiol. Chem., 1930, **191**, 86—88).—The deoxycholic acid compound of vitamin-A was obtained according to the method of Shimizu and Hatakeyama (A., 1929, 726). The equivalent titration corresponds with a deoxycholic acid content of 8 molecules; Shimizu's figure points to 5 mols.

J. H. BIRKINSHAW.

**Statistical methods in the biological assay of vitamins. I. Effect of variables. II. Number**

of animals. M. H. IRWIN, A. E. BRANDT, and P. M. NELSON (J. Biol. Chem., 1930, 88, 449—459, 461—470).—I. A statistical study of the growth records of a large number of rats used in vitamin-A and -B tests revealed that the amount of basal diet consumed was the main factor in determining the variability of change in weight in individual animals. The initial weight and the duration of the experiment were found to be relatively unimportant.

II. A method is described by which the number of animals in each group necessary to obtain significant differences in change of weight may be calculated. Rats used in vitamin-B tests showed more uniform weight changes than those in vitamin-A tests.

G. F. MARRIAN.

**Formation of vitamin-B by *B. mycoides*, Flüge, and *B. mycoides ruber*, Matzuschita.** M. SCHIEBLICH (Biochem. Z., 1930, 225, 212—215).—The formation of vitamin-B by *B. mycoides*, Flüge, is poor, smaller even than with *B. mesentericus* (Flüge), Lehm. and Neum., but is good with *B. mycoides ruber*, Matzuschita, although not as good as with *B. vulgaris* (Flüge), Migula.

P. W. CLUTTERBUCK.

**Vitamin-B<sub>2</sub> content of cereals and the supposed connexion between human pellagra and deficiency of this vitamin.** W. R. AYKROYD (Biochem. J., 1930, 24, 1479—1488).—Two samples of whole rice and two samples of milled rice, "raw" and "parboiled," and whole millet are poor sources of vitamin-B<sub>2</sub>. Amongst the control rats, which remained stationary in weight, only two animals developed dermatitis. Diets containing 65% of maize endosperm and 50% of whole rice, respectively, did not alleviate the symptoms. S. S. ZILVA.

**Conversion of ergosterol into vitamin-D under the influence of radium emanation.** J. MAISIN, W. MUND, Y. POURBAIX, and A. CASTILLE (Compt. rend. Soc. Biol., 1930, 103, 534—536; Chem. Zentr., 1930, i, 2755).—After exposure to radium emanation while dissolved in paraffin, ergosterol possessed antirachitic properties. A. A. ELDRIDGE.

(1) **Distillation of vitamin-D.** (2) **Further irradiation of radiation products of ergosterol.** F. A. ASKEW, R. B. BOURDILLON, H. M. BRUCE, R. G. C. JENKINS, and T. A. WEBSTER (Proc. Roy. Soc., 1930, B, 107, 76—90, 91—100).—I. Resins obtained by the removal of unchanged sterol from ergosterol after irradiation were distilled in a high vacuum. Redistillation of the active fractions and crystallisation from aqueous alcohol yielded crystals, m. p. 113—115°, which were highly antirachitic. It is not claimed that this substance is vitamin-D, since resinous mixtures of the same potency were obtained. It is considered possible that the substance may consist of mixed crystals of the vitamin and an inactive substance, or that it may be one of a number of antirachitic substances.

II. Various irradiation products of ergosterol were irradiated with "short" rays (210—280 mμ) and with "long" rays (longer than 280 mμ). The resin obtained by the removal of unchanged ergosterol from the irradiated mixture, on re-irradiation with

short rays, showed a large increase in absorption at 280 mμ and a decrease in antirachitic potency. On re-irradiation with long rays, the absorption at 280 mμ was slightly decreased, whilst the activity was unchanged. By dissolving such resins in alcohol and adding water, an active granular solid was obtained showing a maximum absorption at 251 mμ. After re-irradiation with short and long rays, the absorption measured at 255 mμ fell rapidly. The crystalline distillation product (see above) showed a relatively slow change in absorption on re-irradiation with short rays.

The results on the ergosterol-free resins prove that the substance absorbing at 280 mμ is not vitamin-D. Evidence is advanced that this substance (probably identical with the substance "A" of Bourdillon and others; A., 1929, 727) is formed simultaneously with vitamin-D from ergosterol on irradiation and is not a precursor of the latter. G. F. MARRIAN.

**Physiological effect of irradiated ergosterol and its transformation products.** F. HOLTZ and E. SCHREIBER (Z. physiol. Chem., 1930, 191, 1—22).—The poisoning produced by excessive doses of irradiated ergosterol (so-called hypervitaminosis) is due not to the excess of vitamin-D administered, but to an excess of the "calcinosis factor," which is also produced by irradiation of ergosterol. The amounts of the vitamin and of this factor found under varying conditions of irradiation are closely proportional. The calcinosis factor may be isolated and its effect studied by heating the activated ergosterol to 160° or by reduction with sodium in alcohol, whereby the antirachitic factor alone is destroyed. The symptoms produced by the toxic factor: calcium deposition, hypercalcaemia, hyperphosphataemia, circulatory deficiency, are those characteristic of "hypervitaminosis." J. H. BIRKINSHAW.

**"Ergosterism" in puppies suckled by mothers given excessive doses of irradiated ergosterol.** M. COMEL (Arch. Ist. Biochim. Ital., 1930, 2, 481—492).—"Ergosterism"—the toxic effects of excessive doses of irradiated ergosterol—has been produced in puppies by giving excessive doses to the mothers, which themselves showed unusual resistance. Thus the toxic constituent, which may or may not be different from the vitamin, is also transferred by way of the milk. R. K. CALLOW.

**Hypervitaminosis-D: calcium-phosphorus intake a determining factor.** L. J. HARRIS (Lancet, 1930, 218, 236).—The occurrence or severity of hypervitaminosis is determined not only by the excess of vitamin-D administered and the time of administration, but also by the calcium and phosphate contents of the diet. Contrary to the suggestion of Hess, no loss of calcium or phosphorus from bones accounts for the rise in the blood figure.

L. S. THEOBALD.

**Vitamin content of breads baked with baking-powder and with yeast.** A. BERNFELD and E. SCHIFF (Biochem. Z., 1930, 224, 434—436).—Bread baked with yeast contains more vitamin than that baked with baking-powder (cf. Scheunert and Schiebllich, A., 1929, 221, 1344). W. MCCARTNEY.

**Germination of seeds. I. Transformation of nitrogenous compounds during germination of soya-bean seeds. II. Starch produced during the germination of soya-bean seeds.** S. SASAKI (Bull. Agric. Chem. Soc. Japan, 1928, 4, 75—77; 1929, 5, 6—7).—During germination the protein was gradually decomposed; the nitrogen insoluble in concentrated hydrochloric acid increased, whilst amide-nitrogen decreased slightly. The nitrogen in the filtrate from heat-coagulated protein increased. The nitrogen precipitated from the filtrate by phosphotungstic acid increased at a slower rate than that not precipitated. During germination in the dark 0.4—7.7% of starch was produced. The saccharification velocity of the paste was intermediate between that of potato starch and that of wheat starch.

#### CHEMICAL ABSTRACTS.

**Energy-storage of plants in relation to the carbon and nitrogen contents. II.** V. HÖNL (Biochem. Z., 1930, 225, 94—114).—In all the investigated plants, the caloric, carbon, and nitrogen contents of 1 g. of ash-free dry substance gradually decreased during development. This decrease is much greater with non-leguminous (buckwheat, maize, turnip) than with leguminous plants (lupin, pea). The C/N ratio during development remains constant for leguminous but increases for non-leguminous plants. The mineral content of the plant substance changes but slightly in the leguminous and decreases in the non-leguminous plants. With oats, a decrease of nitrogen and phosphorus supply causes a decrease of carbon and caloric content of the crop. With increased supply of nitrogen, the C/N ratio increases at first and then decreases, whilst with increasing supply of phosphorus it decreases (cf. A., 1928, 559).

P. W. CLUTTERBUCK.

**Synthesis of proteins by higher plants. J.** BJÖRKSTÉN (Biochem. Z., 1930, 225, 1—80).—The utilisation of a large number of substances as sources of carbon and nitrogen for protein synthesis was investigated with germinating wheat plants, the substances in very great dilution being injected into the intercellular spaces of the leaves by the evacuation method, the experiment stopped by heating after at least 6 hrs., and the protein-nitrogen determined. The formation of carbon dioxide in the leaves is very greatly increased by the infiltration of hydrogen peroxide, but of protein is scarcely affected in so short a time. Protein synthesis is not affected by the differences in acidity and osmotic pressure of the substances used nor by the presence of potassium, sodium, and chlorine ions in the concentrations used. Many of the simple aliphatic acids and hydroxy-acids are unable to act as a source of carbon for protein synthesis. Pyruvic acid, but not its homologues, is readily utilised and does not undergo decarboxylation during the synthesis. Formaldehyde, acetaldehyde, glyceraldehyde, and dihydroxyacetone are not, but dextrose is, utilised. Aliphatic amides, amino-acids, lower amines, substituted amides, nitrites, and ammonium salts of aliphatic organic acids are all readily utilised as a source of nitrogen, nitrites and ammonium salts of mineral acids only feebly, whilst nitriles and certain cyclic compounds are not utilised.

Hydroxynitriles and acetaldehyde- and propaldehyde-cyanohydrins are readily, but hydrogen cyanide is not, utilised. The cyanide strongly inhibits heat production in the leaves. From determinations of amino-nitrogen it appears probable that protein synthesis occurs by way of amino-acids. Irradiation did not affect protein synthesis from amides and ammonium salts and bright diffused daylight did not accelerate synthesis from nitrites and nitrates.

P. W. CLUTTERBUCK.

**Early and late ripening and the acids of fruit.** R. NUCCORINI [with A. ZACCAGNINI] (Annali Chim. Appl., 1930, 20, 302—309).—There is a relationship between the times of ripening of the varieties of any one species of fruit and their qualitative and quantitative acid content. When ripening occurs during the warmer months of the year, the proportion of malic acid is less and that of tartaric acid greater than with varieties ripening during the cooler months.

T. H. POPE.

**Physical chemistry of vegetable sap. E.** CANALS, J. CANAYÉ, and E. CABANES (Bull. Soc. Chim. biol., 1930, 12, 1022—1024).—Calcium, potassium, magnesium, sodium, and phosphate have been determined in the sap of various plants before and after dialysis, in presence of toluene. Sodium, potassium, magnesium, and phosphate were almost completely dialysable and therefore presumably these constituents exist in the sap in a simple crystalloid form, but except in special cases, e.g., carrot, the calcium largely exists in a non-dialysable form.

W. O. KERMAK.

**Exchange of ions between vegetable cells and salt solutions.** P. GENAUD (Rev. gén. Colloid., 1930, 8, 241—250).—When yeast-cells are immersed in inorganic salt solutions exchange of cations between the inorganic constituents of the cells and the external solution takes place. This exchange comes to a definite equilibrium and is in accordance with the law of mass action. The cell is characterised not by the quantity and nature of the different cations contained, but by the total amount of cations available for exchange. When placed in a dilute solution of lead nitrate, dead yeast-cells take up about four times as much lead as the live cells, and this observation provides a useful means of diagnosis. Further, subsequent treatment with hydrogen sulphide shows that in the live cell the lead ions penetrate only the membrane and the vacuole, whilst in the dead cell the entire structure is penetrated. It is considered that the cell membrane is composed of regularly disposed molecules, leaving definite spaces, and that both the membrane and vacuole behave like insoluble organic acids, exchanging their cations for those of the surrounding medium.

E. S. HEDGES.

**Penetration of dyes. IV. Penetration of brilliant-cresyl-blue into *Nitella flexilis*. V. Why does azure-B penetrate more readily than methylene-blue or crystal-violet?** M. IRWIN (J. Gen. Physiol., 1930, 14, 1—17, 19—29).—IV. The average sap of *Nitella* has  $p_H$  5.36 *in vitro*, which increases by about 0.55 when 0.07% of the dye is dissolved in it. A similar increase is observed in the sap of living cells.



V. Azure-B penetrates the vacuole as the free base and raises the  $p_H$  of the sap, whilst between  $p_H$  5.0 and 9.2 both crystal-violet and methylene-blue exist mainly as salts which are unable to penetrate readily and do not raise the  $p_H$  of the sap.

P. G. MARSHALL.

**Accumulation of electrolytes. I. Entrance of ammonia into *Valonia macrophysa*.** W. C. COOPER and W. J. V. OSTERHOUT (J. Gen. Physiol., 1930, 14, 117—125).—Cells of *V. macrophysa* rapidly absorb ammonium chloride when placed in sea-water containing this salt, so that the specific gravity of the cell-sap decreases and the cells float. The higher is the concentration of undissociated ammonia in the sea-water, the more rapidly does the  $p_H$  of the cell-sap rise. Corresponding with the rise in ammonia there is a fall in the potassium concentration. The increase in halide content is not parallel to that of ammonia, showing that the substance entering is largely ammonia.

P. G. MARSHALL.

**Micro-determination of iron in leaves lacking chlorophyll.** D. RUNEJELM (Biochem. Z., 1930, 224, 481—486).—The total iron content of leaves is determined in the ash by a combination of the methods of Lachs and Friedenthal (A., 1911, ii, 542) and of Schönheimer and Oshima (A., 1929, 341). In the case of barley there is no difference in the iron content between normal leaves and those lacking chlorophyll, but white leaves of *Tradescantia* lacking chlorophyll contain twice as much iron as do its normal leaves.

W. MCCARTNEY.

**Fluorescent substances in seeds and fruits.** P. METZNER (Biochem. Z., 1930, 224, 448—458).—When seeds and fruits are steeped in water, fluorescent substances, most of which exhibit weak photodynamic activity, go into solution.

W. MCCARTNEY.

**Distribution of lutein in the vegetable kingdom.** R. KUHN and A. WINTERSTEIN (Naturwiss., 1930, 18, 754).—Lutein, the yellow dye in egg-yolk, is widely distributed in the vegetable kingdom; in most cases the yellow colouring-matter in leaves, formerly described as xanthophyll, contains also lutein. Esterification with palmitic acid yields a red dipalmitate, m. p. 92°. Lutein can be obtained from methyl alcohol in an ochre-brown modification which is free from alcohol, and in a glittering violet modification which contains 1 mol. of methyl alcohol. The dye of egg-yolk is probably obtained from the food.

W. R. ANGUS.

**Sterols of ergot. II. Occurrence of dihydroergosterol.** F. W. HEYL and O. F. SWOAP (J. Amer. Chem. Soc., 1930, 52, 3688—3690).— $\alpha$ -Dihydroergosterol, m. p. 172.5—175°,  $[\alpha]_D^{25}$  -20.6° (acetate, m. p. 176—177°; benzoate, m. p. 153—155°), has been isolated from the ergosterol-free ether-light petroleum solution of the unsaponifiable matter of ergot fat (this vol., 910). H. BURTON.

**Chemical examination of the seeds of *Cassia Tora*, Linn.** I. H. S. JOIS and B. L. MANJUNATH (J. Indian Chem. Soc., 1930, 7, 521—526).—The fatty oil obtained by extracting the seeds of *C. Tora* with light petroleum gives on saponification oleic, linoleic,

palmitic, and lignoceric acids; the unsaponifiable matter contains sitosterol. H. A. PIGGOTT.

**Saponin of soya bean.** I. Y. SUMIKI (Bull. Agric. Chem. Soc. Japan, 1929, 5, 27—32).—The saponin consists of 1 mol. each of sapogenin, dextrose, rhamnose, arabinose, and another substance, possibly mesoxalic acid.

CHEMICAL ABSTRACTS.

**Chemistry of the products of *Cocos nucifera*.** I. J. P. C. CHANDRASENA (Biochem. J., 1930, 24, 1493—1495).—The water content of the kernel diminishes with age. The oil of the latest stage is either less than or equal to that at the preceding stage. The quantity of "residue," mainly cellulose, varies only slightly during all stages of development. The quantity of pentosans calculated on the dry material is nearly the same in all cases and in the haustorium it is comparatively high. The residue is lignin-free. The lignin content is high. Oil constants do not vary much except for the iodine and acid values, which are high in the oil from the youngest bunch. The oil from the haustorium has an even higher iodine value.

S. S. ZILVA.

**Determination of cellulose in straws.** S. H. JENKINS (Biochem. J. 1930, 24, 1428—1432).—The straw is treated with hot dilute alkali and acid and cold sodium hypochlorite. A product similar to Cross and Bevan's chlorination product, except that it contains slightly less xylan than the latter, is obtained.

S. S. ZILVA.

**Decomposition of cellulose and lignin in fallen leaves and needles by fungi and its rôle in the formation of the humic material of the forest floor.** R. FALCK (Cellulosechem., 1930, 11, 198—202).—The decomposition occasioned by *Agaricus nebularis* in sterile pine needles or beech leaves is of the type classified as "corrosion" where both the lignin and the polysaccharides (cellulose and the pentosans) disappear at the same time. With *Coniophora cerebella*, however, the polysaccharides alone are removed, leaving the lignin unattacked; "destruction" is the name given to this type of biological decomposition of wood. During this process the alkali-solubility of the lignin increases, denoting an increased acidity. This type of decomposition results in the formation of humic material. Pine needles, which are not a natural habitat of *A. nebularis*, do not so easily suffer corrosion as do beech leaves. From the needles lignin and cellulose are removed in approximately equal amounts, but from the leaves the ratio of lignin to cellulose removed is 1.4 to 2.3, thus tending to give a material richer in cellulose and poorer in lignin. During the process of destruction organic acids are produced, but with corrosion the product of decomposition is neutral or but slightly acid.

T. H. MORTON.

**Mannitol from *Haptophyton cimidum*.** N. L. DRAKE and J. R. SPIES (J. Amer. Chem. Soc., 1930, 52, 3739).—Mannitol has been isolated from the crude crystalline material (0.75% of dry plant) which separates from a concentrated alcoholic extract of the plant.

H. BURTON.

**Occurrence of mannitol in spike disease of *Santalum album*.** M. SREENIVASAYA (Nature,

1930, 126, 438).—Slow evaporation of the water-soluble constituents of the spiked leaf of sandal yields mannitol (2–3% by weight of green material), but only in the case of diseased samples.

L. S. THEOBALD.

**Unedoside**, a  $\beta$ -glucoside from fresh leaves and branches of *Arbutus Unedo*, L. M. BRIDEL and C. BOURDOUIL (J. Pharm. Chim., 1930, [viii], 12, 241–253).—Enzyme experiments on alcoholic extracts do not give clear indications as to the nature of the glucosides present (cf. Bourquelot and Fichtenholz, A., 1913, i, 1141). When the extracts, after treatment with lead acetate, are evaporated to dryness, and extracted with moist ethyl acetate and then with aqueous acetone, the latter contains *unedoside* (0.01% of the original material) (C, 48.0%, H, 6.5%), m. p. 225.5° (Maquenne block),  $[\alpha]_D -112.4^\circ$ . This reduces Fehling's solution, 1 g. being equivalent to 0.853 g. of dextrose. It is hydrolysed by dilute sulphuric acid at 100° to dextrose and *unedol*, which resinifies and is precipitated. This accounts for the observation that hydrolysis of the crude solutions causes a decrease in laevorotation accompanied by a decrease in reducing power towards Fehling's solution. *Unedol*, obtained crystalline from ethereal extracts of emulsin hydrolysates, gives a blue colour with ferric chloride and reduces Fehling's solution. H. E. F. NOTTON.

**Presence of rutin (rutoside) in the leafy stems of *Bupleurum falcatum***. J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 974–977).—Rutin (cf. Charaux, A., 1924, i, 1272), a glucoside yielding quercetin, rhamnose, and dextrose, has been identified in the dried leafy stems of *B. falcatum*. W. O. KERMACK.

**Salicinerin from *Salix cinerea*. Its identity with piceoside**. J. RABATÉ (Bull. Soc. Chim. biol., 1930, 12, 965–973).—Salicinerin described by Johansson (Diss., Dorpat, 1875) and Jacoby (Diss., Dorpat, 1890) from the bark of *S. cinerea* is identical with piceoside, the glucoside of *p*-hydroxy-acetophenone (cf. this vol 258, 825).

W. O. KERMACK.

**Pollen and pollen extracts. I. Distribution of nitrogen extracted by various solvents**. E. E. MOORE and M. B. MOORE (J. Amer. Chem. Soc., 1930, 52, 3591–3596).—Nitrogen determinations have been made by the method of Koch and McMeekin (A., 1924, ii, 871) on the extracts obtained by successive extraction of the pollens of timothy (*Phleum pratense*, L.), orchard grass (*Dactylis glomerata*, L.), short ragweed (*Ambrosia elatior*, L.), and giant ragweed (*A. trifida*, L.) with ether, water, 10% sodium chloride solution, 75% alcohol, and 0.2% sodium hydroxide solution. Only a very small amount of nitrogen (probably non-protein) is extracted by ether. The aqueous extracts contain most nitrogen, of which only a small percentage is non-dialysable. About one half of the non-dialysable nitrogen is precipitated during dialysis; the precipitated material is probably globulin. Similar results are obtained for the sodium chloride extract. Only a small amount of nitrogen is extracted by 75% alcohol, and about half of that extracted by alkali is precipitated on acidification; the precipitated material is probably a

glutelin. Approximately one half of the nitrogen originally present in the pollens remains in the residue after the above extractions. The ragweed pollens contain much more ether-soluble, but less water-soluble, material than the grass pollens.

H. BURTON.

**Picric acid as a destaining agent for iron alum hæmatoxylin**. H. C. TUAN (Stain Tech., 1930, 5, 135–138).—A saturated aqueous solution of picric acid is used to differentiate paraffin sections and smeared pollen-mother-cells stained in hæmatoxylin, iron alum being replaced by picric acid in the destaining process. H. W. DUDLEY.

**Methylated nitrogen compounds in sea-weed**. R. KAPPELLER-ADLER and T. CSATÓ (Biochem. Z., 1930, 224, 378–383).—Sea-weed (*Fucus vesiculosus* and *F. serratus*) contains ammonia, methylamine, and trimethylamine, all in the combined state, or substances which break down rapidly into these bases after the death of the plants. W. MCCARTNEY.

**Degradation of nicotine in tobacco**. A. FAITEL-LOWITZ (Biochem. Z., 1930, 224, 459–470).—The quantity of potassium mercuric iodide solution which must be added before the precipitate first formed just dissolves is an approximate measure of the nicotine content of aqueous extracts of tobacco. This content decreases first quickly, then slowly, since the acidity of the extracts also decreases as a result of the increase in the total content of bases other than nicotine. When the extracts thus become strongly alkaline decomposition of the nicotine ceases, but can be renewed and completed if the basic degradation products are removed. As the decomposition proceeds the activity of the catalase present increases. If chloroform is present decomposition of the nicotine does not take place. The results prove that the process is bacterial and two species of bacteria from tobacco leaves have been distinguished. One species is aerobic and decomposes proteins; the other is anaerobic and decomposes carbohydrates with formation of acids. W. MCCARTNEY.

**Relation of sunlight to the light of luminous wood**. S. R. BOSE (Naturwiss., 1930, 18, 787).—When a sample of *Sterculia* wood was kept in a moist atmosphere between sterilised Mango wood-chips, white luminous hyphæ appeared and attached themselves to the chips. The luminosity was entirely due to the fungus and autoclaving the wood destroyed the luminosity. Luminescence was intermittent, depending on the general stimulation of the living hyphæ in the presence of sunlight. Over-exposure to sunlight and storage dry in the dark led to decreased luminescence. No phosphorescent metal could be detected either spectroscopically or microchemically. The light emitted by the wood showed a short continuous spectrum between 0.465 and 0.380  $\mu$ , with the maximum emission in the greenish-blue region.

P. W. CLUTTERBUCK.

**Aucuba or yellow mosaic of the tomato: metabolism**. B. D. BOLAS and W. F. BEWLEY (Nature, 1930, 126, 471).—Observations on the course of infection are recorded and a sequence of metabolism is suggested. L. S. THEOBALD.

**Chemistry of white rots of wood. I. Effect on wood substance of *Polystictus versicolor*, (Linn) Fr.** W. G. CAMPBELL (Biochem. J., 1930, 24, 1235—1243).—The decayed wood produced by the fungus is more soluble in water than the original wood. In the early stages of decay the residue is slightly more soluble in alkali than the original wood, but alkali-solubility tends to decrease as decay becomes more advanced. The pentosans of wood substance and lignin are the first components to be attacked and of these the pentosans, not the cellulose, suffer most depletion. As decay becomes more advanced the rate at which pentosans are depleted is diminished and preferential attack is made on the cellulose proper as well as on the lignin. The effects of the decay on wood substance are closely comparable with those produced by acid alcoholic solution under certain conditions. The fungus probably secretes an oxidase which acts on lignin and pentosans producing acid.

S. S. ZILVA.

**How does the copper-ion concentration influence the poisoning action of copper salt solutions for grain?** M. BIROLAND (Ann. Sci. agronom., 1929, 46, 733—741; Chem. Zentr., 1930, i, 2147).—The germinating power of grain is diminished by moistening with solutions of copper salts. The poisoning effect increases with an increase in concentration of the solution and for the same concentration of copper varies with different anions. The most highly dissociated salts are the most toxic and the poisoning power follows the order acetate < chloride < sulphate < fluosilicate. At the same concentration of copper ion, however, the toxicity of different salts is still different. The addition of alkali salts with the same anion diminishes the poisoning effect.

L. S. THEOBALD.

**Cutting microscopic sections of wood without previous treatment in hydrofluoric acid.** I. H. CROWELL (Stain Tech., 1930, 5, 149—150).—Steam is directed against the surface of the wood while the sections are being cut.

H. W. DUDLEY.

**Gas-analysis technique.** A. J. ANTHONY (Z. Biol., 1930, 90, 633—636).—The use of an apparatus of the Haldane type using mechanically shaken absorption burettes is described; its application to respiratory gases and the difficulties associated with the determination of nitrous oxide are discussed.

F. O. HOWITT.

**Conductivity apparatus for biological fluids.** F. W. SUNDERMAN (J. Biol. Chem., 1930, 88, 61—66).—An apparatus for use on a 60-cycle 110-volt circuit is described.

C. R. HARRINGTON.

**Limits of availability of the quinhydrone electrode in the examination of human body-fluids.** K. REIMERS (Z. ges. exp. Med., 1929, 67, 327—371; Chem. Zentr., 1930, i, 2929—2930).—The development of a red colour in protein solutions is due to the presence of benzoquinone; quinol gives no coloration. The appearance of the coloration is retarded by quinine. Human serum forms a stiff jelly 8—10 hrs. after the addition of much quinhydrone. The effect of ammonia (alkaline urine) on the determination is small. The quinhydrone electrode is unsuitable for the examination of whole

blood; irregular results appear to be due to interaction between haemoglobin and quinhydrone. Serum and plasma also give variable results, the maximum deviation from those with the hydrogen electrode being  $p_H$  0.14 on the acid side. The use of the quinhydrone electrode in the examination of sweat, exudates, wound secretions, and cerebrospinal fluid is described.

A. A. ELDRIDGE.

**Indication [unit] of hydrogen-ion concentration in biological studies.** G. JOOS (Klin. Woeh., 1929, 8, 2129—2132; Chem. Zentr., 1930, i, 2926).—The units  $[H^+] = 10^{-9} = 1p$ ;  $1000p = 1r$ ;  $1000r = 1R$  are proposed.

A. A. ELDRIDGE.

**Determination of carbon dioxide in fluids and tissues by micro-titration.** A. KROGH and P. B. REIBERG (Biochem. Z., 1930, 225, 177—182).—The carbon dioxide is set free in a vacuum by means of acid, absorbed by standard baryta, and titrated, using a micro-burette. Two types of apparatus are described, the first suitable for determinations of 700—30 mm.<sup>3</sup> of carbon dioxide in 3—20 c.c. of water or similar fluid and the second for similar amounts of carbon dioxide in 0.1—0.15 c.c. of fluid or in 50—100 mg. of tissue.

P. W. CLUTTERBUCK.

**Micro-determination of unsaturated fatty acids containing four double linkings.** H. TANGI (Biochem. Z., 1930, 226, 180—184).—Blood or serum is dropped into alcohol-ether, and after a time filtered and the filtrate treated with bromine. The precipitated bromo-compounds are washed with hot benzene, which removes bromine derivatives containing two, four, and six but not eight bromine atoms. The bromine of the insoluble fraction is determined. The fasting values for ox and dog's blood vary from 16 to 22 mg. per 100 c.c. and correspond with 10% of the total fatty acid of the blood. The method is adapted for determinations in heart, kidney, liver, etc., and the amounts of unsaturated acid are summarised in a table. The results compare favourably with those of Hartley (A., 1908, ii, 210; 1909, ii, 597) obtained with much larger amounts of material.

P. W. CLUTTERBUCK.

**Adaptation of the Van Slyke-Palmer method of titration of organic acids to solutions which contain proteins.** E. E. MARTINSON and A. A. MARKOVA (Ark. biol. 1930, 30, 181—187).—Trichloroacetic acid is used.

CHEMICAL ABSTRACTS.

**Colorimetric determination of nitrogen by direct nesslerisation: a modified Nessler-Folin reagent.** L. S. WALTERS (Austral. J. Exp. Biol., 1930, 7, 113—116).—The method, which is based on that of Folin (A., 1916, ii, 573) and includes a modification of the protective technique of Chiles (A., 1928, 312), is suitable for barley, malt-worts, etc. The digestion product, obtained in the normal way, is treated with gum ghatti, and the mercuric iodide reagent of Koch and McMeekin (A., 1924, ii, 871) which has been rendered alkaline by lithium hydroxide is then added.

F. O. HOWITT.

**Colorimetric determination of urea [in serum or urine].** S. Aoi (Nagoya J. Med. Sci., 1928, 3, 13—18).—The colour obtained with Ehrlich's reagent is compared with that of a 0.02% potassium chromate

solution; a positive reaction is obtained with 0.0005 *M*-urea, and the results agree ( $\pm 5\%$ ) with those obtained by the urease method. Human serum contains 40–52 mg. per 100 c.c.

#### CHEMICAL ABSTRACTS.

**Improved design of Van Slyke apparatus for the determination of amino-nitrogen.** S. J. FOLLEY (Biochem. J., 1930, 24, 961–964).—Rubber connexions are obviated in the deaminising chamber and in the Hempel pipette of this design.

S. S. ZILVA.

**Detection of alkaloids in viscera by Florence's method.** N. J. IOANID (Bull. Soc. Chim. biol., 1930, 12, 1001–1013).—The method of Florence (cf. A., 1927, 1219) tends to give low results and has no real advantage over the classical procedure.

W. O. KERMACK.

**Should lipins be calculated as fat?** H. FINCKE (Chem.-Ztg., 1930, 54, 598).—Polemical against Rewald (cf. *ibid.*, 134); the author supports his opinion that lipins should not be included in determinations of "fat content" of materials.

E. LEWKOWITSCH.

**Permanent colour standards for bilirubin.** M. S. NICHOLS and J. W. JACKSON (J. Lab. Clin. Med., 1930, 15, 672–677).—The standards consist of acidified solutions of cobalt chloride.

#### CHEMICAL ABSTRACTS.

**Determination of lead in biological material.** R. W. TANNAHILL (Med. J. Austral., 1929, I, 195–201).—For the determination of small quantities of lead in urine the colorimetric method of Avery, Hemingway, and Anderson is preferred; for that of larger quantities in tissues, faeces, etc., Fairhall's titrimetric method is preferred.

#### CHEMICAL ABSTRACTS.

**Colorimetric determination of manganese in biological material.** M. B. RICHARDS (Analyst, 1930, 55, 554–560).—The method of Willard and Greathouse (A., 1918, ii, 84) for the determination of manganese by means of periodate has been modified for application to the very small proportions found in biological material. The acidity of the solution must not exceed 16% sulphuric acid, 5–6% being most satisfactory unless large quantities of manganese are present. Chlorides should be destroyed before the oxidation by repeated evaporation with sulphuric acid. For substances containing much calcium (e.g., milk) and for those with much iron and very little manganese (e.g., blood) certain modifications of the general process are necessary. D. G. HEWER.

**Analysis. XI. Determination of silver in organic material.** L. PINCUSSEN and W. ROMAN (Biochem. Z., 1930, 225, 447–451).—The silver which is found in the animal organism after the metal or one of its salts has been injected may be present in at least three forms. If the material to be investigated is treated with dilute sodium thiosulphate solution and the residue from this treatment extracted with dilute ammonia solution three fractions containing, respectively, silver halides and water-soluble silver salts,

silver-protein compounds, and metallic silver are obtained. The silver content of the fractions may then be determined by evaporation to dryness, ignition, destruction of organic matter with nitric acid and hydrogen peroxide, and titration of the silver nitrate formed with ammonium thiocyanate solution. W. MCCARTNEY.

**Histochemical detection of gold.** O. MICHAELIS (Biochem. Z., 1930, 225, 478–488).—In their original forms the methods of Christeller (Verhandl. deut. Path. Ges., 1927, 173) and Borchardt (Virchow's Archiv, 1928, 267, 272) are not always satisfactory. The methods are improved and detection of gold is made certain if, in the first, nitric acid replaces hydrochloric acid in the stannous chloride solution and, in the second, the metal is precipitated at a higher temperature and more concentrated nitric acid is used for dissolution of the silver. W. MCCARTNEY.

**Determination of gold in animal organs.** S. TUKATO and M. LEINZINGER (Magyar Gyó. Társ. Ért., 1930, 6, 43–54; Chem. Zentr., 1930, i, 2283–2284).—The organ (or urine) is treated with a small quantity of fuming nitric acid and ignited in an electric furnace at 600–800°. The residue is treated with 25% hydrochloric acid (3 c.c.), freshly prepared chlorine solution (30 c.c.), and a filtered aqueous extract (2 c.c.) of bleaching powder (10 g. with 90 c.c. of water, finally diluted to 100 c.c.) and evaporated to dryness. The residue is gently heated with 1–2 drops of 25% hydrochloric acid, 2 c.c. of chlorine solution, and 5 c.c. of water and filtered; the filtrate is boiled with 1–2 drops of phosphoric acid until the chlorine is removed. Microelectrolytic, iodometric, and gravimetric methods for the determination of the gold are described.

A. A. ELDRIDGE.

**Colorimetric determination of silica.** E. J. KING (Bull. Soc. Chim. biol., 1930, 12, 903–909).—Observations have been made on the effect of phosphate on the determination of silicate by the method of Isaacs (A., 1924, ii, 499), and a modification is proposed, applicable to the determination of silica in tissues, in which the reduction of the silicotungstate is effected by quinol in the presence of sulphite at the ordinary temperature, the phosphate being precipitated previously as ammonium magnesium phosphate. W. O. KERMACK.

**Determination of bromides in biological material.** L. D. BEHR, J. W. PALMER, and H. T. CLARKE (J. Biol. Chem., 1930, 88, 131–135).—The material is incinerated in a platinum dish with potassium hydroxide at 460–475°, an aliquot portion of the aqueous solution of the mass is treated with phosphoric acid and potassium permanganate, the liberated bromine is extracted with carbon tetrachloride, the extract is shaken with sodium sulphite solution, and the oxidation and extraction are repeated; after one further repetition of the process, the carbon tetrachloride extract is treated with potassium iodide solution and the liberated iodine is titrated.

C. R. HARRINGTON.

# BRITISH CHEMICAL ABSTRACTS

## A.—PURE CHEMISTRY

DECEMBER, 1930.

### General, Physical, and Inorganic Chemistry.

The ground term of the two-electron problem of  $H^-$ , He,  $Li^+$ ,  $Be^{++}$ , etc. E. A. HYLLERAAS (Z. Physik, 1930, 65, 209—225; cf. this vol., 267).—The ionisation energy of normal helium and of atoms with a similar configuration was calculated.

A. J. MEE.

Absorption of the fine structure of the  $H_\alpha$  line in excited hydrogen. V. VON KRÜSSLER (Ann. Physik, 1930, [v], 7, 225—256).—Absorption measurements in excited hydrogen were carried out at very low pressures and very small current densities, a Lummer-Gehrcke plate being used. The apparatus was cooled in liquid air, the discharge tube being then filled with atomic hydrogen. The metastability of the  $2S_1$  level is not in agreement with the results of Ornstein, Zernike, and Snoek (cf. A., 1928, 449). The ratio of the absorption coefficients of the two components of  $H_\alpha$  is independent of the current density and of the pressure in the discharge tube. The ratio obtained for the absorption coefficients is in agreement (within the experimental error) with that derived by Sommerfeld and Unsöld.

A. J. MEE.

New lines in the arc and spark spectrum of helium. P. G. KRÜGER (Physical Rev., 1930, [ii], 36, 855—859).—The arc and spark spectra of helium were investigated in an attempt to excite the  $1s^2$  electrons of He I into the  $2p^2$ ,  $2s^2$ , and corresponding states, using the glow inside a Paschen hollow cathode as the light source. The  $1s^2S_1-np^2P_{1,1,1}$  series of He II was extended to 9 members, and wave-lengths of the intensity maxima were calculated as standards. Lyman's line at 600.019 Å. was found to be a He band; the forbidden line  $1s^2^1S_0-1s2s^1S_0$  is present; another line, probably  $1s2s^1S_0-2s^2^1S_0$ , was observed. The line 320.392 Å. is probably the helium line corresponding with the transition  $1s2p^3P_{0,1,2}^0-2p^2^3P_{0,1,2}$ . The 303 series is the strongest for pure helium, but is weakened in presence of slight impurities of oxygen or carbon, when the 584 series of He I and the 600.019 Å. band are enhanced. The presence of the forbidden line is probably due to the levels concerned being metastable and to the very low gas pressure.

N. M. Blich.

Hyperfine structure of the lithium II spectrum. P. GÜTTINGER (Z. Physik, 1930, 64, 749—759).—Theoretical. The energy due to the interaction of lithium nuclei of masses 6 and 7 and of spin momenta  $3/2(h/2\pi)$  with one and with two extra-nuclear electrons is calculated. The results are applied to  $2s-2p$  transitions of the lithium spark

spectra. Intensities are also calculated and are consistent with experimental determinations. This overcomes the discrepancy that the lithium spark spectra required a nuclear spin momentum of  $1/2(h/2\pi)$ , whilst the molecular band spectrum required nuclear spin momentum of  $3/2(h/2\pi)$ . A. B. D. CASSE.

Absorption spectrum of lithium vapour. R. W. FRANCE (Proc. Roy. Soc., 1930, A, 129, 354—360).—The spectrum has been photographed on a Rowland grating spectrograph in the region 2250—3400 Å. (which includes the principal series from the second member to the series limit), the metal being vaporised in the presence of hydrogen in an electrically heated double-walled steel tube, with a carbon arc as the source of continuous radiation. The wave-lengths and wave-numbers of 30 lines are tabulated, the estimated error being about 0.01 Å. The value  $2298.837 \pm 0.015$  Å. is derived from a Hicks formula for the wave-length of the series limit. A peculiar spectrum was observed at temperatures higher than  $950^\circ$  in the neighbourhood of the second member of the principal series (3233 Å.); this is probably analogous to that observed by Wood near the second member of the principal series of sodium.

L. L. BIRCHSHAW.

Stark effect of aluminium and carbon. Y. ISHIDA and M. FUKUSHIMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 123—143).—The Stark effect in aluminium and carbon was photographed, using an aluminium cathode in gaseous carbon dioxide. The wave-lengths, quantum analysis, shifts, and polarisation are tabulated for 26 lines of aluminium and 8 lines of carbon in the  $P-P, S, D$  and  $D-F, S-P, P-D, D-F$  series, respectively.

N. M. Blich.

Oxygen spectrum O I. F. PASCHEN (Z. Physik, 1930, 65, 1—3; cf. this vol., 1227).—Three new lines have been found in the O I spectrum at 6300.03, 6364.07, and 6391 Å., corresponding, respectively, with the transitions  $2(p)^4^3P_2 \rightarrow 2(p)^4^1D_2$ ,  $2(p)^4^3P_1 \rightarrow 2(p)^4^1D_2$ , and  $2(p)^4^3P_0 \rightarrow 2(p)^4^1D_2$ . The wave-numbers of the lines are in complete agreement with calculated values.

W. R. ANGUS.

Anomalous dispersion of gases in the excited state. V. Negative dispersion in excited neon. H. KOPFERMANN and R. LADENBURG (Z. Physik, 1930, 65, 167—188; cf. A., 1928, 577).—By increasing the current density in the positive column of a neon discharge there is first an increase in the anomalous dispersion of the reddish-yellow  $s-p$  lines. If, how-

ever, the current density is increased above about 0.1 amp./sq. cm. (for a neon pressure of 1 mm.) the  $N$  value decreases slowly, and in a markedly different way for the different lines. The differences are explained.

A. J. MEE.

**Anomalous dispersion of gases in the excited state. VI. Control experiment for detection of negative dispersion.** R. LADENBURG and S. LEVY (Z. Physik, 1930, 65, 189—206; cf. preceding abstract).—The explanations for the differing effects of current density in excited neon put forward in the preceding work are amplified. Negative dispersion can be proved in two ways: first, by proving the anomalous dispersion of the line 7059 Å. ( $p_{10}-s_1''$ ) and determining its absorption, which in the critical current range becomes markedly increased; secondly, by measurement of the intensity increase of the  $s-p$  lines. The investigation of the distribution of intensity in the inner line for short and for very long layers by means of the Fabry-Perot etalon shows that it is conditioned by the Doppler effect. From the data thus obtained and a knowledge of the  $N$  value it is possible to calculate the increase in density of the  $p_K$  atoms with the current, the results being at least in qualitative agreement with those previously obtained.

A. J. MEE.

**Dispersion of mercury vapour.** R. LADENBURG and G. WOLFSOHN (Z. Physik, 1930, 65, 207—208).—New dispersion measurements with mercury vapour lead to the result that the life period of the  $^3P_1$  state is  $(1.14 \pm 0.02) \times 10^{-7}$ , a value about 14% greater than that formerly obtained. For the characteristic frequency 1190 Å. in the normal dispersion of mercury vapour, the  $f$  value is high (2.591). This can be explained as due to the effect of the simultaneous quantum transition of both valency electrons.

A. J. MEE.

**Nuclear moment of sodium.** S. FRISCH and A. FERCHMIN (Naturwiss., 1930, 18, 866).—The nuclear moment of sodium can be found by a consideration of the spark spectrum of the metal. The spectrum of Na II in the near ultra-violet consists of a series of intensive lines which correspond with combinations of the terms  $^1P_1$  and  $^3P_{0,1,2}$  with a group of higher terms. The hyperfine structure of these lines has been investigated, using a quartz Lummer plate. From this the nuclear moment is shown to be 0.5.

A. J. MEE.

**3400 Å. band of phosphorus hydride.** R. W. B. PEARSE (Proc. Roy. Soc., 1930, A, 129, 328—354).—The 3400 Å. band obtained by Geuter from a discharge tube containing phosphorus and hydrogen, and attributed by him to a hydride of phosphorus (cf. A., 1907, ii, 725), has been photographed, and a table is given of the measured wave-lengths with the corresponding intensities, wave-numbers, and classification. The central maximum lies at 3420 Å. The isolated nature of the band and its widely-spaced rotational structure confirm its assignment to a hydride. Its points of resemblance to and differences from the NH band at 3360 Å. are discussed. The band has been completely analysed into 27 branches, and is believed to afford the most complete data available for a  $^3\Pi \rightarrow ^3\Sigma$  transition.

The fine structure arising from the  $^3\Sigma$  level has been resolved and the observed separations have been found to be in good agreement with Kramers' theoretical formula. The  $3\Pi$  levels are inverted. An approximate calculation of the electronic energy separations between the three component levels shows that they are not equally spaced;  $2\Pi_2 - ^2\Pi_1 = -121$  cm.<sup>-1</sup> and  $2\Pi_1 - ^2\Pi_0 = -111$  cm.<sup>-1</sup>

L. L. BIRCUMSHAW.

**Analysis of the  $S_2$  spectrum.** R. ROMPE (Z. Physik, 1930, 65, 404—429).—An analysis of Henri and Teves' results (A., 1925, ii, 87) shows that these bands originate in a  $^1\Sigma_0$  level and terminate in a  $^1\Pi_1$  level. A ground level of  $^1\Sigma$  type also fits Gilles' bands (A., 1929, 866) in the ultra-violet. The resonance spectra of sulphur vapour at temperatures between 350° and 900° excited by the mercury lines 2967, 3020, 3131, and 3655 Å. were investigated and fitted to a band series. Anti-Stokes lines appear, and, except for the 3655 Å. series, agree with the series allocation for the Stokes lines. The intensity distribution, which deviates from predictions of Condon's theory, is fully discussed. The behaviour of resonance series of  $S_2$  and  $Se_2$  in the presence of nitrogen and helium was investigated, and the results are discussed.

A. B. D. CASSIE.

**Terms of the arc and spark spectra of chromium.** C. C. KIESS (Bur. Stand. J. Res., 1930, 5, 775—779).—Tables of terms are given. Babcock's unpublished Zeeman effects have aided in establishing many of them. Combinations of these terms account for nearly all the stronger lines of Cr I and Cr II. All the terms which have been identified conform to the requirements of Hund's theory.

W. E. DOWNEY.

**Some series in the extreme ultra-violet spark spectra of copper.** F. C. CHALKLIN (Phil. Mag., 1930, [viii], 10, 711—721; cf. A., 1928, 692; this vol., 655).—The arrangement of critical potentials for metals in the soft X-ray region in series of the type  $A - b/n^2$  is extended to available data for the vacuum spark lines of copper. The  $A_1$  level agrees with the  $X_1$  level for the critical potentials; one value of  $b$  is very close to the critical potential value 2360. The scheme covers three arbitrary final levels  $A_1, A_2, A_3$ , and two sets of levels of the form  $b/n^2$ , described as  $\alpha(n)$  and  $\beta(n)$ ; the transitions between these levels are discussed. The effective nucleus involved in the  $\alpha(n)$  terms is 13.3e, and for the  $\beta(n)$  terms 4.13e, the former corresponding with the critical potential 13.2e. The intensities of the lines lead to a curve for the sensitiveness of the photographic plate as a function of the wave-length.

N. M. BLIGH.

**Continuous and band spectra of zinc and mercury vapours.** H. VOLKINGER (Ann. Physique, 1930, [x], 14, 15—81; cf. A., 1929, 226; this vol., 124).—Investigations previously reported on the spectra of mercury and zinc vapours excited by an electrodeless discharge are continued. The mercury spectra can be divided into two groups. The first, at low pressure and strong excitation, extends from 200  $\mu$  to the red and is independent of the temperature at constant pressure; with increase of pressure the energy partition of the spectrum is



modified; bands were found with maxima at  $\lambda$  2537 and 2265 Å. The second group, at higher pressures, consists of arc lines, narrow bands, and a main band continuous from the resonance line to the red. The wave-lengths of diffuse bands in the weak part of the continuous spectrum and the energy distribution curve of the main band were determined; the latter showed an agreement, good in the visible but less exact in the ultra-violet, with the distribution calculated as a function of the wave-length. The spectrum of zinc gave two groups under corresponding conditions; the first extends from the violet to the absorption limit of quartz, and with increase of pressure a series of fine bands appears between  $\lambda$  3980 and 4890 Å. At maximum pressure corresponding with the red, the spectrum is continuous from  $\lambda$  2750 to the resonance line  $\lambda$  2139, with a maximum at  $\lambda$  2570 Å. The phosphorescence of the silica containing tube is discussed. N. M. BLIGH.

**Hyperfine structures of some cadmium lines and the hypothesis of nuclear spin.** C. L. ALBRIGHT (Physical Rev., 1930, [ii], 36, 847—854).—Measurements were made of the hyperfine structures of the cadmium lines  $\lambda$  5086, 4800, 4078, 3614, 3613, 3610, 3468, 3466, 3404, and 6438 Å. ( $2^3P_{2,1,0}$ — $3^3S_1$ ,  $2^3P_2$ — $3^3D_{1,2,3}$ ,  $2^3P_1$ — $3^3D_{1,2,3}$ ,  $2^3P_0$ — $3^3D_1$ , and  $2^1P_1$ — $3^1D_2$ ), and results are compared with those of MacNair (cf. A., 1926, 986) and Schrammen (cf. A., 1927, 998). The structures ascribed to  $\lambda$  3466 and 3613 belong to  $\lambda$  3468 and 3614, respectively. Schüller and Brück's hypotheses (cf. A., 1929, 967; this vol., 124) are extended with fair success to the  $3P$ — $3D$  lines, but certain anomalies are noted.

N. M. BLIGH.

**Spectrum of trebly-ionised selenium.** K. R. RAO (Nature, 1930, 126, 568).—The spectrum of selenium from 700 to 7000 Å., using different intensities of discharge, and the spark spectrum between 500 and 1400 Å. have been investigated. The doublet system of trebly-ionised selenium due to the configurations  $4s^24p$ ,  $4s^24d$ , etc. and  $4s4p^2$  has been identified. The characteristic separations are  $4p^2P_1$ — $4p^2P_2$ , 4378;  $5p^2P_1$ — $5p^2P_2$ , 1198;  $4d^2D_2$ — $4d^2D_3$ , 389, etc. L. S. THEOBALD.

**Spectrum of xenon in the far ultra-violet (2700—1850 Å.).** G. DÉJARDIN (Ann. Physique, 1930, [x], 14, 82—93).—The second spectrum was investigated, particularly in the previously unexplored region 2400—1850 Å., using the electrodeless discharge. The wave-lengths and intensities of more than 350 new lines are tabulated, together with their grouping according to resemblance to the spark spectra of X II, III, and IV. N. M. BLIGH.

**Absorption of light by gaseous, liquid, and solid xenon.** J. C. McLENNAN and R. TURNBULL (Proc. Roy. Soc., 1930, A, 129, 266—283).—Previous work on the absorption of light by gaseous, liquid, and solid oxygen, and by mercury vapour, is discussed. It has been established that in the case of oxygen, and probably also with other diatomic elements, the electronic configurations giving rise to the normal energy levels of the molecules when isolated or in the gaseous state persist throughout the processes of liquefaction and solidification without any important

modification. Measurements have now been made with xenon in its three phases, the gas being enclosed in a small brass cell with fluorite windows, liquefied in the cell by compression, and finally frozen there. Light of suitable wave-length is passed through the cell, and the wave-length limits of the absorption are determined by means of a fluorite spectrograph. Two types of cell are described, one adapted for working at pressures below 1 atm. and the other for high pressures. With gaseous xenon, increase of pressure causes a rapid broadening of the bands and a shift towards the longer wave-lengths. A similar behaviour is observed in the case of mercury vapour (cf. McLennan and Edwards, Trans. Roy. Soc. Canada, 1915, 9, 167). The probable significance of this broadening of the bands is discussed. Owing to experimental difficulties encountered when dealing with liquid and solid xenon, determinations have been made only of the limits of the absorption bands on the long wave-length side; these are found to be at approximately 1783 and 1800 Å., respectively.

L. L. BIRCHUMSHAW.

**Stark effect in the resonance line of mercury and its behaviour in magnetic fields.** P. BRAZDZUNAS (Ann. Physik, 1930, [v], 6, 739—771).—A method which demonstrates the splitting of the resonance line (2536.7 Å.) of mercury and detection of small Zeeman effect is described. The magnitudes and directions of the displacements of the  $\sigma$  and  $\pi$  components for given fields were determined. The amount of splitting is proportional to the square of the electric field strength. In combined electric and magnetic fields the splitting resulting from the Stark effect could not be detected above definite strengths of the magnetic field. The degree of polarisation for the resonance radiation of mercury was experimentally estimated to be about 84%. It was uninfluenced by electric fields up to 140,000 volts per cm.

W. GOON.

**Quenching of mercury resonance radiation. I. Saturated hydrocarbons.** J. R. BATES (J. Amer. Chem. Soc., 1930, 52, 3825—3832).—The quenching by methane, ethane, propane, and butane has been investigated and collision radii of the hydrocarbons for collisions of the second kind with excited mercury atoms have been evaluated. The relative probability of a transfer of the energy of a mercury atom to a hydrocarbon decreases from butane to a very small value for methane. With increase of pressure of methane from 10 to 200 mm. the apparent quenching effect became independent of pressure and then gradually decreased. Methane therefore quenches the resonance radiation in the same manner as does the more inert type of gas molecules by causing transition of the mercury atom to the metastable ( $2^3P_0$ ) state. The quenching effect of ethane increases regularly as the pressure is increased to 20 mm. The results are consistent with the decompositions of these hydrocarbons photosensitised by mercury (cf. Taylor and Hill, this vol., 46).

J. G. A. GRIFFITHS.

**Variation of intensities in the mercury spectrum.** E. LÜBCKE (Wiss. Veröff. Siemens-Konz., 1930, 9, 246—251).—Cooling the cathode space of a vacuum mercury arc causes a change in colour of the

emitted light. This change is due to intensification of lines arising from singlet states and a weakening of those from triplet states. W. E. DOWNEY.

**Measurement of the light yield in the mercury spectrum by excitation through electron collision.** W. HANLE and W. SCHAFFERNICHT (Ann. Physik, 1930, [v], 6, 905—931).—The light yield of a number of lines in the visible region of the mercury spectrum has been measured photo-electrically by an apparatus which is fully described. The number of light quanta arriving per second in an electron collision tube divided by the total number of collisions between electrons and mercury atoms is termed the light yield. At 60 volts electron velocity the light yields per 1000 collisions for the mercury lines at 4348, 4358, 5461, 5675, 5769, and 5789—5790 Å. are 2.7, 5.4, 4.4, 0.85, 3.4, and 6.9 quanta, respectively. A photo-electric method of determining the excitation function has been developed. W. R. ANGUS.

**Variations of intensity distribution in resonance spectra.** L. NATANSON (Z. Physik, 1930, 65, 75—83).—The intensity of resonance spectra excited in tellurium and selenium vapours, at different temperatures and pressures, by a mercury arc was studied. The effect of absorption (reversal) was allowed for by varying the relative positions of the resonance vessel and mercury arc and by introducing a subsidiary absorption vessel. The probability of transitions between different rotation and oscillation levels appears dependent on the environment of the molecule, probably due to an intermolecular resonance, which could be studied by similar experiments.

A. B. D. CASSIE.

**Influence of foreign gases on selective reflexion of the mercury resonance lines.** O. SCHNETTLER (Z. Physik, 1930, 65, 55—66).—Selective reflexion, which is identical with coherent scattering, and resonance radiation, which is characteristic radiation, are distinguished by a difference in the extinguishing power of foreign gases. Selective reflexion is diminished to a much smaller degree by the presence of foreign gases than is resonance radiation, and is, therefore, not dependent on the actual excitation of an atom. A. B. D. CASSIE.

**Possible interpretations of the hyperfine structure of the mercury spectrum.** H. SCHÜLER (Naturwiss., 1930, 18, 895).—The hyperfine structures of the mercury arc lines at  $\lambda$  4047, 4078, 4916, 5461, 5769, and 5791 Å. and the Hg II lines at 6150 and 7944 Å. have been investigated. Comparison of the intensity relations in the hyperfine structure with the relative abundance of the several isotopes of mercury leads to the conclusion that, as in the case of cadmium previously investigated (A., 1929, 967), the hyperfine structure of mercury can be explained by an isotope effect. J. W. SMITH.

**Zeeman effect and the absorption coefficients of the hyperfine structure components of the mercury resonance line.** S. MROZOWSKI (Nature, 1930, 126, 684).—The results obtained for magnetic fields from 0 to 8 kilogauss are described. L. S. THEOBALD.

**Transition probability of "forbidden line" 2656 Å. of mercury.** E. GAVIOLA (Univ. nac. La Plata, Estud. Cienc., 1929, No. 89, 67—75).—The intensity of the line 2656 Å. compared with that of the line 2537 Å. is  $10^{-6}$ ; hence the life of undisturbed metastable atoms in the level  $2^3P_0$  is 10 sec. Under laboratory conditions the life of metastable atoms is considerably shorter ( $10^{-2}$  to  $10^{-5}$  sec.) owing to collisions of the first and second kinds with the solid walls and with other metastable atoms.

CHEMICAL ABSTRACTS.

**Hyperfine structure in some spectral lines from highly ionised atoms of thallium and bismuth.** G. ARVIDSSON (Nature, 1930, 126, 565—566).—The separations of some previously classified lines in the spectra of Tl III and Tl IV, and of bismuth between 800 and 1400 Å., are recorded.

L. S. THEOBALD.

**Effect of pressure on absorption of spectral lines.** S. DATTA and S. N. ROY (Indian J. Physics, 1930, 5, 365—370).—The absorption of continuous radiation from a carbon arc fed with a uranium salt in potassium vapour at different pressures was examined in a quartz spectrograph. At low pressures continuous absorption on the short wave-length side is almost absent and only about 7 or 8 absorption lines were found. With increase of pressure continuous absorption sets in and the intensity and number of absorption lines increase, the continuous absorption gradually masking the latter. The bearing of the results on the question of the development of orbits with high quantum value limited by interatomic distances is discussed. W. GOOD.

**[Abnormal] low-voltage arcs.** M. J. DRUYVEN-STEYN (Z. Physik, 1930, 64, 781—798).—The theory of abnormal low-voltage arcs, which burn in dilute gases between a hot cathode and an anode which is maintained at a potential above the cathode less than the ionisation potential of the gas, is discussed with reference to the mechanisms suggested by Holst and Oosterhuis (Physica, 1924, 42, 1924) and by Compton and Eckart (cf. A., 1925, ii, 253). In the emission spectrum of the low-voltage arc in argon the quadruplet lines 4013.9, 4282.9, 4348.1, 4430.2, 4431.0, 4735.9, 4806.0, 4847.8, and 5009.2 Å. are much more intense than in the glow discharge, whilst the doublet lines 4545.0, 4579.3, 4657.9, 4726.8, 4764.8, and 4965.1 Å. are weak or undetectable. The arc is characterised by a high electron concentration and low velocities, and the converse holds for the glow discharge; it is also suggested that the excitation probabilities of  $A^+$  ions and of argon molecules are very different.

R. W. LUNT.

**Effect of an electric field on resonance radiation.** M. WINKLER (Z. Physik, 1930, 64, 799—805).—The polarisation of the sodium  $D$  lines emitted by atoms in an electric field and excited by mercury radiation was studied in directions parallel and normal to the electric field. Results show the  $\sigma$  component in an electric field to be incoherent radiation. Similar experiments on the 2967 Å. mercury resonance line gave no definite result. A. B. D. CASSIE.

**Appearance of forbidden lines in spectra.** L. D. HUFF and W. V. HOUSTON (Physical Rev.,

1930, [ii], 36, 842—846; cf. Rubinowicz, A., 1929, 615; this vol., 653).—Theoretical. The quadrupole term in the radiation of a forbidden line is usually larger than the dipole produced by an external electric field, except when there is an intermediate state with which both initial and final states combine, and lies close to one of them. If the  $J$  selection rule is violated and the Laporte rule obeyed, the radiation must be due to the octopole and not to the quadrupole term, as in the case of the mercury 2270 Å. line. The Zeeman effect of an octopole transition will differ from that of a dipole or quadrupole. N. M. BUGH.

**Structure of emission lines.** F. HOYT (Physical Rev., 1930, [ii], 36, 860—870).—Mathematical. A method for obtaining the intensity distribution in a spectral line is derived from Dirac's quantum theory of the radiation field. N. M. BUGH.

**Intensities of doublet lines according to the Dirac theory.** K. BECHERT (Ann. Physik, 1930, [v], 6, 700—720).—Theoretical. W. GOOD.

**Theory and calculation of screening constants.** C. ECKART (Physical Rev., 1930, [ii], 36, 878—892).—Mathematical. N. M. BUGH.

**Rotation structure of light molecules.** W. WEIZEL (Physikal. Z., 1930, 31, 880—882).—Theoretical. It is shown how conclusions respecting the electronic configuration of a light molecule can be reached from considerations of the rotation structure. A. J. MEE.

**Analysis of scattered X-rays with the double-crystal spectrometer.** N. S. GINGRICH (Physical Rev., 1930, [ii], 36, 1050—1059).—X-Rays from a molybdenum target scattered by graphite at angles approximately  $109^\circ$  and  $161^\circ$  were analysed by a double-crystal spectrometer. At  $109^\circ$  the fine structure lines reported by Davis and others (cf. A., 1929, 986) were not confirmed. At  $161^\circ$  the modified  $K\alpha_1$  and  $K\alpha_2$  lines were separated. Values found were  $\delta\lambda = 0.04721 \pm 0.00003$  Å.,  $(1 - \cos \phi) = 1.9479$ , giving  $h/mc = 0.02424 \pm 0.00004$  Å. N. M. BUGH.

**Energy of  $K\alpha_2$  of copper as a function of applied voltage with the double-crystal spectrometer.** J. W. M. DUMOND and A. HOYT (Physical Rev., 1930, [ii], 36, 799—809).—Using a special type of double-crystal spectrometer an investigation was made of the dependence of intensity of the satellite  $K\alpha_2$  and the parent  $K\alpha_1$  lines of copper on voltage with constant current, the ratio of intensities of satellite to parent, and the dependence of satellite intensity on current at constant voltage, in order to determine the origin of the satellite. It was found that the difference in excitation voltage for the two lines was immeasurably small, the intensity ratio  $\alpha_1 : \alpha_2$  was about 1:120, and the intensity of the satellite was proportional to the current at constant voltage. These results were against the Wentzel-Drayvesteyn but in agreement with the Richtmyer theories of satellite origin. A doublet structure with component separation about  $2X$  was observed in  $K\alpha_2$ . N. M. BUGH.

**Scattering of X-rays by copper and silver.** A. A. RUSTERHOLZ (Z. Physik, 1930, 65, 226—232).—The scattering functions for copper and silver for the

$K\alpha$  radiation of copper were determined by measuring the integral X-ray interference by crystalline powders. Fine powders are used owing to the difficulties occurring when large crystals are employed (primary and secondary extinction). The scattering function of copper has already been found by Armstrong (A., 1929, 1354). The agreement between her result and that obtained by the present method justifies its use. For silver there is agreement with the scattering function calculated on the assumption of the Thomas-Fermi atom model (A., 1928, 456, 685, 933).

A. J. MEE.

**Natural width of X-ray emission lines. III.** H. MARK and G. VON SUSICH (Z. Physik, 1930, 65, 253—265).—A double spectrometer was used with various crystals and Mo  $K\alpha_1$  lines. The fine structure lines in the  $K$  series of molybdenum described by Davis and Purks (A., 1928, 451) were not found. A. J. MEE.

**Double-crystal study of scattered X-rays.** J. A. BEARDEN (Physical Rev., 1930, [ii], 36, 791—798).—With a view to detect possible fine structure in unmodified scattered X-rays copper and silver  $K$  radiation was scattered by blocks of graphite and aluminium, with negative results. The change in wave-length was found to agree within 1% with that predicted by the quantum theory of X-rays scattered by free electrons, but the width of the modified line was about twice that which should be due to the divergence of the scattering angle. N. M. BUGH.

**Intensity of X-ray satellites.** F. K. RICHTMYER and L. S. TAYLOR (Physical Rev., 1930, [ii], 36, 1044—1049).—With high resolving power, using the two-crystal ionisation spectrometer, measurements were made of the wave-lengths and intensities relative to  $K\alpha_1$  of the satellites  $K\alpha_{3,4}$  of copper, which was shown to contain probably more than two components (four are indicated by comparison with results for nickel). The wave-lengths of the components  $K\alpha_3$  and  $K\alpha_4$  were found to be 1531.15 and 1530.15 X, respectively, and their intensities at 40 kilovolts, of the order 0.25% that of  $K\alpha_1$ . N. M. BUGH.

**Inertia of gas-filled photo-electric cells.** F. SCHRÖTER and G. LUNSZYNSKI (Physikal. Z., 1930, 31, 897—904).—An apparatus for investigating the inertia of gas-filled photo-electric cells is described. When the cell was filled with helium, neon, or a mixture of the two gases, there was a considerable period before the attainment of full conductivity; with argon and hydrogen, however, there was no trace of such an "induction" period. Conclusions are reached concerning recombination of ions in the different gases. A. J. MEE.

**Unidirectional layer photo-cells. I.** O. VON AUWERS and H. KERSCHBAUM (Ann. Physik, 1930, [v], 7, 129—175; cf. this vol., 1254).—A photo-cell was constructed with a thin layer of cuprous oxide formed by oxidation on a copper plate, and an opposite electrode of gold or some other metal placed in contact with the oxide layer. When this cell is illuminated an  $E.M.F.$  is set up which produces a current in an internal resistance. The cell is a typical example of a dipole. Three different phenomena are to be dis-

tinguished in the unidirectional layer photo-cell. First, the unipolarity of the conduction in the combination Cu-Cu<sub>2</sub>O in the dark. Secondly, the change in cell resistance on illumination (the inner photo-electric effect, such as is found with the selenium cell). Thirdly, the *E.M.F.* due to the illumination (the outer photo-electric effect). The theory of the dipole is given and is then applied to the special case of the photo-cell described. It is shown that in consequence of the non-linear resistance it is possible to distinguish between the potential source and the current source. By the aid of the theory of the homogeneous chain conductor, the effect of distance of the light source from the electrode is explained theoretically, and tested practically.

A. J. MEE.

#### Critical potentials of the hydrogen molecule.

J. E. ROBERTS (Proc. Leeds Phil. Soc., 1930, 2, 39—45).—Theoretical. The observed critical potentials of the hydrogen molecule are considered in the light of the potential energy curves for the various states and the Franck-Condon transition principle, giving an explanation of the changes as the electron velocity is gradually increased. The most probable energy change requires 12.8 volts, the critical potential being at 11—12 volts. The potential between 8 and 9 volts (cf. Jones and Whiddington, A., 1929, 115) is probably due to the excitation of the triplet states, with subsequent dissociation of the molecule and emission of the continuous spectrum.

N. M. BUGH.

**Ionisation potential and spectroscopic evidence.** M. PIERUCCI (Nuovo Cim., 1929, 6, 412—417; Chem. Zentr., 1930, i, 2055).—Franck and Herz' rule that the strongest radiating component has the smaller ionisation potential is only a special case of a general law which applies to many components over wide limits of temperature and pressure.

L. S. THEOBALD.

**Scattering of fast electrons by metals. I. Sensitivity of the Geiger point-discharge counter. II. Polarisation by double scattering at right angles.** C. T. CHASE (Physical Rev., 1930, [ii], 36, 984—987, 1060—1065; cf. this vol., 6).—I. The velocity-sensitivity of the point-discharge counter, as tested by a magnetic spectrograph, is discussed. It is shown to depend on the voltage applied to the counter, a fact which probably influences investigations on electron polarisation.

II. Using radium-*E* as a source of electrons and a sensitive gold-leaf electroscope as detector, the polarisation of electron beams scattered twice at right angles by lead targets was investigated. The complex type of polarisation observed is described and discussed.

N. M. BUGH.

**Electron impacts in argon.** J. E. ROBERTS and R. WHIDDINGTON (Proc. Leeds Phil. Soc., 1930, 2, 46—49; cf. *ibid.*, 1929, 2, 12).—Experiments previously reported on electron impacts in gases are extended, using argon. Energy losses are found at 11.6, 13.0, and 14.1 volts. Fundamental differences in the appearance and width of "loss lines" obtained in diatomic and monatomic gases are described and discussed in the light of the theory of atomic and molecular electronic levels.

N. M. BUGH.

**Energy and electron transfer in resonance in impacts of the second order between neutral particles.** H. BEUTLER and W. EISENSCHMIDT (Z. physikal. Chem., 1930, B, 10, 89—105).—The conservation principles deduced by Wigner by the methods of quantum mechanics (Nachr. Ges. Wiss. Göttingen, 1927, 375) lead to the conclusion that in the transfer of energy in a binary impact accompanied by resonance the multiplicity of the system as a whole is not changed. It therefore follows that if in one of the colliding atoms a triplet-singlet intercombination occurs and the energy conditions permit a similar intercombination in the other atom, then the two intercombinations will occur simultaneously in preference to the one intercombination accompanied by a "permitted" transition in the other atom. Experiments on the transfer of energy from excited krypton to mercury have verified this deduction, the multiplicity being maintained by the exchange of two electrons of antiparallel spin without change in the direction of spin. The application of the above theory to certain other reactions is also outlined.

R. CUTHILL.

**Application of diffraction of electrons to study of organic compounds; structure of cellulose.** A. DAUVILLIER (Compt. rend., 1930, 191, 708—711).—The method used to render visible electron diffraction rings produced by zinc oxide (cf. this vol., 129) is applied to organic compounds by using a film of the substance a few Å. thick so as not sensibly to absorb the electrons, thus avoiding the acquisition of any appreciable charge. On passing a stream of cathode rays perpendicularly through such a film of cellulose nitrate or acetate or celluloid, diffraction haloes—some ten times as diffuse as those obtained with a crystalline mineral powder—are obtained. The diagrams differ from those obtained with X-rays, resembling rather the spots of a Laue photograph, and appear to indicate that the film consists of minute crystals definitely oriented, the chains being perpendicular to the film surface, with a 3.8 Å.

C. A. SILBERRAD.

**Electron exchange of slow ions. II. H. KALLMANN and B. ROSEN (Z. Physik, 1930, 64, 806—816).**—An apparatus has been devised in which a beam of positive ions of any required kind, magnetically resolved, is allowed to enter a chamber which contains a gas of the same or of a different kind than that from which the ions are originally derived. Data are given for N<sup>+</sup>, N<sub>2</sub><sup>+</sup>, A<sup>+</sup>, and A<sup>++</sup> ions in nitrogen, argon, and nitrogen-argon mixtures; for A<sup>+</sup> and A<sup>++</sup> ions in helium, and for Hg<sup>+</sup> and Hg<sup>++</sup> ions in nitrogen and in mercury vapour. The results obtained by this method agree with those of the authors, using an absorption method (this vol., 514). N<sup>+</sup> ions are but slightly absorbed in nitrogen and in argon, whilst N<sub>2</sub><sup>+</sup> ions in nitrogen and A<sup>+</sup> ions in argon are strongly absorbed. In argon the absorption of A<sup>++</sup> and N<sub>2</sub><sup>+</sup> ions is approximately equal; it is greater than that of N<sup>+</sup> ions and less than that of A<sup>+</sup> ions. In nitrogen the A<sup>++</sup> ions are absorbed about half as much as N<sub>2</sub><sup>+</sup> ions. The absorption of Hg<sup>+</sup> and Hg<sup>++</sup> ions is about the same, and in nitrogen is slightly less than in mercury vapour.

R. W. LUST.

**Relationship between electron diffraction and [the critical potential of] soft X-rays.** E. RUPP (Naturwiss., 1930, 18, 880).—Apparatus for measuring the electron diffraction and the critical potential of soft X-rays is described. Using an angle of incidence of  $10^\circ$  for the electron stream, it was found that the electron diffraction from the (111) face of a nickel crystal gave maxima at 66.5 and 132 volts. The values for the critical potential of soft X-rays (measured from the photo-electric effect) fell at exactly the same voltages. This relation is not accidental, because when the voltage was kept constant and the incident angle varied, the diffraction maxima and the critical potential for soft X-rays occurred at  $10^\circ$ . Similar results were obtained for tungsten and copper.

W. R. ANGUS.

**Angle and energy distribution of electrons scattered by helium, argon, and hydrogen.** J. H. McMILLEN (Physical Rev., 1930, [ii], 36, 1034—1043; cf. Harnwell, A., 1929, 1211).—Using an electrostatic refocussing method of analysis, the distribution of electrons rebounding at definite angles from gaseous molecules was investigated. Energy losses in helium were identified at 21.12, 22.97, and 23.62 volts for a primary electron beam of 50 volts. The number of electrons rebounding without loss of energy was measured for angles from  $7^\circ$  to  $60^\circ$  in each gas, for the energy range 50—150 volts, and plotted per unit solid angle. With increase of angle and electron energy the number scattered generally decreased. Results are compared with existing experimental and theoretical data (cf. Mitchell, A., 1929, 969; Mott, *ibid.*, 1122).

N. M. BLIGH.

**Causality in the behaviour of the electron.** J. STARK (Ann. Physik, 1930, [v], 6, 681—699).—The concept of swarm motion of the electron mathematically developed by Sommerfeld on the basis of Schrödinger's differential equation is criticised especially in regard to cause in the behaviour of the electron.

W. GOOD.

**Matrix mechanics of the spinning electron.** G. TEMPLE (Proc. Camb. Phil. Soc., 1930, 26, 496—506).—Mathematical.

**Behaviour of silica under the influence of slow cathode rays.** H. PETERS and T. SCHULTES (Z. Elektrochem., 1930, 36, 837—839).—When a discharge, excited by a high-frequency electric field, takes place in highly-evacuated glass tubes provided with external electrodes, there appears on the walls a red luminescence which is more strongly deflected than is the ordinary green fluorescence by a magnetic field. It is therefore considered to be due to slowly-moving electrons. The same phenomenon is observed with different varieties of glass, and with silica. When the discharge is continued for about 70 hrs. the red luminescence gradually disappears and cannot be restored either by leaving the tube in an atmosphere of air, oxygen, hydrogen, or water vapour for a week, or by heating the quartz in a blowpipe flame. It is therefore considered to be due to the transformation of silica into a different modification.

F. L. USHER.

**Passage of an electron beam through a field-free enclosure.** F. L. ARNOT (Proc. Roy. Soc., 1930,

A, 129, 361—377).—Using two independent methods of measurement, an experimental investigation has been made of the fields set up by the passage of an electron beam through an otherwise field-free enclosure. Positive ions and slow electrons, the latter having a Maxwellian velocity distribution corresponding with a temperature of several thousand degrees Abs., diffuse out of the beam. The intensity of the positive-ion current and the mean velocity of the ions at a point outside the beam are both approximately linear functions of the density of ionisation along the path of the beam.

L. L. BIRCUMSHAW.

**Collisions of the second kind between electrons and excited mercury atoms.** G. D. LATISCHEV and A. I. LEIPUNSKI (Z. Physik, 1930, 65, 111—123).—The probability of collisions of the second kind between electrons of known velocity and mercury atoms in the metastable  $2^3P_0$  state has been investigated by measuring the fraction of an electron beam which is able to reach an anode after traversing a region containing excited mercury atoms, and an opposing field greater than the accelerating field by an amount not greater than the excitation energy of mercury atoms in the  $2^3P_0$  state. The probability exhibits a well-defined maximum at 2.8 volts, the region investigated being 2—7 volts. This maximum value is 0.7, and in agreement with the theory of Klein and Rosseland (cf. A., 1921, ii, 291) exceeds the maximum value for collisions of the first kind, which is 0.5.

R. W. LUNT.

**Energy [of electric inertia] of the electron.** W. HEISENBERG (Z. Physik, 1930, 65, 4—13).—Mathematical. Velocities such that the "rest" mass of an electron is negligible give an energy of electric inertia that is independent of the electron radius. Conditions for the vanishing of this energy were investigated.

A. B. D. CASSIE.

**Electromagnetic radiation and properties of the electron.** R. D. KLEEMAN (Science, 1930, 72, 225—226).—The conditions under which electronic internal energy is converted directly into radiant energy are examined.

L. S. THEOBALD.

**Doppler effect of hydrogen positive rays.** F. NEY-VALERIUS (Ann. Physik, 1930, [v], 6, 721—738).—The Doppler effect in hydrogen canal rays has been investigated between 400 and 1200 volts. The maximum velocity fixed by the limits of the effect agrees on the whole with the velocity calculated from  $mv^2/2 = eV$  for  $e/m = 9650$ . The ratio of the two velocity maxima between 400 and 1200 volts was found to be dependent on the pressure (cylindrical tube). Between 1000 and 1200 volts four maxima were observed, whilst in a spherical discharge tube only three of these four maxima are obtained. Other slight differences in the results for cylindrical and bulb discharge tubes were found and explained. A Doppler effect which also possesses two velocity maxima was observed in the reversed canal rays.

W. GOOD.

**Discharge of hydrogen canal rays by passage through gases and solids.** H. BARTELS (Ann. Physik, 1930, [v], 6, 957—984).—The apparatus used and the methods of preparing and purifying the gases

and solid films are described in detail. The influence of a unidirectional field on the intensity of the stream of canal rays is considered. The vacuum relationships and the effects of diaphragm edges and residual vapours on the discharge are discussed. The influence of pressure and velocity on the discharge of hydrogen canal rays in hydrogen, oxygen, nitrogen, and air has been studied. The equilibrium of the discharge ( $w$ ) in hydrogen, oxygen, air, and nitrogen for hydrogen canal rays gave the values 0.38, 0.96, 0.75, and 0.70, respectively. Within the region 13–25 kilovolts  $w$  varies approximately linearly with the kinetic energy of the positive  $H$ -particles; at higher voltages this linear relationship does not hold. The logarithm of the intensity diminishes with the pressure. At a pressure of  $10^{-3}$  mm. of mercury the mean free paths of positive and neutral  $H$ -particles in hydrogen, oxygen, and nitrogen are 77 and 124, 86 and 52, and 45.5 and 36.5 cm., respectively; the value of the mean free path varies inversely with the pressure. The pressure and voltage dependence of the number of effective collisions is discussed and compared with the pressure dependence of the number of effective collisions of molecular canal rays in hydrogen. The discharge of hydrogen and molecular canal rays by thin films of celluloid has been investigated and the influence of velocity, at. wt., and film thickness on the discharge is discussed. W. R. ANGUS.

**Reflexion of cadmium and zinc atoms from sodium chloride crystals.** H. A. ZAHL (Physical Rev., 1930, [ii], 36, 893–903; cf. A., 1929, 1125).—The specularly-reflected part of a beam of zinc atoms reflected from a sodium chloride crystal was investigated by measuring the velocity distribution of the atoms composing it, and by examination after reflexion from a second crystal. Velocity selection or a space-grating type of reflexion is probably very small. Double reflexions of cadmium from sodium chloride crystals indicate both space and surface-grating phenomena. The possible influence of individual differences in crystals is discussed. N. M. BLIGH.

**Formation of neutral particles of high velocity by transference [of charge].** H. KALLMANN and B. ROSEN (Naturwiss., 1930, 18, 867–868).—When ions of medium velocity are passed through a gas a transference occurs between ions and neutral molecules similar to the phenomenon in canal rays. As a result of this resonance process there are formed from an originally stationary molecule and a rapid ion, a slowly moving ion and a neutral particle which has practically the same velocity as the first rapid ion. That this process actually takes place can be shown by direct measurement. Experiments and apparatus are described by means of which the determination can be carried out. The intensity of the neutral rays can be as great as that of the original ionic radiation. A. J. MEE.

**Occurrence of double positively-charged molecules in canal rays.** R. CONRAD (Physikal. Z., 1930, 31, 888–892).—A new apparatus for the production of sharp canal-ray parabolas is described in detail. With the apparatus it was possible to show the presence of double positive charges on the molecules  $\text{CH}$ ,  $\text{CH}_3$ ,  $\text{C}_2$ ,  $\text{C}_2\text{H}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_3$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}$ ,

$\text{O}_2$ ,  $\text{C}_2\text{O}$ ,  $\text{CO}_2$ . It is obvious that the rule concerning the non-existence of doubly-charged molecules in canal rays is no longer tenable. Chlorine atoms with at least five positive charges were obtained. A photograph was taken with both chlorine and helium in the tube. There was an extension of the helium parabolas, proving the existence of  $\text{He}^{++}$  in the tube. A. J. MEE.

**Canal-ray and electron excitation of the band spectrum of nitrogen.** H. D. SMYTH and E. G. F. ARNOTT (Physical Rev., 1930, [ii], 36, 1023–1033).—The possibility of variation in intensity distributions in the excitation of band spectra by canal-ray and by electron impact was investigated for nitrogen. The relative intensities of the lines in the 3914 negative band indicated a small weakening of the lower rotational lines in the canal-ray excitation. The relative intensities of the second positive group and of the negative group were observed in a canal-ray beam, and transitions from high initial vibrational states were abnormally great; excitation by a beam of 700-volt electrons gave an unusual intensity distribution with nearly all the energy in the 0–0 and 0–1 bands of the negative group and in the second positive group. It is concluded that the parabolic intensity distribution is maintained under all types of excitation; being probably characteristic of the transition probabilities, it is independent of excitation conditions, but the distribution along the parabola shows wide variations. The electrodeless discharge, supposedly purely electronic, gives a distribution resembling that of canal-ray excitation. N. M. BLIGH.

**Ionisation of inert gases by slow alkali ions.** O. BEECK (Ann. Physik, 1930, [v], 6, 1001–1024).—The apparatus is described and discussed. The stream of alkali ions was produced by melting together iron oxide and the oxide or salt of the appropriate alkali; this was cooled, pulverised, mixed into a paste with paraffin oil, and deposited on platinum-iridium foil 2 mm. broad and 0.01 mm. thick; the paraffin oil was vaporised by electrically heating the foil, which was subsequently annealed at a bright red heat. The process was repeated until a sufficiently thick layer was obtained. These foils could then be used directly for the propagation of the ionic streams. A description is given of the method of producing the magnetic fields, the arrangement of measuring apparatus, the control of ionic velocity, and the arrangement of electrometers. Sources of error are discussed. A systematic study of the ionisation of helium, neon, and argon has shown that an inert gas atom is most easily ionised by the alkali ion which has the same number of external electrons as the inert gas (this vol., 1083). The amount of ionisation by ionic bombardment is very small and the lower limit of ionisation has not been determined. The ionising power of ions is less than that of electrons. W. R. ANGUS.

**Molecular ray experiments. Chemical activity of molecular and atomic oxygen.** W. R. RODEBUSH and W. A. NICHOLS, jun. (J. Amer. Chem. Soc., 1930, 52, 3864–3868).—Beams of molecular oxygen produced no visible effects on targets of metallic silver, copper, and sodium, phosphorus,



indigotin, and a number of lower oxides, including those of lead and molybdenum. Of many metallic oxides, including that of silver and the trioxide of tungsten, only molybdenum trioxide was affected by beams of atomic oxygen (Kurt and Phipps, this vol., 137). A slate-blue image, similar to that due to atomic hydrogen, is produced and is attributed to the reaction  $3\text{MoO}_3 + \text{O} = \text{Mo}_3\text{O}_8 + \text{O}_2$ . The Stern-Gerlach experiment did not yield any images due to deflected beams of atoms. J. G. A. GRIFFITHS.

**Effective cross-sections for the quenching of mercury resonance radiation.** M. W. ZEMANSKY (Physical Rev., 1930, [ii], 36, 919—934; cf. A., 1928, 687; Stuart, A., 1925, ii, 629).—The mathematical theory of the quenching of resonance radiation is developed on the basis of an extension of Milne's theory of diffusion of radiation. A curve is obtained relating the number of impacts of the second kind and experimental values of the quenching. The effect of metastable atoms is discussed. The scattered radiation emerging from an absorption cell containing mercury vapour in presence of a foreign gas was measured as a function of the gas pressure, using a modification of Stuart's apparatus. The effective cross-section for quenching was calculated for five elementary and eight compound gases; values are tabulated with those for depolarisation of resonance radiation and for collision broadening. The quenching cross-sections for the compound gases are connected with the difference between the energy of the transition  $2^3P_1 \rightarrow 2^3P_0$  of mercury and the vibrational energy of the molecules, in qualitative agreement with the theory of Kallmann and London (cf. A., 1929, 487). N. M. BLIGH.

**Effective cross-section of the gas molecule with respect to electrons below 1 volt.** C. RAMSAUER and R. KOLLATH (Ann. Physik, 1930, [v], 7, 176—182; cf. A., 1929, 1123; this vol., 269).—Determinations with nitrous oxide are given. The character of the curves for carbon dioxide and nitrous oxide is similar, like those for nitrogen and carbon monoxide, for electrons below 1 volt. Comparative determinations for ortho- and para-hydrogen are given. It is concluded that both forms have the same effective cross-section. A note on the results of Normand (cf. this vol., 973) indicates some discrepancy. A. J. MEE.

**"Practical" atomic weights.** R. J. MEYER and F. STRUWE (Z. angew. Chem., 1930, 43, 928—930).—It is suggested that "mean at. wt." is a preferable term to "practical at. wt." It is pointed out that the use of air at. wt. in place of vacuum at. wt. has no advantage in practice and may lead to incorrect results. J. W. SMITH.

**Atomic nomenclature.** A. GÜNTHER-SCHULZE (Naturwiss., 1930, 18, 881—882).—The term metalloid is criticised and, instead of it, a new term—"binder"—is suggested with the proposal that the same term be used in English also. Both in English and in German such a term would convey the idea of the electrons being "bound." W. R. ANGUS.

**Relative abundance of the elements and the existence of nuclear periodicity.** R. A. SONDER (Naturwiss., 1930, 18, 939—940).—The results of

Noddack and Noddack (this vol., 1341) are discussed from the viewpoint of a nuclear periodicity theory postulated by Sonder (*ibid.*); both sets of results are in good agreement. The existence of an abundance period from iron to uranium, which has previously been regarded as an "unexpected" result, is explained. W. R. ANGUS.

**Determination of the abundance ratios of isotopes from band spectra.** G. STENVINKEL (Nature, 1930, 126, 649).—When several vibrational states of the molecules come into play on raising the temperature, the abundance ratio will not remain fixed. With boron monoxide,  $\text{B}^{11}\text{O}$  and  $\text{B}^{10}\text{O}$ , the abundance ratio,  $m$ , of the normal state ( $v=0$ ) becomes  $1.3m$  in the first excited vibrational state ( $v=1$ ). In general, correct values of  $m$  from spectroscopic band data give determinations of  $m$  as a function of  $v$ . Correct values are also obtained by intensity measurements on absorption bands belonging to  $v=0$  in the normal state, provided that the gas is kept at a low temperature. L. S. THEOBALD.

**Actino-uranium and the ratio of actinium to uranium in minerals.** A. F. KOVARIK (Science, 1930, 72, 122—124; cf. Holmes, this vol., 1339).—The need for considering the amount of ordinary lead present in a mineral in calculations of the age of a mineral or of the disintegration constant of actino-uranium is emphasised. Actino-uranium appears to be an independent isotope of uranium;  $T$  is  $2.7 \times 10^8$  years; and the amount in minerals conforms to the view that initially it is of a definite amount in proportion to the uranium, the relative proportion decreasing with age of the mineral. L. S. THEOBALD.

**Artificial disintegration of certain elements.** C. PAWLOWSKI (Compt. rend., 1930, 191, 658—660).—The "retrograde" method has been used for the study of artificial disintegration by means of  $\alpha$ -particles from polonium sources corresponding in activity with 0.3—30 mg. of radium. The apparatus contained two sources of different intensities, which could be used singly or together, with cellulose acetate absorption screens of different thickness, and was adjusted so as to suppress the effect of rays due to hydrogen present as an impurity. Absorption curves were plotted, and by elimination of the effect of reflected  $\alpha$ -particles by calculation of their paths from the Rutherford-Darwin theory of elastic shock, evidence of disintegration was shown to exist for carbon, magnesium, aluminium, silicon, and sulphur, but not for iron, zinc, silver, or lead. In general, the ratio of the number of  $H$  disintegration-particles to the number of  $\alpha$ -particles striking the radiator was in good agreement with values found by other workers (cf. Bothe and Fränzl, A., 1928, 343, 1302). J. GRANT.

**Fine structure of  $\alpha$ -radiation.** J. THIBAUD (Compt. rend., 1930, 191, 656—658).—The experiments of Rosenblum (this vol., 837) on the varying speeds of  $\alpha$ -particles emitted by radioactive disintegration may be related with displacements of helium nuclei between the energy nucleus of the radioactive atom and with the moment of rotation of the latter. The various components constituting the fine structure

of the complex  $\alpha$ -radiation are shown to be multiples of the fundamental energy unit expressed by  $h^2/8\pi^2A$ . Rosenblum's value 40.6 kilovolts is confirmed by calculating the moment of inertia  $A$  from the value  $2.7 \times 10^{-13}$  cm. for the radius of the spherical nucleus. It follows that  $\gamma$ -radiations may result from analogous energy-level changes of positive charges, and also from variations in the nuclear rotational energy (for penetrating  $\gamma$ -rays). J. GRANT.

**Scattering of hard  $\gamma$ -radiation.** G. BECK (Naturwiss., 1930, 18, 896).—It is shown that the scattering of hard  $\gamma$ -radiation produced by heavy nuclei must be of the same order as the Compton scattering by the shell electrons. J. W. SMITH.

**Polonium  $\gamma$ -radiation.** W. BOTHE and H. BECKER (Naturwiss., 1930, 18, 894—895).—It is now shown that the weak  $\gamma$ -radiation from polonium previously described (cf. this vol., 1086) cannot be attributed either to foreign ions or to radioactive impurity in the polonium. Within experimental error its intensity is proportional to the polonium content of the preparation, irrespective of its origin or age. Hence it must be attributed to the polonium itself. The polonium  $\gamma$ -radiation can be absorbed with about the same facility as the weak filtered  $\gamma$ -radiation of radium-B+C. The intensity of the  $\gamma$ -radiation from 1 millicurie of polonium is about equal to that from  $6.6 \times 10^{-6}$  mg. of radium in equilibrium with its disintegration products. The simplest explanation of this  $\gamma$ -radiation is that the energy of disintegration of the polonium nucleus is not wholly given to  $\alpha$ -particles of normal range, but is divided between a slow  $\alpha$ -particle and one or more  $\gamma$ -rays (e.g., by self-excitation of the disintegrating polonium nucleus). It is therefore to be expected that besides the principal line in the velocity spectrum, there will also be one or more weak lines of lower velocities. Such lines have been observed by Rosenblum in the case of thorium-C radiation (this vol., 837). An alternative explanation is that the radium disintegration series shows slight branching at this stage.

J. W. SMITH.

**Activity of potassium and rubidium determined by means of the electron counter.** W. MÜHLHOFF (Ann. Physik, 1930, [v], 7, 205—224).—The electron counter has been used to determine the weak radiation from potassium and rubidium. The absorption coefficient of  $\gamma$ -radiation from potassium was determined by comparison with the known  $\gamma$ -radiation from radium-C and thorium-C. Comparative experiments with a standard radium preparation of 0.03 mg. of radium showed that the intensity of the  $\gamma$ -radiation from radium-C in equilibrium with radium was  $3 \times 10^{10}$  as great as that from potassium. Determinations of the  $\beta$ -activity of potassium and rubidium gave for the ratio of the intensities for potassium:rubidium:uranium the values 1:16:500, only the one  $\beta$ -ray component (i.e., uranium-X 1) being used for uranium.

A. J. MEE.

**Probability law of radioactive disintegration at very small concentrations.** G. I. POKROWSKI (Z. Physik, 1930, 65, 133—138).—In continuation of earlier work (cf. this vol., 9) the apparatus used was

the same, except that the eyepiece had a field of view containing 250 mm.<sup>2</sup> of the fluorescent screen. As the concentration of radioactive atoms is diminished so does the deviation from the exponential laws increase. The deviation is systematic, fewer atoms disintegrating per second than theory predicts, and is greater than the experimental error.

A. B. D. CASSIE.

**Nature of cosmic rays.** P. S. EPSTEIN (Proc. Nat. Acad. Sci., 1930, 16, 658—663).—Mathematical.

**Structure of cosmic radiation.** I. W. S. PFORTE (Z. Physik, 1930, 65, 92—101).—An automatically registering compensation apparatus for measuring cosmic radiation is described. Compensation for stray effects is attained by use of two ionisation chambers. The apparatus was tested in a mine 406 m. deep, where the stray ion currents registered by the system fell to approximately 0.03 times the current to be measured, and remained constant. Currents registered at sea level, and on the earth's surface, must therefore be due to cosmic rays.

A. B. D. CASSIE.

**Frequency shifts in dispersing media.** G. BREIT and E. O. SALANT (Physical Rev., 1930, [ii], 36, 871—877).—Mathematical. The propagation of a light wave through a dispersing medium is investigated by methods of quantum mechanics.

N. M. BLIGH.

**Quantum theory of chemical forces.** M. BORN (Z. Physik, 1930, 64, 729—740).—Theoretical. Slater's method (this vol., 126) may be used to determine the chemical binding forces of two unlike atoms without resort to group theory.

A. B. D. CASSIE.

**Statistical evaluations of the coulomb energy of interaction in a molecule.** L. GOLDSTEIN (Compt. rend., 1930, 191, 606—608; cf. this vol., 1093).—If the Fermi function for atomic distribution is used to calculate the coulomb energy of interaction of two atoms in a molecule, an expression of the electrical coupling of the electrons concerned is obtained. Expressions are derived for the potential energy of each atom in the field of the other, and by combination of these two quantities, the total coulomb energy of the molecule as a function of the nuclear distance is obtained. The special case of a homopolar molecule is considered.

J. GRANT.

**Mechanical theories in physics and chemistry** A. KORN (Scientia, 1930, 47, 315—324).—Speculative.

CHEMICAL ABSTRACTS.

**Electronic structure of atoms.** F. CROZE (Bull. Soc. chim., 1930, [iv], 47, 1017—1124).—A lecture.

**Are resonance phenomena possible in physico-chemical periodicity?** N. VON RASCHESKY (Z. Physik, 1930, 65, 270—272).—Mathematical. By analogy with physical systems displaying periodic fluctuations, e.g., wave motions, physico-chemical periodic reactions should show resonance phenomena. Such a chemical resonance would play an important part in the mechanism of the nerve-centres. The conditions for such resonance phenomena are worked out.

A. J. MEE.

**Spectroscopic investigations on nitric oxide and nitrogen peroxide.** M. LAMBREY (Ann. Physique, 1930, [x], 14, 95—183).—Measurements have been

made of the wave-lengths of the lines in the  $\beta$ - and  $\gamma$ -bands in the absorption spectrum of nitric oxide. The lines in the  $\gamma$ -band are expressed by the formula  $\nu = [44079/44201] + n'(2349.5 - 11.5n') - n''(1888 - 13.8n'')$ , which agrees with observations better than that of Guillery (A., 1927, 496). From analysis of the  $^3S-^2P_1$  component of the (0.0) and (0.1) bands of the  $\gamma$ -system the rotational energy term of the state  $^2P_1, n''=0$  is given by  $b=1.663$ . This is in agreement with the value obtained by extrapolation of the measurements of Guillery, but differs from that of Schmid (A., 1928, 931) and also from that found by Jenkins, Barton, and Mulliken (A., 1927, 916) from analysis of the  $\beta$ -band. Absorption coefficient measurements have been made between 2400 and 2100 Å. Outside the  $\beta$ - and  $\gamma$ -bands general absorption is observed, the intensity varying as a power of pressure between 1.5 and 2. A similar pressure variation also appears in the  $\gamma$ -band where the absorption varies as  $p^{1.61}$ . Introduction of a foreign gas increases the absorption coefficient considerably. These phenomena are explained by supposing that the nitric oxide molecules become absorbent for a short time at the moment of their collisions with one another or with other molecules. The intensity of the  $\beta$ -band, however, seems to be independent of pressure and it is concluded that the initial  $^2P$  state of this band is different from the initial  $^2P'$  state of the  $\gamma$ -band, the former being capable of existence for a molecule alone and the latter being produced only through collisions. The change in the relative intensities of the absorption bands with temperature is also anomalous.

The ultra-violet absorption spectrum of nitrogen peroxide consists of two broad bands attributable to  $N_2O_4$  and bands of complex structure attributable to  $NO_2$ . The wave-lengths of the absorption maxima of these bands are tabulated.

J. W. SMITH.

**High-frequency discharges. II. Methane and its chloro-derivatives.** P. N. GHOSH and B. D. CHATTERJEE (Z. Physik, 1930, 65, 102-106; cf. this vol., 1074).—The authors' earlier investigations on the radiation emitted by oxygen and nitrogen in discharges excited by potentials of high frequency have been extended to methane and its chloro-derivatives. In a narrow range of pressure, depending on the vapour, the discharge is characterised by striations the number of which in a given discharge tube varies with the pressure. If the pressure at which a given number of striations appears be plotted against the mol. wt. of the vapour the points lie on a smooth curve which is approximately of the form  $p=p_0e^{-km}$ , where  $m$  is the mol. wt. and  $k$  a constant.

R. W. LUNT.

**Explanation and prediction of molecular spectra.** F. HUND (Physikal. Z., 1930, 31, 876-880).—Theoretical. From a consideration of the relative sizes of forces within the molecule (e.g., rotation, oscillation, electron forces) the type of spectrum obtainable from the molecule can be predicted. The work is applied to diatomic molecules. A summary of methods of ordering spectra is given.

A. J. MEE.

**Line spectra of ions in solid state in visible and ultra-violet regions of the spectrum. Ab-**

**sorption spectra of  $GdBr_3 \cdot 6H_2O$  at the ordinary temperature and at that of liquid air and their comparison with those of  $GdCl_3 \cdot 6H_2O$ .** S. FREED and F. H. SPEDDING (J. Amer. Chem. Soc., 1930, 52, 3747-3756).—It is considered that ions of the transition elements should be regarded as polyatomic in the solid state and in solution, whilst those of the rare earths may be treated as atomic. The absorption spectrum of  $GdBr_3 \cdot 6H_2O$  at the ordinary temperature consists of very sharp lines confined almost entirely to the ultra-violet and a few faint diffuse lines in the visible. With reduction of temperature the lines shift slightly towards the red and show greater separation of the lines of each multiplet due to contraction of the crystal bringing the ions closer together; at the same time the lines in the visible became narrower and sharper. The widely-separated multiplets are regarded as corresponding with single lines of the spectrum of gaseous  $Gd^{III}$  ions. Complete results are tabulated. The corresponding lines of  $GdCl_3 \cdot 6H_2O$  (A., 1929, 490, 1362) are a little less widely separated and slightly to the shorter wave-length side of those of the bromide. These effects are attributed to the greater deformability of the bromide ion.

J. G. A. GRIFFITHS.

**Ultra-violet absorption of alkali and alkaline-earth halides, zinc iodide, cadmium bromide, cadmium iodide, mercuric bromide, and mercuric iodide in aqueous and non-aqueous solutions.** E. LEDERLE (Z. physikal. Chem., 1930, B, 10, 121-141).—Experimental evidence in support of Franck and Scheibe's theory that the ultra-violet absorption spectra of the halogen ions in aqueous solution are electron-affinity spectra (Z. physikal. Chem., 1928, 139, 22; cf. A., 1929, 1363) is described. Absorption measurements with aqueous solutions of the alkali and alkaline-earth halides down to 1860 Å. show that except at high concentrations the absorption is independent of the cation. Compounds such as the alkyl halides, in which the halogen linking is non-polar, exhibit a different type of absorption. The absorption bands of zinc iodide, cadmium bromide, cadmium iodide, mercuric bromide, and mercuric iodide in solution in non-aqueous solvents, such as ethyl alcohol, also differ from those observed in aqueous solutions, and are ascribed to neutral molecules. The absorption data for mercuric iodide, taken in conjunction with Terenin's results (A., 1927, 1009), make it appear probable that the photo-reaction leads to the dissociation  $HgI_2 \rightarrow HgI + I$ , in which both products of dissociation may appear in the excited state.

R. CUTBILL.

**Further absorption spectra of chemically simple halide crystals.** H. FESEFELDT (Z. Physik, 1930, 64, 741-748; cf. this vol., 1343).—Absorption spectra in the region 160-600 m $\mu$  were studied by means of Hilsch and Pohl's condensed surface layer method (this vol., 395) in the cases of halides of lead, thallium, cadmium, nickel, and cobalt, silver chloride, zinc iodide, barium bromide, and indium chloride. The lead halides give distinct bands, showing these halides to be simple ionic crystals. The bands are sharper at liquid-air than at the ordinary temperature, their maxima are shifted to shorter wave-lengths, and

the longer wave-length maxima are diminished in intensity. These results agree with those obtained from ordinary compressed layers. Halides of thallium do not give distinct bands, and the results do not agree with those of the compressed layer method. A lowering of temperature neither increased the resolution nor shifted the position of absorption. Absorption of cadmium and zinc iodides is like that of lead iodide. The halides of alkaline-earths appear, from barium bromide, to have distinct absorption bands in the region of wave-lengths less than 160  $\mu$ .

A. B. D. CASSIE.

**Light absorption in crystals of silver and copper halides.** H. FESEFELDT and Z. GYULAI (Nachr. Ges. Wiss. Göttingen, 1929, 226—230; Chem. Zentr., 1930, i, 2846—2847).—The absorption spectra of copper and silver chlorides, bromides, and iodides 100—1000 molecular layers thick have been determined down to 185  $\mu$ . Cuprous halides and silver iodide give corresponding results for the longer waves. For the shorter waves there is a maximum at about 400  $\mu$ . The results are discussed with reference to the lattice type. The correlation between the position of the first absorption band of alkali halide phosphors containing thallium and lead and that of the thallium or lead halide does not hold in the case of addition of silver and copper. Fajans and Karagunis' supposed connexion between the silver iodide maximum and the adsorption of free silver ions is not accepted.

A. A. ELDRIDGE.

**Comet-tail bands of carbon monoxide.** L. R. MAXWELL (J. Franklin Inst., 1930, 210, 427—436).—The method used is the same as that used to determine the average duration of the excited state of mercury spark lines (cf. A., 1929, 112). It enables bands produced by ions to be distinguished from those due to neutral molecules, it being assumed that an excited ion is formed at the first collision, and then moves an appreciable distance before radiating and producing the displaced band in the spectrum. Twelve comet-tail bands were observed and their quantum numbers,  $n'$  and  $n''$ , determined. The results indicate that these bands are due to  $\text{CO}^+$  ions, thus agreeing with previous results (cf. Birge, A., 1927, 184). With helium also present at a pressure of  $2.8 \times 10^{-3}$  mm. (Hg) or upwards these bands disappear, which is in disagreement with some previous observations (cf. Baldet, A., 1925, ii, 469; Duffendack and Fox, A., 1928, 6). Two bands (2883 and 2896) of Deslandres' first negative group were also observed, but the duration of the excited state of the  $\text{CO}^+$  group producing them was far shorter than that for the comet-tail bands.

C. A. SILBERRAD.

**Energies of the C-I and C-Br linkings.** T. IREDALE and A. G. MILLS (Nature, 1930, 126, 604).—The absorption spectra of methyl, ethyl, and isoamyl iodides consist in the near ultra-violet of broad, continuous bands with maxima near 2550 Å. and at high vapour pressures a long wave-length limit at 3340 Å. The energy of the C-I linking from these data, after allowing for the energy of excitation of the iodine atom, is 64 kg.-cal.; using Berthelot's values for the heats of combustion of the alkyl iodides the energy of the C-I linking is 65 kg.-cal. The long wave-length limit of ethyl bromide appears to be 2800 Å.,

giving for the energy of the C-Br linking a value of 91 kg.-cal. as against 80 kg.-cal. from the thermochemical data.

L. S. THEOBALD.

**Absorption spectra of organic dyes.** J. AUSCHKAP (Latvian Univ. Raksti, 1930, 1, 279—368).—A spectrophotometric study has been made of the absorption spectra of aqueous solutions of 79 organic dyes. Their molecular absorption constants are expressed as a function of the wave-length over the range 720—410  $\mu$ . Beer's law holds for dilute solutions and applies equally in the presence of small quantities of colourless inorganic salts.

F. J. WILKINS.

**Raman effect.** S. BHAGAVANTAM (Indian J. Physics, 1930, 5, 237—307).—A review with bibliography.

W. GOOD.

**Constitution of hydrogen cyanide.** A. DADIEU (Naturwiss., 1930, 18, 895).—Besides the previously known Raman frequency of 2094  $\text{cm}^{-1}$  (cf. Dadieu and Kohlrausch, this vol., 1162) two other vibration bands have been observed with hydrogen cyanide, at 2062 and 3220  $\text{cm}^{-1}$ . The 2062 line is independent of the dissociation of the molecule and remains unaltered in the aqueous solution. The frequency 3220  $\text{cm}^{-1}$  is attributed to the vibration of the hydrogen atom with respect to the cyanide residue, this carbon-hydrogen frequency being, as in the case of acetylene, increased by the proximity of the triple linking. The frequency 2094  $\text{cm}^{-1}$  is supposed to arise from the normal form  $\text{H}\cdot\text{C}\equiv\text{N}$ , which occurs in excess, and the 2062  $\text{cm}^{-1}$  line from the carbylamine form occurring only in a very small proportion. This interpretation indicates that a triple linking exists between the nitrogen and carbon atoms in both the normal and *iso*-forms; this is in agreement with the conclusions reached by Lindemann (this vol., 1171) from parachor measurements.

J. W. SMITH.

**Raman effect of optically active liquids.** A. KASTLER (Compt. rend., 1930, 191, 565—566).—The Raman spectra of *d*- and *l*-pinene produced with ordinary and with polarised light are identical, differences found by other workers (e.g., Bhagavantam and Venkateswaran, this vol., 275) being attributed to impurities. If the Raman effect is dependent on the variation of a quantum of vibration affecting only a local linking between two atoms of the molecule (as distinct from the four linkings of the asymmetric carbon atom involved in polarisation phenomena), then the above results are consistent with the Curie principle.

J. GRANT.

**Splitting of the frequency of light scattered by liquids and the optical anisotropy of molecules.** E. GROSS (Nature, 1930, 126, 603—604; cf. this vol., 1345).—Of the light scattered by benzene the two lines nearest the unmodified line are strongly polarised, but the outer components are not polarised. In carbon disulphide and chlorobenzene the outer components are almost as intense as the inner, but with liquids of small optical anisotropy such as water, alcohol, and ethyl ether, the outer components have not been definitely established. The existence of outer components is associated with depolarisation and their appearance is supposed to be due to the

diffraction of light by lattices with a constant less than one half the wave-length of the incident light.

L. S. THEOBALD.

**Raman effect of diatomic molecules.** F. RASERTI (Nuovo Cim., 1929, 6, 356—370; Chem. Zentr., 1930, i, 2057).—The Raman spectra of the mercury line 2536 Å. in hydrogen, nitrogen, oxygen, carbon monoxide, and nitric oxide at 1—15 atm. have been photographed. The results are in harmony with quantum mechanics, and the moments of inertia and oscillation frequencies have been determined.

L. S. THEOBALD.

**Raman effect and the constitution of molecules.** II. B. TRUMPY (Z. Physik, 1930, 64, 777—780; cf. this vol., 1091).—The Raman spectra of solutions in water of the sodium salts of fumaric, maleic, mesaconic, and citraconic acids were determined. Lines corresponding with frequency displacements of 1405 and 1650  $\text{cm}^{-1}$  appear in both the *cis*- and *trans*-isomerides, and may be ascribed to the C:O linking. Displacements of 1447 and 2900  $\text{cm}^{-1}$  appear in the salts of mesaconic and citraconic acids, and may be due to the  $\text{CH}_3$  group. The 1650  $\text{cm}^{-1}$  line has a greater intensity in the *trans*- than in the *cis*-form, but no other characteristic difference between the Raman spectra of these two isomeric forms is apparent.

A. B. D. CASSIE.

**Raman spectrum of certain isomeric substances.** H. MŁODZIANOVSKA (Z. Physik, 1930, 65, 124—129).—Experiments have been made to ascertain whether *ortho*-, *meta*-, and *para*-disubstituted benzene derivatives exhibit characteristic Raman spectra. It is known that *o*-, *m*-, and *p*-xylene each have different Raman spectra. The three isomerides of dichlorobenzene, nitrotoluene, and toluidine were examined. It was found for each substance that some Raman lines appear in each isomeride; that some lines were given by two isomerides only, and in the same substance such lines might be exhibited by the *o*- and *m*-, the *m*- and *p*-, or the *o*- and *p*-isomerides. In each substance single lines characteristic of one isomeride were found. The origin of these lines is discussed. It follows that the position of the substituent group exerts an influence on the characteristic vibration of the group.

W. R. ANGUS.

**Raman effect of crystallised and dissolved sulphates and carbonates.** N. EMBIRIKOS (Z. Physik, 1930, 65, 266—269).—The Raman effect for a number of sulphates and carbonates, both in the solid state and in solution, was investigated by the method due to Gerlach (cf. this vol., 663). The frequency displacement due to the acid radical is much smaller for the substance in solution than for the crystalline solid. For crystals containing a large quantity of water of crystallisation the value for the frequency lies considerably closer to that for the solution, as has already been observed in the case of nitrates. The fact that for magnesium sulphate crystals the value for the frequency is lower in the crystal than in a 2*N*-solution can probably be explained by the strong tendency to hydration displayed by magnesium ions. For magnesium and lithium sulphates there was a marked difference in

displacement with different concentrations. A relationship between the displacement and the atomic number of the cation, such as holds for nitrates, is doubtless present here. The sharpness of the Raman lines is greater the less water is contained in the crystal. For solutions the lines were fairly diffuse.

A. J. MEE.

**Raman effect in crystals.** C. SCHAEFER, F. MATOSI, and H. ADERHOLD (Z. Physik, 1930, 65, 289—318).—The Raman spectra due to carbonates, nitrates, chlorates, and bromates, and to sulphates, selenates, phosphates, and the positive  $\text{NH}_4$  radical were determined with a spectrometer of dispersion 1 mm. per 13 Å., and slit width 0.03 mm. Calcite gave lines corresponding with 65, 35.5, 14, 9.2, 6.96, and 5.7  $\mu$ . These fit the infra-red bands assuming the residual ray method to give frequencies greater than the proper frequencies. The 11 and 94  $\mu$  infra-red bands do not appear. A 5.7  $\mu$  Raman displacement corresponds with a combination tone. Aragonite appears to have a similar Raman spectrum. Magnesite shows the inactive frequency, 9.2  $\mu$ , of the complex cation diminished with an increased mass of anion. Cerussite verifies this rule, and gives outer frequencies 56.5, 68.5, 85, 98.5, 135, and 169  $\mu$ . The first four displacements correspond, in doublets, with the observed residual ray wave-lengths. Taking the inactive frequency as that of least symmetrical elastic displacement, the Raman intensity decreases as the symmetry of elastic displacement increases. Sodium nitrate gives 5.99, 7.2, 9.35, 13.75, 54, and 105  $\mu$ , the inner frequencies being displaced towards longer wave-lengths compared with the carbonates. Solutions of nitric acid have the inner frequencies displaced towards longer wave-lengths compared with the crystal. The chlorate group gives displacements corresponding with 9.75, 10.15, 10.3, 10.7, 16, 20, and 80  $\mu$ ; 10.3  $\mu$  is the first harmonic of 20.6  $\mu$ ; 10.7  $\mu$  is most intense and optically inactive. Sodium bromate gives 11.90, 12.5 (inactive), and a doublet 27 and 28  $\mu$ ; cadmium bromate gives only the inactive frequency at 12.7  $\mu$ . The increase in wave-length of the natural vibration of the cation from carbonate to chlorate, and to bromate, and from sodium to cadmium is apparent.

Barium sulphate shows five displacements 8.8, 10.15, 15.6, 16.3, and 21.7  $\mu$ . These correspond with infra-red frequencies, assuming 10.15 and 20.7  $\mu$ —the most intense Raman lines—to be the optically inactive frequencies of sulphates. Barium sulphate shows no outer frequencies, and this seems characteristic of all sulphates examined. Lithium potassium sulphate gives two frequencies corresponding with 9 and 9.9  $\mu$ . Gypsum, copper sulphate, and potash alum show only inner frequencies and the water frequency equivalent to 2.9  $\mu$ . The  $\text{NH}_4$  radical shows a doublet 3.17 and 3.30  $\mu$  equivalent to the infra-red band at 3.24  $\mu$ .

A. B. D. CASSIE.

**Polarisation of Raman radiation in crystals.** C. SCHAEFER, F. MATOSI, and H. ADERHOLD (Z. Physik, 1930, 65, 319—329).—The Raman spectra from calcite and sodium nitrate, and their dependence on the orientation of the crystal axis, were determined. The degree of depolarisation for different orientations of the crystal axis is given. Leontowitsch's theory might fit the results if his simplifying assumption of a

symmetrical tensor system is modified. Gypsum was similarly investigated. The water bands show anomalous changes in intensity with different orientations of the crystal axis, and the polarisation of the  $\text{SO}_4$  vibrations could not be theoretically interpreted.

A. B. D. CASSIE.

**Scattering of light in aqueous sodium silicate solutions.** L. L. BURGESS and K. KRISHNAMURTI (Trans. Faraday Soc., 1930, 26, 574—577).—The intensity of light scattered by filtered solutions of commercial sodium silicate has been determined for constant ( $2M$ )  $\text{SiO}_2$  concentration as a function of the molar ratio  $\text{SiO}_2/\text{Na}_2\text{O}$ . At ratios up to 2.5 the Tyndall intensity is small and practically constant, but thereafter the intensity increases at an increasing rate. Colloidal complexes are formed at ratios exceeding 3, and at higher ratios the particles become coarser and may be removed by filtration. Silicic acid sols treated with sodium hydroxide remain clear until the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio exceeds 3.8, when the intensity of scattered light shows a marked increase.

H. F. GILLBE.

**Experiments with filters in the (long-wave) infra-red.** H. G. HIRSEKORN (Ann. Physik, 1930, [v], 6, 985—1000).—Films of sodium, ammonium, potassium, and thallous chloride were prepared by allowing the vapours of these substances to impinge on a very thin varnish film until a filter was obtained consisting of very thickly packed particles of the order of magnitude of  $1 \mu$ . The transmissivity of these thin films has been determined by means of a spectrometer with a copper wire grating and a micro-radiometer. These substances function as selective filters throughout the spectral range 40—140  $\mu$ . Each of them shows a region of absorption the breadth of which increases in the order sodium, ammonium, potassium, thallous chloride. The transmission curve is less steep on the long-wave side of the absorption region. Potassium chloride exhibits three absorption maxima, whilst the other substances each show two maxima. The reflexion spectrum of natural rock salt was examined, but did not yield results which explained the significance of the appearance of these absorption maxima. The existence of a complicated interaction between absorption, reflexion, and scattering effects is suggested as a possible explanation of the observed peculiarities.

W. R. ANGUS.

**Reststrahlen of univalent and bivalent fluorides.** O. REINKOBER and M. BLUTH (Ann. Physik, 1930, [v], 6, 785—792).—The wave-lengths of the "Reststrahlen" of some univalent and bivalent fluorides have been determined using the reflexion method with grating spectrometer.

W. GOOD.

**Luminosity in the gas space in heterogeneous reactions.** W. FRANKENBURGER and W. ZIMMERMANN (Z. physikal. Chem., 1930, B, 10, 238—240).—In the formation of lithium nitride by passing nitrogen over gently heated lithium, a bluish-green to yellowish-green luminosity is obtained above the pieces of lithium, provided that a very small quantity of oxygen (a few parts per 1000) is introduced into the nitrogen stream. The effect is increased by reduction of pressure, or by heating the lithium electrically in a molybdenum gauze placed in the middle of a large bulb. When

examined spectrographically the light gives the red and sometimes the blue lithium line, and also the yellow sodium line. The bluish-green light corresponds with a band spectrum stretching from green to violet. Active nitrogen strengthens the red lithium line but not the green. The luminosity is strongest while a considerable excess of metallic lithium is still present. The phenomenon may be due to the presence of intermediate active substances, such as atomic nitrogen, excited nitrogen molecules,  $\text{LiN}$  or similar molecules in an excited state, which cause the emission of light on passage to the normal state through collisions of the second kind with lithium or other molecules capable of emission.

M. S. BURR.

**Continuous (or band) fluorescence emission spectrum which accompanies change of colour.** W. D. HARKINS and H. E. BOWERS (J. Amer. Chem. Soc., 1930, 52, 4170—4172).—The Raman effect has been observed by means of the mercury arc in  $\alpha$ - and  $\beta$ -bromobutane,  $\alpha$ -bromo- $\beta$ -methylpropane,  $\beta$ -bromo- $\beta$ -methylpropane,  $\alpha$ - and  $\beta$ -bromopropane, and *n*- and *iso*-amyl bromide. In addition to lines of modified wave-length, a continuous emission spectrum between 4000 and 5800 Å. was obtained with each liquid, providing the exposure was sufficiently prolonged. The production of the continuous spectrum (maxima at 4358—4916 and 5460—5769 Å.) was always accompanied by the appearance of a yellow colour in the liquid even if oxygen were excluded. Under similar conditions methyl alcohol, but not ethyl alcohol, when saturated with ammonia gave analogous results. The pure alcohols did not exhibit the phenomenon.

J. G. A. GRIFFITHS.

**Quenching of the fluorescence of nitrogen dioxide.** W. P. BAXTER (J. Amer. Chem. Soc., 1930, 52, 3920—3927; cf. Norrish, A., 1929, 1022).—The intensity of the fluorescence emitted by nitrogen peroxide at pressures between 0.001 and 18 mm. when illuminated with light of  $\lambda$  4358 and 4047 Å. of the mercury arc has been determined, and the quenching of the fluorescence by added gases has been investigated. Nitrogen peroxide itself quenches the fluorescence, which is half damped in the pure gas at 0.02 mm. The product of the square of the effective collision diameter,  $\sigma$ , and the life of the excited molecule,  $\tau$ , is  $9.3 \times 10^{-21}$  cm.<sup>2</sup> sec. and hence, if  $\tau = 10^{-7}$  sec.,  $\sigma = 30 \times 10^{-8}$  cm., which is ten times the diameter given by the kinetic theory. The specific quenching effects on the fluorescence of added carbon dioxide, nitrogen, oxygen, and hydrogen are, respectively, 0.87, 0.29, 0.24, and 0.15 times that of nitrogen peroxide.

J. G. A. GRIFFITHS.

**Fluorescence of cellulose acetate, cellulose nitrate, and gelatin in ultra-violet light.** J. G. McNALLY and W. VANSELOW (J. Amer. Chem. Soc., 1930, 52, 3846—3856).—The intensity of fluorescence excited by ultra-violet light ( $\lambda$  280—334  $m\mu$ ) in cellulose nitrate films decreases as the films are dried under increased tension, and the optical properties show parallel changes. The fluorescences of cellulose di- and tri-acetate films are similar except for light of wave-length 334  $m\mu$ , for which the former yields lower intensities than the latter. This change of intensity is closely parallel to the progressive hydrolysis of the



triacetate to the diacetate. The results indicate that fluorescence is more closely related to degree of acetylation than to viscosity in acetone. The fluorescence of acetone solutions of cellulose acetate in 365 m $\mu$  light is independent of viscosity, and that of gelatin sols decreases during the part of hydrolysis causing a change of micellar magnitude, and increases later owing to a secondary change.

J. G. A. GRIFFITHS.

**Dielectric constant of bromine vapour.** A. BRAMLEY (J. Franklin Inst., 1930, **210**, 421—426).—From earlier work (cf. A., 1926, 886; 1927, 293) it is deduced that the values of the dielectric constant of (gaseous) bromine for the lowest *P.D.* are the most accurate. The values deduced for  $(D-1) \times 10^3$  for 126 mm. (Hg) and 77°, 295 mm. and 82°, and 144 mm. and 120° arc, respectively, 8.5, 6.5, and 11.1, whilst that for low pressure and 28.5° is  $4.7 \pm 0.3$ . It is inferred that the dielectric constant increases with rise of temperature and decreases with pressure, that the electric moment of the molecules is greater at higher temperatures (corresponding with higher energy levels), and that the molecules which are raised to these higher levels by absorption of radiation must lose this on collision with other molecules. These deductions are in conformity with those of Zahn for acetic acid (cf. this vol., 841). C. A. SILBERRAD.

**Dielectric constant and dipole moment of gaseous hydrogen cyanide.** K. FREDENHAGEN and F. MASKE (Z. physikal. Chem., 1930, **B**, **10**, 142—148; cf. Werner, A., 1929, 1217).—The dielectric constant of hydrogen cyanide vapour between 30° and 200° has been measured. The molecular polarisation calculated from the results fulfils the requirements of Debye's equation above 95°, and the value of  $2.1 \times 10^{-18}$  e.s.u. is deduced for the dipole moment. Lange's equation (A., 1925, ii, 840) yields practically the same value. R. CUTHILL.

**Change of the dielectric constant of ethyl ether with temperature.** J. MAZUR (Nature, 1930, **126**, 649).—The dielectric constant of ethyl ether increases with a fall in temperature from 4.18 at 30.6° to 12.39 at -105.4°. At this point a sharp break occurs and the dielectric constant then decreases rapidly to a minimum at the m. p., -117.2°, after which a slight increase occurs. Below -118.9°, the values are practically constant at 2.04. L. S. THEOBALD.

**Dipole moments of *o*-dihalogen derivatives of benzene.** E. BERGMANN, L. ENGEL, and S. SÁNDOR (Z. physikal. Chem., 1930, **B**, **10**, 106—120).—The dipole moments of the ten *o*-dihalogen derivatives and the four monohalogen derivatives of benzene have been obtained from measurements of the dielectric constant and refractive index in benzene solution at the ordinary temperature. As would be expected in view of the theory previously advanced (this vol., 979), the "ortho-effect" is most marked with iodine as substituent, and least marked with fluorine. The results are, however, also in satisfactory agreement with Smallwood and Herzfeld's theory (*ibid.*, 841). It is pointed out that X-ray data and measurements of dipole moment demonstrate the existence of distortion in molecules even as simple as chloroform and methylene chloride. R. CUTHILL.

**Polar properties of the carboxyl group in some aliphatic acids and in benzoic acid.** (Dipole moment, association, solubility, and electrochemical behaviour.) G. BRIEGLEB (Z. physikal. Chem., 1930, **B**, **10**, 205—237).—The dipole moments of formic, acetic, propionic, butyric, isovaleric, and benzoic acids in benzene solution have been determined by Wolf's method (A., 1929, 244; this vol., 523). A consideration of molar polarisation measurements, mol. wt. and vapour density determinations, and measurements of the distribution between carbon tetrachloride and water indicates that complete dissociation of the fatty acids to simple molecules is not reached in infinitely dilute solutions and that the proportion of simple molecules diminishes with increasing mol. wt. Further, dipole association between molecules of the same kind results in the formation not only of definite binary and ternary complexes, but also of a series of mixed complex or dipole solvates corresponding with ion solvates. Measurements of the dipole moment by the method of dilute solutions gives only the moment of double molecules. In the fatty acid series the moment falls from formic to acetic acid and then remains practically constant. The molar polarisation of the lower members of the series is much more influenced by concentration than is that of the higher members, and calculation of the effective radius of dipole action indicates an increasing steric screening of the moments with increasing length of chain. The moment of the simple molecules might be determined from measurements on the esters.

By adding water to the solutions a strengthening of the dipole field ensues, but the effect diminishes with increasing mol. wt. of the acid. Determinations have been made of the solubility of water in the acid benzene solutions. M. S. BURR.

**Natural optical activity of liquids.** H. VOLK-MANN (Z. physikal. Chem., 1930, **B**, **10**, 161—188).—The Born-Gans theory of natural optical activity has been further confirmed (cf. A., 1929, 743) by rotation measurements in solutions of *d*-limonene in solvents in which the active molecule, as indicated by measurements of the dipole moment and of the shift in the ultra-violet absorption lines, is only slightly deformed. Measurements of rotation in solutions of menthone and camphor, substances with a large dipole moment, indicate deviations from the theory. These are attributed to the influence of intermolecular forces, but in all cases the deviations are larger than observed in refraction measurements. This is ascribed to a stronger influence or rotation of the weak specific vibrations in the long-wave ultra-violet, as is evident from the calculation of the optical centre of gravity of the separate wave-lengths for rotation and refraction. Further, since the asymmetry of the molecule is of primary importance for rotation, the latter must be more sensitive than refraction to external influences. On the assumption that the rotation of menthone in dilute heptane solution approaches most closely to that of the free menthone molecule, there appears to be a marked similarity between the variations in magnitude and direction, with concentration of solution and character of solvent, of rotation and spectroscopic absorption. Agreement with the Born-Gans

theory, when solvent and solute have the same moment and similar polar groups, is probably due to the action of similar electric fields. The marked influence of acid solvents on rotation may be due to the strong electric fields of the ions, and the formation of more or less stable solvates may occur.

M. S. BURR.

**Co-ordination value of multivalent negative radicals.** P. PFEIFFER (Z. anorg. Chem., 1930, 192, 366—368).—Theoretical. In certain complex compounds it is difficult to explain the presence of bivalent acid radicals, except by assigning the co-ordination valency 1 to the latter, e.g., in  $[(H_3N)_5Co(C_2O_4)]X$ . It is suggested that this difficulty may be overcome by adopting the betaine formula (A., 1928, 1132) and writing  $+[ (H_3N)_5Co(C_2O_4) ]^- X^-$ . Thus in the singly-charged state the bivalent acid radical has a co-ordination value 1 and in the uncharged state a value 2 as in the compound  $[(H_3N)_4Co(C_2O_4)]X$ . If doubly charged, its co-ordination value must be zero.

M. S. BURR.

**Heat of formation and electronic properties of atoms.** R. D. KLEEMAN (Z. anorg. Chem., 1930, 193, 106—112).—Theoretical. By considering the energy changes consequent on the changes of the distances between the electrons and their nuclei which occur when two atoms combine, a quantitative treatment of the heat of formation of a chemical compound is given. The changes of heat tone with variation of atomic and molecular concentration, and the heat of formation at infinitely small molecular concentration, are discussed.

H. F. GILLBE.

**Problem and results of the newer investigations of free radicals.** K. ZIEGLER (Z. angew. Chem., 1930, 43, 915—919).—The manifold influences which determine whether any particular substance shall be strongly or weakly dissociated are discussed. The principal are the energy of activation of ethane, and radical and steric factors.

J. W. SMITH.

**Determination of structure from characteristic acoustic oscillations.** A. MEISSNER (Z. Physik, 1930, 65, 145—157).—By applying a high-frequency electric field perpendicular to one of the electric axes in quartz it is found that there are two frequencies, of the ratio 1 : 1.4, which excite resonance in the quartz. It is possible to find the positions of the lattice planes by this method. An approximately cubic structure for silicon was derived. The position of the oxygen atoms was derived by a consideration of the polarity of the elementary cells and of the size of the lattice structure. The elementary cell, the smallest geometrical unit in the quartz which still preserves the symmetry of the macroscopic crystal, contains three  $SiO_2$  "molecules" lying in different planes, and three dipoles are present, of which the positions and the linkings give to quartz its physical properties. The results are compared with those obtained by the X-ray method. Both methods lead to the same results. The method may be used for other crystals.

A. J. MEE.

**Constitution of borates.** F. L. HAHN (Z. anorg. Chem., 1930, 193, 316—320; cf. Wiberg, this vol., 1096).—Theoretical. Simple borates, polyborates, and

complex borates can be satisfactorily represented by constitutional formulæ similar to those proposed by Menzel (A., 1927, 1043). Boric acid in solution behaves invariably as a monobasic acid, to which is assigned the formula  $[B(OH)_4]H$ , and the more complex borates can be similarly represented. Formulæ of acids corresponding with the known borates are given.

F. L. USHER.

**Molecular diameters of nitrogen pentoxide.** L. S. KASSEL (J. Amer. Chem. Soc., 1930, 52, 3972).—Eyring and Van Valkenburgh's result (this vol., 1105) is discussed in relation to theories of the unimolecular decomposition of the gas.

J. G. A. GRIFFITHS.

**Precision measurements in the soft X-ray region.** M. SÖDERMAN (Phil. Mag., 1930, [viii], 10, 600—616).—Various attempts during the last 10 years to join the ultra-violet and soft X-ray regions are examined and discussed. Using improved apparatus, results previously reported (cf. A., 1929, 366) of the investigation of the  $K$  series of light elements have been revised with increased accuracy with the help of gratings for each group of elements under examination, and giving different dispersions for the various groups. Wave-lengths calculated from different orders and different plates are tabulated. The mean errors of the values obtained vary from 0.02 to 0.15%.

N. M. BLIGH.

**Standard ionisation chamber.** L. S. TAYLOR and G. SINGER (Bur. Stand. J. Res., 1930, 5, 507—516).—A modification of the open-air parallel-plate ionisation chamber is described. Narrow guard-plates are supplemented by a system of ten guard-wires across the ends of the chamber. Direct comparisons between this chamber and a primary standard are given and show that the Röntgen can be reproduced by the former with the same accuracy as the primary standard.

W. E. DOWNEY.

**Absorption measurements of the X-ray general radiation.** L. S. TAYLOR (Bur. Stand. J. Res., 1930, 5, 517—538).—Copper absorption curves for heterogeneous X-rays have been obtained using a standard and two thimble ionisation chambers. On the basis of the effective wave-length determinations it is found that, contrary to the accepted views, the greater part of the highly filtered energy is not concentrated in the tungsten  $K$ -lines.

W. E. DOWNEY.

**Reflexion of X-rays at cleavage plane of crystals. IV. Complete spectral diagrams.** H. SEEMANN (Ann. Physik, 1930, [v], 6, 793—824).—The evaluation of X-ray spectral diagrams for an unknown asymmetrical orientation of the crystal in rotating-crystal methods is treated at length.

W. GOOD.

**Dependence of width and intensity of Debye lines and rings on dimensions of X-ray source etc.** M. A. BREDIG (Z. Physik, 1930, 65, 430).—Polemical against Busse (this vol., 1240).

A. B. D. CASSIE.

**X-Ray diffraction study of the series calcite-rhodochrosite.** P. KRIEGER (Amer. Min., 1930, 15, 23—29).—Values of  $n$  and  $d$  for manganocalcite increased proportionally to the percentage of manganoous carbonate; the length of the edge of the unit

rhombohedron decreases from calcite to rhodochrosite.

CHEMICAL ABSTRACTS.

**X-Ray investigation of the system sulphur-selenium.** I. Rhombic mixed crystals of sulphur and selenium. F. HALLA and F. X. BOSCH (Z. physikal. Chem., 1930, B, 10, 149—156).—The densities, facial angles, axial ratios, and spacing of the (111) planes in rhombic mixed crystals of sulphur with up to 7% selenium have been determined. All the linear lattice dimensions are increased similarly on the introduction of selenium, pointing to a statistical distribution within the crystal, and the sulphur is activated.

R. CUTHILL.

**X-Ray investigations on the modifications of manganese.** E. ÖHMAN (Svensk Kem. Tidskr., 1930, 42, 210—216).—A review of recent work on the structure of the different modifications of manganese. The  $\alpha$ -form is stable at ordinary temperatures; this changes to  $\beta$ -manganese at 742°, and to  $\gamma$ -manganese at 1191°, the rate of conversion being appreciably retarded by the presence of impurities. Technical manganese consequently often consists of a mixture of the  $\alpha$ - and  $\beta$ -modifications, or occasionally of the  $\beta$ -modification alone, but the  $\gamma$ -form is never present.

H. F. HARWOOD.

**X-Ray study of some tungsten magnet steel residues.** W. A. WOOD (Phil. Mag., 1930, [viii], 10, 659—667).—The carbide constituents of 20 tungsten magnetic steels were identified from the X-ray spectra of the residues, using the iron  $K\alpha$  radiation. The steels contained W 6, C 0.72, Ni 0.19, Mn 0.28, Si 0.14, S 0.023, P 0.027%. The carbides were identified by the fact that variations in heat treatment of the steels resulted in large differences in the distribution of intensity among the lines of the spectra without alteration in their position. Tungsten carbide, the mixed carbide  $Fe_4W_2C$ , and a compound probably due to the silicon content were found, but no cementite. The tungsten carbide spacings were slightly smaller than normal, indicating that in this, as well as in the mixed carbide, atomic replacement occurs. Chemical analysis of the residues as an indication of steel constituents was of doubtful value.

N. M. BLYTH.

**Loosening of the [crystal] lattice and reactivity in the solid state.** J. A. HEDVALL (Z. Elektrochem., 1930, 36, 853—861; cf. this vol., 559).—The various ways in which the structural units of a crystal lattice may be rendered more mobile are discussed, and attention is especially directed to the loosening produced by the introduction of small quantities of a foreign substance which can form mixed crystals with the material under consideration. The reaction between barium oxide and lead chloride especially has been studied at temperatures at least 140° below the m. p. of the most fusible constituent of the reaction mixture. At the temperatures used (228—298°) the amounts of lead chloride transformed in a given time were considerably (20—100%) greater when the lead chloride contained initially 0.1% of barium chloride. This result is ascribed to the loosening of the lead chloride lattice by barium chloride, an interpretation which is in harmony with the marked increase in the

electrolytic conductivity of solid lead chloride caused by the presence of small proportions of other chlorides.

F. L. USHER.

**Crystal structure in the system copper-bismuth.** W. F. EHRET and R. D. FINE (Phil. Mag., 1930, [viii], 10, 551—559; cf. Bernal, A., 1929, 987; Hanson and Ford, B., 1927, 280).—The structure of alloys of bismuth and copper, covering the whole range, was examined by powder photographs. All the alloys were heterogeneous, and showed the superimposed diffraction patterns of copper and bismuth; the lattices of each metal remain unchanged in the alloys, indicating low mutual solubility. The lattice constant of the face-centred unit cube of copper was redetermined,  $a_0$   $3.607 \pm 0.004$  Å. Using rhombohedral reference axes, mutually inclined at  $57^\circ 16'$ , the length of the edge of the elementary rhombohedron of bismuth was found to be  $4.749 \pm 0.005$  Å.

N. M. BLYTH.

**Lattice distortion at slip planes; X-ray examination of rock salt.** W. BERG (Wiss. Veröff. Siemens-Konz., 1930, 9, 119—143).—Simple reflexion of X-rays from the surface of a crystal is used to examine the nature of the surface layer. From the character of the pattern it is concluded that lattice distortion takes place at slip planes.

W. E. DOWNEY.

**Crystal forms of single crystals of copper. I. Crystals produced by stress-annealing method.**

II. Crystals deposited on the surface of a single-crystal plate by electrolysis. S. TAKEYAMA (Mem. Coll. Sci. Kyoto, 1930, A, 13, 353—362, 363—367).—I. The outer forms of single crystals of copper prepared by the stress-annealing method have been studied. The crystalline faces developed by etching depend on the method of etching.

II. An attempt has been made to cause single crystals of copper to grow by electro-deposition. In favourable conditions the copper first deposited has the same orientation as the mother crystal, but when the deposit has become about 0.5 mm. thick subsequent deposition occurs as micro-crystals of more or less random orientation.

R. CUTHILL.

**Laue photographs of iridescent crystals of potassium chlorate.** S. C. SIKKAR (Indian J. Physics, 1930, 5, 337—343).—Laue patterns from the (001) planes of a single crystal of potassium chlorate and of the same crystal heated almost to the m. p. and then cooled were compared. Each of a particular group of spots in the Laue diagram of the ordinary crystal appeared as two and sometimes as three spots in the case of the heat-treated crystal. The pattern given by the latter was identical with that given by a coloured crystal of potassium chlorate and a thick twinned crystal. It is shown from a study of the X-ray diagrams that on heating a single crystal of potassium chlorate, twinned strata, almost parallel to each other, are produced and that these strata are also present in the coloured crystals.

W. GOON.

**Structure of aluminium chloride.** V. E. LASCHKEV (Z. anorg. Chem., 1930, 193, 270—276).—The unit cell is hexagonal rhombohedral,  $a$   $3.475 \pm 0.007$  Å.;  $c/a$   $2.45 \pm 0.01$ ; space-group  $D_{3d}$ ;  $d_{calc}$  2.47;  $d_{obs}$  2.44.

F. L. USHER.

**Crystal forms of monobasic fatty acids.** Y. TANAKA, R. KOBAYASHI, and K. SHIMIZU (J. Soc. Chem. Ind. Japan, 1930, 33, 364—365B).—The fundamental crystal of stearic, palmitic, and myristic acids is rhombic, the adjacent angles being  $70 \pm 1^\circ$  and  $110 \pm 1^\circ$ , and it exhibits double refraction and parallel extinction. The crystals are orthorhombic, but the oblong and needle forms are produced by excessive growth in a direction parallel to one side, and not in the direction of the angles, as with paraffin. The concentration range over which the fundamental rhombic crystallisation takes place has been determined for the fatty acids, and agrees with the theoretical considerations derived previously from observation of the crystallisation of paraffin.

H. F. GILLBE.

**X-Ray diffraction in liquids. III. Influence of temperature.** S. TANAKA and A. TSUJI (Mem. Coll. Sci. Kyoto, 1930, A, 13, 337—342; cf. this vol., 672).—An investigation of the effect of temperature on the diffraction of X-rays by various organic liquids has shown that as the temperature rises the diffraction ring of the X-ray diagram diminishes in radius, becoming at the same time broader and more diffuse at the edges; the inner scattering increases, and the diffracted X-rays decrease in intensity.

R. CUTHILL.

**X-Ray study of natural and fossil resins.** C. MAHADEVAN (Indian J. Physics, 1930, 5, 345—357).—The two classes of resin show no distinct difference in their X-ray patterns. Observed variations in the intensity of the diffraction halo are correlated with the physical characteristics of the resins.

W. GOOD.

**Thickness of oxide film producing temper colour on iron.** M. KURODA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 145—152).—Interference measurements showed that a thickness of  $40.5 \text{ m}\mu$  is removed on slightly polishing the tarnished blue surface of mild steel until the yellowish-brown temper colour appears. The refractive index of the tarnish film is 1.99 for the mean between  $\lambda 450 \text{ m}\mu$  and  $\lambda 630 \text{ m}\mu$ .

S. K. TWEEDY.

**Electrical resistance of nickel and permalloy wires as affected by longitudinal magnetisation and tension. Electrical resistance and magnetostriction.** L. W. MCKEEHAN (Physical Rev., 1930, [iii], 36, 948—977; cf. A., 1926, 891).—Available data for nickel and alloys rich in nickel indicate abnormal changes in the resistance of ferromagnetic as compared with non-ferromagnetic metals in magnetic fields and under mechanical stresses. Simple cases of these effects were investigated in 45—90% nickel permalloys, and indicate a common origin in the orientation of atomic magnetic axes associated in each atom with mechanical asymmetry. The connexion between these resistance effects and magnetostriction, the kinds of re-orientation involved in magnetising, and the relative importance of intra-atomic and inter-atomic magnetic fields are discussed.

N. M. BLIGH.

**Variation with field strength of back *E.M.F.* and of true conductivity in ion crystals.** O. BERAN and F. QUITTNER (Z. Physik, 1930, 64, 760—776).—If a specimen of a material which exhibits

dielectric absorption is allowed to attain a steady state due to the electric field between two electrodes arranged at opposite faces of the specimen, and if then these electrodes are short-circuited, the back *E.M.F.* of dielectric polarisation may be defined as the initial value of the ratio of the current that then flows, to the true conductivity of the material. This *E.M.F.* has been measured by an electrometer method, using a Helmholtz pendulum contact maker, from  $0.5 \times 10^{-3}$  to  $6.0 \times 10^{-3}$  sec. after the cessation of the polarising field, during which period it is sensibly constant. If  $V_1$  is the value of this *E.M.F.* corresponding with a steady state characterised by a current  $I$  and arising from an electrode *P.D.*  $V$ , then the true conductivity of the specimen is given by  $\rho = I(V - V_1)$ . Data are given for the variation of  $V_1$  and  $\rho$  for polarising fields  $E$  in the range 4—34 kilovolts  $\text{cm}^{-1}$ , and in the temperature range 110—300°. The results show that  $(dV_1/dE)_T$  is relatively small and negative,  $(dV_1/dT)_E$  is large and negative, and  $(d\rho/dE)_T$  and  $(d\rho/dT)_E$  are both positive; they are held to sustain Smekal's theories of the mechanism of conduction in such crystalline materials as those examined, namely, artificial and natural rock salt and sylvine.

R. W. LUNT.

**Dielectric breakdown in crystals.** (Miss) L. INGE and A. WALTER (Z. Physik, 1930, 64, 830—844).—The mechanism of dielectric breakdown in crystalline substances has been examined by photographing the light emitted in the regions of local breakdown when such materials are placed in an electric field of sufficient intensity between point and plane electrodes immersed in insulating oil. Impulse discharges of a duration of  $3 \times 10^{-8}$  sec. were used. Rock salt, Iceland spar, aragonite, fluorspar, barytes, beryl, and sylvine were investigated. The breakdown appears to take place at a single point within the crystal initially and then bifurcates in directions which are related to the crystal structure of the material and to the direction of the electric field.

R. W. LUNT.

**Cross-sectional resistance of the oxide layer of hot cathodes.** J. KROCZEK and E. LÜBCKE (Wiss. Veröff. Siemens-Konz., 1930, 9, 252—261).—The resistance of the oxide layer has been measured by the heating corresponding with the cooling effect due to emission.

W. E. DOWNEY.

**Variation of magnetic resistance and the Hall effect of cuprous oxide with and without exposure to light.** O. VON AUWERS (Wiss. Veröff. Siemens-Konz., 1930, 9, 294—299).—The influence of light on the Hall effect of cuprous oxide is very small, but the effect itself is great. The variation of resistance in a magnetic field is very small, but the influence of light on the variation is very great.

W. E. DOWNEY.

**Electrical and optical properties of semi-conductors. III. Electrical determinations with cuprous oxide.** W. VOET (Ann. Physik, 1930, [v], 7, 183—204).—Experiments were carried out with cuprous oxide, which is a semi-conductor (*i.e.*, a substance which conducts feebly, and is thus in the transition stage between conductors and insulators), to determine its conductivity, Hall constant, thermoelectric force, and heat conductivity within the

range  $-70^{\circ}$  to  $70^{\circ}$ . The numerical values of the conductivity and Hall constant are tabulated, together with the dissociation work  $\epsilon$ , and the maximum electron number  $n_0$ . The effect of temperature on the free wave-length and on the thermoelectric force is given.

A. J. MEE.

**Influence of adsorbed gas on the high-frequency resistance of platinum wires.** H. DOBRETSBERGER (Z. Physik, 1930, 65, 334—357).—The electrical conductivity of platinum wires at the frequency  $1.5 \times 10^{-7}$  has been measured with reference to the gas adsorbed on the wire. The effects due to water vapour, hydrogen, air, oxygen, nitrogen, and carbon dioxide were examined. The results show that a de-gassed platinum wire increases in resistance due to the adsorption of gases and the resistance attains its original value when the gas is removed from the wire. The phenomenon is particularly marked in the case of hydrogen, for which it is possible to detect extremely small amounts of adsorption.

R. W. LUNT.

**Activation and adsorption of rare gases by palladium (argon, neon, helium).** M. E. KLARMAN (Z. Physik, 1930, 65, 358—384).—The adsorption of argon, neon, and helium on palladium has been investigated by measuring the resistance of palladium strips before and after adsorption. The results show that although untreated palladium surfaces do not adsorb, after "activation" consisting of various forms of heat treatment and ionic bombardment the adsorption is very marked, argon and neon being adsorbed, respectively, to the extent of 319 and 446 times the volume of the metal. Helium shows an appreciable adsorption, but it has not yet been possible to examine this quantitatively.

R. W. LUNT.

**Electrical conductivity of nickel and steel in nitrogen and hydrogen atmospheres at high pressures.** T. SKUTTA (Z. Physik, 1930, 65, 385—403).—The variation of the electrical conductivity of nickel and of steel in nitrogen and hydrogen has been examined in the pressure range 1—30 atm. The metal is first activated by repeated gas adsorption and de-gassing; it is then found that the resistance of steel and nickel increases in hydrogen and nitrogen atmospheres. In a hydrogen atmosphere a stable solution is formed with steel and an unstable one with nickel.

R. W. LUNT.

**Ferromagnetism and electrical properties. I. Resistance, magnetic change of resistance, and true magnetisation at the Curie point.** W. GERLACH and K. SCHNEIDERHAN (Ann. Physik, 1930, [v], 6, 772—784).—Systematic measurements of the resistance of nickel in magnetic fields and at various temperatures in the immediate neighbourhood of the Curie point have been made with the view of increasing the trustworthiness and the interpretation of results showing the dependence of resistance on field strength and temperature.

W. GOOD.

**Magnetic properties of metals.** F. BITTER (Physical Rev., 1930, [ii], 36, 978—983).—Divergent values of the susceptibility of metals are attributed to structural variations as well as to impurities. The effect of annealing and drawing is illustrated for copper and silver. It is suggested that partly bound

electrons, as well as the Pauli paramagnetism of the free electrons and the diamagnetism of the ions, should be taken into consideration to explain the susceptibility of the alkali metals.

N. M. BUGH.

**Free electrons and ferromagnetism.** E. C. STONER (Proc. Leeds Phil. Soc., 1930, 2, 50—55).—Theoretical. The probability of ferromagnetism being due to free electrons or the electron gas of Sommerfeld's theory is considered. On this view the Curie temperature would have a minimum value many times the observed value. Ferromagnetism is attributed, not to free electrons, but to Heisenberg's interchange interaction electrons. If the "magnetic" electrons are the same as the conduction electrons, as indicated by Dorfman's experiments (cf. A., 1929, 751), conductivity may be due to interchange electrons. The relation of this view to the theory of magnetic and electric properties of metals is discussed.

N. M. BUGH.

**Interchange interaction theory of ferromagnetism.** E. C. STONER (Proc. Leeds Phil. Soc., 1930, 2, 56—60; cf. preceding abstract).—Theoretical. The atoms in a crystal are considered as separate systems interacting with neighbouring atoms, as opposed to Heisenberg's consideration of the whole crystal as a single system, and a simple treatment of the interchange interaction theory of ferromagnetism is given, the magnetisation energy expressions being formally equivalent to those of the Weiss theory. Good agreement with observations on ferromagnetics is shown.

N. M. BUGH.

**Statistical theory of para- and dia-magnetism.** E. HOWELLS (Phil. Mag., 1930, [viii], 10, 698—711).—Mainly mathematical. Langevin's statistical theory of magnetisation is generalised on the assumption that the magnetisation of the molecules arises from their angular motions and is influenced by the magnetic force. Paramagnetism appears as the Curie term, varying inversely with absolute temperature, and is due to the permanent molecular angular momentum. The diamagnetism, independent of the temperature, is constant, and is ascribed to the induced angular momentum. With the introduction of a molecular field permanent magnetisation is accounted for. The theory demonstrates, even at low temperatures, the character of the typical deviations. The introduction of Planck's function indicates the probability of saturation over a range of temperature just above  $0^{\circ}$  Abs., in agreement with experiment.

N. M. BUGH.

**Magnetic susceptibility of certain complex molybdenum compounds.** P. R. RAY (J. Indian Chem. Soc., 1930, 7, 741—743).—The magnetic susceptibilities of certain complex compounds of quinquivalent molybdenum have been measured. Although the chemical instability of these substances has been attributed to the smaller effective atomic number of the central molybdenum atom, the susceptibilities are lower than those of the tervalent complexes. Two explanations of this anomaly are suggested, one based on the assumption that the quinquivalent complexes are true co-ordination compounds, and the other on the view that they are loosely combined molecular compounds.

H. F. GILLBE.

**Nature of remanence and [magnetic] hysteresis loss.** N. S. AKULOV (Z. Physik, 1930, 64, 817—829).—A theory is developed to account for the experimental observation that remanence and hysteresis loss are characteristic of polycrystalline ferromagnetic materials only; general equations are given for the potential energy, remanence, and hysteresis loss of deformed crystals. The theory also affords an explanation of the reversible magnetisation of Gans and of the Barkhausen and the Arkkieff effects. The form of the hysteresis loop when the remanence is vanishingly small is deduced, and is shown to be identical with that observed experimentally.

R. W. LUNT.

**Thermal variation of coefficient of magnetisation of water.** B. CABRERA, W. JOHNER, and A. PICCARD (Compt. rend., 1930, 191, 589—591).—Divergencies in the results of previous workers are due to the neglect of such factors as the variation in the partial pressure of atmospheric oxygen with the vapour pressure of water, and the dilatation of the water. The present authors have taken the necessary precautions, and have used a U-tube type of apparatus in which the meniscus is outside the field. The sensitiveness obtained for the coefficient of magnetisation was 0.01%, the final corrected value of the thermal variation (for water) being  $+0.131 \pm 0.01$  per 1000 per degree between 0° and 100°. J. GRANT.

**Relations of the magnetic and thermal constants of ferromagnetic substances.** J. R. ASHWORTH (Phil. Mag., 1930, [viii], 10, 681—694).—Theoretical. Relations existing between the fundamental constants in the general equation of ferromagnetism and their allied thermal constants are discussed for iron, cobalt, nickel, Heusler's alloy, and magnetite.

N. M. BLIGH.

**Change in temperature accompanying change in magnetisation of iron.** W. B. ELLWOOD (Physical Rev., 1930, [ii], 36, 1066—1082).—An apparatus, sensitive to a temperature change of  $2.26 \times 10^{-3}$ , for the investigation of the change in temperature of a ferromagnetic material when the magnetic state is altered is described. Results for two specimens of carbon steel containing 1.08 and 1.35% C, respectively, showing the relation between temperature change and magnetising field for various symmetric and asymmetric cycles of magnetisation, are given. Sharply-defined regions of heating and cooling were found; the total amount of hysteretic heat developed depended on the rate of performance of the cycle.

N. M. BLIGH.

**Barkhausen effect.** A. CIŞMAN (Ann. Physik, 1930, [v], 6, 825—851).—The Barkhausen effect in discs of ferromagnetic materials rotating in magnetic fields of different strengths has been investigated experimentally. An angle  $2\alpha$  is found within which no Barkhausen effect is observed, and this is independent of the velocity of motion.

W. GOOD.

**Temperature variation of crystal plasticity. II.** W. FAHRENHORST and E. SCHMID (Z. Physik, 1930, 64, 845—855; cf. Boas and Schmid, this vol., 845).—The temperature variation of stress-strain (compression) curves for zinc crystals was determined in the

range  $-253^{\circ}$  to  $250^{\circ}$ . In the range of normal stress-strain the energy of compression is independent of temperature, and amounts to 0.97 g.-cal. per g. The fracture of crystals at different temperatures and its relation to the motion of the crystal planes were also studied.

A. B. D. CASSIE.

**Recrystallisation [of metals].** G. TAMMANN (Z. Metallk., 1930, 22, 224—226).—A lecture, in which the author outlines his theory of the mechanism of recrystallisation of deformed metals on annealing.

A. R. POWELL.

**Atomistic principles of recrystallisation [of metals].** U. DEHLINGER (Z. Metallk., 1930, 22, 221—223).—A summary of the author's recent work (cf. A., 1929, 1220).

A. R. POWELL.

**Character of recrystallisation nuclei.** A. E. VAN ARKEL (Z. Metallk., 1930, 22, 218—220).—Several experiments on the recrystallisation of deformed aluminium sheet are described showing that new crystals which grow on annealing after a strong local deformation lose their power to grow further when the metal is subjected to stretching just sufficient to cause the fine crystals outside the deformed region to grow on subsequent annealing. This indicates that the theory that recrystallisation nuclei are tiny crystal fragments which remain undeformed during the working of the metal is untenable. Masing's assumption that the points of greatest deformation form nuclei for the growth of new crystals appears also to be contradicted by the author's work, which, however, is in agreement with van Liempt's suggestion that the spontaneous formation of new undeformed crystals takes place at the points of maximum lattice disturbance owing to the presence of a local excess of stress energy.

A. R. POWELL.

**Deformation and solidity of materials.** E. SCHMID (Physikal. Z., 1930, 31, 892—896).—An attempt is made to explain plasticity and deformation on an atomistic basis, and to apply the results of work on single metallic crystals to multicrystalline materials. The actual extent of the deformation is known for a number of crystals, so that it is possible to prophesy to a fair degree of certainty the magnitude of the effect in other crystals. No quantitative theory is available in explanation of many of the phenomena.

A. J. MEE.

**Crystal growth.** W. KOSSEL (Naturwiss., 1930, 18, 901—910).—A lecture. Modern theories of the relation of crystal growth to lattice-structure and -energy are discussed.

E. S. HEDGES.

**Uniaxial orientation of crystalline liquids.** D. VORLÄNDER and J. FISCHER (Ber., 1930, 63, [B], 2506—2510).—The behaviour\* of a large number of crystalline liquid substances with symmetrical or similarly terminated molecules has been examined in a quartz chamber of 0.01 mm. thickness with quartz cover-slip. The substances are melted and observed in convergent polarised light when cooling. Twenty-one of these compounds yield a uniaxially oriented, optically positive crystalline liquid layer, so that this property is not peculiar to dissimilarly terminated molecules. Monotropy, enantiotropy, and extent of crystalline liquid range appear to have little influence



and factors other than molecular structure are probably of greater importance.

**4-Carboxybenzenediazo-1-anisylideneaminonaphthalene** forms a crystalline, optically anisotropic glass.

H. WREN.

**Metastability of matter and the so-called physico-chemical constants.** E. COHEN (Z. physikal. Chem., 1930, 150, 418—420).—Polemical. The necessity of ensuring the physical, as well as the chemical, purity of substances employed for the determination of physico-chemical constants is emphasised.

H. F. GILLBE.

**What is an insulator?** A. MEISSNER (Z. Physik, 1930, 65, 158—166; cf. this vol., 1502).—By considering quartz as an insulator, the general properties which should be possessed by all insulators are derived. The structure of the elementary cell must be such that positive and negative ions lie close together, and there must be a high binding force preventing the loss of the "conductivity" electron. The second requisite of an insulator is polar axes. The effect is distorted by the insertion of electrodes into the material, and by dissociation ions, which in the case of liquid dielectrics collect around the electrodes as a space charge.

A. J. MEE.

**Anisotropy of the electrical resistance of mercury crystals.** O. SCKELL (Ann. Physik, 1930, [v], 6, 932—956).—Single crystals were obtained by the glass-tube method operating at  $-78.5^{\circ}$ . The electrical resistance was measured parallel, normal, and at  $45^{\circ}$  to the axis of the main crystal tube. A minimum was found parallel to the tube, and a maximum normal to the tube. If the crystal axis does not coincide with the tube axis, the formula  $R_{\phi} = R_{\parallel} \cos^2 \phi + R_{\perp} \sin^2 \phi$  with three determinations of  $R$  for different  $\phi$ , should give the inclination of these axes. This showed the crystal axis to be parallel to the tube axis, and the specific resistances parallel and perpendicular to this direction are 0.1527 and 0.2034, respectively,  $\pm 1\%$ . These resistances decrease linearly with fall of temperature in the range  $-78^{\circ}$  to  $-192^{\circ}$ . They were also studied between  $-78^{\circ}$  and the m. p., and are nearly linear in this range. This anisotropy of the electrical resistance of mercury crystals accounts for the inconsistent results of other workers.

A. B. D. CASSIE.

**Diamagnetic susceptibility of dissolved substances.** S. FREED and C. KASPER (Physical Rev., 1930, [ii], 36, 1002—1004).—A simple modification of the Gouy method, applicable to various investigations, is described for accurate determination of the diamagnetic susceptibility of dissolved substances. The effect produced by the solvent is largely eliminated; independent determinations with sodium iodide agreed to  $\pm 0.06\%$ .

N. M. BLIGH.

**Ultrasonic velocity and absorption in oxygen.** W. H. PIELEMEIER (Physical Rev., 1930, [ii], 36, 1005—1007; cf. this vol., 23).—The velocity and absorption in oxygen were measured at five ultrasonic frequencies in the two octaves 316—1264 kilocycles/sec. Values of the velocity reduced to  $0^{\circ}$  agree within 0.2% with Dulong's value for audible sound, 317.2 m./sec., compared with 314.76 (theoretical); values of

the absorption vary with frequency and show greater deviations from the theoretical.

N. M. BLIGH.

**Velocity of sound in soft and brittle substances.** E. J. IRONS (J. Sci. Instr., 1930, 7, 323—326).—The velocities of sound in the following substances have been measured by a modification of Stefan's method, with the results stated: ebonite ( $1.56 \times 10^5$  cm./sec.), paraffin wax (1.39), beeswax (0.808), rosin (1.60), red sealing wax (1.37), Swedish pitch (1.31), plaster of Paris (2.31), compressed cork (0.535).

C. W. GIBBY.

**Determination of the heat conductivity of metals, particularly at high temperatures.** R. HOLM (Wiss. Veröff. Siemens-Konz., 1930, 9, 300—311).—A variation of the methods of Kohlrausch, Diesselhorst, and Meissner is described (see following abstract).

W. E. DOWNEY.

**Heat conductivity of a platinum test-piece between  $19^{\circ}$  and  $1020^{\circ}$ .** R. HOLM and R. STÖRMER (Wiss. Veröff. Siemens-Konz., 1930, 9, 312—322).—Using the method of Holm (see preceding abstract), it is found that the specific resistance of 99.95% pure platinum (Heraeus) can be expressed in the form  $r = 1.048 \times 10^{-5} [1 + 3.695 \times 10^{-3} (t - 15) - 5.98 \times 10^{-7} (t - 15)^2 + 5.25 \times 10^{-11} (t - 15)^3]$  and the heat conductivity  $k = 0.699 [1 + 2.83 \times 10^{-4} (t - 19.5)]$ . The error of the latter constant varies from  $\pm 7 \times 10^{-3}$  at  $19.5^{\circ}$  to  $\pm 2.7 \times 10^{-2}$  at  $1020^{\circ}$ .

W. E. DOWNEY.

**Measurements with liquid helium. IX. Superconductivity of carbides and nitrides.** W. MEISSNER and H. FRANZ (Z. Physik, 1930, 65, 30—54).—Temperatures below  $4.5^{\circ}$  Abs. were determined from the helium vapour pressure; above  $7.3^{\circ}$  Abs. a lead resistance thermometer was used. Vanadium nitride becomes superconductive at  $1.3^{\circ}$  Abs., zirconium nitride at  $3.2^{\circ}$  Abs., and titanium nitride at  $1.6^{\circ}$  Abs.; the resistance-temperature curve is irregular near  $20^{\circ}$  Abs., probably due to a carbide impurity. The mixed crystal TiN-ZrN becomes superconductive in a smaller temperature interval than the pure crystal, and loses its measurable resistance near  $3^{\circ}$  Abs. Scandium nitride does not become superconductive. Cadmium oxide, molybdenum pentoxide, and tungsten oxide do not become superconductive. Vanadium carbide does not become superconductive; titanium carbide might become so at temperatures below  $1.5^{\circ}$  Abs., whilst tungsten carbide shows no superconductivity above  $2.4^{\circ}$  Abs.  $\text{Mo}_2\text{C}$  becomes superconductive at  $2.4^{\circ}$  Abs.,  $\text{MoC}$  at  $7.6^{\circ}$  Abs.,  $\text{TaC}$  at  $9.3^{\circ}$  Abs.,  $\text{NbC}$  at  $10^{\circ}$  Abs. Niobium carbide is superconductive in the exceptionally small temperature interval of  $0.25^{\circ}$ . Compounds generally become superconductive at higher temperatures than the metal, and this temperature does not depend on the crystal form.

A. B. D. CASSIE.

**Measurement of temperature with the platinum-resistance thermometer to  $1100^{\circ}$ .** H. MOSER (Ann. Physik, 1930, [v], 6, 852—874).—Measurement of temperatures up to  $1100 \pm 0.1^{\circ}$  with the platinum-resistance thermometer is made possible by suitable construction of the instrument and by an appropriate application of a formula connecting the electrical resistance of the platinum with temperature.

The alteration of the physical properties of the platinum wire at temperatures higher than 660° is then found to be without influence on the temperature measurements. The advantage of the platinum-resistance thermometer over the platinum-platinum-rhodium thermo-element at high temperatures is pointed out.

W. GOOD.

**Specific heats of gases at high pressures.** III. Results for nitrogen to 150° and 700 atm. B. H. MACKAY and N. W. KRASE (Ind. Eng. Chem., 1930, 22, 1060—1062).—Values for the specific heat at constant pressure of nitrogen at 30—150° and 50—700 atm. are recorded. Up to 100° the heat capacity changes only slightly as the pressure is increased above 400 atm.

R. CUTHILL.

**Variation of the specific heats of gases with pressure.** E. J. WORKMAN (Physical Rev., 1930, [ii], 36, 1083—1090).—A method is described, using the continuous-flow principle and avoiding the measurement of gas flow and heat input, for the determination of the ratio of  $C_p$  at high pressure to  $C_p$  at 1 atm. Results for commercial oxygen at 26° and pressure range 15—100 atm. indicate a pressure coefficient of this ratio of  $0.00165 \pm 0.00005$  per atm.

N. M. BLIGH.

**Pressure variation of specific heats of gases derived from compressibility data.** L. G. HORTON (Physical Rev., 1930, [ii], 36, 1091—1095; cf. preceding abstract).—Theoretical. Experimental values for the rate of variation of  $C_p$  with pressure at constant temperature are compared with those calculated from  $p$ - $v$ - $T$  data for the pressure range 20—100 atm. at 26°. Good agreement is shown, but the calculated values are very sensitive to small variations in the coefficients of the equation of state, and to methods of approximation used. It is concluded that the rate probably diminishes slowly with increased pressure for oxygen and that experimental results are of superior accuracy to those calculated.

N. M. BLIGH.

[M. p. of] krypton and xenon. F. J. ALLEN and R. B. MOORE (J. Amer. Chem. Soc., 1930, 52, 4173—4174).—Pure krypton (m. p.  $-156.6^\circ$ , vapour pressure at m. p., 558 mm.) and xenon (m. p.  $-111.5 \pm 0.5^\circ$ , vapour pressure at m. p.  $600 \pm 20$  mm.) have been obtained by working up liquid air residues by means of charcoal. Xenon probably has a transition point near the m. p. Preliminary density determinations indicate that krypton and xenon have at. wt. 83.6 and 131.4, respectively.

J. G. A. GRIFFITHS.

**Thermodynamic treatment of chemical equilibria in systems composed of real gases.** II. Relation for the heat of reaction applied to the ammonia synthesis reaction. Energy and entropy constants for ammonia. L. J. GILLESPIE and J. A. BEATTIE (Physical Rev., 1930, [ii], 36, 1008—1013; cf. this vol., 1357).—Mathematical. The energy and entropy constants for gaseous ammonia are calculated as  $-10,058.1$  and  $-16,649.1$  g.-cal.<sup>15</sup> per mol., respectively, referred to zero value for the energy and entropy of hydrogen and nitrogen, at 0° and 1 atm. Values of the thermodynamic function are given in this system for hydrogen, nitrogen, and ammonia. A simple relation is given

for the variation with pressure and temperature of the heat absorbed in a chemical reaction at constant pressure in systems of real gases, and values are computed for several pressures and temperatures for the ammonia synthesis.

N. M. BLIGH.

**Expansion of metals at high temperatures.** F. L. UFFELMANN (Phil. Mag., 1930, [viii], 10, 633—659).—An optical interference method for measurements in three perpendicular directions on the specimen, and for use up to 800°, is described, observations being taken during both heating and cooling. Tin, cadmium, and zinc showed marked anisotropic properties, and over extended temperature ranges the cubical expansion coefficient curves did not fit the quadratic or Thiesen's formula. The curve for lead has changes in slope at 170° and 245°; the mean aluminium and copper curves fit the quadratic relation, but that for brass, with a maximum at 460°, does not. For cobalt, nickel, and steel the curves during heating are different from those during cooling, cobalt showing a sharp peak at 450° on heating, and at 330° on cooling; nickel has a maximum in the heating curve at 340—360° (the Curie point).

N. M. BLIGH.

**Saturation vapour pressure [and isotopes] of lithium.** A. BOGROS (Compt. rend., 1930, 191, 560—561; cf. this vol., 829).—The expression  $\log p = -(6173/T) + 5.44$ , gives the vapour pressure ( $p$  in mm. of mercury) of lithium at 450—575°. It is suggested that the atomic-jet method might be used for the separation of isotopes of lithium, the atoms present in the vapour being collected on vertical plates placed at varying distances from the jet so as to retain either the lightest atoms (which have the greatest mean speed), or all of these plus varying proportions of the heavier atoms.

J. GRANT.

**Vapour pressure and critical temperature of fluorine.** G. H. CADY and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, 52, 3839—3843).—The vapour pressure at temperatures between 72° and 86° Abs. is given by  $\log_{10} P(\text{cm.}) = 7.3317 - 406.8/T - 0.007785T$ , from which the b. p.  $84.93^\circ$  Abs./760 mm. is calculated. The latent heat of vaporisation at the b. p. calculated by means of the Clausius-Clapeyron equation is about 1600 g.-cal. per mol., or 1540 if corrected for deviations from the ideal gas laws. The critical temperature is about 144° Abs. and  $p_c$  is approximately 55 atm.

J. G. A. GRIFFITHS.

**Vapour pressure of antimony trioxide.** W. B. HENCKE (J. Amer. Chem. Soc., 1930, 52, 3869—3877).—The vapour pressures of cubic (m. p. 642°) and orthorhombic (m. p. 655°) antimony trioxide determined by means of the gas saturation method at temperatures between 470° and 645° are reproduced by the equations  $\log_{10} p(\text{mm.}) = 12.195 - 10357/T$  and  $\log_{10} p = 11.318 - 9625/T$ , respectively, from which the corresponding heats of vaporisation,  $L_v$ , 47,370 and 44,080 g.-cal. per mol. ( $\text{Sb}_2\text{O}_3$ ), are calculated. The heat of transition ( $\Delta H_{830}$ ) of cubic to orthorhombic is 3240 and the respective latent heats of fusion are 29,490 and 26,250. The vapour pressure of the liquid determined by means of a new type of quartz static balanced tensimeter at temperatures between

656° and 800° is given by the relation  $\log_{10} p = 5.137 - 3900/T$ , from which  $L_v$  is computed to be 17,830.

J. G. A. GRIFFITHS.

**Effect of temperature on viscosity of air.** W. G. SHILLING and A. E. LAXTON (Phil. Mag., 1930, [viii], 10, 721—733).—The coefficient of viscosity of air has been measured by the comparative transpiration method over the temperature range 23—850°, and vindicates the results of Williams (cf. A., 1926, 234). The results show a small steady deviation from Sutherland's law over the range considered.

N. M. BLIGH.

**Temperature variation of viscosity of liquids.** M. P. V. IYER (Indian J. Physics, 1930, 5, 371—383).—The significance of the constants  $A$  and  $B$  in the formula  $\eta = Ae^{B/T}$ , connecting the coefficient of viscosity of a liquid with temperature, is discussed and the formula examined with reference to existing experimental data for 87 liquids. Except in a few cases good agreement between theory and experiment is found. The relationship of the constants to chemical constitution is pointed out and also their manner of variation in a homologous series.

W. GOOD.

**Diffusion. I. Determination of diffusivities in gaseous systems.** J. H. ARNOLD (Ind. Eng. Chem., 1930, 22, 1091—1095).—The diffusivity,  $D$ , of a gas of mol. wt.  $M_1$  into a gas of mol. wt.  $M_2$  at the temperature  $T$  has been calculated from the Stefan-Maxwell-Sutherland equation  $D = B(1/M_1 + 1/M_2)^{1/2} / \{S^2(T+C)\}$ , where  $S$  is the distance between the centres of molecules of two different kinds in contact,  $C$  is Sutherland's constant, and  $B$  is a constant. The value of  $C$  may be calculated from the b. p. (Abs.),  $T_B$ , by the equation  $C = 1.47T_B$  (Vogel, A., 1914, ii, 342). In computing  $S$  from  $V_1$  and  $V_2$ , the mol. vols. at the b. p. in the liquid state, derived from the equation  $S = V_1^{1/3} + V_2^{1/3}$ , in which the values of  $V_1$  and  $V_2$  are deduced from the at. vol. by Kopp's law, correspond closely with those deduced from viscosity data. Finally,  $B$  may be obtained by Chapman's theory (A., 1912, ii, 340). Values of  $D$  derived by this method are in satisfactory agreement with observed values.

R. CUTHILL.

**Equation of state for gas mixtures. II. Methods of combination of the constants of the Beattie-Bridgeman equation of state.** J. A. BEATTIE and S. IKEHARA (Proc. Amer. Acad. Arts Sci., 1930, 64, 127—176).—A study of the relative merits of linear, Lorentz, and linear square-root combinations for  $B_0$  in the equation  $p = [RT(1-\epsilon)/v^2](v+B) - (A/v^2)$  for mixtures of ethylene with oxygen or argon, nitrogen with hydrogen or methane, and hydrogen with carbon monoxide.

CHEMICAL ABSTRACTS.

**Diffusion. II. Kinetic theory of diffusion in liquid systems.** J. H. ARNOLD (J. Amer. Chem. Soc., 1930, 52, 3937—3955).—The factors to be considered in applying the classical kinetic theory to diffusion in liquid systems are discussed. Experimental data are consistent with the assumption that resistance to diffusion is due wholly to binary collisions and that the shortening of the mean free path due to the volume occupied by the molecules is the same for all systems. The retarding effect of

intermolecular forces is represented by a factor,  $F$ , which, for dilute solutions, is nearly independent of the nature of the diffusing substance and is directly proportional to the square root of the viscosity of the solvent. If either the solvent or solute is "abnormal" specific corrections have to be applied to  $F$ . In such cases, the data are not satisfactorily interpreted by the assumption of molecular association or solvation. The temperature coefficient of diffusivity is, for dilute solutions, a function of the properties of the solvent only and converges to a limiting value of 0.03 at zero concentration.

J. G. A. GRIFFITHS.

**Diffusion of metals in the solid state. I.** S. TANAKA and C. MATANO (Mem. Coll. Sci. Kyoto, 1930, A, 13, 343—351).—The diffusion of copper and gold into each other at various temperatures has been studied by following the change in resistance with time of a thin sheet composed of alternate layers of gold and copper. Diffusion is very slow at 140°, but rapid above 250°, and at any given temperature the increase,  $R$ , in resistance in time  $t$  is given by the equation  $R = Ae^{-\alpha t}$ , where  $A$  and  $\alpha$  are constants. The formation of an alloy has also been confirmed by X-ray analysis.

R. CUTHILL.

**Molar volume relationships in liquid mixtures.** W. HERZ (Z. Elektrochem., 1930, 36, 850—852; cf. A., 1925, ii, 101).—If the molar volumes of substances present in liquid mixtures are calculated from the densities of the latter, and the "true volumes" of the molecules from the refractivities of the mixtures in accordance with an additive law, the values so obtained do not in general coincide with the corresponding values for the pure components, and the differences are attributed to contraction or expansion on mixing. Tables are given to show the nature and magnitude of the effect in a number of mixtures.

F. L. USHER.

**System lead-silver.** F. YOLDI [with D. L. DE A. JIMENEZ] (Anal. Fis. Quim., 1930, 28, 1055—1065).—Lead-silver alloys containing 5—10% Ag have been studied by means of cooling curves. The eutectic mixture, which separates at 300—305°, contains 2.3% Ag. The cooling curves show no evidence of compound formation, and photomicrographs of alloys containing 1.84—97% Ag indicate that in the liquid state the components are completely miscible. The Brinell hardness changes continuously for alloys containing 25—100% Ag, and there is no evidence of compound formation.

H. F. GILLBE.

**Thermal diagrams of the systems silver-strontium and silver-barium.** F. WEIBKE (Z. anorg. Chem., 1930, 193, 297—310; cf. Baar, A., 1911, ii, 611).—Thermal analysis of the systems silver-strontium and silver-barium (up to 60% Ba) shows the occurrence of the following compounds:  $Ag_2Sr$ , m. p. 781°,  $d_4^{25}$  7.99;  $Ag_5Sr_3$ , m. p. 757°,  $d_4^{25}$  6.49;  $AgSr$ , m. p. 680°,  $d_4^{25}$  5.70;  $Ag_2Sr_3$ , m. p. 666°,  $d_4^{25}$  5.15;  $Ag_4Ba$ , m. p. 729°,  $d_4^{25}$  7.93;  $Ag_5Ba_3$ ,  $d_4^{25}$  6.70;  $Ag_3Ba_2$ , m. p. 848°,  $d_4^{25}$  6.60. The m. p. of a very pure specimen of strontium was  $757 \pm 1^\circ$ . F. L. USHER.

**X-Ray investigations on copper-arsenic alloys.** N. KATOH (Bull. Chem. Soc. Japan, 1930, 5, 275—282).—X-Ray data, obtained by the powder method,

are given for alloys containing 19.6 and 30.86% As. The 30.86% alloy showed only the lines of the  $\beta$ -phase, although a specimen quenched from 630° gave a number of new lines. The homogeneity range from 28.6 to 29.6% As is confirmed for the  $\beta$ -phase. For 29.1% As,  $a=7.118$ ,  $c=7.279$  Å. For  $\text{Cu}_3\text{As}$   $d_{\text{calc.}} = 8.22$ .

O. J. WALKER.

**X-Ray study of constitution of copper-nickel-aluminium-manganese alloys.** L. J. WOOD (J. Amer. Chem. Soc., 1930, 52, 3833—3838; cf. B., 1928, 18).—The data for alloys containing 1% Mn and 2.6% Al, and with nickel-copper ratios varying from 1.5 to 2.4, are in agreement with the assumption of a face-centred cube, the edge of which generally increases with rising aluminium content and falls with rising nickel-copper ratio. For most of the alloys it appears that all the aluminium is not present in the  $\alpha$ -solid solution, but the second phase has not been identified.

J. G. A. GRIFFITHS.

**X-Ray determination of the solubility of copper in silver.** N. AGEEV and G. SACHS (Z. Physik, 1930, 63, 293—303).—Using the precision method of Sachs and Weerts (this vol., 527) the lattice constants of pure silver and of five alloys of copper with silver up to 17 at.-% Cu were determined with an accuracy of  $\pm 0.025\%$ . The alloys were heated at 770° in high vacuum; neglect of this procedure probably affected the results of Weinbaum (this vol., 149). The lattice constant decreases linearly with increase in the proportion of copper up to about 13 at.-% Cu, after which further addition of copper causes no alteration. From the resulting curve the limits of mixed crystal formation for lower temperatures could be obtained by investigating a supersaturated alloy and then extrapolating horizontally to this curve. The X-ray method has an advantage over other methods, for with supersaturated alloys equilibrium is attained more quickly. For the lower temperatures the alloy was first heated to 800°, then quenched and maintained at the low temperature until equilibrium was reached. In this way the solubility was determined for temperatures down to 200°. The curve obtained was extrapolated and the solubility of copper in silver at 0° found to be 0.2 at.-%. The results are compared with those of Hansen (this vol., 405) and are shown to give smaller solubilities at all temperatures below that of the eutectic point.

H. A. JAHN.

**Structure of mixed crystals of iron with beryllium and aluminium.** F. WEVER and A. MÜLLER (Z. anorg. Chem., 1930, 192, 337—345; cf. this vol., 148).—Thermal and microscopic data relating to the iron side of the equilibrium diagrams for the binary systems iron-beryllium and iron-aluminium indicate that both belong to the group of iron alloys with completely closed  $\gamma$ -field. The mixed crystals of  $\alpha$ -iron with beryllium and aluminium are formed by atomic substitution, and a similar mode of formation may be assumed for the mixed crystals of  $\gamma$ -iron with the same two elements. There is no analogy between the behaviour of beryllium or aluminium and that of carbon in the formation of alloys with iron.

M. S. BURR.

**Crystal structure, electrical conductivity, thermo-electric force, and compensation pheno-**

**mena of the system Ag-Pt in relation to the phase-rule diagram.** C. H. JOHANSSON and J. O. LINDE (Ann. Physik, 1930, [v], 6, 458—486; 7, 408).—Observations have been made of the electrical resistance and crystal structure of alloys of known composition which had been heated to known high temperatures and subsequently quenched. Resistance measurements were also made at higher temperatures, and the thermo-electric force in contact with pure silver was determined at the ordinary temperature. The data in general confirm the phase diagram given by Doerinkel (A., 1907, ii, 785). Evidence is obtained of the existence of a series of mixed crystals, the limits of which have been determined approximately. Below about 750° in this mixed crystal range there appear to be three or perhaps four homogeneous phases with regular distributions of both atoms. The ductilities of the silver-platinum alloys have also been measured and are discussed with reference to the phenomenon of compensation. This system affords an interesting example of possibilities of this kind.

J. W. SMITH.

**Hardness of metal alloys at different temperatures.** V. SCHISCHOKIN and V. AGEJEVA (Z. anorg. Chem., 1930, 193, 237—244; cf. this vol., 985).—The Brinell hardness of bismuth-tin, bismuth-cadmium, lead-cadmium, tin-cadmium, lead-tin, tin-zinc, and cadmium-zinc alloys has been measured at temperatures from 16° to 170° and for various compositions. As with the alloys previously examined, there is a linear relation between log (Brinell hardness) and temperature for an alloy of any given composition. In general, the highest temperature coefficient of hardness occurs at and near the eutectic composition. The results are shown in diagrams.

F. L. USHER.

**Electrolysis of alloys.** R. KREMANN (Archiv Hemiju, 1930, 4, 61—72).—On passage of currents of 100—1000 amp./cm.<sup>2</sup> through fluid alloys, two types of conductivity may be observed—one due to the conductivity of the fused metal and the other to electrolysis of the alloy, leading to changes in its composition in the vicinity of the electrodes, the metal of higher ionisation potential being deposited on the anode. The latter effect becomes more marked as the density of current increases and as the distance between the electrodes is greater. In ternary alloys the electrolytic effect due to each component increases within certain limits inversely with its concentration.

R. TRUSZKOWSKI.

**Complex phenomena observed during the recovery of hypertempered steels.** A. PORTEVIN and P. CHEVENARD (Compt. rend., 1930, 191, 608—610).—An improved differential dilatometer has been applied to the study of isothermal recovery, and it is shown that the results obtained may be explained by the simultaneous decomposition of a saturated  $\gamma$ -solution of carbon into (1) cementite+ a less carburised  $\gamma$ -solution, and (2) cementite+ a slightly carburised  $\alpha$ -solution, accompanied by a contraction and an expansion, respectively (cf. this vol., 1069). The  $\gamma$ -solution is stable at high temperatures, whilst the  $\alpha$ -phase+ cementite is stable in the cold. The dilatation-time curves are represented by the ex-

pressions  $\delta L/L_0 = a \log(1+bt)$  at fairly high temperatures when the system is remote from its equilibrium state, and  $\delta L/L_0 = \alpha(1-e^{-\beta t})$  at higher temperatures, when equilibrium is attained more rapidly.

J. GRANT.

**Reactions in the melting of glass batches.** G. TAMMANN and W. OELSEN (*Z. anorg. Chem.*, 1930, 193, 245—269).—The changes occurring at different temperatures during the fusion of mixtures yielding three typical glasses (soda, lead, and sulphate glasses) have been studied. (1) In the case of soda glass, the double carbonate,  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$ , is first formed at about 600°, and the evolution of carbon dioxide begins at the same temperature (solid reaction), becoming very active after the fusion of the eutectic of sodium carbonate and the double carbonate at 780°. The latest chemical reaction to take place is the combination of silica with lime. A clear homogeneous liquid is formed at 1200°. (2) On heating a lead glass mixture (red lead 5.2, potassium carbonate 2.85, silica 10) oxygen is first evolved, and the resulting litharge then combines with silica, chiefly at 670—750°. At 750°, potassium carbonate and silica react. Liquid potassium carbonate (m. p. 894°) is not miscible with liquid lead monoxide (m. p. 835°), but dissolves in the eutectic silicate mixture (m. p. 675°). (3) The heating curve of a sulphate glass mixture (silica 100, calcium carbonate 40, sodium sulphate 40, sugar charcoal 2.5) shows seven discontinuities, the most important of which are connected with (a) the beginning of the evolution of carbon dioxide at 620°, (b) the reaction of the Leblanc process which occurs at 740—800°, (c) melting of the eutectic of sodium sulphate and sodium silicate at 865°, (d) formation of calcium silicate at 1010°, and (e) dissolution of the calcium silicate to form a homogeneous liquid at 1240°. In the absence of charcoal (and therefore of sodium or calcium sulphides), reaction of the sulphates with silica becomes appreciable only at about 1200°. Phase diagrams of a number of binary systems occurring in the glass mixtures are given.

F. L. USHER.

**Electrical conductivity of glasses. System  $\text{B}_2\text{O}_3\text{--Na}_2\text{O}$ .** S. A. SCHTSCHUKAREV and R. L. MÜLLER (*Z. physikal. Chem.*, 1930, 150, 439—475).—The conductivities of glasses containing only boric oxide and 0.01—32% of sodium oxide have been measured at 25—323° by employing sodium amalgam electrodes, which compensate the mobile ions in the glass and yield a steady current proportional to the conductivity due to the cations in the glass. With the apparatus used neither high-resistance nor polarised films are formed, surface conduction is excluded, and the times of heating and of passing the current are without influence on the conductivity; no temperature hysteresis effect is observed. Although the results are reproducible for glasses of the same composition even after many months, the individual measurements vary by about 15%. For all the glasses examined  $\log k = -A/T + B$ , where  $k$  is the specific conductivity,  $T$  is the temperature, and  $A$  and  $B$  are constants. With increase of the concentration of sodium oxide,  $k$  at constant temperature increases slowly up to a certain value, at which there

is an inflexion in the curve, and  $k$  thereafter rapidly increases, but there are no sharp breaks in the curve indicative of compound formation. The inflexion point corresponds with the crystallisation limits of the glass. Comparison of the conductivities and viscosities with the crystallisation of the glasses suggests that there exist within the material groups of ions separated by excess of boric oxide. The initial slow changes of conductivity are ascribed to the viscosity of the glass, and the later rapid change to the increase in the number of non-solvated sodium ions.

H. F. GILLBE.

**Solubility relations in gas-liquid systems.**  
**IV. Solubility of oxygen in water as found by an analytical method.** J. L. R. MORGAN and A. H. RICHARDSON (*J. Physical Chem.*, 1930, 34, 2356—2365; cf. this vol., 1362).—The solubility of oxygen in water has been determined at 25° and 1 atm. by a modification of Winkler's method. The value obtained, 0.04080 g. of oxygen per litre, is in agreement with the value 0.04047 obtained by Morgan and Pyne (this vol., 1106) by physical measurements. The solubility of oxygen at pressures from 175 to 760 mm. at 25° has also been determined; the Ostwald solubility coefficient is 0.3077 (cf. *loc. cit.*) and Henry's law holds. The effect of hydrostatic pressure on the solubility has also been investigated and the solubility found to be proportional to the hydrostatic pressure exerted by the column of water. L. S. THEOBALD.

**Solubility of silver iodide in solutions of alkali iodide in acetone.** F. K. V. KOCH (*J.C.S.*, 1930, 2385—2386).—The solubility of silver iodide in solutions of sodium iodide in acetone has been determined. It is found that three molecules of silver iodide are taken up by one molecule of sodium iodide. It is suggested that this is due to the formation of a complex anion  $\text{I}(\text{IAG})_3^-$ . On electrolysis of these solutions iodine and silver iodide are deposited at the anode. The conclusion also seems to be supported by determinations of the specific conductivity of sodium iodide in acetone before and after saturation with silver iodide. Mercuric iodide behaves similarly. A filtering apparatus is described in which the solution is kept at constant temperature during filtration, and evaporation of the solvent is prevented.

M. S. BURR.

**Solubility of sodium chloride-silver chloride mixed crystals in pyridine and X-ray analysis of the mixed crystals.** M. LE BLANC and J. QUENSTÄDT (*Z. physikal. Chem.*, 1930, 150, 321—348).—The quantities of silver chloride dissolved by pyridine from mixed crystals of silver chloride with sodium chloride containing 34.72—91.62%  $\text{AgCl}$  and of various particle sizes have been determined. The fraction  $p$  of the original silver chloride content which dissolves diminishes with increase of the sodium chloride content of the crystals, and for the untempered crystals shows only a small linear increase with time after about 100 hrs. The tempered crystals having a sodium chloride content of less than 62.5 mol.-% yield much higher values of  $p$  than the untempered crystals, but at high sodium chloride contents the reverse obtains. With decrease of the particle size from 550—1280  $\mu$  to 55  $\mu$ ,  $p$  increases and

the initial part of the  $p$ - $t$  curves become steeper. For crystals rich in silver chloride  $p$  diminishes as a result of tempering under pressure, even for mixtures which, according to Tammann's theory, should be completely resistant to attack by solvents; even the most resistant mixtures are attacked to some extent. No evidence could be obtained of the existence of sharp limits to the resistance, as required by the theory, there being a gradual transition from the most to the least resistant melts. X-Ray study of mixtures containing 17.75–75 mol.-% NaCl show the lattice constants to be in accordance with Vegard's additive law, and the diagrams show only the lines of the normal face-centred silver and sodium chloride lattices; Tammann's "normal partition" therefore does not occur. Ageing for 6 weeks does not alter the structure of the crystals. H. F. GILBE.

**Effect of added salts on the solubility of other salts in ethyl alcohol.** R. P. SEWARD [with W. C. SCHUMB] (J. Amer. Chem. Soc., 1930, **52**, 3962–3967; cf. Kraus and Seward, A., 1928, 1182).—The solubilities of potassium chloride, potassium perchlorate, and barium nitrate in ethyl alcohol at 25° have been measured in the presence of ammonium salts. The solubility increases when the added salt has no common ion, but is depressed by a salt with a common ion. The results show marked deviations from the predictions of the original Debye-Hückel theory, but are in approximate agreement with the theory as developed by Gronwall, LaMer, and Sandved (A., 1928, 841), or by Bjerrum. J. G. A. GRIFFITHS.

**Reciprocal influence of the presence of sodium sulphate and of potassium sulphate on the solubilities of each other in water.** E. J. SALSTROM and G. MCP. SMITH (J. Physical Chem., 1930, **34**, 2241–2249).—The solubility of potassium sulphate in water and in solutions of sodium sulphate of concentrations up to 2 wt.-normal has been determined at  $25 \pm 0.02^\circ$ , as well as that of sodium sulphate in water and in solutions of potassium sulphate of concentrations up to 1.20 wt.-normal. The respective solubilities increase up to a concentration of approximately 1 wt.-normal of the salt originally present in the solution, and, in the case of potassium sulphate in sodium sulphate solutions, the solubility falls rapidly beyond this to a value less than that for potassium sulphate in water. Indications of the formation of the double salt,  $2\text{Na}_2\text{SO}_4 \cdot 5\text{K}_2\text{SO}_4$ , were obtained. L. S. THEOBALD.

**Rôle of the liquid stationary film in batch absorptions of gases.** I. Absorptions involving no irreversible chemical reactions. II. Absorptions involving irreversible chemical reactions. H. S. DAVIS and G. S. CRANDALL (J. Amer. Chem. Soc., 1930, **52**, 3757–3768, 3769–3785; cf. Davis and Schuler, this vol., 549; Lewis and Whitman, A., 1925, ii, 106).—I. Further evidence is adduced of the existence of a thin unstirred layer, or liquid stationary film, at the gas-liquid interface. The effective thickness depends on absorption conditions and for oxygen and water varies between 0.02 and 0.002 cm. Contact between a pure gas and liquid results in the rapid setting up through the film of a gradient of dissolved gas, tending to uniformity.

When the gradient conditions become constant the rate of absorption is the maximum rate at which the dissolved gas can reach the main body of solution. The initial constant rate of absorption and the liquid film diffusion coefficients have been calculated from data for the dissolution of oxygen, air, carbon dioxide, and hydrogen in water and a few organic liquids, using the methods of (a) stirring (authors; Becker, A., 1923, ii, 228), (b) gas bubbles (Adeney and Becker, A., 1919, ii, 510), and (c) shaking. With stirring, the liquid film diffusion coefficient of water is less than, but of the same order as, those of organic liquids. The coefficients obtained by shaking are practically identical for all liquids. The greater absorbing power of the head of a bubble as compared with its sides is attributed to the introduction of fresh solvent into the liquid stationary film at the head. Other relationships are discussed.

II. If the rates of the irreversible reactions are very fast compared with the rates of diffusion of the gas through the liquid film, reactions take place in this film in zones parallel to the liquid surface. The rate of absorption due to reaction may be much greater than that due to physical dissolution. If the reaction occurs in one or two instantaneous irreversible stages, the primary reaction product is present between the surface and the first reaction zone in uniform concentration equivalent to that of the solute in the main body of the solution. The product will be precipitated if the metastable limit of its solubility is exceeded. A general equation for calculating the initial steady rate of absorption of a pure gas by a liquid from a knowledge of the solubility, the concentration of the solute, and the liquid film diffusion coefficient is supported by calculations from existing data. The rates of absorption of carbon dioxide by water and aqueous sodium and potassium hydroxides have been determined. It is considered that the reaction to sodium hydrogen carbonate is rapid and the precipitation of this substance in the film has been demonstrated. The results of Ledig and Weaver (A., 1924, ii, 318) and of Hatta (A., 1929, 150, 1229) are discussed, and the effects of products and of the heat produced by reactions in the film are examined. The reactions between the olefines and sulphuric acid take place mainly in the liquid stationary film. The more rapid absorption of isobutylene by unstirred as compared with stirred 60% sulphuric acid is attributed to a greater accumulation of *tert.*-butyl alcohol in the liquid stationary film of the quiescent acid. J. G. A. GRIFFITHS.

**Dimeric distribution.** D. B. HAND (J. Physical Chem., 1930, **34**, 1961–2000).—The distribution of a consolute liquid between two immiscible liquids and the effect of such a liquid on the solubility of two immiscible liquids have been investigated with especial reference to the systems acetic acid–water–benzene, alcohol–water–benzene, acetic acid–chloroform–water, and acetone–chloroform–water. Data for these four systems have been re-determined. The tie-lines for such systems become horizontal when certain arbitrary units are selected for one of the immiscible liquids. This makes possible the prediction of the composition of all pairs of conjugate phases when the isotherm and one tie-line are known. The



equation  $a_1/(b_1+kc_1)=a_2/(b_2+kc_2)$ , where  $a$ ,  $b$ , and  $c$  are the weights in grams of consolute liquid and immiscible liquids, respectively,  $k$  is a constant, and the subscripts denote the upper and lower phases, holds for distribution in concentrated but not in very dilute solutions. This leads to the assumption that the ratio of the weights of the consolute component held by unit quantities of the other components is a constant for each phase. The above equation becomes identical with that of Nernst in the limiting case in which the immiscible liquids are entirely in separate phases but none of the four systems studied supports the simple form of the Nernst equation in dilute solution. Association of the consolute liquid in one phase must be assumed to make the distribution of acetic acid between chloroform and water obey this equation up to concentrations of 1% of acetic acid in chloroform. All cases investigated conform to the empirical equation  $(b_1/a_1)^m=k'a_2/c_2$ . The isotherm for saturated solutions of benzene, water, and acetic acid does not follow the mass law equation  $\log(b/a)+n \log(c/a)=\log \text{ constant}$ . L. S. THEOBALD.

**Adsorption of methane and hydrogen on charcoal at high pressure.** P. K. FROLICH and A. WHITE (Ind. Eng. Chem., 1930, 22, 1058—1060).—The adsorption by activated charcoal of hydrogen at 25° and 100° and of methane at 25°, 50°, 100°, and 180° has been measured, the pressure range with each gas being 1—150 atm. In each case the Langmuir isotherm, but not the Freundlich isotherm, is applicable, the adsorbent approaching saturation under a pressure of 80—100 atm. At 25° the maximum volume of gas adsorbed is about three times as great for methane as for hydrogen. In a mixture of the two gases, increase in pressure favours the preferential adsorption of the methane, and from a mixture of methane with 50—90% of hydrogen at 25° and under about 100 atm. pressure, methane only is adsorbed, the amount taken up being approximately the same as if the methane had been present alone at its partial pressure in the mixture. Methane adsorbed under high pressures can be recovered merely by reducing the pressure, but adsorbed hydrogen is held more firmly. R. CUTHILL.

**Sorption of carbon tetrachloride at low pressures by activated charcoals.** II. Isothermals at 25°. III. Isosteres. Discussion. A. J. ALLMAND and R. CHAPLIN (Proc. Roy. Soc., 1930, A, 129, 235—251, 252—266).—I. By means of the experimental method previously described (Chaplin, A., 1929, 133), determinations have been made at 25° of the low-pressure adsorption isothermals for carbon tetrachloride on six different charcoals. The data are plotted in the form of  $\log q$  against  $\log p$  (where  $q$  is the carbon tetrachloride charge). Besides the directly determined isothermals, a number are derived from isostere measurements. The effect of the gradual removal of gases from the charcoal surface during the processes of sorption and desorption is studied in detail.

III. Isostere measurements have been made for different charges of carbon tetrachloride on five different charcoals, and heats of adsorption are calculated therefrom. The molecular heat of sorption

is given by the slope of the linear curve obtained by plotting each isostere in the form of  $\log p$  against  $1/T$ . It is found that at carbon tetrachloride pressures of about 10<sup>-1</sup> mm. both the isothermals and the heats of adsorption show a discontinuous change with further rise of pressure, in the direction of greater  $q/p$  and lower  $\lambda$  values, respectively. The experimental results are discussed, and the view is advanced that a clean charcoal surface consists of areas or points of varying adsorption potential, and that a freshly evacuated charcoal has a residual oxygen charge occupying the regions of highest potential, its nature and density depending on the temperature and the thoroughness of the outgassing. This is gradually displaced in the form of carbon monoxide or dioxide by the action of the sorbate. The removal of these gases is normally accompanied by a gradual drift of the isothermals towards higher  $q$  and lower  $p$  values, and only when removal is complete does this drift cease and the isothermal become truly reversible. Such definitive isothermals are possibly only slightly dependent on the prior evacuation temperature (up to 800°) of the charcoal. L. L. BIRCUMSHAW.

**Relation between the gas content and the adsorption of electrolytes by activated charcoal.** IV. Adsorption of acids by degassed charcoal and by charcoal saturated with hydrogen. R. BURSTEIN, A. FRUMKIN, and D. LAVROVSKAJA (Z. physikal. Chem., 1930, 150, 421—438; cf. this vol., 683, 684).—By heating activated charcoal in a vacuum at 1000° for about 36 hrs. a material is obtained which in the absence of oxygen does not adsorb hydrochloric acid from dilute (0.02*N*) solution; with increase of the acid concentration, the adsorption increases very rapidly. The loss of adsorptive power increases with rise in the ignition temperature from 850° to 1000°. With neutral salts such as potassium chloride negative adsorption is observed. In presence of oxygen or air the charcoal adsorbs, even from the dilute acid solutions, a quantity of hydrochloric acid which is proportional to the quantity of oxygen available, provided that this does not exceed a certain limit; the process probably involves the formation of water at the carbon interface, but carbon dioxide is not produced in either the solution or the gas phase. Degassing in vacuum reduces the ability of the charcoal to adsorb hydrochloric acid from very dilute solutions, even in presence of oxygen, but for more concentrated solutions the adsorptive power is increased. Platinised charcoal saturated with hydrogen shows in dilute solutions of sulphuric, hydrochloric, or hydrobromic acid negative adsorption, the magnitude of which diminishes in the order given; at high acid concentrations the adsorption changes sign and assumes the character of molecular adsorption as does the adsorption by degassed charcoal from the more concentrated hydrochloric acid solutions. In presence of air the quantities of the three acids adsorbed are greatly increased. H. F. GILLBE.

**Determination of sorption isothermals of vapours on charcoal.** L. J. BURRAGE (J. Physical Chem., 1930, 34, 2202—2217; cf. B., 1929, 153).—The method previously described (*loc. cit.*) has been further investigated and from a study of the changes in the

concentration gradient in the charged column of charcoal with the amount of air passed the retentivity test has been modified so as to give true sorption isotherms. These are discontinuous, consisting of a series of loops cutting one another at definite pressures.

L. S. THEOBALD.

**Chemical activation of quartz surfaces.** P. G. NUTTING (Science, 1930, 72, 243—244).—Quartz or sea-sand can be made an adsorbent for oil by a brief treatment with hydrofluoric acid or by exposure to fused potassium hydroxide at 350° for 1—2 min. followed by boiling in hydrochloric acid, washing, and drying.

L. S. THEOBALD.

**Adsorption at crystal-solution interfaces.** V. Effect of adsorbed dye on the lattice size of potassium alum crystals. F. G. FOOTE, F. C. BLAKE, and W. G. FRANCE (J. Physical Chem., 1930, 34, 2236—2240; cf. this vol., 684).—The lattice constants for pure potassium alum and for the alum having dye adsorbed on the cubic faces only are the same, showing that the adsorption of the dye by the growing crystal does not affect the plane spacings to a measurable extent. This supports the assumption that the dye is adsorbed interstitially. L. S. THEOBALD.

**Adsorption of cholesterol.** L. LEPIN (Biochem. Z., 1930, 226, 195—202).—The mutual effect of cholesterol (molecular) and hydrochloric acid on the adsorption of these substances from alcoholic solutions by charcoal is explained in terms of the differences of their adsorption velocities. Adsorption of colloidal cholesterol or charcoal is independent of the amount of adsorbed acid. The peptising action of salt solutions on cholesterol increases with the alkalinity of the solution and adsorption of suspended cholesterol is brought about by the simultaneous adsorption of acid. The cholesterol is changed in alkaline solution probably into metacholesterol.

P. W. CLUTTERBUCK.

**Adsorption by titanium hydroxide sol.** L. S. BHATIA and S. GHOSH (J. Indian Chem. Soc., 1930, 7, 687—697).—Titanium hydroxide sol prepared by dropping titanium tetrachloride into water and containing 15.2 g. of titanium oxide per litre coagulates during dialysis when the  $p_H$  exceed 4.1. The adsorptive power of the sol for the anions of sodium and potassium salts decreases in the order  $Fe(CN)_6^{4-}$ ,  $NO_2^-$ ,  $SO_4^{2-}$ ,  $Cl^-$ ,  $S_2O_3^{2-}$ ,  $Cr_2O_7^{2-}$ ,  $Br^-$ ,  $Fe(CN)_6^{3-}$ ,  $IO_3^-$ ,  $CrO_4^{2-}$ ,  $OH^-$ , whilst the coagulating power of the anions diminishes in the order  $Fe(CN)_6^{4-}$ ,  $Fe(CN)_6^{3-}$ ,  $OH^-$ ,  $SO_4^{2-}$ ,  $Cr_2O_7^{2-}$ ,  $CrO_4^{2-}$ ,  $IO_3^-$ ,  $S_2O_3^{2-}$ ,  $NO_2^-$ ,  $Cl^-$ ,  $Br^-$ ; a strongly adsorbed ion does not therefore necessarily possess a high coagulating power. Hydroxyl ions are adsorbed to only a small extent, the high coagulating power being due to removal of the stabilising hydrogen ions. Anions are adsorbed in preference to cations, and the resultant liberation of hydroxyl ions causes an increase of  $p_H$  of the solution. Ageing of a sol prepared at 18° causes increase of the charge on the particles and a consequent increase of stability and decrease of the viscosity; the free hydrochloric acid present in the solution gradually forms titanium tetrachloride, and the resulting titanate ions are completely adsorbed by the sol. This view is supported by the reduction of conductivity which occurs on ageing.

Ageing of a sol prepared at 55° has but little influence on its properties, on account of the reduced chemical activity and adsorptive power. H. F. GILLBE.

**Sorption experiments with cellulose nitrate.**

**I. Sorption of vapours by cellulose nitrate.** W. J. JENKINS and H. B. BENNETT (J. Physical Chem., 1930, 34, 2318—2329). **II. L. RUBENSTEIN** (*ibid.*, 2330—2342).—I. The sorption of acetone by cellulose nitrate of varying nitrogen content has been investigated in its dependence on temperature and pressure. The temperature of the adsorbent varied from 27° to 60°, and that of the acetone from 10° to 57°. Sorption increases as the difference in temperature between liquid and adsorbent decreases and varies only slightly with the direction of approach to equilibrium. The sorption of acetone by stable cellulose nitrate increases with an increased nitrogen content up to a maximum at 12% N and then decreases. For a given nitrogen content, the sorption is independent of the viscosity of the nitrate solution. A sorption pipette eliminating the disadvantages of the sorption balance is described.

**II.** The sorption of the vapours of acetone, methyl acetate, ethyl acetate, methyl ethyl ketone, and methyl alcohol by cellulose nitrate of varying nitrogen content has been determined. With the adsorbent at 30° and the liquid at 20°, the sorption increases to a maximum (between 11.5 and 12% N) and then decreases in the case of the esters and ketones; with methyl alcohol (at 40°) absorption is much less in amount and decreases with an increase in the nitrogen content of the adsorbent (at 20°). The time taken to establish equilibrium depends on the b. p. of the liquids absorbed and, except for acetone, the equilibrium itself depends, to some extent, on the manner in which it is reached.

L. S. THEOBALD.

**Adsorption of anions of acid dyes by soil colloids.** J. G. SMITH and P. L. GILE (J. Agric. Res., 1930, 41, 401—413).—Adsorption of simple anions from neutral solutions by soils is negligible, but appreciable adsorption of the anions of acid dyes has previously been reported. Experiments on the adsorption of anions of sodium carminate, orange II, and ponceau from water and from weakly acid solutions by soils and by gels of ferric and aluminium hydroxides indicate that the amount of adsorption is almost negligible. From a 0.05N-acid solution large quantities of ponceau were removed by some soils, but this appears to be due to precipitation of the dye with bases dissolved by the colloid rather than to a true adsorption process. The conclusion is that the true adsorption of the anions of acid dyes by soil colloids is negligible and that the contrary results obtained by earlier investigators are to be ascribed to the use of colloidal dyes and to precipitation of the dyes by acids or bases released from the soil colloids. Some freshly prepared gels of alumina and of ferric hydroxide showed an appreciable adsorptive capacity for anions. This may be due to exchange with hydroxyl ions left in the surface of the gel. Such ions are not present in aged soils. E. S. HEDGES.

**Electrocapillarity.** **I. Electrocapillarity curves of organic acids and their salts.** J. A. V. BUTLER and C. OCKRENT. **II. Selective adsorption in**

solutions containing two active substances. C. OCKRENT and J. A. V. BUTLER (J. Physical Chem., 1930, **34**, 2286—2296, 2297—2306).—I. The electrocapillary curves of trichloroacetic, fumaric, maleic, and the commoner aromatic acids and of their sodium salts have been determined at the ordinary temperature in 0.5*M*-sodium sulphate. The maximum adsorption of salts of weak acids occurs at *P.D.* which are approximately 0.1 volt more positive than those for the acids alone, whilst strong acids give maxima in the same region. The displacement of the potential of maximum adsorption of organic anions towards positive potentials is less than the corresponding displacement observed with organic cations. Mixtures of benzoic acid and sodium benzoate show that the effect is not one of hydrolysis. The electrocapillary viscosity shown by solutions of the acids is due apparently to the alkalinity produced in the solution owing to discharge of hydrogen ions at the mercury surface.

II. The electrocapillary curves of solutions containing two active substances have been determined at the ordinary temperature in 0.5*M*-sodium sulphate. When the components produce practically the same lowering of surface tension, both are adsorbed from the mixture, but if, in mixtures of the same type (ions or non-ionised molecules), one compound produces a greater lowering over the entire range of *P.D.*, this only is adsorbed. Excepting those solutions which contain active positive and negative ions, *e.g.*, *p*-toluenesulphonic acid and tetramethylammonium hydroxide, the lowering of surface tension of the mixture is less than the sum of the lowerings produced by the components separately. L. S. THEOBALD.

Colour reaction of Japanese acid clay with leucomalachite-green hydrochloride. N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1930, **33**, 335—336B; cf. this vol., 538).—When an acid solution of leucomalachite-green is added to Japanese acid clay the blue colour develops around the brownish-black granular constituent, whilst the body of the clay becomes tinged only with a faint green. The brown particles contain manganese dioxide, which is probably adsorbed as a salt of the acid clay from water percolating through the clay; later, by exposure to the air, the salt is converted into colloidal manganese dioxide, which is disseminated throughout the clay and is capable of bringing about the benzidine reaction, but only when aggregated into the brown particles is its concentration sufficiently high to oxidise the leucomalachite-green. H. F. GILLBE.

Effect of various salts on the surface tension of sodium taurocholate solutions. M. ITOI (J. Biochem., Japan, 1930, **12**, 83—105).—The effect at  $p_H$  6.8 is greatest when tervalent, and least when univalent, cations are added; the differences disappear at  $p_H$  3.0. When larger quantities of salts are added the effect depends largely on the anions, with which Hofmeister's series is followed. The addition of small quantities of sodium hydroxide increases the surface tension by suppressing hydrolysis, whilst larger quantities diminish it by increasing the quantity of undissociated taurocholate.

CHEMICAL ABSTRACTS.

Capillary activity of organic substances in aqueous salt solutions. P. P. KOSAKEVITSCH and N. S. KOSAKEVITSCH (Z. physikal. Chem., 1930, **150**, 370—380).—The surface tension-concentration curves of aqueous thymol solutions containing lithium chloride, bromide, and iodide are parallel; the lowering of the surface tension increases in the order iodide, bromide, chloride, for thymol, *o*-cresol, and phenol solutions. The surface tension of menthol solutions diminishes rapidly as the salt concentration is increased from *N* to 3*N*, and the maximum on the interfacial adsorption-concentration curve becomes increasingly pronounced and occurs at diminishing concentrations. The function  $\Delta\sigma A/RT$ , where  $\Delta\sigma$  is the surface tension lowering, and *A* the surface area containing 1 mol. of the adsorbed substance, increases in all cases with  $\Delta\sigma$  and is found to be independent of dissolved salts; menthol alone gives a curve concave to the  $\Delta\sigma$  axis. By comparison of the concentrations of the phenol at which the surface tension of water and of the salt solutions are depressed to the same extent, the degrees of hydration of the lithium halides have been calculated and the results are in good agreement with the values obtained from adsorption measurements. Calculations of the activity of phenol in solutions of sodium and lithium chlorides determined (1) by the partition method, (2) by measurements of adsorption on carbon, and (3) from the surface-tension measurements are in good agreement. Menthol yields anomalous results, since it does not conform to Rideal's equation. H. F. GILLBE.

Cohesion of quartz fibres. G. A. TOMLINSON (Phil. Mag., 1930, [viii], **10**, 541—544; cf. A., 1928, 1316; 1929, 1137).—Experiments are described which show that in a dry and dust-free atmosphere the adhesion of quartz fibres persists indefinitely, and is not due to a film of moisture as found by Stone for glass beads (cf. this vol., 686). Films of metals on glass show similar cohesive properties. N. M. BLIGH.

Creeping of crystals. H. ERLÉNMEYER (Helv. Chim. Acta, 1930, **13**, 1006—1008; cf. A., 1929, 503).—Observations previously recorded have been extended. With potassium chloride, in addition to crystal aggregates composed of cubes, hollow needles and hairs attaining a length of 1 cm. are often met with. A mechanism of their formation is suggested.

F. L. USHER.

Surface energy of barium sulphate. B. BRUŽS and A. JANKAUSKIS (Latvian Univ. Raksti, 1930, **1**, 272a—272d).—Sparingly soluble substances show a marked decrease in grain size if they are precipitated from concentrated solutions of reagents producing them. The changes of surface energy of barium sulphate due to change in particle size have accordingly been investigated by studying the heat of precipitation when solutions of zinc sulphate and barium chlorate in concentrations varying from 0.1*N* to 4*N* are mixed. Up to a concentration of *N* the heat of precipitation rises, indicating an increase in surface energy due to decreasing particle size of 2000 g.-cal./mol. Concentrations greater than *N* appear to show an unexpected decrease in surface energy. The possible causes of this decrease are discussed. F. J. WILKINS.

**Microphotometric study of the Liesegang rings.** (MILLER.) S. VEIL (Compt. rend., 1930, 191, 611—612).—A microphotometric study has been made of the Liesegang rings obtained after drying when a drop of silver nitrate solution is placed on a glass plate coated with a mixture of gelatin and potassium dichromate. The darkest portions of the rings are represented in the resulting diagram by vertical acute angles, whilst vertical serrations in the almost horizontal portions correspond with secondary rings in the clear intervals, which are invisible under the microscope. The square roots of the distances between the successive primary rings are in arithmetical progression. With potassium chromate the rings are finer and more numerous. J. GRANT.

**Supersaturated solutions. III. Rhythmic precipitates of silver halides and thallous iodide.** W. M. FISCHER (Latvij. Univ. Raksti, 1930, 1, 263—271).—The conditions necessary for the formation of banded precipitates of silver halides and thallous iodide have been investigated.

F. J. WILKINS.

**Electro-osmotic "de-salting" of concentrated solutions.** R. HOFFMANN (Wiss. Veröff. Siemens-Konz., 1930, 9, 339—351).—The "de-salting" of sodium sulphate solutions has been examined. Increasing current density leads to a decrease in transference number corresponding with an increase of the specific charge of the diaphragm. Addition of sugar also decreases the transference number. The influence of current density on the "de-salting" of molasses is not definite. At 20° the current yield falls with increasing current density, at 40° the yield is independent of C.D., whilst at 60° the yield increases with increasing C.D.

W. E. DOWNEY.

**Partial specific volume of potassium n-octoate in aqueous solution.** D. G. DAVIS and C. R. BURY (J.C.S., 1930, 2263—2267).—The densities of aqueous solutions of potassium octoate (0—28%) have been measured and partial specific volumes calculated. The partial specific volume of the soap begins to rise rapidly at concentrations above approximately 0.47*N*, which is shown by f.p. and dew-point measurements to be the concentration at which an appreciable formation of micelles takes place. The behaviour closely resembles that of aqueous solution of butyric acid (A., 1929, 638). Further evidence that this rapid rise of the partial specific volume is due to micelle formation is given by the fact that it is not shown by the alkali salts of the lower fatty acids.

M. S. BURR.

**Increase of rotation of tartaric acid produced by zirconium and hafnium in alkaline solution.** J. H. DE BOER and H. EMMENS (Rec. trav. chim., 1930, 49, 955—961).—The molecular rotation of alkali tartrates decreases in presence of excess of alkali. The influence of sodium hydroxide is greater than that of potassium hydroxide and with sufficient excess of the former a change from dextro- to levorotation may be produced. In presence of zirconium or hafnium oxychlorides the rotation of the alkali tartrates is increased as a consequence of the formation of complex compounds. With zirconium the increase in the molecular rotation ( $\Delta M$ ) is dependent

on the relative amounts of tartaric acid and zirconium and decreases with excess of alkali. With hafnium  $\Delta M$  is much smaller and varies only slightly with the ratio tartaric acid : hafnium, but depends greatly on the amount of alkali present. Under suitable conditions it is possible to estimate the amounts of the two metals present in zirconium-hafnium mixtures by measurements of  $\Delta M$  of the mixture.

O. J. WALKER.

**Compounds of tartaric acid with copper.** J. GIUNTINI (Compt. rend., 1930, 191, 778—779; cf. Gabiano, A., 1927, 543).—Determinations of the specific rotatory powers of mixtures containing 0.001 part of tartaric acid and  $x \times 0.001$  part of cupric hydroxide per 100 c.c. show that the solution is dextrorotatory for  $\lambda$  5780 and 5460 and that  $[\alpha]$  increases with  $x$  to a maximum at  $x=1$ , then decreases to zero at  $x=1.75$ , and becomes strongly levorotatory for  $x=2$ . A zero value was not obtained for  $\lambda$  4358 over the range  $x=0-2$ , although the maximum was observed at  $x=1$ . The solutions change in colour from pale blue ( $x=1.25$ ) to intense blue (above 1.5), and are non-dichroic for the composition  $C_4H_4O_6Cu$ , and dichroic for  $C_4H_4O_6Cu_2$  ( $p_H$  5). After addition of ammonia or sodium hydroxide to solutions of the latter, minimum values of  $[\alpha]$  are observed for the compositions  $C_4H_4O_6NH_4Cu_2$  and  $C_4H_4O_6NaCu_2$ , the rotations being strongly levo-, whilst those obtained under analogous conditions with solutions corresponding with  $C_4H_4O_6Cu$  are strongly dextrorotatory.

J. GRANT.

**Size of gas bubbles and liquid drops in liquids.** S. HALBERSTADT and P. H. PRAUSNITZ (Z. angew. Chem., 1930, 43, 970—977).—An apparatus and method for the accurate measurement of the size of gas bubbles and liquid droplets is described. Gas bubbles were formed in water and in ether by forcing the gas through a diaphragm, and it was found that the size of bubble varies with the liquid, depending on the surface tension and viscosity, but not on the dielectric constant. Capillary-active substances reduce the size of the bubbles. With increasing pressure of gas the size of the bubbles produced decreases. Experiments on similar lines were carried out with droplets of ethyl ether and of ethyl acetate in water. The ethyl acetate drops were larger than the ether drops, using the same diaphragm. In other respects the behaviour of the liquid droplets was similar to that of the gas bubbles.

E. S. HEDGES.

**Measurements of suspensions and deposits.** P. MERCIER (J. Phys. Radium, 1930, [vii], 1, 292—305).—Measurements of the rate of fall of suspensions have been made. The apparatus consisted of a delicate cylindrical float attached by a hair to a lever; the position of the float in the suspension can be adjusted by means of a rider on the lever. Movements of the float, as the suspended solid falls, are recorded optically. From the results curves representing the upward pressure on the cylinder as a function of time, and of concentration as a function of velocity of fall, are obtained. The nature of the curves to be expected for homogeneous and heterogeneous suspensions is worked out mathematically.

C. A. SILBERRAD.

**Spatial conceptions of the structure of carbon compounds and their application to the chemistry of high polymerides.** K. H. MEYER (Kolloid-Z., 1930, 53, 8—19).—A lecture on the three-dimensional structure of complex organic molecules and on the inter-molecular cohesive forces which are held to be responsible for polymerisation. A sketch of the process of polymerisation to form highly complex substances such as cellulose and the proteins is given. The orientation of structure due to stretching is considered. E. S. HEDGES.

**Behaviour of high polymerides in solution.** H. MARK (Kolloid-Z., 1930, 53, 32—46).—A résumé of published work on the properties of colloidal solutions of organic substances of high mol. wt., dealing with viscosity and its relations to concentration, temperature, and length of molecule, lowering of vapour pressure and its relations to concentration and mol. wt., spreading coefficient, and X-ray spectrographic investigation. E. S. HEDGES.

**Highly polymerised compounds. Organic chemistry and colloid chemistry.** H. STAUDINGER (Kolloid-Z., 1930, 53, 19—32).—A lecture on the structure of colloids of the highly polymerised organic type, especially from the point of view of organic chemistry. The author differs from Meyer (see above) by supposing that in most of these colloids the particle is a single molecule, all the atoms being joined by ordinary covalent linkings, and not an associated group of units joined together by a separate cohesive force. Three kinds of organic colloids are recognised: (1) suspensoids and emulsoids, where the disperse phase is completely insoluble in the dispersion medium, (2) association or micellar colloids, which are heteropolar compounds giving an ion of colloidal dimensions, and (3) molecular colloids, which are constituted in the way described above. E. S. HEDGES.

**Deformation of high-molecular compounds.** R. O. HERZOG (Kolloid-Z., 1930, 53, 46—57).—The essential features of the high-molecular organic colloids are their small kinetic motion, their tendency to form a chain (not leaf-like) structure, their structure as a periodic repetition of a simpler form, and the presence of a mixture of homologous polymerides. The influence of these features on plasticity, elastic deformation, and deformation accompanying solidification is discussed and illustrated by examples taken from published work. E. S. HEDGES.

**Kohlschütter's method of preparing silver hydrosol.** M. R. NAYAR and P. S. MACMAHON (J. Indian Chem. Soc., 1930, 7, 699—707).—Pauli's views on the preparation of silver sols by Kohlschütter's method are criticised and certain of his experimental observations are contradicted; the presence of free alkali is not essential for sol formation, and metallic silver has a marked anticatalytic influence. Reduction of silver oxide in a silvered glass vessel results in the formation of a thin white unstable sol, but in silica or glass vessels a stable red sol is always obtained. The mechanism of the process is probably  $\text{Ag}_2\text{O} \rightarrow \text{Ag} + \text{AgO}'$  and  $\text{AgOH} \rightarrow \text{Ag} + \text{OH}'$ , the  $\text{AgO}'$  ion becoming the nucleus of the colloidal particle. The influence of metallic silver is

due to an increase of the silver-ion concentration in the neighbourhood of the walls of the vessel and consequent reversal of the first equation and removal of the  $\text{AgO}'$  nuclei. A stable sol may be prepared by reduction at  $85^\circ$ , but at the b. p. a coarse suspension is formed. After dialysis of the sol for 18 months no coagulation takes place. H. F. GILLBE.

**Colour and particle size of colloidal silver, especially hydrogen peroxide silver sols.** E. WIEGEL (Kolloid-Z., 1930, 53, 96—101).—A summary of recent experiments and observations on the coloured silver sols produced by the action of hydrogen peroxide on dextrin silver sols (cf. A., 1929, 643). With increase in particle size between 10 and  $130 \mu$ , the colour of the sols as viewed in transmitted light passes through the sequence: yellow, red, reddish-violet, bluish-violet, blue, green. E. S. HEDGES.

**Galvano-colloids. III. Formation of iron hydroxide hydrosols.** A. V. DUMANSKI and Z. P. TSCHESCHEVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1131—1136).—The passage of a current through a ferric chloride solution, using a platinum cathode and an iron amalgam anode, results in the production of a mixed ferrous and ferric hydroxide sol. Iron amalgam, when shaken with a potassium hydroxide solution containing mannitol and a few drops of hydrogen peroxide, also yields a mixed ferric-ferrous hydroxide sol, the particles of which are charged negatively. Such sols on keeping deposit a greenish-black gel, containing chiefly mixed ferric and ferrous hydroxide, leaving a clear supernatant layer of ferric hydroxide sol. R. TRUSZKOWSKI.

**Coagulation of pure ferric hydroxide sols.** N. R. DHAR (J. Amer. Chem. Soc., 1930, 52, 4170; cf. A., 1929, 506).—Polemical against Judd and Sorum (this vol., 1116). J. G. A. GRIFFITHS.

**Flocculation of ferric hydroxide sols by various electrolytes and the Schultze-Hardy law.** A. BOUTARIC and J. BOUCHARD (Compt. rend., 1930, 191, 613—615).—The quantities of electrolyte required to flocculate a ferric hydroxide sol (1.28 g. per litre) prepared by hydrolysis of a warm solution of ferric chloride have been determined by extrapolation of the curves representing the connexion between electrolyte concentration and the duration of flocculation. Results are given for a large number of compounds of the same cation ( $\text{K}'$ ), and it is shown that, contrary to the conclusion of Duclaux, flocculation cannot be explained by a chemical reaction between the added electrolyte and that present in the micelle. The Schultze-Hardy valency law is not obeyed by all the electrolytes used, and there are indications that the flocculating power of an active ion increases with the structural complexity for ions of equal valencies. J. GRANT.

**Sodium nitrate as a reagent for the salting out of colloids.** I. A. OBERHARD and L. T. SOLOVIEV (Ark. biol. nauk, 1930, 30, 83—99).—The coagulation of colloids by means of sodium nitrate is described; colloidal silver may thus be removed from solutions. Blood- and serum-proteins are removed at complete saturation (48%) and at  $p_{\text{H}}$  values less than 3.5.

CHEMICAL ABSTRACTS.

**Reversal of charge of serum and its coagulation and gelatinisation with acids.** S. PRAKASH and N. R. DHAR (J. Indian Chem. Soc., 1930, 7, 723—732).—Blood-serum exhibits one coagulation point with dilute acids (0.01—0.04*N*), corresponding with the precipitation of globulin only, and another with more concentrated acid (0.1—6.0*N*) which results in the precipitation also of serum-albumin; the coagulating power of the concentrated acids diminishes in the order trichloroacetic, nitric, sulphuric, hydrochloric, hypophosphorous, monochloroacetic, acetic, formic. When coagulated by concentrated acid the serum behaves abnormally towards dilution, on account of adsorption of similarly charged ions. By adsorption of hydrogen ions on the addition of acid the serum is rendered unstable and easily coagulable by dilute ammonium sulphate solution. Reversal of charge, at  $p_H$  5—5.3, and continued adsorption of hydrogen ions occur if the acid concentration be increased. The coagulate produced by dilute acids is flocculent and hydrated to a smaller extent than the gelatinous precipitate obtained with concentrated acid. Stable translucent or opaque jellies, which do not exhibit syneresis, may be obtained by coagulation of serum with concentrated solutions of weak acids; the amount of acid required diminishes as the serum concentration increases. Two distinct coagulation points are obtained also with solutions of electrolytes such as aluminium nitrate, copper sulphate, and thorium nitrate. H. F. GILLBE.

**Thermodynamics of lyophilic colloids.** H. KROEPELIN (Kolloid-Z., 1930, 53, 86—88).—A theoretical treatment of osmotic and swelling pressures.

E. S. HEDGES.

**Soap solutions. VIII. Protective activities of soaps on Congo-rubin sol.** J. MIKUMO (J. Soc. Chem. Ind. Japan, 1930, 33, 369—370 B).—The rubin numbers of a series of pure sodium soaps (*n*-valeric to myristic, oleic, and ricinoleic) have been measured at 25° on a Congo-rubin sol, in presence of potassium chloride. The  $C_{12}$  soap shows protective activity, but the  $C_8$ ,  $C_9$ , and  $C_{10}$  soaps have little effect. The  $C_7$  and especially the  $C_6$  and  $C_5$  soaps have a marked coagulating effect, the influence of the sodium ion prevailing over the peptising action of the soap. The protective activity of soap on a hydrophobic sol appears to be intimately related to its adsorptive activity. E. LEWKOWITSCH.

**Positive and negative habituation in the coagulation of ferric hydroxide sols.** V. N. KRESTINSKAJA and O. S. MOLTCHANOVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1223—1236).—Differences in the coagulating effect of electrolytes on ferric hydroxide sols, according to whether they are added in one portion or gradually, are due to the formation of more or less soluble salts with the nucleus of the micelles. When the product is more soluble, the nucleus diminishes, and the active portion of the micelle increases, leading to greater stability of the sol, and vice versa. Apparent negative habituation is due to the coagulative effect of certain electrolytes in low concentrations. R. TRUSZKOWSKI.

**Structure of gelatin sols and gels. III. Isoelectric points of gelatin.** S. E. SHEPPARD

and R. C. HOUCK (J. Physical Chem., 1930, 34, 2187—2201; cf. this vol., 858).—The isoelectric points of de-ashed calfskin gelatin determined from the maximum turbidity in dilute solutions, the optimum flocculation by alcohol, and the point of minimum electric migration have the  $p_H$  values  $4.9 \pm 0.05$ ,  $4.9 \pm 0.05$ , and  $4.9 \pm 0.10$ , respectively; no evidence of a second isoelectric point at  $p_H$  7.7 (Wilson and Kern, A., 1923, i, 68) was obtained. When the above-mentioned methods are applied to the gelatins obtained from alkali- and acid-treated pigskins different values for the isoelectric points are obtained.

L. S. THEOBALD.

**Freezing of gels.** K. KINOSHITA (Bull. Chem. Soc. Japan, 1930, 5, 261—266).—Measurements of the rate of cooling and the f. p. of gels containing 5—60% of gelatin have been made. Super-cooling is very marked and the structure of the frozen gel depends on its concentration. With gels containing less than 15% of gelatin concentric layers of ice and gel are obtained, whereas gels above 20% solidify as a pale brownish-white hard mass, in which small ice crystals can only be observed microscopically. Up to about 15% gelatin the f. p. is only a little lower than that of pure water; between 15 and 30% the f. p. falls rapidly as the concentration rises, whereas at still higher concentrations the f. p. falls slowly. The bearing of these results on the hydration of the gels is discussed. O. J. WALKER.

**Absorption of water by gelatin. IV. Influence of temperature.** D. J. LLOYD (Biochem. J., 1930, 24, 1460—1471).—In hydrochloric acid the swelling of gelatin at 0° rises to a maximum at  $p_H$  2.6 and falls with increasing hydrogen-ion concentration to a value which becomes stationary over a wide range of  $p_H$ . Gelatin does not dissolve in concentrated solutions of the acid at 0°. At 0° the swelling of gelatin in sodium hydroxide solutions rises with increasing value of  $p_H$  from 5, the point of minimum swelling, to 7.5. Between  $p_H$  7.5 and 10 variation of the alkalinity has little effect on the swelling. In solutions more alkaline than  $p_H$  10 there is a well-defined peak of maximum swelling at  $p_H$  11.5. Gelatin dissolves at 0° in alkaline solutions at  $p_H$  13 and upwards. The  $p_H$  of maximum swelling in acid solutions is not affected by temperature, but that in alkaline solutions increases as the temperature falls. In solutions of sodium chloride or nitrate at or near the isoelectric point the absorption of water by gelatin increases with rising temperature. Unless the system is on the verge of dissolution, the influence of temperature is the same over a wide range of concentration. Coagulation of gelatin gels by concentrated solutions of sodium sulphate does not occur at 0° owing to the decreased solubility of the sulphate. At 25° gelatin dissolves in acid solution of  $p_H < 3$ ; in alkaline solutions of  $p_H > 9.5$ . There is no maximum of acid swelling, but a maximum of alkaline swelling occurs at  $p_H$  7.2. S. S. ZILVA.

**Absorption of water by gelatin. V. Influence of calcium hydroxide.** W. B. PLEASS (Biochem. J., 1930, 24, 1472—1478).—Gelatin swells more at higher temperatures than at low. The  $p_H$  value at which maximum swelling occurs is dependent on the tem-



perature. At 0° it occurs at  $p_H$  11.5 and at 25° at  $p_H$  10.5. The magnitude of the swelling in solutions of calcium hydroxide is always less than, but greater than half, that of the swelling in solutions of sodium hydroxide at the same temperature and  $p_H$  value. At 0° the maximum increase in water absorption from solutions of calcium hydroxide above that of the water of imbibition of the gelatin at the same temperature is about half as great as that in the sodium hydroxide system. At this temperature maximum swelling occurs at  $p_H$  11.5 in both the calcium hydroxide and sodium hydroxide systems, and at this  $p_H$  value the hydroxyl-ion concentration is approximately equal to the hydrogen-ion concentration of maximum swelling in hydrochloric acid and nitric acid.

S. S. ZILVA.

**Syneresis of silica gel.** J. FERGUSON and M. P. APPLEBEY (Trans. Faraday Soc., 1930, 26, 642—655).—The volume of liquid exuded in the syneresis of silica gel is independent of the shape and free external surface of the gel, in contradiction to the results of Holmes, Kaufmann, and Nicholas (A., 1919, ii, 454), but is identical with the contraction in volume of the solid gel. As the total volume of the system does not change, the process is probably a squeezing out of the liquid enmeshed in the structure and not a decrease in the degree of hydration of the micelles. Experiments on the time-course of syneresis of gels of constant hydrogen-ion concentration showed that syneresis does not begin immediately after setting, and when once started it follows an S-shaped autocatalytic curve. The velocity of syneresis and the total volume of liquid exuded increase with the concentration of the gel. The velocity is also approximately doubled for each 10° rise in temperature. Syneresis starts almost immediately in alkaline gels and proceeds very rapidly, but the final volume of liquid exuded is less than in acid gels. In neutral gels the hydration of the micelles is 1 mol. of water to 1 mol. of silica, but increases with the alkalinity, being 2 mols. of water to 1 mol. of silica at  $p_H$  10. Syneresis is due to the mutual attraction of micelles through residual valencies and is therefore greater in concentrated than in dilute gels.

E. S. HEDGES.

**X-Ray study of the gelatinisation of cellulose nitrate.** DESMAROUX and M. MATHIEU (Compt. rend., 1930, 191, 786—788).—Whilst the X-ray diagram (Cu-K radiation) of cellulose nitrate films (12.06% N) deposited from acetone or mixtures of ether and alcohol is a single diffused diffraction ring (this vol., 539), the addition of 40—50% of a gelatinising agent may produce another sharp and smaller ring, the outer ring always being sharper and narrower than that produced by the cellulose nitrate itself. The classification of gelatinising agents in terms of the power of absorption by cellulose nitrate, or the disappearance of orientation in poured films, gives results similar to those afforded by X-ray data.

J. GRANT.

**"Melting curve" of natural caoutchouc.** G. VON SUSICH (Naturwiss., 1930, 18, 915—916).—Unstretched natural caoutchouc gives an X-ray interference diagram below 35—38°, but not above that

temperature. With increasing degree of stretching the temperature at which the substance is truly amorphous rises. By plotting the degree of stretching against the temperature at which an X-ray pattern ceases to be obtained, a "melting curve," showing the transition from crystalline to amorphous caoutchouc, is obtained.

E. S. HEDGES.

**Solvent effect with caoutchouc.** P. STAMBERGER and C. M. BLOW (Kolloid-Z., 1930, 53, 90—95).—A method for measuring the swelling pressure of caoutchouc is described. The experimental results show that specimens of caoutchouc from different sources give identical values and that no difference is to be observed between the behaviour of sols and gels. Variations in the viscosity of caoutchouc described are attributed to changes in mol. wt. E. S. HEDGES.

**Structure of celluloid.** J. J. TRILLAT (Compt. rend., 1930, 191, 654—656).—The curve obtained by plotting the camphor content of celluloid films and the corresponding intermolecular distances of the outside rings of the X-ray diagrams shows a very slow rise in the former with increase in the latter up to 10—15% of camphor (5.3 Å.), followed by a rapid rise towards the point corresponding with pure camphor (6.1 Å.). This indicates that an amorphous combination of cellulose nitrate and camphor, capable of dissolving excess of camphor in solid solution, is produced when the camphor content exceeds 15%. Examination of the films in three perpendicular directions showed an orientation corresponding with a marked birefringence, which decreases gradually on addition of camphor until the structure is isotropic in all directions. Tests with other plasticisers suggest that simple mechanical mixtures are involved.

J. GRANT.

**Methyl alcohol equilibrium.** E. F. VON WETTERBERG and B. F. DODGE (Ind. Eng. Chem., 1930, 22, 1040—1046).—Examination of the recorded values of the equilibrium constant,  $K_p$ , for the reaction  $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{MeOH}$  shows that the experimental data differ widely, not only amongst themselves, but also from the values calculated thermodynamically. The fact that  $K_p$  varies with the pressure will account for only slight deviations, and it appears that the discrepancies are due mainly to the equilibrium being complicated by side reactions, and to the use of inaccurate thermal data in the calculations (cf. this vol., 292). A new direct determination of  $K_p$  at 260—330°/170 atm. has given results agreeing fairly well with those obtained by Smith and Branting (A., 1929, 265).

R. CUTHILL.

**Associations in solution.** J. MEISENHEIMER and O. DORNER (Annalen, 1930, 482, 130—160).—The association of a large number of simple organic substances, representing many different types of compounds dissolved in nitrobenzene, dioxan, and benzene has been determined by the cryoscopic method. The factor of association increases linearly with the concentration of the solution, and this is regarded as the general course of association. The same result is also reached theoretically from kinetic considerations. In certain instances, however, such as in a solution of benzoic acid in nitrobenzene, the association factor at first increases rapidly with the

concentration and later more slowly. This behaviour is due to a special type of association leading to the formation of new double or triple molecules in accordance with the law of mass action. The curve obtained is never simple, because the general association process is always superimposed on the special association. A study of the association of mixed molecules has also been made. The association of hydrogen chloride with water, a series of alcohols, ether, and acetone has been followed by preparing solutions of the components in nitrobenzene or in dioxan and determining the alteration in the f. p. on mixing. Hydrogen chloride associates strongly with water, and a series of alcohols examined does so to a smaller extent. Those substances which show the greatest specific association of their own molecules also associate most strongly with hydrogen chloride, and the order of the tendency to associate with hydrogen chloride is the same for the series of alcohols in both solvents. Acetone associates strongly and benzophenone weakly with hydrogen chloride, and in general association is less in the case of aromatic compounds. In a few cases no change of f. p. occurs on mixing the solutions and in other instances a very slight further lowering takes place. The nature of the forces involved in molecular association is discussed and it is pointed out that, for example, the association of hydrogen chloride with water does not depend on the number of single water molecules, but on the number of associated water complexes. The degree of specific association of the solute does not depend on the dielectric constant of the solvent, but on the extent of solvation of the solute in the particular solvent. E. S. HEDGES.

**Dissociation of strong electrolytes in non-aqueous solution.** R. SCHNEXITZ (Z. Elektrochem., 1930, 36, 861—874).—Theoretical. The behaviour of strong electrolytes in non-aqueous solution is discussed from the point of view of the theory of Debye and Hückel. The conclusion reached is that, whilst the theory accounts satisfactorily for the influence of the dielectric constant and the interionic field on the osmotic or activity coefficient, the evidence available indicates that dissociation of even the strongest electrolytes is incomplete. F. L. USHER.

**Hydrogen exponent of water.** A. KLING and A. LASSIEUR (Compt. rend., 1930, 191, 788—789).—The elimination of carbon dioxide (cf. A., 1929, 1384) has been achieved by distillation of the water from a platinum still in the presence of sodium hydroxide, the distillate being received directly in a protected hydrogen electrode vessel containing pure hydrogen, and the  $p_H$  value determined at once by the zero-potential method using hydrogen electrodes containing liquids of known  $p_H$  values. The previous value (5.8) is confirmed, and shown to be unaffected either by boiling or by subsequent freezing. J. GRANT.

**Acidity of mono- and di-ammonium phosphates.** T. R. BALL (J. Amer. Chem. Soc., 1930, 52, 3901—3905).—The  $p_H$  values of mono- and di-ammonium phosphate in dilute solution are found to be 4.35 and 7.75, respectively. The  $p_H$  of diammonium phosphate solutions increases to 8.01 (cresol-red and phenol-red indicate  $p_H$  8.3 and 8.1, respectively)

when the concentration is raised to 100 g. per litre. The colour produced in 10 c.c. of this solution by the addition of 2 drops of 1% phenolphthalein was removed by 0.3 c.c. of 0.1*N*-sulphuric acid.

J. G. A. GRIFFITHS.

**Equilibrium of cerous and perceric salts.** G. LEJEUNE (Compt. rend., 1930, 191, 665—667).—The author's method (A., 1927, 736, 833) has been applied in the measurement of the *E.M.F.* of the cell  $\text{Hg}|\text{HgCl}, \text{sat. KCl}|\text{sat. K}_2\text{SO}_4|\text{K}_2\text{CO}_3, 2.5M\text{-cerous-perceric}|\text{Pt}$ , in nitrogen at 25°. On the assumption that the equilibrium involves a unit valency change Nernst's formula is approximately confirmed and the equation  $\text{Ce}^{\text{III}} + \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{CeO}^{\text{IV}} + 3\text{H}$  is suggested, since the change  $\text{Ce}^{\text{III}} \rightleftharpoons \text{Ce}^{\text{IV}}$  involves three hydrogen ions. This does not preclude the existence of  $\text{Ce}^{\text{IV}}$  ions, which probably account for the more intense red colour obtained on oxidation of cerous compounds by hydrogen peroxide as compared with  $\text{CeO}^{\text{IV}}$  ions produced by air. J. GRANT.

**Hydrochloric acid solutions of iodine monochloride.** F. A. PHILBRICK (J.C.S., 1930, 2254—2260).—The distribution of iodine between hydrochloric acid and a hydrochloric acid solution of iodine monochloride has been investigated by bringing both into equilibrium with a carbon tetrachloride solution of iodine. The iodine monochloride was prepared in the solution by the action of hydrochloric acid on potassium iodate. A corresponding amount of potassium chloride was added, therefore, to the hydrochloric acid solution alone. From the results it appears that iodine monochloride is highly ionised in solution to  $\text{I}^+$  and  $\text{Cl}^-$ . In 3*N*-hydrochloric acid the degree of ionisation of an approximately *M* solution of iodine chloride is about 80% of that of the acid, and in 7*N*-acid it is considerably greater. This confirms the view that the formation of electrovalencies is promoted by a large cation and a small anion, and the ionisation of iodine mono- and tri-chlorides in non-aqueous solvents also supports this conclusion. There is no evidence for the existence of  $\text{HICl}_2$  or its anion in solution. A vessel for the microtitration of iodine is described; 3 mg. can be titrated with an accuracy of 0.1%. M. S. BURR.

**Activity coefficients of caesium chloride and hydroxide in aqueous solution.** H. S. HARNED and O. E. SCHUPP, jun. (J. Amer. Chem. Soc., 1930, 52, 3886—3892).—From *E.M.F.* determinations at 25° with the cells  $\text{Ag}|\text{AgCl}|\text{CsCl}(0.001\text{--}3.0M)|\text{Cs}(0.01\text{ and }0.1\%)|\text{Hg}|\text{CsCl}(0.1M)|\text{AgCl}|\text{Ag}$  and  $\text{H}_2|\text{CsOH}(0.01\text{--}1.3M)|\text{Cs}(0.01\text{ and }0.1\%)|\text{Hg}|\text{CsOH}(0.05M)|\text{H}_2$ , the activity coefficients of aqueous caesium chloride and caesium hydroxide have been computed. The constants of the equation of Hückel (A., 1925, ii, 513) and of Harned (A., 1922, ii, 255) have been evaluated. Values of the activity coefficients of caesium chloride lie below those of the other alkali chlorides, and those of caesium hydroxide are slightly greater than those of potassium hydroxide.

J. G. A. GRIFFITHS.

**Activity coefficient and dissociation of water in caesium chloride solutions.** H. S. HARNED and O. E. SCHUPP, jun. (J. Amer. Chem. Soc., 1930, 52, 3892—3900).—From *E.M.F.* determinations at 25°

with the cell  $H_2|HCl(0.01M), CsCl(0-3M)|AgCl|Ag$  it is found that values of the activity coefficient of hydrochloric acid in caesium chloride solutions are lower than in solutions of other alkali chlorides. The activity coefficient of caesium hydroxide in caesium chloride solutions has been computed from *E.M.F.* data for the cell  $H_2|CsOH(0.05 \text{ or } 0.1M), CsCl(0.0-3.7M)|Cs_2Hg|CsOH(0.05 \text{ or } 0.1M)|H_2$  at  $25^\circ$ . The ionic activity coefficient product and dissociation of water in caesium chloride solutions have been computed and the results are in accord with values based on determinations of the *E.M.F.* of the cell  $H_2|CsOH(0.022M), CsCl(0.02-1.35M)|AgCl|Ag$  at  $25^\circ$  (cf. Roberts, this vol., 1525) and conform to values previously obtained with other alkali halide solutions.

J. G. A. GRIFFITHS.

Free energy of stannous hydroxychloride and the activity coefficient of stannous chloride and stannous ion. M. RANDALL and S. MURAKAMI (J. Amer. Chem. Soc., 1930, 52, 3967-3971).—Determinations of the equilibrium  $Sn^{++} + Cl^- + 2H_2O(l) = Sn(OH)Cl, H_2O(s) + H^+$  have been made at  $25^\circ$ . The free energy of the reaction,  $\Delta F_{298.1}$ , is  $-3750$  g.-cal. and the free energy of formation of  $Sn(OH)Cl, H_2O(s)$  is  $-154,491$ . The activity coefficients of stannous chloride and stannous ion have been calculated; the values of the latter are smaller than those for the alkaline-earth ions.

J. G. A. GRIFFITHS.

Theoretical shape of the solubility isotherm of a solid in a complex solvent. N. I. STEPANOV (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1926, 3, 466-468).

CHEMICAL ABSTRACTS.

Shape of the isothermal solubility curve of a solid in a ternary system. N. I. STEPANOV (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1926, 3, 482-483).—The theoretical shape of the isothermal solubility curves in a ternary system is considered in relation to Roozeboom's triangular diagram. If the two apices of the triangular diagram corresponding with the two components of the liquid solvent are made to coincide with the corresponding points in the binary system, then the intersection of the lines joining the homologous points in the two systems gives an easy means of constructing isothermal curves in a ternary system. CHEMICAL ABSTRACTS.

Isotherm of the solubility of a binary compound in a ternary system. N. I. STEPANOV (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1928, 4, 306-308).—Mathematical. For a non-dissociated compound the curve consists of two intersecting straight lines, whilst for a partly dissociated compound it is a hyperbola, parabola, or ellipse. The m. p. of the compound which is dissociated in the liquid phase falls with increase in the degree of dissociation.

CHEMICAL ABSTRACTS.

Theoretical m.-p. curves of a binary compound both undissociated and dissociated in the liquid phase. N. I. STEPANOV (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1928, 4, 327-330).—Mathematical expressions have been deduced theoretically.

CHEMICAL ABSTRACTS.

Distortion of curves in connexion with m.-p. diagrams; m.-p. diagrams with curvilinear co-

ordinates. N. V. LIPIN (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1928, 4, 308-310).—A complicated theoretical solution of Kurnakov's problem has been obtained. By a study of deviations of the curves with Schröder logarithmics as a basis the position of the m. p. can be determined.

CHEMICAL ABSTRACTS.

Distortion of the curve of the thermodynamic potential with the change of components in a binary system. N. I. STEPANOV (Ann. Inst. Anal. Phys.-Chim., Leningrad, 1928, 4, 325-327).—The relation between the distortion of the curve of the thermodynamic potential and the change of components in the system  $A+B \rightleftharpoons ApBq$  from  $A$  and  $B$  to  $B+ApBq$  has been developed mathematically.

CHEMICAL ABSTRACTS.

Solidifying points of binary mixtures of fatty acids and esters. L. A. BHATT and H. E. WATSON [with Z. H. PATEL] (J. Indian Inst. Sci., 1930, 13A, 141-146).—F.-p. curves are given for the acid pairs acetic-*n*-butyric; behenic-stearic; dodecoic-stearic; deoic-stearic; dodecoic-lignoceric; dodecoic-myristic; and for methyl dodecoate-methyl myristate. The lignoceric acid used was isolated from *Aden-anthera pavonia*; it is not the *n*-acid. H. BURTON.

Connexion between the melting curve and the composition of a binary mixture. K. POSTHUMUS (Rec. trav. chim., 1930, 49, 885-914).—A discussion of the various forms of m.-p. diagrams for binary mixtures in which the two components exist in a single molecular form and give rise to only one new kind of molecule in the mixtures. O. J. WALKER.

Binary systems. II. J. H. KOERS and F. E. C. SCHEFFER (Rec. trav. chim., 1930, 49, 915-954; cf. this vol., 861).—Mathematical. The equilibria in systems in which the solid phase corresponds with one of the two components are discussed and illustrated by means of numerous pressure-temperature, pressure-composition, and volume-composition diagrams. The differences between the critical temperatures and between the triple-point temperatures of the two components are considered with reference to their influence on the equilibrium conditions.

O. J. WALKER.

F. p. of the system water-hydrogen fluoride. G. H. CADY and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1930, 52, 3843-3846).—F.-p. data are given for the entire range of solutions, and the compounds  $H_2O, 2HF$ , and  $H_2O, 4HF$  (m. p.  $172.8^\circ$  Abs.) as well as  $H_2O, HF$ , m. p.  $237.7^\circ$  Abs. (cf. Metzner, A., 1895, ii, 108), have been obtained. J. G. A. GRIFFITHS.

System water-silicon dioxide. I. A. SMITS (Rec. trav. chim., 1930, 49, 962-966).—The work of van Nieuwenburg (this vol., 1262) on the volatility of silicic acid in steam is discussed, and it is shown that the system water-silicon dioxide is of the same type as the system ether-anthraquinone, although complicated by the fact that the second component, silicon dioxide, can exist in several modifications. Some points for further investigation are suggested.

O. J. WALKER.

Iodine and potassium iodide. T. R. BRIGGS and W. F. GEIGLE (J. Physical Chem., 1930, 34, 2250—

2259).—The temperature-composition diagram for the system iodine-potassium iodide has been determined from 70° to 191°, the b. p. of the saturated fused mass. No polyiodides exist as stable phases in equilibrium with the mass. The system is of the simple type with a eutectic at 80.8° and 22.2 mol.-% KI. The solubility curve of potassium iodide in iodine is practically parallel to the temperature axis and as a result temperature arrests are not found in the usual cooling curves. Parsons' conclusions (A., 1908, ii, 89) that certain mixtures supposed to be liquid were not homogeneous is now shown to be correct, but the non-homogeneous mixtures actually consist of solid potassium iodide and saturated solution. Polyiodides of potassium and in particular the tri-iodide do not exist as stable solids above 25°. L. S. THEOBALD.

**Polyiodides of caesium. II. Iodine and caesium iodide.** T. R. BRIGGS (J. Physical Chem., 1930, 34, 2260—2266; cf. this vol., 1374).—The temperature-composition diagram for this system has been determined from 60° to 303°, the b. p. of the saturated fused mass. The four solid phases are iodine, the tetraiodide, the tri-iodide, and caesium iodide, but neither polyiodide is stable at its m. p. The transition temperature between the tri-iodide and the mono-iodide is 211° and that between the polyiodides is 136° approximately; the eutectic for iodine and the tetraiodide lies at  $71.5^\circ \pm 1^\circ$ . L. S. THEOBALD.

**Physico-chemical studies of complex acids. IV. Vanadates of silver.** H. T. S. BRITTON and R. A. ROBINSON (J.C.S., 1930, 2328—2343).—Potentiometric titrations of silver nitrate, using a silver electrode, have been carried out with sodium vanadate solutions in which the values of the ratio  $\text{Na}_2\text{O} : \text{V}_2\text{O}_5$  varied. Reverse titrations of vanadate solutions with silver nitrate have also been made and conductometric titrations of sodium vanadates with silver nitrate. The results indicate that the insoluble vanadates,  $3\text{Ag}_2\text{O} \cdot \text{V}_2\text{O}_5$ ,  $2\text{Ag}_2\text{O} \cdot \text{V}_2\text{O}_5$ , and  $\text{Ag}_2\text{O} \cdot \text{V}_2\text{O}_5$ , are definite chemical individuals. The product  $[\text{Ag}]^2[\text{HVO}_4]'$  has a constant value of the order of  $2 \times 10^{-14}$  and shows that the 2:1 sodium vanadate solutions contain the  $\text{HVO}_4''$  ion rather than the  $\text{V}_2\text{O}_4'''$  ion. The solubility product  $[\text{Ag}][\text{VO}_3']$  is  $5 \times 10^{-7}$ . Hydrolysis of 3:1 sodium vanadate prevents the determination of the solubility product of the corresponding silver salt, but, on the assumption that this hydrolysis is complete, the product  $[\text{Ag}]^3[\text{HVO}_4''][\text{OH}']$  has a constant value of the order of  $10^{-24}$ . Addition to silver nitrate of solutions of sodium vanadate of the composition  $x\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$  first precipitates mixed vanadates of silver of a mean composition  $x\text{Ag}_2\text{O} \cdot \text{V}_2\text{O}_5$ . Addition of excess of sodium vanadate, however, results in the precipitation of either the 3:1 or the 2:1 silver vanadate, depending on the composition of the precipitant used. There appears to be definite evidence of the existence in solution of the ions  $\text{VO}_4'''$ ,  $\text{HVO}_4''$ , and either  $\text{H}_2\text{VO}_4'$  or  $\text{VO}_3'$ . M. S. BURR.

**Thermal dissociation.** J. KRUSTINSONS (Latvian Univ. Raksti, 1929, 1, 29—63).—A compensation method is described by which the dissociation of the following compounds in the liquid state have been studied: thallous carbonate and lithium, sodium,

potassium, rubidium, and caesium nitrates. The isochores of the liquid compounds approximate to straight lines for the pressure interval 200—900 mm. If a compound with a common ion, e.g., thallous oxide or a carbonate, is dissolved in thallous carbonate, the dissociation temperature is raised and the well-known formula for the relative lowering of the vapour tension is shown to be applicable. A very large rise in the dissociation temperature of the nitrates is observed when the corresponding nitrites are dissolved in them. Binary mixtures of compounds with unlimited reciprocal solubility, e.g.,  $\text{NaNO}_3 + \text{LiNO}_3$ ,  $\text{KNO}_3 + \text{LiNO}_3$ ,  $\text{KNO}_3 + \text{NaNO}_3$ , and  $\text{LiNO}_3 + \text{CsNO}_3$  have a minimum dissociation temperature at a certain definite composition. The temperature at which the dissociation of zinc spar begins rises as dissociation proceeds, and this is due to the formation of a solid solution with the zinc oxide formed. M. S. BURR.

**Dependence of the dissociation temperature of a solid on the size of the crystal grains.** J. KRUSTINSONS (Latvian Univ. Raksti, 1930, 1, 273—277).—Mercuric oxide has been separated into four specimens of differing grain size. A difference of 6° was found in the dissociation temperatures of the coarsest and finest specimens. Using Thomson's formula the surface tension of solid mercuric oxide is calculated to be 1146 dynes/cm. F. J. WILKINS.

**Equilibrium between phosphine, phosphorus, and hydrogen.** V. I. IPATIEV and A. V. FROST (J. Russ. Phys. Chem. Soc., 1930, 62, 1123—1129).—Drummond's values (A., 1927, 940) for the equilibrium constant of the system  $4\text{PH}_3 \rightleftharpoons \text{P}_4 + 6\text{H}_2$  are too high. Using an improved experimental method, the values of  $K_p$  are found to be expressed by the equation  $\log K_p = A/T + B$ , where  $T$  is the temperature,  $A$  is —4956, and  $B$  is —18.68. R. TRUSZKOWSKI.

**Dissociation pressures of metal pyridine thiocyanates.** T. L. DAVIS and H. R. BATCHELDER (J. Amer. Chem. Soc., 1930, 52, 4069—4074).—The dissociation pressures of di- and tetra-pyridinecobaltous, mono- and di-pyridinecupric, di- and tetra-pyridinenickelous, and tetrapyridinezinc thiocyanates have been measured at 20—80°. The curves (log. pressure against  $1/T$ ) for the cobaltous salts are practically parallel to the vapour-pressure curve for pyridine, indicating that the affinities of these salts for pyridine are approximately constant over the range of temperature studied. The curves for the copper salts approach that for pyridine at the higher temperatures, indicating that the affinity of cupric and monopyridinecupric thiocyanates for pyridine decreases with rise in temperature. The nickelous and zinc salts show increasing affinity with rise in temperature. Tetrapyridinenickelous thiocyanate decomposes spontaneously below —3°. H. BURTON.

**Pyrogenic decomposition of the alkaline-earth bromates.** HACKSPILL and WINTERER (Compt. rend., 1930, 191, 663—665).—Continuous photographic records of the increase with rise of temperature of the pressure of the oxygen evolved from the anhydrous salts show that all the oxygen is evolved from barium and calcium bromates at 265—315° and 247—275°, respectively, all the bromine being retained. Stront-

ium bromate, however, yields all but 1—3% of oxygen at 240—287°, the residue being fixed as SrO, and a little bromine liberated in its place. With barium bromate, decomposition is slow up to 300°, and then explosive.

J. GRANT.

**Ternary system potassium sulphate-magnesium sulphate-water.** B. A. STARRS and H. H. STORCH (J. Physical Chem., 1930, 34, 2367—2374).—The isotherms for 85° and 100° have been determined. The stable solid phases at 85° are potassium sulphate, leonite ( $K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ ), langbeinite ( $K_2SO_4 \cdot 2MgSO_4$ ), and kieserite, whilst at 100° they are potassium sulphate, langbeinite, and kieserite. All available data for 30—100° are incorporated in a diagram.

L. S. THEOBALD.

**Hydrated potassium sesquicarbonate,**  $K_2CO_3 \cdot 2KHCO_3 \cdot 1.5H_2O$ . A. E. HILL (J. Amer. Chem. Soc., 1930, 52, 3817—3825; cf. following abstract).—Isotherms at 5°, 25°, 35°, and 50° for the ternary system  $K_2CO_3$ — $KHCO_3$ — $H_2O$  have been determined. The double salt  $K_2CO_3 \cdot 2KHCO_3 \cdot 1.5H_2O$  exists within a very narrow range of concentrations from -9.2° (lower transition point) to above 50°.

J. G. A. GRIFFITHS.

**Double salt formation among carbonates and hydrogen carbonates of sodium and potassium.** A. E. HILL (J. Amer. Chem. Soc., 1930, 52, 3813—3817; cf. A., 1929, 884).—A further study of the system  $K_2CO_3$ — $NaHCO_3$ — $Na_2CO_3$ — $KHCO_3$ — $H_2O$  shows that a rise of temperature from 25° to 35° increases the range of concentrations within which the salt  $K_2CO_3 \cdot 2KHCO_3 \cdot 1.5H_2O$  is stable and decreases the range for the salt  $K_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ .

J. G. A. GRIFFITHS.

**System copper sulphate-lithium sulphate-water.** H. D. CROCKFORD and M. M. WEBSTER (J. Physical Chem., 1930, 34, 2375—2377).—The isotherms for 0°, 25°, and 55° have been determined. The data are in general agreement with those obtained for 30° by Schreinmakers (cf. A., 1909, ii, 559) and show that the solubility of each salt is depressed by the presence of the other. The solid phases are the hydrates  $CuSO_4 \cdot 5H_2O$  and  $Li_2SO_4 \cdot H_2O$ , no double salts being obtained at the temperatures used.

L. S. THEOBALD.

**System sodium chloride-magnesium sulphate-water at 35°.** N. K. VOSKRESSENSKA (J. Appl. Chem., Russia, 1930, 3, 321—336).—The following systems, each with water, were investigated at 35°: sodium chloride-magnesium chloride, magnesium chloride-magnesium sulphate, magnesium sulphate-sodium sulphate, magnesium sulphate-magnesium chloride-sodium sulphate-sodium chloride.

CHEMICAL ABSTRACTS.

**High-temperature equilibrium of titanium dioxide and carbon with titanium carbide and carbon monoxide.** L. R. BRANTLEY and A. O. BECKMAN (J. Amer. Chem. Soc., 1930, 52, 3956—3962).—The equilibrium pressure of carbon monoxide in the system  $TiO_2$  (rutile modification) +  $3C$  (graphite) =  $TiC + 2CO$  at temperatures between 1278° and 1428° Abs. is given by the relation  $\log_{10} p(\text{atm.}) = 3.829 - 5024/T$ , from which the increase of free energy and of heat content attending the reaction at 1 atm.

are computed to be  $\Delta F = 45,930 - 35.01T$  and  $\Delta H = 45,930$  g.-cal., respectively. The equilibrium pressure is 1 atm. at 1312° Abs. The solid phases in the reaction mixtures were identified by means of X-ray powder photographs.

J. G. A. GRIFFITHS.

**Double decomposition in the absence of a solvent. XII. Fusion curves of the systems silver iodide-metal chlorides of group I.** V. P. RADISOVTSHEV (J. Russ. Phys. Chem. Soc., 1930, 62, 1063—1072).—A study of the fusion diagrams of the systems  $AgI$ — $CsCl$  ( $RbCl$ ,  $LiCl$ ,  $CuCl$ ) shows that in no case does double decomposition take place. All systems are of the eutectic type with the exception of lithium chloride, in which two layers separate. The miscibility of fused salts and the character of the fusion diagram are closely connected with the thermal data for the double decomposition reactions.

R. TRUSZKOWSKI.

**Thermodynamics of high pressures.** V. NJEGOVAN (Arhiv Hemiju, 1930, 4, 49—61).—Van der Waals' equation cannot be applied at high pressures, as it does not take into account the variation of  $C_V$ . A modification of van Laar's equation is given, in which  $a=f(T)$ . In the Haber-Bosch process  $C_V$  is constant up to 100 atm., but at 1000 atm. the yield of ammonia is greater than theoretical; this is ascribed to variation of  $C_V$  with pressure.

R. TRUSZKOWSKI.

**Gibbs-Helmholtz equation.** S. E. G. SUBERO (Anal. Fis. Quím., 1930, 28, 1089—1097).—A résumé of a paper by Boutaric (Radium, 1919, 257), and a criticism of the derivation given by Palacios (this vol., 698).

H. F. GILLBE.

[Gibbs-Helmholtz equation.] J. PALACIOS (Anal. Fis. Quím., 1930, 28, 1098—1099).—A reply to Subero (preceding abstract).

H. F. GILLBE.

**Application of optical data to the calculation of heats of activation.** H. EYRING (Naturwiss., 1930, 18, 915).—For the calculation of heats of activation, the total energy of diatomic molecules as a function of the distance between the atomic nuclei can be derived from optical data.

E. S. HEDGES.

**Calculation of heats of activation.** H. EYRING and M. PÓLÁNYI (Naturwiss., 1930, 18, 914—915).—London's calculation for the reaction between a single atom and a diatomic molecule involves the neglect of several terms in the energy equations and leads to the value  $0.13\beta_0$ , where  $\beta_0$  is the valency energy of the diatomic molecule. A new method of calculation, which avoids these neglected terms, leads to the value  $0.25\beta_0$ .

E. S. HEDGES.

**Heat of formation of molecular oxygen.** L. C. COPELAND (Physical Rev., 1930, [ii], 36, 1221—1231).—Using a direct calorimetric method previously described for molecular hydrogen (cf. A., 1928, 712) the heat of formation of molecular from atomic oxygen was determined for the pressure range 0.1—0.55 mm. of mercury, and gave values of  $131,000 \pm 6000$  g.-cal. or  $5.7 \pm 0.3$  volts per mol. Mercury vapour is readily oxidised to yellow mercuric oxide by atomic oxygen; traces of nitrogen give a green afterglow due to metastable molecules, and a compound, probably an oxide of nitrogen, is formed.

Palladium, platinum, and nickel, palladium being the most active, acted catalytically in the recombination of atomic oxygen. The possibility of long-lived metastable states is discussed. N. M. BLIGH.

**Thermochemistry of sulphur. III.** W. A. ROTH, R. GRAU, and A. MEICHNER (Z. anorg. Chem., 1930, 193, 161—175).—The heat of decomposition of hydrogen peroxide at 20° is 22.68 kg.-cal per mol., and its heat of dilution is negligibly small (0.017—0.034 kg.-cal. per mol.). The following thermochemical data have been obtained by measurement of the heat of oxidation of gaseous sulphur dioxide by 0.05*N*-hydrogen peroxide solutions at 20—21°:  $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3(\text{liquid}) + 33.66 \pm 0.06$  kg.-cal.;  $\text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 54.88 \pm 0.05$  kg.-cal.;  $\text{S}_{\text{rhombic}} + \frac{1}{2}\text{O}_2 = \text{SO}_3(\text{liquid}) + 104.57 \pm 0.07$  kg.-cal.;  $\text{S}_{\text{rhombic}} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 125.79 \pm 0.10$  kg.-cal.;  $\text{S}_{\text{rhombic}} + 2\text{O}_2 + \text{H}_2 = \text{H}_2\text{SO}_4 + 194.1(5) \pm 0.1$  kg.-cal. The heats of dilution per mol. of sulphuric acid with 0.02*N*-hydrogen peroxide are  $\text{H}_2\text{SO}_4, 10.36\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4, 2200\text{H}_2\text{O} + 3.38$  kg.-cal. and  $\text{H}_2\text{SO}_4, 10.36\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4, 2535\text{H}_2\text{O} + 3.49$  kg.-cal.; dilution with  $\text{HCl}, 900\text{H}_2\text{O}$  gives  $\text{H}_2\text{SO}_4, 10.36\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4, 1940\text{H}_2\text{O} + 2.48$  kg.-cal. and  $\text{H}_2\text{SO}_4, 10.36\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4, 1860\text{H}_2\text{O} + 2.46$  kg.-cal. Earlier thermochemical data are criticised, especially those involving the heat of dissolution of sulphur dioxide. H. F. GILLBE.

**Determination of heats of dissociation from pre-dissociation spectra and the heat of dissociation of  $\text{O}_2$ .** G. HERZBERG (Z. physikal. Chem., 1930, B, 10, 189—192).—Since only an upper limiting value of the heat of dissociation can be obtained from pre-dissociation spectra (this vol., 831), Henri's value for the heat of dissociation of oxygen, determined from the pre-dissociation spectra of nitrogen peroxide and sulphur dioxide (this vol., 272, 388), is too high. Frerichs' value of  $5.09 \pm 0.02$  volts (117.3 kg.-cal.) (cf. this vol., 1328) must therefore be regarded as the correct one. On this basis the work of separation of the first oxygen atom from nitrogen peroxide is 71.5 kg.-cal. (3.1 volts). M. S. BURR.

**Heats of dilution and of dissolution of potassium nitrate and chloride, rubidium fluoride, and calcium sulphate at high dilutions.** E. LANGE and J. MONHEIM (Z. physikal. Chem., 1930, 150, 349—369).—The heats of dilution at very low concentrations of potassium nitrate, rubidium fluoride, and calcium sulphate at 25°, and of potassium nitrate at 12.5°, have been measured, and the heats of dissolution of potassium nitrate at 12.5° and 25°, potassium chloride at 12.5°, and calcium sulphate at 25° have been determined. The results, together with the differential heats of dissolution and dilution, are presented in tabular and graphical form for a range of dilutions. H. F. GILLBE.

**Heats of neutralisation by the continuous-flow calorimeter.** L. J. GILLESPIE, R. H. LAMBERT, and J. A. GIBSON, jun. (J. Amer. Chem. Soc., 1930, 52, 3806—3813).—Heats of neutralisation of hydrochloric acid by sodium hydroxide at 20°, 25°, 32°, and 50° and by potassium hydroxide at 20° have been determined by means of the continuous-flow calorimeter (cf. Keyes, Gillespie, and Mitsukuri, A., 1922,

ii, 424). The determinations at 20° are in good agreement with the results of Richards and co-workers (A., 1929, 511; 1922, ii, 425), but values computed by extrapolation from the other temperatures with the aid of temperature coefficients are in poor agreement, probably owing to uncertainties in the temperature coefficients. J. G. A. GRIFFITHS.

**Thermochemistry of compounds in the system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . IV. Heat of dissolution of tricalcium aluminate and its hydrates in hydrochloric acid.** T. THORVALDSON, W. G. BROWN, and C. R. PEAKER (J. Amer. Chem. Soc., 1930, 52, 3927—3936).—Heats of dissolution in  $\text{HCl}, 20\text{H}_2\text{O}$  at 20° of tricalcium aluminate ( $3\text{CaO}, \text{Al}_2\text{O}_3$ ), the hexahydrate ( $3\text{CaO}, \text{Al}_2\text{O}_3, 6\text{H}_2\text{O}$ ), and hydrates containing 8, 10.2, and 11.6 mols. of water per mol. of  $3\text{CaO}, \text{Al}_2\text{O}_3$  have been determined. The values computed for heats of dissolution of the first two in  $\text{HCl}, 200\text{H}_2\text{O}$  are 732.8 and 518.8 g.-cal (20°) per g. of  $3\text{CaO}, \text{Al}_2\text{O}_3$ , respectively. The heat of hydration of the anhydrous compound to the hexahydrate is 214 g.-cal per g., and the heat of formation of  $3\text{CaO}, \text{Al}_2\text{O}_3$  from calcium and aluminium oxides at 20° is 20.7 kg.-cal. per g.-mol. The specific heat of  $\text{HCl}, 20\text{H}_2\text{O}$  compared with water between 16° and 20° is 0.8507 (cf. Richards, Mair, and Hall, A., 1929, 652). J. G. A. GRIFFITHS.

**Conductivity of aqueous solutions of electrolytes in the presence of sucrose.** H. POSSNER (Ann. Physik, 1930, [v], 6, 875—902).—The conductivities of salts in sucrose solutions of high viscosity have been determined. Kohlrausch's square-root law remains valid up to relatively high concentrations of the electrolyte. The concentrations at which deviations from the law occur are found to be lower as the valencies of the salt radicals increase. The observed effects for the influence of concentration on conductivity are found to agree satisfactorily, within the range of validity of the square-root law, with those obtained by calculation on the basis of the theory of Debye and Onsager. The Wien effect (deviation from Ohm's law) and the frequency effect were also investigated. Their dependence on the concentration of the salts shows qualitative agreement with theory. W. GOOD.

**Mobility of some ions containing iron. III. Complex ions of the salts  $\text{Na}_3[\text{Fe}^{++}(\text{CN})_5\text{OH}_2]$  and  $\text{Na}_3[\text{Fe}^{+++}(\text{CN})_5\text{OH}_2]$ .** F. HÖLZL (Monatsh., 1930, 56, 253—260; cf. this vol., 1253).—Measurements have been made at 5° and 25°, over a wide concentration range, of the conductance of solutions of sodium aquopentacyanoferrate, sodium hydroxypentacyanoferrate, sodium aquopentacyanoferroate, and sodium hydroxypentacyanoferroate. These conductance measurements confirm the acid character of the two salts  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{OH}_2] \cdot \text{H}_2\text{O}$  and  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{OH}_2] \cdot \text{H}_2\text{O}$  inferred from titration experiments with sodium hydroxide. These salts behave as monobasic acids and contain one non-co-ordinated water molecule which forms a hydroxonium ion with the hydrogen ion of the acid salt. They are represented best by the formulae  $\text{Na}_3\text{H}_2\text{O} \cdot \text{H}[\text{Fe}(\text{CN})_5\text{OH}]$  and  $\text{Na}_2\text{H}_2\text{O} \cdot \text{H}[\text{Fe}(\text{CN})_5\text{OH}]$ , and the neutralisation of them by sodium hydroxide by the equations  $\text{Na}_3\text{H}_2\text{O} \cdot \text{H}[\text{Fe}(\text{CN})_5\text{OH}] + \text{NaOH} = 2\text{H}_2\text{O} +$



$\text{Na}_3[\text{Fe}(\text{CN})_5\text{OH}]$  and  $\text{Na}_3\text{H}_3\text{O}\cdot\text{H}[\text{Fe}(\text{CN})_5\text{OH}]+\text{NaOH}=2\text{H}_2\text{O}+\text{Na}_3[\text{Fe}(\text{CN})_5\text{OH}]$ .

F. G. TRYHORN.

**Electron-sharing ability of organic radicals. Conductivity of organo-mercuric nitrates and chlorides.** I. B. JOHNS, W. D. PETERSON, and R. M. HIXON (*J. Physical Chem.*, 1930, **34**, 2218—2225; cf. A., 1927, 814).—The conductivities of mercuric methyl, ethyl, butyl, benzyl, *p*-tolyl, and phenyl nitrates in water, and of mercuric ethyl, benzyl, and phenyl nitrates in absolute alcohol have been determined at 25°. In the first series, the values of the dissociation constants  $\times 10^{-4}$  are 75, 72, 12 (approx.), 20, 15, and 8.5, respectively. Conductivity data for mercuric methyl, benzyl, and phenyl chlorides in absolute alcohol, and in alcohol-water mixtures are also recorded. The m. p., approximate decomposition temperatures, and the solubilities in water at 25° are tabulated for the nitrates. The regular diminution of the conductances of aqueous solutions of the nitrates from radical to radical supports the generalisation that the electrical properties of a polar organic derivative should be a function of the electron-sharing ability of the various radicals to which it is linked (*loc. cit.*). L. S. TIEBOLD.

**Electrical conductivities of dilute sodium amalgams at various temperatures.** W. J. DAVIES and E. J. EVANS (*Phil. Mag.*, 1930, [viii], **10**, 569—599; cf. Boohariwalla and others, A., 1929, 1225).—Using pyrex four-electrode tubes the electrical resistances of pure mercury and eleven dilute liquid sodium amalgams have been measured over the range 0.307—5.27 at.-% Na between 0° and 302°. The resistance of an amalgam relative to mercury increases at first with the sodium concentration, then remains fairly constant, and finally diminishes. The resistance-concentration curves are somewhat irregular near the maxima, with indications of small discontinuities. The average temperature coefficient of resistivity of the amalgams is greater than that of pure mercury for the same temperature range, and, for an amalgam of given concentration increases with the temperature range; the variation of this coefficient is somewhat irregular, but the tendency is for an increase with concentration. The results are discussed in relation to Skaupy's theory of the conductivity of amalgams. N. M. BLIGH.

**Ionisation constant of water at 25° from the *E.M.F.* of cells without liquid junction.** E. J. ROBERTS (*J. Amer. Chem. Soc.*, 1930, **52**, 3877—3881).—From determinations of the *E.M.F.* of the cells  $\text{Pt}, \text{H}_2 | \text{NaOH}(m_1) + \text{NaCl}(m_2) | \text{AgCl}, \text{Ag}$  and  $\text{Pt}, \text{H}_2 | \text{HCl}(m_3) | \text{AgCl}, \text{Ag}$  at 25° ( $m_1=m_2=0.0063$ — $0.135M$ , and  $m_3=0.0016$ — $0.138M$ ) the ionisation constant of water at 25° is computed to be  $0.988 \pm 0.004 \times 10^{-14}$ . Similar measurements with the aqueous medium containing sodium chloride with a weak acid and its sodium salt in equimolar proportions lead to the ionisation constant,  $K_A$ , of the acid if  $K_A$  is between  $10^{-5}$  and  $10^{-9}$ . J. G. A. GRIFFITHS.

**Platinum-hydrogen electrode.** M. TRIALINGER and M. VOLMER (*Z. physikal. Chem.*, 1930, **150**, 401—417).—Measurements of the cell  $\text{Pt}, \text{H}_2 | 0.01N\text{-H}_2\text{SO}_4 | \text{PbO}_2$  show that polished platinum exhibits

very similar behaviour to that of readily polarised metals such as iron and nickel, but the passivity is caused, not by metallic ions, but by hydrogen ions. The current falls rapidly at first to about 70% of its initial value, remains constant for a time, falls again rapidly, and then rises abruptly; the frequency of the cycle diminishes with time. In presence of arsenious oxide or of sulphur dioxide the frequency diminishes considerably, but the amplitude remains unchanged, and in presence of hydrogen sulphide the current falls steadily to zero; hydrogen peroxide and lead ions are without influence. If the electrolyte contains hydrochloric acid at *N*-concentration the frequency decreases, and the periodic fluctuations appear at higher currents, but with 0.01*N*-hydrochloric acid the electrode becomes completely passive. The polarisation is induced by a unimolecular layer of oxygen resembling that formed on tungsten filaments at high temperatures, and the layer becomes thicker and more stable as the polarisation progresses. The oxygen film inhibits amalgamation of the platinum surface. Unlike the passive films on base metals, the oxygen film on platinum cannot be detected by optical methods, but as the hydrogen layer increases in thickness optical properties become evident. By cathodic dispersion, platinum films of a spongy structure are obtained. H. F. GILLBE.

**Chloroplatinate-chloroplatinite electrode.** E. R. SMITH (*Bur. Stand. J. Res.*, 1930, **5**, 735—740).—A platinum electrode immersed in 0.1*N*-potassium chloride solution containing a mixture of potassium chloroplatinate and potassium chloroplatinite has a definite *E.M.F.* corresponding with the electrode reaction  $\text{PtCl}_6^{--} + 2\text{Cl}^- = \text{PtCl}_6^{--} + 2e^-$ . This *E.M.F.* was measured against the 0.1*N*-calomel electrode and extrapolated to pure 0.1*N*-potassium chloride solution. The experimental results show that this electrode functions reversibly.

W. E. DOWNEY.

**Normal potential of beryllium.** M. PRYTZ (*Z. anorg. Chem.*, 1930, **193**, 113—118).—Dilute beryllium amalgams have been prepared by electrolysis at 0° of a paste made from hydrochloric acid and a large excess of beryllium hydroxide, using a *P.D.* of 7 volts and a current of 1 amp. Calculations based on measurement of the *P.D.* between the amalgam and beryllium, employing a solution of beryllium acetylacetonate in propylamine, yield for the normal potential of beryllium 1.9(6) volts. H. F. GILLBE.

**Concentration cells in ethyl alcohol.** V. Cells without liquid junctions. J. R. PARTINGTON and H. G. SIMPSON (*Trans. Faraday Soc.*, 1930, **26**, 625—634; cf. A., 1929, 269).—The liquid junction in the cell  $\text{Ag} | \text{AgI}, \text{NaI} c_1, | \text{NaI} c_2, \text{Ag} | \text{Ag}$ , where  $c_1$  and  $c_2$  are the concentrations of sodium iodide in ethyl-alcoholic solution, have been eliminated by separating the sodium iodide solutions by means of (a) a saturated solution of potassium thiocyanate and (b) two streaming sodium amalgam electrodes receiving amalgam from the same reservoir, one electrode being in each solution. An attempt to eliminate the junction by means of a thin glass membrane was not successful. The *E.M.F.* of the cell agrees with the formula  $E = (\sqrt{RT/F}) \log \lambda_1 c_1 / \lambda_2 c_2$ , where  $\lambda_1$  and  $\lambda_2$  are the

equivalent conductivities of the sodium iodide solutions at concentrations  $c_1$  and  $c_2$ , and  $\nu$  is 1 in the case of (a) and 2 in the case of (b). Assuming the formula  $E = (2RT/F) \log_e f_1 c_1 / f_2 c_2$ , in which  $f_1$  and  $f_2$  are the activity coefficients of the sodium iodide at concentrations  $c_1$  and  $c_2$ , for the *E.M.F.* of the cell with the amalgam electrode, the equation obtained for the activity coefficient of sodium iodide in ethyl-alcoholic solutions of concentrations between 0.1 and 0.01M at 25° is  $-\log_{10} f = 1.63\sqrt{c} - 2c$ . It is concluded that sodium iodide is not completely dissociated in these solutions.

E. S. HEDGES.

**Interaction of molecules with the silver ion.** F. K. V. KOCH (Phil. Mag., 1930, [viii], 10, 559—564).—The free energies of solvation of the silver ion have been derived ( $A_E$ ) from measurements of the variation of the electrode potential with the solvent in ten organic liquids (cf. A., 1928, 370), and are compared with those ( $A_T$ ) calculated by Born's method for the ideal case assuming that the ion is a rigid sphere in a continuous medium of dielectric constant  $\epsilon$ . Since the absolute value of  $A_E$  cannot be determined experimentally,  $A_E$  is chosen for acetone so that  $A_E = A_T$ , and the values for the other solvents are found by difference. Uncertainties due to values of  $\epsilon$  and the radius of the silver ion are discussed. The values of  $A_c - \chi$ , where  $A_c = A_E - A_T$  and  $\chi$  is a constant, fall into three classes, which merge into one another, and show that the transition from solvation to complex formation is gradual. The results are discussed.

N. M. BUGH.

**Electron-sharing ability of organic radicals. Concentration cells using organo-mercuric iodides.** I. B. JOHNS and R. M. HIXON (J. Physical Chem., 1930, 34, 2226—2235; cf. this vol., 1525).—The reaction  $2RHgI \rightleftharpoons R_2Hg + HgI_2$ , where R is an organic radical, has been shown to be reversible. Concentration cells of the type  $Hg|HgI_2(0.005M), KI(0.05M)||2RHgI \rightleftharpoons R_2Hg + HgI_2(c), KI(0.05M)|Hg$  have been investigated and the value of  $c$  [Hg] has been determined on the assumption that the organo-mercuric ions give no *E.M.F.* with metallic mercury. The equilibrium constants of the above reaction for the cells in which R is methyl, ethyl, butyl, benzyl, tolyl, and phenyl can be correlated with the dissociation constants of the acid and amine derivatives of the same radicals. The *E.M.F.* of the cells  $Hg|HgI_2(0.005M), KI(0.05M)||HgI_2(c), KI(0.05M)|Hg$  in alcoholic solution are recorded.

L. S. THEOBALD.

**Apparatus for determining potentials of cells with very high internal resistance.** G. SCHWARZENBACH (Helv. Chim. Acta, 1930, 13, 865—869; cf. Stadie, A., 1929, 1262).—In a Wheatstone bridge in which two thermionic valves form one pair of arms, a balance is obtained by means of adjustable resistances forming the other two. If the same grid potential as was previously used is now applied to one of the valves through a potentiometer system containing a cell with a very high internal resistance and the potentiometer adjusted until a balance is again obtained, the potentiometer reading does not give the true *E.M.F.* of the cell, owing to the variation with external resistance of the (anode current/grid potential)

characteristic from its normal value; but by carrying out two measurements, in the second of which the connexions of the potentiometer system are reversed, the additional potential required to produce a balance is in one case added to, and in the other subtracted from, the true potential of the cell, which is therefore the arithmetic mean of the two potentiometer readings. The method, which is of especial value in working with glass electrodes, was tested on a standardised cell through resistances varying from 3 to 26 megohms, the maximum deviation found being 0.3 millivolt.

F. L. USHER.

**Activity of protons and electrons in any solvent.** G. SCHWARZENBACH (Helv. Chim. Acta, 1930, 13, 870—896).—Theoretical. An expression formally similar to that which connects the potential of an indifferent metal electrode with the activities of the constituents of a mixture of oxidising and reducing agents in which it is immersed is proposed for the potential of a hydrogen electrode in solutions of an acid, viz.,  $E = E_0 + (RT/F) \log_e (\text{acid}/\text{base})$ , in which the words "acid" and "base" refer to the molar concentrations, multiplied by the respective activity coefficients, of substances which can respectively donate and accept protons. The "normal acidity potential,"  $E_0$ , is the potential of a hydrogen electrode in an equimolecular (with respect to activities) mixture of the "acid" and "base," and depends on the dielectric constant of the solvent but not on its acidity or basicity, for which reason the above expression is more generally applicable than the functions hitherto employed. The formula is used to calculate hydrogen potentials in solutions of hydrogen chloride in mixtures of water and alcohol, and the values so obtained agree with the measurements of Hardman and Lapworth (J.C.S., 1911, 99, 2242). The behaviour of acids in non-basic solvents is explained partly by the relatively large effect of minute traces of basic impurities, and partly by a "self-buffering" action due to their assumption of amphoteric properties when dissolved in non-aqueous solvents. This conception is shown to account for the increase of the molecular conductivity of acids with concentration, observed in non-basic solvents such as ether or hydrocarbons.

F. L. USHER.

**Measurements of potential of the hydrogen electrode in solutions of acids in ether.** G. SCHWARZENBACH (Helv. Chim. Acta, 1930, 13, 896—907).—The potential of the hydrogen electrode in ethereal solutions of sulphuric, hydrochloric, acetic, and trichloroacetic acid have been determined. The measurements are regarded as only approximately quantitative, on account of the large variations observed and the magnitude of some of the liquid contact potentials. The reference electrodes used were (a) a calomel electrode in a saturated solution of phenyltrimethylammonium chloride in chloroform or (b) a mercurous sulphate electrode in a 2N-solution of sulphuric acid in ether. The acidity of all the acids studied is much greater in ether than in water, sulphuric acid being more than 10,000 times as strong in the former as in the latter. The phenomenon of "self-buffering" was observed in all the acids excepting trichloroacetic, and is so marked in sulphuric acid

that the acidity is nearly independent of the concentration. The acidity of trichloroacetic acid rises steeply with concentration, and in 2*N* ethereal solution is equal to that of ethereal sulphuric acid and greater than that of ethereal hydrochloric acid. The acidity of ethereal sulphuric acid is lowered by the addition of either alcohol or acetic acid, the effect varying directly with the amount added, and inversely with the concentration of sulphuric acid. F. L. USHER.

**Polarographic studies with the dropping mercury cathode. XV. Positive and negative maxima on current-voltage curves.** J. HEYROVSKÝ and M. DILLINGER (Coll. Czech. Chem. Comm., 1930, 2, 626—638).—The maxima exhibited by the current-voltage curves obtained during the electrolysis with the dropping mercury cathode of solutions containing reducible substances may be positive, when the cathodic deposition potential is greater than the electrocapillary zero, or negative, when the deposition potential is algebraically less than the zero. The type in any given case is indicated by the shape of the electrocapillary curve obtained with the polarised dropping mercury cathode. The positive maxima only are suppressed by acid dyes, negative colloidal micelles, and by anions, for which a law analogous to that of Hardy and Schulze is valid, viz., the dilution at which the maximum vanishes is proportional to the valency of the ion. The negative maxima only are suppressed by multivalent cations. At equivalent concentrations the suppressive powers of the hydroxyl and sulphate ions are identical and are much greater than that of the nitrate ion. In certain cases there appears to be a protective action produced by the ions of one metal on the maxima of another.

H. F. GILLBE.

**Theory of passivity. XII. Passage of current through anodes covered with an insoluble surface layer.** W. J. MÜLLER (Monatsh., 1930, 56, 191—196; cf. A., 1929, 146, 886).—By the application of Kirchhoff's law to the distribution of the current between the surface film and the pores of a coated anode, an expression is derived for the magnitude of the current in the pores in a state of stationary equilibrium. The formula shows that with a surface film of low conductance the whole of the current is concentrated in the pores. With increasing conductance of the film the current tends to shift towards the surface, and, with a good conductor, only a small percentage of the total current remains in the pores. There is practically no current transfer across the interface metal-electrolyte in the pores of the surface layer until the discharge potential of the anion is reached, and it amounts at most to a few milliamperes. These views are applied qualitatively to the anodic behaviour of iron in strongly alkaline solutions.

F. G. TRYHORN.

**Electrochemical behaviour of metals. I. Passivity and corrosion of iron.** J. F. CHITTM (J. Physical Chem., 1930, 34, 2267—2285).—Defining passivity as a tendency on the part of iron to exhibit a potential less than that of an iron amalgam under the same conditions, a theory of passivity has been developed from a consideration of the curves which are obtained when samples of iron are immersed in

solutions of varying hydrogen-ion concentration. Soft irons, annealed and alloy steels are in equilibrium with the ions  $\text{Fe}(\text{OH})^+$  between  $p_{\text{H}}$  1.0 and 6.0 when no oxidising agent is present. The slope of the curve is one half that of the hydrogen electrode and its position is different for chlorides and sulphates. Tempered steels are in equilibrium with a higher oxide of iron between  $p_{\text{H}}$  3.0 and 6.0, and in the presence of oxidising agents, soft iron as well as annealed and alloy steels are in equilibrium with the ion  $\text{Fe}(\text{OH})^+$  between  $p_{\text{H}}$  1.0 and 3.0, and with the higher oxide of iron between  $p_{\text{H}}$  4.0 and 6.0. When the  $p_{\text{H}}$  is greater than 6.0 the species of iron with which the metal is in equilibrium is soluble and its solubility increases as the cathodic potential increases to a nearly constant value. In such cases iron behaves as an electrode:  $\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{FeO}_3^- + 6\text{H}^+ + 4e$ ; in cases where the oxide dissolves or is reduced it behaves as an electrode:  $\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{FeO}_2 + 4\text{H}^+ + 4e$ . The iron electrode has its greatest anodic potential when it is covered with a film of water and has its greatest cathodic potential when covered by a solution of a strong acid or an oxidising agent. The general explanation of passivity lies in the behaviour of iron as a higher oxide electrode and its solubility in the higher state of oxidation. The nine reactions involved are summarised. The detailed mechanism of corrosion processes based on this theory of passivity is considered with reference to the  $p_{\text{H}}$  of the solution. The known characteristics of passive iron, many of which are in accord with the present theory, are summarised. Various theories of corrosion are also discussed and the oxide film theory of passivity is criticised and held to be untenable.

L. S. THEOBALD.

#### Time factor in anodic passivation of metals.

W. J. SHUTT and V. J. STIRRUP (Trans. Faraday Soc., 1930, 26, 635—642).—The passivation of a gold anode in 2*N*-hydrochloric acid has been studied by the oscillographic method and a few experiments on the passivation of an anode of Swedish iron in 2*N*-sulphuric acid were also carried out. The electrolyte was stirred in order to avoid the formation of relatively thick layers of salt at the anode surface and under these conditions the rise of potential on passivation was almost instantaneous. A study was made of the "time of passivation," representing the time elapsing between the start of electrolysis and the moment the passive potential is developed, and also the "time of recovery," or reversion of the anode potential to the normal value after stoppage of the passivating current. The time of passivation increases with rise of temperature and is inversely proportional to the current density diminished by some constant amount which appears to represent the minimum current density which will bring about passivation at all. The experimental curves diverge from the rectangular hyperbola form at high current densities, the observed times being less than those required by the equation. The time of recovery is independent of the current density, but decreases rapidly with rise of temperature. The results are considered to support the oxygen theory of passivity.

E. S. HEDGES.

**Bimolecular reactions.** H. B. FRIEDMAN and H. K. FULMER (J. Amer. Chem. Soc., 1930, 52,

3973—3974).—Mathematical. The expression for the velocity coefficient when only one reactant is present is derived from that for the case involving two reactants at different initial concentrations.

J. G. A. GRIFFITHS.

**Velocity of ignition of gaseous mixtures.** K. BUNTE and W. LITTELSCHIEDT.—See B., 1930, 1053.

**Ignition of electrolytic gas.** F. HABER (Naturwiss., 1930, 18, 917).—An error in previous work (A., 1929, 278) is pointed out, making the results consistent with other work on the influence of hydrogen atoms on the explosion of hydrogen-oxygen mixtures.

E. S. HEDGES.

**Explosions in detonating gas mixtures. I. Calculation of rates of explosions in mixtures of hydrogen and oxygen and the influence of rare gases.** B. LEWIS and J. B. FRIAUF (J. Amer. Chem. Soc., 1930, 52, 3905—3920).—The reaction chain theory developed by Lewis (this vol., 1255) affords an interpretation of the extremely rapid chemical reaction in the wave front, but does not lead to the quantitative prediction of the velocity of detonation waves slower than that corresponding with the mixture of optimum composition. By means of the theory of Chapman (A., 1899, ii, 591) and Jouguet (A., 1925, ii, 1169) and employing recent thermal data, velocities of the detonation wave have been calculated for explosive mixtures of hydrogen and oxygen diluted with several gases. It is assumed that the composition of the burned gases corresponds with equilibrium for the dissociation of water vapour into hydrogen and oxygen or hydrogen and hydroxyl, and the dissociation of molecular into atomic hydrogen at the temperature and pressure attained in the wave front. The velocities calculated for stoichiometric mixtures of hydrogen and oxygen diluted with 1—5 mols. of oxygen or nitrogen generally deviate less than 1% from the experimental values recorded by Dixon and others. The less satisfactory agreement between calculated and observed values for mixtures diluted with hydrogen may arise from incomplete reaction in the wave front.

The theory requires that if the explosive mixture is diluted with helium, the velocity of the detonation wave shall increase, but with argon the contrary shall occur. This has been verified qualitatively in preliminary experiments by means of direct and Schlieren photographs of the detonation waves. If the threefold dissociation equilibrium in water vapour is not considered, much poorer agreement is obtained between calculated and observed velocities in all the cases investigated.

J. G. A. GRIFFITHS.

**Ignition of electrolytic gas [ $2H_2 + O_2$ ] by quartz or porcelain, under reduced pressure.** H. N. ALYEA and F. HABER (Z. physikal. Chem., 1930, B, 10, 193—204).—If currents of hydrogen and oxygen cross each other at right angles, at temperatures between 435° and 540° and at pressures of 10—200 mm., no ignition takes place in the free gas space. At walls of quartz, porcelain, or glass, however, between the same temperatures and at the lower pressures considered, explosion readily occurs. Iron and copper have a similar effect, but aluminium is inactive. A variation in the procedure was there-

fore made by allowing a hydrogen-oxygen mixture of the required composition to pass through a heated aluminium tube into a large space containing nitrogen at the required pressure. When necessary, a piece of porcelain tube could be inserted in the aluminium tube and heated at the same temperature. Previous treatment of the porcelain wall with hydrogen for some time reduces its power to cause explosion, but increases the tendency to bring about quiet combination. Treatment with oxygen has the opposite effect.

M. S. BURR.

**Inflammability of hydrogen. XI. Prevention of flame propagation in hydrogen-air mixtures by wire gauze.** Y. TANAKA and Y. NAGAI (J. Soc. Chem. Ind. Japan., 1930, 33, 361—364B).—The extinction of the flame in hydrogen-air mixtures by copper gauze is facilitated by the presence of small quantities of tin or lead tetraethyl, or of benzene, owing to the rise of the theoretical flame propagation temperature. The size of the mesh necessary for extinction diminishes with increase of the content of the anti-knock compound up to about 1%, with decrease of the hydrogen percentage from 60 to 20%, and with decrease of the speed of the flame.

H. F. GILLBE.

**Gaseous oxidations. I. Homogeneous uncatalysed reaction between oxygen and acetylene.** G. B. KISTIAKOWSKY and S. LENHER (J. Amer. Chem. Soc., 1930, 52, 3785—3796; cf. Bone and Andrew, J.C.S., 1905, 87, 1232).—The oxidation of acetylene by oxygen at temperatures between 253° and 356° has been investigated in a pyrex vessel by a flow method. The yields of all products decreased with increased rates of flow, but the proportions changed in such a manner as to indicate that the reaction proceeds by the following steps: acetylene  $\rightarrow$  glyoxal  $\rightarrow$  formaldehyde  $\rightarrow$  formic acid. The gaseous products consisted mainly of carbon monoxide with some carbon dioxide and hydrogen; the first probably originated from direct decomposition of glyoxal, the second from oxidation or decomposition of formic acid, whilst the origin of the traces of hydrogen is uncertain. The velocity of reaction is proportional to the square of acetylene concentration and is very slightly retarded by oxygen. The reaction exhibits an induction period and is homogeneous and of the chain type, since packing the bulb with glass leads to a marked decrease of reaction rate. The increase of surface leads to a predominating heterogeneous reaction with no induction period. The main direct products are carbon dioxide and water. The velocity is approximately independent of rate of flow and directly proportional to the concentrations of oxygen and acetylene.

J. G. A. GRIFFITHS.

**Thermal decomposition of nitrous oxide.** C. N. HINSHELWOOD (Z. physikal. Chem., 1930, B, 10, 157—158).—In reply to Volmer and Kummerov (this vol., 1255), it is contended that a unimolecular reaction and a bimolecular reaction probably occur simultaneously, the decomposition as a whole being effectively bimolecular except at very low pressures.

R. CUTHILL.

**Low-temperature oxidation. III. Lag in ignition of some hydrocarbons.** J. S. LEWIS

(J.C.S., 1930, 2241—2254).—Anomalies are found if the ignition temperature of a hydrocarbon is taken as a measure of its ignitability. It is shown from experiments made by the crucible method that the lag in the ignition, i.e., the interval of time between the rapid heating of the hydrocarbon to or above the ignition temperature and the appearance of the flame, is a much more trustworthy indication of the ignitability, since it is a function of the mol. wt. or the boiling range. Metals such as copper, aluminium, and lead at about 230° raise the temperature of ignition and increase the lag, although at higher temperatures the reverse happens. Both pro-knock compounds, such as nitrogen peroxide and amyl nitrite, and anti-knock compounds, such as lead tetraethyl and aniline, raise the ignition temperature and increase the lag at low temperatures, but at high temperatures the former reduce the lag, whilst the behaviour of the latter is unchanged. When members of these two classes are present together each neutralises the effect of the other.

F. J. WILKINS.

**Kinetics of gaseous oxidation reactions.** R. FORT and C. N. HINSHELWOOD (Proc. Roy. Soc., 1930, A, 129, 284—298).—To investigate the influence of chemical configuration on the mechanism of oxidation reactions, the oxidation of methane, methyl alcohol, and formaldehyde has been studied by the method previously described (Hinshelwood and Thompson, A., 1928, 483). The influence of concentration and of surface on the rate of reaction was determined, and for methyl alcohol the relation between the reaction rate and size of vessel was investigated. All these substances exhibited an induction period, which was considerable with methane; the reaction rate varied greatly with the concentration of the combustible gas, but oxygen had relatively small influence. The reaction rate decreased as the capacity of the reaction vessel decreased. The results are best explained by the assumption of a chain mechanism, which does not depend on the particular configuration of the reacting molecules as long as the requisite energy is available. An approximate quantitative treatment is attempted for methyl alcohol. In the oxidation of this substance the chains appear to end only at the walls of the vessel, in contrast with benzene, where they end principally in the gas unless the vessel is very small; with methyl alcohol the efficiency of the walls in breaking the chains depends on a layer of adsorbed oxygen. Heats of activation are calculated in the usual way and found to be 61,500, 62,500, and 20,600 g.-cal. for methane, methyl alcohol, and formaldehyde, respectively.

L. L. BIRCHENSHAW.

**Kinetics of chlorine bleaching.** H. KAUFFMANN.—See B., 1930, 1062.

**Kinetics of the reduction of permanganate by formaldehyde in neutral solution.** J. HOLLETA and A. MUTSCHIN (Z. physikal. Chem., 1930, 150, 381—400).—In neutral solution the reduction of 0.016—0.008*M*-potassium permanganate solution by formaldehyde is a reaction of the second order and is in accordance with the equation  $4\text{MnO}_4' + 3\text{CH}_2\text{O} = 4\text{MnO}_2 + 2\text{HCO}_3' + \text{CO}_3' + 2\text{H}_2\text{O}$ ; in presence of an excess of formaldehyde the reduction proceeds

further, and if a large excess be present the reaction is  $2\text{MnO}_4' + 2\text{CH}_2\text{O} = \text{Mn}_2\text{O}_3 + 2\text{HCO}_3' + \text{H}_2\text{O}$ . The reduction involves two consecutive reactions, which are both bimolecular, of which the first results in the formation of formic acid and the second in the rapid oxidation of the acid. The bimolecular velocity coefficient of the total reaction changes rapidly in the early stages of the reaction on account of the production of hydrogen ions, but this effect disappears on addition of a relatively small quantity of hydroxyl ions, which accelerate considerably the total reaction. In the later stages of the reaction the velocity coefficient increases as a result of the rapid oxidation of the formic acid. The influence of neutral salts is only partly in accordance with theory, and increases in the later stages of the reaction, but the variation is due only partly to the occurrence of consecutive reactions.

H. F. GILLBE.

**Chain reactions produced by physical structure.** N. VON RASCHESKY (Z. Physik, 1930, 64, 556—558; cf. this vol., 420, 698).—The hysteresis phenomena of drops containing more than one substance have been studied. Under certain conditions the substances concerned can form themselves into a definite sequence only, so that the formation of another substance can set in only if a certain amount of the original substances is present. These circumstances are quite independent of the chemical nature of the reactions concerned and are governed only by the interplay of diffusion and solution phenomena.

W. R. ANGUS.

**Velocity of decomposition of diazo-compounds in water.** VI. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1930, 33, 358—360B; cf. this vol., 1128).—The velocity coefficients at 0° (*k*) and the temperature coefficients of the velocity (*A*) have been determined for the decomposition in aqueous solution of the following diazo-compounds: *m*-nitrobenzenediazonium chloride, *k*  $4.0 \times 10^{-8}$ , *A* (60—80°) 13,600; *p*-nitrotoluene-*o*-diazonium chloride, *k*  $6.8 \times 10^{-7}$ , *A* (40—60°) 12,750; *p*-nitrobenzenediazonium chloride, *k*  $6.9 \times 10^{-8}$ , *A* (50—70°) 14,150; the calculated velocity coefficients are tabulated for 0—110°, 0—90°, and 0—100°, respectively.

H. F. GILLBE.

**Speed of reaction of benzoyl peroxide with secondary amines.** O. CIALTIKIAN (Bull. univ. état R.S.S. Armenie, 1930, No. 5, 253—258).—The reactions  $\text{NHR}_2 + \text{Bz}_2\text{O}_2 \rightarrow \text{NR}_2\text{OBz} + \text{BzOH}$ , where R=Et, Pr, Bu<sup>n</sup>, or CH<sub>2</sub>Ph, and the reaction between benzoyl peroxide and piperidine are bimolecular, except that involving dibenzylamine. The longer is the alkyl radical the slower is the reaction. When the carbon chain is closed the velocity increases 15-fold.

CHEMICAL ABSTRACTS.

**Shrinkage of metallic leaves on heating.** I. SAWAI, Y. UEDA, and M. NISHIDA (Z. anorg. Chem., 1930, 193, 119—132; cf. this vol., 991).—The velocities of shrinkage of gold and silver foils in a vacuum, and in atmospheres of carbon dioxide, nitrogen, and air, have been investigated. At constant temperature (600°) the velocity of shrinkage of gold leaf falls rapidly with time and becomes zero after 40—60 min., the effect being most marked with very thin foils ( $1.2 \times 10^{-4}$  mm.); after shrinkage the foil

shows minute cracks and becomes translucent, but recrystallisation is not the main cause of the shrinkage. The shrinkage temperatures of the thinnest gold and silver foils studied are, in a vacuum 600° and 725°, in nitrogen 450° and 600°, in carbon dioxide 400° and 600°, and in air 250° and 220–270°, according to the rate of heating. The shrinkage coefficients are of the same order in vacuum and in nitrogen, but are greater in carbon dioxide and air. Adsorption of gas, and particularly of oxygen, influences the shrinkage considerably, especially in the case of silver foil. The shrinkage temperature may be defined as that at which the velocity of shrinkage becomes greater than the velocity of thermal expansion. The ultimate cause of the effect, which is purely physical, is discussed; dissolution of oxygen in the foil is a possible cause.

H. F. GILLBE.

**Changes of length of glass threads at high temperatures.** I. SAWAI and M. NISHIDA (*Z. anorg. Chem.*, 1930, 193, 133–143; cf. A., 1929, 756).—Measurement of the rate of change of length of glass threads at constant high temperature (600–625°) shows that  $\log(l_t/l_0) = kt$ , where  $l_t$  is the length at time  $t$ ,  $l_0$  is the original length, and  $k$  is constant.  $k$  has been measured as a function of the load on the thread at 600°, 625°, and 675°; at the lowest temperature there is no contraction even at zero load, but at all temperatures there are two inflexion points on the  $k$ -load curve. The force of contraction of threads from 0.7 to 0.27 mm. diameter is smaller at 600–625° than at 650–675°, but the viscosity diminishes continuously as the temperature rises. Calculation of the critical force from the minimum load necessary to cause a change of length shows that at relatively low temperatures (550–600°) the glass becomes plastic. It is suggested that between the critical temperature of the glass, i.e., the temperature of maximum contraction, and the aggregation temperature, there lies the temperature above which the glass is a viscous liquid and below which it is plastic; at this temperature the chain arrangement of the molecules completely breaks down. The theoretical significance of the results is further discussed.

H. F. GILLBE.

**Rate of dissolution of magnesium in acids.** M. KILPATRICK, jun., and J. H. RUSHTON (*J. Physical Chem.*, 1930, 34, 2180–2186).—The rate of dissolution of magnesium in strong acids such as hydrochloric and in buffered solutions of weak acids such as formic, acetic, glycollic, and aromatic acids has been determined at  $25 \pm 0.01^\circ$  by measuring the volume of gas evolved. With the buffered solutions of the weak acids the rate is practically proportional to the concentration of acid and independent of the concentration of the buffering ion. With the strong acids, the rate of evolution of hydrogen is proportional to the ion  $H_3O^+$  and the effect of added electrolyte (salt) is small. The reaction is unimolecular and there appears to be a general relationship between the velocity coefficient and the acid strength as measured by  $K_A = [\text{Base}][H_3O^+]/[\text{Acid}]$ , using Brønsted's definition of an acid.

L. S. THEOBALD.

**Corrosion of light metals and alloys.** R. CAZAUD and others.—See B., 1930, 1072.

**Influence of radiation on combustion of colloidal powders in a closed vessel.** H. MURAOV (*Compt. rend.*, 1930, 191, 713–715).—It has already been shown (cf. B., 1926, 722; 1928, 770) that for high densities of loading the integral  $\int p dt$  ( $p$ =pressure,  $t$ =time) is practically constant, but for low densities falls rapidly to less than half the "constant" value. To explain this on the theory that the energy necessary to decompose the powder is imparted by molecular collisions, the hypothesis that in such cases the requisite additional energy is imparted by radiation from the explosion gases is examined. Experiments with a powder of very low explosion temperature (2020° Abs.) show, however, that the energy supplied in this way, on the most favourable estimate, is not more than half what is requisite.

C. A. SILBERRAD.

**Catalysis.** A. W. PORTER (*Nature*, 1930, 126, 349).—The values which  $E$ , the energy of activation of reacting molecules, may have in various cases are discussed.  $E$  may retain its normal value and not suffer the reduction which the facts of catalysis are generally supposed to demand.

L. S. THEOBALD.

**Influence of hydrogen ions on the Fenton reaction.** W. H. HATCHER and M. G. STURROCK (*Canad. J. Res.*, 1930, 3, 214–223).—The course of the oxidation of tartaric acid by hydrogen peroxide in presence of ferrous sulphate as catalyst has been studied by observation of the conductivity changes of the solution. The smallness of the yield of dihydroxymaleic acid, which does not exceed 30%, is due partly to inactivation of the catalyst by the increased hydrogen-ion concentration of the solution, caused by the relatively strong dihydroxymaleic acid. The  $p_H$  of the reaction mixture shows a sudden decrease when about 60% of the theoretically necessary quantity of hydrogen peroxide has been added, and from the effect of heat on the solution it appears that a stable acid, probably oxalic, is formed at this stage. The remaining 30% loss is probably the result of the production of the tautomeric keto-form of the dihydroxymaleic acid.

H. F. GILLBE.

**Decomposition of hydrogen peroxide under the simultaneous influence of several catalysts.** I. IRON and copper salts. E. I. SPITALSKI and B. A. KONOVALOV (*J. Russ. Phys. Chem. Soc.*, 1930, 62, 1033–1049).—The catalytic action of copper salts on the decomposition of acid solutions of hydrogen peroxide is insignificant; the addition of copper to systems containing iron catalyst greatly enhances the action of the latter. In such systems the velocity of reaction at first rises to a maximum, and then falls linearly, as for a reaction of the first order. The velocity is directly proportional to the concentration of peroxide at the point of maximum velocity. When fresh portions of peroxide are added to systems in which the reaction has proceeded almost to completion, the velocity of reaction is greater than when fresh catalyst is taken. This effect is not observed if the system is first boiled, pointing to the presence of an active intermediate compound. The velocity of reaction is within certain limits proportional to the concentration of copper (constant values being obtained in 0.02M solutions of copper) and to that



of iron; in the presence of iron salts alone it is also inversely proportional to the hydrogen-ion concentration. The presence of traces of impurity in the peroxide, undetectable by ordinary analytical methods, greatly reduces the action of the mixed catalysts.

R. TRUSZKOWSKI.

**Eighth report of the Committee on Contact Catalysis.** J. C. W. FRAZER (J. Physical Chem., 1930, 34, 2129—2179; cf. A., 1929, 1488).—A general survey of the field is made. Subjects of especial prominence are the application of quantum mechanics to the elucidation of the nature of the homopolar linking and the activation occurring at a catalytic surface, the theoretical views of Balandin (A., 1929, 1245) and of Lennard-Jones and Dent (A., 1928, 8), and, finally, the polarising influence of surfaces.

L. S. THEOBALD.

**Heterogeneous catalysis and chemical sorption.** E. SAUTER (Z. Elektrochem., 1930, 36, 874—881).—A general discussion of the results of recent work on adsorption and catalysis at solid surfaces.

F. L. USHER.

**Mechanism of catalysis.** L. V. PISARSHVSKI (Ber. Ukrain. wiss. Forsch.-inst. physikal. Chem., 1929, 2, 10—35).—Adsorption plays an important part in the mechanism of heterogeneous catalysis. Also in the surface of the catalytic metal which possesses groups of unactivated electrons there occurs a transition of electronic isomerides from the "active" to the "passive" electrons, with simultaneous development of a state of equilibrium between the isomerides. An active isomeride is one which has dissociated into ions and electrons. The influence of electronic isomerisation on catalytic action is discussed.

CHEMICAL ABSTRACTS.

**Influence of the removal from catalytic agents (through pressure reduction) of adsorbed gases on the rate of catalysis of hydrogen peroxide.** V. A. ROITER (Ber. Ukrain. wiss. Forsch.-inst. physikal. Chem., 1929, 2, 42—54).—The catalytic decomposition of hydrogen peroxide proceeds more rapidly under reduced than under normal pressure, but excessive reduction of pressure and removal of adsorbed gases irreversibly decreases the activity of the catalyst. Platinum foil saturated with hydrogen remains an active catalyst for many hours regardless of the generation of oxygen; during the catalytic action oxygen is absorbed only very slowly. It is possible that the catalytic effect is promoted by the presence of a small amount of adsorbed gas.

CHEMICAL ABSTRACTS.

**Catalytic reduction of carbon monoxide at ordinary pressure.** VI. Hydrocarbon-forming action of iron catalyst. S. KODAMA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 169—183).—Iron-copper catalysts containing a small quantity of sodium carbonate convert the carbon monoxide in a mixture with hydrogen into carbon dioxide, coloured hydrocarbon oils (probably high-molecular or unsaturated hydrocarbons) being produced at the same time. The final gas always contains more hydrogen than carbon monoxide. Water is not formed, contrary to the results of Berl and Jüngling (B., 1930, 650).

Cobalt catalysts cause reaction at lower temperatures than iron catalysts, but the reverse results are obtained. The best yield of liquid products (illuminating oil and benzine) is obtained with a catalyst comprising equal parts of iron and copper together with a small quantity of sodium carbonate. The alkali appears to be essential; in its absence only lower hydrocarbons are formed. The catalytic action of copper-iron catalysts is impaired by the addition of magnesium oxide.

S. K. TWEEDY.

**Fission of carbon monoxide by cobalt.** H. A. BAHR and V. JESSEN (Ber., 1930, 63, [B], 2226—2237).—Weighed quantities of cobalt oxide of differing origin are treated with hydrogen in the reaction vessel until constant in weight. The metallic powder is heated at a fixed temperature in carbon monoxide (99.2% CO, 0.8% N) at a steady rate of 0.75 litre per hr. The process of carburisation is followed by weighing the vessel. At temperatures below about 225°, finely-divided metallic cobalt is unable to catalyse the decomposition of carbon monoxide. Reaction appears to occur only when the metal is converted into the carbide  $\text{Co}_3\text{C}$  with 9.24% C. Above 225° the carbide decomposes at a rate which increases with rising temperature with separation of part or all of the carbide carbon in the elementary form. In consequence of this behaviour, the amount of carbide carbon present in carburised cobalt diminishes with rise of temperature of preparation. Higher contents of carbide carbon can be obtained at higher temperatures if the metallic powder has been pre-carburised at a lower temperature. Above 300°, the carbide decomposes rapidly, but traces of carbide carbon can be detected at far higher temperatures. Treatment of finely-divided cobalt preparations, which have been carburised by carbon monoxide, with molecular hydrogen at 240—250° permits the determination of carbide carbon in the form of methane; free carbon simultaneously present does not react with hydrogen at this temperature. Above 400° the free carbon can be converted into methane.

H. WREN.

**Reactions at the surface of hot metallic filaments.** IV. Reaction  $\text{CO}_2 + \text{H} \rightarrow \text{H}_2\text{O} + \text{CO}$  on tungsten and thoriated tungsten. B. S. SRIKANTAN (J. Indian Chem. Soc., 1930, 7, 745—757).—The reaction between carbon dioxide and hydrogen at a tungsten surface maintained at 965° has a unimolecular velocity coefficient of 0.00046 at a total pressure of 204 mm. The temperature coefficient of the reaction falls from 1.18 at 965—1080° to 1.03 at 1100—1280°, and the heat of activation from 54 to 9.7 kg.-cal. The reaction velocity increases rapidly with increase of the hydrogen pressure from 100 to 500 mm. At pressures below 200 mm. the tungsten surface becomes saturated with carbon dioxide, and increase of the carbon dioxide pressure beyond this point does not influence the velocity of the reaction, except in as far as a slight displacement of hydrogen from the surface occurs. The reaction is brought about by the independent adsorption of the two gases, and involves the rapid consecutive reactions:  $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ ,  $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ , and possibly also in presence of an excess

of hydrogen the slow reaction  $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ , since methane is found among the products to the extent of about 8% towards the end of the reaction. The tungsten surface becomes pitted during the reaction, due probably to volatilisation of tungsten as carbonyl, but it is possible that surface complexes are formed and subsequently decomposed.

H. F. GILLBE.

**Catalytic activity of nickel in the form of aerosol and aerogel.** W. E. GIBBS and H. LIANDER (Trans. Faraday Soc., 1930, 26, 656—662).—Nickel aerosols, prepared by vaporisation of nickel in a continuous direct-current arc or by heating the vapour of nickel carbonyl, and nickel aerogels prepared by the condensation of these aerosols have little or no catalytic effect on the reduction of carbon monoxide or ethylene by hydrogen.

E. S. HEDGES.

**Electrochemical preparation of sodium hyposulphite.** M. RABINOVITSCH and A. S. FOKIN (Z. Elektrochem., 1930, 36, 839—845).—A continuous process for preparing sodium hyposulphite by electrolytic reduction of sodium hydrogen sulphite is described. A platinum anode and a mercury cathode are used. The cathode liquid is a 1–2% solution of sodium hydrogen sulphite through which sulphur dioxide is bubbled at a rate depending on the current used. The anode liquid is concentrated sodium hydroxide solution. The concentration of hyposulphite can be made to reach the saturation value, when crystals of the dihydrate are deposited. The current yield is 70–80%, the loss being chiefly due to the decomposition of the hyposulphite into thiosulphate and metabisulphite. This decomposition is markedly retarded by sodium silicate (1 g.  $\text{Na}_2\text{SiO}_3$  in 100 c.c. of solution).

F. L. USHER.

**Electrodeposition of cobalt-nickel alloys.** I. S. GLASSTONE and J. C. SPEAKMAN.—See B., 1930, 1074.

**Electrodeposition of gold alloys.** G. GRUBE.—See B., 1930, 1073.

**Electrochemical preparation of formates from carbonic acid.** M. RABINOVITSCH and A. MASCHOVETZ (Z. Elektrochem., 1930, 36, 846—850; cf. Fischer and Prziza, A., 1914, ii, 198).—The current yield of formate in the electrolytic reduction at a mercury cathode of a solution of sodium hydrogen carbonate into which carbon dioxide is introduced at atmospheric pressure is only 3%. By using as cathode an amalgam containing 0.2% of lead the initial current yield can reach 95%. The yield decreases with increasing concentration of formate. It is important to keep the amalgam vigorously stirred.

F. L. USHER.

**Gaseous combustion in electric discharges.** V. Spectrographic examination of the cathodic combustion of carbon monoxide. G. I. FINCH and H. H. THOMPSON (Proc. Roy. Soc., 1930, A, 129, 314—319; cf. Finch and Hodge, A., 1929, 890, 1401).—Steady direct current discharges, maintained between electrodes of various metals, were passed through "detonating gas" ( $2\text{CO} + \text{O}_2$ ), carbon monoxide, oxygen, and steam, the discharges being examined by means of a Bellingham and Stanley

quartz spectrograph. The spectra show that in pure oxygen, singly-ionised oxygen molecules and atoms and neutral oxygen atoms are present within the discharge; that oxygen atoms are probably also formed in "detonating gas"; and that carbon monoxide molecules, although strongly excited, are not ionised. These facts indicate that the cathodic combustion of "detonating gas" proceeds without a prior ionisation of the carbon monoxide, and therefore the suggested mechanism of the process previously advanced (*loc. cit.*) must be revised.

L. L. BIRCUMSHAW.

**Combination of nitrogen and hydrogen activated by electrons.** G. F. BRETT (Proc. Roy. Soc., 1930, A, 129, 319—327).—The experimental method used was that of Caress and Rideal (A., 1927, 943), with certain modifications which are detailed. The rate of reaction increases sharply at the following electron speeds: 17.0, 18.5, 20.5, 24.5, and 27.0 volts, corresponding with the production of  $\text{N}_2^+$ ,  $\text{H} + \text{H}^+$ ,  $\text{N}_2^{++}$ ,  $\text{N}^+ + \text{N}^+$ ,  $\text{N}^+ + \text{N}^+$  and/or  $\text{H} + \text{H}^+$ , respectively. The most probable mechanism for the formation of ammonia appears to be the combination of atomic hydrogen with one or other of the active states of nitrogen given above.

L. L. BIRCUMSHAW.

**Action of high-speed electrons on methane, and on oxygen and carbon monoxide [mixtures].** J. C. McLENNAN and J. V. S. GLASS (Canad. J. Res., 1930, 3, 241—251).—Methane at 20 mm. pressure when subjected to the action of cathode rays is only slightly decomposed, about 16% of hydrogen and 14% of ethylene being produced; the reaction is but slightly influenced by moisture. Mixtures of methane and oxygen react to form water, carbon monoxide and dioxide, hydrogen, and formic acid, but no tar or oil is formed. Pressure changes show the reaction to be unimolecular. The reaction velocity shows a linear increase with voltage up to a certain critical value, above which it is but slightly influenced by further changes; the critical point represents the saturation point of the gas by electrons. The ratio of carbon monoxide to dioxide is practically independent of pressure, composition of the gas mixture, and energy of the rays, possibly on account of the removal of carbon dioxide by formation of formic acid. By the action of cathode rays on carbon monoxide the reaction  $5n\text{CO} \rightarrow 2n\text{CO}_2 + (\text{C}_3\text{O})_n$  takes place; the carbon suboxide is a brown solid of inappreciable vapour pressure, and is very soluble in water. In presence of water vapour no suboxide is formed, carbon dioxide and hydrogen being the main products. In carbon monoxide-oxygen mixtures carbon dioxide is the sole product of the action of cathode rays; its formation is greatly retarded by the presence of water, but the retardation is independent of the water vapour pressure. For mixtures of constant composition the reaction velocity is proportional to the pressure. In the dry gases the carbon dioxide yield increases with the proportion of carbon monoxide present, but in presence of water the carbon dioxide yield is independent of the composition. The reaction is due primarily to the formation of oxygen ions and carbon atoms from the carbon monoxide and of oxygen ions and atoms from the oxygen.

H. F. GILLBE.

**Chemical action in the glow discharge. V. Oxidation of hydrogen.** A. K. BREWER and J. W. WESTHAVER (J. Physical Chem., 1930, 34, 2343—2355; cf. this vol., 1003).—The synthesis of water from electrolytic gas in the glow discharge has been investigated by the methods previously described. For the negative glow the rate of reaction is independent of pressure over the range 0.3–7 mm. In the positive column, the rate of reaction is high at higher pressures and the critical explosion pressure depends largely on the electrode separation, being the smaller the greater is the separation. The rate for the negative glow expressed as molecules per electron of current increases slightly with an increase in current and the proportionality found between current and rate for ammonia and nitrogen dioxide (this vol., 304, 553) thus does not hold for water over the whole current range; further, the rate depends on the cathodic material, being higher for iron than for aluminium. The maximum rate of reaction occurs with an excess of hydrogen. Helium (less than 50%) is without effect, and argon, nitrogen, and oxygen decrease the rate in proportion to the partial pressure of the excess of gas. At high pressures, oxygen accelerates the reaction. In the positive column, an excess of oxygen is preferable to one of hydrogen and the rate of reaction is markedly decreased by an excess of nitrogen, argon, or helium. The water synthesised in the negative glow is charged when it reaches the walls. The reaction is initiated by  $H_2^+$  ions at pressures below 7.0 mm., whilst at higher pressures the ions  $O_2^+$ ,  $N_2^+$ , and  $A^+$  are effective reaction nuclei. A mechanism involving ionic clusters in the negative glow and an ionic chain reaction in the positive column is suggested.

L. S. THEOBALD.

**Second Report of the Committee on Photochemistry, National [U.S.A.] Research Council.** H. S. TAYLOR (J. Physical Chem., 1930, 34, 2049—2091; cf. A., 1928, 600).—A systematic analysis of the total photo-process in terms of the initial process of quantised absorption and the secondary processes of chemical change which follow it. Under the former are discussed (i) absorption by atomic systems, (ii) continuous absorption by atomically-bound or homopolar molecules, (iii) continuous absorption by ionically-bound or heteropolar molecules, (iv) discontinuous fine-structure band absorption, and (v) discontinuous diffuse-structure band absorption; under the second heading the chemical processes succeeding these different types of absorption are discussed.

L. S. THEOBALD.

**Photochemical reaction between sulphur and yellow arsenic.** C. HAENNY (Helv. Chim. Acta, 1930, 13, 725–730).—An attempt has been made to prepare new sulphides of arsenic analogous to those of phosphorus by the interaction of sulphur and yellow arsenic dissolved in carbon disulphide. No reaction takes place in darkness, but on exposure to light a powder, the colour of which varies between yellow and orange, is slowly precipitated. After prolonged extraction with carbon disulphide the powder contains both elements in a proportion which depends on that in the original solution. As the ratio S/As in the

solution varies from 1 to 18, the corresponding ratio in the precipitate is 0.69 to 1.45. Iodine exercises no influence either on the composition or on the reaction time. No free arsenic or sulphur could be detected, nor could the presence of any of the known sulphides be established. It is suggested that the substance is a mixture of sulphides not hitherto described.

F. L. USHER.

**Photochemical reduction of tungstic and molybdic acids.** S. GHOSH and A. K. BHATTACHARYA (J. Indian Chem. Soc., 1930, 7, 717–721).—The photochemical reduction of molybdic and tungstic acid solutions by ethyl alcohol is a reaction of zero order, in contradiction to Wassiljewa's observation (A., 1913, ii, 265), and the reduction does not take place in the dark. On ageing of molybdic acid sol for 2 days the velocity coefficient at 26.5° falls from 0.0291 to 0.0260, but if the sol be heated at 70° for 8 min. the velocity coefficient rises to 0.035, on account of the breakdown of the polymerised molecules formed during the ageing process. In presence of chlorides of the alkali metals the velocity coefficient of the reduction of both molybdic and tungstic acid sols decreases in the order rubidium, potassium, sodium, lithium.

H. F. GILLBE.

**Photochemical reaction between sodium nitrite and iodine.** A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1930, 7, 709–715).—In the dark the reaction between sodium nitrite and iodine is bimolecular, the temperature coefficient being 2.7 at 30–40°; the temperature coefficients at 4725, 5650, 7304, and 8500 Å. are 2.07, 2.20, 2.29, and 2.35, respectively, and the quantum efficiency varies from 36 to 119, according to the wave-length and temperature. The ratio of radiation absorbed to reaction velocity varies from about 0.25 to 1.5 and is dependent on the ratio of the velocities in the dark and in the light. The error of the titration of iodine by sodium thiosulphate in presence of sodium nitrite becomes appreciable only at high nitrite concentrations.

H. F. GILLBE.

**Catalytic action of light on the efflorescence of some salts.** E. BEUTEL and A. KUTZELNIGG (Monatsh., 1930, 56, 184–190).—Irradiation by ultra-violet light accelerates the efflorescence of many salts. Sodium sulphate and sodium ferrocyanide lose practically all their water of crystallisation after irradiation for an hour or two. The rate of efflorescence is 3–3.5 times as great as for a non-irradiated control sample at the same temperature. Ferrous sulphate effloresces 5.14 times as fast when irradiated, losing completely three molecules of water of crystallisation in 2 hrs. The acceleration is marked also with zinc sulphate, iron alum, and sodium carbonate.

F. G. TRYHORN.

**Chemical reactions in infra-red radiations. II.** A. K. BHATTACHARYA and N. R. DHAR (J. Indian Chem. Soc., 1930, 7, 677–685).—Sixteen photochemical reactions of various types, including oxidation processes, sugar inversion, and the decomposition of complex salts, have been found to be accelerated by radiation of wave-length 8500 Å.; four are accelerated also by radiation at 7304 Å. In each case the quantum yield increases with rise of temperature,

and the temperature coefficient of the reaction velocity is less for the reaction in the light than for the dark reaction. In several cases Einstein's law is applicable at 8500 Å.; it appears, therefore, that a quantum of small energy content can activate only one or two molecules, and Einstein's law is probably valid for longer wave-lengths. Calculations of the threshold frequency from the temperature coefficient of a number of photochemical reactions indicate that frequencies greater than the threshold limit are absorbed and are capable of accelerating the reaction. Thus the radiation hypothesis of reaction is supported. The mean wave-length transmitted by a saturated solution of potassium dichromate in a cobalt-glass cell is 8500 Å., all wave-lengths shorter than 8000 Å. being suppressed. H. F. GILLBE.

**Reflexion and transmission of light by photographic plates.** D. B. McRAE and R. C. TOLMAN (J. Opt. Soc. Amer., 1930, 20, 565—572).—The percentage transmission and reflexion of light by Eastman 40 plates have been determined by photographic methods, for red, green, blue, and "actinic" light. The absorption of light by the plate, obtained by difference, corresponded with the sensitivity, being greatest for blue light (66%). The reflexion and transmission did not alter during the course of exposures insufficient to produce visible darkening.

J. LEWKOWITSCH.

**Interpretation of solarisation phenomena. III. Silver content, covering power, grain distribution, and grain size in the region of solarisation.** H. ARENS and K. KIPPAN (Z. wiss. Phot., 1930, 28, 229—238).—The density, silver content, and grain distribution in peptised silver bromide emulsions have been measured over the range of normal exposure and solarisation. From these data the covering power and mean grain size are calculated. In the region of solarisation, with chemical development, all the characteristics pass through a minimum, except the covering power, which shows a maximum; with physical development, the covering power decreases with the other characteristics, but the grain size increases slightly. The grain distribution in the region of maximum density is, with chemical development, less than half, and with physical development, nearly equal to, the original silver bromide grain distribution, the maximum density being the same in the two cases. The upper limit for the size of primary silver nuclei is calculated to be a cube of edge  $1.7 \times 10^{-6}$  cm. (cf. Arens and Eggert, B., 1930, 1047).

J. LEWKOWITSCH.

**Adsorption as the primary process of photographic development.** P. WULFF and K. SEIDL (Z. wiss. Phot., 1930, 28, 239—291).—Since quinol cannot be used for adsorption experiments on account of its developing action, resorcinol, which has no action, was employed. Resorcinol is adsorbed on silver bromide from alkaline solution, being determined directly by titration of the moist silver bromide complex with potassium permanganate in acid solution. The adsorption increases with increased specific surface of the silver bromide and decreases with rise of temperature. It is reduced in the presence of bromine, chlorine, and sulphite ions, and increased

by silver and thallium ions; parallel results are obtained for the influence of these ions on the rate of development of an emulsion (by quinol), except for the sulphite ion, which has no effect. The rate of development by quinol, pyrogallol, or *p*-aminophenol is reduced by resorcinol, phloroglucinol, or *m*-aminophenol. The silver salts of the latter three compounds are sparingly soluble and decompose after a short time. Experiments on development with equimolecular mixtures of quinol and resorcinol and with varying concentrations of quinol alone indicate that the adsorptions of the two isomerides on silver bromide are of the same order. These results support Sheppard's theory that development is the intramolecular rearrangement and subsequent decomposition of an adsorption complex.

J. LEWKOWITSCH.

**Optical sensitising of silver halides by colloidal silver.** S. E. SHEPPARD (J. Franklin Inst., 1930, 210, 587—607).—Theoretical. Previous theories are inadequate. It is now suggested that the effect should be attributed to minute Volta condenser fields set up between free and absorbed silver particles, with silver bromide as dielectric, causing sensitised photoelectric emission by the silver amicros and ultramicros.

J. LEWKOWITSCH.

**Mechanism of formation of the latent photographic image.** A. P. H. TRIVELLI (Nature, 1930, 126, 760).—A reply to Toy and Harrison's criticism (this vol., 1005) of the concentration speck theory.

L. S. THEOBALD.

**Inhibition and mechanism of photochemical reaction in Eder's solution.** E. SHPOLSKY (Nature, 1930, 126, 647—648).—Ferric chloride (concentration  $> 10^{-2}$  g./c.c.), potassium permanganate, uranyl nitrate or acetate, fluorescent dyes such as uranin, cosin, and erythrosin, and quinine hydrogen sulphate are strong inhibitors of the reaction in Eder's solution when X-rays are used. The dyes are the most potent inhibitors, their inhibiting power increasing at the same rate as does their sensitising action in ordinary light. Eder's reaction appears to be a chain reaction with a mechanism similar to that of the combination of hydrogen and chlorine.

L. S. THEOBALD.

**Geometrical inversion in light.** B. K. VAIDYA (Proc. Roy. Soc., 1930, A, 129, 299—313).—Quantum efficiency determinations for the inversion of the following geometrical isomerides have been made: maleic and fumaric acids, citraconic acid, *o*-coumaric acid, cinnamic and *isocinnamic* acids. The inversion in each case was followed by conductivity measurements on a Wheatstone bridge, the percentage conversion of one isomeride into the other on exposure to light being determined by measuring the conductivity of mixtures of pairs of isomerides containing varying amounts of each. Besides the conductivity method it was also possible, in the case of cinnamic acid, to follow the change spectroscopically; a measurable displacement of the absorption curve takes place. Velocity measurements were also carried out for the cinnamic=*isocinnamic* acid change, which showed that the direct as well as the reverse reaction belongs to the zero order. The equilibrium point, which may be attained from either direction after

about 10 hrs.' exposure, corresponds with 72% of isocinnamic acid in the case of a 0.003*M* solution, and 75% in the case of a 0.002*M* solution. Measurements of the absorption of energy were carried out with a Hilger linear thermopile and a Moll galvanometer, and the following mean values were obtained for the quantum efficiencies ( $\phi$ ) for the wave-length 313 $\mu$ : 0.01 maleic acid, 0.048; 0.005 maleic acid, 0.0525; 0.01 fumaric acid, 0.1175; 0.005 fumaric acid, 0.083; 0.01 citraconic acid, 0.182; 0.005 citraconic acid, 0.219; 0.005 coumaric acid, 0.0305; 0.002 coumaric acid, 0.0225; 0.003 cinnamic acid, 0.0095; 0.002 cinnamic acid, 0.5305; 0.003 isocinnamic acid, 0.206; 0.002 isocinnamic acid, 0.153. The concentrations are given in g.-mol. per litre. All the acids investigated, with the exception of maleic and citraconic acids, show a marked decrease in  $\phi$  with increase in dilution. It is suggested that in substances showing selective absorption the value of  $\phi$  would approach unity as the exciting radiation decreases in wave-length within one of the photochemically active bands. Substances showing general absorption, or those in which the exciting radiation fails to fall within an active band, appear to have a low quantum efficiency. L. L. BIRUMSHAW.

**Alleged effect of polarised light on films of starch.** A. E. NAVEZ (*Science*, 1930, 72, 13).—The hydrolysis of boiled starch by moonlight claimed by Semmens (*ibid.*, 1929, 70, xiv) could not be confirmed. L. S. THEOBALD.

**Photographic activity of cod-liver oil.** J. W. WOODROW (*Physical Rev.*, 1929, [ii], 33, 119).—The oxidation of cod-liver oil is accompanied by the emission of particles which affect a photographic plate. The particles are completely absorbed by a few cm. of air and their absorption by cellophane follows the usual exponential law. The effect is increased by a rise in temperature. L. S. THEOBALD.

**Oxidation-reductions with chlorophyll and other sensitizers.** F. ALLISON (*Helv. Chim. Acta*, 1930, 13, 788–805; cf. Böhi, A., 1929, 278).—Further experiments based on Baur's theory, according to which an optical sensitizer induces simultaneous oxidation and reduction such as occurs at the anode and cathode in electrolysis, are described. Chlorophyll cannot be substituted for eosin as a sensitizer in Eder's solution, since it is rendered inactive by the mercuric chloride, but when oxalic acid and cochineal in methyl-alcoholic solution are exposed to light in the presence of chlorophyll the cochineal is decolorised (reduced). Attempts to effect photo-reduction of various dyes by hydrogen in the presence of chlorophyll or other sensitizers gave negative results unless the hydrogen was activated by platinum or palladium. Electrolytic gas combines when illuminated in a methyl-alcoholic solution of chlorophyll to which a little of the hydroxide of calcium, barium, or sodium has been added, but photolysis of water could not be induced by adding only a single depolariser, whether cathodic or anodic. Fluorescein or certain triphenylmethane colouring matters can often be substituted for chlorophyll without loss of effect. Blank experiments were performed in all cases.

F. L. USHER.

**Hydrates of metallic oxides and salts.** L. HACKSPILL and A. P. KIEFFER (*Ann. Chim.*, 1930, [x], 14, 227–282).—The dehydration of a large number of metallic oxides and salts has been investigated by heating them in a vacuum in a special apparatus, which is described, and determining the amount of water evolved at each temperature by means of the increase in pressure. Dehydration-temperature curves of the following are plotted and discussed: hydrated  $\text{Cr}_2\text{O}_3$ ;  $\text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ;  $\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ;  $\text{BeO} \cdot \text{H}_2\text{O}$ ;  $\text{CdO} \cdot \text{H}_2\text{O}$ ;  $\text{ZnO} \cdot \text{H}_2\text{O}$ ;  $\text{MgO} \cdot \text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_2\text{Na}_2\text{O} \cdot 4\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_2\text{Na}_2\text{O} \cdot 10\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_2\text{Na}_2\text{O} \cdot 5\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_3\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_2\text{Na}_2\text{O} \cdot 4\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_3\text{Na}_2(\text{K}_2\text{O}) \cdot 4\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_2\text{Cs}_2\text{O} \cdot 5\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_3\text{Na}_2\text{O} \cdot 10\text{H}_2\text{O}$ ;  $(\text{B}_2\text{O}_3)_5\text{M}_2\text{O} \cdot 8\text{H}_2\text{O}$  ( $\text{M}=\text{K}, \text{Rb}, \text{Cs}$ );  $\text{MSO}_4 \cdot 7\text{H}_2\text{O}$  ( $\text{M}=\text{Mg}, \text{Co}, \text{Ni}, \text{Fe}$ );  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ;  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ;  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ;  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ;  $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ;  $\text{Cr}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ;  $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ ;  $\text{K}_2\text{SO}_4 \cdot \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ ; and  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . For detailed results and conclusions in individual cases the original must be consulted, but on the basis of the results hydrated substances are classified into the following five categories. (1) Occluded water retained as a saturated solution between the crystal lamellae. This is lost slowly but continuously in a vacuum. (2) Water of adsorption retained on the surface of the crystals when these are in very fine grains or as a gel. Dehydration in this case is slow and continuous, but varies with concentration. Hydrated chromium oxide falls within this category. (3) Water of crystallisation the loss of which involves disintegration of the crystal. Dehydration in this case occurs suddenly, often with almost explosive violence (e.g., orthoboric acid at 100°), the dehydration-temperature curve becoming almost vertical at a temperature which varies only slightly with the conditions of the experiment. (4) Water of semi-constitution which, although its loss (which does not occur readily) does not involve decomposition of the anhydrous salt, yet seems to form an integral part of the molecule. Such cases are exemplified in the alkali diborates and sulphates of nickel and cobalt etc. Thus ordinary borax loses 80% of its water at 60°, whilst the remainder is given off only slowly, dehydration not being complete until about 400°, the structure of borax being represented as  $[(\text{B}_2\text{O}_3)_2 \cdot \text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}] \cdot 8\text{H}_2\text{O}$ . Similar types of curves are obtained with the other alkali borates. (5) Water of constitution, elimination of which involves complete disruption of the molecule as in the alkali hydroxides and 98.5% sulphuric acid. The water of hydration in a particular compound may thus fall into two or more categories. In the cases studied the number of molecules of water of crystallisation never exceeds and is nearly always equal to the number of molecules of water liberated in the formation of the salt by neutralisation. The reversibility of dehydration has also been studied and far from being the rule is rather the exception. The following phenomena may oppose rehydration: (a) crystalline cohesion which opposes the loss of water and is overcome only at a certain critical temperature; (b) false equilibria, and (c) polymerisation of the

dehydrated substance, which becomes more rapid the higher is the temperature. Thus aluminium hydroxide loses its water of crystallisation at  $220^{\circ}$  and can reabsorb only water of absorption, and even this property is lost when it is calcined at  $1000^{\circ}$ . In the rehydration of boron trioxide the subsequent dehydration curve shows that equal proportions of ortho- and meta-boric acids are produced. The existence of a definite hydrate  $\text{Bi}(\text{OH})_3$  is considered very doubtful, whilst the existence of a basic nitrate,  $(\text{Bi}_2\text{O}_3)_4\text{N}_2\text{O}_5$ , is confirmed. J. W. BAKER.

**Ammines. IV. Cuprammine salts of monobasic acids.** H. J. S. KING (J.C.S., 1930, 2307—2319).—Measurements of the mol. wt. of triammine and diammine salts of bivalent copper with monobasic acids in aqueous solution, using the cryoscopic method, give values of  $i$  which indicate that both are tri-ionic salts. This suggests that the acid radicals are ionised, and this is supported by the chemical properties of the salts. In concentrated solutions a progressive diminution is observed in the value of  $i$  which may mean that a small proportion of the salt is present in the acido-ammine form, in which the acid radicals are co-ordinated with the copper atom. The following new compounds are described: *tetramminocupric formate*, m. p.  $157^{\circ}$  (decomp.); *diamminocupric formate* m. p.  $152^{\circ}$  (decomp.); *dipyridinocupric formate monohydrate*; *pentamminocupric iodide hemihydrate*; *diamminocupric iodide*; *hexapyridinocupric iodide*; *tetrapyridinocupric iodide*; *cupric o-nitrobenzoate* with its *tetrammino-* and *tripyridino-*salts; *tetramminocupric m-nitrobenzoate*; *tetramminocupric picrate*; *tetrammino-* and *diquinolino-cupric trichloroacetate*.

The m. p. of the cuprammines indicate that they are non-polar in the solid state. F. J. WILKINS.

**Ammonates of copper selenite.** L. C. HURD, G. I. KEMMERER, and V. W. MELOCHE (J. Amer. Chem. Soc., 1930, 52, 3881—3886; cf. Boutzoureano, A., 1891, 262).—The following compounds have been prepared and their properties recorded:  $\text{CuSeO}_3 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ ;  $\text{CuSeO}_3 \cdot \text{NH}_3$  (decomp.  $150^{\circ}$ ); transition occurs between  $\text{CuSeO}_3 \cdot 4\text{NH}_3$  and  $\text{CuSeO}_3 \cdot 3\text{NH}_3$  at  $-25 \pm 1^{\circ}$  and between the latter and  $\text{CuSeO}_3 \cdot 2\text{NH}_3$  at  $19.8^{\circ}$ . The hydrate,  $\text{CuSeO}_3 \cdot 3\text{NH}_3 \cdot x\text{H}_2\text{O}$ , has been obtained.

J. G. A. GRIFFITHS.

**Ammonates of copper selenate.** L. C. HURD and V. LENHER (J. Amer. Chem. Soc., 1930, 52, 3857—3864; cf. Dennis and Koller, A., 1919, ii, 336).—Copper selenate pentammonate and diammonate have been prepared and are described. The transition point between the former and copper selenate tetrammonate is  $19 \pm 0.3^{\circ}$ . The existence of copper selenate tetrammonate dihydrate is doubtful (cf. Lange, A., 1926, 1112).

J. G. A. GRIFFITHS.

**Position of beryllium and magnesium in the periodic classification of elements.** P. PFEIFFER, T. FLEITMANN, and R. HANSEN (J. pr. Chem., 1930, [ii], 128, 47—62).—From a comparison of complex coordination compounds of the calcium, strontium, barium, zinc, cadmium, magnesium, and beryllium salts of various aromatic sulphonic acids, it is concluded that magnesium and beryllium should be

placed with zinc and cadmium in the same long period. The following salts are described: *calcium*  $+0.5\text{H}_2\text{O}$ , *strontium*  $+ \text{H}_2\text{O}$ , *hexa-aquo-cobalt*, *tetra-aquoberyllium*, *tetramminoberyllium*, *hexa-aquo-* and *hexammino-magnesium naphthalene-1-sulphonates*; *calcium*  $+ \text{H}_2\text{O}$ , *strontium*, *hexa-aquomanganese*, *hexa-aquo-ferrous*, *hexa-aquocobalt*, *hexa-aquoberyllium*, *tetramminoberyllium*, *hexa-aquo-* and *hexammino-magnesium naphthalene-2-sulphonates*; *calcium*  $+ \text{H}_2\text{O}$ , *barium*  $+ \text{H}_2\text{O}$ , *hexa-aquoberyllium*, *tetramminoberyllium*, *hexa-aquo-* and *hexammino-magnesium benzenesulphonates*; *calcium*  $+4\text{H}_2\text{O}$ , *strontium*  $+ \text{H}_2\text{O}$ , *hexa-aquoberyllium*, *tetramminoberyllium*, *hexa-aquo-* and *hexammino-magnesium p-toluenesulphonates*. J. W. BAKER.

**Principles of the genetic development of material.** V. KOHLSCHÜTTER. I. **Structural forms of calcium oxalate.** V. KOHLSCHÜTTER and J. MARTI. II. **Course of chemical reactions in crystals.** I. **Compounds of copper.** V. KOHLSCHÜTTER and M. LÜTHI (Helv. Chim. Acta, 1930, 13, 929—978, 978—1006).—I. A systematic study of the crystalline form and habit of growth of calcium oxalate when formed under different conditions has been undertaken with the object of gaining an insight into the widely-varying modes of occurrence of this substance in plants. For this purpose the reaction between calcium and oxalate ions has been examined (a) under different conditions of acidity, (b) in the presence or absence of foreign ions, (c) when localised at a solid surface, and (d) when caused to take place with extreme slowness. The last-named condition was secured either by the slow introduction of oxalate ions into a large volume of highly-diluted calcium ions or by the interaction of a solution of one of the ions with the other in the form of a sparingly soluble solid compound. In the course of these experiments a new crystalline variety was observed, probably triclinic and containing more water than the monoclinic monohydrate but less than the tetragonal trihydrate. It is more readily dissociated and more soluble than the other hydrates. The rate of formation of nuclei increases in the order monoclinic, tetragonal, triclinic, whilst the rate of crystal growth increases in the reverse order. It is thus possible by careful addition of one of the reagents to grow large crystals of the triclinic variety. In acid solution ( $p_{\text{H}}$  2.5—5) the triclinic and monoclinic forms are produced; at  $p_{\text{H}}$  6 tetragonal crystals are formed together with smaller triclinic ones, and in alkaline solution ( $p_{\text{H}}$  8) the former greatly preponderate. The presence of foreign ions exerts a characteristic influence on the habit of single crystals of the triclinic variety, very little on the monoclinic, and none on the tetragonal form. The varied shapes of calcium oxalate crystals, of which numerous photographs are given, are largely determined by the process of transformation of the unstable phase. If this transformation takes place topochemically the crystals of the stable variety (tetragonal or monoclinic according to the  $p_{\text{H}}$ ) are not at first well developed, but are rather to be regarded as "somatoids," the actual shape depending chiefly on that of the parent crystal. Growths formed in this way assume characteristic



habits not observed in tetragonal or monoclinic crystals formed directly from solution.

II. The course of decomposition of a number of hydrated cupric salts and of non-hydrated basic compounds has been observed microscopically and photographs illustrating the characteristics of these topochemical changes are given. The observations are discussed theoretically. F. L. USHER.

**Calcium chloro-, bromo-, and iodo-aluminates.** (MILE.) FORET (Compt. rend., 1930, 191, 711—713).—By mixing solutions of calcium aluminate,  $\text{CaX}_2$ , where X is a halogen or  $\text{NO}_3$ , and calcium hydroxide in proportions such that the concentrations are limited by the relations  $[\text{CaO}] > 3[\text{Al}_2\text{O}_3]$  and  $[\text{CaX}_2] > [\text{Al}_2\text{O}_3]$  (to avoid formation of  $\text{Ca}_3\text{Al}_2\text{O}_6$  the concentration of  $\text{CaX}_2$  must be three times that theoretically sufficient), the salts  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaX}_2 \cdot n\text{H}_2\text{O}$ , where  $n=8$  for  $\text{X}=\text{I}$ , 9.5 for  $\text{X}=\text{Br}$ , and 10 for  $\text{X}=\text{Cl}$  or  $\text{NO}_3$ , are obtained when the products are dried over calcium chloride (cf. Friedel, A., 1899, ii, 366; Wells, B., 1929, 173). All are decomposed by water. Phase relations are the same as for the nitroaluminates, and are shown for the chloroaluminate by curves, those for the bromo- and iodo-derivatives being similar. C. A. SILBERRAD.

**Purification of mercury.** A. O. JONES (J.S.C.I., 1930, 49, 437—438r).—A simple type of mercury purifier working on the principle of Record's motorless circulator (J. Sci. Instr., 1928, 5, 299) is described. It combines the advantages of aerial oxidation and electrolytic interchange. A more permanent form suitable for large quantities of mercury is also illustrated.

**Gallium sulphides.** A. BRUKL and G. ORTNER (Monatsh., 1930, 56, 358—364).—A more detailed account of work already abstracted (this vol., 720).

**Hydrates of silicic acid.** W. D. TREADWELL and W. WIELAND (Helv. Chim. Acta, 1930, 13, 842—864).—The method of potentiometric titration has been used in an attempt to determine the number of acidic groups in solutions of silicic acid under varying conditions. In the titration of aqueous sodium metasilicate with hydrochloric acid a break in the curve occurs at a point corresponding with sodium hydrogen metasilicate. The ionisation coefficients of the acid found from the titration curve are  $K_1=10^{-9.7}$ ,  $K_2=10^{-12}$  (cf. Hägg, A., 1926, 924). There was no indication of the presence of orthosilicic acid. In 50% alcoholic solution rapid titration furnishes a curve similar to that given by the aqueous solutions, but when the addition of acid is extended over 3 hrs. no break corresponding with an acid silicate occurs. This behaviour is attributed to progressive hydrolysis of the acid silicate owing to polymerisation of the silicic acid by the alcohol. Experiments on the time of gelatinisation of salt-free silicic acid sols, and a study of various physical properties of the sols during gelatinisation, indicate that the process is purely physical. It is considered that the acidic character of silicic acid is due to two co-ordinatively linked molecules of water, separated by hydroxyl groups attached by the principal valencies. Polymerisation occurs chiefly by elimination of water from the latter groups. F. L. USHER.

**Oxidations with fluorine. XVII. Preparation of pertitanic, pervanadic, and permolybdic acids; reduction of per-acids by ozone.** F. FICHTER and A. GOLDACH (Helv. Chim. Acta, 1930, 13, 1200—1207; cf. this vol., 1140).—Molybdic acid dissolved in hydrofluoric acid is oxidised by fluorine to permolybdic acid. Rise of temperature favours the reaction. The yield was from 4 to 29% calculated on the fluorine used, the highest values referring to experiments of the shortest duration. A similar solution of titanium dioxide gave still smaller yields of pertitanic acid, and vanadic acid dissolved in sulphuric acid was oxidised only to the extent of about 1%. Ozonised oxygen reduces solutions of the three per-acids in sulphuric acid, and the diminution of yield with increase in duration of the oxidation experiments is thus accounted for. Ozone also reduces solutions of sodium perborate, but since the latter substance is produced by means of fluorine in an alkaline solution the same explanation is not obviously applicable, the formation of ozone never having been observed under these conditions. F. L. USHER.

**Germanium. V. Complex compounds of germanium.** R. SCHWARZ and H. GIESE (Ber., 1930, 63, [B], 2428—2432).—Sodium metagermanate is treated with ammonium molybdate in boiling water and the cooled mixture is acidified with 60% sulphuric acid and extracted with ether. Slow evaporation of the ethereal solution after addition of a little water leads to isolation of the acid  $\text{H}_8[\text{Ge}(\text{Mo}_2\text{O}_7)_6] \cdot 28\text{H}_2\text{O}$ , m. p.  $40^\circ$  [guanidinium salt,  $(\text{CN}_3\text{H}_3)_3 \cdot \text{H}_8[\text{Ge}(\text{Mo}_2\text{O}_7)_6]$ ]. Treatment of germanium dioxide gel with normal sodium tungstate in hot solution, removal of undissolved dioxide, and treatment of the solution with 60% sulphuric acid and ether yield the acid  $\text{H}_8[\text{Ge}(\text{W}_2\text{O}_7)_6] \cdot 28\text{H}_2\text{O}$  (anhydrous guanidinium salt). In the absence of silicon (cf. Oberhauser and Schormüller, A., 1929, 414) traces of germanium may be detected by the blue coloration produced when the solution of an alkali germanate is treated with excess of ammonium molybdate, feebly acidified, and then treated with a strongly alkaline stannite solution. Germanium can be separated from tungsten by distillation in a stream of hydrogen chloride from 70% sulphuric acid solution; germanium is precipitated as sulphide from the distillate. Molybdenum is separated from germanium by conversion into the pure oxides by heating the complex compound at  $500^\circ$ ; at  $1000^\circ$ , molybdenum is volatilised in oxygen as the trioxide, leaving the non-volatile germanium dioxide.

Anhydrous or hydrated germanium tetrachloride appears incapable of adding hydrogen chloride.

H. WREN.

**Germanium. VIII. Sulphides of germanium.** W. PUGH (J.C.S., 1930, 2369—2373).—The reaction between sulphur vapour and germanium dioxide begins at about  $400^\circ$ ; at  $800^\circ$  the reaction is fast enough to give a practicable amount of the product, which is germanium disulphide. Hydrogen sulphide reacts with germanium dioxide at  $700^\circ$  to form a mixture containing germanium mono- and disulphides in the ratio 1:10. Germanium monosulphide may be prepared conveniently by passing a

mixture of hydrogen sulphide and hydrogen in the ratio of 1:2 over germanium dioxide at 800–850°. The product contains about 5% of the disulphide. Germanium disulphide is best prepared by the sublimation of the monosulphide in sulphur. The monosulphide melts at about 530° and volatilises readily above 650°. It has  $d_4^{25}$  4.012; its hardness is 2 on Moh's scale. Crystalline germanium disulphide has  $d_4^{25}$  2.942, m. p. 800° (approx.). F. J. WILKINS.

**Heteropoly-acids of germanium.** I. A. BRUKL (Monatsh., 1930, 56, 179–183).—A solution of 12-tungstogermanic acid,  $\text{GeO}_2 \cdot 12\text{WO}_3 \cdot 32\text{H}_2\text{O}$ , is obtained by the addition of sulphuric acid to a boiled mixture of solutions of sodium paratungstate and sodium metagermanate. The acid is isolated by extraction with ether, with which it forms an oxonium salt of high density. This salt may be decomposed by water, and the free acid obtained, by evaporation of the aqueous solution over sulphuric acid, as pale yellow, easily soluble crystals. The ammonium, rubidium, and caesium salts are sparingly soluble, whilst the sodium,  $\text{Na}_3\text{H}_3[\text{Ge}(\text{W}_2\text{O}_7)_6] \cdot 19\text{H}_2\text{O}$ , and barium,  $\text{Ba}_2\text{H}_4[\text{Ge}(\text{W}_2\text{O}_7)_6] \cdot 22\text{H}_2\text{O}$ , salts are isomorphous with the corresponding molybdosilicates. From hot solutions of the free acid, after neutralisation with silver carbonate, the silver salt ( $+7\text{H}_2\text{O}$ ) separates, whilst from cold solutions the decahydrate, isomorphous with the corresponding molybdosilicate, is obtained. F. G. TRYHORN.

**Behaviour of thorium oxide in tungsten filaments.** W. G. BURGERS and J. A. M. VAN LIEMPT (Z. anorg. Chem., 1930, 193, 144–160).—X-Ray investigation shows that in drawn multi-crystalline tungsten filaments containing 3% of thorium oxide, before ignition, the thorium is present as oxide and exhibits no definite orientation. Part of the oxide is reduced to thorium by heating the filament to above 2500° Abs., and the X-ray diagram shows the appearance also of a face-centred lattice having  $a$  5.15  $\pm$  0.005 Å., i.e., between the parameters of the metal and the oxide; the same type is produced also by heating a superficially oxidised thorium wire in a vacuum, the parameter varying from 5.31 to 5.24 according to the time of heating. Possibly intermediate oxides are formed, but the effect may be due to a type of mixed crystal formation.

[With J. C. M. BASART.]—The following lattice constants have been determined: thorium oxide, ignited,  $a$  5.585  $\pm$  0.001 Å.; thorium, prepared by reduction of the chloride by sodium,  $a$  5.074  $\pm$  0.002 Å.; thorium, prepared by thermal decomposition of the iodide,  $a$  5.081  $\pm$  0.002 Å. H. F. GILLBE.

**Zirconium oxyiodides.** E. CHAUVENET and J. DAWIDOWICZ (Bull. Acad. Polonaise, 1930, A, 195–197).—The product obtained by evaporating a solution of zirconium hydroxide in concentrated hydriodic acid is  $\text{ZrOI}_2 \cdot 5\text{H}_2\text{O}$ ; when dried at 15° in a vacuum this forms  $\text{ZrOI}_2 \cdot 5\text{H}_2\text{O}$ . This is stable at 40°, but at a higher temperature slowly loses iodine. These products are all decomposed by water with precipitation of zirconium hydroxide and re-formation of zirconyl iodide. A dilute aqueous solution hydrolyses with formation of  $\text{ZrIO}_2 \cdot \text{ZrO}_2$  (cf. A., 1929, 1154).

C. A. SILBERRAD.

**Thoryl nitrate.** E. CHAUVENET and (MME.) SOUTEYRAND-FRANCK (Bull. Soc. chim., 1930, [iv], 47, 1428–1431).—The following hydrates of thorium nitrate have been prepared:  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Th}(\text{NO}_3)_4 \cdot 3\text{H}_2\text{O}$ , and  $\text{Th}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ . By heating the trihydrate at 125–150°, *thoryl nitrate*,  $\text{ThO}(\text{NO}_3)_2 \cdot 0.5\text{H}_2\text{O}$ , is obtained, and the same substance appears also to be formed by hydrolysis in aqueous solution. R. CUTHILL.

**Oxide hydrates. XXXII. Vanadium pentoxide-water. XXXIII. Niobium pentoxide-water. XXXIV. Tantalum pentoxide-water.** G. F. HÜTTIG and A. KÖNIG (Z. anorg. Chem., 1930, 193, 81–92, 93–99, 100–105).—XXXII. Thermal dehydration isobars of vanadium pentoxide at 10 mm. pressure show in general a continuous loss of water at temperatures up to about 280°, when about 0.4 mol. of water is retained; at higher temperatures oxygen is evolved from the oxide. At temperatures up to 100° the loss of water is reversible. When prepared by decomposition of ammonium vanadate with nitric acid the oxide behaves as a typical colloid, both as regards its dehydration and its X-ray diagram, but on ageing the X-ray diagrams show the appearance of a crystalline structure, and the residual water is less readily given up; the compound tends either to the anhydrous oxide or to the monohydrate. The monohydrate,  $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , prepared by vigorous shaking during the precipitation, gives a characteristic X-ray diagram, and decomposes at 258°  $\pm$  1° at 10 mm. pressure;  $\text{V}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$  decomposes at 275°.

XXXIII. Niobium pentoxide containing 5.6–6.9 mols. of water loses water continuously when heated at constant (10 mm.) pressure from 21° to 500°, but if it be aged by heating at 150° for 6 hrs. with an excess of water there is a break in the dehydration curve at 200° corresponding with the decomposition of a hydrate  $\text{Nb}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$ ; none of these preparations gives a definite X-ray diagram, but by ignition at a high temperature a definite structure is developed. Only a small fraction of the water in hydrated niobium pentoxide is combined chemically, and the material behaves as a typically colloidal substance. As with vanadium pentoxide, the amorphous hydrated oxide on ageing tends to form either the anhydrous oxide or a mono- or hemi-hydrate.

XXXIV. Tantalum pentoxide containing 4.04 mols. of water shows a break in the thermal dehydration curve at 210° corresponding with  $\text{Ta}_2\text{O}_5 \cdot 0.5\text{H}_2\text{O}$ , but the material does not give a characteristic X-ray diagram; ageing under water does not induce crystallisation, but ageing by heating with water under pressure causes the dehydration curve to assume a different form, the monohydrate being formed. After ignition the pentoxide shows a characteristic X-ray diagram and when aged under water for 28 days absorbs about 0.25 mol. of water, but there is no evidence of hydrate formation. H. F. GILLBE.

**Sulphur fluoride,  $\text{S}_2\text{F}_2$ .** K. STRENK (Latvian Univ. Raksti, 1930, 1, 233–260).—Sulphur fluoride,  $\text{S}_2\text{F}_2$ , is prepared by heating together silver fluoride and sulphur. It attacks glass forming sulphur, silicon tetrafluoride, thionyl fluoride, and sulphur dioxide. The earlier work on the physical constants of this

compound which has been carried out in glass vessels cannot, therefore, be trusted. Sulphur fluoride has no action on zinc, iron, steel, or platinum. It is decomposed by water according to the equation  $2S_2F_2 + 3H_2O = 3S + H_2SO_3 + 4HF$ . F. J. WILKINS.

**Nitrogenation of chromium.** L. DUPARC, P. WENGER, and W. SCHUSSELÉ (Helv. Chim. Acta, 1930, 13, 917—929).—The absorption of nitrogen by chromium has been studied with reference to the factors temperature, duration of heating, pressure, and degree of purity of the metal. Both the temperature at which absorption begins and the temperature of maximum absorption are raised by the presence of impurities in the chromium. Absorption is practically complete in 2 hrs. The total amount of nitrogen taken up is increased by about 18% when the pressure of nitrogen is increased from 1 to 70 atm. Lithium nitride acts as a positive catalyst, although it slightly diminishes the quantity of nitrogen absorbed at a given temperature. F. L. USHER.

**Complex chromiselenates.** I. P. B. SARKAR and S. N. BHATTACHARYA (J. Indian Chem. Soc., 1930, 7, 765—769).—Chromoselenic acid,  $H[Cr(SeO_4)_2]$ , prepared by mixing green chromium selenate solution with selenic acid and evaporating to dryness, forms green, very hygroscopic crystals. Chromiseleno-mono-, -di-, and -tri-sulphuric acids,  $H_2[Cr_2(SO_4)(SeO_4)_3]$ ,  $H_4[Cr_2(SO_4)_2(SeO_4)_3]$ , and  $H_6[Cr_2(SO_4)_3(SeO_4)_3]$ , are obtained as green hygroscopic crystalline powders by treating chromium selenate with the theoretically necessary quantity of sulphuric acid. If the sulphuric acid be replaced by potassium sulphate the three potassium salts, similar to the acids but less hygroscopic, are obtained. A mixed chromisulphoselenic alum has been prepared. By concentrating in a vacuum over sulphuric acid a mixed solution of violet chromium sulphate and sodium selenate violet octahedral crystals of the alum  $Cr_2(SO_4)_3 \cdot Na_2SeO_4 \cdot 24H_2O$  are formed; 12 mols. of water are lost over sulphuric acid at 27°, and the solution becomes green when heated to above 60°. H. F. GILBE.

**Formation of green manganous sulphide.** II. Influence of ammonium hydrosulphide, hydroxide, and sulphide on the transition of the pink to the green sulphide. G. LANDESEN [with M. REISTAL] (Z. anorg. Chem., 1930, 193, 277—296; cf. A., 1924, ii, 186).—The spontaneous colour changes in pink manganous sulphide kept undisturbed in the original reaction mixture have been observed over a period of 6.5 years. In all the specimens precipitated without the addition of ammonia solution the transformation into the green variety was initiated after about 6 days, and proceeded with extreme slowness, being still incomplete after 6.5 years. An orange-coloured modification is formed from the pink sulphide simultaneously with, but independently of, the pink-green change, the former process being complete in 6 months. Increase in the proportion of ammonium hydrosulphide used for precipitation accelerated the progress of the pink-green transformation without shortening the period of induction. Ammonia solution added to the precipitated sulphide was without effect, but if added before pre-

cipitation it shortened both the period of induction and, if present in sufficient concentration, the velocity of transformation also. Precipitates formed from ammonium sulphide were generally transformed more slowly than those produced by the hydrosulphide. The mechanism of these changes is discussed.

F. L. USHER.

**Reaction between iodic acid and hypophosphorous and phosphorous acids or their salts.** II. V. HOVORKA (Coll. Czech. Chem. Comm., 1930, 2, 609—625).—The presence of a cadmium salt retards the separation of iodine from an acid solution containing iodate and hypophosphite or phosphite; the reduction does not proceed at temperatures below 50° and is slower with phosphorous than with hypophosphorous acid. In presence of silver perchlorate a sparingly soluble precipitate is formed and part of the silver is reduced, especially by hypophosphorous acid, to the metallic state; the silver salt increases the extent of the oxidation of both acids at the ordinary temperature, but the rate of oxidation of phosphorous acid is very slow. In presence of mercuric salts the reactions which occur are complex; free iodine cannot exist in presence of an excess of mercuric perchlorate, but forms mercuric iodide and iodate, and the actual oxidation of the phosphorous acids involves first the reduction of the mercuric salt to the mercurous state, and subsequent reoxidation by the iodic acid and the liberated perchloric acid. Mercurous iodide is not formed, nor does any direct reduction of iodic acid take place. The velocity of the oxidation depends only on the concentration of mercury salt present, the proportion of iodate having no appreciable influence, and is greater for phosphorous than for hypophosphorous acid; both acids are oxidised quantitatively by the mercury salt, and at the b. p. the reaction is complete within a few minutes. H. F. GILBE.

**[Metallic] carbonyls and nitrosyls.** IV. H. REHLEN, A. GRUHL, G. VON HESSLING, and O. PFRENGLE (Annalen, 1930, 482, 161—182).—The compound to which Manchot and Gall (A., 1929, 1027) attributed the formula  $Fe(NO)_2 \cdot 2MeOH$  is more accurately represented as  $Fe_2(NO)_2(OMe)_2 \cdot OH$ . It is decomposed almost exclusively to ferrous salt by dilute sulphuric acid in the cold if the nitric acid simultaneously formed is immediately removed. The interaction of nickel carbonyl with methyl alcohol and nitric oxide in presence of a trace of sulphuric acid, and with exclusion of moisture and atmospheric oxygen, gives the compound  $Ni(NO)(OMe) \cdot OH \cdot MeOH$ , which readily loses a molecule of methyl alcohol. It does not undergo autoxidation as readily as the iron compound, but is less stable to hydrolysis. The interaction of iron pentacarbonyl with boiling methyl alcohol in ultra-violet light gives  $Fe(CO)_3 \cdot MeOH$  and the compound  $[Fe(CO)(OMe)OH]_n$ , which tends to lose carbon monoxide, but not methyl alcohol, in a high vacuum. Long heating of iron pentacarbonyl with butadiene at 135° gives the compound  $Fe(CO)_3 \cdot C_4H_6$ , b. p. 29.5—30° in a high vacuum. Less well-defined compounds, approximating to  $Fe(CO)_3 \cdot (C_5H_8)_3$ ,  $Fe(CO)_3 \cdot (C_5H_8)_2$ , and  $Fe(CO)_3 \cdot (C_6H_{10})_2$  are obtained with isoprene and  $\beta$ -dimethylbutadiene. H. A. PIGGOTT.

**High-carbon carbides of the iron group.** F. FISCHER and H. BAHR (Ges. Abh. Kennt. Kohle, 1928, 8, 255—269; Chem. Zentr., 1930, i, 2862).—When carbon monoxide is passed at 270° over finely divided cobalt or cobaltous oxide there is obtained a mass which appears to contain the carbide  $\text{Co}_3\text{C}_2$ . This substance is decomposed by hydrogen at 270°, half the carbon (presumably derived from the carbide  $\text{Co}_3\text{C}$ ) being evolved as methane. Similar addition of carbon to an equimolecular mixture of cupric and ferric oxides affords the carbide  $\text{Fe}_3\text{C}_4$  in addition to iron carbonyl. Hydrogen liberates methane in proportion corresponding with the formula  $\text{Fe}_2\text{C}$ , formed apparently by separation of carbon from the unstable carbide  $\text{Fe}_3\text{C}_4$ . Small quantities of hydrocarbons are also formed. The iron, but not the cobalt, carbide affords, when treated with acids, a mixture of hydrocarbons. A. A. ELDRIDGE.

**Cobaltic cobalticarbonate.** C. DUVAL (Compt. rend., 1930, 191, 615—616).—*Cobaltic cobalticarbonate* was prepared by the interaction in complete darkness of saturated solutions containing 5 g. of cobaltous chloride hexahydrate and 8 g. of sodium hydrogen carbonate, followed by the addition of 50 c.c. of 100-vol. hydrogen peroxide. After 1 min. 100 g. of aqueous glycerol ( $d$  1.262) were added to inhibit the decomposing action of the sodium, and the precipitate was filtered after several hours and washed well with absolute alcohol. It is an olive-green powder stable to light, and soluble in alkali hydrogen carbonate solutions, but insoluble and unstable in water. The formula,  $\text{Co}[\text{Co}(\text{CO}_3)_3]$ , was confirmed by chemical and electrophoretic analysis. *Sodium cobaltipercarbonate*,  $\text{Na}[\text{CoCO}_4]$ , a red complex compound, was produced by substitution of ozone for hydrogen peroxide. J. GRANT.

**Constitution of aqueous pink and blue cobaltous chloride solution.** II. Spectrometric research. R. BRDČKA (Coll. Czech. Chem. Comm., 1930, 2, 545—558).—The absorption spectra of aqueous solutions of cobaltous chloride containing calcium chloride have been determined. The concentration of the substance responsible for the absorption in the red is proportional to that of the complexes from which cobalt deposits reversibly at the dropping mercury cathode (cf. this vol., 1254). The change from pink to blue is explained on the basis of the theory of Fajans (this vol., 399). C. W. GIBBY.

**Compounds of nickel and cobalt salts with  $\beta$ -diaminobutane.** J. FREJKA and (MLLE.) L. ZAHLOVÁ (Coll. Czech. Chem. Comm., 1930, 2, 639—651).—The following complex salts have been prepared by mixing the appropriate nickel salt with  $\beta$ -diaminobutane ("bn") and recrystallising from water:  $[\text{Ni bn}_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , red;  $[\text{Ni bn}_3]\text{Br}_2 \cdot \text{H}_2\text{O}$ , violet-red;  $[\text{Ni bn}_3]\text{I}_2 \cdot 4\text{H}_2\text{O}$ , violet-red;  $[\text{Ni bn}_3](\text{CNS})_2 \cdot \text{H}_2\text{O}$ , violet;  $[\text{Ni bn}_3]\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , violet-blue;  $[\text{Ni bn}_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , violet-red. By treatment of a solution of the complex sulphate with potassium thiocyanate,  $[\text{Ni bn}_3](\text{CNS})_2 \cdot \text{H}_2\text{O}$  separates as violet needles. Addition of the diamine to nickel cyanide yields  $[\text{Ni bn}_3](\text{CN})_2 \cdot \text{Ni}(\text{CN})_2$ , as rose-coloured, almost insoluble crystals. By heating a mixture of chloro-

pentamminecobaltic chloride with the diamine at 120—140°, dissolving the product in water, and concentrating, a solution is obtained which is difficult to crystallise, but on addition of concentrated hydrobromic acid  $[\text{Co bn}_3]\text{Br}_3$  separates as orange-red crystals; if potassium iodide be used  $[\text{Co bn}_3]\text{I}_3 \cdot 2\text{H}_2\text{O}$ , brownish-yellow, is obtained, whilst with potassium thiocyanate  $[\text{Co bn}_3](\text{CNS})_3 \cdot 6\text{H}_2\text{O}$ , orange-yellow, is precipitated. H. F. GILLBE.

**Higher oxides of group VIII elements. II. Octavalent nickel compounds.** D. K. GORALEVITSCH (J. Russ. Phys. Chem. Soc., 1930, 62, 1165—1188).—Fusion of a mixture of barium nitrate and peroxide with nickelous oxide and extraction of the fused mass with dilute acetic acid yields an insoluble residue, which has the formula  $\text{BaNiO}_5$ , and is a salt of *pernickelic acid* containing octavalent nickel. Acidified solutions of barium pernickelate lose nickel on concentration; this is due to the volatility of the free acid, which may be collected as a white sublimate by the evaporation of such solutions. The sublimate is, however, extremely unstable, and is almost instantaneously converted into nickelous oxide. Nickel pentoxide is isolated as a bright green powder from the fused mass by extraction with hot concentrated hydrochloric acid. A white precipitate of *pernickelic anhydride*,  $\text{NiO}_4$ , separates from the hydrochloric acid solution of the pentoxide on dilution with water. Nickel pentoxide appears to be a compound of bi- and octo-valent nickel,  $\text{NiNiO}_5$ . R. TRUSZKOWSKI.

**Ammines and amides of quadrivalent platinum as acids and bases.** A. A. GRÜNBERG and G. P. FAERMANN (Z. anorg. Chem., 1930, 193, 193—236; cf. Tschugaev, A., 1924, ii, 769).—Hexamine-, pentamine-, and tetrammine-platinic chlorides possess weakly acidic properties which are due to a secondary dissociation of the cation according to the equation  $[\text{Pt}(\text{NH}_3)_n\text{Cl}_{6-n}]^{(n-2)+} \rightarrow [\text{Pt}(\text{NH}_3)_{n-1}\text{Cl}_{6-n}\text{NH}_2]^{(n-3)+} + \text{H}^+$ . The acidity increases with the valency of the cation, and in the case of the hexamine and pentamine compounds is of the same order as that of boric acid. It also increases with rise of temperature. The replacement of ammonia by amino-groups leads, on the other hand, to the appearance of basic properties. The alkalinity increases with the number of ammonia molecules replaced, and in the compound  $[\text{en}(\text{NO}_2)_2\text{NH}_2\text{ClPt}]$  is about the same as that of aqueous ammonia. The alkalinity decreases reversibly with rising temperature in consequence of the secondary change referred to above. Hydroxyammines exhibit an amphoteric character, since the ammonia molecules can provide, and the hydroxyl groups combine with, hydrogen ions. The results are discussed theoretically. F. L. USHER.

**X-Ray spectroscopic microanalysis.** G. VON HEVESY (Mikrochem., Emich Festschr., 1930, 163—165).—The advantages of X-ray spectroscopic methods for the detection and determination of quantities of material as small as 0.001 mg., or even less, are described. The lines of the L series should preferably be sought, on account of the relatively low tube voltage necessary for their production. H. F. GILLBE.

**Quantitative analysis by monochromatic transmission.** M. BARNARD and P. McMICHAEL (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 363—365).—From Lambert's law the equation  $n_a = \log(T_m/T_b) / \log(T_a/T_b)$ , where  $T_a$ ,  $T_b$ , and  $T_m$  are the transmission factors of the components  $a$  and  $b$  and of the mixture  $m$ , at any given wave-length, respectively, and  $n_a$  is the fraction of  $a$  in the mixture, has been derived; if  $T_a$  and  $T_b$  are known, the composition of the mixture may be determined by measurement of  $T_m$ . For accurate results a wave-length should be chosen at which the transmission factors of the components differ widely and do not change rapidly with wave-length. Measurements with mixtures of potassium chromate and ammoniacal copper solutions and of spearmint oil and peppermint oil show that the error does not exceed about 1—2%. The method may be applied to three-component mixtures if the transmission curves of two of the components intersect; by measurement of  $T_m$  at the wave-length at which the intersection occurs the proportion of the third component may be calculated, and those of the others may be determined at any other convenient wave-length.

H. F. GILLBE.

**Magneto-optic method of chemical analysis.** F. ALLISON and E. J. MURPHY (*J. Amer. Chem. Soc.*, 1930, 52, 3796—3806; cf. Allison, A., 1929, 1365).—The phenomenon interpreted as the differential time lag of the Faraday effect behind the magnetic field has been investigated in a comprehensive series of aqueous solutions of metallic chlorides, nitrates, sulphates, and hydroxides. Each chemical compound, independently of other substances present, produces a minimum (or minima) of light intensity at a point on the scale characteristic of the compound even at concentrations as low as 1 part in  $10^{11}$  parts. In general, the time lag is an inverse function of the equivalent of the metallic element. Elements which have two different valencies exhibit, as a rule, two minima, or two series of close minima, in different regions of the scale corresponding with the equivalents in the two cases. The number of minima in a series is generally equal to the number of known isotopes of the metal in the compound. Hydrochloric, nitric, and sulphuric acids each produce two minima for which no explanation is offered. Ferric sulphate exhibits anomalies. The application of the method to qualitative and quantitative analysis is discussed.

J. G. A. GRIFFITHS.

**Analytical significance of ageing phenomena.** H. FISCHER (*Z. angew. Chem.*, 1930, 43, 919—922).—Freshly-formed precipitates which have no definite crystal structure adsorb foreign ions to a very much greater extent than aged precipitates, where a definite crystal structure can be observed. This leads to considerable inaccuracies in quantitative analysis. Where possible, therefore, precipitation should be brought about slowly so as to allow ageing to occur. It is suggested that the best results can be attained when the precipitation process is accompanied by another, simultaneous reaction, e.g., by an oxidation or reduction reaction, so as to cause the precipitate formation to occur more slowly.

J. W. SMITH.

**Colorimetric determination of hydrogen ions.** F. R. McCURMB and W. R. KENNY (*J.S.C.I.*, 1930, 49, 425—431r).—The more recent developments in the colorimetric determination of hydrogen ions are discussed with respect to the selection of indicators, salt effect, protein effect, and specific errors of indicator substances. The problems encountered in determining the  $p_H$  of dilute and unbuffered solutions are treated. The practical side of the tests is emphasised.

**Sulphates of aromatic amines as primary standards in alkalimetry.** E. STRASSER (*Z. anal. Chem.*, 1930, 82, 114—116).—Sulphates of such aromatic bases as aniline and toluidine serve satisfactorily as primary standards in alkalimetry owing to their high equivalent weight and non-hygroscopic character. Sulphates of relatively acid bases, such as *o*-chloroaniline, are, however, unsuitable.

R. CUTHILL.

**Calculation of mineral water analyses.** L. FRESSENIUS and O. FUCHS (*Z. anal. Chem.*, 1930, 82, 226—236).—Formulae are derived for calculating the state of combination of the constituents in mineral waters based on the dissociation constants of the acid radicals present and the  $p_H$  of the water. Tables are given showing the effect of temperature on the dissociation constants of some of the commoner acids present in mineral waters.

A. R. POWELL.

**Analysis of a water containing arsenic, molybdenum, and bismuth, and the colorimetric determination of small amounts of molybdenum.** O. STEINER (*Z. anal. Chem.*, 1930, 81, 389—391).—The water is evaporated to dryness and the residue gently ignited and dissolved in hydrochloric acid for the removal of silica. The filtrate is saturated with hydrogen sulphide, the precipitate collected and dissolved in ammonia, and the solution evaporated to dryness. The residue is dissolved in nitric acid and the arsenic precipitated as magnesium ammonium arsenate in ammoniacal solution. The filtrate is boiled, neutralised with acetic acid, cooled, and treated with 10 c.c. of a 1% tannin solution. The colour developed is compared with that produced in a similar way in solutions containing known amounts of molybdenum.

A. R. POWELL.

**Determination of chlorine in bromides.** A. V. FROST (*Trans. Inst. Pure Chem. Reagents, U.S.S.R.*, 1929, No. 300, 187—193).—Chlorine (0.05—25.0%) in bromides may be determined by Berg's method, preferably volumetrically. The accuracy of Merck's method is 0.3%.

CHEMICAL ABSTRACTS.

**Determination of hydrogen chloride and of silver by Mohr's method and tests on the accuracy of the determination of silver in mints by Mohr's and by Volhard's method.** H. RUOSS (*Z. anal. Chem.*, 1930, 81, 385—389).—In the determination of chloride by Mohr's method exact neutrality is essential; this is obtained by the addition of calcium carbonate in slight excess. Using 2 drops of 5% potassium chromate solution as indicator in 50 c.c. of solution a definite colour change is obtained with 0.4 c.c. of 0.01N-silver nitrate. In the determination of silver by Gay-Lussac's method the end-point may be more rapidly determined by adding the usual deficiency of sodium chloride solution and

finishing the titration with thiocyanate (1 c.c. = 0.005 g. Ag) using iron alum as indicator, or by adding an excess of sodium chloride, neutralising with calcium chloride, and titrating the excess by Mohr's method. A. R. POWELL.

**Bromo-iodometric investigations. III. Determination of iodate and bromate present together.** J. H. VAN DER MEULEN (Chem. Weekblad, 1930, 27, 578—579; cf. this vol., 1392).—Addition of hydrobromic acid followed by potassium hydrogen carbonate leaves the iodate unchanged, forming from the bromate potassium hypobromite, which may be reduced by addition of excess of carbamide, hydrogen peroxide, formate, or oxalate; the unchanged iodate is then determined iodometrically. By subtracting the iodine value of the iodate from the total value of the iodate and bromate together, the amount of bromate present is calculated.

S. I. LEVY.

**Micro-iodometry.** R. W. TEISS (Z. anal. Chem., 1930, 82, 116—122).—In the micro-titration with iodine of thiosulphate or a mixed solution of arsenious acid, bromine, and sodium hydrogen carbonate, the maximum precision is attained by using a 0.002*N*-iodine solution, provided that sufficient potassium iodide is present (cf. Geilmann and Höltje, A., 1927, 1159). R. CUTHILL.

**Volumetric determination of fluorine.** A. KURTENACKER and W. JURENKA (Z. anal. Chem., 1930, 82, 210—217).—The solution is neutralised to phenolphthalein, saturated with sodium chloride, and titrated with aluminium chloride at 70—80°, using methyl-red as indicator; during the titration the fluorine is precipitated as  $\text{Na}_3\text{AlF}_6$ . Equally good results are obtained by titrating the neutral fluoride solution with cerous nitrate at 80°, cerous fluoride being precipitated. On treating a neutral fluoride solution with boric acid the fluorine is converted into fluoborate thus:  $4\text{F}^- + \text{B}(\text{OH})_3 = \text{BF}_4^- + 3\text{OH}^-$ ; the solution is treated with 10—20 g. of potassium chloride and with an equal volume of alcohol and the free alkali titrated with sulphuric acid, using methyl-orange as indicator. A. R. POWELL.

**Effect of iron on the accuracy of the determination of dissolved oxygen [in water] by Winkler's method.** O. M. URBAIN and J. N. MILLER.—See B., 1930, 1094.

**Radiometric microanalysis. Sulphide determination and oxidimetry.** R. EHRENBERG (Mikrochem., Emich Festschr., 1930, 120—124).—The radiometric determination of sulphides by precipitation as lead sulphide, and the application of the method to the determination of other metals of the hydrogen sulphide and ammonium sulphide groups, are described. The method may be adapted also for the determination of free iodine, permanganate, ferric iron, and copper; it is simpler and more rapid than the precipitation of residual oxalate, and if conducted in acetic acid solution the liberated sulphur is without influence on the radiometric determination. For the iodine and copper determinations the activity curves are approximately linear, but with permanganate and iron the relative activity decrease diminishes at low

concentrations, and calibration curves must therefore be obtained for the relevant concentration range.

H. F. GILLBE.

**Determination of sulphate ion in the presence of lead in hydrochloric acid solution.** B. TEZAR (Arhiv Hemiju, 1930, 4, 78—86).—The solution, of volume not greater than 50 c.c., and containing 0.1—0.3 g. of lead and 0.1—0.2 g. of sulphate ion, is acidified with 10 c.c. of concentrated hydrochloric acid, and heated to boiling, when 25 c.c. of hot 2.5% barium chloride solution are added, and the mixture is diluted to 180 c.c., after which it is kept for 5 hrs. at 100°. The precipitate of barium sulphate is washed, collected, ignited, and weighed. R. TRUSZKOWSKI.

**Application of the dilution method to micro-analysis.** J. B. NIEDERL, O. R. TRAUTZ, and W. J. SASCHEK (Mikrochem., Emich Festschr., 1930, 219—232).—By employing a 1% solution in, e.g., carbon tetrachloride of the material to be analysed, Pregl's, Dubsy's, or any similar method for the determination of nitrogen may be conducted without the use of a micro-balance. The arrangement of apparatus described involves the use of a gasometer between the carbon dioxide generator and the combustion tube, and permits the renewal and removal of the generator acid without admission of air; a standard quantity of carbon dioxide of known purity may thus be used for each combustion. H. F. GILLBE.

**Systematic investigation of the reaction of diphenylbenzidine in sulphuric acid with nitric acid in the presence of chlorides. Comparison with the diphenylamine reaction.** H. RIEM (Z. anal. Chem., 1930, 81, 439—447).—The reaction of nitric acid with diphenylbenzidine follows a course exactly similar to that between nitric acid and diphenylamine, but the colour produced is about twice as intense and is much more affected by an excess of diphenylbenzidine (cf. B., 1930, 1149).

A. R. POWELL.

**Potentiometric study of the reaction between sodium ferrocyanide and nitrite.** J. V. ROMÓN (Anal. Fis. Quim., 1930, 28, 1045—1049).—The reaction  $\text{Na}_4\text{Fe}(\text{CN})_6 + \text{NaNO}_2 + \text{H}_2\text{SO}_4 = \text{Na}_3\text{Fe}(\text{CN})_6 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{NO}$  in dilute (0.3*M*) solution proceeds quantitatively and may be employed for the potentiometric determination of either the nitrite or the ferrocyanide ion, a very sharp break being obtained.

H. F. GILLBE.

**Reagent capillaries and their application to the detection of nitrate and nitrite.** F. L. HAHN (Mikrochem., Emich Festschr., 1930, 143—147).—Capillary tubes 5—6 mm. × 1—2 mm. are recommended for the storage of reagents such as diphenylamine which are unstable in solution. The diphenylamine solution may be prepared by mixing 1 part of the solid and 20 parts of sodium chloride, and adding to 20 mg. of the mixture 1 c.c. of water and 2 c.c. of concentrated sulphuric acid; when the evolution of gas has subsided the reagent is ready for use, and may be kept for a long period without becoming coloured. The 2:4-diamino-6-hydroxypyrimidine reaction may be applied to the micro-detection of nitrite, the limiting concentration being about 10<sup>-5</sup> g. per c.c.

H. F. GILLBE.



**Separation of phosphoric acid as bismuth phosphate in quantitative analysis.** A. KEŠANS (Latvij. Univ. Raksti, 1929, 1, 65—126).—The determination of phosphoric acid by precipitation as bismuth phosphate,  $\text{BiPO}_4$ , in the presence of the following cations, has been investigated: sodium, potassium, magnesium, calcium, strontium, barium, zinc, manganese, cobalt, nickel, aluminium, chromium, and iron. Although the solubility of bismuth phosphate in dilute nitric acid solution is fairly high, by using excess of solid bismuth oxynitrate,  $\text{BiONO}_3$ , phosphoric acid can be precipitated until not more than 0.1 mg.  $\text{P}_2\text{O}_5$  remains in 100 c.c. of solution. In low initial concentrations of phosphoric acid (less than 20 mg.  $\text{P}_2\text{O}_5$  per 100 c.c.) separation takes place either very slowly or not at all, unless freshly precipitated bismuth phosphate is added. Precipitation takes place in two stages. The main precipitation is carried out in a small quantity of hot or cold 2*N*. to 5*N*. nitric acid; the exact conditions depend on the nature of the cations present. The reagent is added a little at a time and the solution vigorously shaken. The solution is then diluted with hot or cold water until the concentration of nitric acid is 0.5*N* and the solution is warmed for 6—8 hrs. on a water-bath, cooled, and left until next day. The particular conditions to be observed in the presence of different cations are given. Exceptional precautions are necessary in the presence of iron. M. S. BURR.

**Determination of boron in natural waters and plant materials. Modification of the Chapin method.** L. V. WILCOX (Ind. Eng. Chem. [Anal.], 1930, 2, 358—361).—Chapin's method has been improved by the employment of copper flasks and beakers for concentration of the sample and for separation of the methyl alcohol from the alkaline distillate, and of hard (Kavalier) glass vessels for the hot alkaline solutions; methyl-red is preferable to *p*-nitrophenol as indicator for the titration. No boric acid is lost during the process of boiling to remove carbon dioxide. During the distillation of the methyl borate it is unnecessary to collect more than 200 c.c. of distillate, as 98.5% of the boron is recovered in the first 150 c.c. The method is quantitative when applied to pure compounds of boron containing not more than 5 mg. of the element, and by addition of boron to a natural water 90—95% of the total boron may be recovered. The analytical error for determinations of boron in water is of the order of 0.1 in 10<sup>3</sup>. H. F. GILLBE.

**Volumetric determination of small quantities of carbon dioxide.** J. LINDNER and F. HERNLER (Mikrochem., Emich Festschr., 1930, 191—196).—A vessel suitable for the absorption of small quantities of carbon dioxide by barium hydroxide solution is described, together with details of the determination of carbon dioxide by titration of the excess of hydroxide with 0.05*N*-acid and phenolphthalein. Quantities of from 0.1 to 1.0 mg. may be determined with a mean error of 2.0—0.2%. H. F. GILLBE.

**Helium. VII. Microanalysis of helium-neon mixtures.** F. PANETH and W. D. URRY (Mikrochem., Emich Festschr., 1930, 233—240).—By employing a heated wire manometer and a compensating manometer as two arms of a Wheatstone bridge the composition of helium-neon mixtures may be determined at pressures down to  $6 \times 10^{-6}$  mm. with an accuracy of 2%. The galvanometer deflexion bears a linear relationship both to the total pressure and to the percentage of helium in the mixture at constant pressure, and it is therefore sufficient to determine the deflexions with pure helium, pure neon, and with the mixture. H. F. GILLBE.

**Determination of rubidium and caesium with potassium chloroplatinate solution; specific reaction for caesium.** H. GRAVESTEIN (Mikrochem., Emich Festschr., 1930, 135—142).—The types of crystalline precipitate produced with chloroplatinic acid or with potassium chloroplatinate and potassium, rubidium, and caesium salts are described with special reference to the size of crystal developed under different conditions of concentration. It is possible with a saturated solution of potassium chloroplatinate to detect rubidium and caesium, and to differentiate between these metals and potassium, but not between one another. A solution of 5 g. of silver nitrate and 20 g. of sodium iodide in 20 c.c. of water is a specific reagent for caesium salts, with which it gives, in presence of alcohol, a faintly yellow precipitate resembling in form precipitated lead chloride; 1% of caesium chloride in rubidium chloride may thus be detected. Potassium, rubidium, or lithium does not give a similar precipitate, but on dilution the reagent is liable to deposit silver iodide, which should be redissolved by addition of sodium iodide. H. F. GILLBE.

**Iodometric determination of small quantities of silver, especially in presence of chlorides, bromides, and cyanides.** E. SCHULEK (Mikrochem., Emich Festschr., 1930, 260—267).—To 30 c.c. of a neutral solution containing 0.25—5 mg. of silver is added sufficient 2% potassium cyanide solution to redissolve the precipitate at first formed, and the excess of cyanide is destroyed by formaldehyde. The solution is acidified with 5 c.c. of 20% phosphoric acid, without allowing the silver cyanide to coagulate, and treated with bromine water until a permanently yellow solution is obtained; after 10 min. the excess of bromine is removed by addition of phenol solution, and the cyanogen bromide is determined by adding potassium iodide and titrating with 0.01*N*-sodium thiosulphate. Bromides and iodides do not interfere. The method may be applied to the determination of silver chloride in a mixture by extraction of the silver with 2% potassium cyanide solution, and of silver in organic mixtures by heating with sulphuric acid and hydrogen peroxide until a clear, colourless solution is obtained, and cooling and neutralising with sodium hydroxide using thymolphthalein as indicator; combustion of the organic matter with subsequent dissolution of the silver leads to low results. H. F. GILLBE.

**Micro-determination of calcium.** M. MOUSSE-ROU (Bull. Soc. Chim. biol., 1930, 12, 1014—1021).—The calcium is precipitated by potassium nickelinitrite as  $\text{K}_2\text{CaNi}(\text{NO}_2)_6$ , the precipitate after being washed with dilute acetone and with a mixture of alcohol and ether is reduced in dilute sodium hydroxide solution

with aluminium powder in presence of a small quantity of zinc powder, and the ammonia formed is carried over in a current of steam, collected in dilute sulphuric acid, and titrated. W. O. KERMACK.

**Separation of barium from lead sulphate by means of ammonium acetate.** I. MAJDEL (Arhiv Hemiju, 1930, 4, 76—78).—Lead sulphate cannot be separated from barium sulphate by extraction with ammonium acetate solution, owing to the presence of the insoluble double sulphate,  $\text{BaSO}_4 \cdot \text{PbSO}_4$ . The proportion of lead present as double compound rises with increase in the proportion of barium to lead in the precipitate; when Ba:Pb is 7:1 or more, lead is present exclusively as double compound. Separation can be effected by the use of hydrogen sulphide.

R. TRUSZKOWSKI.

**Volumetric determination of barium by direct titration with potassium chromate.** S. BALACHOVSKI (Z. anal. Chem., 1930, 82, 206—210).—The method is based on the fact that potassium chromate reacts alkaline to bromothymol-blue and phenol-red, so that when a neutral solution of barium salt is titrated with potassium chromate in the presence of one of these indicators the end-point is marked by a characteristic colour change. Good results are obtained on a microchemical scale, using 1—2 c.c. of barium solution and 0.04—1N-potassium chromate in a special micro-burette provided with a three-way stopcock above the usual stopcock so that the burette can be filled from the bottom from a tubular reservoir parallel to the burette.

A. R. POWELL.

**Applications of hexamethylenetetramine, ammonia, and hydrazine as micro-chemical reagents.** P. RAY and P. B. SARKAR (Mikrochem., Emich Festschr., 1930, 243—253).—Hexamethylenetetramine in presence of ferro- or ferri-cyanide or of nitroprusside yields with magnesium salts well-defined crystalline precipitates, the sensitivity being 0.0005—0.008 microgram; calcium and lithium may be detected by the same reagents, but the sensitivity for lithium is only 0.065 microgram. Molybdenum (0.065 microgram) in sulphuric acid solution yields with hexamethylenetetramine characteristic white needles. Silver (0.065), manganese (0.02), nickel (0.15), and cobalt (0.02 microgram) yield with sodium dithionate and hexamethylenetetramine characteristic white or coloured crystals. From a solution of copper thiocyanate gaseous ammonia causes the separation of blue needles of composition  $\text{Cu}(\text{SCN})_2 \cdot 2\text{NH}_3$ , the limit of sensitivity being 0.065 microgram of copper; zinc and cadmium yield with ammonium thiocyanate and hydrazine colourless crystals of  $\text{M}(\text{SCN})_2 \cdot 2\text{N}_2\text{H}_4$ , the sensitivity limits being 0.15 and 0.065 microgram, respectively.

H. F. GILLBE.

**Colour reactions for magnesium.** I. M. KOLTHOFF (Mikrochem., Emich Festschr., 1930, 180—190).—Titan-, Clayton-, and brilliant-yellow are delicate reagents for magnesium, with which in alkaline solution they give a red coloration; the sensitivity with Titan-yellow is about 0.2 mg. per litre, and the colour is intensified by small quantities of calcium salts. A mixture of magnesium chloride with Titan-yellow provides a sensitive indicator, there being a sharp colour change over the range  $p_{\text{H}}$  2.5—3; the sensi-

tivity increases with the magnesium concentration. Nickel and cobalt give a similar coloration, which does not develop in presence of potassium cyanide, and manganese also interferes; for maximum sensitivity it is best to remove all three metals as sulphide. Beryllium does not interfere except to reduce the sensitivity. 1:2:5:8-Tetrahydroxyanthraquinone yields with magnesium salts a blue colour, but the reaction is not very specific. 2:4-Dihydroxybenzeneazo-*p*-nitrobenzene, besides being a fairly specific reagent for magnesium, is a useful indicator over the range  $p_{\text{H}}$  10.8—13.0; beryllium, aluminium, lanthanum, zinc, cadmium, cobalt, and nickel all interfere to some extent with the detection of magnesium by this reagent. Congo-corinth in alkaline solution gives, in presence of magnesium, cobalt, and nickel, a brilliant violet coloration. Aniline-yellow S in slightly acid solution (about  $p_{\text{H}}$  5) yields a violet colour with a number of metals, but is especially sensitive to copper (0.4 mg. per litre). A number of other dyes has been investigated, and in all cases cobalt and nickel give the same reactions as magnesium.

H. F. GILLBE.

**Gravimetric microanalysis of beryllium silicate rocks.** A. BENEDETTI-PICHLER and F. SCHNEIDER (Mikrochem., Emich Festschr., 1930, 1—17).—Methods available for the determination of phosphate, aluminium, iron, beryllium, and magnesium have been critically examined with the view of establishing a satisfactory system of separation. In the method proposed, silica is removed by treating the mineral with hydrofluoric and sulphuric acids, and the phosphate is determined by the ammonium phosphomolybdate method. The excess of molybdate is removed by hydrogen sulphide, and aluminium and iron are precipitated by 8-hydroxyquinoline, the excess of the reagent being destroyed by concentrated sulphuric acid; beryllium and aluminium are then determined together as anhydrous sulphate. After dissolution of the sulphate the beryllium is precipitated as hydroxide by blowing a current of air containing ammonia against the surface of the hot solution; the magnesium, none of which is precipitated by this procedure, is finally determined by precipitation as magnesium ammonium phosphate. In the determination of beryllium as sulphate it is advisable to moisten the residue, after evaporating to dryness, with concentrated sulphuric acid, to evaporate to dryness at 250°, and heat at 320° for 15 min. in a current of air; by this means the anhydrous salt is obtained without decomposition to basic salt.

H. F. GILLBE.

**Quantitative precipitations at very high concentrations.** II. V. NJEGOVAN and V. MARJANOVIĆ (Z. anal. Chem., 1930, 82, 154—161; cf. A., 1928, 978).—The precipitation of magnesium ammonium phosphate has been studied, using very concentrated solutions with the view of obtaining minute crystals and thus minimising the error due to internal adsorption. As a result, the following procedure for the determination of magnesium has been worked out. The solution of magnesium sulphate or chloride, containing not more than 0.12—0.18 g. of magnesium, is evaporated to dryness, and any hydrochloric or oxalic acid removed by warming with 5 c.c. of con-

centrated sulphuric acid. After addition of the requisite amount of a cold saturated solution of disodium hydrogen phosphate, sufficient of a mixture of equal volumes of concentrated ammonia solution and 96% alcohol to make the solution alkaline is added all at once. By diluting with 150–200 c.c. of water and warming for 1 hr. the precipitate is caused to become coarser, and after cooling is collected in a porcelain filtering-crucible, washed with 2.5% ammonia solution, and dried to constant weight at about 850°.

R. CUTHILL.

**Determination of zinc as oxide, silicate, ferrite, sulphate, and sulphide.** V. TAFEL and G. SILLE (*Z. angew. Chem.*, 1930, **43**, 948–951).—Zinc silicate can be separated from zinc ferrite and sulphide by stirring the mixture in boiling 6% acetic acid. The zinc silicate is decomposed by the acid; the ferrite and sulphide are not untouched, but the separation is sufficient for practical purposes. Attempts to separate zinc ferrite and sulphide by means of sulphuric acid or aqueous sodium hydroxide were not sufficiently effective, but directions are given for their separation by means of fused sodium hydroxide. Under optimum conditions, this converts zinc ferrite into sodium zincate and ferric oxide, whilst zinc sulphide is unchanged.

E. S. HEDGES.

**Analytical applications of reaction of ammonia with resorcinol in presence of cations.** L. BEY (*Bull. Soc. chim.*, 1930, [iv], **47**, 1192–1193; cf. A., 1929, 1064).—On addition of a 5% ethereal solution of resorcinol to an aqueous solution of cadmium chloride containing just sufficient ammonia to keep the hydroxide in solution a transient blue ring soon develops at the surface of contact of the two liquids, this reaction being obtained with concentrations of the chloride as low as 0.0011%. If copper is present in not too great amount it may be prevented from interfering by addition of potassium cyanide. Stannic tin produces a blue coloration on addition of ammonia and 2–3 c.c. of a 5% aqueous solution of resorcinol, this test being applicable even in presence of a considerable excess of antimony. The limit of sensitivity is represented by a 0.0015% solution of stannous chloride oxidised with bromine water.

R. CUTHILL.

**Titration of lead by means of a thermionic titrometer.** R. W. GELBACH and K. G. COMPTON (*Ind. Eng. Chem. [Anal.]*, 1930, **2**, 397–398).—A device employing three thermionic valves, by means of which rapid potentiometric titration of lead with potassium chromate solution may be carried out, is described. Calomel and platinum electrodes are used and are connected across the grid and filament of the first valve; the current in the anode circuit of the third valve is adjusted to give a mid-point reading on a sensitive milliammeter, and the equivalence point is that at which the deflexion of the needle becomes a maximum. A sensitivity of 1 millamp. for 120 millivolts change of potential in the titration cell may readily be obtained, whilst for null-point determinations the sensitivity may be increased to 60 microamp. per millivolt. In place of three triodes one tetrode and one triode may be employed.

H. F. GILLBE.

**Titration of lead salts.** R. C. WILEY, P. M. AMBROSE, and A. D. BOWERS (*Ind. Eng. Chem. [Anal.]*, 1930, **2**, 415–416).—The neutral solution, containing lead but no other metals yielding insoluble molybdates, is neutralised with ammonia solution, any precipitated lead hydroxide being dissolved by boiling with ammonium nitrate solution, and titrated while hot with standard ammonium molybdate solution, a saturated solution of pyrogallol in chloroform being employed as an external indicator. One drop of neutral 0.000005*N*-molybdate solution gives with this indicator a definite brown coloration, but in acid solution the molybdate-ion concentration must be not less than 0.002*N* before it can be detected. The indicator is not influenced by the precipitated lead molybdate, nor, in contrast to the stannous chloride-thiocyanate indicator, by ammonium salts; a solution in carbon tetrachloride serves equally well, but the aqueous solution is only one tenth as sensitive.

H. F. GILLBE.

**Sensitivity of chemical reactions.** W. BÖTTGER [with (FRL.) B. M. SCHALL] (*Mikrochem., Emich Festschr.*, 1930, 29–38).—The influence of the total volume of solution and of illumination on the sensitivity of the detection of certain ions by precipitation reactions has been investigated; with a few exceptions the sensitivity is greatly increased if the reaction mixture be observed under strong illumination. With a total volume of 10 c.c. the lead ion may be detected by the chromate method at a concentration of  $1 \times 10^{-6}M$  if the solution is observed directly, whereas under illumination a concentration of  $1 \times 10^{-8}M$  is sufficient for its detection. With a total volume of 1 c.c., lead at  $1 \times 10^{-9}M$  concentration may be detected, and with about 0.2 c.c. at  $0.5 \times 10^{-9}M$ . Analogous results are obtained for the determination of cobalt by means of nitroso- $\beta$ -naphthol; the minimum concentration falls from  $1 \times 10^{-7}M$  for a volume of 10 c.c., observed ordinarily, to  $1 \times 10^{-10}M$  for 1 c.c. observed under illumination. The nephelometric method is thus more sensitive than the spot method, but at these very low concentrations cannot be regarded as specific and should be employed only for quantitative work. An apparatus whereby 0.06 microgram of boron may be detected by the boric ester flame coloration is described. H. F. GILLBE.

**Quantitative separation of lead and bismuth.** H. FUNK and J. WEINZIERL (*Z. anal. Chem.*, 1930, **81**, 380–385).—Lead may be precipitated as chromate free from bismuth by the addition of potassium chromate to a boiling solution of the metals containing 25 c.c. of glacial acetic acid and 15 g. of sodium acetate in a volume of 150–200 c.c. Bismuth is recovered from the filtrate, after destroying the excess of chromate with alcohol and hydrochloric acid, by saturation with hydrogen sulphide. A. R. POWELL.

**Micro-determination of thallium and lead.** L. MOSER and W. REIF (*Mikrochem., Emich Festschr.*, 1930, 215–218).—To 6–8 c.c. of the solution containing thallium are added a few drops of ammonia solution and, at the b. p., an excess of potassium chromate solution; if much ammonium salt is present a little alcohol should be added to depress the solubility of the thallous chromate. The precipitate is

washed with alcohol and dried at 120°. Lead is precipitated by ammonium phosphate from a hot, slightly alkaline solution containing sulphosalicylic acid. The precipitate need not be ignited, but should be washed with ammonia solution and dried at 150°.

H. F. GILLBE.

**Application of microchemical methods to the determination of traces of substances.** R. LUCAS and F. GRASSNER [with E. NEUKIRCH] (*Mikrochem., Emich Festschr.*, 1930, 197—214).—The microelectrometric method of Pregl is suitable for the determination of small quantities of copper, but where traces only (1 microgram) are concerned, the cathodically deposited metal is dissolved in nitric acid and precipitated as potassium lead copper nitrite by evaporation of the solution with lead acetate and treatment of the residue with a solution of potassium nitrite, ammonium acetate, and acetic acid; the product is compared with that given by a known amount of copper. Quantities of lead down to 25 micrograms, even at very high dilutions, may be determined by precipitation with copper as sulphide, dissolution of the precipitate in nitric acid, and deposition as lead peroxide on a stationary anode; the precipitate is titrated with potassium iodide and 0.01*N*-sodium thiosulphate. Traces of copper, nickel, and iron, simultaneously present in oils, are best determined by electrolytic separation of the copper, precipitation of the nickel with dimethylglyoxime, and colorimetric determination of the iron with thiocyanate. Details are given of the determination of hydrogen in iron by titration of the hydrochloric acid evolved from phosphorus naphthylchloride by the action of the gas liberated by the heated metal, and of carbon monoxide by dissolution of the metal in an acid copper ammonium chloride solution, oxidation of the evolved gas by iodine pentoxide at 130°, and titration of the liberated iodine; traces of metallic carbonyls in air may be determined by a modification of this process. By freezing out with liquid air the carbon dioxide produced by combustion and measuring the pressure change on allowing the gas to re-evaporate into an evacuated vessel of known volume, the quantity of organic vapour present in air may be determined.

H. F. GILLBE.

**Microelectrolytic determination of copper in organic substances.** E. PHILIPPI and F. HERNLER (*Mikrochem., Emich Festschr.*, 1930, 241—242).—Pregl's method is applicable to organic substances after ignition, and is satisfactory as regards accuracy, rapidity, and the quantity of material needed.

H. F. GILLBE.

**"Direct-green B,"** a very sensitive reagent for detection of copper. P. SISLEY and DAVID (*Bull. Soc. chim.*, 1930, [iv], 47, 1188—1192).—As little as 1 part of copper in 10<sup>7</sup> parts of aqueous solution produces a reddish-violet colour when a 0.1% solution of direct-green B is added and the mixture heated on a boiling water-bath. The solution should be at  $p_H$  6—9, and colloids and salts of iron, chromium, mercury, and silver should be absent. The test is most satisfactory when the ratio of dye to copper in the mixture is about 10 : 1, and is particularly suitable for the detection of copper in distilled water.

R. CUTHILL.

**Applicability of chemical reactions to micro-analysis. I. Colorimetric micro-determination of metals with 8-hydroxyquinoline.** [With W. WOLKER and E. SKOPP.] **II. Detection and determination of small quantities of silicic and selenious acids with pyrrole.** [With M. TETTERBAUM.] **III. Gravimetric micro-determination of copper and titanium with 5 : 7-dibromo-8-hydroxyquinoline.** [With H. KÜSTENMACHER.] R. BERG (*Mikrochem., Emich Festschr.*, 1930, 18—22, 23—26, 26—28).—I. The magnesium is precipitated with 8-hydroxyquinoline in presence of ammonium chloride; after being heated for 10 min. on the water-bath the precipitate is removed by centrifuging and dissolved in *N*-hydrochloric acid. Sodium hydroxide solution and a special reagent are added, and after heating the mixture at 80° for 30 min. the colour is compared with that given by a known amount of magnesium. The reagent is prepared by dissolving 100 g. of sodium tungstate, 20 g. of phosphomolybdic acid, and 50 c.c. of 85% phosphoric acid in water, boiling for 2 hrs., and diluting to 1 litre. The method yields good results in presence of 40 times the quantity of calcium, but an excess of 8-hydroxyquinoline must be used to allow for the formation in solution of the calcium compound.

II. In presence of selenious acid pyrrole yields a deep blue coloration; in phosphoric acid solution the sensitivity is about 1 in 500,000, but in presence of iron this is increased to 1 in 12 × 10<sup>5</sup>. To the selenious acid solution (1—2 c.c.) is added 1 c.c. of 5% ferric chloride solution and the volume is made up to 10 c.c. with phosphoric acid (*d* 1.85); 5—10 drops of a 1% solution of pyrrole in alcohol are then added. If 2 c.c. of 8% ammonium molybdate solution and 10 c.c. of 1 : 1 sulphuric acid are used instead of phosphoric acid the sensitivity is about 1 in 30 × 10<sup>5</sup>, but the reaction is less specific. The second method serves also for the detection of silica, but arsenious acid interferes. Both selenious and silicic acids may be determined colorimetrically by the pyrrole reaction, but the colour fades rather rapidly.

III. 5 : 7-Dibromo-8-hydroxyquinoline will detect 1 in 10<sup>6</sup> of copper or titanium and 2 in 10<sup>6</sup> of iron. For the determination a 0.1% solution of the reagent in acetone is added to the slightly acid solution, at about 50°, containing the metal and about 30% of acetone; after boiling for 3—5 min., the precipitate is removed and washed with a warm, slightly acid 30% solution of acetone, and dried at 110—120°. H. F. GILLBE.

**Poulsen arc as a means of detecting traces of impurities in metals.** H. E. REDEKER and P. A. LEIGHTON (*J. Amer. Chem. Soc.*, 1930, 52, 4169—4170; cf. Stowell and Redeker, *A.*, 1929, 1359).—With the non-oscillating arc in hydrogen the spectra of the cathode metals (copper and sodium) were revealed, but with the oscillating circuit these spectra were suppressed and spectra due to traces of zinc, titanium (0.005%), and aluminium (0.0045%) in the cathode became greatly accentuated. A gold-tipped copper cathode in an atmosphere of ammonia gave somewhat similar results. J. G. A. GRIFFITHS.

**Volumetric determination of mercury.** O. PROČKE (*Coll. Czech. Chem. Comm.*, 1930, 2, 593—

608).—Denigès' cyanide method for the determination of mercury has been modified. At the end-point the complex formed is not  $\text{Hg}(\text{CN})_2 \cdot 2\text{KCN}$ , as assumed by Denigès, but  $\text{Hg}(\text{CN})_3^-$ , of which the dissociation constant  $k = [\text{Hg}(\text{CN})_2][\text{CN}^-]/[\text{Hg}(\text{CN})_3^-]$  is  $3.0 \times 10^{-4}$  at  $20^\circ$ , within the limits of concentration of the iodide ions from  $2 \times 10^{-2}$  to  $10^{-3}N$ . From this value of  $k$  a theoretical factor  $f$  has been derived to replace the empirical factor of Denigès; tabulated values of  $f$  are given for a range of volumes of silver nitrate employed. The following procedure is recommended: to 50 c.c. of a solution containing not more than 0.5 g. of mercury are added a slight excess of 10% ammonia solution, 25 c.c. of 0.2M-potassium cyanide solution, and 1 c.c. of 0.1N-potassium iodide solution. The solution is titrated with 0.1N-silver nitrate solution until turbidity appears, and is then diluted to 100 c.c. and titrated further until opalescence reappears. If considerable quantities of salts are present the solution should be still further diluted, as otherwise the end-point may be rendered less distinct owing to flocculation of the silver iodide. The method is not recommended for the analysis of cinnabar or of mercuric cyanide. H. F. GILLBE.

**Gravimetric determination of aluminium using hydrazine carbonate.** A. JÍLEK and J. LUKAS (Chem. Listy, 1930, 24, 365—369).—The solution containing 0.1—0.2 g. of alumina is made feebly acid and 2—3 c.c. of 50% hydrazine carbonate are added. The mixture is heated for 60 min. at  $100^\circ$ , filtered, and the precipitate of basic aluminium carbonate is washed with hot water or with hot neutral 1% ammonium nitrate solution. The precipitate is calcined to constant weight, and weighed as aluminium oxide. R. TRUSZKOWSKI.

**Determination of manganese in cobalt steels.** P. KRÜGER.—See B., 1930, 1069; J. KASSLER.—See B., 1930, 1071.

**Analytical chemistry of rhenium. I. Determination of soluble per-rhenates by means of nitron.** W. GEILMANN and A. VOIGT (Z. anorg. Chem., 1930, 193, 311—315).—The solubility of nitron per-rhenate in water at  $0^\circ$  is 0.018 g. per 100 c.c., and practically zero in a 0.3% solution of nitron acetate. A procedure for determining soluble per-rhenates by means of nitron acetate is described and examples of the method are given in which the maximum error was 0.2 mg. Re. F. L. USHER.

**Hydroxylamine as a precipitation agent.** J. C. ROLDÁN (Anal. Fis. Quím., 1930, 28, 1080—1083).—Addition of hydroxylamine to neutral solutions of iron, nickel, cobalt, aluminium, or zinc salts yields precipitates which are apparently identical with those produced by ammonia, and may result from decomposition of the hydroxylamine; precipitates are not formed with silver, gold, and manganese salts. Platinum yields a crystalline precipitate similar to that obtained by boiling a dilute chloroplatinic acid solution with hydroxylamine. With copper salts a copious gelatinous green precipitate is formed; when kept it becomes white and crystalline, but the precipitation is not complete. Chromium salts give a similar result. On addition of hydroxylamine to a

colloidal solution of copper ferrocyanide a reddish-violet substance which exhibits green fluorescence in diffused light and blue fluorescence in sunlight is produced. Cadmium salts yield slowly a white crystalline precipitate different from that obtained with ammonia. H. F. GILLBE.

**Quantitative analysis of steels by spectrum analysis.** F. TWYMAN and A. A. FITCH.—See B., 1930, 1032.

**Sensitive colour reactions for cobalt.** E. EEGRIWE (Z. anal. Chem., 1930, 82, 150—154).—As little as 0.0003 mg. of cobalt in 1 c.c. of neutral solution causes a violet coloration on adding to 1 drop 5—10 drops of a 0.02% aqueous solution of eriochrome-blue-black B (G) and 1 drop of a solution of 3.5 g. of sodium nitrite in 100 c.c. of water and acidifying with acetic acid. In presence of nickel the colour appears only after a little time, and copper, vanadium, and tungsten also produce violet colorations. Under similar conditions eriochrome-red B (G) gives a permanent orange-red colour, the minimum amount of cobalt required being 0.0001 mg. Chromium salts and vanadates produce similar colorations, which are, however, transient. In detecting cobalt in presence of a large amount of nickel the solution is boiled after addition of concentrated sodium hydroxide solution and glycerol, and under these conditions the cobalt remains in solution (cf. Donath, A., 1901, ii, 389) and may be detected in the neutralised filtrate by the above tests. R. CUTHILL.

**Determination of chromium in special steels.** P. KLINGER.—See B., 1930, 1069.

**Detection of traces.** F. FEIGL (Mikrochem., Emich Festschr., 1930, 125—134).—Traces (1 in 6000) of chromate may be detected by acidifying the solution with sulphuric acid, reducing the permanganate with a crystal of sodium azide, and adding an alcoholic solution of diphenylcarbazide to the colourless solution; a violet to red coloration indicates chromate. Traces of nickel in cobalt salt solutions may be detected by adding just enough potassium cyanide solution to dissolve the precipitate first formed, oxidising with hydrogen peroxide, and adding dimethylglyoxime; after evaporation to a syrup formaldehyde is added, and on shaking with ether a red precipitate at the interface indicates the presence of nickel. The reaction depends on the stability of potassium cobalticyanide towards dimethylglyoxime and formaldehyde, but as in presence of excess of potassium cyanide the nickel-ion concentration is reduced and the test is rendered less sensitive, the cyanide must be destroyed by formaldehyde. By adaptation of this method cobalt salts absolutely free from nickel may be prepared. Traces of hydrogen sulphide in water may be removed by shaking with mercury, and the presence of sulphur may be demonstrated by the evolution of nitrogen when the mercury is covered with an acidified solution of sodium azide and iodine; 0.05 microgram of hydrogen sulphide in 10 c.c. of water may thus be detected. A similar process may be employed to detect free sulphur in carbon disulphide, but the mercury must be heated on the water-bath to ensure removal of carbon

disulphide, which also catalyses the azide-iodine reaction. If the carbon disulphide is evaporated to dryness and the residue is treated with sodium sulphite solution, free sulphur, if present, forms sodium thiosulphate, which also may be detected by the azide-iodine reaction; this method is, however, much less sensitive than that employing mercury.

H. F. GILLBE.

**Permanganometric determination of molybdenum.** T. DÖRING (Z. anal. Chem., 1930, 82, 193—206).—Accurate results for molybdenum are obtained by the methods of Kassler (A., 1929, 165) and Reissaus (Metall u. Erz, 1924, 21, 118), but each method requires rather careful manipulation. The latter method has been modified by collecting the reduced molybdenum solution from the Jones reductor directly in an excess of ferric alum solution containing sulphuric and phosphoric acids and titrating the resulting ferrous salt with permanganate; this procedure avoids the inconvenience of filling the apparatus with carbon dioxide and gives good results with 0.0025—0.33 g. of molybdenum.

A. R. POWELL.

**Volumetric determination of the rarer metals by visual conductivity titration.** E. ROTHER and G. JANDER (Z. angew. Chem., 1930, 43, 930—933).—Conductometric titration methods of determining molybdenum, tungsten, and thallium are shown to be not less exact and much more rapid than gravimetric methods. The molybdenum is titrated in the form of sodium molybdate against lead acetate. The determination of tungsten by titration of sodium tungstate with lead nitrate is much more accurate than any gravimetric method in use for this purpose. Thallium is determined by titration of thallous sulphate with sodium chromate.

J. W. SMITH.

**Luminescence test for tin.** F. L. HAHN (Z. anal. Chem., 1930, 82, 113—114).—Evidence is adduced to show that it is very unlikely that tin hydride is formed in the above reaction (cf. Meissner, this vol., 882).

R. CUTHILL.

**Gravimetric determination of vanadium in high-speed steel.** S. CINBERG.—See B., 1930, 1069.

**Micro-balance with proportional swings and damped oscillations.** J. DONAU (Mikrochem., Emich Festschr., 1930, 39—42).—A new type of micro-balance, in which the oscillations are air-damped, can be adjusted to give practically uniform sensitivity over the whole range of deflexions and at varying loads. Correction curves are unnecessary. The balance may be adjusted to give a movement of 1 division per 0.05 mg., and may be loaded up to 500 mg.

H. F. GILLBE.

**Use of filter pencils.** E. S. VON BERGKAMPF (Mikrochem., Emich Festschr., 1930, 268—274).—Filter pencils made of tightly-rolled ashless filter-paper placed in a glass tube serve for the separation of precipitates such as silica which have to be further treated after ignition.

H. F. GILLBE.

**Sublimation apparatus, using sintered glass.** A. SOLTYS (Mikrochem., Emich Festschr., 1930, 275—279).—An apparatus is described wherein saturation of the current of air by the vapour of the subliming substance is ensured by spreading the

material on a plate of sintered glass; the maximum sublimation velocity at any given temperature is thus obtained. The plate is fused into a glass tube, which is fitted at the lower end with a water-cooled tube for condensing the vapour and at the upper end with a capillary for the admission of the air current.

H. F. GILLBE.

**Instrument for measuring and recording the concentration of hydrogen and other ions.** P. WULFF and W. KORDATZKI.—See B., 1930, 1077.

**Apparatus for determining aboard ship the salinity of sea-water by the electrical conductivity method.** F. WENNER, E. H. SMITH, and F. M. SOULE (Bur. Stand. J. Res., 1930, 5, 711—732).

**Simple aqueous electrode.** C. P. HEINLEIN (Science, 1930, 72, 16—17).—An electrode suitable for laboratory use with high-frequency E.M.F. is described.

L. S. THEOBALD.

**Dark-field microscopy with many-sided illumination.** C. SPIERER (Kolloid-Z., 1930, 53, 88—90).—The advantages of a method of ultramicroscopy previously described (*ibid.*, 51, 162) are pointed out.

E. S. HEDGES.

**Impervious tubes of pure alumina.** F. ADCOCK and D. TURNER (J. Sci. Instr., 1930, 7, 327).—Tubes are made by extrusion through dies, and fired at about 1900° in a carbon resistance furnace, being supported by packing with powdered alumina. They are then glazed by careful heating with an oxyhydrogen flame, and are practically impervious to gases at the ordinary temperature.

C. W. GIBBY.

**Visual spectrophotometer.** H. BUCKLEY and F. J. C. BROOKES (J. Sci. Instr., 1930, 7, 305—317).—A detailed account of the construction of a visual spectrophotometer is given. The guiding principles are that (1) the photometric scale must not involve the use of moving optical media, (2) the Maxwellian method of view must be used, (3) the light sources must be uniformly bright and of high brightness, (4) the wave-length scale must be free from errors introduced by changes in slit width. The average deviation from the mean of spectral transmissions measured over the greater part of the spectrum is about 0.5%.

C. W. GIBBY.

**Improved Victor Meyer mol. wt. apparatus.** M. M. HICKS-BRUUN (Bur. Stand. J. Res., 1920, 5, 575—584).—The apparatus is modified to permit measurements at 1 and 0.5 atm. By using Berthelot's method of limiting density most of the effects of departure from the perfect gas laws are eliminated. Hydrocarbons gave values for mol. wt. differing from the theoretical by the following maximum deviations: benzene (16 experiments), 0.2%; hexane (4), 0.24%; naphthalene (4), 0.06%.

W. E. DOWNEY.

**Micro-manometer of high sensitivity.** E. OWEY (Phil. Mag., 1930, [vii], 10, 544—551).—The manometer, sensitive to pressure differences of the order 0.00001 in. of water, is constructed on the Chattock tilting-cup principle, the applied pressure difference being measured in terms of the displacement of a bubble in the liquid in a capillary tube connecting the two cups. Xylene was found to be the most satisfactory manometric liquid.

N. M. BLIGH.



**Rotatable manometer for high vacua.** M. BRUNNER (Helv. Chim. Acta, 1930, 13, 915—917).—A mercury manometer of the McLeod type, reading from 0.001 to 1 mm., is described. It is cheaper in construction and less fragile than the usual forms. The total weight, including mercury, is 150—300 g.

F. L. USHER.

**Universal luminoscope (fluoroscope, phosphoroscope) and nepheloscope.** S. MOHORVIČIĆ (Arhiv Hemiju, 1930, 4, 73—76).

R. TRUSZKOWSKI.

**Laboratory apparatus of amber.** C. PLONAT and A. EISENACK (Chem. Fabr., 1930, 422).—Beakers etc. constructed of amber are completely resistant to concentrated hydrofluoric acid and to 50% potassium hydroxide solution at the temperature of the water-bath. After 4 weeks' use a slight gain in weight was recorded owing to absorption of hydrofluoric acid, but this caused no inconvenience. In extractions with this acid it is desirable to cover the liquid with a film of molten paraffin to prevent fuming. C. IRWIN.

**Small apparatus for attaining very low temperatures.** M. RUHEMANN (Z. Physik, 1930, 65, 67—74).—A simple apparatus which, by use of Linde's principle, attains liquid hydrogen temperatures in liquid air surroundings, and liquid helium temperatures in liquid hydrogen surroundings, is described. The possibilities of the apparatus, which gives only small quantities of liquid helium, are discussed.

A. B. D. CASSIE.

**Evaporation of large quantities of solution in the laboratory.** P. FUCHS (Chem. Fabr., 1930, 421—422).—The best arrangement for providing a slow continuous feed of liquor to an evaporating basin, distillation flask, or filter consists of a form of Mariotte's bottle set up so that the level to be maintained in the basin etc. is in a line with the bottom of the two tubes within the bottle. The feed is started by blowing into the air tube. For smaller quantities of liquid an inverted flask with a long open neck dipping beneath the surface of the liquid in the basin is sufficient. Apparatus with large inverted aspirators is objectionable. C. IRWIN.

**Rapid evaporation.** H. N. NAUMANN (Biochem. Z., 1930, 226, 164—165).—A reply to Jantzen and Schmalfuss (this vol., 1152). P. W. CLUTTERBUCK.

**Apparatus for distillation in a high vacuum.** S. FRÄNKEL and H. MATHIS (Biochem. Z., 1930, 226, 157—161).—A modification of the usual apparatus is described. P. W. CLUTTERBUCK.

**General utility laboratory still.** G. PITMAN (Ind. Eng. Chem. [Anal.], 1930, 2, 418).—A flask fitted with a suction drain tube, a fractionating column, and a feed tube from a convenient reservoir is recommended for the semi-continuous recovery of solvents. The flask is immersed in a constant-level water-bath fed from the condenser outlet. H. F. GILLBE.

**Theory, design, and construction of sensitive vacuum thermopiles.** C. H. CARTWRIGHT (Rev. Sci. Instr., 1930, 1, 592—604).—Various methods of designing thermopiles are discussed; the design for maximum sensitivity depends on the type of galvanometer available. A method of calculating the optimum

number of junctions is discussed; a large number is desirable if the galvanometer resistance is high, or if the radiant energy cannot all be concentrated into a small receiver. The construction of a vacuum thermocouple having a sensitivity of 1 microvolt for  $10^{-8}$  g.-cal./sec. is described. The vacuum sensitivity is 20—40 times that in air. The receiver is made of thin blackened gold lead, and the thermocouple wires of alloys of 97% bismuth-3% antimony, and 90% bismuth-10% tin. C. W. GIBBY.

**Micro-furnace for temperatures above 1000°.** H. S. ROBERTS and G. W. MOREY (Rev. Sci. Instr., 1930, 1, 576—580).—A strip of alloy (Pt 60%, Rh 40%), 0.01 mm. thick, is bent into a U about 1.2 mm. wide and 10 mm. deep, and is heated electrically. The temperature is measured with an optical micro-pyrometer, and the m. p. of a few mg. of substance placed upon it is observed. Calibration of the pyrometer is necessary, as the strip is not a black body, and in addition to the usual standard temperatures the following are recommended: a mixture of 15% calcium oxide and 85% silica,  $1698 \pm 5^\circ$ ; 15% magnesium oxide and 85% silica, m. p.  $1695 \pm 5^\circ$ . The mixtures must be free from alkalis and alumina, and sintered for some time below their m. p. The furnace cannot be used above  $1850^\circ$ . C. W. GIBBY.

**Quartz monochromator and its spectral transmission.** W. E. FORSYTHE and B. T. BARNES (Rev. Sci. Instr., 1930, 1, 569—575).—The construction of the instrument is described in detail. It contains two Cornu prisms mounted and rotated so that each remains in the position of minimum deviation. The transmission is 25% at 2600 Å. and 47% at 6000 Å. C. W. GIBBY.

**Method for determining critical constants, and its application to diphenyl.** J. M. CORK (Rev. Sci. Instr., 1930, 1, 563—568).—After a preliminary approximate determination of the critical density, three calibrated glass tubes are sealed off containing such amounts of diphenyl that at the critical temperature the densities will be respectively slightly less than, slightly greater than, and as nearly as possible equal to the critical density. The tubes are mounted in a copper block, and heated in an electric furnace, in the side of which is a slit for observing the position of the meniscus with a cathetometer. Three sets of equations involving the densities of the gaseous and liquid phases are solved graphically. The critical temperature is determined by heating until the meniscus in the third-mentioned tube disappears. For diphenyl, possibly slightly impure, the following values were obtained: m. p.  $70.4^\circ$ ,  $p_c$  31,400 mm.,  $t_c$   $528^\circ$ ,  $d_c$  0.343 g. per c.c., coefficient of expansion between  $100^\circ$  and  $150^\circ$ , 0.00080. C. W. GIBBY.

**New mechanical disintegrator.** E. W. SCHULTZ and F. D. BANHAM (Science, 1930, 72, 147).—A pestle and mortar grinding machine, especially suitable for virus tissues, is described. L. S. THEOBALD.

**Rapid positive control method of handling small quantities of liquids.** E. L. HARRINGTON (Science, 1930, 72, 201—202).—An all-glass pipette operated by a mercury plunger is described.

L. S. THEOBALD.

**Peculiar action of photographic flashlight.** W. ZIMMERMANN (*Naturwiss.*, 1930, 18, 867).—Experiments with a "vacuum" flashlight, made up of 0.08 g. of aluminium foil, 0.5  $\mu$  thick in a glass bulb, filled with oxygen under 140 mm. pressure, with an electric firer, are described and an explanation of its action is given. A. J. MEE.

**Thermostat for temperatures below 20°.** D. H. MATHESON (*Chemist-Analyst*, 1930, 19, No. 3, 22).

#### CHEMICAL ABSTRACTS.

**Laboratory filter press.** P. MEDVEDCHUK (*Masloboino Zhir. Delo*, 1929, No. 2, 25—27).—An apparatus suitable for the extraction of fat by hot-pressing is described. CHEMICAL ABSTRACTS.

**Wash-bottle for organic, poisonous, or corrosive liquids.** W. FERMAZIN (*Chem.-Ztg.*, 1930, 54, 804).—A stopper bearing three fused-in tubes, of which the blowing tube is provided with a valve, is employed. S. I. LEVY.

**Methods of dialysis.** A. A. SCHMIDT (*Biochem. Z.*, 1930, 225, 216—226).—Methods for the preparation of collodion sacs, for the dialysis of 500—1000 c.c. of fluid, and for warming the dialysis water are described. P. W. CLUTTERBUCK.

**Alumina in a new form as laboratory desiccant.** J. B. BARNETT, R. B. DERR, and E. W. SCRIPTURE, jun. (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 355—357).—A crystalline form of aluminium hydroxide, which when suitably treated acquires marked adsorptive properties, has been prepared. Owing to its high porosity, dehydration of, e.g., crystallised copper sulphate over the alumina takes place at about the same rate as over sulphuric acid, and is much more rapid than over calcium chloride or phosphorus pentoxide. Comparative tests are given for the change of weight of the ignited desiccant over other drying agents and for the rate of removal of moisture from air. The material is recommended as a drying agent on account of its relative inertness, non-deliqescence, and freedom from any volume or other physical change during the adsorption; it will normally adsorb 15—20% of its own weight of water, and may be reactivated by heating for 6—8 hrs. at 175°; it may be prepared in any required particle size. H. F. GILLBE.

**Chemical micrurgy.** R. N. TITUS and H. L. GRAY (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 368—371).—The preparation of various tools, including needles, hooks, and crucibles, suitable for the manipulation of small particles under the microscope, is described. Glass is recommended for the smallest hooks on account of its rigidity. A micro-pipette may be constructed from a glass capillary tube containing a mercury piston which is operated by the plunger of a small syringe to which the capillary is attached; the plunger may be controlled by a micrometer screw. Methods of dissolving, evaporating the solution, and crystallising minute particles are described. H. F. GILLBE.

**Apparatus for percolation at a uniform rate and automatic collecting device.** P. L. HIBBARD (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 404—405).—An apparatus is described for the percolation of small quantities (20 g.) of soil at a uniform rate for 30 hrs., the percolate being automatically collected in a series

of receivers. The distribution apparatus permits the operation of two or more percolators at the same rate from one source of supply. H. F. GILLBE.

**Accessories for use with the Saybolt universal viscosimeter.** C. WINNING (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 417—418).—An adaptor which is suitable for inserting into the Saybolt universal or Furol viscosimeter tube is described; it reduces the volume of the sample required to 15 c.c. and the time of efflux to about one seventh. By employing a flask of 28.6 c.c. capacity the efflux time may be reduced to one third of that necessary for 60 c.c. without any loss of accuracy. H. F. GILLBE.

**Improved thermionic valve falling-ball viscosimeter.** L. P. MOORE and A. C. CUTHBERTSON (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 419).—An improved viscosimeter of the type recommended by Symmes and Lantz is described. Variable condensers, each of 0.0005 microfarad capacity, are placed across the telephones and the anode coil, and by adjustment of the capacity across the telephones the note frequency may be varied to suit the observer. The most sensitive condition of the apparatus is produced by allowing the circuit to oscillate feebly by adjustment of the anode condenser, passage of the ball through the tube being then sufficient to suppress the oscillation. Steel balls of 3.2 mm. diameter yield satisfactory results, but aluminium balls do not give consistent results. H. F. GILLBE.

**Improved Bartell-Osterhof cell.** C. C. DE WITT (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 424—425).—A cell avoiding certain undesirable mechanical features of the original has been devised; the external yoke mechanism for holding the plunger in position is eliminated, and there is only one plunger, which is secured by a single nut while the material is under pressure. The cell is open at both ends and permits free flow of the wetting agent, the manometer being attached not via a plunger but by means of a gasket. The plunger, except for the collar, is smooth outside and is bored centrally to admit a  $\frac{1}{8}$ -in. diameter copper tube and yet leave an annular space for return flow of the liquid to the observation tube. The results obtained with this apparatus are as consistent as, and in accord with, those given by the original cell. H. F. GILLBE.

**Large constant-temperature bath containing a removable glass front.** T. H. TREMEARNE (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 426—427).—Details are given of the construction of a large wooden copper-lined thermostat having a glass front, which, being held against a rubber tubing gasket by means of screws tapped through the welded angle iron framework, is readily removable. A type of bushing suitable for sealing glass apparatus through the walls of the vessel, and a springy brass snap clamp for holding glassware and yet permitting its easy removal, are also described. H. F. GILLBE.

**Rinsing pipettes.** G. M. KLINE (*Ind. Eng. Chem. [Anal.]*, 1930, 2, 427).—Pipettes are rapidly rinsed by sucking water through by the filter pump. Pipettes of uniform bore may be rinsed by standing them in a cylinder fitted with an intermittent automatic siphon overflow. H. F. GILLBE.

## Geochemistry.

**Radon in the atmosphere.** W. KOSMATH (Gerland's Beitr. Geophys., 1930, 25, 95—117).—The radon content of the atmosphere increases with increasing pressure and rising temperature; near the earth's surface it decreases with increasing wind strength. The mean radon content 10 cm. above the ground is  $173 \times 10^{-18}$  curie per c.c.

### CHEMICAL ABSTRACTS.

**Phenolphthalein and pyrocatechol-*o*-carboxylic acid reactions for the detection of "activity" of mineral waters.** L. FRESenius and K. LEDErER (Biochem. Z., 1930, 226, 139—146).—The reactions of mineral water with phenolphthalein and pyrocatechol-*o*-carboxylic acid can be reproduced artificially, manganous and ferrous hydrogen carbonates serving as activating agents, and do not indicate the existence of a specially active condition of the inorganic salts of the mineral water.

### P. W. CLUTTERBUCK.

**Blue colour of sea-water.** R. WILLSTÄTTER (Naturwiss., 1930, 18, 868).—The blue colour of sea-water may be due to dissolved complex copper compounds, *e.g.*, ammines. Sea-water is known to contain copper and ammonia, which could be formed from organic amino-compounds and the decomposition of proteins. It is suggested that a spectroscopic examination would decide the matter.

### A. J. MEE.

**Metallographic study of certain minerals of Yugoslavia.** S. PAVLOVITCH (Compt. rend., 1930, 191, 720—722).—As a result of the examination of some hundred specimens of metallic minerals of Yugoslavia with the polarising microscope, they are classified as follows: (1) Cupriferous, in northern Serbia, (a) associated with andesites or dacites, deposits of Maidan Peck and Bor, consisting, at depth, respectively, of pyrites, mispickel, pyrrhotite, galena, and tetrahedrite, and of pyrites, enargite, erubescite, chalcocite, and covellite; (b) associated with serpentines and lherzolites, deposits of Podgorina and Planinitza, native copper, secondary chalcocite, and cuprite. (2) Cupro-plumbo-argentiferous, in central and southern Serbia, associated with cretaceous or tertiary andesites or dacites, (a) deposits of Rudnik and Kratovo, consisting mainly of pyrites with varying proportions of galena, blende, mispickel, and argentiferous tetrahedrite; (b) deposits of Dobrovo, as the preceding but with chalcopyrite in place of pyrites.

### C. A. SILBERRAD.

**Violarite and other rare nickel sulphides.** M. N. SHORT and E. V. SHANNON (Amer. Min., 1930, 15, 1—22).—Violarite from Sudbury contained Ni 38.68, Co 1.05, Cu 1.12, Fe 17.01, S 41.68, insoluble 0.40, total 99.94%, corresponding with the formula  $\text{FeS}_2\text{Ni}_2\text{S}_3$ . Millerite, polydymite, siegenite, and bravoite are described.

### CHEMICAL ABSTRACTS.

**Occurrence of beryllium in the zinc deposits of Franklin, New Jersey.** C. PALACHE and L. H. BAUER (Amer. Min., 1930, 15, 30—33).—Beryllium was found in vesuvianite, cyprine, and berylite. Vesuvianite, *d* 3.385, contained  $\text{SiO}_2$  34.25,  $\text{CaO}$  33.15,  $\text{BeO}$  9.20,  $\text{MgO}$  3.17,  $\text{MnO}$  4.84,  $\text{ZnO}$  4.86,  $\text{Al}_2\text{O}_3$  9.70,

$\text{H}_2\text{O}$  1.31,  $\text{FeO}$  trace, total 100.48%, corresponding with the formula  $2\text{RO}_2\cdot 6\text{CaO}\cdot 4\text{BeO}\cdot \text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$  ( $\text{R} = \text{Mg}:\text{Mn}:\text{Zn}$  in equal proportions). Berylite, *d* 4.066, contained  $\text{SiO}_2$  36.42,  $\text{BaO}$  46.49,  $\text{BeO}$  15.77,  $\text{FeO}$  0.19,  $\text{MgO}$  0.29,  $\text{PbO}$  0.11,  $\text{H}_2\text{O}$  (110°) 0.40,  $\text{ZnO}$  present, total 99.67%, corresponding with the formula  $2\text{BeO}\cdot \text{BaO}\cdot 2\text{SiO}_2$ . CHEMICAL ABSTRACTS.

**Phenocrysts of volcanic rocks and Tertiary fossils in Quelpart (Saishu) Island.** K. HARAGUCHI (Chikyū, 1928, 10, 350—356).—Augite, olivine, and labradorite are described. CHEMICAL ABSTRACTS.

**Sodalite in nepheline-syenite of Fukushimazan, Korea.** K. HARAGUCHI (Chikyū, 1928, 10, 262—265).—The sodalite, *d*  $2.298 \pm 0.0001$ ,  $n_D$   $1.48271 \pm 0.000027$ , contained  $\text{SiO}_2$  37.42,  $\text{Al}_2\text{O}_3$  3.14,  $\text{FeO}$  trace,  $\text{CaO}$  0.93,  $\text{MgO}$  0.39,  $\text{Na}_2\text{O}$  21.68,  $\text{K}_2\text{O}$  0.13,  $\text{Cl}$  7.12,  $\text{H}_2\text{O}$  (+) 2.46,  $\text{H}_2\text{O}$  (−) 0.45, total 100.12%, corresponding with the formula  $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ .

### CHEMICAL ABSTRACTS.

**Two minerals from the Belgian Congo. I. Non-pyroelectric tourmaline with special facies.**

II. Colourless untwinned chrysoberyl. J. MELON (Bull. Acad. roy. Belg., 1930, [v], 16, 996—1000).—I. A non-pyroelectric tourmaline, *d* 3.0,  $n$  1.636 approx., of fairly high birefringence, has been found in a sand from Bas-Uele.

II. A colourless chrysoberyl has been found in a concentrate from Katanga.

### C. W. GIBBY.

**Structure and form of fresh-water limestone.** E. ROSENSTEIN (Latvian Univ. Raksti, 1929, 1, 13—27).—The microstructure of fresh-water limestone from different sources has been investigated and it is shown that the presence or absence of gypsum has an important morphological influence. By allowing calcium carbonate to precipitate slowly from a saturated solution of the hydrogen carbonate, in presence and in absence of gypsum, lamellar aggregates, grouped in the form of rosettes round granular nuclei, are observed in the former case, whilst in the latter the typical rhombohedral calcite crystals are obtained. The same specific differences are not necessarily observed in natural limestones because other factors come into play.

### M. S. BURR.

**Soil survey of Woorinen Settlement, Swan Hill Irrigation District, Victoria.** J. K. TAYLOR and F. PENMAN (Counc. Sci. Ind. Res. Comm. Australia, Bull. 45, 41 pp.).

**State of water and the active surface of Japanese acid clay.** Y. TANAKA and M. NAKAMURA (J. Soc. Chem. Ind. Japan, 1930, 33, 365—366b).—The thermal dehydration of Japanese acid clay has been determined from 0° to 1300°; there is an arrest in the dehydration curve at 300—450°, and a rapid loss at 70—250° and at 450—700°, the latter temperature corresponding with loss of the water of constitution, since the curve resembles that of kaolin. The water contents of air-dried clay and of clay in equilibrium with air saturated with water at 20° become identical at 100°; the water evolution at 450—500° is partly reversible. Silica gel gives an

almost linear dehydration curve from 150° to 600°, and alumina gel a linear curve from 100° to 500°; there is no evidence of the formation of mono-, di-, or tri-hydrates of aluminium oxide. Since the aluminium exists in the clay in two forms, of which one is easily removed by hydrochloric acid, it is suggested that the superficial silicon and aluminium atoms have free valencies, whereas those in the crystalline interior are fully saturated. The superficial atoms are those responsible for the adsorptive power of the clay, and form the part removable by acid, whilst the crystalline interior gives rise to the *X*-ray diagram.

H. F. GILLBE.

**Basis for computing the age of a radioactive mineral from the lead content.** A. F. KOVARIK (Amer. J. Sci., 1930, [v], 20, 393).—A correction (see this vol., 1155).

**Radioactive properties of rocks, soils, crude oil, and waters from Southern California.** J. L.

BOHN (J. Franklin Inst., 1930, 210, 461—472).—The method of determining the radioactivity of solid materials was substantially that of Joly (A., 1911, ii, 685); of liquids that of Boltwood. Sources of the Pasadena water supply gave results averaging five times that of the same water as supplied in taps ( $0.97 \times 10^{-10}$  curie per litre); whilst 10 varieties of rock or soil in the catchment averaged from 0.8 to  $3.9 \times 10^{-12}$  g. of radium per g. of soil. The greatest activity was found in the Harlem Hot Springs ( $18.0 \times 10^{-10}$  curie per litre), the lowest in Lake Arrowhead ( $0.54 \times 10^{-12}$ ), whilst Pacific sea-water showed  $0.94 \times 10^{-12}$ . Two samples of crude oil from the Montebello field gave 1.9 and  $2.2 \times 10^{-10}$  curie, respectively. The very low activity of Lake Arrowhead water makes it eminently suitable for cosmic radiation determinations, its activity being only about 1% of the minimum detectable by the electroscope used for that purpose by Millikan and Cameron (cf. A., 1928, 1303).

C. A. SILBERRAD.

## Organic Chemistry.

**Paraffinisation of alcohols.** G. RAZUBAIEV (Trans. State Inst. Appl. Chem. Sci. Tech. Dep. U.S.S.R., 1929, No. 300, 25—28).—Saturated hydrocarbons were obtained by reduction of alcohols with hydrogen in presence of nickelic oxide or nickelic oxide with alumina, methane being obtained from ethyl or methyl alcohol. Alumina does not affect the velocity of the reaction in presence of nickelic oxide. For pressures of 25—100 atm. the evolution of methane commences at 250°, but the yield at higher temperatures (80% at 310—330°) is not quantitative, since the catalyst becomes coated with tarry products. The yield of methane depends only on the initial pressure of the hydrogen. The unchanged alcohol contained acetaldehyde or formaldehyde, respectively. A mixture of copper oxide and alumina was ineffective as a catalyst.

### CHEMICAL ABSTRACTS.

**Action of fuming sulphuric acid on hexane, cyclohexane, and some of their derivatives.** G. N. BURKHARDT (J.C.S., 1930, 2387—2399).—When pure *n*-hexane, cyclohexane, or methylcyclohexane is vigorously stirred with fuming sulphuric acid (35 or 65% free SO<sub>3</sub>) at 0—10° almost the whole of the sulphuric anhydride is used in the reaction that takes place, approximately 1 mol. of sulphur dioxide being formed for each mol. of hydrocarbon attacked. Isolation of single substances from the complex mixture of barium salts obtained by neutralisation of the acid layer was not generally possible, but the general nature of the products was determined from the analytical data of the mixed barium salts and the derived sulphonyl chlorides, and partial separation is effected by fractional precipitation of their concentrated aqueous solution with alcohol. The mixed barium salts obtained from hexane and cyclohexane are partly unsaturated and contain sulphuric ester groups, probably as salts of sulphato-sulphonic acids formed by the action of fuming sulphuric acid on unsaturated compounds.

After hydrolysis of these the product contains 2 mols. of disulphonate per mol. of monosulphonate, 5% of the hexane chains are unsaturated, and about 30% contain a hydroxyl group, whilst in the case of cyclohexane small quantities of derivatives of benzenesulphonic acid can be isolated. Similar products are obtained from methylcyclohexane, which, however, is more readily attacked. Concentrated sulphuric acid converts cyclohexene into cyclohexanol and cyclohexyl hydrogen sulphate (isolated as its barium salt). The latter is almost the sole water-soluble product obtained when 35% oleum is dropped into cyclohexene, although sulphato-sulphonic acids are obtained when the hydrocarbon is added to excess of the acid. Similar polysulphonated products are obtained by the action of oleum on cyclohexanol and cyclohexyl hydrogen sulphate, and it appears that prior formation of a sulphuric or pyrosulphuric ester is followed by sulphonation. *cyclo*Hexyl hydrogen sulphate (sodium + H<sub>2</sub>O, decomp. to cyclohexanol and sodium hydrogen sulphate at 120—130°, and barium + 3H<sub>2</sub>O, salts) is prepared from cyclohexanol either by the action of 12% oleum at 20—35°, or by treatment with chlorosulphonic acid and dimethylaniline. *cyclo*Hexanesulphonic acid is obtained either by the action of sulphur dioxide on the Grignard derivative of cyclohexyl chloride and subsequent oxidation of the sulphinic acid with cold potassium permanganate (yield 15—20%, together with 30—40% of dicyclohexyl) or by prolonged shaking of cyclohexene with 0.5*N*-ammonium hydrogen sulphate (Kolker and Lapworth, A., 1925, i, 353). Sodium 1-cyclohexanol-2-sulphonate, prepared from cyclohexene oxide (Brunel, A., 1905, i, 869), is stable to boiling, dilute potassium permanganate solution, and is only partly acetylated by boiling with acetyl chloride for several hours.

J. W. BAKER.

**Catalytic hydration of olefines.** S. SWANN, R. D. SNOW, and D. B. KEYES (Ind. Eng. Chem.,

1930, 22, 1048—1051).—The hydration of ethylene and propylene by aqueous solutions of hydrochloric, hydrobromic, and hydriodic acids, chlorides, and silver nitrate at 100—200° and under pressure has been investigated. Even at a pressure of 800 lb. per sq. in. the equilibrium concentration of alcohol never exceeded 0.6%, and increase in the concentration of hydrobromic or hydriodic acid favoured the formation of alkyl halides without having much effect on the yield of alcohol, from which it is concluded that the action of the acid is catalytic.

R. CUTHILL.

**Conjugated systems. V. Preparation and chlorination of butadiene.** I. E. MUSKAT and H. E. NORTHRUP (J. Amer. Chem. Soc., 1930, 52, 4043—4055).—The preparation of  $\Delta^{\alpha\gamma}$ -butadiene by Perkin's method (A., 1912, i, 636) is developed; the best yield (about 30%) is obtained from the  $\alpha\gamma$ -dichlorobutane fraction by distillation over soda-lime at 700—730°. Treatment of the butadiene with chlorine in chloroform, carbon disulphide, or light petroleum solution gives a mixture of  $\alpha\beta$ -dichloro- $\Delta^{\gamma}$ -butene, b. p. 115°, 45—45.5°/40 mm.,  $n_D^{20}$  1.4550 (ozonolysis products,  $\alpha\beta$ -dichloropropaldehyde and formaldehyde),  $\alpha\delta$ -dichloro- $\Delta^{\delta}$ -butene, b. p. 75—76°/40 mm.,  $n_D^{20}$  1.4745 (oxidation product chloroacetic acid), and two stereoisomeric  $\alpha\beta\gamma\delta$ -tetrachlorobutanes, b. p. 110—111°/40 mm. and b. p. 130—134°/40 mm., m. p. 72°, respectively. Further addition of chlorine to the  $\alpha\beta$ -dichlorobutene gives the tetrachloro-derivative, b. p. 110—111°/40 mm., whilst the  $\alpha\delta$ -dichlorobutene yields a mixture of tetrachloro-compounds in which the form of m. p. 72° predominates. All the above chlorides are reduced by zinc dust and alcohol to  $\Delta^{\alpha\gamma}$ -butadiene. When either of the dichlorobutenes is heated with powdered potassium hydroxide at 90°,  $\alpha$ -chloro- $\Delta^{\alpha\gamma}$ -butadiene, b. p. 85°, is obtained. The above dichlorobutenes undergo no rearrangement when heated at 90° in sealed tubes. A theory is developed to explain additive reactions of conjugated systems (cf. this vol., 451, 769).

H. BURTON.

**Formation of diisobutylene from acetone at high pressures.** A. D. PETROV and F. Z. IVANOV (J. Russ. Phys. Chem. Soc., 1930, 12, 1489—1492).—On heating acetone under pressure to 300° in the presence of zinc chloride, a mixture of unsaturated hydrocarbons is obtained, of which a large proportion is diisobutylene, which is contained in the fraction of b. p. 100—110°,  $d_4^{18}$  0.7198,  $n_D^{18}$  1.416. Hydrogenation of this hydrocarbon gave a good yield of  $\beta\beta\delta$ -trimethylpentane, b. p. 100°,  $d_4^{20}$  0.6959,  $n_D^{18}$  1.397, which is useful as a standard of comparison for the anti-knock properties of motor fuels, since it has a lower anti-knock value than any of them. The bearing of the results on the mechanism of formation of petroleum is discussed.

M. ZVEGINZOV.

**Quantitative investigation of the Schotten-Baumann reaction.** F. A. MENALDA (Rec. trav. chim., 1930, 49, 967—995).—The Schotten-Baumann reaction is considered as consisting of the two simultaneous reactions (1)  $X \cdot COCl + 2NaOH = X \cdot CO_2Na + NaCl + H_2O$ ; (2)  $X \cdot COCl + EtOH + NaOH \rightarrow X \cdot CO_2Et + NaCl + H_2O$ . By treat-

ment of aqueous-alcoholic alkali hydroxide with an acid chloride, followed by titration of the excess of alkali at the end of the reaction, the amount of ester formed can be determined. From observations at several temperatures, using potassium and sodium hydroxides, methyl, ethyl, allyl, and benzyl alcohols, glycerol, sucrose, and phenol, on the one hand, and acetyl, benzoyl, and benzenesulphonyl chlorides on the other, it is concluded that for the yield of ester to be as high as possible the temperature must be as low as possible and the acid chloride must be added in portions to prevent the sudden evolution of heat. Potassium hydroxide should be used in preference to sodium hydroxide, although the latter affords excellent results; the alkali must be as concentrated as possible. After the reaction, the ester must be removed from the sphere of reaction as rapidly as possible, to prevent hydrolysis. An excess (1.2—1.5 times the theoretical) of acid chloride should be used except in the case of such alcohols as ethyl alcohol, in which it is best to add small quantities of acid chloride and alkali, shake until the reaction is complete, and repeat the process until 3—4 times the theoretical amount of acid chloride has been used. It is suggested that the Schotten-Baumann reaction carried out quantitatively as described above can be used to determine the composition of alcohol-water mixtures.

J. D. A. JOHNSON.

**Relative loading of the molecule [with groups] and its solvent power in the case of alcohols, aldehydes, ketones, and carbohydrates.** M. A. RAKUSIN (Biochem. Z., 1930, 226, 133—138).—A theoretical discussion of the variation of solvent power of molecules of organic substances with the number of hydroxyl ions and water molecules they are carrying.

P. W. CLUTTERBUCK.

**Reactions that occur on a methyl alcohol catalyst.** D. F. SMITH and L. L. HIRST (Ind. Eng. Chem., 1930, 22, 1037—1040).—When a mixture of carbon dioxide and hydrogen is passed over a zinc oxide-chromic oxide catalyst at 304°, partial reaction, with formation of methyl alcohol, carbon monoxide, and water, occurs, and under similar conditions carbon monoxide and water give carbon dioxide and hydrogen. It seems possible that the formation of methyl alcohol from carbon monoxide and hydrogen is more complicated than the equation  $CO + 2H_2 = MeOH$  suggests.

R. CUTHILL.

**Catalysts for formation of alcohols from carbon monoxide and hydrogen. VI. Investigation of mechanism of formation of alcohols higher than methyl alcohol.** P. K. FROLICH and D. S. CRYDER (Ind. Eng. Chem., 1930, 22, 1051—1057; cf. B., 1930, 49).—In the reaction of carbon monoxide with hydrogen under high pressure in presence of a mixture of potassium chromate and the basic carbonates of zinc and manganese as catalyst, methyl alcohol is an intermediate product in the synthesis of higher alcohols, which are probably formed mainly by successive condensations of the lower alcohols, e.g.,  $MeOH + EtOH = PrOH + H_2O$ . Of these condensations, that leading to the formation of ethyl alcohol appears to have the lowest velocity, and therefore determines the rate of the process as a whole. The

fact that the formation of higher alcohols is favoured by high concentrations of carbon monoxide is explained by supposing that the water formed in the alcohol condensations is selectively adsorbed by the catalyst, thus acting as an inhibitor, but in presence of excess of carbon monoxide is removed by the reaction  $\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$ , a theory which also accounts for the high percentage of carbon dioxide formed in the synthesis of higher alcohols. No evidence of ethers being intermediate products has been obtained. Acids are produced in comparatively small amounts, chiefly as esters, which probably result from the polymerisation of aldehydes.

R. CUTHILL.

**Action of halogen acids on acetylenic glycols.** J. S. SALKIND and S. V. NIEDZVIETZKI (J. Russ. Phys. Chem. Soc., 1930, 62, 1011—1019).—Hydrogen iodide reacts with the stereoisomeride of  $\beta$ -diphenyl-hexene- $\beta$ -diol, m. p. 163°, to yield 3-iodo-2:5-diphenyl-2:5-dimethyl-2:5-dihydrofuran (an oil) and  $\gamma$ - $\delta$ -di-iodo- $\beta$ -diphenyl- $\Delta^{86}$ -hexadiene, m. p. 145—146°; the same di-iodide is obtained from the isomeride of m. p. 126°. The di-iodide is converted on reduction in acetone solution into the moniodide, m. p. 84°, and into 2:5-diphenyl-2:5-dimethyl-2:5-dihydrofuran, m. p. 103—104°.

R. TRUSZKOWSKI.

**New "acetone" glycerol [ $\alpha$ -isopropylideneglycerol].** N. M. CARTER (Ber., 1930, 63, [B], 2399—2400).— $\alpha$ -isoPropylideneglycerol  $\beta$ -benzoate is converted by alkaline hydrolysis into  $\alpha$ -isopropylideneglycerol, b. p. 90—91°/13 mm.,  $d_4^{20}$  1.0911,  $n_D^{20}$  1.4427, re-benzoated to the initial material.

H. WREN.

**Preparation of solid derivatives for identification of ethers.** H. W. UNDERWOOD, jun., O. L. BARIL, and G. C. TOONE (J. Amer. Chem. Soc., 1930, 52, 4087—4092).—Small amounts (1 c.c.) of dialkyl ethers can be identified by treatment with 3:5-dinitrobenzoyl chloride (0.5 g.) and anhydrous zinc chloride (0.1—0.15 g.) (cf. this vol., 320), when the alkyl 3:5-dinitrobenzoate is produced; the method is illustrated, using diethyl, di-*n*- and -iso-propyl, di-*n*- and -iso-butyl, di-*n*- and -iso-amyl, and di-*n*-hexyl ethers. Anisole and phenetole are characterised by warming 1 c.c. with *p*-nitrobenzoyl chloride (0.8 g.), carbon disulphide (1 c.c.), and aluminium chloride (0.1 g.), whereby 4-nitro-4'-methoxy- and 4-nitro-4'-ethoxy-benzophenones are produced, respectively. Such nuclear acylation is, however, not general for aromatic ethers. The following ethers are identified by bromination in presence of various solvents, the derivative formed being given in parentheses: *o*-tolyl methyl (monobromo-derivative, m. p. 63—64°);  $\alpha$ - and  $\beta$ -naphthyl methyl (monobromo-derivatives, m. p. 46° and 62—63°, respectively);  $\alpha$ -naphthyl ethyl (4-bromo-derivative);  $\beta$ -naphthyl ethyl (1-bromo-derivative); dibenzyl (dibromo-derivative, m. p. 107—108°); veratrole, resorcinol dimethyl, quinol dimethyl, and diphenyl (dibromo-derivatives); guaiacol (tribromo-derivative); anethole, isosafrole, and eugenol methyl (monobromo-derivative dibromides); safrole (tribromo-derivative dibromide), and isoeugenol methyl (dibromide). *p*-Tolyl methyl, and *o*- and *p*-tolyl

ethyl ethers are oxidised with potassium dichromate and dilute sulphuric acid to *p*-anisic, and *o*- and *p*-ethoxybenzoic acids, respectively. H. BURTON.

**Two modifications of liquid ethyl ether.** M. WOLFFKE and J. MAZUR (Nature, 1930, 126, 684—685).—The curve showing the change of temperature with time during the gradual heating of ethyl ether exhibits a transformation point at  $-105.4^\circ$ .

L. S. THEOBALD.

**Ether and ester. III. Diethylene dioxide (dioxan).** J. VAN ALPHEN (Rec. trav. chim., 1930, 49, 1040—1044; cf. this vol., 738, 1270).—Ethylene glycol is partly converted into dioxan under the catalytic influence of ferric chloride (hydrated), ferric sulphate (anhydrous), aluminium sulphate (anhydrous), or concentrated sulphuric acid. A "continuous" process for the conversion of glycol into dioxan using ferric sulphate as catalyst is described. Dioxan with concentrated nitric acid at  $-10^\circ$  yields a nitrate,  $(\text{C}_4\text{H}_8\text{O}_2)_3 \cdot 4\text{HNO}_3$ , m. p. 14°.

J. D. A. JOHNSON.

**Alkyl peroxides. V. Barium methyl peroxide.** A. RIECHE and F. HITZ (Ber., 1930, 63, [B], 2504—2505; cf. A., 1929, 1268).—Barium methyl peroxide may be prepared by the addition of an excess of crystalline barium hydroxide to 30—50% aqueous methyl hydrogen peroxide in an atmosphere free from carbon dioxide; after removal of the excess of barium peroxide, the filtrate is heated with alcohol and cooled, when the barium compound crystallises; it is washed with alcohol, from which it should not be freed completely, since the dry material is violently explosive. When dissolved in water and treated with terephthalyl chloride in benzene it yields methyl diperterephthalate,  $\text{C}_6\text{H}_4(\text{CO}-\text{O}-\text{Me})_2$ , m. p. 125°, hydrolysed to terephthalic acid and methyl hydrogen peroxide.

H. WREN.

**Alkyl peroxides. VI. Monohydroxydialkyl peroxides.** A. RIECHE [with F. HITZ] (Ber., 1930, 63, [B], 2642—2652; cf. preceding abstract).—Monohydroxydialkyl peroxides,  $\text{R}-\text{CH}(\text{OH})-\text{O}-\text{O}-\text{R}$ , are readily obtained by the interaction of molar quantities of alkyl hydrogen peroxides with aldehydes. They are remarkably stable, distil almost without decomposition in a vacuum, are stable in organic solvents, and almost unchanged by boiling water. Methyl hydroxymethyl peroxide is exceptional, since it decomposes slowly on contact with glass and is moderately explosive. In aqueous solution the hydroxy-compounds are less readily reduced than the dialkyl peroxides and complete reaction of peroxidic oxygen is not observed with hydriodic acid or titanium trichloride. They are very sensitive towards alkali. Hydrogen and formic acid are invariably produced from a hydroxymethyl group, whereas other hydroxyalkyl groups do not yield hydrogen. When warmed, they are decomposed by salts of bivalent iron; the hydroxymethyl derivatives occupy an isolated position, since the group yields formic acid and the liberated hydrogen atom is available for reduction of the other half of the molecule. The other hydroxyalkyl compounds decompose in a different manner. The following individual compounds are described: methyl hydroxy-



*methyl peroxide*, b. p. 45°/17 mm.,  $d_{20}^{25}$  1.112,  $n_D^{25}$  1.39827, from 80% methyl hydrogen peroxide and formaldehyde in anhydrous ether: its decomposition by potassium hydroxide into hydrogen, methyl alcohol, and formic acid confirms its postulated intermediate production during the alkaline decomposition of methyl hydrogen peroxide (A., 1929, 1268); *hydroxymethyl ethyl peroxide*, b. p. 46–48°/13 mm.,  $d_{20}^{25}$  1.0453,  $n_D^{25}$  1.40435; *methyl  $\alpha$ -hydroxyethyl peroxide*, b. p. 25–27°/17 mm.,  $d_{20}^{25}$  1.029,  $n_D^{25}$  1.39301; *ethyl  $\alpha$ -hydroxyethyl peroxide*, b. p. 65–70°/65 mm. (slight decomp.),  $d_{20}^{27}$  0.9902,  $n_D^{27}$  1.39643; *ethyl  $\alpha$ -hydroxypropyl peroxide*. H. WREN.

***n*-Butyl phosphite.** A. ARBUSOV and J. ARBUSOV (J. Russ. Phys. Chem. Soc., 1930, 62, 1533–1536).—Sodium *n*-butoxide reacts with the calculated quantity of phosphorus trichloride to give a 68.6% yield of tri-*n*-butyl orthophosphite, b. p. 119.5–120°/8 mm.,  $d_4^{20}$  0.9309. With bromine the ester yielded the metaphosphite and butyl bromide. When heated in a sealed tube at 150–160° with *n*-butyl iodide, *n*-butyl *n*-butylphosphinate, b. p. 150–151°/10 mm.,  $d_4^{20}$  0.9634, was obtained, which on hydrolysis with concentrated hydrochloric acid gave *n*-butylphosphinic acid, m. p. 101–103° (barium salt).

M. ZVEGINTZOV.

**Preparation and physical properties of  $\alpha$ -monoglycerides.** R. S. REWADIKAR and H. E. WATSON (J. Indian Inst. Sci., 1930, 13A, 128–140).— $\alpha$ -Monoglycerides of octoic, decaic, dodecoic, myristic, palmitic, and stearic acids have been prepared by Fischer's method (A., 1920, i, 805), by oxidation of the allyl esters of the fatty acids, and from glycerol and the methyl esters of the fatty acids. The variation of  $d_4^{20}$ ,  $n_D^{25}$ , m. p., and viscosity with number of carbon atoms in the acid is regular. The parachors are all lower than those calculated from Sugden's data. The monoglycerides of dodecoic, myristic, palmitic, and stearic acids exhibit two definite m. p. (cf. Fischer, *loc. cit.*); the rate of change of the more fusible ( $\beta$ ) modification into the less fusible ( $\alpha$ ) form increases with decrease in mol. wt. The solidifying points of the glycerides are invariably lower than the m. p. of the  $\alpha$ -form (cf. B., 1929, 101). The following are new: *allyl stearate*, m. p. 35° (*dibromide*, m. p. 45°); *allyl dodecoate*, b. p. 162–164°/20 mm. (*dibromide*, b. p. 220–222°/10 mm.); *diphenylcarbimide*, m. p. 101°, and *di-p-nitrobenzoyl* derivatives, m. p. 94°, of  $\alpha$ -glyceryl decaate; *diphenylcarbimide*, m. p. 114°, and *di-p-nitrobenzoyl* derivatives, m. p. 91.5°, of  $\alpha$ -glyceryl octoate. H. BURTON.

**Synthesis of  $\beta$ -glycerides.** M. BERGMANN and N. M. CARTER (Z. physiol. Chem., 1930, 191, 211–221).— $\beta$ -Benzoyl- $\alpha\gamma$ -benzylideneglycerol on reduction with hydrogen and palladium yields  $\beta$ -benzoylglycerol, m. p. 72.5°, reconverted into the benzylidene compound with benzaldehyde and hydrogen chloride. With *p*-nitrobenzoyl chloride and pyridine it gives  $\beta$ -benzoyl- $\alpha\gamma$ -di-*p*-nitrobenzoylglycerol, m. p. 153° (corr.). With acetone in presence of hydrochloric acid,  $\beta$ -benzoylglycerol forms  $\beta$ -benzoyl- $\alpha\gamma$ -isopropylideneglycerol, m. p. 33°.  $\alpha\gamma$ -Benzylideneglycerol with pyridine and acetic anhydride gives the  $\beta$ -acetyl derivative, m. p. 101°, which on catalytic hydrogen-

ation furnishes  $\beta$ -acetylgllycerol, b. p. 117–118°/0.3 mm. The latter forms  $\beta$ -acetyl- $\alpha\gamma$ -di-*p*-nitrobenzoylglycerol, m. p. 161–162° (corr.).  $\beta$ -Palmityl- $\alpha\gamma$ -benzylideneglycerol, m. p. 63.5°, and  $\beta$ -palmitylgllycerol, m. p. 69°, are described.  $\alpha$ -Palmitin condensed with benzaldehyde gives  $\alpha$ -pamityl- $\beta\gamma$ -benzylideneglycerol, m. p. 35°;  $\beta$ -palmitin with acetone in presence of copper sulphate forms  $\beta$ -palmityl- $\alpha\gamma$ -isopropylideneglycerol, m. p. 44°; in presence of hydrogen chloride and sodium sulphate it furnishes  $\alpha$ -palmityl- $\beta$ -isopropylideneglycerol (migration of the acyl group).  $\alpha$ -Palmitin gives the  $\alpha$ -palmityl product in presence of copper sulphate. J. H. BIRKINSHAW.

**Physical properties of pure triglycerides.** R. B. JOGLEKAR and H. E. WATSON (J. Indian Inst. Sci., 1930, 13A, 119–127).—Mainly an account of work previously reviewed (B., 1929, 101). The parachors for the triglycerides of decaic, dodecoic, myristic, palmitic, and stearic acids are all higher than those calculated from Sugden's data. H. BURTON.

**Mechanism of carbohydrate oxidation. XIII. Action of potassium hydroxide on calcium hexosediphosphate. Comparison with that of dextrose and lævulose.** W. L. EVANS and R. C. HOCKETT (J. Amer. Chem. Soc., 1930, 52, 4065–4069).—The production of lactic acid from calcium hexosediphosphate and 5*N*-potassium hydroxide at 50° is similar to its formation from dextrose (A., 1926, 1228) and lævulose (A., 1928, 741); the amount increases rapidly to a maximum after rather more than 24 hrs. and then remains constant up to 22 days. Formic and acetic acids are produced in small amounts. The hexosediphosphate is probably hydrolysed to lævulose, which undergoes 3:4-enediol formation, resulting in the production of lactic acid. The acetic acid may arise from glycollaldehyde formed either by fission of the hexose-2:3-enediol or a triose-1:2-enediol. H. BURTON.

**Action of magnesium ethyl bromide and of oxidising agents on diethyl polysulphides.** A. BARONI (Atti R. Accad. Lincei, 1930, [vi], 11, 905–909).—The action of magnesium ethyl bromide on diethyl polysulphides results in complete breakdown of the molecules with formation of ethyl sulphide and mercaptan. Treatment of diethyl trisulphide with nitric acid ( $d$  1.2) yields *diethyl trisulphoxide*, Et·[SO]<sub>3</sub>·Et, b. p. 154–155°/20 mm.,  $d_4^{20}$  1.2844, which is reduced to mercaptan by zinc and dilute acid. When oxidised with either fuming nitric acid, or aqueous permanganate or hydrogen peroxide, diethyl disulphide and trisulphide yield respectively *diethyl disulphone*, Et·SO<sub>2</sub>·SO<sub>2</sub>·Et, b. p. 128°/26 mm.,  $d_4^{20}$  1.3035, and *diethyl trisulphone*, Et·[SO]<sub>3</sub>·Et, m. p. 32°,  $d_4^{20}$  1.5048 (cf. A., 1929, 1039, 1270). T. H. POPE.

**Influence of the sulphur atom on the reactivity of adjacent atoms or groups. IV. Direct polar effects.** G. M. BENNETT and A. N. MOSSES (J.C.S., 1930, 2364–2369).—Fuming hydrobromic acid reacts, under identical conditions at the ordinary temperature, with phenyl  $\gamma$ -hydroxypropyl,  $\delta$ -hydroxybutyl, and  $\epsilon$ -hydroxyamyl sulphides to cause, respectively, 1.0, 90, and 1.3% conversion into the bromosulphide,

that from the  $\delta$ -compound being isolated, by addition of potassium bromoaurate, as *phenyltetramethylenesulphonium bromoaurate*, m. p. 120° (decomp.). The original suggestion (A., 1927, 355) that the hydroxyl group in the  $\delta$ -position to a sulphur atom is much more reactive with hydrobromic acid than one in the  $\gamma$ - or  $\epsilon$ -position is thus confirmed, since the alternative possibility that the hydroxysulphide is first converted into the cyclic sulphonium hydroxide is negated by the complete absence of tendency to ring closure with phenyl  $\delta$ -hydroxybutyl sulphide at 100°. Moreover, with conditions under which the  $\gamma$ -hydroxy-sulphide suffers only 3.7% conversion by dry hydrogen chloride at 50° into the chloro-sulphide, the  $\delta$ -hydroxy-sulphide, after subsequent treatment with sodium phenyl sulphide, affords a 33.2% yield of  *$\alpha$* - $\delta$ -diphenylthiobutane, m. p. 85° (similarly synthesised from pure phenyl  $\delta$ -chlorobutyl sulphide), indicating that this proportion of the  $\delta$ -chloro-sulphide formed had not undergone ring closure. Hence in the reaction with hydrogen chloride the  $\delta$ -hydroxy-sulphide was converted first into the halogenated sulphide and reacted much faster than the  $\gamma$ -hydroxy-sulphide. This effect is ascribed to the direct polar effect of the sulphur atom transmitted through space to the  $\delta$ -hydroxy-group. The anomalous direct effect of the methyl group on the strength of *o*-toluic ( $k$   $11.7 \times 10^{-5}$ ) compared with benzoic ( $6.2 \times 10^{-5}$ ) and *m*-toluic ( $5.0 \times 10^{-5}$ ) acids is discussed, and is explained by the suggestion that the small dipole which exerts an electron repulsion towards the remainder of the molecule along the line of its attachment will result in an electron attraction along the same line in the opposite direction outside the group. The application of this idea to the direct polar effects of the halogens and to the valency-deflexion effects of the *gem*-dialkyl group are discussed.

J. W. BAKER.

**Chlorination of formylmethionine (formylmethanedisulphonic) acid.** H. J. BACKER (Rec. trav. chim., 1930, 49, 1054—1056; cf. A., 1929, 792; this vol., 1270).—Potassium formylmethionate when chlorinated in warm aqueous solution gives a 67% yield of *potassium formylchloromethanedisulphonate*,  $\text{CH}(\text{OH})_2 \cdot \text{CCl}(\text{SO}_3\text{K})_2$  (oxime and semicarbazone dihydrate). Treatment of this salt (but not of the oxime) with aqueous potassium hydroxide at the ordinary temperature results in the formation of potassium formate and methionate, the latter being isolated as its strychnine salt (yield 78%).

J. D. A. JOHNSON.

**Bromomethanetrissulphonic acid.** H. J. BACKER and K. H. KLAASSENS (Rec. trav. chim., 1930, 49, 1045—1047).—*Bromomethanetrissulphonic acid* ( $+3\text{H}_2\text{O}$ ), m. p. 179° (decomp.), is obtained in 40% yield by bromination of methanetrissulphonic acid in aqueous solution at 150°. The *barium* salt [ $+9\text{H}_2\text{O}$ ; and  $+8\text{H}_2\text{O}$  (stable in air)] is soluble in water at 25° to the extent of 4.19 g. of anhydrous salt in 100 g. of water. For the *potassium* salt ( $+ \text{H}_2\text{O}$ , piezoelectric, solubility at 25°, 1.890 g. in 100 g. water), full crystallographic data are given. The anhydrous *thallous* and *heptahydrated lanthanum* salts are described. With potassium sulphite, potassium bromomethanetrissulphonate reverts to potassium methanetrissulphonate.

J. D. A. JOHNSON.

**Thiolmethanetrissulphonic acid.** H. J. BACKER (Rec. trav. chim., 1930, 49, 1048—1053).—Attempts to prepare methanetrissulphonic acid from thiolmethanetrissulphonic acid by regulated oxidation at the ordinary temperature and at 0° by means of chlorine or bromine in presence of aqueous potassium carbonate were unsuccessful. One mol. of thiolmethanetrissulphonic acid requires six atoms of halogen and not eight for regulated oxidation (cf. Albrecht, A., 1872, 403). Full crystallographic data for the potassium thiolmethanetrissulphonate dihydrate are given (solubility at 25° 3.21% of anhydrous salt).

J. D. A. JOHNSON.

**Velocity of esterification in mixed solvents.** B. W. BRIDE.—See this vol., 1379.

**Electrochemical preparation of formates from carbonic acid.** M. RABINOVITSON and A. MASCHOVETZ.—See this vol., 1532.

**Preparation and purification of ethyl acetate.** II. M. S. ROSHDESTVENSKI, A. G. PUKIREV, and V. V. LONGINOV (Trans. Inst. Pure Chem. Reagents, U.S.S.R., 1929, No. 300, 123—142).—The composition of the crude ester prepared by various methods was determined. Wade's method (J.C.S., 1905, 87, 1656) does not afford an azeotropic ternary mixture of b. p. 70.3°. The preparation of the crude ester and its purification are described in detail; ethyl acetate has b. p. 77.15°,  $d_4^{25}$  0.90725 (in air),  $n_D^{25}$  1.37234.

CHEMICAL ABSTRACTS.

**Optical rotatory power of configuratively related substances.** W. KUHN, K. FREUDENBERG, and I. WOLF (Ber., 1930, 63, [B], 2367—2379).—Analysis of the graphs showing the optical activity and absorption of methyl azidopropionate and azidopropiondimethylamide shows that the azido-bands contribute 45% and 23% of the optical rotation respectively, but are responsible only for  $1/10^5$  of the total absorption. The optical activity of a compound is therefore regarded as the sum of the contributions of the individual bands or substituents whereby particular weight is laid on the weak and medium strong bands proximate to the visible portion of the spectrum. Exchange of methoxyl for dimethylamido-groups causes a change in the magnitude and sign of the anisotropy of the carboxyl bands, whereas the vicinal action of the azido-bands is approximately retained. The alteration of rotation caused by transformation of a substituent depends mainly on the change of the band-anisotropy of the substituent and to a smaller extent on the modified rotation components of the remaining substituents due to vicinal action. The graphs of methyl chloro- and bromo-propionate and of chloro- and bromo-propiondimethylamide are similarly considered. Consideration of the optical displacement rule from an analogous point of view establishes theoretically the necessity for a very close chemical relationship among the compounds under comparison. Under certain conditions, the principle of optical superposition can be predicted.

H. WREN.

**Steric series. XI. Configuration of the halogenopropionic acids and alanine.** K. FREUDENBERG, W. KUHN, and I. BUMANN [in part with

F. SOHNS (Ber., 1930, **63**, [B], 2380—2390).—The optical displacement rule is formulated as follows. Derivatives of  $\alpha$ -substituted fatty acids or other compounds with a centre of asymmetry which are analogous among themselves do not possess mobile hydrogen atoms, and can be examined in the absence of solvent, undergo a similar change in activity when corresponding substituents of the asymmetric atom are similarly changed in such a manner that a large change in activity results. The following compounds are shown to belong to the *d*-series: (+)-azido-, (+)-chloro-, (+)-bromo-, (+)-iodo-propionic acid, benzoyl-*d*-, acetyl-*d*-, and toluenesulphonyl-*d*-lactic acid, *d*(-)-lactic acid and *d*(-)-alanine. The following data are recorded: (-)- $\alpha$ -azidopropionyl chloride, b. p. 46—47°/13 mm.,  $[\alpha]_{D}^{25} +49.9^\circ$ , from the *l*-acid and thionyl chloride; methyl (-)- $\alpha$ -azidopropionate, b. p. 53°/13 mm.,  $[\alpha]_{D}^{25} -18.35^\circ$ , from the acid and diazomethane or the chloride and methyl alcohol; ethyl (-)- $\alpha$ -azidopropionate, b. p. 62—63°/12 mm.,  $[\alpha]_{D}^{25} -18.69^\circ$ ; propyl (-)- $\alpha$ -azidopropionate, b. p. 82°/35 mm.,  $[\alpha]_{D}^{25} -20.68^\circ$ ; (-)- $\alpha$ -azidopropiondimethylamide, b. p. 80°/2 mm.,  $[\alpha]_{D}^{25} +182^\circ$ ; (-)- $\alpha$ -azidopropiondiethylamide, b. p. 93—94°/2 mm.,  $[\alpha]_{D}^{25} +180.8^\circ$ ; methyl *l*(+)- $\alpha$ -aminopropionate, b. p. 35—36°/12 mm.; methyl *l*(+)- $\alpha$ -acetamidopropionate, b. p. 88—90°/2 mm., m. p. 45°,  $[\alpha]_{D}^{25} -54.46^\circ$ , from the ester and acetic anhydride in ether at -15°; *l*(+)- $\alpha$ -acetamidopropiondimethylamide, b. p. 110°/2 mm., m. p. 88—90°,  $[\alpha]_{D}^{25} -46.8^\circ$ ,  $[\alpha]_{D}^{25} -58.7^\circ$  in alcohols, by acetylation of *l*(+)- $\alpha$ -aminopropiondimethylamide, b. p. 64—66°/0.5 mm.,  $[\alpha]_{D}^{25} +14.0^\circ$ , obtained by reduction of *l*(-)-azidopropiondimethylamide with aluminium amalgam in ether or (partly racemised) by the action of dimethylamine on methyl *l*(+)- $\alpha$ -acetamidopropionate; ethyl *l*(-)- $\alpha$ -aminopropionate,  $[\alpha]_{D}^{25} -2.1^\circ$ ; ethyl *l*(+)- $\alpha$ -benzamidopropionate, m. p. 100—101°,  $[\alpha]_{D}^{25} +39.3^\circ$  ( $\pm 0.3$ ) in *s*-tetrachloroethane,  $[\alpha]_{D}^{25} +5.89^\circ$  in pyridine; (-)- $\alpha$ -bromopropiondimethylamide (readily racemised),  $[\alpha]_{D}^{25} +86.8^\circ$ ; (-)- $\alpha$ -chloropropionic acid,  $[\alpha]_{D}^{25} -15.4^\circ$ , by resolution of the *r*-acid with cinchonine in aqueous solution; (-)- $\alpha$ -chloropropionyl chloride, b. p. 50—53°/90 mm.,  $[\alpha]_{D}^{25} +4.1^\circ$ ; methyl (-)- $\alpha$ -chloropropionate, b. p. 80—82°/110 mm.,  $[\alpha]_{D}^{25} -27.8^\circ$ ; (-)- $\alpha$ -chloropropiondimethylamide, b. p. 89°/10 mm.,  $[\alpha]_{D}^{25} +60.4^\circ$ ;  $\alpha$ -iodopropionyl chloride, b. p. 44—45°/12 mm.,  $[\alpha]_{D}^{25} +54.34^\circ$ , from the *d*-acid and thionyl chloride; methyl  $\alpha$ -iodopropionate,  $[\alpha]_{D}^{25} +97.31^\circ$ ,  $[\alpha]_{D}^{25} +87.50^\circ$  in hexane, from the acid and diazomethane in hexane;  $\alpha$ -iodopropiondimethylamide, m. p. 67°/2 mm.,  $[\alpha]_{D}^{25} -6.08^\circ$ , -10.8° in hexane.

Attempts to resolve  $\alpha$ -cyanopropionic acid by means of brucine were only partly successful and the active acid became racemised with great readiness.  $\alpha$ -Cyanopropionyl chloride, b. p. 68°/25 mm., methyl  $\alpha$ -cyanopropionate, b. p. 80°/12 mm., and  $\alpha$ -cyanopropiondimethylamide, b. p. 84°/2 mm., are described.

Methyl *d*(-)-toluenesulphonyl-lactate,  $[\alpha]_{D}^{25} +51.64^\circ$ , and lactidimethylamide, b. p. 78°/1 mm., have been prepared. H. WREN.

**Preparation of pure palmitic and stearic acids in large quantities.** H. DUBOVITZ (Chem.-Ztg., 1930, **54**, 814).—Very pure palmitic acid (titer

62.6°, iodine value 0.45, acid value 219.2) can be obtained from *Stillingia* tallow as follows: the liberated fatty acids (by the autoclave or Twitchell process) are cold-pressed to remove liquid acids and neutral oil, and then pressed warm in cakes 1 cm. thick; the product, dissolved in its own weight of 90% alcohol, is cast into cakes 3 cm. thick, which are warm-pressed (without previous melting). The residue is broken up and the alcohol evaporated. Stearic acid, titer 69.7°, acid value 197.5, iodine value 0.41, unsaponif. matter 0.1%, can be prepared by the same method from shea butter or from olive oil fatty acids that have been partly hydrogenated (iodine value 35—40). E. LEWKOWITSCH.

**Purification [isolation] and properties of naturally occurring higher fatty acids.** D. HOLDE and W. BLEYBERG (Z. angew. Chem., 1930, **43**, 897—902; cf. A., 1929, 294; B., 1929, 667, 785).—An individual fatty acid is best isolated, particularly from a complex mixture, by fractional distillation of the mixed acids or their esters at a very low pressure; and in any case this should precede attempts at separation by crystallisation. The separation may be controlled by measuring the m. p. of successive fractions, a rapid fall in m. p. of the first few indicating the presence of an individual in fair purity. Acids of lower mol. wt. may then be separated by fractional crystallisation, but any of higher mol. wt. still present are best removed by distillation. The lithium acetate method fails with sparingly soluble acids of high mol. wt. A micro-distillation apparatus for use with low pressures is described, by aid of which the tendency of the higher fatty acids and their esters to decompose on distillation is avoided. As additional criteria of purity to those already implied, the identity of m. p. of crystals and mother-liquor, and the tendency of pure fatty acids to form coarse crystals (as against that of mixtures to form glassy microcrystalline masses) are suggested.

Fractional distillation of the methyl esters of crude "cerotic" acid from beeswax gave a series of fractions of steadily increasing m. p., but the acid itself gave three initial fractions of decreasing m. p., from which *n*-tetracosic acid, identical with the synthetic product, was readily isolated in a pure state. An apparently homogeneous acid,  $C_{27}H_{54}O_2$ , obtained by fractional distillation of the ethyl esters of the acids from Chinese insect wax and crystallisation of the main fraction, when distilled gave initial fractions of rapidly falling m. p., from which *n*-hexacosic acid was finally isolated. H. A. PIGGOTT.

**Action of acetyl bromide on ethyl ethoxyacetate.** R. LYDÉN (Finska Kemistsamf. Medd., 1930, **38**, 68—71; Chem. Zentr., 1930, i, 3171).—The chief products are ethyl bromide and ethyl acetoxycetate, ethyl acetate and ethyl bromoacetate also being formed. A. A. ELDRIDGE.

**Decarboxylation of pyruvic acid.** I. U. BOKLUND (Biochem. Z., 1930, **226**, 56—61).—Pyruvic acid in presence of ammonia and of a number of amino-compounds, e.g., aniline, methylamine, aminobenzoic acid, toluidine, etc., is catalytically decomposed into carbon dioxide and acetaldehyde, the reaction occurring in dilute aqueous solution at the ordinary temper-

ature. With aniline, the reaction has an optimal  $p_H$  at 3.6 and shows close resemblance to the decomposition by carboxylase. P. W. CLUTTERBUCK.

**Behaviour of polyhydroxy-aliphatic acids on heating.** K. H. BAUER and A. EBERLE (Z. angew. Chem., 1930, 43, 902—904).—Dihydroxystearic acid, m. p. 133°, when heated at 140—200° in a stream of carbon dioxide, evolves water and gives gelatinous products of lower acid value and with an acquired saponification value, and regarded therefore as esters of varying complexity produced by elimination of water intermolecularly between the hydroxyl and carboxyl groups of the acid ("estolides"). These products, or the original dihydroxy-acid, when heated at 300° are converted into  $\alpha$ -ketostearic acid (Baruch, A., 1894, i, 170) in yields of about 60%. The same product is obtained, in slightly better yield, from the dihydroxystearic acid, m. p. 98°. Corresponding products are not obtained from sativic or linusic acids, decarboxylation apparently occurring with the production of hydrocarbons. H. A. PIGGOTT.

**Oxidation of dibasic acids.** W. H. HATCHER and W. H. MUELLER (Canad. J. Res., 1930, 3, 291—305).—The rates of oxidation of malonic, tartronic, succinic, malic, tartaric, maleic, and fumaric acids by aqueous hydrogen peroxide at 100° have been determined by the method previously described (A., 1927, 425; 1929, 424). Oxidation appears to take place through an acid-hydrogen peroxide complex. The  $\alpha$ -hydroxy-acids are oxidised twice as rapidly as the unsubstituted acids; malic acid, however, behaves as a  $\beta$ -hydroxy-acid. Maleic acid is oxidised more rapidly than fumaric acid. In presence of hydrochloric acid, fumaric acid is the only one to show no velocity change; the rate is increased for maleic acid and decreased for all the other acids. The sodium or potassium salts are unsuitable for oxidation studies owing to the catalytic decomposition of the peroxide. The formation of peracids is not a stage in the oxidation, but is due to side reactions.

The rate of oxidation of tartronic acid by acidified potassium permanganate at 25° increases with rise in acidity (cf. A., 1928, 249); succinic acid is not attacked by potassium permanganate in presence of sulphuric acid. H. BURTON.

**Optical activity and polarity of substituent groups.** XVI. Application of the Thorpe-Ingold valency deflexion hypothesis to optically active compounds. H. G. RULE and J. HARROWER (J.C.S., 1930, 2319—2328).—The influence exerted by the *gem*-dialkyl group on the rotatory powers (in the homogeneous state and in alcohol and benzene solutions) of the *l*-menthyl esters,  $CR_2X \cdot CO_2C_{10}H_{19}$ , has been investigated in the cases where  $X = CO_2C_{10}H_{19}$ ,  $CO_2H$ ,  $CO_2Na$ , and  $OMe$ . These menthyl esters are best prepared by the action of *l*-menthol on the corresponding methyl esters at 140—150° in the presence of a little sodium methoxide, and thus are obtained: *l*-menthyl dimethyl-, b. p. 210—212°/2 mm.,  $d_{40}^{20}$  0.9712,  $[M]_{5461}^{20}$  —271.9° (converted by 1 mol. of sodium hydroxide at 80° into the *l*-menthyl hydrogen ester,  $d_{40}^{20}$  1.029  $[M]_{5461}^{20}$  —205.0°), and diethyl-, m. p. 52—53°,  $d_{40}^{20}$  0.9705,  $[M]_{5461}^{20}$  —279.1° (*l*-menthyl hydrogen ester,  $d_{40}^{20}$  1.013,  $[M]_{5461}^{20}$  —224.7°) -malonate; *l*-menthyl  $\alpha$ -

methoxyisobutyrate, b. p. 124—126°/10 mm.,  $d_{40}^{20}$  0.9466,  $[M]_{5461}^{20}$  —197.9° [the methyl ester, b. p. 134—137°/755 mm. (corr.), is obtained by the action of methyl iodide and silver oxide on hydroxyisobutyric acid, m. p. 79°, which, in turn, is prepared by hydrolysis of acetonecyanohydrin with fuming hydrochloric acid at the ordinary temperature], and *l*-menthyl  $\alpha$ -methoxy- $\alpha$ -ethylbutyrate, b. p. 139—141°/8 mm.,  $d_{40}^{18}$  —76.23°  $l = 100$  mm.) (methyl ester, b. p. 165—168°,  $n_D^{18}$  1.4194), all rotations being in the homogeneous state. The rotatory powers for other wave-lengths and in alcohol and benzene are also given. The increasing proximity of the groups  $X$  and  $CO_2C_{10}H_{19}$  resulting, on the basis of the Thorpe-Ingold valency deflexion hypothesis, from the change  $CH_2 \rightarrow CMe_2 \rightarrow C(Et)_3$ , leads to a marked fall in the rotations of the menthyl malonates ( $X = CO_2C_{10}H_{19}$ ) and of the sodium menthyl malonates ( $X = CO_2Na$ ), and to a rise in the hydrogen malonates ( $X = CO_2H$ ) and in the methoxy-esters ( $X = OMe$ ). The depression following the conversion of the acids into their sodium salts increases continually in magnitude from the malonate to the diethylmalonate. With the exception of the methoxy-esters these observations are in agreement with the known influence of the substituents  $X$  in the *p*- and *o*-substituted benzoic esters on the assumption that the characteristic *o*-effects are related to the proximity of  $X$  to the ester group (Rule and others, A., 1928, 765, 884). The absence of a similar parallelism in the case of the methoxy-esters is discussed in the light of possible complicating factors, and the influence of steric effects on the yields and ease of hydrolysis of the various esters are noted. J. W. BAKER.

**Polymerisation and ring formation.** VI. Adipic anhydride. J. W. HILL (J. Amer. Chem. Soc., 1930, 52, 4110—4114).—Mainly an account of work previously reviewed (Carothers, this vol., 1272). The following is new. Polymeric adipic anhydride reacts with phenol forming *phenyl adipate*, m. p. 105.5—106° (cf. Voerman, A., 1905, i, 13). H. BURTON.

**Preparation of thio-acids, particularly chlorothioacetic acid.** F. ARNDT and N. BEKER (Ber., 1930, 63, [B], 2390—2393).—Chloroacetyl chloride is converted into chlorothioacetic acid,  $CH_2Cl \cdot CO \cdot SH$ , b. p. 46°/16 mm., in good yield by the action of dry hydrogen sulphide in presence of aluminium chloride at a low temperature. The method appears general, since acetyl chloride affords thioacetic acid in poor yield under similar conditions. The constitution of chlorothioacetic acid follows from its conversion by diazomethane into methyl chlorothioacetate, b. p. 160°/atm. pressure, 58°/15 mm., also obtained from chloroacetyl chloride and methyl mercaptan. Chlorothioacetic acid and chloroacetyl chloride in boiling carbon tetrachloride yield dichlorodiacetyl sulphide, b. p. 130°/11 mm., m. p. 47°. The product of m. p. 38° obtained by von Auwers and Arndt (A., 1909, i, 668) by the action of chloroacetyl chloride on *p*-thiocresol is shown to be *p*-tolyl chlorothioacetate, and not *p*-tolylthiolacetyl chloride as stated by Stollé (A., 1914, i, 992), since it is only slowly attacked by water, by which *p*-tolylthiolacetyl chloride, b. p. 149°/16 mm., derived from the acid and phosphorus pentachloride, is immediately hydrolysed.

Thiolacetic acid and phosphorus trichloride appear to yield the substance,  $\text{CH}_2\text{S} \cdot \text{CO}-\text{O} > \text{PCl}$ , b. p.  $93^\circ/13 \text{ mm.}$ , immediately decomposed by water with formation of hydrogen chloride and thiolacetic acid. H. WREN.

**Product of interaction of formaldehyde with ammonium sulphate.** A. MACHADO (Revista Chim. pura appl., 1928, 3, 129—133; Chem. Zentr., 1930, i, 2421—2422).—The crystalline product of  $\text{CH}_2\text{S}-\text{CH}_2$  interaction of formaldehyde and ammonium sulphate in aqueous solution  $\text{N}-\text{CH}_2-\text{N}$  has a composition corresponding with  $\text{CH}_2\text{S}-\text{CH}_2$  the formula  $\text{C}_5\text{H}_{10}\text{N}_2\text{S}_2$ ; the annexed formula is proposed in place of Délépine's formula.

A. A. ELDRIDGE.

**Condensation reactions of acetaldehyde over certain oxide catalysts at pressures from 1 to 500 atm. of hydrogen.** H. ADKINS, M. E. KINSEY, and K. FOLKERS (Ind. Eng. Chem., 1930, 22, 1046—1048).—When a mixture of the vapours of ethyl alcohol and acetaldehyde is subjected to the action of the chromite of zinc, manganese, or copper as catalyst at  $360^\circ$  in an atmosphere of hydrogen under 500 atm. pressure, a great variety of products, mainly aliphatic alcohols and the ethyl esters of fatty acids, are formed. Ethyl alcohol treated similarly but in absence of acetaldehyde yields mainly hydrogen and ethylene; the effect of variation in the experimental conditions on the ratio and rate of formation of these substances has been studied. R. CUTHILL.

**Aliphatic acyloins. I. Preparation.** B. B. CORSON, W. L. BENSON, and T. T. GOODWIN (J. Amer. Chem. Soc., 1930, 52, 3988—3995).—The following acylalkylcarbinols are prepared in about 50% yield by adding gradually 2 mols. of the ethyl ester of the requisite fatty acid to a stirred mixture of sodium (4 atoms) and ether (1—1.5 litres); the mixture is kept gently boiling. After 24 hrs. the mixture is poured into ice and the resultant ether-soluble neutral product fractionated (cf. Bouveault and Locquin, A., 1906, i, 782): propionylethylcarbinol, b. p.  $50-53^\circ/3 \text{ mm.}$ ,  $d_4^{25}$  0.9310,  $n_D^{25}$  1.4183; *n*-butyryl-*n*-propylcarbinol, b. p.  $80-82^\circ/10 \text{ mm.}$ ,  $d_4^{25}$  0.9160,  $n_D^{25}$  1.4242; isobutyrylisopropylcarbinol, b. p.  $55-57^\circ/3 \text{ mm.}$ ,  $d_4^{25}$  0.8990,  $n_D^{25}$  1.4159; *n*-valeryl-*n*-butylcarbinol, b. p.  $90-92^\circ/3 \text{ mm.}$ ,  $d_4^{25}$  0.9000,  $n_D^{25}$  1.4298; isovalerylisobutylcarbinol, b. p.  $94-97^\circ/12 \text{ mm.}$ ,  $d_4^{25}$  0.8930,  $n_D^{25}$  1.4260; *n*-hexoyl-*n*-amylcarbinol, b. p.  $105-107^\circ/3 \text{ mm.}$ ,  $d_4^{25}$  0.8900,  $n_D^{25}$  1.4339; isohexoyl-isoamylcarbinol, b. p.  $101-103^\circ/3 \text{ mm.}$ ,  $d_4^{25}$  0.8865,  $n_D^{25}$  1.4326;  $\beta$ -methylvaleryl- $\beta$ -methylbutylcarbinol, b. p.  $102-104^\circ/3 \text{ mm.}$ ,  $d_4^{25}$  0.8880,  $n_D^{25}$  1.4330, and  $\alpha$ -dimethylbutyryl- $\alpha$ -dimethylpropylcarbinol, b. p.  $96-97^\circ/3 \text{ mm.}$ , m. p.  $\pm 12^\circ$ ,  $d_4^{25}$  0.9300,  $n_D^{25}$  1.4471. Some of the corresponding diketone is usually produced and during distillation of the carbinol a high-boiling compound is formed. When the carbinols are exposed to sunlight the carbon and hydrogen contents decrease (with one exception) whilst the values of  $d$  and  $n$  remain constant; the pale yellow colour of the carbinols disappears, but returns in the dark.

H. BURTON.

**Cleavage of  $\alpha$ - $\gamma$ -diketones.** W. M. KUTZ and H. ADKINS (J. Amer. Chem. Soc., 1930, 52, 4036—

4042; cf. this vol., 1273).—Nine  $\alpha$ - $\gamma$ -diketones,  $\text{CHRAc}\cdot\text{CO}\cdot\text{R}'$ , have been hydrolysed with 0.1*N*-sodium hydroxide and an alcoholic solution of hydrogen chloride (0.5 mol. per 1 mol. of diketone) at  $60^\circ$ , and the amounts of acetic acid (or ester) and the acid  $\text{R}'\cdot\text{CO}_2\text{H}$  (or ester) determined from the partition ratio of the acids involved between benzene and water containing 0.15 mol. of sodium sulphate per litre. The percentages of ethyl acetate in the mixture of esters produced by alcoholysis are: acetylbutyrylmethane, 43.5; acetyl-*n*-valerylmethane, 61; acetylisovalerylmethane, 65.5; acetyl- $\alpha$ -methylbutyrylmethane, 81; acetyltrimethylacetylmethane, 91; benzoylacetylmethane, 100; cyclohexanecarboxylacetylmethane, 58.5;  $\alpha$ -benzoyl- $\alpha$ -acetyl- $\beta$ -phenylethane, 100; furoylacetylmethane, 100. The corresponding figures for the percentages of acetic acid produced on alkaline hydrolysis are 49, 55, 67, 58, 86, 56, 69, and 100, respectively. The results show that there is no close relationship between the amounts of the acids produced and their strengths. Increased branching in the acetylvalerylmethanes causes a progressive diminution in the amount of the ethyl valerate produced during alcoholysis; such branching has, however, little effect on the amount of the valeric acid formed on alkaline hydrolysis. It is suggested that the ratio of esters is a measure of the extent of enolisation of the carbonyl groups (cf. *loc. cit.*). Determinations of the partition of cyclohexanecarboxylic, benzoic, trimethylacetic, *n*-valeric, isovaleric,  $\alpha$ -methylbutyric, and *n*-butyric acids between equal volumes of benzene and water containing 0.15 mol. of sodium sulphate per litre have been made. Acetyl- $\alpha$ -methylbutyrylmethane, b. p.  $62-65^\circ/5 \text{ mm.}$ ,  $d_4^{25}$  0.9160, and furoylacetylmethane, m. p.  $30-31^\circ$ , are prepared by the method previously described (*loc. cit.*). H. BURTON.

**Catalytic hydrogenation of azines. V. Hydrogenation of ketazines.** The relative affinities of the methyl and ethyl groups. K. A. TATPALE and P. W. USATSCHEV (J. Russ. Phys. Chem. Soc., 1930, 62, 1241—1258; cf. A., 1926, 157; 1927, 260).—Bisdimethyl ketazine, bisdimethyl ethyl ketazine, and bisdiethyl ketazine were investigated in the same way as the aldazines (*loc. cit.*); the rate of hydrogenation of the dimethyl was greater than for the methyl ethyl, and the rate of the latter greater than for the diethyl compound, the quantitative results of the former investigation being confirmed.

Bisdimethyl ethyl ketazine, b. p.  $171-172^\circ$ ,  $d_4^{25}$  0.8404,  $n_D^{25}$  1.4551, on hydrogenation gave NN-di-sec-butylhydrazine, b. p.  $168.5-169^\circ/769 \text{ mm.}$ ,  $d_4^{25}$  0.8214,  $n_D^{25}$  1.4283; this formed a dihydrochloride readily decomposing into the monochloride, m. p.  $147^\circ$ , which yielded a semicarbazide, m. p.  $48-49^\circ$ , with potassium cyanate, and the phenylthiosemicarbazide, m. p.  $78-78.5^\circ$ , with phenylthiocarbimide. The hydrazine can be converted into the corresponding azo-compound, azo- $\alpha$ -methylpropane, b. p.  $140-142^\circ/756 \text{ mm.}$ ,  $d_4^{25}$  0.7904,  $n_D^{25}$  1.4127, either by cautious oxidation with mercuric oxide or with nitrous acid by way of the nitroso-compound. If the alcoholic solution of the azo-compound is saturated with hydrogen chloride, sec-butylhydrazine hydrochloride is obtained, whilst heating with benzoyl chloride yields dibenzoyl-sec-butylhydrazine, m. p.  $169-170^\circ$ . The hydrochloride

of the primary hydrazine and potassium thiocyanate on heating give the *sec.-butylsemicarbazide*, m. p. 97.5—98°.

Bisdiethyl ketazine, b. p. 196—197°/762 mm.,  $d_4^{20}$  0.8419,  $n_D^{20}$  1.4574, on hydrogenation yields NN'-di-tert.-amylhydrazine, b. p. 193—193.5°/753 mm., which is very similar to the lower homologue, readily giving the *benzoyl* derivative, b. p. 184—185°/15 mm., *semicarbazide*, m. p. 57—57.5°, *azo-compound*, b. p. 181—182°/751 mm., primary *hydrazine* and its *dibenzoyl* derivative, m. p. 199.5—200°, and *semicarbazide*, m. p. 107—108°, with the corresponding reagents. M. ZVEGINZOV.

**Xylan.** J. REILLY, P. P. DONOVAN, and K. BURNS (Proc. Roy. Irish Acad., 1930, 39B, 505—514).—Xylan is conveniently prepared from wheat straw by extraction with 5% sodium hydroxide solution, after the preliminary removal of incrusting materials by repeated application of the chlorine dioxide-sodium sulphite process. The crude polysaccharide is purified by precipitation from aqueous solution by alcohol and final extraction with boiling alcohol and ether. Cryoscopy of a 0.5% solution of xylan in molten acetamide indicates a mol. wt. corresponding with xylose anhydride, but in more concentrated solutions the apparent mol. wt. is somewhat greater. The depolymerised xylan, "xylanane," may be recovered from solution in acetamide by precipitation with alcohol; in the moist condition it is soluble in cold water, but after drying it may only be dispersed above 50°. Cryoscopy of an aqueous solution of xylanane, dried at 112° in a vacuum, indicates  $M$  345, increasing after repeated freezing of the solution to  $M$  485. Similar cryoscopic measurements on solutions of the original xylan are impossible, since the solute is precipitated on cooling to 0°. Analogous results are obtained when xylan is depolymerised in formamide at 90°. Xylanane is indistinguishable from xylan either by ultimate analysis or by rotation,  $[\alpha]_D^{25}$  —111°, in dilute sodium hydroxide solution. Xylanane, dispersed in molten acetamide, is formulated as xylopyranose 1 : 4-anhydride. T. H. MORTON.

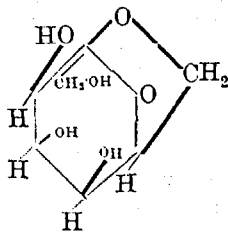
**Determination of aldose sugars by titrating with standard iodine and alkali.** G. M. KLINE and S. F. ACREE (Ind. Eng. Chem. [Anal.], 1930, 2, 413—415).—Slow addition of an alkali to a solution containing an aldose and a small quantity of iodine causes oxidation of the sugar without the formation of iodate, and by alternate additions of iodine and alkali solutions in small quantities the reaction may be rapidly completed without over-oxidation of the sugar; rapid production of iodate indicates the completion of the oxidation. In the procedure recommended 5 c.c. of 0.1*N*-iodine and 7.5 c.c. of 0.1*N*-sodium hydroxide are added alternately to the sugar solution, which should be neutral to phenolphthalein, until the reaction is complete, and after acidification the liberated excess of iodine is titrated with 0.1*N*-thiosulphate solution, of which 1.5—2.0 c.c. should be required. Back-titration of the excess of acid added indicates the quantity of alkali used during the oxidation, which serves as a check on the iodine titre. Ketonic and non-reducing sugars do not interfere unless an excess of iodine and alkali is used. The error does not exceed 0.2—0.3%. H. F. GILLBE.

**Simple proof of the stereochemical configurations of *d*-glucose and of *d*-galactose.** J. A. AMBLER (J. Chem. Educ., 1930, 7, 1599—1601).—A discussion. CHEMICAL ABSTRACTS.

**Precipitation of dextrose by copper sulphate and barium hydroxide. Generalisation to sugars and polyoses.** P. FLEURY and P. AMBERT (J. Pharm. Chim., 1930, [viii], 12, 289—301).—The precipitation of dextrose by copper sulphate and sodium hydroxide is liable to be prevented by the dissolution of the colloidal complex to form a blue solution: this difficulty can be obviated by the use of barium hydroxide. As the proportion of sodium hydroxide to sugar and copper sulphate is increased a maximum precipitation is rapidly reached at which 78% of the sugar is removed, but with further addition of alkali the amount of sugar precipitated decreases. With progressive additions of barium hydroxide the removal of sugar increases regularly and tends towards a maximum precipitation of 96%. Addition of barium salts to the blue "peptised" solution results in immediate precipitation of the sugar. When excess of barium hydroxide is added a certain amount of alkali is "fixed" by the precipitate, the amount being proportional to the amount of sugar withdrawn; the sugar and alkali are, however, reformed on dilution and the former may be recovered. The amount of dextrose removed by a fixed amount of copper has a maximum value linearly proportional to the amount of copper and amounting, approximately, to 466 mg. of dextrose per 1 g. of copper sulphate. H. J. DOWDEN.

**Reactions relating to carbohydrates and polysaccharides. XXXII. Constitution of sedosan (anhydrosedoheptose).** H. HIBBERT and C. G. ANDERSON (Canad. J. Res., 1930, 3, 306—317).—Methylation of anhydrosedoheptose (sedosan) (La Forge and Hudson, A., 1917, i, 444; La Forge, A., 1920, i, 595) with methyl iodide and silver oxide, first in presence of and then in absence of methyl alcohol, gives a *tetramethyl* derivative, m. p. 48—49°,  $[\alpha]_D^{25}$  —137° in water, which on successive oxidation with nitric acid ( $d$  1.42) at 90° and esterification with methyl-alcoholic hydrogen chloride yields an inactive methyl trimethoxyglutarate (*methylamide*, m. p. 145—146°) and possibly a methyl hydroxydimethoxyglutarate (non-crystalline *methylamide*). The crystalline methylamide differs from trimethoxyglutarmethylamide (Haworth and Jones, A., 1927, 1059), and the absence of dimethoxysuccinic acid in the oxidation product suggests that sedosan is a 2:7-anhydropyranose. The presence of a primary hydroxyl group in sedosan is illustrated by its forming a *triphenylmethyl ether*, m. p. 147°,  $[\alpha]_D^{25}$  —33.25° in chloroform. Sedosan is given the annexed constitution.

Attempted epimerisation of trimethyl- $\delta$ -arabonolactone into trimethyl- $\delta$ -ribonolactone by Haworth and Long's method (A., 1929, 426) was not successful. H. BURTON.





Reactions relating to carbohydrates and polysaccharides. XXX. Comparative hydrolysis of disaccharides and polysaccharides. H. HIBBERT and E. G. V. PERCIVAL (J. Amer. Chem. Soc., 1930, 52, 3995—4005).—The rates of hydrolysis of cellulose, cellobiose, cellodextrin (cellobiosan), starch, maltose, and lactose by a solution of anhydrous zinc chloride (1 part) in hydrochloric acid (*d* 1.18; 2 parts) have been determined polarimetrically at 23°. With the exception of cellulose and cellodextrin, the reactions are unimolecular and the velocity coefficients ( $K \times 10^4$ ) are: cellobiose (1.0), starch (2.45), maltose (2.4), and lactose (2.84). No relationship appears to exist between the rate of hydrolysis of a disaccharide and the mode of linking of the sugar units (cf. Freudenberg and others, A., 1928, 1222). Cellulose is hydrolysed slowly, probably owing to the slow hydrolysis of cellobiose. Hydrolysis of sucrose, lævan, and inulin with 0.1*N*-oxalic acid at 65° proceeds at approximately the same rate in each case, indicating that each substance contains  $\gamma$ -fructose residues.

H. BURTON.

Phillyrin. F. KOLLE and T. HJERLOW (Pharm. Zentr., 1930, 71, 705—708).—*Phillyrin*,  $C_{39}H_{47}O_{16} + 2H_2O$ , m. p. 152° (decomp. 160° partly to a substance of m. p. 178—180°),  $[\alpha]_D^{20} + 49.11^\circ$ , the glucoside from *Forsythia suspensa* and *Olea fragrans* (cf. Eykman, A., 1886, 1040), is hydrolysed by  $\alpha$ -glucosidase, rhamnase, or dilute aqueous acids to dextrose and *phillygenin*,  $C_{33}H_{35}O_{10}$ , m. p. 131—131.5°,  $[\alpha]_D^{20}$  about +130°. R. CHILD.

Glucosides of *Digitalis lanata*, Ehrh. C. MANNICH, P. MOHS, and W. MAUSS (Arch. Pharm., 1930, 268, 453—476).—Four glucosides, none of which is identical with digoxin (Smith, this vol., 583), have been isolated from the alcoholic extract of the dried leaves. The principal glucoside, *lanadigin*,  $C_{41}H_{66}O_{17} + 4H_2O$ , m. p. 245° (rapid heating),  $[\alpha]_D^{20} + 33.3^\circ$  in alcohol, gives a yellow *sodium* derivative, from which it is not recovered on acidification. It is hydrogenated with difficulty (palladium) to a *dihydro*-derivative, m. p. 245° (decomp.),  $[\alpha]_D^{20} + 27.6^\circ$  in alcohol, and hydrolysed by dilute hydrochloric acid to digitoxose, a small quantity of a disaccharide (below), and lanadiginin,  $C_{23}H_{34}O_5$ , m. p. 220—222° (also  $+2H_2O$ , froths at 130—135°, resolidifying with m. p. 206—207°),  $[\alpha]_D^{20} + 23.6^\circ$  in alcohol (*dibenzoyl*, m. p. 256—257°,  $[\alpha]_D^{20} + 5^\circ$ , and *diacetyl*, m. p. 210°, derivatives), probably identical with digitoxigenin (Smith, *loc. cit.*). This is a monolactone and gives when treated with boiling 0.1*N*-sodium hydroxide and reacidified a *product*, m. p. 255° (also  $+H_2O$ ). With concentrated hydrochloric acid it forms an *anhydro*-derivative,  $C_{23}H_{32}O_4$  (also  $+2H_2O$ ), m. p. 186—187°, readily converted in presence of palladised charcoal into a *dihydro*-derivative, m. p. 184°, isomeric with digitoxigenin. Lanadiginin is hydrogenated to a *dihydro*-derivative ( $+0.5H_2O$ ), m. p. 220°, sintering and frothing from 155°, which is also a lactone. The *disaccharide*,  $C_{12}H_{22}O_9$ , m. p. 220°,  $[\alpha]_D^{20} + 31.7^\circ$  in water (*hexa-acetate*, m. p. 196—196°), is non-reducing, but gives reducing sugars after vigorous hydrolysis. *Lanata glucoside-II* (C, 60.3%; H, 8.0%), m. p. 243—245°,  $[\alpha]_D^{20} + 32.6^\circ$  in alcohol,

closely resembles lanadigin, but yields on hydrolysis digitoxigenin in addition to the three products obtained from the latter. Systematic fractional crystallisation failed to separate it into simpler glucosides. The amorphous *Lanata glucoside-III*, m. p. 228—229°,  $[\alpha]_D^{20} + 14.2^\circ$  in alcohol, is probably identical with "digitalinum verum," Kiliani. It is hydrolysed to a digitaligenin,  $[\alpha]_D^{20} + 566^\circ$ , characterised by analysis and hydrogenation, also sugars, of which only dextrose can be identified. *Lanata glucoside-IV*,  $C_{42}H_{66}O_{16}$ , or  $C_{29}H_{48}O_{11}$ , sintering at 195° and resolidifying with m. p. 225—250°,  $[\alpha]_D^{20} + 5.5^\circ$  in methyl alcohol, gives none of the usual colour reactions of the *Digitalis* glucosides and is hydrolysed by aqueous-alcoholic hydrochloric acid to a *genin*,  $C_{32}H_{32}O_3$ , or  $C_{30}H_{42}O_4$ , m. p. 190°, optically inactive (*dihydro*-derivative, m. p. 213—214°), and dextrose only. Acidification of an alkaline solution of the glucoside gives an isomeric *product*, m. p. 278°. The colour reactions of the new products are described. The glucosides have physiological activities by the timeless method of 200,000, 250,000, 150,000, and 50,000 frog units, respectively. H. E. F. NOTTON.

Polysaccharides. III. Acetamide as a polysaccharide solvent. J. REILLY, R. WOLTER, and P. P. DONOVAN (Sci. Proc. Roy. Dublin Soc., 1930, 19, 467—473).—An apparatus for the mol. wt. determination in acetamide is described (cf. A., 1929, 1282); the molten acetamide is cooled in boiling alcohol vapour. Determinations of the molecular depression constant of acetamide give the following values: sucrose (40.6 and 44.1 when the concentration of the solute is 0.767 and 2.009%, respectively); acetanilide (40.2 and 40.7 with concentrations of 1.208 and 2.148%, respectively); mannitol (42.7;  $c = 2.112\%$ ); naphthalene (37.8;  $c = 1.27\%$ ). Determinations of the mol. wt. of depolymerised polysaccharides and their acetates by the modified method of Freudenberg (this vol., 198) give the same results as with the older method (cf. Hess, *ibid.*, 456). H. BURTON.

Starch. XXIV. New polyamyloses. H. PRINGSHEIM, A. WIENER, and A. WEIDINGER (Ber., 1930, 63, [B], 2628—2636; cf. this vol., 895).—Determinations of the mol. wt. of  $\alpha$ -tetra-amylose in freezing acetamide give values corresponding closely with those required for a hexose anhydride. Similar results are obtained in freezing formamide provided that the solvent has been freed so far from traces of formic acid that it has m. p.  $+1.8^\circ$  to  $+2^\circ$ ; with unpurified formamide much higher values are obtained. Addition of alcohol to the formamide solution causes precipitation in 80% yield of  $\alpha$ -amylosan,  $C_6H_{10}O_5 \cdot H_2O$ ,  $[\alpha]_D^{20} + 149^\circ$  in water, which gives characteristic, long, green needles with iodine in potassium iodide. Removal of alcohol and the bulk of the formamide from the filtrate followed by addition of alcohol and ether gives  $\beta$ -amylosan,  $C_6H_{10}O_5 \cdot H_2O$ ,  $[\alpha]_D^{20} + 173^\circ$  in water, which in formamide or water has the mol. wt. of a disaccharide anhydride. It is most easily distinguished from  $\alpha$ -amylosan by the additive *product* with iodine, which forms brownish-red prismatic rods. Similar observations with  $\beta$ -hexa-amylose in acetamide or form-

amide give mol. wts. corresponding with the  $2 \times C_6$  stage. Addition of alcohol and ether to the formamide solution precipitates, in 90% yield,  $\beta$ -amylosan identical with that derived from  $\alpha$ -tetra-amylose. The amylosans form sparingly soluble additive compounds with organic solvents, for example trichloroethylene, by aid of which they can be withdrawn from their aqueous solutions.  $\alpha$ -Amylosan triacetate,  $[\alpha]_D^{20} +120^\circ$  in chloroform, mol. wt. 256 in glacial acetic acid, and  $\beta$ -amylosan triacetate,  $[\alpha]_D^{20} +130.5^\circ$  in chloroform, mol. wt. 332 in glacial acetic acid, are described. Repeated evaporation of aqueous solutions of  $\alpha$ -amylosan on the water-bath results in the production of  $\alpha$ -isoamylosan,  $[\alpha]_D^{20} +133^\circ$  in water, mol. wt. in formamide corresponding with  $C_6H_{10}O_5$ .  $\beta$ -Amylosan requires only protracted heating of its aqueous solution to effect the conversion into  $\beta$ -isoamylosan,  $[\alpha] +151^\circ$  in water, mol. wt. in formamide corresponding with the  $2 \times C_6$  stage; the compound is precipitated unchanged from formamide solution. In aqueous solution the isoamylosans exhibit a pronounced tendency towards molecular aggregation, becoming colloiddally disperse within a few days. The artificial production of polyisoamylosans thus appears to be indicated and to receive support from the ability of  $\alpha$ -polyisoamylosan to form a gel in concentrated aqueous solution. On the other hand, these products appear to be convertible into the characteristic  $\alpha$ - and  $\beta$ -amylosans from which the respective iodine products are formed.

$\alpha$ -Amylosan passes when heated in formamide for 6 hrs. at  $100^\circ$  into a substance crystallising from aqueous alcohol in hexagonal plates which gives a very characteristic blackish-green, prismatic compound with iodine (photomicrograph).  $\alpha$ -Tetra-amylose,  $\beta$ -hexa-amylose, and the two amylosans have identical optical activities ( $[\alpha]_D^{20} +133^\circ$ ) in aqueous pyridine (7:3). H. WREN.

**Inulin.** X. H. PRINGSHEIM and J. REILLY [with W. G. HENSEL, W. BURMEISTER, P. P. DONOVAN, and (MISS) N. HAYES] (Ber., 1930, 63, [B], 2636—2642; cf. this vol., 896).—Re-examination of the products used previously (*loc. cit.*) in consequence of the criticisms of Berner (*ibid.*, 1025) has shown that the inulin used was free from ethyl alcohol as judged by the failure of the iodoform reaction and that air-dried inulin,  $C_6H_{10}O_5 \cdot H_2O$ , generally becomes completely dehydrated within 30 min. when preserved over phosphoric oxide in a vacuum at  $78^\circ$ . The inulin was free from acetamide when tested by distillation with sodium, hydroxide and treatment of the distillate with Nessler's solution. Cryoscopic observations of the mol. wt. of inulin in acetamide and purified formamide indicate the formula  $2 \times C_6H_{10}O_5$ , although occasionally double this value is found. Inulin from acetamide or formamide in sufficiently dilute aqueous solution has the  $2 \times C_6$  formula.

Examination of the action of iodine on l  vulose under the conditions of Willst  tter shows reaction to occur to an extent corresponding with about 2.8% of dextrose. When this correction is applied to the product obtained by the acid hydrolysis of inulin (cf. Schlubach and Elsner, A., 1929, 915; Jackson

and Goergen, *ibid.*, 1280) about 5% of dextrose appears to be present. Application of the same method to the product of the hydrolysis of inulin by inulinase shows the absence of dextrose. The possibility that dextrose is a component of natural inulin is not thereby excluded, since fermentative hydrolysis cannot be caused to proceed beyond 90%, as judged from the behaviour of the product towards Fehling's solution. H. WREN.

**Views of the constitution of cellulose and their experimental foundations.** K. HESS (Kolloid-Z., 1930, 53, 61—75).—An account of old and new views of the constitution of cellulose is given and recently published experimental work on the swelling of cellulose and on its examination by the X-ray spectrographic method is summarised. It is concluded that the work reviewed does not justify definite views of the constitution of the cellulose molecule.

E. S. HEDGES.

**Chemical sorption. IV. Complex sorption process and hydrolysis.** S. LIEPATOV [with N. SOKOLOVA] (Z. anorg. Chem., 1930, 192, 383—390).—Investigation of the adsorption of sodium hydroxide by cellulose indicates that 1 mol. of cellulose fixes 3 mols. of sodium hydroxide and that the sodium atom can attach itself to the surface of the cellulose only at a point where there is a hydroxyl group. The swelling of cellulose which takes place in sodium hydroxide solution reaches a maximum in a 10% solution of the hydroxide. Comparison of the swelling of cellulose in sodium hydroxide solution and pure water, respectively, indicates that, in the former case, water is adsorbed until the cellulose is covered with a unimolecular layer, whilst in the latter the water merely enters the capillaries of the cellulose film. Both conclusions are confirmed by X-ray measurements.

M. S. BURR.

**Action of heat on ethylamine and benzylamine.** C. D. HURD and F. L. CARNAHAN (J. Amer. Chem. Soc., 1930, 52, 4151—4158).—When ethylamine is passed through a pyrex-glass tube at  $600^\circ$ , acetonitrile and hydrogen are the main products formed, together with some ethylene, ammonia, hydrogen cyanide, and methane. At  $890$ — $900^\circ$ , using quartz tubes, acetonitrile is not produced; the amount of ethylene diminishes with increase in the time of contact; hydrogen and paraffin hydrocarbons are also formed. When ethylamine is passed over kaolin at  $900^\circ$ , little or no ethylene is produced but carbon monoxide is found. Contrary to the statement of Upson and Sands (A., 1922, i, 1121), butane is not formed during the pyrolysis. The following changes probably occur:  $NH_3 + C_2H_5 \leftarrow NH_2Et \rightarrow H_2 + CH_3C \equiv NH \rightarrow CH_4 + HCN$  or  $H_2 + MeCN$ .

Benzylamine is recovered unchanged when passed through a pyrex-glass tube at  $535^\circ$  (contact time 54 sec.). At  $630^\circ$  (contact time 160 sec.), hydrogen, nitrogen, hydrogen cyanide, ammonia, benzene, toluene, benzonitrile, and small amounts of carbon monoxide and saturated gaseous hydrocarbons are formed. Much benzylamine is recovered at  $700^\circ$  (contact time 49 sec.) and practically no benzonitrile is produced. The following changes take place:  $CH_2Ph \cdot NH_2 \rightarrow H_2 + CHPh \cdot NH$ ;  $2CH_2Ph \cdot NH_2 \rightarrow$

$\text{NH}_3 + \text{Ph} \cdot \text{Me} + \text{CHPh} \cdot \text{NH} ; \text{CHPh} \cdot \text{NH} \longrightarrow \text{Ph} \cdot \text{H} + \text{HCN} \text{ or } \text{H}_2 + \text{Ph} \cdot \text{CN}.$

*p*-Toluenesulphon-benzylamide and -dibenzylamide have m. p. 119° (corr.) and 81.3° (corr.), respectively.

H. BURTON.

**Synthesis of ethylenediamine.** N. PUTCHIN (Trans. Inst. Pure Chem. Reagents, U.S.S.R., 1929, No. 300, 119—122).—Phthalimide and potassium carbonate are used instead of potassium phthalimide, and the water formed in the reaction is trapped. The yield is 55—60% (cf. A., 1929, 1168).

CHEMICAL ABSTRACTS.

**Quaternary ammonium iodide derivatives of ethyl iodoacetate.** P. FREUNDLER, L. PIAUX, and (MLLE.) M. PILAUD (Bull. Soc. chim., 1930, [iv], 47, 1147—1150).—When 1 mol. of silver oxide is added to a solution of 1 mol. of a quaternary iodide of the type  $(\text{NPhRR}' \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Et})\text{I}$  only a part of the iodide is decomposed; for the complete conversion into betaine addition of 2 mols. of silver oxide is required (cf. this vol., 594). The reaction has been observed with the methyl and ethyl derivatives and with phenyldimethylethylammonium iodide. A hydroxyiodide,  $\text{AgI} \cdot \text{AgOH}$ , appears to be formed; it is stable in the cold in presence of water and in exclusion from light, but the dry product is unstable.

When the aqueous solutions of the betaines obtained by use of a slight excess of silver oxide are exposed to daylight they assume a rose and then a brown colour, and yield a brown precipitate with a high silver content and also containing tin (spectrographic). Comparative experiments with the quaternary iodides gave negative results and it is suggested that the betaines concentrate the stannous tin which is present in too dilute a form in the reagents to give the reactions. The formation of this precipitate is regarded as analogous with that observed when silver is used in the combustion of algæ containing volatile tin or in Ditte's purple reaction between stannous nitrate and silver nitrate.

R. BRIGHTMAN.

**Preparation of glycine.** P. W. BOUTWELL and L. F. KUCK (J. Amer. Chem. Soc., 1930, 52, 4166—4167).—Chloroacetic acid (189 g.) is treated with ammonia (8 litres, *d* 0.9) at the ordinary temperature for 48 hrs., the excess of ammonia recovered by distillation, and the residual solution evaporated to about 500 c.c. This is mixed with methyl alcohol (800 c.c.) and pyridine (140 c.c.); glycine (64% yield) separates from the mixture. The glycine is crystallised from water (1 part) and methyl alcohol (2 parts).

H. BURTON.

**Electrolytic separation of arginine and alanine.** W. HENDRY and T. B. JOHNSON (Biochem. Z., 1930, 226, 47—55).—Tables indicate the results of electrolysis of a mixture of known amounts of arginine and alanine under varying conditions of  $p_{\text{H}}$ , temperature, *E.M.F.*, etc. At  $p_{\text{H}}$  5.5, 95% of the arginine present is recovered at the cathode in a high degree of purity.

P. W. CLUTTERBUCK.

**Preparation of prolylalanine and prolylpeptides.** M. FRANKEL and S. KUK (Biochem. Z., 1930, 226, 221—232).—Details are given for the preparation in quantity of allyl alcohol and its conversion successively into allyl and trimethylene bromides.

The preparation of prolylalanine is then described. Trimethylene bromide is condensed with ethyl sodio-malonate and the product brominated and hydrolysed to give  $\alpha$ -dibromovaleric acid, m. p. 172—174°. This acid is converted by the action of phosphorus pentachloride into the acid chloride, which is condensed with *DL*-alanine and the product treated with aqueous ammonia.

P. W. CLUTTERBUCK.

**New synthesis of creatine and alacreatine.** H. KING (J.C.S., 1930, 2374—2377).—The synthesis of glycoamine (guanidinoacetic acid) from glycine (Wheeler and Merriam, A., 1903, i, 524) has been extended to the synthesis of creatine and alacreatine by use of sarcosine and alanine, respectively. The amino-acid in *N*-potassium hydroxide (1 mol.) is treated with methylisothiocarbamide hydriodide (1 mol.) and the solution evaporated at 50° under reduced pressure. Thus are obtained glycoamine (90% yield), not melting at 300° [Wheeler and Merriam, *loc. cit.*, give m. p. 250—260° (decomp.)] [hydrochloride, m. p. 200° (decomp.) (lit. m. p. 191°)], which yields a picrate, m. p. 210° (decomp.) (Wheeler and Merriam, *loc. cit.*, give m. p. 202°), and a *semi-picrate*, m. p. 242° (decomp.), thus rendering unnecessary Söll and Stutzer's postulation of a bimolecular guanidinoacetic acid (A., 1910, i, 14). Glycoamine is converted by heating with concentrated hydrochloric acid under pressure at 150° into glyco-cyamidine, darkens at 240° and chars up to 300°, isolated (66% yield) as its hydrochloride and its dimorphous picrate. Similarly are obtained alacreatine (65% yield), m. p. 246—247° (decomp.) (lit. m. p. 180° and 226°) [*picrate*, m. p. 187° (decomp.)], and creatine, m. p. 303° [*picrate*, m. p. 218—220° (decomp.)], which are converted into alacreatinine and creatinine, respectively. The latter gives a picrate which has the same m. p. as creatine picrate and gives no depression on admixture, this observation explaining the uncertainty existing in the literature with regard to creatine picrate (cf. Wörner, A., 1899, ii, 438; Folin, A., 1914, i, 665).

J. W. BAKER.

**Reactions of cystine.** J. A. SÁNCHEZ (Semana Med., 1930, II, 31—32).—(1) Cystine (0.1—1.2 mg.) is heated with 3 drops of 10% sodium nitrite solution and 2 drops of hydrochloric acid, the mixture diluted, and extracted with ether. The residue after evaporation of the ether gives an orange-red colour with sodium or potassium hydroxide or ammonia solution; if heated with phenol and sulphuric acid it gives a blue colour with alkali. (2) Cystine, when heated with sodium hydroxide, potassium iodide, and iodine, affords iodoform. In each case pyruvic acid may be formed.

CHEMICAL ABSTRACTS.

**Non-identity of natural muscarine with synthetic betainealdehyde.** R. VOLT (Arch. Int. Pharm. Ther., 1929, 36, 205—224; Chem. Zentr., 1930, i, 2724—2725).—Betainealdehyde does not produce the physiological effects typical of muscarine, but behaves like nicotine and curare. Trimeric betainealdehyde is without action, as also is the homologue  $\text{OH} \cdot \text{NMe}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$ .

A. A. ELDRIDGE.

$\psi$ -Halogens. X. Dichlorodioxycyanogen, ethyl *N*<sup>w</sup>-mono- and -di-chloroallophanate, and *N*<sup>w</sup>-chloroallophanyl chloride. XI. Iodo-oxy-cyanogen, di-iododioxycyanogen, and tri-iodo-cyanuric acid. L. BROCKENBACH and M. LINHARD (Ber., 1930, 63, [B], 2528—2544, 2544—2558; cf. A., 1929, 1285; this vol. 876).—X. Silver cyanate, dry or suspended in well-cooled ethyl chloride, is converted by chlorine into *dichlorodioxycyanogen*,  $\text{NCl}_2\cdot\text{CO}\cdot\text{N}\cdot\text{CO}$ , a mobile, highly-refractive liquid,  $d_{20}^{20}$  1.64, which slowly solidifies at  $-80^\circ$  to an indistinctly crystalline mass, m. p.  $-50^\circ$ . It may be preserved unchanged at  $-80^\circ$ , but at the ordinary temperature it polymerises quantitatively and more or less rapidly, according to its purity, to trichloro-cyanuric acid, hydrolysed by water to cyanuric acid. In phosphoryl chloride the mol. wt. corresponds with the formula  $(\text{OCN}\cdot\text{Cl})_2$ . It inflames when mixed with alcohol, but by suitable cooling and admixture with an indifferent solvent the reaction may be conducted so as to lead to *ethyl N*<sup>w</sup>-*dichloroallophanate*,  $\text{NCl}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , m. p.  $41-42^\circ$ , *ethyl N*<sup>w</sup>-*chloroallophanate*,  $\text{NHCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , m. p.  $148^\circ$ , and ethyl allophanate, ethyl hypochlorite being produced during the last two reactions. Dichlorodioxycyanogen is transformed by hydrogen chloride into *N*<sup>w</sup>-*chloroallophanyl chloride*,  $\text{NHCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{COCl}$ , and chlorine and by further action into allophanyl chloride; the production of dichloroallophanyl chloride could not be observed. Dichlorodioxycyanogen reacts vigorously with water, giving nitrogen trichloride and chlorine; very cautious treatment permits the isolation of *NN*'-dichlorocarbamide, formed by the subsequent action of chlorine or hypochlorous acid on chloro-carbamide. With dilute alkali hydroxide dichlorodioxycyanogen reacts in the same manner as does bromo-oxy-cyanogen (*loc. cit.*), but more slowly, so that the side reactions are more pronounced; the production of cyanate from the undoubtedly dimeric products is remarkable. Dichlorodioxycyanogen is rapidly and quantitatively reduced by aqueous sulphurous acid to the chloride; it liberates iodine from acidified potassium iodide,  $(\text{OCN}\cdot\text{Cl})_2 + 4\text{HI} + \text{H}_2\text{O} = 2\text{I}_2 + \text{CO}(\text{NH}_2)_2 + \text{CO}_2 + 2\text{HCl}$ . With neutral potassium iodide the change is more complex.

Ethyl *N*<sup>w</sup>-*dichloroallophanate* liberates 4 atoms of iodine from acidified potassium iodide and is reduced by sulphurous acid to hydrogen chloride and ethyl allophanate. It is slowly decomposed by water with evolution of nitrogen chloride. Ethyl *N*<sup>w</sup>-*chloroallophanate* behaves similarly to the dichloro-compound, but is very much more stable, so that it may be recovered partly unchanged after short treatment with boiling water. *N*<sup>w</sup>-*Chloroallophanyl chloride* reacts violently with alcohol and water, giving ethyl allophanate and carbon dioxide, chlorine, and carbamide hydrochloride, respectively. With aqueous potassium iodide the change proceeds according to the scheme:  $\text{NHCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{COCl} + \text{H}_2\text{O} + 2\text{KI} = \text{CO}(\text{NH}_2)_2 + \text{I}_2 + 2\text{KCl} + \text{CO}_2$ .

XI. Reaction between silver cyanate and iodine scarcely proceeds in solvents which dissolve iodine to a violet solution, although reaction can be caused by addition of ether, methyl or ethyl alcohol. *Iodo-oxy-cyanogen* is best prepared by mixing approxi-

ately equal weights of silver cyanate, iodine, and ether at a temperature not exceeding  $-20^\circ$ . From this solution the ether can be so far distilled at  $-30^\circ$  that the unused iodine almost completely separates on subsequent cooling. In consequence of the difficulty of removing the last traces of ether, the homogeneity of the product is not guaranteed. The substance polymerises under carefully-regulated conditions to a mixture of *di-iododioxycyanogen*,  $\text{NI}_2\cdot\text{CO}\cdot\text{N}\cdot\text{CO}$ , an unstable orange-yellow powder, and *tri-iodo-cyanuric acid* (the final product of the polymerisation of iodo-oxy-cyanogen); unchanged iodo-oxy-cyanogen is removed by treatment with ethyl chloride at  $-80^\circ$ , whereas the two polymerides are separated by ether, in which the former dissolves. Reactions of iodo-oxy-cyanogen in water are generally simpler than those of the dimeric chloro- and bromo-compounds on account of the less powerful oxidising action of the hypiodous acid. In dilute sulphuric acid the change follows the course  $5\text{I}\cdot\text{CNO} + 8\text{H}_2\text{O} = 2\text{I}_2 + \text{HIO}_3 + 5\text{CO}_2 + 5\text{NH}_3$ . In water, nitrogen iodide is produced in considerable amount. In alkaline solution reaction is expressed by the equation  $3\text{I}\cdot\text{CNO} + 6\text{KOH} = 2\text{KI} + \text{KIO}_3 + 3\text{KCNO} + 3\text{H}_2\text{O}$ . From acid potassium iodide, 1 mol. of iodo-oxy-cyanogen liberates 2 atoms of iodine. With alcohols it yields alkyl hypochlorites and alkyl carbamates with probable intermediate production of very unstable iodourethanes,  $\text{NHI}\cdot\text{CO}_2\text{Alk}$ . Treatment of iodo-oxy-cyanogen with ethyl ether in presence of silver cyanate involves the reactions  $\text{Et}\cdot\text{O}\cdot\text{Et} + \text{I}\cdot\text{NCO} = \text{HI} + \text{OCN}\cdot\text{C}_2\text{H}_5\cdot\text{OEt}$ ,  $\text{I}\cdot\text{NCO} + \text{HI} = \text{I}_2 + \text{HCNO}$ ,  $\text{AgCNO} + \text{I}_2 = \text{AgI} + \text{I}\cdot\text{CNO}$ . After addition of magnesium oxide and ignited sodium sulphate, the  $\alpha$ -ethoxyethylcarbimide can be isolated as a colourless, mobile liquid characterised by conversion into  $\alpha$ -ethoxyethylcarbamide,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{OEt}$ , m. p.  $116^\circ$ .

Di-iododioxycyanogen is characterised by its conversion by ethyl alcohol into ethyl hypiodite and ethyl allophanate with probable intermediate production of ethyl iodoallophanate. In aqueous solution it reacts according to the equation  $5(\text{OCN}\cdot\text{I})_2 + 11\text{H}_2\text{O} = 4\text{I}_2 + 2\text{HIO}_3 + 5\text{CO}(\text{NH}_2)_2 + 5\text{CO}_2$ .

Tri-iodocyanuric acid when cautiously treated with water or organic compounds which readily lose hydrogen affords cyanuric acid and the reagent merely determines the fate of the positive iodine. It is converted by chlorine into iodine trichloride and trichlorocyanuric acid. H. WREN.

Ketenimines and tautomerism of nitrites. G. MIGNONAC and C. HOFFMANN (Compt. rend., 1930, 191, 718—720).—Treatment of acetonitrile with magnesium ethyl bromide gives ethane and a crystalline magnesium derivative, probably  $\text{CH}_2\cdot\text{C}\cdot\text{N}\cdot\text{MgBr}$ , which, when decomposed with water at  $0^\circ$ , affords an appreciable amount of acetamide. It is assumed that water is added across the ethylenic linking. Benzoyl chloride reacts with the sodium derivative of benzyl cyanide, forming probably the *N*-benzoyl derivative, m. p.  $146.2^\circ$  (corr.), of benzoyl-phenylketenimine. When this is treated with  $\beta$ -phenylethylamine in toluene the *N*-benzoyl group is eliminated and a yellowish-green solution of the compound,  $\text{CPhBz}\cdot\text{C}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$ , m. p.  $99^\circ$ ,

results. When this solution is heated at 90°, the colour disappears owing to the production of benzoylphenylacetone nitrile and  $\beta$ -phenylethylamine; the same change occurs very readily when the coloured solution is treated with mineral acid. Treatment of the above *N*-benzoyl derivative with ammonia in an anhydrous medium furnishes the substance  $\text{CPhBz:C:N-NH}_2$ , decomp. about 72°.

H. BURTON.

**Bromine chloride; action of mixtures of chlorine and bromine on aliphatic diazo-compounds.** T. W. J. TAYLOR and L. A. FORSEY (J.C.S., 1930, 2272—2277).—Ethyl diazoacetate reacts readily with an equivalent quantity of an equimolecular mixture of chlorine and bromine in carbon tetrachloride at 0° to yield a mixture of ethyl dichloro-, dibromo-, and chlorobromo-acetate, converted by concentrated ammonia into the corresponding acetamides. Fractional crystallisation of the latter indicates that more than 50% of the mixture is chlorobromoacetamide, m. p. 129°, identical with a synthetical specimen, and shown by thermal analysis not to be an equimolecular compound of the dichloro- and dibromo-acetamides. Similarly, the action of bromine and chlorine in carbon tetrachloride on benzoylphenyldiazomethane affords a mixture of dichloro-, dibromo-, and chlorobromo-deoxybenzoin, m. p. 85°, the last-named being synthesised by the action of bromine in glacial acetic acid on chlorodeoxybenzoin at 100°. The halogeno-deoxybenzoins cannot be completely separated by fractional crystallisation, since they all form solid solutions with each other, but the composition of the product was determined by thermal analysis, the m.-p. curve of an equimolecular mixture of the dichloro- and dibromo-compounds with the chlorobromo-compound being plotted. On the assumption that the composition of the reaction products expresses the proportion of the molecules in the equilibrium  $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$ , 80% of the chlorine-bromine mixture exists as bromine chloride. The discrepancy of this result with that obtained by Barratt and Stein (A., 1929, 411) from spectrophotometric measurements is discussed.

J. W. BAKER.

**Effect of excess of magnesium on the volume of gas liberated in the preparation of magnesium alkyl halides.** H. GILMAN and R. E. FOTHERGILL (Iowa State Coll. J. Sci., 1930, 4, 351—353).—Measurement of the amount of gas evolved during the preparation of magnesium methyl iodide and magnesium ethyl bromide confirmed the observation that the use of an excess of finely-divided magnesium gives practically quantitative yields of some  $\text{RMgX}$  compounds.

CHEMICAL ABSTRACTS.

**Purification, properties, and methods of using zinc diethyl.** A. W. LAUBENGAYER and R. H. FLECKENSTEIN (Z. anorg. Chem., 1930, 191, 283—288).—Zinc diethyl, purified by fractional distillation of the crude material under reduced pressure at 0°, has vapour density 5.553 g. per litre,  $d_{20}^{18}$  1.1826, m. p. -39°. Its vapour pressure from -10° to 118° is expressed by the equation  $\log p = -2080/T + 8.209$ , where  $p$  is the vapour pressure in mm. and  $T$  the

absolute temperature. The most convenient methods for storing and handling the material are described.

H. F. GILLBE.

**Tin alkyl compounds. IV. Properties of the complex hydroxy-bromide**

$(\text{Me}_3\text{SnOH})_2, \text{Me}_3\text{SnBr}$ . C. A. KRAUS and R. H. BULLARD (J. Amer. Chem. Soc., 1930, 52, 4056—4065).—The complex hydroxybromide, m. p. 115° (slow decomp.), previously described (A., 1925, i, 1254) is most conveniently prepared from tin trimethyl hydroxide (2 mols.) and tin trimethyl bromide (1 mol.) in chloroform at the ordinary temperature. Mol. wt. determinations in naphthalene show that the salt is largely dissociated in this solvent. The complex is not appreciably affected by dissolution in liquid ammonia, but treatment of a chloroform solution with ammonia gas gives ammino-tin trimethyl bromide. When a solution of the complex in liquid ammonia is treated with sodium, some hydrogen is evolved; the amount is about one third of that producible if the salt contains 1 mol. of water. The complex decomposes above 115° into its constituents, which sublime and then recombine; a small amount of the hydroxide is, however, converted into tin dimethyl oxide, tin tetramethyl, and water. The conductivity of an alcoholic solution of the complex is the same as that of an alcoholic solution of its components, but much greater than that of either of the components alone. The conductivity of a solution of tin trimethyl bromide (1 mol.) in acetone is increased 30 times by the addition of 0.1 mol. of tin trimethyl hydroxide and 300 times by the addition of 2 mols. Treatment of an aqueous solution of the complex with silver oxide gives the corresponding hydroxide, which is a comparatively weak electrolyte; this hydroxide decomposes gradually into tin trimethyl hydroxide.

The conductivity of a solution of tin trimethyl hydroxide in acetone increases when methyl iodide is added, indicating the formation of an ionisable complex; the equivalent conductivity of the complex is of the same order as that of lithium or silver nitrate.

H. BURTON.

**Action of reduced nickel and hydrogen on aromatic hydrocarbons under high pressure and temperature.** T. OGAWA and T. YOKOTA (Bull. Chem. Soc. Japan, 1930, 5, 266—275).—The action of hydrogen in presence of reduced nickel on benzene, cyclohexane, naphthalene, tetra- and deca-hydro-naphthalenes has been investigated up to 500° with pressures up to about 100 atm. cycloHexane is stable under these conditions, but with the other substances various reduction products are obtained.

O. J. WALKER.

**Condensation of acetone with sulphuric acid.** D. TISTCHENKO (Bull. Soc. chim., 1930, [iv], 47, 1137—1147).—When acetone (900 c.c.) is condensed with cold sulphuric acid (900 c.c.) diluted with 500—600 c.c. of water for 24 hrs. and the reaction mixture distilled with steam, yields of 23.4—25.6% of mesitylene, b. p. 150—210°, are obtained, 82% of which is obtained pure, b. p. 58—60°/16 mm.,  $d_{20}^{20}$  0.856, by distillation over sodium to remove a little isodurene. Fractionation of the distillate and tar yields a portion b. p. 99—103°/13 mm., 218—220°/

760 mm., containing isophorone and an unsaturated hydrocarbon (I),  $C_{12}H_{16}$ ,  $d_4^{20}$  0.892, which is regarded as 3:5-dimethyl- $\Delta^2$ -isobutenylbenzene, since it contains a double linking and on oxidation with potassium permanganate yields mesitylenic and uvitic acids. A fraction (II) b. p. about 137–142°/60 mm. contains 1:1:3:6:8-pentamethyl-1:2-dihydronaphthalene. When heated in a current of hydrogen II yields a considerable amount of naphthalene, whilst with aluminium chloride at 260° a fraction, b. p. 190–205°,  $d_4^{25}$  0.874, yielding isodurene dibromide is obtained. The hydrocarbon contains one double linking and on oxidation with dilute nitric acid at 155–165° yields benzene-1:3:4:5-tetracarboxylic acid. With benzoyl hydrogen peroxide it yields an oxide,  $C_{15}H_{20}O$ , b. p. 167–173°/20 mm., and when heated with sulphur or selenium a hydrocarbon,  $C_{12}H_{16}$ , m. p. 84–85° (picrate, m. p. 151–152°), together with methyl mercaptan or the corresponding selenium compound. All the condensation products except mesitylene are resinified by concentrated sulphuric acid.

R. BRIGHTMAN.

**Polymethylbenzenes. IV. Preparation and physical properties of  $\psi$ -cumene [1:2:4-trimethylbenzene].** L. I. SMITH and A. P. LUND (J. Amer. Chem. Soc., 1930, 52, 4144–4150).—Magnesium *m*-4-xylyl iodide and methyl sulphate give 37% of the theoretical yield of 1:2:4-trimethylbenzene, b. p. 68°/22 mm., f. p.  $-45.0 \pm 0.05^\circ$  (corr.),  $n_D^{25}$  1.5032. The vapour-pressure curve for the hydrocarbon is given (cf. Woringer, A., 1900, ii, 709).

H. BURTON.

**New orientation rule and the anomaly of the nitroso-group.** D. L. HAMMICK and W. S. ILLINGWORTH (J.C.S., 1930, 2358–2364).—The directive action of single atoms or groups attached to the benzene nucleus may be expressed by the following rule, which is free from theoretical implications. If, in a benzene derivative  $PhXY$ ,  $Y$  is in a higher group of the periodic table than  $X$ , or if, being in the same group,  $Y$  is of lower atomic weight than  $X$ , the group  $XY$  is *m*-directing, whilst in all other cases, including that in which the group  $XY$  is a single atom, it is *op*-directing. The only apparent exception is the nitroso-group, but it is shown that the *op*-directive influence of this group is due to association. Thus the mol. wt. of nitrosobenzene determined by the ebullioscopic method in pure carbon disulphide is 116.4, indicating an average degree of association of 16%. On the other hand, cryoscopic determinations show that nitrosobenzene is unimolecular in acetic acid. Bromination in carbon disulphide at  $-5^\circ$  confirmed Ingold's result (A., 1925, i, 646), the *p*-bromo-derivative being formed, but in acetic acid at  $0^\circ$  no bromination occurs, prolonged action at the ordinary temperature giving only a substance, m. p. 123°, probably tribromoazoxybenzene. It is suggested that this indicates that unimolecular nitrosobenzene would be *m*-directive if the fragility of the molecule did not preclude the use of the more drastic conditions necessary to effect the much slower *m*-substitution. The possibility of interaction with the solvent to form either (a) the complex  $Ph\dot{N}H\cdot O\}CH_3\cdot CO_2$  or (b)  $Ph\cdot N\cdot O \rightarrow HOAc$ , is negated, (a) by the fact that the

electrical resistance of pure acetic acid is unaffected by addition of nitrosobenzene and (b) by an investigation of the solid-liquid equilibria in the system acetic acid-nitrosobenzene, the small variation with composition of the normal heats of dissolution  $Q$ , calculated from the formula  $\log_e S/S_1 = Q(T_1 - T)/2T^2$  (Sidgwick and Ewbank, J.C.S., 1921, 119, 979), indicating that the system is of the normal type where neither combination between the components nor dissociation of either of them occurs. In suggested confirmation of the *m*-directive influence of the nitroso-group in unimolecular nitrosobenzene it is shown that with conditions under which *o*- and *p*-bromonitrosobenzene react with silver nitrate in pure acetic acid in an atmosphere of nitrogen to give silver bromide, the *m*-bromo-derivative is unaffected. J. W. BAKER.

**Condensation of benzyl chloride in presence of chlorides of metals.** S. N. USHAKOV and A. V. KON (J. Appl. Chem., Russia, 1930, 3, 69–79; cf. G.P. 280595, 416904).—Benzyl chloride and chlorinated *p*-xylene (b. p. 199–202°) when condensed in presence of catalysts (iron, zinc, aluminium, and their chlorides) gave products, m. p. 70–100°, of composition corresponding approximately with the formula  $C_7H_6$ , which were stable to light and soluble in benzene and oils. Within certain limits the yield of resins is independent of the amount of catalyst used. The presence of catalysts is indispensable. CHEMICAL ABSTRACTS.

**Parallelism between mobility of hydrogen in the benzene nucleus and that of chlorine in the side-chain.** S. J. C. OLIVIER (Rec. trav. chim., 1930, 49, 996–1002; cf. A., 1923, i, 908; this vol., 1028).—The rule that the position of a substituent in the benzene nucleus influences the reactivity of the chlorine in the side-chain has been further exemplified by experiments on  $\omega$ -chloro-*m*-toluamide, m. p. 129.5–130°, and  $\omega$ -chloro-*p*-toluamide, m. p. 181–182°, and on *o*-, *m*-, and *p*-cyanobenzyl chloride. The observed rates of hydrolysis in acetone were respectively ( $k \times 10^3$ ) at 60°, 0.203, 0.146, 0.049, 0.062, 0.058, and at 50°, 0.077, 0.055, 0.0181, 0.0237, and 0.0214. A table showing the relative rates of hydrolysis of substances so far determined is given.

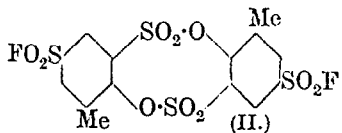
J. D. A. JOHNSON.

**Aromatic sulphonyl fluorides. II.** W. STEINKOPF and P. JAEGER (J. pr. Chem., 1930, [ii], 128, 63–88; cf. A., 1927, 963).—*m*-Iodobenzenesulphonyl fluoride is converted by heating with "copper powder" at 200–230° into diphenyl-3:3'-disulphonyl fluoride, m. p. 133–134°, converted by chlorosulphonic acid into the corresponding disulphonyl chloride. *o*-Toluidine-4-sulphonyl fluoride is converted by the Sandmeyer reaction into *o*-iodotoluene-4-sulphonyl fluoride, m. p. 35–36°, from which 2:2'-dimethyldiphenyl-5:5'-disulphonyl fluoride, m. p. 146–147° (bisdimethylamide, m. p. 244–247°), is obtained, whilst 2-iodoanisole-4-sulphonyl fluoride, m. p. 58–58.5° (from the 2-amino-compound), affords 2:2'-dimethoxydiphenyl-5:5'-disulphonyl fluoride, m. p. 205–206°. Reduction of nitromesitylenesulphonyl fluoride (loc. cit.) with tin and hydrochloric acid at 45–55° affords the corresponding amino-compound, m. p. 62°. Nitration of mesitylene-



sulphonyl fluoride with fuming nitric and sulphuric acids at 20–25° gives the *dinitro-derivative*, m. p. 157–158°, reduced to *diaminomesitylenesulphonyl fluoride*, m. p. 142–143°. Benzenesulphonyl fluoride reacts with magnesium methyl iodide to yield phenyl methyl sulphone together with (*phenylsulphonyl-phenylmethylsulphonic acid* (type I), m. p. 123–124° (potassium salt; methyl ester, m. p. 102–103°). With magnesium phenyl bromide the chief product is diphenyl sulphone, together with a little diphenyl. Toluene-2:4-disulphonyl fluoride and magnesium phenyl bromide afford *toluene-2:4-di-(phenylsulphone)*, m. p. 192–192.5°, and 2 (or 4)-(*phenylsulphonyl*)tolyl-4(or 2)-*diphenylsulphonic acid* (type I), decomp. 125–126°. The formation of these products is represented by the schemes:  $R \cdot SO_2X + 2R'MgI \rightarrow MgXI + RR'S'O(OMgI) \xrightarrow{H_2O}$  either (a)  $R \cdot SO_2 \cdot R' + Mg(OH)I + RH$  or (b)  $RR'S'O(OH) + Mg(OH)I$  and  $RR'S'O(OMgI) + R \cdot SO_2X \rightarrow R'X + RR'S'O(OMgI)(SO_2R) \xrightarrow{H_2O}$  either (a)  $R \cdot SO_2 \cdot SO_2R + Mg(OH)I + R'H$  or (b)  $RR'S'O \cdot SO_2R$  (I) +  $Mg(OH)I$ .  $O \nabla OH$

*m*-Aminobenzenesulphonyl fluoride is converted by diazotisation and treatment with arsenic trichloride into *m*-fluorosulphonylphenylarsinic acid, m. p. 160° (sulphonamide, not melting at 300°), converted by reduction with sulphurous acid in hydrochloric acid in the presence of iodine into *m*-fluorosulphonylphenyldichloroarsine, b. p. 183–184°/10 mm., m. p. 42° (corresponding *m*-chlorosulphonyl compound, b. p. 200–205°/10 mm., m. p. 61–62.5°). Similarly, from phenyldichloroarsine is obtained *m*-fluorosulphonylphenylphenylarsinic acid, m. p. 150–152°, reduced to *m*-fluorosulphonylphenylphenylchloroarsine, b. p. 168–179°/high vac. *o*-Cresolsulphonyl fluoride reacts with fluorosulphonic acid at 80–90° to give 4:4'-difluorosulphonyl-2:2'-dimethyl-*o*-phenylene sulphonyl-ide (II), decomp. above 240°, whilst *m*-cresolsulphonyl fluoride yields *m*-cresol-2:6(or 4:6)-disulphonyl fluoride,



m. p. 125–126.5° (ammonium salt, m. p. 163–165°; disulphonamide, m. p. 244–245.5°), nitrated with hot, concentrated nitric acid to the 2(or 4)-nitro-derivative, m. p. 99–100°. *p*-Cresol-3-sulphonyl fluoride reacts with fluorosulphonic acid at 80–90° to give 2:2'-difluorosulphonyl-4:4'-dimethyl-*o*-phenylene sulphonyl-ide (as II), decomp. 260–265°, converted by excess of ammonia into *p*-cresol-3:5-disulphonamide, m. p. 219.5–220.5°. Fluorosulphonic acid converts 1:3:5-xenol into its 2(or 4)-sulphonyl fluoride, m. p. 107–108° (sulphonamide, m. p. 161–162°), and 1:3:4-xenol into a sulphonyl fluoride, b. p. 71–73°/high vac., whilst an attempt to prepare the disulphonyl fluoride with 40% fluorosulphonic acid at 45° gave only 4:6:4':6'-tetramethyl-*o*-phenylene sulphonyl-ide (as II), decomp. 243–245°. *o*-Chlorophenol gives a 2(or 4)-sulphonyl fluoride, m. p. 83–84°. Benzenesulphonyl fluoride reacts with sodium benzoate at 240° to give benzoic anhydride (33%) and benzoyl fluoride (67%), which cannot be separated from the excess

of the sulphonyl fluoride and are isolated only as benzanilide.

J. W. BAKER.

**Sulphonic esters. Configuration of the nitrogen atom.** M. FRÈREJACQUE (Ann. Chim., 1930, [x], 14, 147–226).—Aromatic methyl sulphonates (A., 1926, 1251) are characterised by their additive compounds with hexamethylenetetramine; the additive compound of methyl benzenesulphonate has m. p. 149°. The following derivatives of the new camphorsulphonic acid (*loc. cit.*) are described: *methyl ester*, m. p. 76°,  $[\alpha]_D + 98.6^\circ$  in chloroform (additive compound with hexamethylenetetramine, m. p. 192–193°); *sodium* +  $3H_2O$ ,  $[\alpha]_D + 65.5^\circ$  in water; *ammonium*,  $[\alpha]_D + 77.5^\circ$  in water; *aniline* +  $COMe_3$ , +  $CHCl_3$ ,  $[\alpha]_{5461} + 65.5^\circ$  in chloroform, decomposing into camphor and sulphanilic acid when heated; *o-toluidine* +  $CHCl_3$ ,  $[\alpha]_{5461} + 63.9^\circ$  in chloroform; *p-toluidine* +  $CHCl_3$ ,  $[\alpha]_{5461} + 66.6^\circ$  in chloroform; *quinine*,  $[\alpha]_{5461} - 43.2^\circ$ ; and *phenylmethylethyl-n-butylammonium*, very hygroscopic (corresponding chloroplatinate), salts: *chloride*, m. p. 88°; *amide*, m. p. 143–144°,  $[\alpha]_{5461} + 94^\circ$  in water; *anilide*, m. p. 124°,  $[\alpha]_{5461} - 143^\circ$  in chloroform; *o-toluidide*, m. p. 117°,  $[\alpha]_{5461} - 110.6^\circ$  in chloroform; *p-toluidide*, m. p. 196–197°,  $[\alpha]_{5461} - 146.5^\circ$  in chloroform; *ethylanilide*, m. p. 89°,  $[\alpha]_{5461} - 8^\circ$  in chloroform. The rotatory powers of these substituted anilides in 0.1N-potassium hydroxide increase regularly with increasing quantity of alkali until 1 mol. of alkali is present, after which they remain constant; these changes are explained on the basis of enolisation. All attempts to isolate the two stereoisomeric forms required by Dupont's theory of the spatial configuration of tervalent nitrogen (A., 1927, 1128) were unsuccessful. When methyl sulphate and phenol (or anisole) are heated together at 95° without solvent in the absence of moisture, the following products can be isolated from the reaction mixture: potassium methyl sulphate, phenol- and anisole-sulphonic acids (isolated as potassium salts) and their methyl esters, and anisole, whilst methyl ether is evolved, and thus are obtained: *methyl p-hydroxy-*, m. p. 97° [*acetyl*, m. p. 71°, and *benzoyl*, m. p. 104°, derivatives; additive compound with hexamethylenetetramine, m. p. 225° (decomp.)]; *p-methoxy-*, m. p. 30°, b. p. 160°/3 mm. [additive compounds with hexamethylenetetramine, m. p. 195° (decomp.), with dimethylaniline, m. p. 158°, with antipyrine, m. p. 96°, and with pyramidone, m. p. 162°]; *4-hydroxy-3-methyl-*, m. p. 93°, b. p. 200°/1 mm. [*acetyl*, m. p. 56°, and *benzoyl*, m. p. 82°, derivatives; additive compound with hexamethylenetetramine, m. p. 134° (decomp.)], converted by bromine in methyl alcohol into *methyl 5-bromo-4-hydroxy-3-methylbenzenesulphonate*, m. p. 143°; *4-methoxy-3-methyl-*, m. p. 57° [additive compound with hexamethylenetetramine, m. p. 190° (decomp.)]; *5-hydroxy-2-methyl-* (? orientation, from *p*-cresol), m. p. 70° (*benzoyl* derivative, m. p. 68°; *methyl ether*, m. p. 70°); and *4-hydroxy-3-carbomethoxy-*, m. p. 65° [*acetyl* derivative, m. p. 68°; additive compound with hexamethylenetetramine, m. p. 230° (decomp.)]. *-benzenesulphonate*. Quinine reacts with methyl *p*-methoxybenzenesulphonate in cold, anhydrous benzene, carbon disulphide, or ether, to give the

$\alpha$ -form of the additive compound,  $[\alpha]_{5461} -51^\circ$  in chloroform, which is very soluble in chloroform and is unstable, passing readily into the stable  $\beta$ -form,  $[\alpha]_{5461} -60^\circ$  in chloroform, in the presence of chloroform or alcohol, and hence only the  $\beta$ -form is obtained when addition is effected in these solvents. This isomerism is not considered to be due to stereochemical relationships of the nitrogen atom, but it is suggested that the  $\alpha$ -form is a molecular compound, whilst the  $\beta$ -form is the true quaternary salt. No such isomerism is observed in the case of the corresponding compounds with *N*-methylquinine and *N*-methylbrucine, and the *d*-camphor- $\alpha$ -sulphonates of these alkaloids,  $+H_2O$ ,  $[\alpha]_{5461} -46.3^\circ$  in chloroform, and anhydrous,  $[\alpha]_{5461} +52^\circ$  in water, respectively, could not be separated into isomerides by fractional crystallisation. By slight modification of the conditions employed by Speyer and Becker (A., 1922, i, 674) for the action of hydrogen peroxide on quinine, a compound,  $C_{20}H_{24}O_4N_2$ ,  $+CHCl_3$ , m. p.  $152^\circ$ ,  $[\alpha]_D -60^\circ$  in chloroform, is obtained, which appears to be a *quinine peroxide*, since it has peroxidic properties and is converted by crystallisation from acetone into quinine oxide, m. p.  $195^\circ$ ,  $[\alpha]_D -19.5^\circ$  in chloroform (*loc. cit.*,  $[\alpha]_D -30^\circ$ ), and is readily transformed into the nitrate and chloroplatinate of the oxide. These results are discussed in relation to Dupont's theory (*loc. cit.*) of the configuration of the nitrogen atom.

J. W. BAKER.

**Polymerisation of *as*-diphenylethylene. Preparation of 1:1:3-triphenyl-3-methylhydrindene.** C. S. SCHORFFLE and J. D. RYAN (J. Amer. Chem. Soc., 1930, 52, 4021–4030; cf. Bergmann and Weiss, this vol., 901).—Polymerisation of *as*-diphenylethylene with stannic chloride in benzene solution at the ordinary temperature gives 77% of the theoretical amount of  $\alpha\gamma\gamma$ -tetraphenyl- $\Delta^a$ -butene, the formation of which can be explained by the production of unstable 1:1:3:3-tetraphenylcyclobutane. When the polymerisation is carried out in benzene containing hydrogen chloride, 90% of 1:1:3-triphenyl-3-methylhydrindene results. The butene is converted into the hydrindene only by treatment with stannic chloride and benzene containing hydrogen chloride; in the absence of hydrogen chloride partial depolymerisation occurs. 1:1:3-Triphenyl-3-methylhydrindene is prepared in almost quantitative yield when *as*-diphenylethyl chloride is treated with stannic chloride in benzene at the ordinary temperature for 1 week. Reaction is presumed to occur through the formation of the

radicals  $\dot{C}Ph_2\cdot CH_2$  and  $\dot{C}MePh\cdot C_6H_4\ldots$  (o), which subsequently combine. The saturated dimeride of  $\alpha$ -methylstyrene (Staudinger and Breusch, A., 1929, 434) is prepared similarly from phenyldimethylcarbinyl chloride. Oxidation of 1:1:3-triphenyl-3-methylhydrindene with chromic and acetic acids gives a mixture of benzoic acid, benzophenone, 2-benzoylbenzophenone, and the following unidentified compounds:  $C_{16}H_{12}O_2$ , m. p.  $120^\circ$ ;  $C_{20}H_{14}O_2$ , m. p.  $146^\circ$ ;  $C_{23}H_{20}O_2$ , m. p.  $190^\circ$  (acidic);  $C_{21}H_{14}O_3$ , m. p.  $225^\circ$ ;  $C_{24}H_{22}O_4$ , m. p.  $245^\circ$ , which may be  $\alpha\gamma\gamma$ -triphenyl- $\alpha$ -methylglutaric acid;  $C_{22}H_{15}O_3$ , m. p.  $279^\circ$ , and  $C_{16}H_{12}O_2$ , m. p.  $285^\circ$ , which has the properties

of anhydro- $\beta$ -benzoyl- $\alpha$ -phenylpropionic acid (Hann and Lapworth, J.C.S., 1904, 85, 1362). Absorption curves for the above butene and hydrindene are given.

H. BURTON.

**Alkali organic experiments.** E. BERGMANN (Ber., 1930, 63, [B], 2593–2597).—The transformation of  $\alpha\alpha\zeta\zeta$ -tetraphenyl- $\Delta^a$ -hexadiene into a potassium derivative which yields  $\alpha\alpha$ -diphenyl- $\Delta^a$ -propene and  $\beta\beta$ -diphenylacrylic acid (Wittig and Leo, this vol., 762) is explained by the hypothesis that addition of the metal occurs initially at the  $\alpha\zeta$  carbon atoms and the free valencies of the  $\beta\zeta$  carbon atoms saturate themselves in pairs by the formation of the cyclobutane derivative,

$CHR\langle\begin{smallmatrix} CHR \\ CH_2 \end{smallmatrix}\rangle CH_2$  ( $R=CPh_2K$ ). By reason of ring tension the latter compound is unstable and yields 2 mols. of potassium diphenylvinyl. The following experimental evidence is cited.

*Methyl suberate*, b. p.  $138$ – $140^\circ/21$  mm., prepared quantitatively by the action of diazomethane on the acid, is converted by magnesium phenyl bromide into  $\alpha\alpha\theta\theta$ -tetraphenyl-octane- $\alpha\theta$ -diol, m. p.  $110^\circ$ , and thence by boiling glacial acetic acid containing a little sulphuric acid into  $\alpha\alpha\theta\theta$ -tetraphenyl- $\Delta^a$ -octadiene, m. p.  $92$ – $93^\circ$ . The hydrocarbon gives a lithium derivative converted into a hydrocarbon,  $C_{32}H_{32}$ , m. p.  $212$ – $213^\circ$ , regarded as 1:2-dibenzhydrylcyclohexane, since it is readily dehydrogenated by treatment with sulphur; the freedom from strain of the cyclohexane system renders a secondary reaction unnecessary. The instability of the cyclobutane system leads to an analogous secondary decomposition during the withdrawal of metal from compounds of the type disodium tetraphenylbutyl,  $(\cdot CH_2\cdot CNaPh_2)_2 \rightarrow CH_2\langle\begin{smallmatrix} CPh_2 \\ CH_2 \end{smallmatrix}\rangle CPh_2 \rightarrow 2CPh_2\cdot CH_2$ .

The presence of the butane skeleton in this compound, previously obtained only by the addition of sodium to *as*-diphenylethylene, is established by the observation that it is obtained by the action of sodium on  $\alpha\delta$ -dimethoxy- $\alpha\alpha\delta\delta$ -tetraphenylbutane, m. p.  $230^\circ$  after softening at  $227^\circ$ , prepared by the action of sulphuric acid on tetraphenylbutanediol in a mixture of methyl alcohol and dioxan. Treatment of the butanediol with potassium and methyl iodide in boiling xylene yields the corresponding *monomethyl ether*, m. p.  $175$ – $176^\circ$ .  $\alpha\alpha\delta\delta$ -Tetraphenyl- $\Delta^b$ -butinene- $\alpha\delta$ -diol is transformed by sulphuric acid in methyl alcohol at the ordinary temperature into the dimethyl ether, m. p.  $115$ – $116^\circ$ , which is hydrogenated in boiling propyl alcohol in presence of palladised barium sulphate to  $\alpha$ -methoxy- $\alpha\alpha\delta\delta$ -tetraphenyl-*n*-butane, m. p.  $140$ – $141^\circ$ . Treatment of the dimethyl ether, m. p.  $115$ – $116^\circ$  (see above), with sodium followed by hydrolysis gives two hydrocarbons, m. p.  $97^\circ$  and  $167^\circ$ , respectively, whilst the sodium derivative with phenylthiocarbimide affords the *dithioanilide* of  $\alpha\alpha\delta\delta$ -tetraphenyl- $\Delta^b$ -butinene- $\alpha\delta$ -dicarboxylic acid, m. p.  $204^\circ$ .

Since sodium diphenylmethyl yields tetraphenylethane when treated with mercury and the reaction is not therefore confined to dialkali compounds, the hypothesis of Ziegler and Colonius (this vol., 590)

that a cyclic mercury compound is intermediately produced is deprived of its foundation.

H. WREN.

**Magnesium benzhydryl chloride and the apparent prior formation of free benzhydryl radicals.** H. GILMAN and E. A. ZOELLNER (J. Amer. Chem. Soc., 1930, 52, 3984—3988).—Magnesium benzhydryl chloride is obtained in 70% yield by the procedure previously described (A., 1929, 800), using the chloride (2.53 g.), magnesium powder (9.12 g.), and ether (74 c.c.). It is considered that free radical formation is the first stage in the production of a Grignard reagent. When benzhydryl chloride is added to an ethereal solution of magnesium benzhydryl chloride in absence or presence of magnesium, a transient, red coloration is produced. This is ascribed to the production of free benzhydryl radicals.

H. BURTON.

**Double linking. I. Action of halogens on fulvenes.** E. BERGMANN and A. FREIHERR VON CHRISTIANI (Ber., 1930, 63, [B], 2559—2571).—In accordance with the previous observations\* that an ethylenic carbon atom adds alkali metal with greatest readiness when it is most saturated according to its behaviour towards bromine, it is shown that the characteristic fulvene carbon atom is almost unable to add halogen.

Diphenylbenzofulvene reacts smoothly with 2 atoms of bromine in chloroform yielding hydrogen bromide and 2(3)-bromo-1-benzhydrylideneindene, m. p. 151°, oxidised by chromic acid to a substance,  $C_{22}H_{14}O_2$ , m. p. 236°. With 4 atoms of bromine, a dibromo-compound could not be isolated, but with 6 atoms 2:3:6-tribromo-1-benzhydrylideneindene, m. p. 168°, is obtained. The compound is oxidised to benzophenone and 2:3:6-tribromoindone, m. p. 145° [oxime, m. p. 231° (decomp.); 6-bromo-2:3-diphenylhydrazinoindone-phenylhydrazone, decomp. 250°]. For purposes of comparison,  $\alpha\beta$ -dibromo- $\beta$ -phenylpropionic acid is converted by distillation with phosphoric oxide in a vacuum into 2:3-dibromoindone, m. p. 123°, which is transformed successively into 2:3-dibromoindoneoxime, m. p. 222° (decomp.), and 2:3:6-tribromoindoneoxime, m. p. 231° (decomp.). By treatment of diphenylbenzofulvene with the requisite amount of chlorine in carbon tetrachloride the following compounds are obtained: 2(?)3-chloro-1-benzhydrylideneindene, m. p. 142—144°; 2:3-dichloro-1-benzhydrylideneindene, m. p. 130—131°, oxidised to 2:3-dichloroindone, m. p. 86°, obtained also from  $\alpha\beta$ -dichloro- $\beta$ -phenylpropionic acid and phosphoric oxide; 2:2:3:3-tetrachloro-1-benzhydrylidenehydrindene, m. p. 170° (decomp.).

3-Phenyl-1-benzhydrylideneindene is converted by an excess of chlorine into 2-chloro-3-phenyl-1-benzhydrylideneindene, m. p. 158—159°, prepared also from acetyl chloride and  $\alpha\delta\delta$ -tetraphenylbutinene- $\alpha\delta$ -diol and converted by bromine in chloroform into 2:6-dibromo-3-phenyl-1-benzhydrylideneindene, m. p. 145—146°, oxidised to 2:6-dibromo-3-phenylindone, m. p. 163°.

Diphenylfulvene with 4 at. of bromine affords 2:3:4:5-tetrabromo-1-benzhydrylidene- $\Delta^{2:4}$ -cyclopentadiene, m. p. 190—191°.

Benzhydrylidene fluorene and 4 atoms of bromine

yield 2:7-dibromo-9-benzhydrylidene fluorene, m. p. 220—222°, oxidised to 2:7-dibromofluorene, m. p. 200°.  $\gamma$ -Diphenylmethylene- $\alpha\epsilon$ -distyryl- $\Delta^{8:9}$ -penta-diene absorbs 7.7 atoms of bromine. Benzylidenexanthene with an excess of bromine gives the unstable tetrabromide,  $O\langle C_6H_4 \rangle CBr(Br_2)CHPhBr$ , m. p. 140° (decomp.), which loses bromine and hydrogen bromide in boiling chloroform, giving  $\omega$ -bromobenzylidenexanthene,  $O\langle C_6H_4 \rangle CPhBr$ , m. p. 110° (decomp.).

H. WREN.

**Dibromonaphthalenes obtained by the action of bromine on naphthalene.** J. S. SALKIND and S. B. FAERMAN (J. Russ. Phys. Chem. Soc., 1930, 62, 1021—1032).—The products of bromination of naphthalene are 1:2-, 1:4-, and 1:5-dibromonaphthalene.

R. TRUSZKOWSKI.

**Preparation of 4-nitronaphthalene-1-sulphonyl chloride.** W. BRUNETTI (J. pr. Chem., 1930, [ii], 128, 44—46).—Addition of a solution of 4-nitronaphthalenediazonium chloride (from 4-nitro- $\alpha$ -naphthylamine) to a stirred, saturated solution of sulphurous acid in the presence of finely-divided copper, affords 4-nitronaphthalene-1-sulphinic acid, m. p. 131°, converted by chlorine in alkaline solution into the corresponding sulphonyl chloride, m. p. 99° (Cleve, A., 1890, 634).

J. W. BAKER.

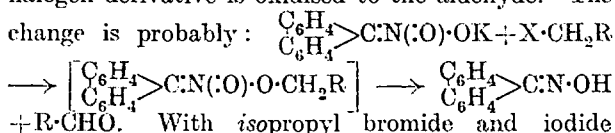
**"Superfluous" isomerides. III. Condensation of fluorene with piperonal and  $p$ -dimethylaminobenzaldehyde.** E. BERGMANN (Ber., 1930, 63, [B], 2598—2599; cf. this vol., 902, 912).—Condensation of fluorene with methylenedioxy-cinnamaldehyde in presence of sodium ethoxide yields 3:4-methylenedioxy-cinnamylidenefluorene, m. p. 196—197°;  $p$ -dimethylaminocinnamylidenefluorene, m. p. 169—170°, is similarly prepared. The compounds are identical with the substances described by de Fazi (A., 1921, i, 568) as by-products of the condensation of fluorene with piperonal and  $p$ -dimethylaminobenzaldehyde, respectively.

H. WREN.

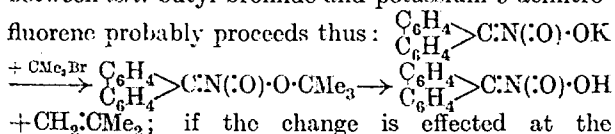
**Action of iodine on halogeno-derivatives of acinitro-alkali compounds.** C. D. NENTZESCU and D. A. ISACESCU (Ber., 1930, 63, [B], 2484—2496; cf. A., 1929, 1433).—Potassium 9-acinitrofluorene is converted by iodine in aqueous alcohol at 0° into 9-iodo-9-nitrofluorene, m. p. 86°. Phenyliodonitromethane,  $p$ -tolylidionitromethane, converted by boiling sodium hydroxide into 4:4'-dimethylstilbene, m. p. 179—180° (also obtained from the sodium derivative of  $p$ -tolylidionitromethane and iodine in presence of excess of sodium hydroxide),  $p$ -chlorophenylidionitromethane, m. p. 30°, decomp. 175° (whence 4:4'-dichlorostilbene, m. p. 174°, and  $p$ -chlorobenzoic acid),  $p$ -bromophenylidionitromethane, m. p. 35°, decomp. 165° after darkening at 135° (whence 4:4'-dibromostilbene, m. p. 208°, and  $p$ -bromobenzoic acid),  $p$ -nitrophenylidionitromethane, m. p. 90°, decomp. 150°,  $\alpha$ -naphthylidionitromethane, m. p. 74°, decomp. 110—135° (whence  $\alpha\beta$ -di-1-naphthylethylene, m. p. 160°),  $\beta$ -naphthylidionitromethane, m. p. 60°, decomp. 105°, diphenylidionitromethane, m. p. 62°.

decomp. 64°, and *iodonitromethane* are described. 9-Iodo-9-nitrofluorene with potassium 9-*acinitrofluorene* and phenyliodonitromethane with sodium *aciphenylnitromethane* afford the corresponding  $\alpha\beta$ -dinitroethanes, but the reaction cannot be extended to the other iodonitro-compounds. Thermal decomposition of the iodonitro-compounds occurs with separation of iodine at a rate which depends on the b. p. of the solvent. Thus iodonitrofluorene affords almost quantitatively  $\alpha\beta$ -dinitro- $\alpha\beta$ -didiphenylene-ethane, the free radical being apparently formed intermediately.

Potassium 9-*acinitrofluorene* reacts with methyl iodide, benzyl chloride, ethyl bromide, or ethyl chloroacetate in boiling alcohol, giving potassium halide and fluorenoneoxime in more than 80% yield; the halogen derivative is oxidised to the aldehyde. The change is probably:



With *isopropyl* bromide and iodide fluorenoneoxime and acetone result with addition of a little  $\alpha\beta$ -dinitro- $\alpha\beta$ -dibiphenylene-ethane in the case of the iodide; ethyl bromomalonate behaves similarly, whereas bromocyclohexane is indifferent. *tert*-Butyl bromide and potassium 9-*acinitrofluorene* react readily with production of *isobutylene*,  $\alpha\beta$ -dinitro- $\alpha\beta$ -didiphenylene-ethane, and fluorenoneoxime. The non-appearance of the expected 9-nitrofluorene has led to a re-examination of its supposed formation by isomerisation of 9-*acinitrofluorene* in boiling alcohol (cf. Wislicenus and Waldmüller, A., 1908, i, 973). The products of the change are fluorenoneoxime and  $\alpha\beta$ -dinitro- $\alpha\beta$ -didiphenylene-ethane, with which the supposed 9-nitrofluorene is identical. Attempts to effect the isomerisation under milder conditions or to prepare 9-nitrofluorene by the action of hydriodic acid on 9-iodo-9-nitrofluorene were unsuccessful. The reaction between *tert*-butyl bromide and potassium 9-*acinitrofluorene* probably proceeds thus:



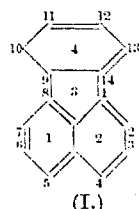
if the change is effected at the ordinary temperature, 9-*acinitrofluorene* can be isolated in good yield. Dimethylbenzylmethyl bromide and triphenylmethyl chloride give  $\alpha\beta$ -dinitro- $\alpha\beta$ -didiphenylene-ethane and fluorenoneoxime, whereas picryl chloride and  $\alpha$ -bromobutyric ester do not react. Methyl iodide reacts less smoothly with sodium phenylacinitromethane and sodium *p*-bromophenylacinitromethane, giving, as sole isolable products, stilbene or 4:4'-dibromostilbene. *tert*-Butyl bromide and sodium phenylacinitromethane yield phenylnitromethane.

The production of stilbenes, occurring smoothly by the action of iodine on primary *acinitro-alkali* compounds in presence of a large excess of alkali hydroxide, does not depend on the intermediate production of iodonitro-compounds. H. WREN.

**Fluoranthene and its derivatives.** J. VON BRAUN and G. MANZ (Ber., 1930, 63, [B], 2608—2612;

cf. A., 1929, 307).—Hydrogenation of fluoranthene (1) occurs successively in rings 2, 4, and 1. Fluoranthene is converted by hydriodic acid at temperatures above 200° into an inseparable mixture of hydrogenated compounds. At 180°, 1:2:3:4-tetrahydrofluoranthene, b. p. 203—205°/12 mm., m. p. 76° (*loc. cit.*), is produced, preferably prepared by the action of sodium amalgam and alcohol on fluoranthene. It does not combine with picric acid. A dihydro-compound could not be isolated. Fluoranthene is not attacked by sodium and moist ether or by hydrogen in presence of platinum or palladium. Hydrogenation in presence of nickel in decahydronaphthalene under pressure at 230° proceeds very rapidly until 12 atoms of hydrogen have been absorbed; sulphonation of the product followed by decomposition of the sulphonic acids with hydrochloric acid at 150° affords 1:2:3:4:9:10:11:12:13:14-decahydrofluoranthene, b. p. 181—183°/12 mm.,  $d_4^{25}$  1.043, the constitution of which follows from its oxidation to benzene-1:2:3-tricarboxylic acid. When distilled with lead oxide it yields fluoranthene; partial dehydrogenation could not be effected. Hydrogenation of fluoranthene at 230° until the rate of absorption of gas slackens followed by distillation and further hydrogenation of the distillate leads to *perhydrofluoranthene*,  $\text{C}_{16}\text{H}_{28}$ , b. p. 168—170°/12 mm.,  $d_4^{25}$  0.9811, which is extensively decomposed by heated lead oxide.

(I.)



H. WREN.  
**Dissociable organic oxides. Dibromorubrene.** C. DUFRASSE and N. DRISCH (Compt. rend., 1930, 191, 619—620).—A *dibromorubrene*, m. p. 310° or (+ $\text{C}_6\text{H}_5$ ) m. p. 195°, obtained from diphenyl-*p*-bromophenylacetylenylcarbinol,  $\text{OH} \cdot \text{CPh}_2 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{Br}$  (cf. Robin, A., 1929, 1175), resembles the parent hydrocarbon in colour (both of solid and solutions), in its fluorescence phenomena (cf. Moureu and others, A., 1926, 945, and elsewhere), and in its absorption spectrum, which shows maxima at 5300, 4950, and 4650 Å. (cf. A., 1928, 53; Willemart, A., 1929, 690); moreover, it is similarly oxidised on irradiation in presence of air to a colourless dissociable peroxide (cf. A., 1928, 53, 594, 628; 1929, 1166; this vol., 335). R. CHILD.

**Catalytic action at high temperatures under high pressures. II. Catalytic hydrogenation of aromatic nitro-compounds.** S. KOMATSU and R. AMATATSU (Mem. Coll. Sci. Kyōtō, 1930, A, 13, 329—336).—Reduction of nitrobenzene with hydrogen in presence of reduced nickel at 100°/50 atm. (the pressures recorded are those determined at 15° prior to heating) gives aniline, but at 200°/100 atm. a mixture of cyclohexylamine (78%), dicyclohexylamine (7%), and aniline (5%) results; a similar mixture is also produced from aniline at 180°/100 atm. *p*-Nitrophenol is reduced similarly at 100°/50 or 100 atm. to *p*-aminophenol, whilst at 160°/30 or 100 atm. the main product is 4-aminocyclohexanol; small amounts of *p*-aminophenol, cyclo-hexane, -hexanol, and ammonia are also formed.  $\alpha$ -Naphthylamine and *ac*-tetrahydro- $\alpha$ -naphthylamine are obtained

by reduction of 1-nitronaphthalene at 50°/30 or 100 atm. and 150°/30 or 100 atm., respectively.

H. BURTON.

**Organic compounds of molybdenum.** S. L. MALOWAN (Arch. Pharm., 1930, **268**, 537—539).—Molybdenum pentachloride and aniline in boiling absolute alcohol give a dark blue solution containing a greyish-black substance (8.9% Mo), m. p. 170°. This gives a blue coloration with chromic acid in sulphuric acid. Its solution in boiling water gradually deposits part of its molybdenum as molybdic acid. After precipitation of the rest with hydrogen sulphide, a substance, m. p. 192°, from which aniline is not liberated by alkali, is obtained. *o*-Toluidine and molybdenum pentachloride give, similarly, a bluish-black compound (7.8% N), which after dissolution in water gives colourless crystals of the same nitrogen content, in which no toluidine can be detected. Removal of molybdenum from the latter by means of hydrogen sulphide affords an acidic substance, m. p. 118°.

H. E. F. NOTTON.

**$\alpha\gamma$ -Migration of the [aryl]amino-group in the arylamino-derivatives of diarylarylethynylcarbinols. Constitution of the compounds obtained.** J. ROBIN (Compt. rend., 1930, **191**, 790—792).—The initial product of the reaction between aniline and  $\alpha$ -chloro- $\alpha\gamma$ -triphenylallylene is the colourless  $\alpha$ -anilino- $\alpha\gamma$ -triphenylallylene, m. p. 87—88°. This is isomerised readily when heated with a trace of aniline hydrochloride to the yellow  $\gamma$ -phenylimino- $\alpha\gamma$ -triphenyl- $\Delta^a$ -propylene (A., 1929, 1056), and converted by treatment with methyl alcohol in presence of dilute sulphuric acid into  $\alpha$ -methoxy- $\alpha\gamma$ -triphenylallylene and thence into phenyl  $\beta$ -phenylstyryl ketone (cf. *loc. cit.*). The following allylenes are prepared similarly and converted into the propylenes:  $\alpha$ -*o*-toluidino-, m. p. 139—140°,  $\alpha$ -*m*-toluidino-, m. p. 117—118°,  $\alpha$ -*p*-toluidino-, m. p. 115—116°,  $\alpha$ -*o*-anisidino-, m. p. 140—141°, and  $\alpha$ -*p*-anisidino- $\alpha\gamma$ -triphenylallylenes;  $\alpha$ -anilino- $\alpha\alpha$ -diphenyl- $\gamma$ -*p*-tolylallylene, m. p. 118—119°;  $\alpha$ -anilino- $\alpha\alpha$ -diphenyl- $\gamma$ - $\beta$ -naphthylallylene, m. p. 146—147°;  $\alpha$ -anilino- $\alpha\alpha$ -diphenyl- $\gamma$ -*p*-bromophenylallylene, m. p. 151—152°;  $\gamma$ -*o*-tolylimino-, m. p. 192—193°,  $\gamma$ -*m*-tolylimino-, m. p. 139—140°,  $\gamma$ -*p*-tolylimino-, m. p. 174—175°,  $\gamma$ -*o*-methoxyphenylimino-, and  $\gamma$ -*p*-methoxyphenylimino- $\alpha\gamma$ -triphenyl- $\Delta^a$ -propylenes, m. p. 148—149°;  $\gamma$ -phenylimino- $\alpha\alpha$ -diphenyl- $\gamma$ -*p*-tolyl- $\Delta^a$ -propylene, m. p. 162—163°;  $\gamma$ -phenylimino- $\alpha\alpha$ -diphenyl- $\gamma$ - $\beta$ -naphthyl- $\Delta^a$ -propylene, m. p. 149—150°;  $\gamma$ -phenylimino- $\alpha\alpha$ -diphenyl- $\gamma$ -*p*-bromophenyl- $\Delta^a$ -propylene, m. p. 138—139°.

H. BURTON.

**Reaction between keto-anils and Grignard reagents and the tautomerism of aliphatic keto-anils.** W. F. SHORT and J. S. WATT (J.C.S., 1930, 2293—2297).—Acetoneanil, m. p. 23.5°,  $d_4^{20}$  (supercooled) 1.0087,  $n_D^{20}$  1.5886, reacts with magnesium methyl iodide in amyl ether forming methane (1 mol.) and a complex, which is decomposed to the original anil. Successive treatment of the complex from acetoneanil and magnesium ethyl bromide with methyl sulphate and ammonia and ammonium chloride solution affords methylisopropenylaniline

(cf. Knoevenagel, A., 1921, i, 785). These observations and the molecular refraction indicate that acetoneanil exists mainly in the enamic form  $\text{CH}_2\text{:CMe:NHPh}$ . The so-called alkiodides of acetoneanil described by Knoevenagel (*loc. cit.*) decompose cold, dilute sodium carbonate solution and appear to be identical with alkylisopropenylaniline hydriodides. Thus, acetoneanil and benzyl chloride in benzene give the hydrochloride, m. p. 195° (decomp.), of benzylisopropenylaniline, m. p. 22—23°, whilst acetone-*p*-tolil and methyl iodide afford the hydriodide, m. p. 145—146° (decomp.) after sintering at 142—143° [Knoevenagel (*loc. cit.*) gives m. p. 80—82°], of methylisopropenyl-*p*-toluidine, also formed from the base and hydrogen iodide in benzene. The ready hydrolysis of acetoneanil and the observation that acetone does not condense with methylaniline suggest that the anil is an instance of the tautomeric system  $>\text{CH}\text{:}\dot{\text{C}}\text{:}\dot{\text{N}}\text{:}\rightleftharpoons>\text{C}\text{:}\dot{\text{C}}\text{:}\dot{\text{N}}\text{H}$  (cf. von Auwers and Susemihl, this vol., 897).

Condensation of acetophenoneanil and magnesium phenyl bromide under the conditions described by Plancher and Ravenna (A., 1907, i, 152) does not give the substance  $\text{C}_{20}\text{H}_{19}\text{N}$  (*loc. cit.*), but affords dynnoneanil (Reddell, A., 1913, i, 1202). This anil is also obtained from magnesium ethyl bromide and acetophenoneanil, indicating that the Grignard reagent acts as a condensing agent, viz.,  $2\text{CMePh:NPh} + \text{R.MgX} \rightarrow \text{CMePh:CH:CPh:NPh} + \text{NHPh.MgX} + \text{RH}$ . Benzophenoneanil is recovered unchanged from its complex with magnesium methyl iodide.

H. BURTON.

**Polynitroarylnitroamines. I. 2:4:6-Trinitrophenylnitroamine.** W. W. JONES and F. G. WILLSON (J.C.S., 1930, 2277—2279).—Treatment of a solution of sulphanilic acid in sulphuric acid ( $d$  1.84) with nitric acid ( $d$  1.5; free from nitrous acid) below 20° affords 75% of the theoretical amount of 2:4:6-trinitrophenylnitroamine, which deflagrates between 80° and 110°; the nitroamine is obtained similarly from picramide or 2:6-dinitrosulphanilic acid. Methylation of the nitroamine with methyl sulphate and 1.5% sodium hydroxide solution furnishes 2:4:6-trinitrophenylmethylnitroamine. Equimolecular quantities of the nitroamine and 2:4-dinitroaniline react in sulphuric acid solution at the ordinary temperature, forming an almost quantitative yield of picramide. The picramide nitrate of Macciotta (this vol., 1032) is identical with 2:4:6-trinitrophenylnitroamine.

H. BURTON.

**Condensations of [aromatic] halogeno-nitrocompounds. I.** G. GALLAS and A. ALONSO (Anal. Fis. Quim., 1930, **28**, 645—690).—Previous work on the condensations of 1-chloro-2:4-dinitrobenzene and analogous compounds with bases is reviewed. Some of this work has been repeated and certain new reactions have been investigated.

Condensation of 1-chloro-2:4-dinitrobenzene by heating with *o*-toluidine in alcohol in presence of sodium acetate yields 2:4-dinitro-2'-methylidiphenylamine, m. p. 117°, or, if heating is prolonged, an isomeride, m. p. 128—129° (lit., 101° and 129°). Similarly are obtained the 3'-methyl derivative, m. p. 161°, in quantitative yield, and the 4'-methyl deriv-

ative, which exists only in one form, m. p. 137°. 2:4-Dinitrophenyl- $\beta$ -naphthylamine has m. p. 171° (lit. 169.5° and 179°). 2:4-Dinitro-2'-methoxydiphenylamine separates from solution first in a red form, m. p. 165° (lit. 151°), which is followed by a yellow form which changes to red at 125–145° and melts at 153–159°. It yields a *benzoyl* derivative, m. p. 115°. Attempts to isolate the monoamino-compound were unsuccessful. The impure *diamino*-compound, m. p. about 116° (*hydrochloride*, m. p. above 210°), is obtained by reduction with aluminium amalgam, and yields a (?) *nitroso*-derivative, m. p. above 200°. 2:4-Dinitro-4'-methoxydiphenylamine, m. p. 141° (*benzoyl* derivative, m. p. above 200°; *acetyl* derivative, m. p. 148°), yields, when reduced with aqueous sodium sulphide, 4-amino-4'-methoxydiphenylamine, m. p. 102° (loss of one nitro-group) (I), and with methyl-alcoholic sodium sulphide, 2-nitro-4-amino-4'-methoxydiphenylamine, m. p. 135° (II). The latter is reduced to I by iron and acetic acid with the formation of (?) 2-amino-4'-methoxydiphenylamine as a by-product. Addition of the dinitro-compound to stannous chloride in hydrochloric acid yields 2:4-diamino-4'-methoxydiphenylamine (III), m. p. 118° (*hydrochloride*, m. p. above 200°), also obtained by reduction with aluminium amalgam, whilst addition of stannous chloride to the dinitro-compound in alcoholic hydrochloric acid yields II, accompanied by I. III yields red azo-dyes when diazotised and coupled and is oxidised to the corresponding phenazine derivative.

Condensation of 1-chloro-2:4-dinitrobenzene with diphenylamine gives an oily mixture of products. The mono- and di-2:4-dinitrophenyl derivatives of benzidine have been prepared; the latter, when it is decomposed by acetic anhydride and the product hydrolysed, yields 2:4-dinitrophenol, m. p. 113°, from which the impure, readily oxidised *nitroamine*, m. p. 201°, and the *diamine*, m. p. 196–197°, are prepared by reduction with sodium sulphide and aluminium amalgam, respectively. Condensation of 1-chloro-2:4-dinitrobenzene with the isomeric aminophenols takes place most readily with the *p*-compound; heating in a sealed tube is necessary in the case of the *o*-compound. Condensation of 1-chloro-2:4-dinitrobenzene with sulphanilic acid is best carried out by heating in a sealed tube. The *product*, m. p. 152–153°, is reduced by aluminium amalgam to the *diamino*-compound, m. p. above 225°. Condensation with sodium naphthionate yields a red *product*, m. p. 86–97°. 1-Chloro-2:4-dinitrobenzene and thiocarbonyl anilide yield only a crude *product*, m. p. 195°; derived from 2 mols. of the former and 1 mol. of the latter, which is apparently changed on recrystallisation, yielding a *compound*, m. p. 225°. Condensation with potassium phthalimide by heating in a sealed tube at 180–200° yields a *compound*, m. p. 194–195°, reduced to the *diamino*-derivative, m. p. above 250°, by aluminium amalgam. When dimethylamine is passed into a xylene solution of 1-chloro-2:4-dinitrobenzene, 2:4-dinitrodimethylaniline, m. p. 87°, is obtained in good yield. 1-Chloro-2:4-dinitrobenzene (2 mols.) and dimethylglyoxime combine in alcoholic solution to give a white, amorphous *compound*.

R. K. CALLOW.

**Tenacity of organic residues.** VII. J. VOX BRAUN and A. FRIEDSAM (Ber., 1930, 63, [B], 2407–2413; cf. A., 1926, 1231).—Any aromatic hydrogen atom of the benzyl group can be replaced by fluorine without causing increased tenacity of the radical to nitrogen or sulphur such as is caused by the substitution of chlorine, bromine, or iodine for hydrogen.

The requisite fluorobenzyl bromides are obtained by converting the three toluidines into fluorotoluenes and bromination in the side-chain. Interaction with the secondary amines (mol. ratio 3–4:1) is effected at the ordinary temperature and finally at 60°. Treatment with cyanogen bromide takes place initially with cooling and finally on the water-bath. The mixture is treated with ether, which precipitates the additive product of the eliminated bromide and original base. The ethereal solution is shaken with dilute acid, distilled, and the distillate is treated with an excess of trimethylamine, whereby the quaternary bromide,  $\text{NMe}_3\text{RBr}$ , is formed and can be readily separated from the cyanamide.

The following compounds are described: *benzyl-p-fluorobenzylmethylamine*, b. p. 168–170°/16 mm. (*hydrochloride*, m. p. 155–156°; *picrate*, m. p. 105°; *methiodide*, m. p. 221°), converted by cyanogen bromide into a mixture of *benzyltrimethylammonium bromide*, m. p. 250°, and *p-fluorobenzyltrimethylammonium bromide*, m. p. 228–229°, and a mixture of the corresponding cyanamides: *p-fluorobenzyl-p-methylbenzylmethylamine*, b. p. 166–168°/10 mm. (very hygroscopic *hydrochloride*, m. p. 183°; *picrate*, m. p. 110–112°; *methiodide*, m. p. 216–217°), yielding *p-methylbenzyltrimethylammonium bromide* and *p-fluorobenzylmethylcyanamide*, b. p. 148–154°/10 mm., *p-methylbenzylethylamine*, b. p. 98–99°/10 mm. (*hydrochloride*, m. p. 189°; *picrate*, m. p. 89°), transformed into *p-fluorobenzyl-p-methylbenzylethylamine*, b. p. about 175°/10 mm. (non-crystalline *hydrochloride* and *picrate*; *methiodide*, m. p. 122–125°), yielding *p-methylbenzyltrimethylammonium bromide*, m. p. 183°, and homogeneous *p-fluorobenzylethylcyanamide*; *benzyl-p-methylbenzylethylamine*, b. p. 82°/11 mm. (non-crystalline salts), affording homogeneous *p-methylbenzyltrimethylammonium bromide* and *benzylethylcyanamide*, b. p. 160°/12 mm.; *p-chlorobenzyl-p-fluorobenzylmethylamine*, b. p. 182–184°/10 mm. (*hydrochloride*, m. p. 160–161°; *picrate*, m. p. 129°; *methiodide*, m. p. 210–212°), giving almost homogeneous *p-fluorobenzyltrimethylammonium bromide* and *p-chlorobenzylmethylcyanamide*, b. p. 166°/10 mm.; *benzyl-o-fluorobenzylmethylamine*, b. p. 158–160°/11 mm. (*hydrochloride*, m. p. 189°; *picrate*, m. p. 99°; *methiodide*, m. p. 213°), yielding a mixture of quaternary bromides and cyanamides (*o-fluorobenzyltrimethylammonium bromide*, m. p. 225°); *p-fluorobenzylmethylamine*, b. p. 80–82°/14 mm. (*hydrochloride*, m. p. 199°; *picrate*, m. p. 131°), transformed into *o-fluorobenzyl-p-fluorobenzylmethylamine*, b. p. 164–166°/12 mm. (very hygroscopic *hydrochloride*, m. p. 130°; *picrate*, m. p. 142°; *methiodide*, m. p. 230°), yielding a mixture of quaternary bromides and cyanamides; *o-fluorobenzylmethylamine*, b. p. 73°/12 mm. (*hydrochloride*, m. p. 160°; *picrate*, m. p. 139–140°).

*Benzyl m-fluorobenzyl sulphide*, b. p. 140–142°;



0.2 mm., very smoothly prepared from benzyl mercaptan and *m*-fluorobenzyl bromide in presence of alcoholic sodium ethoxide, is transformed into a mixture of benzyl- and *m*-fluorobenzyl-trimethylammonium bromide, m. p. 231°, and of benzyl and *m*-fluorobenzyl thiocyanates.

H. WREN.

**Organic sulphur-nitrogen linking.** E. RIESZ (Monatsh., 1930, 56, 239—246).—Oxidation of arylsulphonanilides with 30% hydrogen peroxide or sodium dichromate and acetic acid does not occur unless a free amino-group is present. The formation of quinonoid compounds by similar oxidation of anilinothiolbenzenes (A., 1927, 52; 1928, 168, 748; 1929, 60) substituted in the *o*- and *p*-positions (not *m*-) of the aniline residue involves the thionium condition of the sulphur atom.

[With A. LORENZ, C. MYSCHALOV, and O. STRAKOSCH].—The following compounds, prepared by the usual method, are unaffected by the above oxidants: 4-chloro-2-nitrobenzene-sulphonanilide, *o*- and *p*-hydroxyanilides, m. p. 122—123° and 92—93°, respectively, and *p*-dimethylaminoanilide, m. p. 125°; 4:4'-di-(*p*-chloro-*o*-nitrobenzenesulphonamido)diphenyl, m. p. above 290° (decomp.); 1:2- and 1:4-di-(*p*-chloro-*o*-nitrobenzenesulphonamido)benzene, m. p. 92—94° (decomp.) and 250° (decomp.), respectively; 1-*p*-chloro-*o*-nitrobenzenesulphonamido-4-*p*-chloro-*o*-nitrophenylthiolaminobenzene, m. p. 164—166° (decomp.); 4-chloro-2-nitro-1-*m*-hydroxyanilinothiolbenzene, m. p. 158°; 4-chloro-2-nitro-1-*m*-dimethylaminoanilinothiolbenzene, m. p. 148°. 4-Chloro-2-nitrobenzenesulphon-*o*- and *p*-aminoanilides, m. p. 143° and 161°, respectively, are oxidised by the above reagents.

H. BURTON.

**Coupling of diazonium compounds with 2-methoxy-3-naphthoic acid.** G. B. JAMBUSERWALA and F. A. MASON (J. Soc. Dyers and Col., 1930, 46, 339—341).—Although according to Meyer (A., 1920, i, 97) the ether of a naphtholcarboxylic acid does not couple, the authors have coupled 2-methoxy-3-naphthoic acid in aqueous solution with diazotised *p*-chloroaniline, dichloroaniline, *p*-nitroaniline, 4-nitro-*o*-anisidine, benzidine, tolidine, *o*- and *m*-nitroaniline, sulphanilic acid, and 5-nitro-*o*-anisidine. Whilst the first six give unmethylated dye and the next three approximately equal parts of methylated and unmethylated, the last couples without dealkylation, this being the first instance to be recorded.

L. J. HOOLEY.

**Possible yellow content of the acidic, red solutions of methyl-yellow.** A. THIEL (Ber., 1930, 63, [B], 2453—2455).—Contrary to Hantzsch and Burawoy (this vol., 1280), the author's experience leads him to the conclusion that methyl-yellow, if present at all, is contained only in very small amount in the aqueous, strongly acidic solutions of methyl-yellow. Re-examination of the extinction of methyl-yellow shows the complete analogy of this compound with methyl-orange and hence the maximum yellow content in 0.2*N*-hydrochloric acid in presence of 55% alcohol is not greater than 6%. The "azoid band" of Hantzsch and Burawoy is in reality a second, less pronounced maximum characteristic for the red forms of methyl-yellow and methyl-orange and gives no basis for the

calculation of the yellow content in acid solutions of azo-dyes.

H. WREN.

**Azobenzene-4-sulphonic acid and 4-nitroazobenzene-4'-sulphonic acid.** F. PERKTOLD (Monatsh., 1930, 56, 247—252).—Treatment of azobenzene with fuming sulphuric acid (8—10% SO<sub>3</sub>) at 130—135°, gives a 90—100% yield of azobenzene-4-sulphonic acid (+3H<sub>2</sub>O), m. p. 125—138° according to the rate of heating [sodium (+4H<sub>2</sub>O), carbamide, aniline (+1.5H<sub>2</sub>O), *o*- and *p*-toluidine, and  $\alpha$ - and  $\beta$ -naphthylamine salts]; the anhydrous acid chars at 140° without melting. Nitration of azobenzene-4-sulphonic acid with nitric acid (*d* 1.41) at 75°, affords 4-nitroazobenzene-4'-sulphonic acid (+3H<sub>2</sub>O) (aniline and  $\beta$ -naphthylamine salts), an aqueous solution of which readily gelatinises. Treatment of the nitroacid with bromine in acetic acid at 130—150°(?) furnishes 2:6-dibromo-*p*-nitroaniline and a small amount of 4-bromo-4'-nitroazobenzene. Solubilities of the above salts in water are recorded. H. BURTON.

**Aryl fluorosulphonates, Ar·O·SO<sub>2</sub>F.** W. LANGE and E. MÜLLER (Ber., 1930, 63, [B], 2653—2657).—Aryldiazonium fluorosulphonates decompose when heated according to the scheme [ArN<sub>2</sub>]<sup>+</sup>[SO<sub>2</sub>F]<sup>-</sup> → Ar·O·SO<sub>2</sub>F + N<sub>2</sub>, but the change is accompanied by side reactions so that the yields do not exceed half the theoretical amounts. The products are generally liquids of aromatic odour which do not attack glass when vaporised. They are very stable towards water even in the presence of acid, but slowly decomposed by aqueous alkali hydroxide with formation of alkali aryl sulphates. The following fluorosulphonates are described: benzenediazonium, decomp. 90.0—94.6°, according to the rate of heating, and thence phenyl, b. p. 179.6°/756 mm., *d*<sub>4</sub><sup>20</sup> 1.3361, *n*<sub>D</sub><sup>20</sup> 1.4640; *o*-tolyl, b. p. 191.6—192.6°/754 mm., *d*<sub>4</sub><sup>20</sup> 1.2896, *n*<sub>D</sub><sup>20</sup> 1.4673; diphenylene-4:4'-bis(diazonium), decomp. 132.2—134.2°, and thence 4:4'-diphenylene, m. p. 94.8° after softening; 4-chlorobenzenediazonium, decomp. 120.6°, and thence 4-chlorophenyl, b. p. 208—211°/753 mm., *d*<sub>4</sub><sup>20</sup> 1.4678, *n*<sub>D</sub><sup>20</sup> 1.4888; *o*-nitrobenzenediazonium, m. p. 146.2° (slight decomp.), and *o*-nitrophenyl, b. p. 152°/26 mm.; *m*-nitrobenzenediazonium, decomp. 142—144.3°, and *m*-nitrophenyl, b. p. 154°/12 mm.; *p*-nitrobenzenediazonium, decomp. 145.1—145.7°, and *p*-nitrophenyl fluorosulphonate, b. p. 156°/19 mm.

H. WREN.

**Nitration. IV. Mechanism of nitration of phenol.** S. VEIBEL (Z. physikal. Chem., 1930, B, 10, 22—46; cf. this vol., 1429).—To account for the part played by nitrous acid in the nitration of phenol, it is suggested that the formation of the nitrophenols occurs through oxidation by the nitric acid of the intermediate *o*- and *p*-additive compounds of phenol and nitrous acid produced in nitrosation (cf. this vol., 1033). The fact that the ratio of *o*- to *p*-compound formed in nitrosation is much less than in nitration is explained by supposing that the rate of dissociation of the *o*-additive compound is so high compared with the speed of its conversion into the *o*-nitroso-compound that little of the latter can be formed, but is no greater or even less than the rate of oxidation to the nitro-compound. Reaction velocity measurements at 25° give general support to this

theory. *o*-Nitrosophenol is oxidised by nitric acid far more rapidly than the *p*-compound, the velocity, however, being in each case proportional to the cube of the acid concentration. The rate of nitration of phenol is proportional to the fourth power of the acid concentration, but nitrosation follows the bimolecular law.

R. CUTHILL.

**Action of oxides of nitrogen on ethers. II. Action of nitrogen peroxide on mixed aliphatic-aromatic ethers.** O. I. EGOROVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1097—1100).—The products of the prolonged action of nitrogen peroxide on phenyl isomyl ether on reduction yield isovaleric acid and *p*-aminophenyl isomyl ether, b. p. 274—275° (acetyl derivative, m. p. 103—104°; benzoyl derivative, m. p. 164°).

R. TRUSZKOWSKI.

***o*-Phenetylcarbamide.** E. WERTHEIM (J. Amer. Chem. Soc., 1930, 52, 4167—4168).—*o*-Phenetylcarbamide, prepared from *o*-phenetidine, potassium cyanate, and dilute hydrochloric acid, has m. p. 142—143° after shrinking at 139° (lit. 206°).

H. BURTON.

**Concurrence between principal and subsidiary valency fields.** E. HERTEL and G. H. RÖMER (Ber., 1930, 63, [B], 2446—2452).—The conditions are discussed under which two substances may unite to form a molecular compound or may undergo more intimate chemical reaction, and attempts are described to divert the change into one or other direction by systematic variation of the component molecules. Thus ethyl  $\alpha$ -2 : 4 : 6-trinitrophenoxypropionate yields an additive compound, m. p. 142—143°, with dimethylaniline, and not a quaternary ammonium picrate. 2 : 4 : 6-Trinitroanisole and aniline afford 2 : 4 : 6-trinitrodiphenylamine, m. p. 179°, whereas with  $\alpha$ - and  $\beta$ -naphthylamines and 4-bromo- $\alpha$ -naphthylamine the ether gives only additive compounds (1 : 1); indications of the production of 2 : 4 : 6-trinitrophenyl- $\beta$ -naphthylamine are observed. Replacement of trinitroanisole by ethyl  $\alpha$ -2 : 4 : 6-trinitrophenoxypropionate leads to the formation of 2 : 4 : 6-trinitrophenyl- $\alpha$ - and - $\beta$ -naphthylamine, m. p. 197° and 234°, respectively. The reactivity at the etheral linking depends on the strength of the base, since aniline reacts readily with 2 : 4 : 6-trinitroanisole or ethyl  $\alpha$ -2 : 4 : 6-trinitrophenoxypropionate, whereas *p*-nitroaniline and picramide do not react. 4-Bromo- $\alpha$ -naphthylamine forms an additive compound with ethyl  $\alpha$ -2 : 4 : 6-trinitrophenoxypropionate, whilst diphenylamine gives adducts with the ester (ratio 2 : 1) and 2 : 4 : 6-trinitroanisole (ratio 1 : 1).

Ethyl  $\alpha$ -iodopropionate is converted by silver picrate into ethyl  $\alpha$ -2 : 4 : 6-trinitrophenoxypropionate, m. p. 92°, converted by concentrated nitric acid into  $\alpha$ -2 : 4 : 6-trinitrophenoxypropionic acid, m. p. 164° (decomp.).

H. WREN.

**Organic sulphur compounds. XVIII. Thermal rearrangement of thiocarbonic esters into thiolcarbonic esters. II. Formation of disulphides from phenols.** A. SCHÖNBERG, L. VON VARGHA, and W. PAUL (Annalen, 1930, 483, 107—114; cf. this vol., 320).—Di-*p*-tolyl thiocarbonate is isomerised when heated at 300° in a current of carbon dioxide to *p*-tolyl *p*-tolylthiolformate, m. p. 109°.

Hydrolysis of this with aqueous-alcoholic sodium hydroxide and subsequent oxidation of the *p*-thiocresol produced with hydrogen peroxide affords di-*p*-tolyl disulphide. Thymol and thiocarbonyl chloride in presence of benzene and pyridine give dihythmyl thiocarbonate, m. p. 85° (lit. 110°), isomerised at 300° in an atmosphere of nitrogen to thymyl thymylthiolformate, m. p. 58—59°. Dihythmyl disulphide, m. p. 63°, is obtained as above. 2-Hydroxydiphenyl and thiocarbonyl chloride react in presence of benzene and alcoholic potassium hydroxide, forming di-2-diphenylthyl thiocarbonate, m. p. 106°, converted by rearrangement, hydrolysis, and oxidation into di-2-diphenylthyl disulphide, m. p. 116°.

Treatment of phenyl thiocarbonate with yellow mercuric oxide in boiling benzene furnishes phenyl carbonate.

H. BURTON.

**Di-iodothymol and the decomposition of its salts.** G. H. WOOLLETT and C. H. EVERETT (J. Amer. Chem. Soc., 1930, 52, 4018—4021).—Treatment of iodothymol dissolved in concentrated ammonia with a 0.2*M* solution of iodine in potassium iodide gives a di-iodothymol, not solid at -17° (benzoate, m. p. 112°), which when treated with sodium hydroxide solution passes into a red resinoid, (C<sub>10</sub>H<sub>11</sub>OI)<sub>2</sub> (cf. A., 1921, i, 340). This decomposition is probably due to free iodine in the di-iodothymol, since the change does not occur in presence of alcohol, acetone, or sulphites. The resinoid is also produced by the action of potassium ferrieyanide solution (1 mol.) on the di-iodothymol (1 mol.). Thymol iodide (U.S.P.) contains a small amount of di-iodothymol.

H. BURTON.

**Tenacity of alkyl groups in the benzene nucleus.** K. VON AUWERS and E. JANSSEN (Annalen, 1930, 483, 44—65).—A continuation of previous work (A., 1926, 608; 1928, 416). The Fries transformation of various 2 : 6-dimethyl- and 2-methyl-6-ethyl-4-alkylphenyl acetates has been effected by the methods previously used. *vic*-*m*-Xylenyl propionate, b. p. 234—236°; butyrate, b. p. 248—250°; heptoate, b. p. 162—164°/12 mm.; dodecoate, b. p. 216—218°/12 mm., m. p. 28—29°, and benzoate, m. p. 40.5—41°, are converted by treatment with aluminium chloride into 4-propionyl-, m. p. 106—106.5°; 4-butyryl-, m. p. 124—125°; 4-heptoyl-, m. p. 92—93°; 4-dodecyl-, m. p. 52—53°, and 4-benzoyl-2 : 6-dimethylphenols, m. p. 142—142.5°, respectively. Reduction of these ketones by Clemmensen's method gives 2 : 6-dimethyl-4-propyl-, m. p. 33—34° (acetate, b. p. 252—260°); 4-butyl-, m. p. 32.5—33.5° (acetate, b. p. 268—276°); 4-heptyl-, m. p. 48.5—49° (acetate, m. p. 37.5—38°); 4-dodecyl-, m. p. 65—66° (acetate, m. p. 57—58°), and 4-benzyl-phenols, b. p. 195—200°/20 mm., m. p. 66.5—67.5° (acetate, b. p. 324—326°), respectively. The Fries transformation of the above acetates affords, in all cases, unchanged acetate, the corresponding phenol, and 4-hydroxy-3 : 5-dimethylacetophenone; small amounts of unidentified *o*-hydroxyketones are formed with the propyl, butyl, and heptyl derivatives. 2 : 6-Dimethyl-4-ethylphenyl acetate (A., 1928, 416) gives (mainly) 4-hydroxy-3 : 5-dimethylacetophenone and a small amount of impure 2-hydroxy-3 : 5-dimethylacetophenone.

2-Methyl-6-ethylphenyl propionate, b. p. 244—246°; butyrate, b. p. 258—261°; heptate, b. p. 172—174°/12 mm., and dodecate, b. p. 218—220°/18 mm., m. p. 19—20°, are converted as above into 4-propionyl-, m. p. 101—102°; 4-butyryl-, m. p. 86—87°; 4-heptyl-, m. p. 56—57.5°, and 4-dodecoyl-2-methyl-6-ethylphenols, m. p. 44.5—45.5°, respectively. The Fries transformation of the acetate, b. p. 264—266°, of 2-methyl-6-ethyl-4-propylphenol, b. p. 130—133°/15 mm. (phenylcarbimide derivative, m. p. 140.5—141.5°), gives a little *o*-hydroxyketone and regenerated phenol. 2-Hydroxy-3-methyl-5-propylacetophenone, b. p. 136°/12 mm. (p-nitrophenylhydrazone, m. p. 216—217°), is obtained by the Fries transformation of the acetate, b. p. 125°/11 mm., of 2-methyl-4-propylphenol, b. p. 117°/10 mm. (phenylcarbimide derivative, m. p. 136°). The acetate, b. p. 270—280°, of 2-methyl-6-ethyl-4-butyphenol, b. p. 146—150°/15 mm. (phenylcarbimide derivative, m. p. 117—119°), undergoes the Fries transformation into the last-named phenol and 2-hydroxy-3-methyl-5-butyacetophenone, b. p. 152—154°/13 mm. (p-nitrophenylhydrazone, m. p. 168—170°), synthesised by way of 2-methyl-4-butyphenyl acetate, b. p. 268—270°. *o*-Tolyl butyrate has b. p. 237—240°. The acetate, b. p. 184—194°/16 mm., of 2-methyl-6-ethyl-4-heptylphenol, m. p. 26—28°, is converted (Fries) into the phenol and a little unidentified ketone, whilst the acetate, m. p. 41—43°, of 2-methyl-6-ethyl-4-dodecylphenol, m. p. 51—52°, yields similarly small amounts of the phenol and 4-hydroxy-3-methyl-5-ethylacetophenone. In these transformations, the ethyl group is generally eliminated exclusively.

m-4-Xylenyl heptate, b. p. 180—182°/16 mm., is converted into 6-heptyl-2:4-dimethylphenol, b. p. 186—190°/16 mm., and thence by reduction (Clemmensen) into 2:4-dimethyl-6-heptylphenol, b. p. 172—178°/16 mm., m. p. 39—40°. The acetate, b. p. 180—188°/13 mm., of this undergoes the Fries transformation, yielding mainly 2-hydroxy-3:5-dimethylacetophenone; the heptyl group is replaced by acetyl. 2-Methyl-4-ethylphenyl propionate, b. p. 136—138°/16 mm., affords 6-propionyl-2-methyl-4-ethylphenol, b. p. 152—154°/14 mm., reduced to 2-methyl-4-ethyl-6-propylphenol, b. p. 134—138°/13 mm. (phenylcarbimide derivative, m. p. 131—131.5°). The acetate, b. p. 142—146°/16 mm., of this is converted (Fries) into approximately equal amounts of 2-hydroxy-3-methyl-5-propylacetophenone, m. p. 101° (prepared also by way of 2-methyl-6-propylphenyl acetate, b. p. 117°/11 mm.), and an unidentified *o*-hydroxyketone. The acetates, b. p. 250—260° and 194—198°/12 mm., respectively, of 2-methyl-4-ethyl-6-allylphenol, b. p. 120—125°/15 mm. (prepared by Claisen's method from allyl bromide and the requisite phenol), and 6-benzyl-2-methyl-4-ethylphenol, b. p. 188—194°/12 mm. (phenylcarbimide derivative, m. p. 142—143°), are both converted (Fries) into 2-hydroxy-3-methyl-5-ethylacetophenone.

The results obtained show definitely that the ease of elimination of the ethyl, propyl, and methyl groups is in the order quoted.

The following are also described: *o*-hydroxy-propionophenoneoxime, m. p. 93.5—94°; 2-hydroxy-5-propylacetophenone, b. p. 145—147°/20 mm., reduced

(Clemmensen) to 2-ethyl-4-propylphenol, b. p. 245—246° (acetate, b. p. 244—246°); 2-hydroxy-3-ethyl-5-propylacetophenone, b. p. 140—141°/18 mm. (p-nitrophenylhydrazone, m. p. 152.5—153.5°).

H. BURTON.

Synthesis of lodal and epinine. J. S. BUCK (J. Amer. Chem. Soc., 1930, 52, 4119—4122).—When benzylidenehomoveratrylamine is warmed with methyl iodide in absence of air and moisture at 37°, the hydriodide, m. p. 131°, of *N*-methylhomoveratrylamine, b. p. 159°/11 mm.,  $d_4^{25}$  1.0597,  $n_D^{25}$  1.5362 [picrate, m. p. 162—163°; chloroplatinate, m. p. 190° (decomp.); chloroaurate, m. p. 148° (decomp.); quaternary iodide, m. p. 226°, from the base and methyl iodide in warm alcohol], is obtained. This is demethylated by hydriodic acid ( $d$  1.7) at 120—130° to *N*-methyl- $\beta$ -3:4-dihydroxyphenylethylamine (epinine) (Pyman, J.C.S., 1909, 95, 1266, 1610). A method for preparing 3:4-dimethoxy-5- $\beta$ -methylaminoethylbenzaldehyde (lodal) (Pyman, *loc. cit.*) from *N*-methylhomoveratrylamine and formic acid at 210°, with subsequent treatment of the product formed with phosphoric oxide in boiling toluene, is given.

H. BURTON.

Bromo-derivatives of polyphenols. G. GALLAS and M. ALONSO (Anal. Fis. Quim., 1930, 28, 967—1002).—Bromination of 1:1'-di- $\beta$ -naphthol has been carried out under various conditions, in aqueous suspension or solution, and in organic solvents. From the complex reaction mixtures, in which they are accompanied by resinous products and unchanged di- $\beta$ -naphthol, there have been separated, most readily in the latter conditions, 1-bromo- $\beta$ -naphthol, formed by the rupture of the 1:1'-linking, and a dibromo-1:1'-di- $\beta$ -naphthol, m. p. 120—121° (+AcOH, m. p. 196°) (benzoyl derivative, m. p. 170°; nitro derivative, m. p. above 300°), which reacts with alcoholic potassium hydroxide to give an impure substance, m. p. 75°. Di- $\alpha$ -naphthol yields similarly complex mixtures from which there have been separated a (?)monobromo- $\alpha$ -naphthol, m. p. 85—86°, and a (?)tetrabromodi- $\alpha$ -naphthol, m. p. 150°. Treatment of 2:4-dibromo- $\alpha$ -naphthol with ferric chloride yields a complex product from which fractions of m. p. 70°, 150°, 210°, and above 290° have been separated.

4:4'-Dihydroxydiphenyl yields the 3:3':5:5'-tetrabromo-compound, or mixtures of this with dibromo-compounds of m. p. 115°, 130—132°, or 160—162°. From 2:2'-dihydroxydiphenyl there are obtained dibromo-compounds with m. p. varying from 100—105° to 110—125° and 185°.

The reactions of the substances isolated with ferric chloride, concentrated sulphuric acid, nitric acid, and alcoholic potassium hydroxide are described, and the results are discussed in relation to the constitution of diphenols formed by oxidation of phenols and the orientation of the bromo-derivatives.

R. K. CALLOW.

Stereoisomeric polyhydroxycycloalkanes. II. Stereoisomeric pyrogallitols [cyclohexane-1:2:3-triols]. H. LINDEMANN and A. DE LANGE (Annalen, 1930, 483, 31—43).—Catalytic reduction of pyrogallol by the method previously described (this vol., 209) gives small amounts of cyclo-hexane

and -hexanol, a mixture of *cis*- and *trans*-cyclohexane-1:2-diols (*bisphenylcarbimide* derivatives, m. p. 185° and 212°, respectively), and a mixture of  $\alpha$ -, m. p. 108° (cf. Brunel, A., 1910, i, 476) (tribenzoate, m. p. 142°; *trimenthylcarbimide* derivative, melts at 120° and then re-solidifies with m. p. 213°,  $[\alpha]_D^{25}$  -59.6° in benzene),  $\beta$ -, m. p. 124—125° (cf. Brunel, *loc. cit.*) [tribenzoate, m. p. 184° (lit. 181°)], and  $\gamma$ -cyclohexane-1:2:3-triols, m. p. 148° (tribenzoate, m. p. 142°; *trimenthylcarbimide* derivative, m. p. about 130° re-solidifying with m. p. 208°,  $[\alpha]_D^{25}$  -56.2° in benzene). The  $\gamma$ -triol is identical with that (m. p. 145°) described by Senderens and Aboulenc (A., 1922, i, 337), but the triol, m. p. 95°, of these authors is a cyclohexane-1:2-diol. The cyclohexane-1:2:3-triol, m. p. 67°, of Sabatier and Mailhe (A., 1908, i, 529) could not be prepared; it is probably a mixture of the above diols or triols. Hydrolysis of the above benzoates gives the appropriate triol, which can be re-benzoylated to the corresponding ester; no inversion occurs during hydrolysis. The above triols are the three theoretically possible cyclohexane-1:2:3-triols.

H. BURTON.

**Oxygen affinity of hydrocarbon radicals. IV.** R. LYDEN (Finska Kemistsamf. Medd., 1930, 38, 72—84; Chem. Zentr., 1930, i, 3171—3172).—The relative reactivities towards acetyl bromide were determined: benzyl ethyl ether: diethyl ether (1.52:1); benzyl ethyl ether: phenetole (3.58:1); benzyl *n*-butyl ether: di-*n*-butyl ether (1.83:1); benzyl *n*-butyl ether: phenyl *n*-butyl ether (5.18:1); benzyl *n*-butyl ether: diethyl ether (1.58:1); benzyl ethyl ether: di-*n*-butyl ether (4.71:1).

A. A. ELDRIDGE.

**Preparation of optically active phenylmethylcarbinols.** A. J. H. HOUSSA and J. KENYON (J.C.S., 1930, 2260—2263; cf. Pickard and Kenyon, *ibid.*, 1911, 99, 45; Ott, A., 1928, 1350).—*d*- and *l*-Phenylmethylcarbinols, b. p. 98—99°/20 mm.  $[\alpha]_{5461}^{19}$  +51.36°, and b. p. 93°/14 mm.,  $\alpha_{5461}^{18}$  -13.27° ( $l=0.25$ ), respectively, are obtained from the *dl*-alcohol by fractional crystallisation of the brucine salt of the carbonyl hydrogen phthalate. The *d*-alcohol is obtained only in small quantity.

H. BURTON.

**Action of stannous chloride on aromatic carbinols.** A. VANSCHIEDT and B. MOLDAVSKI (J. Russ. Phys. Chem. Soc., 1930, 62, 1467—1487).—The action of stannous chloride on triarylcabinols was investigated in acetic acid solution, with a view of preparing free triaryl radicals and studying halochromism. The stannous chloride was added in fuming hydrochloric acid solution, stannic chloride being introduced in certain cases to investigate the possibility of complex salt formation. In almost all cases stannous and especially stannic chloride intensified halochromism or induced it strongly. With diphenyl- $\alpha$ -naphthylcarbinol dehydration occurred with the formation of phenylchrysofluorene, m. p. 191—192°, but a hydrocarbon, m. p. 137—138°, was also obtained. With fluorenol derivatives, stannous chloride gave the corresponding arylfluorenyl di-derivatives of the type  $\left[ \begin{smallmatrix} C_6H_5 \\ C_6H_4 \end{smallmatrix} > CAr \right]_2$ , brilliantly coloured when heated in anisole solution.  $\alpha$ -Naphthyl-

fluorenol gave a reddish-brown coloration, which disappeared on keeping in air. A white solid, m. p. 185°, identified as  $\alpha$ -naphthylfluorenyl peroxide was obtained from benzene solution, the original brown coloration being due to free  $\alpha$ -naphthylfluorenyl.

M. ZVEGINZOV.

**Optically active diphenylhydroxyethylamines and isohydrobenzoin. III. Optically active diphenylethylene oxides.** J. READ and I. G. M. CAMPBELL (J.C.S., 1930, 2377—2384).—The quaternary iodides, HO·CHPh·CHPh·NMe<sub>3</sub>I, obtained from *dl*- and *l*-isodiphenylhydroxyethylamine and methyl iodide (cf. Rabe and Hallensleben, A., 1910, i, 317), when treated with silver oxide and then distilled with steam afford *cis*- $\alpha\beta$ -diphenylethylene oxide, m. p. 42°. The corresponding iodide, m. p. 145°,  $[\alpha]_D +92.4^\circ$  in methyl alcohol, from *d*-diphenylhydroxyethylamine furnishes similarly *l*-trans- $\alpha\beta$ -diphenylethylene oxide, m. p. 69—70°,  $[\alpha]_D -306^\circ$  in alcohol, which when kept in alcoholic solution for 14 days passes into *l*-isohydrobenzoin monoethyl ether, m. p. 45—50°,  $[\alpha]_D -34.6^\circ$  in alcohol; ring fission of the oxide is followed by addition of 1 mol. of alcohol. Ring fission can also be effected with hydrogen chloride in chloroform. *d*-trans- $\alpha\beta$ -Diphenylethylene oxide, m. p. 69—70°,  $[\alpha]_D +310^\circ$  in alcohol, is obtained from *l*-diphenylhydroxyethyltrimethylammonium iodide, m. p. 145°,  $[\alpha]_D -102^\circ$  in methyl alcohol. The m.-p. curve of mixtures of the *d*- and *l*-trans-oxides is that of a characteristic racemate. From the above results and the observation that *l*-isohydrobenzoin is formed by the action of nitrous acid on *d*- and *l*-isodiphenylhydroxyethylamines (A., 1929, 1444), it appears that diphenylhydroxyethylamine and isodiphenylhydroxyethylamine are correctly represented by I and II,



respectively. The stereoisomeric oxides are unimolecular; they are markedly stable towards Fehling's solution, potassium permanganate, and chromic acid.

When *l*-isodiphenylhydroxyethylamine is treated with nitrous acid as previously described (*loc. cit.*), a small amount of *l*-isohydrobenzoin and much oil are obtained; the oil contains a small quantity of benzophenone and probably hydrobenzoin (36%). A dark brown oil is obtained as the sole product from the *dl*-iso-derivative, whilst the oil from *d*-diphenylhydroxyethylamine has  $[\alpha]_D -20^\circ$  in benzene (indicating that no unimolecular oxide is present). The above oils probably contain polymerised oxides and hydrobenzoin. Migration of hydrocarbon radicals does not appear to take place during the deamination, since aldehydes or ketones do not occur in the oil.

All rotations were measured at about 15°.

H. BURTON.

**Semi-ethers of benzpinacol.** L. SCHUSTER (Ber., 1930, 63, [B], 2397—2399).—Phenylbenzoin mono-phenyl ether, OPh·CPh<sub>2</sub>Bz, m. p. 134.5°, is prepared by the action of phenol on benzoyldiphenylmethyl bromide. From magnesium phenyl bromide and the requisite phenylbenzoin alkyl (aryl) ether are obtained benzpinacol methyl ether, OMe·CPh<sub>2</sub>·CPh<sub>2</sub>·OH,

m. p. 182.5°, *ethyl ether*, and *phenyl ether*, m. p. 219°. The alkyl ethers are readily transformed by hydrogen bromide in glacial acetic acid to  $\beta$ -benzpinacolin, whereas the phenyl ether is unaffected by this treatment.

H. WREN.

**Organic sulphur compounds. XVII. Sulphur analogues of hexaphenylethane and triphenylmethyl.** A. SCHÖNBERG and T. STOLFF (Annalen, 1930, 483, 90—107).—Treatment of phenylthioldiphenylmethyl chloride (A., 1929, 924) with mercury in presence of benzene and in absence of air and light gives *s*-tetraphenylethylene and diphenylthioldiphenylmethane. Reaction is presumed to occur through the intermediate free radical phenylthioldiphenylmethyl:  $4\text{CPh}_2\text{-SPh} \rightarrow \text{CPh}_2\text{:CPh}_2 + 2\text{CPh}_2(\text{SPh})_2$ . Similar treatment of *o*-nitrophenylthioldiphenylmethyl chloride affords benzophenone, di-*o*-nitrophenylthioldiphenylmethane, and di-*o*-nitrophenyl disulphide; much resinous material is produced. Diazo fluorene and sulphur phenyl chloride in ether give 9-chloro-9-phenylthiofluorene, converted as above into  $\alpha\beta$ -diphenylthiol- $\alpha\beta$ -di(diphenylene)ethane (+AcOEt), m. p. (solvent-free) about 220° (decomp.). This has a normal mol. wt. in chloroform, and, when heated in presence or absence of a high-boiling solvent, decomposes into diphenyl disulphide and di(diphenylene)ethylene. The solid is stable to light, but exposure of a benzene solution to ultra-violet light results in the formation of di(diphenylene)ethylene. 9-Chloro-9-*o*-nitrophenylthiofluorene (*loc. cit.*) is converted by mercury in benzene into  $\alpha\beta$ -di-*o*-nitrophenylthiol- $\alpha\beta$ -di(diphenylene)ethane, m. p. 165—167°, which, when heated in boiling xylene or alone at 170—190°, decomposes into fluorenone and di-*o*-nitrophenyl disulphide. The above results show that intermediate radical formation occurs when the arylthioldiphenylmethyl chlorides are treated with mercury; dimerisation or some other form of stabilisation of the radical then takes place.

9:9-Dichlorofluorene and thiophenol react in boiling benzene in a current of carbon dioxide, yielding 9:9-diphenylthiofluorene, m. p. 115°, which decomposes quantitatively at 240° (bath)/vac. into diphenyl disulphide and di(diphenylene)ethylene. 9:9-Di-*o*-nitrophenylthiofluorene, m. p. 159—160° (from 9-chloro-9-*o*-nitrophenylthiofluorene and *o*-nitrophenyl mercaptan in benzene), decomposes explosively at 200°/vac., forming fluorenone, di-*o*-nitrophenyl disulphide, and much carbonaceous material. Similar decomposition of di-*o*-nitrophenylthioldiphenylmethane furnishes benzophenone, a small amount of di-*o*-nitrophenyl disulphide, and much carbonaceous material.

H. BURTON.

**Migration of hydrogen in cholesterol.** R. SCHÖNHEIMER (Naturwiss., 1930, 18, 881).—When cholesterol, free from ergosterol, is heated at a high temperature, an ergosterol-like substance which possesses antirachitic properties is formed (cf. Koch and others, this vol., 256). Several cholesterol preparations, which had been freed not only of ergosterol but also of the last traces of dihydrocholesterol, when heated at 190—220°/1 mm. after previous removal of all traces of air by oxygen-free nitrogen, showed the presence of 1—2% of a saturated sterol, probably

dihydrocholesterol. The reaction may be explained by the assumption that the dehydrogenation of cholesterol to the ergosterol-like substance and hydrogenation to dihydrocholesterol occur simultaneously. An unknown catalyst probably plays a part, since in a large number of purified cholesterol preparations the formation of saturated sterols could not be observed.

W. R. ANGUS.

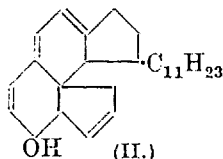
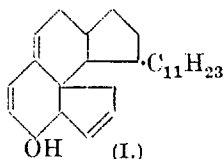
**Crystalline irradiation products of ergosterol and dehydroergosterol.** A. WINDAUS, J. GAEDE, J. KÖSER, and G. STEIN (Annalen, 1930, 483, 17—30).—Prolonged irradiation of an alcoholic solution of ergosterol in an evacuated sealed tube (Uviol glass) affords a small amount of dihydroergosterol (precipitated by digitonin) and physiologically inactive material. Treatment of a solution of this material in benzene with gaseous cyanic acid and keeping the mixture for 14 days gives two *allophanates*, m. p. 219° (amorphous),  $[\alpha]_D^{25} -40^\circ$  (all rotations are in chloroform), and m. p. 224° (crystalline),  $[\alpha]_D^{25} +80^\circ$ , respectively, separable through their differing solubilities in ethyl acetate. The amorphous ester consumes 3 atoms of oxygen when titrated with benzoyl hydrogen peroxide and on hydrolysis with methylalcoholic potassium hydroxide in an atmosphere of hydrogen, gives *suprasterol* I, m. p. 104°,  $[\alpha]_D^{25} -76^\circ$  (*benzoate*, m. p. 96°,  $[\alpha]_D^{25} -50^\circ$ ). This is isomeric with ergosterol, distils unchanged at 190°/0.002 mm., gives an intense reddish-violet colour with chloral hydrate at 100°, an olive-green colour with the Liebermann-Burchard reaction, indefinite colorations with arsenic and antimony trichlorides and trichloroacetic acid, and a negative Tortelli-Jaffé reaction. *Suprasterol* I alters gradually when exposed to air and is unaltered by further irradiation. Catalytic hydrogenation produces neither *allo*- $\alpha$ -ergostanol nor *epi*-ergostanol. Hydrolysis of the crystalline *allophanate* affords *suprasterol* II, m. p. 110°,  $[\alpha]_D^{25} +62.9^\circ$  (*oxalate*, m. p. 165°,  $[\alpha]_D^{25} +75.3^\circ$ ), which is isomeric with, and similar in properties to, *suprasterol* I. Unlike ergosterol, the new sterols are not reduced by sodium and alcohol; *suprasterol* II gives a crystalline dihydroderivative when reduced catalytically (Adams). The new compounds show general absorption below 250 m $\mu$ , thus differing greatly from ergosterol. It is suggested that ergosterol contains a system of conjugated double linkings; the conjugation is destroyed by irradiation.

The alcohol, m. p. 134°,  $[\alpha]_D^{25} +119.5^\circ$ , previously obtained (A., 1928, 1372) from the irradiation of dehydroergosterol contains four double linkings; it is named *photodehydroergosterol* (the *benzoate*, m. p. 160°,  $[\alpha]_D^{25} +134.1^\circ$ , and the *phenylcarbimide* derivative, m. p. 130°,  $[\alpha]_D^{25} +98.7^\circ$ , are described). Catalytic reduction (Adams) of the acetate (*loc. cit.*) in alcohol gives the *acetate*, m. p. 106°,  $[\alpha]_D^{25} +2.9^\circ$  to  $3.8^\circ$ , of *tetrahydrophotodehydroergosterol*, m. p. 123°,  $[\alpha]_D^{25} +26^\circ$  (*benzoate*, m. p. 82—83°,  $[\alpha]_D^{25} +50.2^\circ$ ), which is practically unaffected by sodium ethoxide at 175°. The alcohol, m. p. 175°, previously described (*loc. cit.*) as new, is the known dihydroergosterol. A small amount of a substance,  $\text{C}_{58}\text{H}_{82}\text{O}_4$ , m. p. 257° (hydrolysed to a pinacone), is also found in the irradiation product of dehydroergosterol acetate; it

arises by loss of 2 atoms of hydrogen from 2 mols. of the acetate.

H. BURTON.

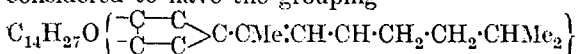
**Positions of the double linkings in ergosterol and its transformation products.** A. WINDAUS (Nachr. Ges. Wiss. Göttingen, 1930, 169—172; Chem. Zentr., 1930, i, 3194—3195).—The following formulæ for ergosterol (I) and dehydroergosterol (II), respectively, are proposed:



A. A. ELDRIDGE.

**Acid from degradation of ergosterol.** F. REINDEL and K. NIEDERLÄNDER (Annalen, 1930, 482, 264—279).—Ergosterol or its acetate gives on prolonged oxidation with nitric acid an acid,  $C_5H_8(CO_2H)_3$ , m. p. 268° (+1½H<sub>2</sub>O), characterised by the following derivatives: *anhydride*, m. p. 268° (by sublimation at 0.1 mm. or by heating with acetic anhydride); *dianiline hydrogen salt* (+2H<sub>2</sub>O), m. p. 300°; *trianilide*, m. p. above 300° (+2NH<sub>2</sub>Ph, red, m. p. above 300°), and its esters. This acid is not produced by oxidation of  $\alpha$ - or  $\beta$ -ergosterols, cholesterol, zymosterol, or sitosterol acetate, and only in traces from irradiated ergosterol. It is stable to further oxidation and catalytic reduction, but sodium amalgam and water reduce it and its trimethyl ester to unidentified oily products: attempts at decarboxylation are without effect or lead to profound decomposition. It is considered to be a cyclopentadienetricarboxylic acid, in which one carboxyl group occupies the 1-position, and two at least are adjacent to each other. The *methyl dihydrogen* (+H<sub>2</sub>O), m. p. 150—152°, and *dimethyl hydrogen* esters, m. p. 140—143°, are obtained with methyl-alcoholic hydrogen chloride, but for the *trimethyl ester*, m. p. 123—124°, diazomethane is required. An isomeric *monomethyl ester* (+H<sub>2</sub>O), m. p. 172°, results from partial hydrolysis of the neutral ester; both monomethyl esters give the anhydride on heating. The trimethyl ester is converted by magnesium methyl iodide into an oily "carbinol," oxidised by chromic and acetic acids to a *substance*,  $C_{11}H_{12}O_3$ , m. p. 235° (+*p*-nitrophenylhydrazine, m. p. 138—139°), probably the triketone,  $C_5H_3(COMe)_3$ .

Ergosterol ozonide is decomposed by water into isooctaldehyde (?) (*semicarbazone*, m. p. 125—127°) and methylglutaric acid. Ergosterol is therefore considered to have the grouping



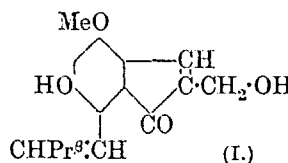
H. A. PIGGOTT.

**Zymosterol.** II. F. REINDEL and A. WEICKMANN (Annalen, 1930, 482, 120—129).—The purification of zymosterol through its dibromide (cf. Heilbron, A., 1929, 1443) is unsatisfactory on account of the instability of the latter. Hydrolysis of the acetate-dibromide (Reindel and Weickmann, *loc. cit.*) with cold alcoholic alkali readily gives zymosterol dibromide, m. p. 157—158°,  $[\alpha]_{5463} + 7.1^\circ$ , and debromination with zinc and acetic acid in the cold yields

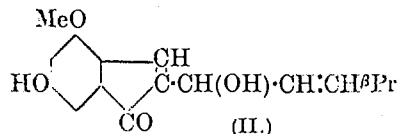
zymosteryl acetate, m. p. 102—104°,  $[\alpha]_{5463} + 38.9^\circ$ , readily hydrolysed to zymosterol, m. p. 107—110°,  $[\alpha]_{5463} + 58.7^\circ$  [*benzoate*, m. p. 125—127° (clear at 130°),  $[\alpha]_{5463} + 51.5^\circ$ ]. Zymosterol is unaffected by irradiation with ultra-violet light, and may be freed from ergosterol by this means, although the method fails occasionally for no apparent reason. Catalytic hydrogenation under the most varied conditions leads only to  $\alpha$ -dihydrozymosterol; this is converted by hydrogen chloride in chloroform into  $\beta$ -*dihydrozymosterol* (+H<sub>2</sub>O), m. p. 99—100°,  $[\alpha]_{5463} + 32.1^\circ$  (*acetate*, m. p. 74—75°,  $[\alpha]_{5463} + 15.3^\circ$ ), which can now be reduced by hydrogen and platinum to *zymostanol*, m. p. 139—140° (+2H<sub>2</sub>O),  $[\alpha]_{5463} + 20.6^\circ$  [*acetate*, m. p. 130—131° (+2H<sub>2</sub>O or +MeOH)]. Zymosterol is oxidised by chromic and acetic acids to *zymostadienone*, m. p. 162—164° (*oxime*, m. p. 238—240°), and an uncrystallisable acid product.

H. A. PIGGOTT.

**Resin of *Garcinia Mangostana*, L.** O. DRAGENDORFF (Annalen, 1930, 482, 280—301).—The benzene-soluble fraction (80—85%) of the resin from the bark of *G. Mangostana* consists of  $\alpha$ -mangostin, m. p. 180—181° [the mangostin of Schmid (Annalen, 1855, 93, 83) and subsequent workers: about 50% of the total resin],  $\beta$ -mangostin, m. p. 175.5°, a *phytosterol*,  $C_{27}H_{46}O$ , m. p. 105—106°, b. p. 270°/11 mm. (*acetate*, m. p. 113°) (a mixture?), and an unsaturated *hydrocarbon*,  $C_{15}H_{24}$ , b. p. about 105°/11—12 mm. The isomeric  $\alpha$ - and  $\beta$ -mangostins have the empirical formula  $C_{16}H_{18}O_4$ ; they contain a methoxyl, and a phenolic and an aliphatic hydroxyl group, and, as their methyl ethers are identical, differ only in the relative positions of the first two. The ultra-violet absorption spectrum indicates the presence of the system  $\cdot C : C \cdot CO \cdot$ , but no oxime can be obtained, although formation of boracetates points to the



the presence of an *isovaleryl* group. The alternative structures I and II are suggested.



The following derivatives of mangostin are described: *O*-methyl, m. p. 123° (*boroacetate*, m. p. 219°) (from both  $\alpha$ - and  $\beta$ -);  $\alpha$ -*monoacetyl*-, m. p. 112° (*boroacetate*, m. p. 206—207°);  $\alpha$ -*diacetyl*-, m. p. 117°; and *acetylmethyl-mangostin*, m. p. 193—194°;  $\beta$ -*monoacetylmangostin boroacetate*, m. p. 188°, and  $\alpha$ -*methyltetrahydromangostin*, m. p. 106°.

H. A. PIGGOTT.

**Benzoic esters and electronic affinities of radicals.** II. Halogenoalkyl benzoates. A. ZAKI (J.C.S., 1930, 2269—2272).—Nitration of the



following halogenoalkyl benzoates gives the following amounts of *meta*-nitro-derivative:  $\alpha$ -chloromethyl, 81.9%;  $\beta$ -chloroethyl, 75.8%;  $\gamma$ -chloropropyl, 77.3%;  $\beta$ -bromoethyl, 71.5%; and  $\gamma$ -bromopropyl, 72.8%. Nitrations and determinations were carried out as previously described (A., 1928, 636). The results agree with the view that the intrinsic negativity of the halogen atom is transmitted by electrostatic induction along the chain. Chlorine shows a greater *m*-orienting effect than bromine. The effect is the greater the nearer the halogen atom is to the nucleus. The alternation observed is explained as for the alkyl benzoates (*loc. cit.*)

When  $\beta$ -iodoethyl benzoate, b. p. 161–163°/17 mm. (from the chloroethyl ester and sodium iodide in 90% alcohol), and  $\gamma$ -iodopropyl benzoate are treated with nitric acid, iodine is eliminated. H. BURTON.

**Anomalies in perbenzoic acid oxidations.** K. BODENDORF (Arch. Pharm., 1930, 268, 491–499).

—Determinations of reaction velocity coefficients in chloroform at 20° show that cinnamyl alcohol is readily oxidised by perbenzoic acid, cinnamaldehyde, cinnamic acid, methyl, ethyl, propyl, isopropyl, and *n*-butyl cinnamates, styryl methyl ketone, and crotonaldehyde are only slowly oxidised, and dimethylpyrone is not attacked. These results in conjunction with those of Böseken (A., 1927, 39) and of Meerwein (A., 1926, 722, 730) indicate that the reactivity of an ethylenic linking towards perbenzoic acid is decreased or completely inhibited by conjugation with a carbonyl radical, whether this be present in a carboxyl, ester, aldehyde, or ketone group. The abnormal behaviour of conjugated polyenes may be due to this cause, the intermediate  $\Delta^2$ -unsaturated ketones, e.g.,  $\text{CH}_2\text{:CMe}\cdot\text{C=OMe}$  from isoprene, being unreactive. Ethyl acetoacetate also is oxidised very slowly, but dibenzoylmethane and benzoylacetone both react more rapidly, taking up 4 atoms of oxygen and giving benzoic acid and benzoic and acetic acids, respectively. The pyruvic acid presumably formed immediately in this last reaction is shown to be very readily oxidised to acetic acid. H. E. F. NOTTON.

**Autocatalysis in oxidation. III. Mechanism of the action of positive catalysts in the autoxidation of abietic acid.** G. DUPONT, J. LÉVY, and J. ALLARD (Bull. Soc. chim., 1930, [iv], 47, 942–952).—The autoxidation of abietic acid in presence of cobalt abietate is a normal autocatalysis, but the reaction velocity is much accelerated. The rate of absorption of oxygen increases rapidly to a maximum and decreases appreciably when one atom of oxygen has been taken up by the abietic acid. The rate of absorption continues to decrease, but less rapidly, until 2 atoms of oxygen have been absorbed per mol. of abietic acid, the absorption then proceeding much less rapidly for the oxidation of the product  $\text{AO}_2$ . This observation indicates the existence of two stages in the oxidation, the first product AO being oxidised much less rapidly than the original abietic acid. The influence of the catalyst depends partly on the proportion present. Although with high concentrations and at high pressures cobalt abietate has a strongly positive catalytic effect, at very low concentra-

tions (0.001% of cobalt oxide) it has a pronounced anti-oxygenic action. These observations are explained on Moureu and Dufraisse's theory as due to the mutual decomposition of abietic acid peroxide and the peroxide of cobalt abietate when the proportion of the latter is only small. Since neutral cobalt abietate in xylene solution is only very slowly oxidised, but is much more rapidly oxidised in presence of excess of abietic acid, it is probable that the catalyst is a complex oxidised acid cobalt abietate.

This conclusion is supported by comparison of the absorption spectra of (a) faintly acid cobalt abietate, showing three bands between 460 and 570  $\mu$ ; (b) cobalt abietate in presence of excess of abietic acid, showing complete absorption at wave-lengths below 500  $\mu$ , and (c) the latter oxidised, showing complete absorption up to  $\lambda$  540  $\mu$ .

R. BRIGHTMAN.

**Naphthyl esters and naphthylamides of chaulmoogric acid.** I. DE SANTOS and A. P. WEST (Philippine J. Sci., 1930, 43, 409–413).—Chaulmoogryl chloride reacts with  $\alpha$ - and  $\beta$ -naphthols at 100° and 125° during 8 and 6 days, respectively, forming  $\alpha$ - and  $\beta$ -naphthyl chaulmoogrates, m. p. 53–54.5° and 49.5–51°, respectively. The  $\alpha$ -, m. p. 93–95°, and  $\beta$ -naphthylamides, m. p. 96–98°, of chaulmoogric acid are formed when chaulmoogramide is heated with  $\alpha$ - and  $\beta$ -naphthylamines at 100° and 115° for 5 and 7 days, respectively.

H. BURTON.

**Physical identity of enantiomerides.** A. N. CAMPBELL and F. C. GARROW (Trans. Faraday Soc., 1930, 26, 565).—A reply to Lowry's criticism of the view that the *d*- and *l*-forms of a compound may differ in energy and rotatory power. (See this vol., 1289.) H. F. GILLBE.

**Isomeric monohydroxyphenylalanines. II. Halogen-substitution products and their reactions.** W. P. DICKINSON and P. G. MARSHALL (J.C.S., 1930, 2289–2293).—3 : 5-Dibromosalicylaldehyde reacts with diketopiperazine in presence of sodium acetate and acetic anhydride at about 40°, forming 2 : 5-diketo-3 : 6-di-(3' : 5'-dibromo-2'-acetoxybenzylidene)piperazine, which exists in *cis*-, m. p. 287°, and *trans*-, m. p. above 300° (decomp.), modifications, separable through their differing solubilities in acetic acid. Reduction of this with zinc dust and acetic acid gives 2 : 5-diketo-3 : 6-di-(3' : 5'-dibromo-2'-acetoxybenzyl)piperazine, m. p. 275° (decomp.), whilst reduction with hydriodic acid causes elimination of bromine. Zinc dust-acetic acid reduction of 2 : 5-diketo-3 : 6-di-(3' : 5'-dibromo-4'-acetoxybenzylidene)piperazine affords no individual product. 2 : 5-Diketo-3 : 6-di-*m*-acetoxybenzylpiperazine, m. p. 191–192°, is hydrolysed by barium hydroxide solution to *m*-hydroxyphenylalanine. Bromination of *o*- and *m*-hydroxyphenylalanines by Zeynek's method (A., 1922, i, 254) affords bromo-derivatives, m. p. 256° and 260° (decomp.), respectively, whilst iodination with a solution of iodine in potassium iodide in presence of ammonia gives di-iodo-derivatives, m. p. 211° (decomp.) and 230° (decomp.), respectively. Colour reactions of the above acids with ferric chloride are given. H. BURTON.

**Reducing action of a Grignard reagent.** H. BURTON (J.C.S., 1930, 2400).—Treatment of benzilamide with magnesium *p*-tolyl iodide in boiling amyl ether gives diphenylacetimide; no *p*-toluoyl-diphenylcarbinol is formed. J. W. BAKER.

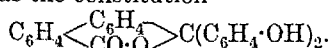
**Methylation process.** M. NIERENSTEIN (J. Amer. Chem. Soc., 1930, 52, 4012—4013).—When 3:4-diacetoxybenzoic acid is treated with diazomethane in alcoholic solution containing piperidine (1 mol. per acetyl group) the acetyl groups are replaced by methyl, and veratric acid is formed; hydrolysis of the product obtained in presence of 1 mol. of piperidine gives isovanillic acid. Similarly, 2:4-diacetoxybenzoic acid furnishes 2:4-dimethoxybenzoic acid or a mixture of monomethylated acids in which 2-hydroxy-4-methoxybenzoic acid predominates. Trimethylgallic acid is prepared from triacetyl gallic acid, m. p. 175° (lit. 171—172°).

H. BURTON.

**Ring closures in the cyclobutane series. II. Cyclisation of  $\alpha\alpha'$ -dibromoadipic esters.** R. C. FUSON, O. R. KREIMEIER, and G. L. NIMMO (J. Amer. Chem. Soc., 1930, 52, 4074—4076).—Treatment of  $\alpha\alpha'$ -dibromoadipyl chloride with phenol (or sodium phenoxide) and  $\beta$ -naphthol in benzene gives *phenyl*, m. p. 146—148°, and  *$\beta$ -naphthyl  $\alpha\alpha'$ -dibromoadipates*, m. p. 165—166·8°, respectively. These esters do not undergo ring closure when treated with various cyanides in acetone, ether, or acetonitrile (cf. A., 1929, 794). Ethyl  $\alpha\alpha'$ -dibromo- $\beta$ -methyladipate and sodium cyanide in alcohol afford *ethyl 1(or 2)-cyano-3-methyleyclobutane-1:2-dicarboxylate*, b. p. 140—143°/3 mm.,  $d_4^{25}$  1·08854,  $n_D^{25}$  1·44735, hydrolysed by hot 20% barium hydroxide solution to *barium 3-methyleyclobutane-1:1(or 2):2-tricarboxylate*.

H. BURTON.

**Diphenic and phthalic acid series. IV.** H. W. UNDERWOOD, jun., and G. E. BARKER (J. Amer. Chem. Soc., 1930, 52, 4082—4087).—Fusion of phenolphthalein with potassium hydroxide gives benzoic acid and 4:4'-dihydroxybenzophenone; phenoldiphenic (A., 1924, i, 176, 1197) (*dipotassium salt*) affords phenol and diphenyl-2-carboxylic acid. Treatment of phenolphthalein with methyl iodide and potassium hydroxide in methyl alcohol at 40—45° yields a *lactone dimethyl ether*, m. p. 100—101°, also formed from phthalic anhydride and anisole in presence of aluminium chloride. Similar methylation of phenoldiphenic furnishes a *lactone dimethyl ether*, m. p. 150—151°, also produced from diphenic anhydride, anisole, and aluminium chloride. Phenoldiphenic has the constitution



Methyl hydrogen and ethyl hydrogen phthalates are converted into phthalic anhydride when heated with acetic acid and anhydride at 145°; methyl and ethyl phthalates are unaffected (cf. A., 1929, 444). Similarly, phthalamic acid gives a mixture of phthalic anhydride and phthalimide, whilst phthalamide affords *o*-cyanobenzamide and phthalimide.

H. BURTON.

**Conjugated double linkings. XIV. Addition of maleic anhydride to polyenes.** R. KUHN and T. WAGNER-JAUREGG (Ber., 1930, 63, [B], 2662—

2679; cf. this vol., 1406).—With unsaturated hydrocarbons containing a large number of conjugated linkings addition of maleic anhydride occurs in such a manner that they are saturated in pairs with the production of six-membered carbon rings. Exclusive addition at the terminal methine groups is not observed. With the diphenylpolyenes the reacting diene groups lie at the end of the chains. Probably, therefore, the addition of maleic anhydride is governed by the same causes as that of hydrogen. Addition of maleic anhydride is initiated by the formation of molecular compounds, recognised by their colour. Stilbene and maleic anhydride in boiling xylene give an amorphous product of high mol. wt.  $\alpha\delta$ -Diphenylbutadiene and the anhydride under similar conditions give 3:6-diphenyltetrahydrophthalic anhydride, m. p. 198°, 200°, and 203°, in different experiments; since the materials can be separated into fractions of identical composition but with maximal variation of 4° in m. p., they appear to be a mixture of isomerides. An *isomeride*, m. p. 212·5—214·5° (corr.), of the compound obtained by Diels and Alder (A., 1929, 1297) by interaction of the molten substances is prepared by isomerisation with dichloroacetic acid in chloroform or crystallisation from trichloroacetic anhydride. After crystallisation from benzene the substance has m. p. 196—198° (corr.). Treatment of the anhydride with 0·5*N*-sodium hydroxide yields 3:6-diphenyltetrahydrophthalic acid, m. p. 209—211° (corr.) after softening with loss of water at 194° (corr.), oxidised by potassium ferricyanide in alkaline solution to *p*-diphenylbenzene. A second, non-crystalline 3:6-diphenyltetrahydrophthalic acid is prepared by the addition of fumaryl chloride to  $\alpha\delta$ -diphenylbutadiene and hydrolysis of the 3:6-diphenyltetrahydrophthalyl chloride, m. p. 143—144° (corr.), thus produced. It is converted by hydrogen chloride in ether into *crystals*,  $\text{C}_{20}\text{H}_{18}\text{O}_4$ , m. p. 230—231° (corr., decomp.). When distilled with soda-lime, it affords diphenylbenzene.

$\alpha\zeta$ -Diphenylhexatriene and maleic anhydride when melted together yield 3-phenyl-6-styryltetrahydrophthalic anhydride, m. p. 199·5—200° (corr.) (cf. Diels and Alder, *loc. cit.*), the structure of which is confirmed by its simultaneous decarboxylation and dehydrogenation by distillation with anhydrous barium hydroxide and selenium to  $\alpha$ -phenyl- $\beta$ -diphenyl-ethylene, m. p. 221—222° (corr.). If addition occurs in boiling xylene, an isomeric 3-phenyl-6-styryltetrahydrophthalic anhydride, m. p. 192—193° (corr.), is obtained, also prepared by distilling the anhydride, m. p. 199·5—200° (corr.), in a vacuum. When ozonised it gives benzoic acid. The corresponding 3-phenyl-6-styryltetrahydrophthalic acid, m. p. 190—191° (corr.) with loss of water, gives  $\alpha$ -phenyl- $\beta$ -diphenyl-ethylene when dehydrogenated with potassium ferricyanide and then decarboxylated or when distilled directly with soda-lime.

$\alpha\delta$ -Diphenyloctatetraene when cautiously melted with maleic anhydride gives 6:6'-di-3-phenylcyclohexene-1:2-dicarboxylic anhydride,

$\left[ \begin{array}{c} \text{CH} \cdot \text{CH} \quad \text{CH} \cdot \text{CO} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{CH} \cdot \text{CHPh} \cdot \text{CH} \cdot \text{CO} \end{array} \right]_2 \text{O}$ , m. p. 275° (corr., decomp.). An *isomeride*, m. p. 264° (corr.), is prepared in boiling xylene. The m. p. of the last-named compound is

raised to 292° (corr., decomp.) by crystallisation from dichloroacetic anhydride, but the original m. p. is regained if the product is crystallised from acetic anhydride or *o*-dichlorobenzene. The anhydride, m. p. 264°, is transformed by successive hydrolysis, dehydrogenation, and decarboxylation to di-*p*-phenyldiphenyl, m. p. 313–314° (corr.). It is hydrolysed by concentrated sodium hydroxide to an amorphous 6:6'-di-3-phenylcyclohexene-1:2-dicarboxylic acid (?), isomerised by formic acid alone or in presence of ether to a *dehydrated acid*, m. p. about 252° (corr.) after loss of water. When treated with dichloroacetic acid at 140° the acid is transformed into the anhydride, m. p. 290° (corr., decomp.). Addition of maleic anhydride to  $\alpha\delta$ -diphenyloctatetraene in the molar ratio 1:1 appears impossible. With fumaryl chloride the hydrocarbon yields the compound  $C_{28}H_{22}O_4Cl_4$ , m. p. 231.5–232.5° (corr.).

$\alpha\kappa$ -Diphenyldecapentaene in boiling xylene adds mainly 2 mols. of maleic anhydride, giving chiefly two crystalline substances,  $C_{30}H_{24}O_6$ , m. p. 235.5° (corr., decomp.) and 255.5° (corr., decomp.), respectively, and an amorphous compound, decomp. 276.5°, apparently derived by addition of 3 mols. of the anhydride. The compound, m. p. 235.5°, is probably obtained by addition in the  $\alpha\delta$  and  $\tau\kappa$  positions. When dehydrogenated and decarboxylated it gives a hydrocarbon, m. p. 302–303°, identical with that obtained by dehydrogenation of di-*p*-diphenylethane, and hence regarded as di-*p*-diphenylethylene.  $\alpha\kappa$ -Diphenyldecapentaene is partly regenerated when its additive compound with maleic anhydride is heated in a vacuum.

$\alpha\mu$ -Diphenyldodecahexaene reacts smoothly with maleic anhydride in boiling tetrahydronaphthalene, but examination of the product is rendered difficult by its sparing solubility in organic media. Its simultaneous dehydrogenation and decarboxylation leads to a hydrocarbon analyses of which agree with the formula  $Ph\cdot[C_6H_5]_2\cdot Ph$ , whereas the m. p. 326° indicates that it possibly has not entirely the linear structure.

$\alpha\gamma$ -Diphenyltetradecaheptaene resembles the hexaene in its behaviour towards maleic anhydride, but a homogeneous product of the reaction has not yet been isolated.

H. WREN.

**Perylene and its derivatives.** XXXI. A. PONGRATZ (Monatsh., 1930, 56, 163–178).—Various diaroylperylene are prepared by the Friedel-Crafts reaction and derivatives of perylene-3:9-dicarboxylic acid are described.

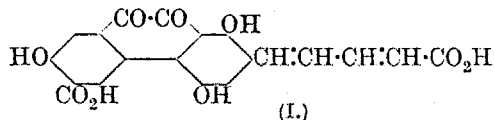
[With A. HALABARDA.]—Perylene reacts with *m*- and *p*-toluoyl chlorides in presence of aluminium chloride, forming di-*m*- and di-*p*-toluoylperylene, m. p. 248–250° and 340–341°, respectively. Neither of these derivatives nor the corresponding di-*o*-toluoyl analogue is identical with the compound obtained from toluene and perylene-3:9-dicarboxyl chloride (A., 1929, 929). The diaroylperylene prepared from the last-named chloride and *o*-, *m*-, and *p*-xylenes, anthracene, and phenanthrene have m. p. 270–273°, 262–264°, 247–249°, above 360°, and above 360°, respectively. Oxidation of perylene-3:9-dicarboxylanilide with lead peroxide in nitrobenzene affords

a compound,  $C_{34}H_{20}O_2N_2$ , probably the oxazole  $NHPh\cdot CO\cdot C_{20}H_{10}\cdot C\begin{smallmatrix} \diagup N \\ \diagdown O \end{smallmatrix} C_6H_4$ . The corresponding *o*-chloroanilide, m. p. 342–345°, is oxidised similarly to a substance,  $C_{34}H_{16}O_4N_2Cl$ , whilst the *methylanilide*, m. p. 270–272°, is unaffected, thus indicating that oxidation proceeds by way of the enol form of the anilides. The *amide* from perylene-3:9-dicarboxyl chloride and 2-aminoanthraquinone dyes cotton (alkaline vat) golden-yellow.

Bromination of perylene-3:9-dicarboxylic acid in the solid state or in boiling nitrobenzene furnishes a *bromo*-derivative, whilst in sulphuric acid a *tetra*-*bromo*-derivative results. Bromination of the acid chloride takes place in the solid state, but crystallisation of the resultant product from benzoyl chloride regenerates the initial chloride. Ethyl perylene-3:9-dicarboxylate, m. p. 275–276° (cf. A., 1927, 1190), from the chloride and alcohol, is brominated to a *dibromo*-derivative, m. p. 248–250°, which when heated with aniline regenerates the original ester.

H. BURTON.

**Fungus dyes. IX. Constitution of thelephoric acid.** F. KÖGL, H. ERLEBEN, and L. JÄNECKE (Annalen, 1930, 482, 105–119; cf. this vol., 606).—Triacetylthelephoric acid, decomp. 330° without melting, is reduced by distillation with zinc dust to an unsaturated hydrocarbon,  $C_{18}H_{14}$ , m. p. 125°, oxidised by permanganate to phenanthrene-2-carboxylic acid (Werner, A., 1902, i, 437) and therefore a 7-phenanthrylbutadiene. Thelephoric acid is oxidised by hydrogen peroxide to hydroxytrimellitic acid, m. p. 240–241° (decomp.); this and adipic acid are similarly obtained from hexahydrothelephoric acid. Oxidation of the triacetyl-acid with chromic and acetic acids, followed by deacetylation of the product, gives only a trace of hydroxytrimellitic acid and 4:3':6'-trihydroxydiphenyl-3:6:2':4'-tetra-carboxylic acid, m. p. 290°, decarboxylated to 4:3':6'-trihydroxydiphenyl, m. p. 234°. Formula I is therefore assigned to thelephoric acid, and is confirmed by the



formation of a colourless *penta*-acetyl-leuco-derivative by reduction with zinc dust and acetic anhydride, and a *heptamethylhexahydro*-derivative, m. p. 246°, by catalytic hydrogenation, followed by methylation.

The orientation of the trihydroxydiphenyl follows from its oxidation to *p*-hydroxybenzoic acid, and its synthesis by reduction and demethylation of *p*-methoxyphenylbenzoquinone, m. p. 110° (from *p*-methoxydiazobenzene and benzoquinone; cf. I.G. Farbenind., U.S.P. 1,735,432) with hydriodic acid. Hydroxytrimellitic acid was synthesised for comparison by oxidation of *p*-cumenesulphonic acid with alkaline permanganate, and fusion of the crude sulphobenzenetricarboxylic acid with alkali at 150–160°.

H. A. PIGGOTT.

**Manufacture of arylaminophenolcarboxylic [arylamino-salicylic] acids.** I. G. FARBENIND. A.-G.—See B., 1930, 1016.

**Manufacture of derivatives of naphthalene [acylnaphthalenes and 4-substituted  $\alpha$ -naphthoic acids].** I. G. FARBERIND. A.-G.—See B., 1930, 1017.

**Oxidation of benzaldehyde.** E. RAYMOND (Compt. rend., 1930, 191, 616—618).—Pure benzaldehyde when shaken with oxygen in a quartz tube is not oxidised unless illuminated; oxidation is energetic in presence of traces of salts of peroxidisable metals (especially manganese). On prolonged exposure to light or when heated, the aldehyde becomes progressively less oxidisable owing to formation of stilbene (the anti-catalytic activity of which is common to ethylenic compounds) and of perbenzoic acid (cf. Jorissen and Beek, A., 1926, 519; 1928, 413), the reaction velocity decreasing according to the equation  $t^{1/3}$ .  $dv/dt = k$  ( $k = 4$  per c.c. of aldehyde, time expressed in min.). The initial reaction velocity is related to the concentration,  $c$ , of anticatalyst by the equation  $u = e^{-kc}$  and thus follows the law deduced by Perrin (A., 1924, ii, 713) relating the fluorescing power of a solution and concentration.

Metallic salts are converted immediately by perbenzoic acid into per-salts, which at once oxidise the aldehyde; since the rapidity of oxidation is proportional to the conductivity of the solution (for a given amount of catalyst) it appears that oxidation is induced by metallic ions and that the removal of perbenzoic acid as formed (by the mechanism described above) allows the oxidation to proceed at a higher rate (cf. also Reiff, A., 1927, 57; Brunner, *ibid.*, 1152; Bäckström, *ibid.*, 737, 1151).

R. CHILD.

**Chloroimines. II. Negatively-substituted aromatic *N*-chloroaldimines.** C. R. HAUSER, M. L. HAUSER, and A. GILLASPIE (J. Amer. Chem. Soc., 1930, 52, 4158—4163).—Arylidenechloroimines are prepared, usually in good yields, when an ethereal solution of the aldehyde is shaken with a cold aqueous solution of monochloroamine (cf. this vol., 916). The following are described: *p*-peronylidene-, m. p. 68—69° (at 72—77°, solid is precipitated; when this is drained on porous earthenware and then crystallised from cold aqueous acetone, pure chloroimine is obtained); *o*-nitrobenzylidene-, m. p. 74—75°, decomp. 84—85°; *o*-methoxybenzylidene-, m. p. 35—36°, decomp. 83—85°; *m*-nitrobenzylidene-, m. p. 79—80° (precipitation occurs at 81—83°); *p*-chlorobenzylidene-, melts at 79—80°, becomes turbid at 90—95°, and re-solidifies at 100—127°; *p*-bromobenzylidene-, melts at 87—88°, becomes turbid at 90—95°, and precipitates at 95—103°, and 2-chloro-5-nitrobenzylidene-chloroimine, m. p. 85—86°, decomp. 110—115°. The rates of decomposition of the chloroimines at 30° indicate that the first three of the above and anisylidenechloroimine, decomp. 60—70° (cf. *loc. cit.*), are less stable than the halogenobenzylidenechloroimines. Decomposition of the chloroimine is, in many cases, catalysed by small amounts of impurities. *o*-Chlorobenzylidenechloroimine (*loc. cit.*) decomposes at 110—118°.

H. BURTON.

**Constitution of cyclanones. III. Abnormal condensation of dihydrocamphorone and benzaldehyde.** R. CORNUBERT and C. BORREL (Bull.

Soc. chim., 1930, [iv], 47, 958—966).—Methylation of 2-isopropylcyclopentanone with methyl iodide in presence of sodamide gives 2-methyl-2-isopropylcyclopentanone, b. p. 97.5°/45 mm.,  $d_{25}^{25}$  0.9067,  $n_D^{25}$  1.4495 (semicarbazone, m. p. 170—172°), separated from unaltered 2-isopropylcyclopentanone by fractionation of the semicarbazones. With benzaldehyde in presence of hydrogen chloride at —15° 2-methyl-2-isopropylcyclopentanone gives a benzylidene derivative, m. p. 61°, b. p. 208—209°/27 mm., which is not identical with the derivative, m. p. 61.5°, b. p. 154°/10 mm., obtained from dihydrocamphorone (5-methyl-2-isopropylcyclopentanone). Since the wide difference in the physical constants makes stereoisomerism improbable and conversion of the cyclopentanone ring in dihydrocamphorone into a cyclohexane ring is also improbable (cf. this vol., 347, 776), it is suggested that the benzylidene group has entered the  $\omega$ - or 3- or 4-position. By agitating for 10 hrs. only and omitting the ether extraction in Vavon and Apchié's method (A., 1928, 1000) 2-isopropylidenecyclopentanone, b. p. 80—82°/12 mm., can be prepared from cyclopentanone and acetone in three days instead of seven. Hydrogenation in alcoholic solution in presence of nickel formate at 60° gives 2-isopropylcyclopentanone, b. p. 86°/40 mm.,  $d_{25}^{25}$  0.9044,  $n_D^{25}$  1.4451. With benzaldehyde in presence of hydrogen chloride at —15° the latter yields only viscous products, including a fraction, b. p. above 250°/15 mm.

R. BRIGHTMAN.

**Three-carbon system. XXV. Effect of the methyl group on the tautomerism of acids and ketones of the cyclopentane and cyclohexane series.** G. A. R. KON and R. S. THAKUR (J.C.S., 1930, 2217—2231).—The effects of a methyl group substituted in the  $\alpha$ -, 2-, 3-, and 4-positions in the tautomeric systems cyclohexylidenecetic acid  $\rightleftharpoons$  cyclohexenylacetic acid and cyclohexylidenecetone  $\rightleftharpoons$  cyclohexenylacetone, and those due to an  $\alpha$ -methyl group in the systems cyclopentylidenecetic acid  $\rightleftharpoons$  cyclopentenylacetic acid and cyclopentylidenecetone  $\rightleftharpoons$  cyclopentenylacetone have been studied. Mobilities and equilibria were determined essentially by the methods of Linstead and others (A., 1927, 1167; 1928, 1214; 1929, 927). Introduction of a methyl group into the  $\alpha$ -positions of both acid systems causes a marked shift in the equilibrium towards the  $\alpha\beta$ -form, and a strong retardation of the mobility. With an  $\alpha$ -methyl group in both ketone systems, the equilibrium is displaced towards the  $\beta\gamma$ -phase; the effect on the mobility is not so marked. Nuclear methylation causes a slight shift towards the  $\beta\gamma$ -side in the case of the cyclohexane acids in the order 4>3>2; a slight retarding effect on the mobility is observed. In the cyclohexane ketone system, introduction of a methyl group into the 2-position stabilises the  $\beta\gamma$ -form to the almost complete exclusion of the  $\alpha\beta$ ; methyl groups in the 3- and 4-positions do not exert a pronounced effect. The following acids and ketones, prepared by methods already recorded, are investigated (the percentages and figures given in parentheses for the  $\alpha\beta$ -compounds are the proportion of this isomeride at equilibrium and the mobility, respectively):  $\alpha$ -cyclohexylidenepropionic acid (32%; 0.0075) (anilide, m. p. 126°; *p*-toluidide, m. p. 161°);

$\alpha$ - $\Delta^1$ -cyclohexenylpropionic acid, b. p. 120—124°/1 mm., m. p. 38°,  $d_4^{20}$  (supercooled) 1.0332,  $n_D^{20}$  1.48405 {anilide, m. p. 123—124° [the m. p. 56° given by Kandiah and Linstead (A., 1929, 1294) is an error]; p-toluidide, m. p. 108°}; 2-methylcyclohexylideneacetic acid, m. p. 68.5° (11.5%; 0.15) (amide, m. p. 112°; anilide, m. p. 99°); 2-methyl- $\Delta^1$ -cyclohexenylacetic acid (amide, m. p. 138°; anilide, m. p. 143°) is oxidised by alkaline potassium permanganate forming adipic acid; 3-methylcyclohexylideneacetic acid, m. p. 90° (9%; 0.27) (amide, m. p. 143—144°; p-toluidide, m. p. 136°); 3-methyl- $\Delta^6$ -cyclohexenylacetic acid (?), b. p. 126°/2 mm., m. p. 38°, oxidised by potassium permanganate to a small amount of probably  $\beta$ -methyladipic acid; 4-methylcyclohexylideneacetic acid (7%; 0.42) (p-toluidide, m. p. 119°); 4-methyl- $\Delta^1$ -cyclohexenylacetic acid (p-toluidide, m. p. 111°);  $\alpha$ -cyclopentylidenepropionic acid (38%; 0.58);  $\alpha$ - $\Delta^1$ -cyclopentenylpropionic acid, b. p. 113—115°/1 mm.,  $d_4^{20}$  1.0366,  $n_D^{20}$  1.47497;  $\alpha$ -methyl- $\Delta^1$ -cyclohexenylacetone ( $\alpha$ - $\Delta^1$ -cyclohexenylethyl methyl ketone), also isolated from attempted preparations of the isomeric  $\alpha$ -cyclohexylidene-ethyl methyl ketone; 2-methyl- $\Delta^1$ -cyclohexenylacetone [semicarbazone, m. p. 168° (lit. 173—174°)], prepared from zinc methyl iodide and 2-methyl- $\Delta^1$ -cyclohexenylacetyl or 2-methylcyclohexylideneacetyl chloride; 3-methylcyclohexylideneacetone (25%; —), b. p. 91—93°/6—7 mm.,  $d_4^{20}$  0.9235,  $n_D^{20}$  1.48571, when regenerated from its semicarbazone, m. p. 191°, is prepared from zinc methyl iodide and 3-methylcyclohexylideneacetyl chloride; 3-methyl- $\Delta^1$ -cyclohexenylacetone, b. p. 86—88°/7—8 mm.,  $d_4^{20}$  0.9200,  $n_D^{20}$  1.46986, when regenerated from its semicarbazone, m. p. 153—154° (lit. 150°); 4-methylcyclohexylideneacetone (13.5%; 600—700), b. p. 94°/9 mm.,  $d_4^{20}$  0.92694,  $n_D^{20}$  1.48594 (semicarbazones, m. p. 145° and 176—177°); 4-methylcyclohexenylacetone, b. p. 85°/8 mm.,  $d_4^{20}$  0.9178,  $n_D^{20}$  1.46836;  $\alpha$ -methylcyclopentylideneacetone (64%; 3000), b. p. 95.5—96°/11 mm.,  $d_4^{20}$  0.9601,  $n_D^{20}$  1.49737 (cf. Bardhan, A., 1928, 1243);  $\alpha$ -methyl- $\Delta^1$ -cyclopentenylacetone, b. p. 74°/10 mm.,  $d_4^{20}$  0.9216,  $n_D^{20}$  1.4635.

Prolonged interaction of the last-named ketone (equilibrium mixture used) with ethyl sodiomalonate and hydrolysis of the resulting product give cyclopentanespiro-2-methylcyclohexane-3:5-dione, m. p. 118—119° (cf. Bardhan, loc. cit.). 3- and 4-Methylcyclohexanespirocyclohexane-3:5-diones, m. p. 135—136° and 168°, respectively, are obtained similarly from 3- and 4-methyl- $\Delta^1$ -cyclohexenylacetones, respectively. 2-Methyl- $\Delta^1$ -cyclohexenylacetone and ethyl sodiomalonate afford a small amount of ethyl 2-methylcyclohexanespirocyclohexane-3:5-dione-6-carboxylate, m. p. 134°.

H. BURTON.

**Constitution of certain compounds formed by the action of alcoholic hydrochloric acid on unsaturated ketones.** B. COFFEY and H. RYAN (Proc. Roy. Irish Acad., 1930, 39, B, 434—439).—The dimeric form of styryl methyl ketone (this vol., 344) yields with hydroxylamine hydrochloride and sodium acetate a monoxime, m. p. 242—243°. This substance does not react further with hydroxylamine hydrochloride, and is hydrolysed by acids to the

original dimeric ketone. Treatment of the monoxime in boiling benzene solution with phosphorus pentoxide affords an isomeric compound, m. p. 249°. This substance reacts with neither bromine nor hydroxylamine hydrochloride and, on acid hydrolysis, does not yield the dimeric ketone; the constitution  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NHEt}$  is suggested.

T. H. MORTON.

**Nuclear synthesis of ketimines and ketones by condensation of nitriles with aromatic and heterocyclic compounds. II. Syntheses with toluene, mesitylene, tetrahydronaphthalene, phenol, 1:4:5-xylene, 3:5-dimethylanisole, thymol, and carvacrol.** J. Houben and W. Fischer (Ber., 1930, 63, [B], 2455—2463; cf. this vol., 89).—Improvements, particularly in the isolation of the ketimines, are frequently effected by decomposing the reaction products (loc. cit.) with alkali hydroxide in place of acid or by using so much crushed ice that a very marked fall in temperature is produced. In this manner p-tolyl trichloromethyl ketimine, b. p. 158°/23 mm. (hydrochloride), is obtained in 86% purity. Trichloroacetimidomesitylene (loc. cit.) is transformed by protracted ebullition with 25% hydrochloric acid into trichloroacetylmesitylene, b. p. 148—149°/10 mm., converted by boiling 40% sodium hydroxide into mesitylenecarboxylic acid, m. p. 150—152°. 1:2:3:4-Tetrahydronaphthalene is converted by aluminium chloride, hydrogen chloride, and trichloroacetonitrile in presence of chlorobenzene into a mixture of 1:2:3:4-tetrahydronaphthyl trichloromethyl 5- or 6-ketimine hydrochlorides, converted by preservation over potassium hydroxide and lime into 1:2:3:4-tetrahydronaphthalene-6-carboxylic acid, m. p. 149—151°, and 5-cyano-1:2:3:4-tetrahydronaphthalene. 1:2:3:4-Tetrahydronaphthyl trichloromethyl 6-ketone, b. p. 170—180°/2 mm., appears to be the main component of a ketonic mixture produced simultaneously. p-Hydroxyphenyl trichloromethyl ketimine hydrochloride is isolated by the "alkaline" treatment of the corresponding reaction product (loc. cit.). 4-Hydroxy-2:5-dimethylphenyl trichloromethyl ketone, m. p. 85—86° [corresponding ketimine, m. p. 170—171° (decomp.)], and its hydrochloride, m. p. about 185° (decomp.), is quantitatively transformed by boiling sodium hydroxide into 4-hydroxy-2:4-dimethylbenzoic acid, m. p. 182—184°. 3:5-Dimethylanisole yields a mixture of ketimine hydrochlorides, slowly transformed by boiling 20% hydrochloric acid into a mixture of 2- and 4-trichloroacetyl-3:5-dimethylanisoles, b. p. 168—170°/11 mm., from which 2-methoxy-4:6-dimethylbenzoic acid, m. p. 163—167°, is obtained (cf. von Auwers and Sauerwein, A., 1922, i, 1032). Partial condensation is thus shown to have taken place in the ortho-position to the methoxyl group and consequently also in the para-position. From thymol are derived 4-hydroxy-2-methyl-5-isopropylphenyl trichloromethyl ketone, m. p. 99—100° (whence p-thymotic acid, m. p. 154—157°), the corresponding ketimine, m. p. 115—117°, and its hydrochloride, m. p. about 170—175° (decomp.). Carvacrol affords 4-hydroxy-5-methyl-2-isopropylphenyl trichloromethyl ketimine hydrochloride, m. p. (indef.)

180—190° (decomp.); the corresponding ketimine and ketone could not be purified, but the latter affords 4-hydroxy-5-methyl-2-isopropylbenzoic acid, m. p. 161—164°.  
H. WREN.

**Preparation of cyclic nitriles by catalytic degradation.** I. J. HOUBEN and W. FISCHER (Ber., 1930, 63, [B], 2464—2472).—Aryl trichloromethyl ketimines are smoothly decomposed by aqueous or alcoholic alkali hydroxide or, preferably, by dry, powdered alkali hydroxide in presence of ether into cyclic nitriles and chloroform,  $R \cdot C(NH) \cdot CCl_3 \rightarrow R \cdot CN + CHCl_3$ . The catalytic function of the alkali hydroxide is established. The isolation of the ketimine is not essential. The crude condensation product from aryl derivative, trichloroacetonitrile, aluminium chloride, and hydrogen chloride may be used. Any ketone present in it becomes transformed into the corresponding acid, which is readily separated from the nitrile. The process has been applied to toluene, *m*- and *p*-xylene, mesitylene, 1:2:3:4-tetrahydronaphthalene, *p*-xylene, 3:5-dimethylanisole, thymol, and carvacrol. The following data are recorded: 2:4-dimethylbenzonitrile, m. p. 24—25°; 2:5-dimethylbenzonitrile, m. p. 6° after softening at -3°; 5-cyano-1:2:3:4-tetrahydronaphthalene, m. p. 48—50°; 4-hydroxy-2:5-dimethylbenzonitrile, m. p. 163—165°; 4-methoxy-2:6-dimethylbenzonitrile, m. p. 85—87°, and an (?) isomeric nitrile, m. p. about 49—55°; *p*-thymonitrile, m. p. 115—116° (sodium salt); 4-hydroxy-3-methyl-6-isopropylbenzonitrile, m. p. 75—77°.  
H. WREN.

**Occurrence of free disubstituted methyl radicals in chemical reactions.** E. BERGMANN and S. FUJISE (Annalen, 1930, 483, 65—80).—Prolonged exposure of a mixture of benzophenone and di-*p*-tolylmethane to sunlight in quartz vessels results in the formation of benzopinacol, also formed from *pp'*-tetramethyldiaminodiphenylmethane and benzophenone in dioxan solution. Phenyl diphenyl ketone and *pp'*-tetramethyldiaminodiphenylmethane in benzene in an atmosphere of nitrogen give a 4:4'-diphenylbenzopinacol, m. p. 212° (cf. Gomberg and Bachmann, A., 1927, 245). Benzophenone and di-*p*-anisylmethane in presence of a little benzene give, after 9 weeks' exposure, a mixture of benzopinacol, *s*-tetra-*p*-anisylethane, m. p. 189—190°, and  $\alpha$ -di-phenyl- $\beta$ -*p*-anisylethyl alcohol, m. p. 182—183° (dehydrated by boiling acetyl chloride to  $\alpha$ -diphenyl- $\beta$ -*p*-anisylethylene, m. p. 154—155°). The production of these compounds is readily explained by the intermediate formation of the radicals  $\dot{C}H(C_6H_4 \cdot OMe)_2$  and  $\dot{C}Ph_2 \cdot OH$ , which either add or dimerise. Benzophenone and benzhydryl methyl ether give, after 3 months, a mixture of benzopinacol and benzopinacol dimethyl ether, m. p. 157—159°. Benzopinacol monomethyl ether, m. p. 127—128°, is not formed, but is synthesised from magnesium phenyl bromide and methyl  $\alpha$ -methoxydiphenylacetate, b. p. 199—200°/27 mm. The last-named compound is produced when  $\alpha$ -bromodiphenylacetyl bromide is boiled with methyl alcohol. Di-*p*-anisylmethyl methyl ether, b. p. 218—219°/15 mm., m. p. 35—37°, undergoes very slow scission when treated with sodium.

When *s*-tetrabenzylidimethyl disulphide is heated with copper-bronze (cf. Manchot and Krische, A., 1905, i, 142), a mixture of  $\alpha$ -diphenyl-propane and -propene is produced; the intermediate free radical (dibenzylmethyl) undergoes disproportionation into  $\alpha$ -diphenylpropane and dibenzylmethylene. The last-named radical is rendered stable by the migration of a hydrogen atom, whereby the propene results. Distillation of the reaction product (di- $\alpha$ -phenylethyl disulphide) from acetophenone and ammonium sulphide (cf. Manchot and Krische, *loc. cit.*) furnishes styrene and ethylbenzene; a small amount of di- $\alpha$ -phenylethyl sulphone (?), m. p. 167—169°, is also formed. These results are explained by disproportionation of free  $\alpha$ -phenylethyl radicals. When 9:9'-difluorenyl disulphide is heated with copper-bronze over a free flame in an atmosphere of nitrogen, fluorene, diphenylenephenanthrene (Klinger and Lonnes, A., 1896, i, 691), and a small amount of  $\alpha$ - $\beta$ -di(diphenylene)-ethane are produced. The 9-methylenefluorene described by Manchot and Krische (*loc. cit.*) is impure fluorene.  
H. BURTON.

**Double linking. III. Aromatic thioketones, in particular, their reaction with diazomethane.** E. BERGMANN, M. MAGAT, and D. WAGENBERG (Ber., 1930, 63, [B], 2576—2584).—Reasons and analyses are cited from the literature in favour of the view that the colour of aromatic thioketones is caused by their existence, wholly or in part, not in the ethylenic form, but in the di-radical state,  $Ar_2C \cdot S \cdot C \cdot Ar_2 \rightleftharpoons Ar_2C \cdot S \cdot C \cdot Ar_2$ , and the following experimental evidence has been adduced.

Contrary to the behaviour of ketones, reduction of thioketones acts initially at the carbon atoms. Thus alcoholic ammonium hydrogen sulphide transforms thiobenzophenone, 4:4'-dimethoxythiobenzophenone, and 4:4'-tetramethyldiaminothiobenzophenone into dibenzhydryl disulphide, m. p. 152°, tetra-*p*-methoxydibenzhydryl disulphide, m. p. 128°, and tetra-*p*-dimethylaminodibenzhydryl disulphide, m. p. 164—165°.

Analogously to the conversion of triphenylmethyl by diazomethane into  $\alpha\alpha\alpha\gamma\gamma\gamma$ -hexaphenylpropane, 4:4'-dimethoxythiobenzophenone is readily transformed by ethereal diazomethane into 4:4':5:5'-tetra-*p*-anisyl-R-trimethylene 1:3-disulphide,  $CH_2 \begin{smallmatrix} S \cdot C(C_6H_4 \cdot OMe)_2 \\ S \cdot C(C_6H_4 \cdot OMe)_2 \end{smallmatrix}$ , m. p. 161—162° to a blue liquid, reduced by zinc and hydrochloric acid in glacial acetic acid to tetra-*p*-anisylethylene, m. p. 177° (probably containing tetra-*p*-anisylethane), identical with the compound derived from 4:4'-dimethoxythiobenzophenone and copper powder. Analogously, thiobenzophenone and xanthione afford 4:4':5:5'-tetraphenyl-R-trimethylene 1:3-disulphide, m. p. 166—167° to a dark blue liquid, and 4:5-dixanthylene-R-trimethylene 1:3-disulphide, m. p. 224°. Michler's thioketone yields a compound, m. p. 144° after slight softening.

The authors do not share Meerwein's views (A., 1929, 681) that the differing behaviour of aromatic ketones and thioketones towards diazomethane is a consequence of difference in dipole moment, since 2:3-diphenylindone does not react with diazomethane, although its dipole moment is greater than that customarily observed with ketones.  
H. WREN.



**Action of sodium diphenylmethyl on aromatic ketones and thioketones.** E. BERGMANN and D. WAGENBERG (Ber., 1930, 63, [B], 2585—2592).—In contrast to their behaviour with Grignard's reagents (cf. Schönberg, A., 1927, 667), aromatic thioketones react with sodium diphenylmethyl in the same manner as ketones, yielding tertiary thioalcohols which readily lose hydrogen sulphide with formation of the corresponding ethylenes. Sodium diphenylmethyl and di-*p*-tolyl ketone yield  $\beta\beta$ -diphenyl- $\alpha$ -di-*p*-tolylethanol, m. p. 155—156°, transformed by boiling acetyl chloride into  $\beta\beta$ -diphenyl- $\alpha$ -di-*p*-tolylethylene, m. p. 161° (a modified method for the preparation of di-*p*-tolyl ketone is given). Similarly, 4:4'-dimethoxybenzophenone is converted successively into  $\beta\beta$ -diphenyl- $\alpha$ -di-*p*-anisylethanol, m. p. 183°, and  $\beta\beta$ -diphenyl- $\alpha$ -di-*p*-anisylethylene, m. p. 155°. Thio-benzophenone affords  $\alpha\beta\beta$ -tetraphenylethanthiol, m. p. 167—168° to a blue liquid, readily transformed into tetraphenylethylene, m. p. 220°.  $\beta\beta$ -Diphenyl- $\alpha$ -di-*p*-anisylethanthiol, m. p. 155°,  $\beta\beta$ -diphenyl- $\alpha$ -di-*p*-anisylethylene, m. p. 155°, and  $\beta\beta$ -diphenyl- $\alpha$ -xanthylene-ethanthiol, m. p. 159°, are described. Michler's thioketone gives  $\beta\beta'$ -diphenyl- $\alpha$ -di-*p*-dimethylamino-phenylethylene, m. p. 214.5°, in place of the expected thiol. When melted, the thiols become converted into diphenylmethane and the thioketone. They cannot be converted into the corresponding methyl sulphides by the action of diazomethane (which reacts smoothly with benzyl mercaptan) or of potassium and methyl iodide. Characteristic derivatives of the ethanols are obtained from the crude sodium compounds. Thus the sodium compound of  $\alpha\beta\beta$ -tetraphenylethanol is converted by phenylthiocarbimide into tetraphenylethylene, whereas phenylcarbimide affords the *phenylurethane*,  $\text{CHPh}_2\cdot\text{CPh}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 163—165° (decomp.); with less than 1 mol. of benzoyl chloride the benzoate,  $\text{CHPh}_2\cdot\text{CPh}_2\cdot\text{OBz}$ , m. p. 155° and about 210° after re-solidifying at about 180°, is produced, whereas tetraphenylethylene results when an excess of the reagent is used.

Addition of sodium diphenylmethyl to di- $\delta$ -phenyl- $\Delta^{\alpha\gamma}$ -butadienyl ketone appears to occur in the 1:4-position with production of  $\alpha$ -diphenyl- $\gamma$ -benzhydryl- $\Delta^{\alpha\delta}$ -nonatrien- $\epsilon$ -one, m. p. 145—146°, in which the presence of three double linkings is established. Under similar conditions, distyryl ketone affords a saturated, hydroxyl-free substance, m. p. 170—172°, regarded as 3:4:4:5-tetraphenylcyclohexanone. H. WREN.

#### Degradation of quaternary ammonium salts.

III. T. S. STEVENS, W. W. SNEDDEN, E. T. STILLER, and T. THOMSON (J.C.S., 1930, 2119—2125; cf. this vol., 1437).—The rearrangement,  $\text{CH}_2\text{R}\cdot\text{NMe}_3\cdot\text{X}\cdot\text{R}' \rightarrow \text{CHR}(\text{NMe}_3)\text{R}'$ , under the influence of alkali occurs readily when  $\text{R}=\text{COMe}$  and  $\text{R}'=\text{CH}_2\text{Ph}$ , and also when  $\text{R}=\text{COPh}$  and  $\text{R}'=\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Br}(p)$  or  $\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2(p)$ , but not when  $\text{R}=\text{CN}$  or  $\text{CO}_2\text{Et}$  and  $\text{R}'=\text{CH}_2\text{Ph}$ . *Acetonylbenzyltrimethylammonium chloride* (+1H<sub>2</sub>O), m. p. 75—77° (picrate, m. p. 141—143°), and *phenacyl-p-bromo-*, m. p. 193°, and *-p-nitro-*, m. p. 169—171°, *-benzyltrimethylammonium bromides*, prepared from the appropriate acyl halide and tertiary amine in benzene, undergo normal rearrangements when heated with alkali, giving  $\alpha$ -dimethylamino- $\alpha$ -

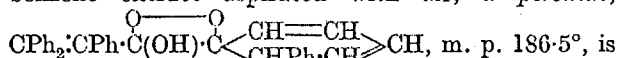
benzylacetone (*picrate*, m. p. 140—144°),  $\omega$ -dimethylamino- $\omega$ -*p*-bromobenzylacetophenone, m. p. 61° (*picrate*, m. p. 149—150°), and  $\omega$ -dimethylamino- $\omega$ -*p*-nitrobenzylacetophenone, m. p. 79—82° (*picrate*, m. p. 144—145°), accompanied in the last case by *p*-nitrotoluene and *pp'*-dinitrodibenzyl. The ketonic products are identified in each case by decomposition of their methosulphates with alkali, benzylacetone, phenyl *p*-bromostyryl and phenyl *p*-nitrostyryl ketones being formed. Benzyltrimethylamine readily unites with ethyl chloroacetate to form *carbethoxymethylbenzyltrimethylammonium chloride*, but with chloroacetonitrile in boiling benzene a dibenzyltrimethylammonium salt is formed, although in cold ether a non-crystalline cyanomethylbenzyltrimethylammonium chloride (*picrate*, m. p. 140—143°) may be obtained. These quaternary chlorides are merely hydrolysed by alkalis (*carboxymethylbenzyltrimethylammonium picrate*, m. p. 146—148°), and no degradation product could be isolated even under anhydrous conditions. *p*-Bromobenzyltrimethylamine (*hydrochloride*, m. p. 219—220°; *picrate*, m. p. 133—135°) may be prepared from *p*-bromobenzyl bromide by the hexamine method (cf. A., 1922, i, 333), but is obtained more readily, accompanied by a little di-*p*-bromobenzyltrimethylammonium salt (*picrate*, m. p. 165—167°) by condensation with dimethylamine. Interaction of benzyltrimethylamine with  $\omega$ -bromoacetophenone gives *phenacylbenzyltrimethylamine*, b. p. 195—205°/15 mm. (*picrate*, m. p. 137—138°). *Benzyl-p-bromobenzyltrimethylamine* has b. p. 194—196°/20 mm. Attempts at bromination and nitration of  $\omega$ -dimethylamino- $\omega$ -benzylacetophenone either gave unchanged material or led to complete decomposition.

H. A. PIGGOTT.

#### Reaction between highly-phenylated compounds and organic magnesium compounds.

E. P. KOHLER and E. M. NYGAARD (J. Amer. Chem. Soc., 1930, 52, 4128—4139).—Phenyl  $\alpha\beta\beta$ -triphenylethyl ketone, prepared from benzylidenedecybenzoin and magnesium phenyl bromide, reacts with ethereal magnesium methyl iodide, forming  $\beta$ -hydroxy- $\beta\gamma\delta\delta$ -tetraphenylbutane, m. p. 140°, dehydrated by treatment with acetic acid containing a small amount of sulphuric acid at the ordinary temperature to  $\beta\gamma\delta\delta$ -tetraphenyl- $\Delta^{\alpha}$ -butene, m. p. 104—106°. Treatment of this with ozonised oxygen in ethyl bromide gives phenyl  $\alpha\beta\beta$ -triphenylethyl ketone, which with magnesium phenyl bromide in ethereal benzene affords  $\alpha\beta\gamma\gamma$ -pentaphenylpropyl alcohol, m. p. 159°, oxidised by chromic and acetic acids to benzoic acid and benzophenone. Treatment of the additive compound from benzylidenedecybenzoin and magnesium phenyl bromide with bromine in cold ether furnishes  $\alpha$ -bromo- $\alpha$ -benzoyl- $\alpha\beta\beta$ -triphenylethane, which with potassium acetate in boiling alcohol yields  $\alpha$ -benzoyl- $\alpha\beta\beta$ -triphenylethylene. This reacts with magnesium methyl iodide only in benzene at 50°, forming  $\beta$ -hydroxy- $\beta\gamma\delta\delta$ -tetraphenyl- $\Delta^{\alpha}$ -butene, m. p. 96.5° [ozonolysis products, benzophenone and a peroxide,  $\text{C}_{28}\text{H}_{24}\text{O}_3$ , m. p. 148° (decomp.)], together with a small amount of 1:2:3-triphenyl-1-methylindene, m. p. 118°. The indene is also obtained when the alcohol is heated with acetic anhydride and sodium acetate. Oxidation of the indene with chromic and acetic acids at 50—60° gives

2- $\alpha$ -benzoyl- $\alpha$ -phenylethylbenzophenone, m. p. 182°, and oily products (oxidised further to 2-benzoylbenzophenone). When  $\alpha$ -benzoyl- $\alpha\beta$ -triphenylethylene is treated with an excess of magnesium phenyl bromide in ethereal benzene at 52°, the product decomposed with ice-cold hydrochloric acid, and the resultant ethereal benzene extract aspirated with air, a peroxide,



obtained (cf. A., 1906, i, 753). This arises by addition of two atoms of oxygen to the unsaturated compound formed by a 1 : 4-addition to the CO·Ph residue in the original unsaturated ketone. Treatment of the peroxide with methyl-alcoholic sodium methoxide at the ordinary temperature affords  $\alpha$ -o-phenylbenzoyl- $\alpha\beta$ -triphenylethylene, m. p. 138°, oxidised by ozonised oxygen in ethyl bromide to benzophenone and 2-phenylbenzil, m. p. 80° (quinoxaline derivative, m. p. 163°, from o-phenylenediamine). 2-Phenylbenzil is oxidised by alkaline hydrogen peroxide to diphenyl-2-carboxylic acid.  $\alpha$ -Hydroxy- $\alpha\beta\gamma\gamma$ -pentaphenyl- $\Delta^2$ -propylene, m. p. 169° (acetate, m. p. 218°), is also formed in relatively small amount in the above reaction; the acetate is best prepared by treating the mixture of  $\alpha$ -benzoyl- $\alpha\beta$ -triphenylethylene and magnesium phenyl bromide with acetyl chloride. H. BURTON.

**Mixed benzoin.** II. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1930, 52, 4107—4109).—The mixed benzoin, m. p. 144°, prepared by the method previously described (this vol., 345) from *p*-dimethylaminobenzaldehyde and anisaldehyde, is oxidised with Fehling's solution to 4-dimethylamino-4'-methoxybenzil, m. p. 128°, and reduced with tin and alcoholic hydrochloric acid containing a trace of copper sulphate to a deoxybenzoin, m. p. 130°. The following benzoin, deoxybenzoin, and benzils are prepared similarly from the appropriate pairs of aldehydes: 4-chloro-3' : 4'-methylenedioxybenzil, m. p. 132° (benzoin, m. p. 110°; deoxybenzoin, m. p. 113°); 2-chloro-4'-methoxybenzil, m. p. 104° (benzoin, m. p. 84°; deoxybenzoin, m. p. 96°); 2-chloro-3' : 4'-dimethoxybenzil, m. p. 117° (benzoin, m. p. 140°; deoxybenzoin, m. p. 110°); 3-chloro-4'-dimethylaminobenzil, m. p. 130° (benzoin, m. p. 140°; deoxybenzoin, m. p. 125°), and 3-bromo-4-methoxybenzil, m. p. 94° (benzoin, m. p. 88°; deoxybenzoin, m. p. 54°). H. BURTON.

**Configurations of the benzilmonoximes.** T. W. J. TAYLOR and M. C. MARKS (J.C.S., 1930, 2302—2307).— $\alpha$ -Benzilmonoxime, m. p. 140° (lit. 137—138°; improved method of preparation given), is converted into the  $\beta$ -oxime (+0.5C<sub>6</sub>H<sub>6</sub>), m. p. 62—63°, m. p. (benzene-free) 112° (lit. 113—114°), when a solution in benzene is heated with 0.1 part of animal charcoal. The pure  $\beta$ -oxime causes no colour change in an aqueous-alcoholic solution of copper acetate. The solubilities of the two oximes in benzene at various temperatures have been measured and the "nominal heats of solution" calculated (cf. Sidgwick and others, J.C.S., 1921, 119, 993; 1922, 121, 1853). The results indicate that the  $\alpha$ -oxime behaves as a hydroxylic solute, whereas the  $\beta$ -oxime does not. These observations support the structures previously

assigned (A., 1927, 58; cf. Meisenheimer and others, A., 1922, i, 152; 1924, i, 432, 433).

The suggested stereochemical change of the  $\alpha$ - into the  $\beta$ -structure during metallic derivative formation (*loc. cit.*) does not appear to occur, since the  $\alpha$ -oxime can be recovered from its copper derivative by treatment with cold, dilute sulphuric acid. The structure proposed by Pfeiffer and Richarz (A., 1928, 291) is more probable. H. BURTON.

**$\alpha$ -Aminoketones. I. Reduction of oximinodibenzoylmethane.** J. PASCUAL and L. REY (Anal. Fis. Quim., 1930, 28, 632—635).—The reduction of oximinodibenzoylmethane under anhydrous conditions with stannous chloride and hydrogen chloride in ether and acetic acid yields phenacylamine as the main product. Rupture of the carbon chain is avoided when reduction is carried out by shaking with stannous chloride in concentrated hydrochloric acid for 24 hrs., and, after removal of tin as sulphide,  $\beta$ -amino- $\alpha\gamma$ -diketo- $\alpha\gamma$ -diphenylpropane hydrochloride, m. p. 213° (corr., decomp.), is isolated in about 25% yield.  $\beta$ -Phthalimido- $\alpha\gamma$ -diketo- $\alpha\gamma$ -diphenylpropane, m. p. 208—209° (corr.), is obtained by condensation of potassium phthalimide with bromodibenzoylmethane in boiling benzene; in alcohol the main product is phenacylphthalimide. The  $\beta$ -phthalimido-compound is unaffected by boiling 20% hydrochloric acid, but is decomposed by cold sodium hydroxide solution, yielding probably a phenacylamine derivative, whilst concentrated hydrochloric acid at 200° gives 2 : 5-diphenylpyrazine among other products. R. K. CALLOW.

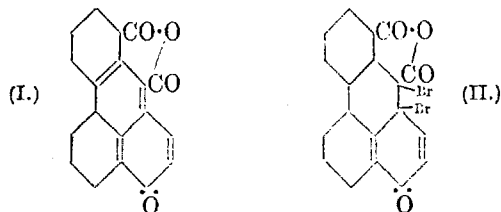
**Synthesis of compounds related to apocynin and apocynol.** H. P. HOWELLS, B. H. LITTLE, and H. P. ANDERSEN (J. Amer. Chem. Soc., 1930, 52, 4076—4082; cf. Finemore, J.C.S., 1908, 93, 1513).—Magnesium *n*-butyl iodide and vanillin benzoate afford 48% of the theoretical amount of 4-benzoyloxy-3-methoxyphenyl-*n*-butylcarbinol, m. p. 109.3° (all m. p. are corr.); the yield is not so good when the bromide is used. Oxidation of the above carbinol with potassium dichromate and dilute sulphuric acid in acetic acid solution gives 4-benzoyloxy-3-methoxyphenyl-*n*-butyl ketone, m. p. 88.1° (phenylhydrazone, m. p. 163°), hydrolysed by 10% alcoholic potassium hydroxide to 4-hydroxy-3-methoxyphenyl-*n*-butyl ketone, m. p. 62.9° (diphenylcarbamyl derivative, m. p. 121.5—123°). 4-Hydroxy-3-methoxyphenyl-*n*-butylcarbinol has m. p. 81.5°. Magnesium *n*-propyl iodide and vanillin benzoate give 31.5% of 4-benzoyloxy-3-methoxyphenyl-*n*-propylcarbinol, m. p. 111.3°, oxidised to 4-benzoyloxy-3-methoxyphenyl-*n*-propyl ketone, m. p. 79° (phenylhydrazone, m. p. 175.5°). 4-Benzoyloxy-3-methoxyphenyl-*n*-amylcarbinol (about 10% yield), m. p. 95.6°, is oxidised to 4-benzoyloxy-3-methoxyphenyl-*n*-amyl ketone (phenylhydrazone, m. p. 134.6°), which was not obtained in sufficient amount for complete identification. H. BURTON.

**2-Benzoylfluorene. Synthesis of 2 : 7-dibenzoylfluorene.** K. DZIEWOŃSKI and A. OBTULOWICZ (Bull. Acad. Polonaise, 1930, A, 399—406).—2-Benzoylfluorene (A., 1903, i, 177; 1905, i, 66) reacts with benzoyl chloride and aluminium chloride to give 2 : 7-dibenzoylfluorene, m. p. 193—194°

[*dioxime*, m. p. 235° (decomp.)], stable to hydrolysis by alcoholic alkali or acetic acid; its orientation is assumed by analogy. It is oxidised by sodium dichromate and acetic acid to 2:7-dibenzoylfluorenone, m. p. 211° (*diphenylhydrazone*, m. p. 142°), and reduced by Clemmensen's method to 2:7-dibenzoylfluorene, m. p. 125°. The following derivatives of 2-benzoylfluorene are prepared by standard methods, no orientation being assigned: 2-benzoylfluorene-sulphonic acid, m. p. 262° (sodium salt; aniline salt, m. p. 282°; chloride, m. p. 145°; amide, m. p. 228°); nitro-, m. p. 206°, and amino-2-benzoylfluorene, m. p. 155° (acetyl derivative, m. p. 217°); and nitro-2-benzoylfluorenone, m. p. 198—199°, by oxidation of the nitrofluorene.

H. A. PIGGOTT.

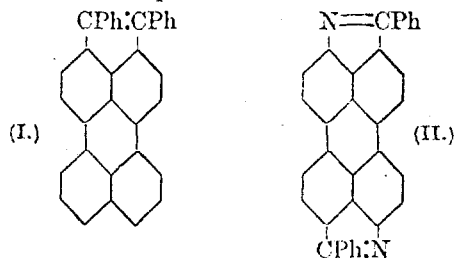
**Perylene and its derivatives. XXIX. Degradation of perylene to benzanthrone.** A. ZINKE and R. WENGER (*Monatsh.*, 1930, 56, 143—152).—Oxidation of perylene with 10% aqueous chromic acid affords in addition to perylene-3:10-quinone and anthraquinone-1:5-dicarboxylic acid (cf. this vol., 608), some 1:9-benzanthrone-(2)-5:10-dicarboxylic anhydride (I), also formed in small amount when the above quinone is oxidised with manganese dioxide and sulphuric acid. The anhydride is separated from the crude quinone by treatment with



hot 4% sodium hydroxide solution; the resultant solution is then acidified. Acidification at 2° gives the free dicarboxylic acid (calcium salt; methyl ester, m. p. 190—191° after sintering at 186°), which readily passes into I on crystallisation from nitrobenzene. When a solution of the acid in dilute aqueous ammonia is heated, a mixture of the ammonium salt and the corresponding imide is produced. Treatment of I with bromine in nitrobenzene suspension affords the dibromide (II) (corresponding dibromide from the free acid), which when dissolved in alkali and then precipitated, or crystallised several times from nitrobenzene, regenerates I. Zinc dust distillation of I furnishes impure 1:9-benzanthrone (Bally and Scholl, A., 1911, i, 677). Oxidation of this with chromic and acetic acids and removal of admixed anthraquinone by reduction with alkaline sodium hyposulphite affords 1:9-benzanthrone. H. BURTON.

**Perylene and its derivatives. XXX.** A. ZINKE and O. BENNDORF (*Monatsh.*, 1930, 56, 152—162).—Treatment of perylene with a large excess of benzoyl chloride in presence of aluminium chloride affords an appreciable amount of 3:4-dibenzoylperylenes, m. p. 329—330°, in addition to the 3:9-isomeride (Scholl, Seer, and Weitzenböck, A., 1910, i, 616); separation is effected by the sparing solubility of the former in boiling xylene. Reduction of the 3:4-derivative by Clemmensen's method gives 1:2-diphenylaceperylene (I), dark brownish-red with violet

reflex, m. p. 315—316°, whilst nitration with potassium nitrate and sulphuric acid in acetic acid affords



a dinitro-derivative. Similar nitration of 3:9-dibenzoylperylenes furnishes 4:10-dinitro-3:9-dibenzoylperylenes, reduced by alkaline sodium hyposulphite to the corresponding diamino-derivative (not isolated), which loses 2 mols. of water forming the pyrrole (II) (impure tetrabromide). Bromination of 3:4-dibenzoylperylenes in acetic acid containing iodine and a trace of ferric chloride gives an impure bromo-derivative, m. p. 326—330°. A dinitro-3:9-diacetylperylenes is also described.

[With W. BLANK.]—Magnesium methyl iodide and 3:9-dibenzoylperylenes afford 3:9-di-( $\alpha$ -hydroxy- $\alpha$ -methylbenzyl)perylenes, m. p. 277°, dehydrated to 3:9-di-( $\alpha$ -phenylvinyl)perylenes, yellow, m. p. 257—258°. The colour of this compound and the non-reducibility of 3:9-dibenzoylperylenes by Clemmensen's method support the structure I.

[With H. KOLMAYR.]—Perylene and chloroacetyl chloride react in presence of aluminium chloride and carbon disulphide forming 3:9-di(chloroacetyl)perylenes. H. BURTON.

**Preparation of methyl ethers of quinone-oximes.** S. VEIBEL and M. H. SIMESSEN (*Ber.*, 1930, 63, [B], 2476—2484).—Under suitable conditions, many nitrosophenols can be transformed in good yield into oxime ethers by the action of methyl sulphate or *p*-toluenesulphonate. Treatment of *p*-benzoquinone with *O*-methylhydroxylamine hydrochloride in alcohol at the ordinary temperature gives the monoxime methyl ether, m. p. 83.5°, in 59% yield. From *p*-nitrosophenol and methyl sulphate in very dilute alkaline solution the compound is prepared in 28% yield, whereas with methyl *p*-toluenesulphonate and sodium hydroxide in methyl alcohol the yield is 27%. Quinonechloroimide and magnesium in methyl alcohol give only traces of the monoxime methyl ether. From 4-nitroso-*o*-cresol the oxime ether  $\text{O}:\text{C}_6\text{H}_3\text{Me}:\text{N}:\text{OMe}$ , m. p. 74°, is derived in 20% and 26% yield by means of methyl sulphate and *p*-toluenesulphonate, respectively. Under similar conditions the yields of the ether  $\text{O}:\text{C}_6\text{H}_3\text{Me}:\text{N}:\text{OMe}$  from 6-nitroso-*m*-cresol are 39% and 42%. Nitrosation of *p*-xylenol and treatment of the product with methyl sulphate affords *p*-xyloquinoneoxime monomethyl ether, m. p. 70.5—71°, in 70% yield; the use of methyl *p*-toluenesulphonate leads to a less uniform product, whereas condensation of *p*-xyloquinone with *O*-methylhydroxylamine gives a difficultly-separable mixture of unchanged material and the mono- and di-oxime ethers. Nitrosocarvacrol is converted by methyl sulphate and sodium hydroxide into thymoquinoneoxime methyl ether,

$\text{O}:\text{C}_6\text{H}_2\text{MePr}^{\beta}:\text{N}:\text{OMe}$  (1:2:5:4), m. p. 38—38.5°, whereas nitrosothymol affords *thymoquinoneoxime methyl ether*,  $\text{O}:\text{C}_6\text{H}_2\text{MePr}^{\beta}:\text{N}:\text{OMe}$ , (4:2:5:1), b. p. 144—145°/18 mm., m. p. 35°. Condensation of thymoquinone with *O*-methylhydroxylamine gives a mixture of these compounds.

Nitrothymol is slowly converted by methyl sulphate into the corresponding *methyl ether*, m. p. 31.5°, b. p. 173°/16 mm.

H. WREN.

**Stereochemistry of diphenylbenzenes. Preparation of stereoisomeric 2:5-dibromo-3:6-di-*m*-4-xylylquinols and derivatives. IX.** E. BROWNING and R. ADAMS (J. Amer. Chem. Soc., 1930, 52, 4098—4107; cf. A., 1929, 1298).—*p*-Benzoquinone and *m*-xylene react in presence of aluminium chloride below 20° yielding 50% of the theoretical amount of 3:6-di-*m*-4-xylylquinol, m. p. 188—189°, which when brominated in chloroform solution at 40—50° affords two (*r*- and *meso*-) 2:5-dibromo-3:6-di-*m*-4-xylylquinols (I), m. p. 236—237°, and (II), m. p. 190—191°. The *diacetate*, m. p. 235—236°, of I gives with nitric acid (*d* 1.48) below −5°, 2:5-dibromo-3:6-di-(2:6-dinitro-*m*-4-xylyl)quinol *diacetate*, m. p. 305—306° (decomp.); the isomeric *tetranitro*-derivative from the *diacetate*, m. p. 193—194° after softening, of II has m. p. 282—283° (slight decomp.). Oxidation (cf. Pummerer and Huppmann, A., 1927, 770) affords the same 2:5-dibromo-3:6-di-*m*-4-xylyl-*p*-benzoquinone, m. p. 197—198°, which on reduction with stannous chloride and hydrochloric and acetic acids furnishes a mixture of I and II. The same quinone is also obtained when 3:6-di-*m*-4-xylyl-*p*-benzoquinone, m. p. 180° (prepared as above from the corresponding quinol), is brominated in chloroform. Application of X-ray data to the dibromoquinone suggest that the quinone oxygen atom and the methyl group of the xylene residue do not impede each other; free rotation of the rings is, therefore, possible. When II is heated at 220° in an atmosphere of nitrogen, a small amount of I is produced. Oxidation of I, II, or the dibromoquinone with alkaline hydrogen peroxide gives 2:4-dimethylbenzoic acid.

H. BURTON.

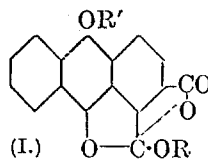
**Synthesis of trihydroxymethylanthraquinone derivatives. IV. Synthesis of 1:5:8-trihydroxy-2-methylanthraquinone.** S. KEIMATSU and I. HIRANO (J. Pharm. Soc. Japan, 1930, 50, 421—426).—The following compounds were prepared (from 3:6-dichlorophthalic anhydride and *o*-chlorotoluene): 3:5:8-, m. p. 261—261.5°, and 1:5:8-, m. p. 244.5—245°, -trichloro-2-methylanthraquinone; 2- $\omega$ -dibromomethyl-1:5:8-trichloroanthraquinone, m. p. 256—256.5°; 1:5:8-trichloroanthraquinone-2-aldehyde, decomp. 248°, and the corresponding carboxylic acid, decomp. 278—279°; 1:5:8-trichloroanthraquinone, m. p. 254°; 1:5:8-trimethoxy-2-methylanthraquinone, m. p. 206.5—207°; 1:5:8-trihydroxy-2-methylanthraquinone, m. p. 253—254° (triacetate, m. p. 215°).

CHEMICAL ABSTRACTS.

**Synthesis of trihydroxymethylanthraquinone. V. 1:5:8-Trihydroxy-4-methylanthraquinone.** S. KEIMATSU, I. HIRANO, and J. YOSHIMI (J. Pharm.

Soc. Japan, 1930, 50, 644—653).—5'-Methyl-2':3:6-trichlorobenzoylbenzoic acid, m. p. 199—200°, obtained in 84—97% yield by condensation of 3:6-dichlorophthalic anhydride and *p*-chlorotoluene in presence of aluminium chloride, when heated with fuming sulphuric acid for 3 hrs. gives 1:5:8-trichloro-4-methylanthraquinone, m. p. 330—331°, in 75—82% yield. This, when heated with sodium methoxide in a sealed tube for 6 hrs. at 160—180° affords 1:5:8-trimethoxy-4-methylanthraquinone, m. p. 249—250.5°; the *hydroxy*-compound has m. p. 278—278.5° and the *acetoxy*-compound m. p. 197°. 1:5:8-Trichloroanthraquinone-4-aldehyde, decomp. 317—318°; 4-carboxylic acid, decomp. 253—254°; 1:5:8-trichloroanthraquinone, m. p. 254°. CHEMICAL ABSTRACTS.

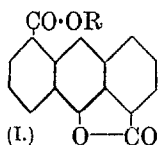
**Blue, carboxylated anthraquinol- $\alpha$ -carboxylactones (II) and the formation of dicyclic, condensed lactol- $\psi$ -carboxylic acids therefrom.** R. SCHOLL and O. BÖTTGER (Ber., 1930, 63, [B], 2432—2440; cf. this vol., 1439).—Treatment of anthraquinone-1:2-dicarboxylic acid with sodium hyposulphite in 4% sodium hydroxide at 40—50°, or in boiling glacial acetic acid affords  $\psi$ -anthraquinol-1:2-dicarboxylactone (I; R=R'=H), m. p. 290° (decomp.) after softening. The constitution follows from its close relationship to anthraquinone-1:2-dicarboxylic anhydride, from which it is obtained under conditions which preclude the rupture of the anhydride ring and into which it is readily converted by oxidation with ferric chloride in presence of glacial acetic acid, and from the similarity of its absorption spectrum with those of anthraquinol-1:4-dicarboxylactone and anthraquinol-1-carboxylactone. The lactol ring is very readily ruptured. The compound is present in anhydrous pyridine for a short time as a blue solution, but in aqueous pyridine or alcohol the colour changes almost immediately to red owing to the formation of anthraquinol-1:2-dicarboxylic anhydride. With sodium hyposulphite in cold and hot dilute sodium hydroxide it gives solutions identical with those obtained similarly from anthraquinone-1:2-dicarboxylic anhydride and the corresponding acid, respectively. In sodium carbonate solution it appears to be present as a mixture of the blue salts of the lactol anhydride and the red salts of the dicarboxylic anhydride. With aqueous ammonia at the ordinary temperature it gives a grey solution, becoming blue and then colourless when shaken with air, owing to the ultimate production of the acid



$\text{C}_6\text{H}_4(\text{CO})_2\cdot\text{C}_6\text{H}_2(\text{CO}\cdot\text{NH}_2)_2\cdot\text{CO}_2\text{H}$ . Short treatment of anthraquinone-1:2-dicarboxylic acid with sodium hyposulphite, glacial acetic acid, and acetic anhydride affords a *monoacetyl* derivative (I; R'=H, R=Ac), m. p. 255—256°, readily soluble in cold, dilute alkali hydroxide or ammonia. The *diacetyl* compound (I; R=R'=Ac), m. p. 284—285°, is prepared from the lactol, acetic anhydride, and anhydrous sodium acetate or by the prolonged action of sodium hyposulphite, glacial acetic acid, and much acetic anhydride on anthraquinone-1:2-dicarboxylic anhydride. It may be crystallised unchanged from boiling acetic

acid, thus excluding the possibility that it is a mixed acetic carboxylic anhydride. H. WREN.

**Behaviour of anthraquinonecarboxylic acids towards sodium hyposulphite; anthranol- $\alpha$ -carboxylactones.** R. SCHOLL and O. BÖTTGER [with J. HORN] (Ber., 1930, 63, [B], 2440—2446).—Anthraquinone-1:5-dicarboxylic acid is converted by boiling alkaline sodium hyposulphite and subsequent acidification into the anthranoldicarboxylic acid, transformed by boiling acetic anhydride into



the mixed lactone anhydride (I; R=Ac), decomp. above 285°. It is transformed by boiling 50% acetic anhydride into anthranol-1:5-dicarboxylactone (I; R=H), decomp. above 310°, which is hydrolysed by boiling 10% sodium hydroxide to anthranol-1:5-dicarboxylic acid, m. p. above 310° (decomp.) after softening.

Anthraquinone-1:4-dicarboxylic acid when similarly reduced and acetylated affords anthranol-1:4-dicarboxylactone,  $C_{15}H_8O_4$ , not molten below 325°, which is hydrolysed in an atmosphere of hydrogen to anthranol-1:4-dicarboxylic acid, becoming dark red without melting at about 250°.

Anthraquinone-1:2-dicarboxylic acid is much more difficultly reducible to the anthranol stage than the 1:4- or 1:5-acid, but by protracted treatment (as outlined above) it yields the yellow anthranol-1:2-dicarboxylic acid, converted by boiling acetic anhydride into  $\psi$ -anthran-9-ol-1:2-dicarboxylactone (formula I of preceding abstract, but with R=H and OR' replaced by H), m. p. 278°, and 10-acetoxy-anthracene-1:2-dicarboxylic anhydride, m. p. 266—267°. H. WREN.

**1-Hydroxyphenanthraquinone.** K. BRASS, E. WILLIG, and R. HANSSEN (Ber., 1930, 63, [B], 2613—2616).—*o*-Methoxybenzaldehyde and benzaldehyde under the influence of potassium cyanide in boiling aqueous alcohol give a mixture of benzoin and *o*-methoxybenzoin, m. p. 56—57°, to which the structure  $Ph-CH(OH)-CO-C_6H_4-OMe$  is assigned; it appears to exist also in a yellow, liquid form. Oxidation of the crude methoxybenzoin with alkaline permanganate yields *o*-methoxybenzil, m. p. 71—72° (2:4-dinitrophenylhydrazone, m. p. 176—177°; tetranitrophenyl-osazone,  $\alpha$ -form, converted with softening at 227—228° into the  $\beta$ -variety, m. p. 295°). Treatment of *o*-methoxybenzil with aluminium chloride at 120° gives 1-hydroxyphenanthraquinone, m. p. 218—219°, in very small yield; the compound  $C_{14}H_8O_3SnCl_3$  is described. The colours produced by 1-, 2-, 3-, and 4-hydroxyphenanthraquinone on mordanted cotton are very pale and fugitive; on mordanted wool the shades are much darker, those of the 2-, 3-, and 4-compounds being fast, those of the 1-derivative fugitive.

*o*-Aminobenzaldehyde and benzaldehyde do not appear to give a substituted benzoin. H. WREN.

**Unsymmetrical ortho-disubstituted benzils and their transformation into the corresponding phenanthraquinones.** K. BRASS and R. STROEBEL (Ber., 1930, 63, [B], 2617—2621).—Benzpiperoin, m. p. 115° (cf. Hörbye, Diss., Dresden, 1917), is pre-

pared in 40% yield by the action of benzaldehyde and potassium cyanide in aqueous methyl alcohol on piperonal at the ordinary temperature. It is oxidised by Fehling's solution to benzpiperil,  $C_{15}H_{10}O_4$ , m. p. 120°, which yields a molecular compound with stannic chloride, a 2:4-dinitrophenylhydrazone, m. p. 183—184°, and a 2:4:2':4'-tetranitrophenylosazone, m. p. 270° (decomp.). Less successful results are obtained by the condensation of benzaldehyde with 3:4-dimethoxybenzaldehyde, since the product contains tetramethoxybenzoin, which can be removed only with difficulty. Oxidation of the crude materials affords a mixture of the corresponding benzils from which 3:4-dimethoxybenzil is isolated as a yellow form, m. p. 117.5°, and a colourless modification; the 2:4:2':4'-tetranitrophenylosazone has m. p. 249°. When heated with aluminium chloride 3:4-dimethoxybenzil affords 2:3-dimethoxyphenanthraquinone, m. p. 303° (corr.), in 6% yield with a little 2:4-dihydroxyphenanthraquinone. Under similar conditions, benzpiperil affords a compound, m. p. 258—259°, regarded as 2:3-methylenedioxyphenanthraquinone; dealkylation of the substance could not be effected. Tetramethoxyphenanthraquinone, m. p. 258°, is described. H. WREN.

**Action of aluminium chloride on *o*-dihydroxybenzils.** K. BRASS, F. LUTHER, and K. SCHÖNER (Ber., 1930, 63, [B], 2621—2627).—Benzpiperil is converted by phosphorus pentachloride at 108—109° and subsequently at 120—125° into 3:4-dihydroxybenzil, m. p. 157.5°, which exists in colourless leaflets and yellow crystals; it is readily converted into the dibenzoyl derivative, m. p. 98.5—99.5°, and 3:4-dimethoxybenzil. A colourless dichlorodihydroxybenzil, m. p. 189—190°, is prepared by chlorination in glacial acetic acid. The dihydroxy-compound is converted by aluminium chloride in nitrobenzene into 2:4-dihydroxyphenanthraquinone, decomp. 240°, m. p. above 300°. The compound is unchanged by pyroboracetate in acetic anhydride, and hence does not contain a hydroxyl group in position 1. It is oxidised to phthalic acid, showing the two hydroxyls to be attached to the same benzene nucleus. With *o*-tolylenediamine it gives a quinoxaline, m. p. 88.5°, readily converted into a diacetyl compound, m. p. 219°, identical with that prepared by the action of *o*-tolylenediamine on 2:4-diacetoxyphenanthraquinone, m. p. 197—198°. The ring closure under the influence of aluminium chloride is therefore accompanied by displacement of a hydroxyl group. The crude product of the reaction contains, in addition to unchanged initial material, small amounts of morpholquinone, so that it is probable that 2:4-dihydroxyphenanthraquinone is a secondary product derived from the latter substance. Further unsuccessful attempts to obtain morpholquinone synthetically are described in outline. H. WREN.

**Manufacture of [halogeno-, nitro-, and hydroxy-]derivatives of benzanthrone.** I. G. FARBENIND. A.-G.—See B., 1930, 1018.

**Manufacture of vat dyes [dibenzpyrenequinones] containing halogens.** I. G. FARBENIND. A.-G.—See B., 1930, 1019.

**Constitution of caoutchouc.** R. PUMMERER (Kolloid-Z., 1930, 53, 75—78).—The available evidence points to a cyclic structure for caoutchouc.

E. S. HEDGES.

**Picrocrocin, the bitter principle of saffron.** H. E. W. LUTZ (Biochem. Z., 1930, 226, 97—128).—The amount of carbon dioxide obtained on hydrolysis of picrocrocin is insignificant, corresponding with only 5.8% of that required for one molecule. Formaldehyde is detected as a product of acid hydrolysis and its amount determined. The mean mol. wt. of picrocrocin is 324.2. Analyses of picrocrocin and of its semicarbazone, m. p. 172.6° (corr.), agree with those of Winterstein and Teleczky (A., 1922, i, 563). Hydrogenation of the saffron camphor product of hydrolysis gave a dihydro-derivative,  $C_{10}H_{16}O$ . The results of analysis, determinations of mol. wt., and the products of hydrolysis, viz., one mol. each of the saffron camphor  $C_{10}H_{14}O$ , dextrose, and formaldehyde, agree best with the formula  $C_{17}H_{28}O_8$  for picrocrocin.

P. W. CLUTTERBUCK.

**Constitution of capraric acid.** G. KOLLER and W. PASSLER (Monatsh., 1930, 56, 212—233).—When capraric acid,  $C_{23}H_{40}O_{12}$  (Hesse, A., 1897, i, 631; 1898, i, 680; 1916, i, 264), is heated with hydriodic acid (*d* 1.17) at 150°, 3 mols. of carbon dioxide are eliminated. Acetylation of the acid with acetic anhydride and pyridine gives a *monacetate*, whilst diazomethane affords *trimethyl caparate monomethyl ether*. The acid therefore contains three carboxyl groups and one hydroxyl group. It is also shown that the acid contains two acetyl groups (Freudenberg's method). These are eliminated during methylation of the above ester with methyl sulphate and potassium hydroxide at 60°, and a *compound*,  $C_{20}H_{10}O_4(OMe)_6$ , results. Capraric acid (*anilide*) also forms a *phenylhydrazone*, m. p. (vac.) 265° (decomp.). The acid is not a depside, since simple fission does not occur when it is heated with concentrated alkali hydroxide in an atmosphere of hydrogen or with acetic acid at 140°. Fission of the acid takes place when it is heated with zinc dust and 15% sodium hydroxide solution in hydrogen at 100° (bath), orcinol and a *substance* (I),  $C_8H_8O_3$ , m. p. 122—123° [*oxime*, m. p. (vac.) 188° (decomp.); *anilide*, m. p. (vac.) 206°], being produced. Alkaline fusion of I gives orcinol, whilst methylation with methyl sulphate and alkali affords a *dimethyl ether*,  $C_{10}H_{12}O_3$ , m. p. 92—93° [*oxime*, m. p. (vac.) 215—216°], and a small amount of a liquid product (A). Since the dimethyl ether is oxidised by alkaline potassium permanganate to 3:5-dimethoxy-*p*-toluic acid, capraric acid must contain an aldehyde group. Similar oxidation of A affords 2:6-dimethoxy-3:4-dimethylbenzoic acid, m. p. (vac.) 185°, synthesised as follows. Reduction of oreylaldehyde by Clemmensen's method gives 3:5-dihydroxy-*o*-xylene, which when heated with potassium hydrogen carbonate and water at 100° (bath) in carbon dioxide is converted into 2:6-dihydroxy-3:4-dimethylbenzoic acid, m. p. 159—160°. Methylation of this with methyl sulphate and alkali hydroxide gives the *methyl ester*, m. p. 40—41° (prepared also from the above dimethoxy-acid and diazomethane), of 2:6-dimethoxy-3:4-dimethylbenzoic acid. These results show that I is essentially 3:5-dihydroxy-*p*-

tolualdehyde, contaminated with a small amount of 2:6-dihydroxy-3:4-dimethylbenzaldehyde. A partial formula for capraric acid is given which accounts for 22 carbon atoms.

H. BURTON.

**Phytochemistry. VI. *alloBetulin*.** O. DISCHENDORFER and H. JUVAN (Monatsh., 1930, 56, 272—281).—When betulin is heated with palladised charcoal at 220—330° or with fuller's earth (activated by heating to 300°) in boiling xylene, *apoallobetulin*, m. p. 200—201° (Schulze and Picroh, A., 1922, i, 1045), is obtained. *Oxyallobetulin* (A., 1929, 449) is also dehydrated by the latter method to *apoxyallobetulin*,  $C_{30}H_{46}O_2$ , m. p. 309° after darkening at 281°,  $[\alpha]_D^{20} + 79.9^\circ$  in chloroform. The presence of a  $\cdot CO \cdot CH_2 \cdot$  grouping in *allobetulinone* (cf. A., 1927, 59; *loc. cit.*) is confirmed by the production of a *m-nitrobenzylideneallobetulinone*, m. p. 137—139°, from the ketone and *m-nitrobenzaldehyde* in acetic acid saturated with hydrogen chloride. Oxidation of *oxyallobetulin* with chromic anhydride in acetic acid at 100° gives *oxyallobetulinone*,  $C_{30}H_{46}O_3$ , m. p. 341—342°,  $[\alpha]_D^{20} - 6.25^\circ$  in benzene [*oxime*, m. p. 333—337° (decomp.)]; *semicarbazone*, m. p. 301° (decomp.)], oxidised further by nitric (*d* 1.52) and acetic acids in the cold to *oxyallobetulinic acid*. Bromination of this acid or its anhydride in presence of chloroform and phosphorus pentachloride affords *bromo-oxyallobetulinic anhydride*, m. p. 315° (decomp.) after sintering at 300°.

H. BURTON.

**Kakishibu. VI. Potassium hydroxide fusion of methylshibuol.** S. KOMATSU and M. KURATA (Mem. Coll. Sci. Kyōtō, 1930, A, 13, 323—327).—Hydrolysis of tetramethylshibuol (A., 1928, 1137, 1138) with alcoholic potassium hydroxide affords gallic acid trimethyl ether and an insoluble, amorphous *compound* (OMe=33.1%) (termed *destetramethylshibuol*), m. p. 298—299° (decomp.); some formic, acetic, and butyric acids are formed also. Fusion of *destetramethylshibuol* with potassium hydroxide at 190—200°, gives gallic acid 3-methyl ether, phloroglucinol, alkali-soluble and -insoluble amorphous products, and small amounts of the above fatty acids. Similar fusion of tetramethylshibuol furnishes gallic acid 3:5-dimethyl ether, formic, acetic, and butyric acids, and amorphous substances.

H. BURTON.

**Action of zinc chloride on abietic acid.** G. ROUIN (Bull. Inst. Pin, 1929, 251—252).—Abietic acid is converted, by heating with 5% of zinc chloride at 150—250°, into octahydroretene, b. p. 202—203°/15 mm., with loss of carbon dioxide and methane.

C. HOLLINS.

**Action of ultra-violet light on terpenes. I. Action on citronellal.** M. T. BOGERT and T. HASSELSTRÖM (J. Amer. Chem. Soc., 1930, 52, 4093—4098).—Exposure of citronellal to ultra-violet light in absence of air and moisture at 40—50° results in the formation of *isopulegol* and polymerised material. The change probably occurs through the enol form of the aldehyde, since citronellal enol acetate is similarly converted into *isopulegyl acetate*. It is suggested that  $\alpha$ -citronellal gives rise mainly to *isopulegol*, whilst the  $\beta$ -form is polymerised.

H. BURTON.



**Permanganate oxidation of nopinene. Preparation of nopinic acid.** G. DU PONT (Bull. Inst. Pin, 1929, 269—270).—Oxidation of nopinene, free from  $\alpha$ -pinene, with alkaline potassium permanganate below 30° gives nopinic acid precipitated as sodium salt, in 36% yield. In neutral solution the yield is 7—8%, in acid solution nil. C. HOLLINS.

**Acetylenic derivatives of the terpene series. Preparation of some ethynylalkylcarbinols.** E. BARBE (Bull. Inst. Pin, 1929, 245—249).—Ketones of the terpene series are treated with sodamide and the resulting sodio-derivatives are condensed with acetylene to give acetylenic carbinols. Methylheptenone, b. p. 72°/16 mm., prepared from citral by means of potassium carbonate gives dehydrolinalool, b. p. 194° or 95°/18 mm. (Ruzicka and Fornasir, A., 1919, i, 193). 2-Ethynylborneol,  $\text{OH}\cdot\text{C}_{10}\text{H}_{16}\cdot\text{C}\equiv\text{CH}$ , m. p. 205°,  $[\alpha] +22.4^\circ$  (in alcohol), from camphor, and 1-ethynynopinol,  $\text{OH}\cdot\text{C}_{10}\text{H}_{14}\cdot\text{C}\equiv\text{CH}$ , b. p. 105—108°/18 mm.,  $d$  0.995,  $n_D^{20}$  1.494, from nopinone, are similarly obtained. The nopinone, prepared from  $\beta$ -pinene, had b. p. 91°/16 mm.

C. HOLLINS.

**Magnesium derivative of pinene hydrochloride [bornyl chloride]. Action of ethyl formate.** R. BOUSSET and (MLLE.) M. VAUGIN (Bull. Soc. chim., 1930, [iv], 47, 986—1003).—Pinene hydrochloride, m. p. 129—130°, with magnesium and ether in an atmosphere of nitrogen is converted into a magnesium chloride, which with ethyl formate at -20° gives 34% of bornylene and 34% of an alcohol,  $\text{C}_{10}\text{H}_{17}\cdot\text{CH}_2\cdot\text{OH}$ , together with a little dibornyl and camphane. The absence of methyl alcohol from the hydrolysis liquors when excess of magnesium is avoided establishes the mechanism of the reaction. No aldehydes were formed and the alcohol  $\text{OH}\cdot\text{CH}(\text{C}_{10}\text{H}_{17})_2$  is not present. Under the conditions of hydrolysis bornylene is not reduced to camphane, and bornylene is not formed in the preparation of the magnesium compound, in its hydrolysis, or in its oxidation or carbonation. The alcohol, *camphanecarbinol*, is isolated by conversion into the *hydrogen phthalate*, fractional crystallisation from benzene, and hydrolysis of the fraction, m. p. 160—161°,  $[\alpha]_D -10.54^\circ$ . The product obtained by hydrolysis has m. p. 88—89°,  $[\alpha]_D -33^\circ$ ; when distilled with steam the product has m. p. 62—64°, raised to 86° on a further distillation and falling to 62—64° on a third distillation. On further distillations the m. p. is raised to 86—87° and does not again fall. The product of m. p. 62—64° has the same rotatory power in acetone as the product of m. p. 88—89°. The *formate*,  $d_4^{25}$  0.9876,  $n_D^{25}$  1.475, *acetate*, b. p. 127.5/18 mm.,  $d_4^{25}$  0.9868,  $n_D^{25}$  1.470, and *p-nitrobenzoate*, m. p. 126°,  $[\alpha]_D -9.27^\circ$ , are described. Oxidation with alkaline potassium permanganate gives 43% of *camphanecarboxylic acid*, m. p. 69—71°,  $[\alpha]_D -10^\circ$  in benzene, also obtained (m. p. 69—70°,  $[\alpha]_D -2^\circ$ ) by the action of carbon dioxide on magnesium bornyl chloride (cf. Houben, A., 1911, i, 61). The *ethyl ester*, b. p. 110—112°/6 mm.,  $d$  0.976,  $[\alpha]_D -2.03$ , obtained by esterification with hydrogen chloride, on reduction with sodium and alcohol is converted into *camphanecarbinol*, m. p. 88—89°,  $[\alpha]_D -25^\circ$ . The latter is also obtained, but in only 0.5% yield, by the action of

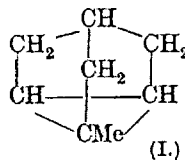
trioxymethylene on magnesium bornyl chloride, and hydrolysis of the hydrogen phthalate, m. p. 157—159°,  $[\alpha]_D -11.98^\circ$ . On further oxidation with alkaline permanganate *camphanecarboxylic acid* gives small amounts of camphor. R. BRIGHTMAN.

**Crystalline complexes obtained from bornyl and isobornyl acetates.** G. BRUS and J. VEBRA (Compt. rend., 1930, 191, 667—669).—Crystalline additive compounds (1 : 1) are formed when bornyl or isobornyl acetate is treated with phosphoric acid, arsenic acid, phosphorus pentachloride, antimony trichloride, bismuth trichloride, stannic chloride, or zinc chloride. Pyrophosphoric acid and isobornyl acetate afford a complex containing 2 mols. of the ester. The compounds are decomposed by water regenerating the original ester. The additive compounds from isobornyl acetate and phosphoric acid and antimony trichloride have m. p. 64—66° and 72—73°, respectively.

H. BURTON.

**Action of organic acids on *d*-pinene.** M. DELÉPINE, J. REESMAN, and E. SUAU (Bull. Soc. chim., 1930, [iv], 47, 966—986; cf. A., 1924, i, 1084, 1088; 1926, 841).—A sample of *d*-pinene,  $[\alpha]_D +48.3^\circ$ , with salicylic acid at 130—135° yields 44% of esters,  $[\alpha]_D +25.4^\circ$ , hydrolysed to a mixture of borneols, m. p. 203—204°, and some liquid alcohols (giving a liquid camphor,  $[\alpha]_D +45.7^\circ$  and  $\beta$ -fenchoneoxime, m. p. 122°,  $[\alpha]_D +112^\circ$ ), together with inactive hydrocarbons, b. p. 157—186°, containing dipentene and terpinolene. With small proportions of acid less racemisation of the borneols and hydrocarbons occurs, but bornyl, isobornyl, and fenchyl salicylates are formed in all cases. Similarly, oxalic acid at 140° in tetrachloroethane yields a mixture of neutral bornyl, isobornyl, and fenchyl oxalates, the mixture of borneols obtained on hydrolysis having  $[\alpha]_D +32.3$ —31.2°, and containing 6—9% of isoborneol. Separation of the hydrocarbons in presence of tetrachloroethane was difficult, but the presence of camphene and of a very active limonene was established; the recovered hydrocarbons when heated with oxalic acid gave further amounts of bornyl esters. With *o*-benzoylbenzoic acid at 140° about 70% of crude esters,  $d$  1.2,  $[\alpha]_D +24.7^\circ$ , are obtained, giving on hydrolysis about 80% of borneols,  $[\alpha]_D +32.25^\circ$ , containing 4% of isoborneol and 20% of fenchyl alcohol. The hydrocarbon fraction contained camphene and limonene.

Chloroacetic acid reacts very slowly with pinene below 100°; at 140—142° it affords 84% of esters,  $[\alpha]_D +8.2^\circ$ , containing about 30% of fenchyl chloroacetate, and a hydrocarbon fraction containing 5% of fenchene, b. p. 49—50°/15 mm.,  $n_D^{20}$  1.4616, 2% of pinene, 17% of camphene, 63% of limonene and dipentene, and 13% of terpinolene. Since the fenchene yields an isofenchyl acetate,  $n_D^{20}$  1.4596, and the alcohol obtained on hydrolysis yields on oxidation an isofenchone (semicarbazone, m. p. 222°), and then isofenchocamphoric acid, the bridged structure (I) is suggested for the fenchene. With dichloroacetic acid at the ordinary temperature 63% esterification is effected in 15 min.; at 90° 90% of bornyl, isobornyl, and fenchyl dichloroacetates are obtained, about



half of the esters decomposing on distillation at 15 mm. The borneols obtained on hydrolysis are very active and contain 10–12% of isoborneol. The hydrocarbon fraction contains limonene and  $\alpha$ -terpinene, but not dipentene. The yield of alcohols obtained from  $\alpha$ -pinene in the five cases is: salicylic acid, 25.3%; oxalic acid, 26.0%; *o*-benzoylbenzoic acid, 21.0%, chloroacetic, 16.0% and dichloroacetic acid, 20%. Austerweil's results with benzoic acid (A., 1927, 1082) are in agreement with these results, since the *l*-pinene,  $[\alpha]_D -45.3^\circ$ , used by him is not optically pure and the borneol obtained,  $[\alpha]_D -25.92^\circ$  (alcohol),  $-26.6^\circ$  (toluene), contains nearly 6% of isoborneol calculated by Haller's method. R. BRIGHTMAN.

[Auto-oxidation of cedrene.] A. BLUMANN (Ber., 1930, 63, [B], 2680; cf. A., 1929, 1076).—The specific rotation of the unsaturated sesquiterpene is incorrectly recorded as  $-125^\circ$ . The hydrocarbon appears to be dextrorotatory, but has not been obtained homogeneous. H. WREN.

Diterpenes kaurene and mirene. J. R. HOSKING (Rec. trav. chim., 1930, 49, 1036–1039; cf. B., 1928, 426, 691).—Kaurene is catalytically hydrogenated (platinum-black in ethyl acetate, or platinum oxide in acetic acid) to dihydrokaurene,  $C_{20}H_{34}$ , m. p.  $86-87^\circ$ ,  $d_4^{20}$  0.9282,  $d_4^{calc}$  0.9330,  $n_D^{20}$  1.4912. The molecular refraction ( $85.2$ ) agrees with that calculated for  $C_{20}H_{34}$  with one double linking ( $85.76$ ). From mirene, by the same methods, is obtained dihydromirene,  $C_{20}H_{34}$ , m. p.  $73-74^\circ$ . Neither of these hydrocarbons gives a coloration with tetranitromethane. When kaurene is dehydrogenated with selenium, pimanthrene (dimethylphenanthrene) is obtained in 50% yield. It is concluded that both diterpenes are tetracyclic, with one double linking, and that one of the phenanthrene rings is a bridged ring. J. D. A. JOHNSON.

Nitration of furfuraldehyde. H. GILMAN and G. F. WRIGHT (J. Amer. Chem. Soc., 1930, 52, 4165–4166).—Nitration of furfuraldehyde by the method previously described for its diacetate (this vol., 1045) gives 33% of the theoretical amount of pure 5-nitrofurfurylidene diacetate. H. BURTON.

Product of oxidation of phloretin. Synthesis of 7-hydroxy-3-benzyl-2-methyl-1:4-benzopyrone. J. SHINODA and T. SATO (J. Pharm. Soc. Japan, 1930, 50, 265–270).—5:7-Diacetoxy-3-*p*-acetoxybenzyl-2-methyl-1:4-benzopyrone, m. p.  $170-171^\circ$ , when treated with hydrogen iodide gave 5:7-dimethoxy-3-*p*-methoxybenzyl-2-methyl-1:4-benzopyrone, m. p.  $163-166^\circ$ , corresponding with Ciamician and Silber's methyl coumarin derivative (cf. A., 1894, i, 471; 1895, i, 538). This, when heated with alcoholic alkali, gave a compound, m. p.  $110^\circ$ , which did not depress the m. p. of 2'-hydroxy-4':6':4-trimethoxyhydrochalcone (oxime, m. p.  $206-207^\circ$ ), of which the acetyl derivative did not afford 5:7-dimethoxy- $\beta$ -4-methoxyphenylvinylcoumarin. The results support the view that the oxidation product of phloretin is of the  $\gamma$ -pyrone rather than of the coumarin type. CHEMICAL ABSTRACTS.

Condensation of aldehydes and phenols. IV. *o*-Chlorobenzylidenedi- $\beta$ -naphthol [*o*-chloro-

phenyldi-2-hydroxy- $\alpha$ -naphthylmethane]. O. DISCHENDORFER (Monatsh., 1930, 56, 261–271).—*o*-Chlorobenzaldehyde and  $\beta$ -naphthol condense in presence of acetic and hydrochloric acids to give a mixture of *o*-chlorophenyldi-2-hydroxy- $\alpha$ -naphthylmethane, m. p.  $184-185^\circ$  (monosodium salt; diacetate, m. p.  $198-199^\circ$ ; dibenzoate, m. p.  $241-242^\circ$ ; monomethyl ether, m. p.  $192-193^\circ$ ), and *ms*-*o*-chlorophenyldi-naphthopyran (9-*o*-chlorophenyl-1:2:7:8-dibenzo-xanthen), m. p.  $221^\circ$ . The last-named compound is also produced when the methane is heated with acetic acid containing a little sulphuric acid or when the initial condensation is carried out in presence of acetic and sulphuric acids. Oxidation of the methane with aqueous alcoholic sodium hypobromite affords dehydro-*o*-chlorobenzylidenedi- $\beta$ -naphthol, m. p.  $258^\circ$ , whilst oxidation of the pyran with manganese dioxide and hydrochloric acid in acetic acid and treatment of the resulting solution with ferric chloride gives *ms*-*o*-chlorophenyldinaphthopyrylium chloride ferrichloride, m. p.  $215^\circ$ . This is decomposed by aqueous acetone to *ms*-*o*-chlorophenyldinaphthopyranol (9-*o*-chlorophenyl-1:2:7:8-dibenzo-xanthihydrol), m. p.  $221^\circ$  (decomp.) after darkening at about  $210^\circ$  [chloride mercurichloride, m. p.  $261-262^\circ$  (decomp.) after sintering and darkening at  $253-254^\circ$ ; perbromide,  $C_{27}H_{16}OClBr_3$ , m. p.  $189-191^\circ$  (decomp.) after sintering and darkening at about  $160^\circ$ ; perchlorate, m. p.  $293-294^\circ$  (decomp.) after sintering at  $250^\circ$  and darkening at  $270^\circ$ ; ethyl ether, m. p.  $236^\circ$  (decomp.), prepared by the action of alcohol on the above ferrichloride; methyl ether, m. p.  $242^\circ$  (decomp.) after darkening at  $225^\circ$  and sintering at  $238^\circ$ ]. Nitration of the above pyran with nitric acid (*d* 1.41) at  $100^\circ$  (bath) gives a dinitro-*ms*-*o*-chlorophenyldinaphthopyranol, m. p.  $290^\circ$  (decomp.) after darkening and sintering at  $272^\circ$ . H. BURTON.

Constitution of cetraric acid. G. KOLLER and E. KANDLER (Monatsh., 1930, 56, 234–238; cf. A., 1929, 1459).—Reductive fission of cetraric acid by zinc dust and dilute sodium hydroxide (cf. Simon, A., 1903, i, 98; 1906, i, 961) at  $100^\circ$  (bath) gives impure 3:5-dihydroxy-*p*-tolualdehyde, as does capraric acid (this vol., 1590). This aldehyde is also identical with atranol (Pfau, A., 1926, 836). H. BURTON.

Syntheses in the thiophen series using stannic chloride. J. L. GOLDFARB (J. Russ. Phys. Chem. Soc., 1930, 62, 1073–1082).—The preparation of a number of thiophen derivatives is described (cf. Stadnikov and Goldfarb, A., 1929, 74). In addition to the above, acetyldibenzhydrylthiophen, m. p.  $152^\circ$ , is described. R. TRUSZKOWSKI.

1-Thio-4-pyrone and derivatives. F. ARNDT and N. BEKIR (Ber., 1930, 63, [B], 2393–2397).—Penthianone (cf. Bennett and Scora, A., 1927, 228) is dehydrogenated by phosphorus pentachloride in presence of benzenetol-1-thio-4-pyrone,  $S \begin{smallmatrix} \text{CH:CH} \\ \text{CH:CH} \end{smallmatrix} \text{CO}$ , m. p.  $110^\circ$  (hydrochloride, m. p. about  $135^\circ$ ; additive compound, m. p.  $189^\circ$ , with mercuric chloride; ferrocyanide). Whereas penthianone is readily oxidised by hydrogen peroxide in presence of glacial acetic acid to the corresponding sulphone, m. p.  $171-172^\circ$ , 1-thio-4-pyrone is much more resistant; its sulphone,

m. p. 174°, is obtained by the action of boiling pyridine on 3:5-dibromopentthianonesulphone, m. p. 220° (decomp.), prepared by brominating pentthianonesulphone in glacial acetic acid. Ethyl 2:6-dithiol-1-thio-4-pyrone-3:5-dicarboxylate (cf. Apitzsch, A., 1909, i, 48) is converted into the corresponding dimethyl ether, which is hydrolysed by boiling hydrochloric acid to 2:6-dimethylthiol-1-thio-4-pyrone-3:5-dicarboxylic acid, m. p. 243—245° (decomp.) (pyridine salt). The acid loses carbon dioxide at 245° with formation of 2:6-dimethylthiol-1-thio-4-pyrone, m. p. 130—131°, which is readily oxidised by hydrogen peroxide to the disulphone,  $C_7H_8O_5S_2$ , m. p. 270°. Treatment of the thiopyrone with phosphorus pentasulphide in boiling benzene gives 2:6-dimethylthiodithiopyrone,  $C_7H_8S_4$ , m. p. 121°.

[With C. MARTIUS.]—Methyl  $\beta$ -chlorobutyrate is smoothly transformed into methyl 2:6-dimethylpentthianone-3-carboxylate, m. p. 86°, converted by water at 175° or 210—220° into 2:6-dimethylpentthianone, m. p. 38.5°, or its liquid stereoisomeride. Either of these substances is dehydrogenated by chlorine or sulphuryl chloride to 3-chloro-2:6-dimethyl-1-thiopyrone, m. p. 96°; dehydrogenation with phosphorus pentachloride yields a dark blue product.

H. WREN.

**Preparation of thioindigo dyes. I. Syntheses in the naphthalene series.** K. DZIEWONSKI, C. BARANIECKI, and L. STERNBACH (Bull. Acad. Polonaise, 1930, A, 198—202).—When  $\alpha$ -naphthyl methyl ketone (3 parts) is heated with sulphur (1 part) at 230—260°, 1:2-naphththioindigotin,

$(C_{10}H_6 \begin{smallmatrix} \diagup CO \\ \diagdown S \end{smallmatrix} \diagup C)_2$ , m. p. (sealed tube) 411—412° after

subliming at 390° (cf. Friedländer and Voroshzov, A., 1912, i, 293), is obtained in 50% of the theoretical amount of the ketone used. This is reduced by zinc dust and acetic anhydride to the diacetyl derivative, m. p. 278° (decomp.), of the corresponding leuco-compound, which when heated with 50% potassium hydroxide solution for a long time regenerates the dye.

2:1-Naphththioindigotin,  $(C_{10}H_6 \begin{smallmatrix} \diagup S \\ \diagdown CO \end{smallmatrix} \diagup C)_2$ , m. p.

(sealed tube) 415—416° after subliming at 403° (cf. loc. cit.), obtained in 40% yield from  $\beta$ -naphthyl methyl ketone and sulphur at 230°, is reduced by zinc dust, acetic acid, and acetic anhydride to the diacetyl derivative, m. p. 318—319° (decomp.), of the corresponding leuco-compound. The above thioindigotins dye cotton (from an alkaline vat) brownish-red and violet-brown, respectively.

H. BURTON.

**By-product from action of sulphuric acid on m-nitro-p-cresol.** I. J. RINKES (Rec. trav. chim., 1930, 49, 1002—1006).—The by-product (m. p. 207°) obtained by Pauly, Gilmour, and Will (A., 1914, i, 485) is shown to be 2-keto-4-methyl-5-carboxymethylene- $\Delta^3$ -pyrroline,  $\begin{smallmatrix} CH:CM \\ CO-NH \end{smallmatrix} > C:CH-CO_2H$ , since its amide, m. p. 214°, was converted by sodium hypochlorite in methyl alcohol into the carbamate, m. p. 187—188°, which on hydrolysis gave an aldehydic substance. Further evidence is afforded by the by-

product yielding citraconimide and oxalic acid when oxidised with acid dichromate.

J. D. A. JOHNSON.

**Piperidine derivatives. X. Piperidylphenylcarbinols [ $\alpha$ -hydroxybenzylpiperidines].** K. E. CROOK and S. M. McELVAIN (J. Amer. Chem. Soc., 1930, 52, 4006—4011).—Benzyl chloride and pyridine react in presence of a small amount of copper powder, first at 70—115°, and then at 240—245°, forming a mixture of 2- and 4-benzylpyridines (cf. Tschitschibabin, A., 1901, i, 484; La Forge, A., 1928, 1260). Reduction of 2-benzoylpyridine, b. p. 170—172°/10 mm. (hydrochloride, m. p. 126—128°), with hydrogen in presence of a platinum oxide-platinum-black catalyst and an excess of hydrochloric acid gives a mixture of 3 parts of a 2- $\alpha$ -hydroxybenzylpiperidine, m. p. 141—142° (hydrochloride, m. p. 200—202°), and 1 part of a diastereoisomeride, m. p. 171—173°; the former is converted into the latter when it is heated with 25% hydrochloric acid at 100° for 2 days. Similar reduction of 3- and 4-benzoylpyridine hydrochlorides, m. p. 160—162° and 195—197°, respectively, in aqueous solution affords 3- and 4- $\alpha$ -hydroxybenzylpiperidine hydrochlorides, m. p. 190—192° and 191—193°, respectively. 4- $\alpha$ -Hydroxybenzylpiperidine has m. p. 166—167°. The above carbinols possess pharmacological properties similar to those of ephedrine.

H. BURTON.

**Local anaesthetics derived from quinoline and isoquinoline.** C. F. BAILEY and S. M. McELVAIN (J. Amer. Chem. Soc., 1930, 52, 4013—4017).—The following quinolinoalkyl benzoate hydrochlorides are prepared from  $\beta$ -chloroethyl and  $\gamma$ -chloropropyl benzoates and the requisite secondary amine:  $\beta$ -1:2:3:4-tetrahydroquinolinoethyl, m. p. 129—131°;  $\gamma$ -1:2:3:4-tetrahydroquinolino- and -isoquinolino-propyl, m. p. 122—124° and 188—189°, respectively;  $\beta$ -cis- and -trans-decahydroquinolinoethyl, m. p. 159—160° and 155—157°, respectively, and  $\gamma$ -cis- and -trans-decahydroquinolinopropyl, m. p. 155—156.5° and 171—173°, respectively. Pharmacological data are given for these compounds.

Details are given for the isolation of cis-decahydroquinoline from the cis-trans-mixture obtained by the complete reduction of quinoline in presence of a nickel catalyst at 200°/150—200 atm. (cf. Hückel and Stepf, A., 1927, 572).

H. BURTON.

**Indoles. I. 5:6-Dimethoxy-2-methylindole.** F. LIONS (J. Proc. Roy. Soc. N.S. Wales, 1929, 63, 168—171).—The dibromide of 5-nitro-4-allylveratrole has m. p. 111°, whilst that of 5-acetamido-4-allylveratrole has m. p. 160—161°. The second is converted by boiling 20% alcoholic potassium hydroxide into 5:6-dimethoxy-2-methylindole, m. p. 91°.

T. H. MORTON.

**N-Substituted oxindoles and isatins.** R. STOLLÉ [with R. BERGDOLL, M. LUTHER, A. AUERHAHN, and W. WACKER] (J. pr. Chem., 1930, [ii], 128, 1—43).—Experimental details of work, a preliminary account of which has already been published (A., 1923, i, 1125), are given. The following compounds and physical data appear to be new: 7-methyloxindole, m. p. 200°; bischloroacetyl-m-phenylenediamide, m. p. 212°; bromoacetyl- $\beta$ -naphthylamide, m. p. 134°; chloroacetyl-, m. p. 218°, and trichloroacetyl-, m. p. 234°.

- $\alpha$ -aminoanthraquinone (the last four compounds could not be cyclised to oxindole derivatives). From 1-methyloxindole are obtained its 3-isonitroso-, m. p. 189° (lit. m. p. 180—183°); 3-benzylidene-, m. p. 71°; 5-bromo-, m. p. 133° (isonitroso-derivative, m. p. 225°); 3-p-dimethylaminobenzylidene-, m. p. 212°; 5:7-dibromo-, m. p. 200° (p-dimethylaminobenzylidene derivative, m. p. 208°); 3:3-dichloro-, m. p. 149°; 3:3-dichloro-5-bromo-, m. p. 155°, and 3:3'-dichloro-5:7-dibromo-, m. p. 182°, -derivatives. 1-Ethyl-oxindole is converted by nitrosodimethylaniline and sodium ethoxide into 1-ethylisatin-3-p-dimethylaminoanil, m. p. 175°. Bromine (1 mol.) in carbon tetrachloride at 0° converts 1-ethyl-oxindole into its unstable 1:1-dibromide, m. p. 94°, but with 2 mols. of bromine in warm solution the 2:2-dibromo-derivative, m. p. 95°, is obtained. With aqueous bromine the product is 5-bromo-1-ethyl-oxindole, m. p. 108°,  $+x$ C<sub>6</sub>H<sub>6</sub>, m. p. 96°, converted by nitrosodimethylaniline into 5-bromo-1-ethylisatin-3-p-dimethylaminoanil, m. p. 174°. Prolonged treatment with 3 mols. of bromine in carbon tetrachloride at the ordinary temperature converts 1-ethyl-oxindole into its 3:3:5-tribromo-derivative, m. p. 144°. Hydrolysis of 1-phenyloxindole affords o-anilinophenylacetic acid, m. p. 109°, which could not be readily reconverted into the oxindole. 1-Phenyloxindole is converted into its 5-, m. p. 162°, 1-, m. p. 98°, 3:5-di-, m. p. 162° (decomp.), 3:3-di-, m. p. 131°, 3:3:5-tri-, m. p. 168°, and 3:3:5:7-tetra-, m. p. 172°, -bromo-derivatives. From the base and the appropriate chloroacetyl chloride are obtained dichloroacetdiphenylamide, m. p. 79°, and -methylanilide, m. p. 69°, and trichloroacetdiphenylamide, m. p. 86°, the last-named being converted into 3:3-dichloro-1-phenyloxindole, m. p. 117° (not m. p. 100°; A., 1914, i, 200). N-Methyloxanilic acid chloride, anhydrous, m. p. 122° (lit. m. p. 130°) (anilide, m. p. 106°), is converted into 1-methylisatin, whilst from the appropriate brominated 3:3-dichloro-1-methyloxindole are obtained 5-bromo- and 5:7-dibromo-, m. p. 175° (lit. m. p. 171°, indefinite), -1-methylisatin. By similar methods are obtained: diethylloxanilide, m. p. 93°; ethyloxanilide, m. p. 116°; diphenyloxanilic acid chloride, m. p. 70°; diphenyloxamic acid, m. p. 146° (lit. m. p. 141.5°); 1-phenylisatin, m. p. 138° (lit. m. p. 134°) (3-oxime, m. p. 221°); 5-bromo-1-phenylisatin, m. p. 205°; 1-p-tolyl-5-methylisatin, m. p. 184° [also from di-p-tolyloxamic acid chloride, m. p. 156° (decomp.), and anilide, m. p. 175°];  $\alpha$ -naphthylphenyloxamic acid chloride, m. p. 105° [ethyl ester, m. p. 124° (decomp.); anilide, m. p. 168°]; 1-phenyl-6:7-benzoisatin, m. p. 217°; 1- $\alpha$ -naphthylisatin, m. p. 176°; phenyl- $\beta$ -naphthylloxamic acid, m. p. 221° (decomp.) (acid chloride, m. p. 225°; ethyl ester, m. p. 103°; anilide, m. p. 219°); 1-anilinonaphthalene-2-, m. p. 236°, and 2-anilinonaphthalene-1-, m. p. 146° (decomp.), -carboxylic acid; 1-phenyl-4:5-benzoisatin, m. p. 229° (lit. m. p. 227°); di- $\beta$ -naphthylloxamic acid, m. p. 169° (decomp.) [acid chloride converted at 110° into 1- $\beta$ -naphthyl-4:5-benzoisatin, m. p. 268° (3-oxime, m. p. 212°); methyl, m. p. 141°, and ethyl, m. p. 110°, esters]; as-di- $\beta$ -naphthylloxamide, m. p. 228° (decomp.). Condensation between the appropriate oxindole and isatin derivative affords 1-methyl-,

m. p. 223°; 1:1'-dimethyl-, m. p. 265°; 3-hydroxy-1:1'-diethyl-3:3'-dihydro-, m. p. 148° with decomp. to 1:1'-diethyl-, m. p. 175°; 5:5'-dibromo-1:1'-diethyl-, m. p. 274°; 3-hydroxy-1:1'-diphenyl-3:3'-dihydro-, m. p. 172° with decomp. to 1:1'-diphenyl-, m. p. 314°; and 5:5'-dibromo-1:1'-diphenyl-, not melting at 360°, -isoindigotin. The following condensation products are described: 1-phenylisatin with 1-hydroxythionaphthen,

$\text{NPh} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{S} \end{array} \text{C}_6\text{H}_4$ , m. p. 237°; 1-ethyl-oxindole with phthalic anhydride,

$\text{NEt} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CO} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{CO}$ , m. p. 208° (previous sintering); and the similar product from 1-phenyloxindole, m. p. 246° (free phthalic acid derivative, m. p. 171° with reversion into the anhydride compound). 7-Bromo-, m. p. 278° (decomp.); 5:6-benzo-, m. p. 286° (decomp.); 7:8-benzo-, m. p. 276° (decomp.); and 1:2:7:8-dibenzo-, m. p. 232° (decomp.), -acridine-9-carboxylic acid, are described.

J. W. BAKER.

**Mercuri-iodides of pyridine.** V. V. ZAPOLSKI (U.S.S.R. State Inst. Tobacco Inv., 1930, Bull. 69, 87—98).—The following compounds are described: C<sub>5</sub>H<sub>5</sub>N, HI, HgI<sub>2</sub>, m. p. 144—145°; 2C<sub>5</sub>H<sub>5</sub>N, HgI<sub>2</sub>, m. p. 103° (decomp.); 2C<sub>5</sub>H<sub>5</sub>N, 2HI, HgI<sub>2</sub>; 3C<sub>5</sub>H<sub>5</sub>N, HI, 2HgI<sub>2</sub>, m. p. 81—82°; 3C<sub>5</sub>H<sub>5</sub>N, 2HI, HgI<sub>2</sub>, m. p. 117°; 3C<sub>5</sub>H<sub>5</sub>N, 2HI, 2HgI<sub>2</sub>, m. p. 87—88°; 2C<sub>5</sub>H<sub>5</sub>N, 2HI, 5HgI<sub>2</sub>, decomp. about 100° (cf. B., 1930, 120). Elementary analysis by combustion with cupric oxide gives low results with these compounds. Various other similar compounds have been prepared, but their composition has not yet been determined.

T. H. POPE.

**Synthesis of 2-hydroxyquinolines.** A. E. TSCHITSCHIBABIN and A. I. KURANOVA (J. Russ. Phys. Chem. Soc., 1930, 62, 1211—1216).—The following hydroxyquinolines are obtained by the action on the corresponding quinolines of anhydrous potassium hydroxide at 225—275°: 2-hydroxy-8-methyl- (m. p. 219—220°) and 2-hydroxy-6-methyl-quinoline (m. p. 232—233°) from o- and p-toluquinoline, hydroxy- $\alpha$ - and - $\beta$ -naphthoquinoline, m. p. 252—253° and 285—286°, from  $\alpha$ - and  $\beta$ -naphthoquinoline, and hydroxyisiquinoline, m. p. 209—210°, from isoquinoline. 2-Hydroxy-8-methylquinoline is oxidised by permanganate to oxalyl-o-methylantranilic acid, m. p. 231°, whilst the 6-methyl compound gives the corresponding p-methyl acid, m. p. 186—187°, together with 5-methylisatin.

R. TRUSZKOWSKI.

**Preparation of benzeneazo-derivatives of 8-hydroxyquinoline.** K. MATSUMURA (J. Amer. Chem. Soc., 1930, 52, 4164—4165; cf. Fox, J.C.S., 1910, 97, 1337).—Alkaline coupling of 8-hydroxyquinoline and benzenediazonium chloride in very dilute solution gives 5-benzeneazo-8-hydroxyquinoline, m. p. 187° [hydrochloride (+1.5H<sub>2</sub>O), m. p. 227° (decomp.)], also obtained when coupling is carried out in presence of acetic acid. When alkaline coupling is effected in presence of a minimal amount of water, 5:7-dibenzeneazo-8-hydroxyquinoline, m. p. 205—206°, is produced.

H. BURTON.

**Trimethoxyquinoline derivatives.** F. LIONS (J. Proc. Roy. Soc. N.S. Wales, 1929, **63**, 159—167).—Nitration of ethyl gallate trimethylether by the method of Hamburg (A., 1899, i, 364) yields the corresponding 2-nitro-derivative, from which the free acid is obtained by alkaline hydrolysis. Reduction by ferrous sulphate and ammonia affords 3:4:5-trimethoxy-anthranilic acid, m. p. 140°, which, when heated in glycerol at 150—200°, gives carbon dioxide and 2:3:4-trimethoxyaniline, b. p. 147—148°/15 mm. (acetyl derivative, m. p. 90°). The condensation of 2:3:4- or 3:4:5-trimethoxyaniline with acetylacetone at 100° affords  $\beta$ -(2:3:4-trimethoxyanilino)-, m. p. 70°, b. p. 206—208°/14 mm., or  $\beta$ -(3:4:5-trimethoxyanilino)-propenyl methyl ketone, m. p. 101°, respectively. These ketones are quantitatively converted by the concentrated sulphuric acid method into 6:7:8-trimethoxy-, m. p. 59.5°, b. p. 198—200°/12 mm., and 5:6:7-trimethoxy-2:4-dimethylquinoline, m. p. 59°, respectively. Reduction with sodium and boiling ethyl alcohol affords 6:7:8-trimethoxy-, b. p. 173—175°/11 mm. (benzoyl and acetyl derivatives), and 5:6:7-trimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinoline, m. p. 89°, b. p. 211—214°/13 mm. (acetyl derivative, m. p. 137°, and nitrosoamine).

T. H. MORTON.

**Quinoline derivatives. VII. Quinic acid.** H. JOHN [with E. ANDRASCHEK] (Ber., 1930, **63**, [B], 2657—2661).—The yields of 6-methoxyquinoline-4-carboxylic acid obtained by the oxidation of conchicine by chromic acid in aqueous sulphuric acid do not exceed 42% of the theoretical. Addition of iron, as ferrous sulphate, increases the yield to 55%, whereas cobalt, nickel, and vanadium are without action. Manganese, added as manganese dioxide or sulphate or as potassium permanganate in concentration of 0.1 mol. per litre of metal, gives as an average a 75% yield of very pure acid. To obtain the maximal yield of 75% it is requisite that the weight of chromic acid used should be at least twice that of the conchicine. The most favourable concentration of sulphuric acid is 8%. Replacement of manganese by magnesium, aluminium, copper, cerium, silver, and lead does not increase the yield to above 48% whereas mercury depresses it to 28%. Chlorine, arsenic, and kieselguhr are not suitable.

H. WREN.

**Derivatives of 2-hydroxy-4-methyl, -4:6-, -4:7-, and -4:8-dimethylquinolines.** I. E. BALABAN (J.C.S., 1930, 2346—2354).—Nitration of 2-hydroxy-4-methylquinoline affords the 6-nitro-derivative, m. p. 340° (decomp.) (also obtained by dehydration of *p*-nitroacetacetanilide), converted through the amine, m. p. 315° (hydrochloride, m. p. above 310°; acetyl derivative, m. p. 314°), by the usual method into 2-hydroxy-4-methylquinoline-6-arsinic acid (+H<sub>2</sub>O), m. p. above 320°. 6-Nitro-2-hydroxy-4-methylquinoline is converted into 2-chloro-6-nitro-4-methylquinoline, m. p. 207°, by phosphorus pentachloride, and by permanganate oxidation into 5-nitro-benzoxazolone, m. p. 242° (also prepared by the nitration of benzoxazolone, and by the action of carbonyl chloride on 5-nitro-2-aminophenol) (Chelmicki, A., 1891, 52, gives m. p. 241°; cf. Bender, A., 1887, 38; Hewitt and King, A., 1926, 746, who give

256° and 255°, respectively); 2-hydroxy-4-methylquinoline is similarly oxidised to benzoxazolone.

3-Nitro-2-hydroxy-4:6-dimethylquinoline, m. p. 294°, is reduced to 3-amino-2-hydroxy-4:6-dimethylquinoline, m. p. 264° (hydrochloride, m. p. 240°; acetyl derivative, m. p. 270°), which fails to give an arsenic acid under the usual conditions; 2-chloro-3-nitro-4:6-dimethylquinoline has m. p. 157°.

Nitration of 2-hydroxy-4:7-dimethylquinoline yields a mixture of the 6-nitro-, m. p. 280°, and the 8-nitro-derivative, m. p. 226°, oxidised respectively to 5-nitro-, m. p. 233° (Benda and Sievers, U.S.P. 1,539,798/25; cf. B., 1925, 653), and 3-nitro-4-methylbenzoxazolone, m. p. 236°, and yielding the respective 2-chloro-compounds, m. p. 164° and 156°. 8-Amino-2-hydroxy-4:6-dimethylquinoline, m. p. 255° [hydrochloride (+H<sub>2</sub>O), m. p. 257° (efferv.); acetyl derivative (+2H<sub>2</sub>O), m. p. 266°], gives with nitrous acid an insoluble diazoimide, from which its orientation, with that of the original nitro-compound, follows; 6-amino-2-hydroxy-4:7-dimethylquinoline, decomp. 320° (hydrochloride, m. p. above 320°; acetyl derivative, m. p. above 320°), gives normally 2-hydroxy-4:7-dimethylquinoline-6-arsinic acid, m. p. above 320°.

6-Nitro-2-hydroxy-4:8-dimethylquinoline, m. p. 310°, gives on oxidation 5-nitro-3-methylbenzoxazolone, m. p. 249°, and with phosphorus pentachloride 2-chloro-6-nitro-4:8-dimethylquinoline, m. p. 195°; 6-amino-2-hydroxy-4:8-dimethylquinoline, m. p. 288° (hydrochloride and acetyl derivative, both m. p. above 320°), yields normally 2-hydroxy-4:8-dimethylquinoline-6-arsinic acid.

Tetrahydro-derivatives have not been obtained by reduction of any of the nitro-, amino-, or chloroquinolines described.

R. CHILD.

**Comparison of the directive powers of elements having consecutive atomic numbers. II. Mononitrations of 2-phenylquinoline and its methosulphate.** R. J. W. LE FÈVRE and F. C. MATHUR (J.C.S., 1930, 2236—2241; cf. this vol., 217).—2-Phenylquinoline methosulphate, m. p. 142—143.5° (corresponding methopicate, m. p. 138—139°), with nitric acid (*d* 1.5) affords exclusively the *m*-nitro-derivative, isolated as 2-*m*-nitrophenylquinoline methopicate, m. p. 181—182°, and identified by conversion into the methochloride, m. p. 203—204°, and thermal decomposition of the latter to 2-*m*-nitrophenylquinoline, m. p. 123—124° (Kinkelin and Miller, A., 1885, 1144).

2-Phenylquinoline affords the last-named (33% crude yield) and 2-*p*-nitrophenylquinoline, m. p. 129—131° (66% crude yield) (synthesised from *p*-nitrocinnamaldehyde, aniline, and hydrochloric acid). 2-*o*-Nitrophenylquinoline (from *o*-nitrocinnamaldehyde) has m. p. 121—123°.

By analogy it is suggested that the three mononitro-derivatives of 4-phenylquinoline described by Königs and Nef (A., 1887, 599):  $\alpha$ , m. p. 187°;  $\beta$ , m. p. 117—118°; and  $\gamma$ , m. p. 135°, are respectively *p*-, *m*-, and *o*-. Synthetic experiments on this point have been so far unsuccessful.

R. CHILD.

**Skraup reaction with azo-compounds.** K. MATSUMURA (J. Amer. Chem. Soc., 1930, 52, 3974—

3977).—When a mixture of 4-benzeneazoresorcinol dimethyl ether (0.05 mol.), glycerol (18 g.), sulphuric acid (18 g.), and arsenic acid (9 g.) is heated at 160–195° (bath), quinoline and *p*-phenanthroline are produced; quinoline is the main product with 4-benzeneazoresorcinol. Similarly, azobenzene gives quinoline and 6:6'-diquinolyl; *p*-aminoazobenzene affords quinoline and *p*-phenanthroline; 4-*p*-nitrobenzenazo- $\alpha$ -naphthol furnishes *p*-phenanthroline; 4-*p*-chlorobenzenazophenol yields 6-chloroquinoline; 5-benzeneazo-8-hydroxyquinoline gives quinoline and a small amount of 10-hydroxy-*m*-phenanthroline, m. p. 157–158° [sulphate, m. p. 273° (decomp.); chloroplatinate (+1.5H<sub>2</sub>O), m. p. 309°; picrate, m. p. 237° (decomp.)], similar to the 2-hydroxy-*m*-phenanthroline of La Coste (A., 1883, 811), and chrysoidine affords quinoline and a small amount of a substance, m. p. 155–156°. H. BURTON.

**Action of lithium alkyls on acridine and other organo-alkali transformations in the acridine series.** E. BERGMANN, O. BLUM-BERGMANN, and A. F. VON CHRISTIANI (Annalen, 1930, 483, 80–89).—Lithium aryls, prepared from lithium and aryl bromides by the method of Ziegler and Colonius (this vol.,

590), form additive compounds  $C_6H_4 \begin{smallmatrix} NLi \\ \diagup \diagdown \\ CHR \end{smallmatrix} C_6H_4$ , with acridine, decomposed by water to 5-aryl-5:10-dihydroacridines. The following are prepared: 5-phenyl-, 5-*p*-anisyl-, m. p. 183–184°; 5-*o*-tolyl-, m. p. 185–186°; 5-*m*-tolyl-, m. p. 148–149°; 5- $\alpha$ -naphthyl- (+C<sub>6</sub>H<sub>6</sub>), m. p. 123° (decomp.). 10-Phenyl-5:10-dihydroacridine has m. p. 123° (lit. 119°). Lithium phenyl and isoquinoline afford an additive compound which on hydrolysis undergoes oxidation yielding 1-phenylisoquinoline. 1-*p*-Anisylisoquinoline (picrate, m. p. 191°) is prepared similarly from lithium *p*-anisyl. When 5:10-dihydroacridine is treated with lithium ethyl at 65°, and the product acted on by methyl iodide at 65°, 10-methyl-5:10-dihydroacridine, m. p. 93–95° (also prepared by reducing 10-methylacridone with sodium and amyl alcohol), is produced. Reduction of acridine-5-carboxylic acid (methyl ester, m. p. 128–130°) with hydrogen in presence of palladised barium sulphate and propyl alcohol affords 5:10-dihydroacridine-5-carboxylic acid, m. p. 205° (decomp.) (methyl ester, m. p. 160–162°), identical with the acid described by Schlenk and Bergmann (A., 1928, 1039); the difference in m. p. is due to the rate of heating. 10-Methylacridone behaves as a normal aromatic ketone towards lithium, yielding first a ketyl and then a dilithium derivative,  $C_6H_4 \begin{smallmatrix} NMe \\ \diagup \diagdown \\ CLi(OLi) \end{smallmatrix} C_6H_4$ . Treatment of the latter with dichlorodiphenylmethane affords the compound,  $NMe \begin{smallmatrix} C_6H_4 \\ \diagup \diagdown \\ C \end{smallmatrix} \begin{smallmatrix} O \\ \diagup \diagdown \\ CPh_2 \end{smallmatrix}$ , m. p. 242°. H. BURTON.

**aci-Form of 5-hydroxy-1-*m*-dinitrophenyl-3-methylpyrazole and its amino- and thio-analogues.** C. A. ROJAHN and H. FEGELER (Ber., 1930, 63, [B], 2510–2519).—5-Chloro-1-*m*-dinitrophenyl-3-methylpyrazole is converted by an equimolecular amount of potassium hydroxide in the requisite alcohol into 5-methoxy-, 5-ethoxy-, and 5-butoxy-1-*m*-dinitrophenyl-3-methylpyrazole, m. p. 182°, 112°, and

99°, respectively. As by-product in these cases, or almost quantitatively if 2 mols. of potassium hydroxide are used, the potassium salt of 2':1':3:4:4'-nitrobenzo-1'':5'':5:6:3''-methylpyrazolo-N<sup>2</sup>-hydroxy-N<sup>2</sup>-oxy-1:2:5-oxadiazine (cf. I), not molten below 359°, is produced (the parent compound has m. p. 126°); it is sometimes accompanied by an unstable red isomeride. With aniline, the chloro-compound yields 5-anilino-1-*m*-dinitrophenyl-3-methylpyrazole, m. p. 190° [occasionally accompanied by a (?) stereoisomeride, m. p. 156°], converted by boiling aqueous or alcoholic potassium hydroxide into the potassium salt described above and reduced by tin and hydrochloric acid to 5-anilino-1-*m*-diaminophenyl-3-methylpyrazole, m. p. 184° (dihydrochloride, m. p. 242° after incipient sublimation at about 200°). Ammonia transforms the chloropyrazole into yellow and red 5-amino-1-*m*-dinitrophenyl-3-methylpyrazoles, of which only the yellow variety, m. p. 204°, can be isolated; since it does not give a picrate or hydrochloride and cannot be acetylated or benzoylated it probably exists in the imino- or aci-form. 5-*p*-Toluidino-1-*m*-dinitrophenyl-3-methylpyrazole, m. p. 166°, is described. 5-Formamido-1-*m*-dinitrophenyl-3-methylpyrazole, m. p. 286°, and 5-phenylhydrazino-1-*m*-dinitrophenyl-3-methylpyrazole, m. p. 216° (decomp.) (also obtained from the 5-hydroxypyrazole, m. p. 126°, and phenylhydrazine at the ordinary temperature), have been prepared. With pyridine the hydroxy-compound affords a substance, C<sub>15</sub>H<sub>13</sub>O<sub>5</sub>N<sub>5</sub>, m. p. 226° (decomp.). 5-Cyano-1-*m*-dinitrophenyl-3-methylpyrazole has m. p. 169°. The chloropyrazole and sodium *p*-toluenesulphinate in dilute alcohol yield 5-*p*-toluenesulphonyl-1-*m*-dinitrophenyl-3-methylpyrazole, m. p. 219°, and is converted by potassium hydrogen sulphide into 5-ethylthio-1-*m*-dinitrophenyl-3-methylpyrazole, m. p. 259°; the last-named compound is accompanied by the potassium compound of 2':1':3:4:4'-nitrobenzo-1'':5'':5:6:3''-methylpyrazolo-N<sup>2</sup>-hydroxy-N<sup>2</sup>-oxy-1:2:5-thiodiazine (cf. I), from which the hydrogen compound, m. p. 179°, is obtained by addition of dilute acid.

H. WREN.

**Colour reactions of thiolglyoxalines (thioliminazoles) with sodium diazobenzene-*p*-sulphonate.** G. HUNTER (J.C.S., 1920, 2343–2346).—The test previously described (A., 1928, 316) for ergothioneine is a general one for 2-thiolglyoxalines containing a displaceable hydrogen or carboxyl group in position 4 (or 5); a free imino-hydrogen may also be necessary (cf. the conditions postulated by Fargher and Pym, J.C.S., 1919, 115, 217, for the coupling of glyoxalines with the diazo-reagent). Blocking the thiol group renders the test negative. Thus, positive reactions are given by ergothioneine, thiolurocanic acid, 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylic acid, and 2-thiol-4(5)-aminomethylglyoxaline, whilst the acetic acid derivatives

$$O-NMe_2 \quad CH-NH \quad \begin{smallmatrix} CO-CH-CH_2-C \\ \diagup \diagdown \end{smallmatrix} \begin{smallmatrix} N \\ \diagup \diagdown \end{smallmatrix} \begin{smallmatrix} C-S-CH_2-CO_2H \\ \diagup \diagdown \end{smallmatrix}$$

and

$$CO_2H-CH-CH_2-C \begin{smallmatrix} CH-NH \\ \diagup \diagdown \end{smallmatrix} \begin{smallmatrix} N \\ \diagup \diagdown \end{smallmatrix} \begin{smallmatrix} C-S-CH_2-CO_2H \\ \diagup \diagdown \end{smallmatrix}$$

respect-



ively, of ergothioneine and of thiolurocanic acid and 2-ethylthiol-5(4)-carbethoxy-4(5)-methylglyoxaline do not respond. The presence of a free thiol group in position 2 inhibits the usual diazo-reactions (Pauly, A., 1904, i, 1068; Koessler and Hanke, A., 1920, ii, 67); blocking the thiol group by replacing the hydrogen atom by an alkyl (or presumably by an aryl) group restores the sensitivity to the diazo-reagent.

R. CHILD.

**Stereoisomerism of carnosine.** V. GULEVITSCH (Z. physiol. Chem., 1930, 191, 126).—The optical form of the histidine present in carnosine was determined by Dietrich in 1915;  $[\alpha]_D^{20}$  was given as  $-38.4^\circ$  (cf. Linneweh and Linneweh, this vol., 1194).

J. H. BIRKINSHAW.

**Local anæsthetics derived from piperazine.** E. FOURNEAU and B. SAMDAHL (Bull. Soc. chim., 1930, [iv], 47, 1003—1016).—Two series of local anæsthetics,  $C_4H_9N_2(CH_2 \cdot CMeR \cdot OH)_2$  and  $C_4H_9N_2[CH_2 \cdot CH(OH) \cdot CH_2 \cdot OR]_2$ , have been obtained by the action of piperazine hydrate (1 mol.) on 2 mols. of the ethylene oxides,  $R \cdot \begin{smallmatrix} CMe \\ \diagup \\ CH_2 \end{smallmatrix} O$ , and

$OR \cdot CH_2 \cdot CH_2 \cdot \begin{smallmatrix} CH_2 \\ \diagup \\ O \end{smallmatrix}$ , respectively. Anæsthetic action

is developed when  $R = Bu^a$  and increases with the mol. wt. to the heptyl derivatives, which have anæsthetic action on the cornea of the rabbit 9.1 and 22.5 times as great as that of cocaine, respectively. The following are described: 1:4-bis- $\beta$ -hydroxy- $\beta$ -methylamylpiperazine, b. p.  $171^\circ/3$  mm. [dihydrochloride, m. p.  $220$ — $221^\circ$  (decomp.); picrate, m. p.  $206^\circ$  (decomp.)], from  $\alpha\alpha$ -methylpropylethylene oxide, b. p.  $108$ — $110^\circ/756$  mm., obtained by the action of sodium hydroxide on methylchloromethylpropylcarbinol, b. p.  $78$ — $80^\circ/30$  mm., from chloroacetone and magnesium propyl bromide; 1:4-bis- $\beta$ -hydroxy- $\beta$ -methylhexylpiperazine, m. p.  $36$ — $37^\circ$ , b. p.  $188^\circ/25$  mm. [dihydrochloride, m. p.  $221$ — $222^\circ$  (decomp.); picrate, m. p.  $202^\circ$  (decomp.)], similarly obtained from methylchloromethylbutylcarbinol, b. p.  $84$ — $86^\circ/20$  mm., through  $\alpha\alpha$ -methylbutylethylene oxide, b. p.  $49$ — $50^\circ/20$  mm.; 1:4-bis- $\beta$ -hydroxy- $\beta$ -dimethylamylpiperazine, b. p.  $181$ — $183^\circ/3$  mm. [dihydrochloride, m. p.  $221$ — $222^\circ$  (decomp.); picrate, m. p.  $206$ — $207^\circ$  (decomp.)], from methylchloromethylisobutylcarbinol, b. p.  $65$ — $95^\circ/25$  mm., and  $\alpha\alpha$ -methylisobutylethylene oxide, b. p.  $120$ — $125^\circ/754$  mm.; 1:4-bis- $\beta$ -hydroxy- $\beta$ - $\epsilon$ -dimethylhexylpiperazine, m. p.  $57$ — $58^\circ$  [dihydrochloride, m. p.  $228^\circ$  (decomp.); picrate, m. p.  $208$ — $209^\circ$  (decomp.)], from methylchloromethylisoamylcarbinol, b. p.  $78$ — $118^\circ/20$  mm., and  $\alpha\alpha$ -methylisoamylethylene oxide, b. p.  $62$ — $64^\circ/17$  mm.; 1:4-bis- $\beta$ -hydroxy- $\beta$ -methyl-*n*-octylpiperazine, m. p.  $36$ — $38^\circ$  [dihydrochloride, m. p.  $230^\circ$  (decomp.); picrate, m. p.  $190$ — $191^\circ$  (decomp.)], from methylchloromethylhexylcarbinol, b. p.  $110$ — $140^\circ/45$  mm., and  $\alpha\alpha$ -methylhexylethylene oxide, b. p.  $77$ — $80^\circ/20$  mm.; 1:4-bis- $\beta$ -hydroxy- $\beta$ -methyl-*n*-onylpiperazine, m. p.  $40$ — $41^\circ$  [dihydrochloride, m. p.  $228$ — $229^\circ$  (decomp.)]. Similarly, 1:4- $\beta$ -hydroxy- $\gamma$ -propoxypropylpiperazine, b. p.  $209$ — $211^\circ/3.3$  mm. [dihydrochloride, m. p.  $223^\circ$  (after slight decomp. at  $213^\circ$ ); picrate, m. p.  $172$ — $174^\circ$  (decomp.)], is obtained from  $\gamma$ -propoxypropylene  $\alpha\beta$ -oxide, b. p.  $75$ — $77^\circ/60$  mm., prepared from  $\alpha$ -chloro- $\gamma$ -propoxypropan- $\beta$ -ol

( $\gamma$ -propoxy- $\alpha\beta$ -chlorohydrin), b. p.  $92$ — $95^\circ/15$  mm., obtained by condensation of propyl alcohol and epichlorohydrin in presence of sulphuric acid.  $\alpha$ -Chloro- $\gamma$ -butoxypropan- $\beta$ -ol, b. p.  $122$ — $124^\circ/40$  mm.,  $\gamma$ -butoxypropylene  $\alpha\beta$ -oxide, b. p.  $79$ — $80^\circ/30$  mm., 1:4-bis- $\beta$ -hydroxy- $\gamma$ -butoxypropylpiperazine, b. p.  $226$ — $228^\circ/2.7$  mm. [dihydrochloride, m. p.  $227^\circ$  (decomp. at  $217^\circ$ ); picrate, m. p.  $176$ — $177^\circ$  (decomp.)],  $\alpha$ -chloro- $\gamma$ -isobutoxypropan- $\beta$ -ol, b. p.  $100$ — $102^\circ/20$  mm.,  $\gamma$ -isobutoxypropylene  $\alpha\beta$ -oxide, b. p.  $58$ — $60^\circ/20$  mm., 1:4-bis- $\beta$ -hydroxy- $\gamma$ -isobutoxypropylpiperazine, b. p.  $210$ — $214^\circ/3$  mm. [dihydrochloride, m. p.  $240^\circ$  (decomp. at  $225^\circ$ ); picrate, m. p.  $177$ — $179^\circ$  (decomp.)],  $\gamma$ -isoamylloxypropylene  $\alpha\beta$ -oxide, b. p.  $78$ — $82^\circ/15$  mm., 1:4-bis- $\beta$ -hydroxy- $\gamma$ -isoamylloxypropylpiperazine, m. p.  $40$ — $42^\circ$  [dihydrochloride, m. p.  $220^\circ$  (decomp.); picrate, m. p.  $186^\circ$  (decomp.)],  $\alpha$ -chloro- $\gamma$ -hexoxypropan- $\beta$ -ol, b. p.  $140$ — $160^\circ/18$  mm.,  $\gamma$ -hexoxypropylene  $\alpha\beta$ -oxide, b. p.  $98$ — $105^\circ/20$  mm., 1:4-bis- $\beta$ -hydroxy- $\gamma$ -hexoxypropylpiperazine, oil [dihydrochloride, m. p.  $233^\circ$  (decomp. at  $220^\circ$ ); picrate, m. p.  $181$ — $184^\circ$  (decomp.)];  $\alpha$ -chloro- $\gamma$ -heptoxypropan- $\beta$ -ol, b. p.  $140$ — $150^\circ/18$  mm.,  $\gamma$ -heptoxypropylene  $\alpha\beta$ -oxide, b. p.  $125$ — $130^\circ/18$  mm., and 1:4-bis- $\beta$ -hydroxy- $\gamma$ -heptoxypropylpiperazine, an oil [dihydrochloride, m. p.  $238^\circ$  (decomp. at  $215^\circ$ ); picrate, m. p.  $180$ — $181^\circ$  (decomp.)], are also described. The anæsthetic power of the dihydrochlorides with reference to cocaine in the first series are 0.05, 0.79, 0.08 (*iso*), 1.60, 10.0, 9.1, respectively, from propyl to heptyl; and in the second series 0.0, 0.45, 0.05 (*iso*), 1.74, 8.3, 22.5.

R. BRIGHTMAN.

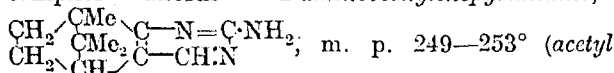
#### Base from 2:5-dimethylpyrazine methiodide.

J. G. ASTON (J. Amer. Chem. Soc., 1930, 52, 4172—4173).—A pure base could not be isolated by treatment of 2:5-dimethylpyrazine methiodide with alkali (cf. Princivalle, this vol., 929); a kinetic study of the reaction between the methiodide and alkali hydroxide, using a conductometric method, indicates the change  $2 \left[ CH \begin{smallmatrix} N=CMe \\ \diagup \\ CMe \cdot NMe \end{smallmatrix} CH \right]^+ + 2OH^- \rightarrow \left[ CH \begin{smallmatrix} N=CMe \\ \diagup \\ CMe \cdot NMe \end{smallmatrix} CH \right]_2 O$ . Treatment of 1:2:2:5:5-pentamethyl- and 1:2:2:3:5:5:6-heptamethyl-2:5-dihydropyrazinium iodides with aqueous alkali affords 6-hydroxy-1:2:2:5:5-pentamethyl-, m. p.  $110^\circ$ , and 1:2:2:3:5:5-hexamethyl-6-methylene-1:2:5:6-tetrahydropyrazines, b. p.  $78^\circ/6.5$  mm., respectively. The reaction involving the formation of the last-named compound is similar to that whereby 6-keto-1:2:4-trimethyl-5-methylene-1:4:5:6-tetrahydropyrazine is produced from 6-keto-1:2:5-trimethyl-1:6-dihydropyrazine methiodide (Gastaldi and Princivalle, this vol., 223); the changes,  $\cdot NMe \cdot CMe \cdot + OH^- \rightleftharpoons \cdot NHMe \cdot \dot{C} : CH_2 + OH^- \rightleftharpoons \cdot NMe \cdot \dot{C} : CH_2 + H_2O$ , probably occur, caused by reduced conjugation in the pyrazine ring.

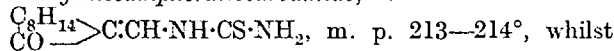
H. BURTON.

**Action of guanidine and carbamide on hydroxymethylene ketones.** E. BENARY (Ber., 1930, 63, [B], 2601—2608).—The action of guanidine on hydroxymethylene ketones appears to lead generally to substituted pyrimidines. The sodium derivative of hydroxymethyleneacetone is transformed when

shaken with guanidine nitrate in absolute alcohol at the ordinary temperature into 2-amino-4-methylpyrimidine (picrate, m. p. 235—236° (decomp.) after darkening), converted by bromine into 5-bromo-2-amino-4-methylpyrimidine, m. p. 195°, in which the bromine atom is very firmly retained. 2-Chloroacetamido-4-methylpyrimidine, decomp. about 235° after darkening about 165°, is transformed by alcoholic ammonia mainly into the parent amine. 2-Amino-4:5-dimethylpyrimidine, m. p. 216—217° [chloroacetyl derivative, m. p. 145—148° (decomp.)], is more conveniently prepared from guanidine carbonate and methyl  $\alpha$ -hydroxymethylene-ethyl ketone in boiling alcohol. Methyl propyl ketone through the sodium derivative of its hydroxymethylene compound yields 2-amino-4-propylpyrimidine, m. p. 122—123°. 2-Amino-4- $\delta$ -methyl- $\Delta^7$ -pentenylpyrimidine, m. p. 155—159°, is derived from methylheptenone. The reaction is applicable to fatty-aromatic ketones; 2-amino-4-phenylpyrimidine, m. p. 165°, 2-amino-4-p-tolylpyrimidine, m. p. 189—191°, and 2-amino-4-p-anisylpyrimidine, m. p. 185—187°, are described. Hydroxymethylene derivatives of cyclic ketones readily yield dicyclic compounds when boiled with guanidine carbonate in alcohol. The amino-compounds do not usually affect litmus, can be subjected without change to protracted ebullition with dilute hydrochloric acid, and are generally without action on nitrous acid. They may be used for the characterisation of ketones which yield hydroxymethylene compounds. Hydroxymethylene-cyclohexanone and cyclopentanone yield respectively 2-amino-5:6:7:8-tetrahydroquinazoline, m. p. 206—210°, and 2-amino-4:5-trimethylenepyrimidine, m. p. 206—208°. 2-Amino-5-methyl-8-isopropyl-5:6:7:8-tetrahydroquinazoline, m. p. 139—141° (acetyl derivative, m. p. 125—127°), is derived from hydroxymethylenementhone and 2-amino-8-methyl-5- $\alpha$ -methyleneethyl-5:6-dihydroquinazoline, m. p. 165—167°, from hydroxymethylene-carvone. In boiling amyl alcohol, hydroxymethylene-camphor affords "2-aminobornylene-pyrimidine,"



derivative, m. p. 154—155°; chloroacetyl compound, m. p. 156—159°. With thiocarbamide in boiling amyl alcohol, hydroxymethylenecamphor gives methylenecamphor-thiocarbamide,



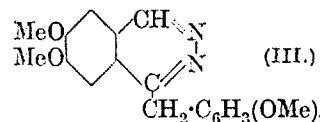
hydroxymethylenecyclohexanone and carbamide in boiling alcohol yield methylenecyclohexanone-carbamide, m. p. about 229—230° (decomp.). Methyl  $\alpha$ -hydroxymethylene-ethyl ketone and carbamide afford  $\gamma$ -keto- $\beta$ -methyl- $\Delta^6$ -butenylcarbamide, m. p. 156°.

Ethyl hydroxymethylenecetoacetate and guanidine yield essentially iminomethyluracil. H. WREN.

**Phthalazines.** II. J. S. AGGARWAL, I. D. KHERA, and J. N. RAY (J.C.S., 1930, 2354—2357; cf. A., 1929, 1314).—Phthalazines having some structural analogy with papaverine have been prepared; the following substances are described: veratraldehyde-phenylacetylhydrazine, m. p. 171—172°, converted by amyl-alcoholic hydrogen chloride into 6:7-di-

methoxy-1-benzylphthalazine, m. p. 191—192°; s-phenylacetyl-3:4-dimethoxybenzylhydrazine, m. p. 129—130° (by reduction of the above hydrazone); piperonaldehydephenylacetylhydrazine, m. p. 210°; 6:7-methylenedioxy-1-benzylphthalazine (I), m. p. 203—204°; anisaldehydephenylacetylhydrazine, m. p. 167°; 7-methoxy-1-benzylphthalazine (II), m. p. 168—169° (picrate, m. p. 208—209°); s-phenylacetyl-4-methoxybenzylhydrazine, m. p. 98—99° (insoluble copper derivative); o- and m-methoxybenzaldehydephenylacetylhydrazones, m. p. 141—142° and 107—108°, respectively, are not converted into phthalazines by the usual treatment; benzaldehydephenylacetylhydrazine, m. p. 148—149°; s-phenylacetyl-benzyl-, 2-methoxybenzyl-, and 3-methoxybenzyl-hydrazine, m. p. 113—114°, 79—80°, and 94—95°, respectively.

3:4-Dimethoxyphenylacetylhydrazine (from ethyl 3:4-dimethoxyphenylacetate and hydrazine hydrate at 100°), m. p. 115—116°, condenses readily with veratraldehyde; the hydrazone (not isolated) is easily converted into 6:7:3':4'-tetramethoxy-1-benzylphthalazine (III), m. p. 192—193° (picrate, m. p. 186—187°).



Phthalazines are hydrolysed by hydrochloric acid in the presence of phthalic acid to o-aldehydoketones and hydrazine (removed as the insoluble phthaloyl derivative); thus, II gives 4-methoxy-2-phenylacetylbenzaldehyde, isolated as the diphenylhydrazone, m. p. 122—133°; whilst from I is obtained 3:4-methylenedioxy-6-phenylacetylbenzaldehydediphenylhydrazone, m. p. 104—105°.

The phthalazine III has no action on tubercle bacilli (E. HESSE, Breslau). R. CHILD.

**Constitution of complex metallic compounds of indigotin.** K. KUNZ (Ber., 1930, 63, [B], 2600; cf. Kuhn and Machemer, A., 1928, 306; Machemer, this vol., 1048, 1193).—A review. H. WREN.

**1:3:4-Triazoles.** K. L. BHAGAT and J. N. RAY (J.C.S., 1930, 2357—2358).—The following compounds have been prepared (for pharmacological investigation) by the reaction of Pellizzari and Alciatore (A., 1901, i, 571): from s-dibenzoylhydrazine and the appropriate amine: 1:2:5-triphenyl-, 2:5-diphenyl-1-p-tolyl-, 2:5-diphenyl-1-p-methoxyphenyl-2:5-diphenyl-1-m-tolyl-, and 2:5-diphenyl-1-p-ethoxyphenyl-1:3:4-triazoles, m. p. 292° (loc. cit., 305°), 296—297°, 246—247°, 250°, and 215°, respectively; from s-phenylacetylbenzoylhydrazine, m. p. 214—215°, and the requisite amine: 1:2-diphenyl-5-benzyl-, 2-phenyl-1-m-tolyl-5-benzyl-, and 2-phenyl-1-p-methoxyphenyl-5-benzyl-1:3:4-triazoles, m. p. 200°, 240°, and 225°, respectively.

Triazoles could not be obtained from sulphanilic and orthanilic acids. s-Acetylbenzoylhydrazine reacts with aromatic amines to give acyl derivatives only. The triazoles are weak bases not forming stable salts with acids. R. CHILD.

**Porphyryns. XXVI. "Hæmoporphyrin."** H. FISCHER, H. HELBERGER, and G. HUMMEL (Z. physiol. Chem., 1930, 191, 251—261; cf. this vol., 1194).—"Hæmoporphyrin" prepared according to Willstätter's method (A., 1913, i, 1251) is a mixture containing mesoporphyrin, deuteroporphyrin, and the two tetramethylmonoethyldipropionic acid porphins derived from ætioporphyrin III. This was shown in the following way. The potassium salt of hæmophyllin on oxidation with chromic anhydride in acetic acid yielded a mixture of methylethylmaleimide and citraconimide. Hæmoporphyrin ester was brominated in acetic acid. Fractionation with hydrochloric acid yielded mesoporphyrin and a mixture of a mono- with a small amount of a di-bromoporphyrin, probably dibromodeuteroporphyrin. Oxidation of the dibrom-ester yielded a mixed imide. The acetylation of the iron salt of hæmoporphyrin ester gave rise to the diacetyldeutero-ester and dimethyl monoacetylmonoethyltetramethylporphindipropionate.

J. H. BIRKINSHAW.

**Porphyryns. XXXIV. Synthesis of isouroporphyrin.** I. H. FISCHER and R. SIEBERT (Annalen, 1930, 483, 1—17).—2:4-Dimethyl-3- $\beta$ -dicarboxyethylpyrrole-5-carboxylic acid, decomp. 85°, is obtained by careful acidification of a solution of its trisodium salt (A., 1926, 178) with hydrochloric acid at  $-5^\circ$  to  $-3^\circ$ . Treatment of this with bromine in acetic acid below  $30^\circ$  gives the hydrobromide, decomp.  $181^\circ$ , of 5-bromo-4:3':5'-trimethyl-3:4'-di-( $\beta$ -dicarboxyethyl)pyrromethene [tetramethyl ester, m. p.  $113^\circ$  (hydrobromide, decomp.  $202^\circ$ ; copper, decomp.  $152^\circ$ ; zinc, decomp.  $149^\circ$ ; nickel, decomp.  $147^\circ$ ; cadmium, decomp.  $115^\circ$ ; manganese, decomp.  $153^\circ$ ; and cobalt, decomp.  $151^\circ$ , salts)]. When this is fused with succinic, methylsuccinic, or tartaric acid, or treated with solutions of hydrogen bromide in acetic acid or methyl alcohol at various temperatures, coproporphyrin I is produced owing to decarboxylation having occurred. Prolonged treatment of the methene ester with a saturated solution of hydrogen bromide in formic acid at  $65^\circ$  and  $75^\circ$  furnishes mixtures of coproporphyrin I and partly decarboxylated isouroporphyrins, but at  $45$ – $50^\circ$ , isouroporphyrin I [1:3:5:7-tetramethyl-2:4:6:8-tetra- $\beta$ -dicarboxyethylporphin] is produced. This is isolated as the octamethyl ester, m. p.  $284^\circ$  (copper salt, m. p.  $289^\circ$  after sintering at  $280^\circ$ ), which differs from natural uroporphyrin octamethyl ester (m. p.  $292^\circ$ ). Treatment of the ester with 1% hydrochloric acid at  $180^\circ$  furnishes coproporphyrin I. It is considered that natural uroporphyrin may contain succinic acid residues rather than malonic acid groups.

Ethyl 2:4-dimethyl-3- $\beta$ -dicarboxyethylpyrrole-5-carboxylate, m. p.  $192^\circ$  (3- $\beta$ -dimethyl 5-ethyl ester, m. p.  $127^\circ$ ), is obtained when the corresponding triethyl ester is hydrolysed with alcoholic sodium hydroxide solution. When a cold, concentrated methyl-alcoholic solution of the above tricarboxylic acid is treated with dry hydrogen chloride, 3:5:3':5'-tetramethyl-4:4'-di-( $\beta$ -dicarboxyethyl)pyrromethene hydrochloride, decomp.  $211^\circ$ , is formed.

H. BURTON.

**Structure of aniline-black. I. Interaction of emeraldine and nigraniline with amines. II.**

**Interaction of nigraniline with aniline. I. S. JOFFE and R. M. METRIKINA (J. Russ. Phys. Chem. Soc., 1930, 62, 1101—1114, 1115—1122).**—I. Nigraniline does not condense with aminosulphonic acids (metanilic, sulphanilic, and  $\alpha$ -naphthylamine-3:6-disulphonic acids) to yield sulpho-derivatives of aniline-black. Nigraniline is converted by weak oxidising agents into products soluble in aqueous alkali. Chromic acid reacts with aniline hydrochloride to produce an insoluble precipitate, and the same effect is obtained by using nigraniline in place of aniline; when the two bases are present together the yield of insoluble products is equal to the sum of that which would be obtained were they treated separately.

II. The yield of insoluble products obtained by the oxidation by chromic acid of systems containing nigraniline and aniline hydrochloride increases with time. This effect is due not to condensation of aniline with nigraniline, but probably to the oxidation of the former by the latter, yielding fresh insoluble products.

R. TRUSZKOWSKI.

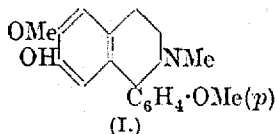
**Reactivity of electropositive hydrogen atoms. IV. Oxido-oxazoles.** W. DILTHEY and J. FRIEDRICHSEN (J. pr. Chem., 1930, [ii], 127, 292—306).—The compounds obtained by Diels and Riley (A., 1915, i, 690) by condensation of diacetylmonoxime with aromatic aldehydes under the influence of aqueous hydrochloric acid are more conveniently prepared when hydrogen chloride in acetic acid is used as condensing agent, unstable hydrochlorides of these weak bases being usually obtained as initial products. Similar compounds are obtained with oximinopropiophenone,  $\text{OH}\cdot\text{N}\cdot\text{CMeBz}$ , and  $\alpha$ - and  $\beta$ -benzilmonoximes; a doubtful sample of oximinobenzyl methyl ketone ( $\text{CPhAc}\cdot\text{N}\cdot\text{OH}$ ) did not, however, react. Formation of these compounds from benzilmonoxime, and the reduction of the benzaldehyde derivative to 2:4:5-triphenyloxazole (Zinin, Annalen, 1840, 34, 191), confirms the structure assigned by Diels and Riley, except in regard to the mode of attachment of the additional oxygen atom, which is still uncertain. The following are described: (from diacetylmonoxime), 2-phenyl-4:5-dimethyloxido-oxazole, m. p.  $103$ – $104^\circ$ ; 2-anisyl-, m. p.  $141^\circ$ ; ( $+2\text{H}_2\text{O}$ ), m. p. about  $80^\circ$  (Diels and Riley, loc. cit.); 2-salicyl-, m. p.  $105$ – $106^\circ$ ; 2-(3':4'-methylene-dioxyphenyl)-, m. p.  $175$ – $176^\circ$ ; 2-m-nitrophenyl-, m. p.  $159$ – $160^\circ$  (decomp.); 2-p-nitrophenyl-, m. p.  $199$ – $200^\circ$ ; 2-styryl-, m. p.  $131^\circ$  (decomp.); and 2-(2':4'-dihydroxyphenyl)-4:5-dimethyloxido-oxazole, m. p.  $225$ – $226^\circ$ ; (from oximinopropiophenone), 2:5-diphenyl-4-methyloxido-oxazole, m. p.  $153^\circ$ ; ( $+1\text{H}_2\text{O}$ ); 2-anisyl-, m. p.  $156$ – $157^\circ$  (decomp.); ( $+3\text{H}_2\text{O}$ ); 2-salicyl-, m. p.  $130$ – $131^\circ$ ; 2-(3':4'-methylenedioxyphenyl)-, m. p.  $168$ – $170^\circ$ ; 2-m-nitrophenyl-, m. p.  $176$ – $177^\circ$  (decomp.); 2-o-nitrophenyl-, m. p.  $157$ – $158^\circ$ ; and 2-p-nitrophenyl-4-methyl-5-phenyloxido-oxazole, m. p.  $188$ – $189^\circ$ ; (from  $\alpha$ - and  $\beta$ -benzilmonoximes), 2:4:5-triphenyloxido-oxazole ( $+3\text{H}_2\text{O}$ ; lost at  $105^\circ$ ), m. p.  $170$ – $171^\circ$ ; (from  $\alpha$ -benzilmonoxime), 2-anisyl-, m. p.  $194$ – $195^\circ$ ; and 2-m-nitrophenyl-4:5-diphenyloxido-oxazole, m. p.  $178$ – $179^\circ$ . 2:4:5-Triphenyl- and 2-anisyl-5-phenyl-4-methyl-oxido-oxazoles, when reduced by the method of Diels and Riley, give 2:4:5-triphenyloxazole, m. p.  $114$ – $115^\circ$ ,

and 2-anisyl-5-phenyl-4-methyloxazole, m. p. 77—78°, respectively. H. A. PIGGOTT.

**Synthesis of thiazole amines possessing pharmacological interest.** V. VI. W. S. HINEGARDNER and T. B. JOHNSON (J. Amer. Chem. Soc., 1930, 52, 4139—4141, 4141—4144).—V. *s*-Dichloroacetone and thioanisamide react in warm alcohol, forming 2-*p*-methoxyphenyl-4-chloromethylthiazole, b. p. 185—188°/3—4 mm., m. p. 55—56°, which with ethyl sodiomalonate gives ethyl 2-*p*-methoxyphenyl-4-thiazolymethylmalonate, b. p. 235—239°/3—4 mm. [free acid (+2H<sub>2</sub>O), m. p. 97°]. β-2-*p*-Methoxyphenyl-4-thiazolylpropionic acid, m. p. 126—127°, is converted by way of its ethyl ester, m. p. 53—54°, hydrazide, m. p. 158—159°, and azide, m. p. 78—79°, into *s*-di-(β-2-*p*-methoxyphenyl-4-thiazolylethyl)carbamide, m. p. 173—174°, which when heated with phthalic anhydride at 220—225° furnishes β-2-*p*-methoxyphenyl-4-thiazolylethylphthalimide, m. p. 120—121°. This is converted by treatment with alcoholic hydrazine hydrate into β-2-*p*-methoxyphenyl-4-thiazolylethylamine, b. p. 292—293°/3—4 mm., demethylated by boiling with 48% hydrobromic acid to β-2-*p*-hydroxyphenyl-4-thiazolylethylamine, an oil (hydrochloride, m. p. 218—222°).

VI. 3:4-Dimethoxythiobenzamide, m. p. 183°, prepared from 3:4-dimethoxybenzonitrile and alcoholic hydrogen sulphide at 100°, is converted as above into 2-3':4'-dimethoxyphenyl-4-chloromethylthiazole, m. p. 89—90°, and thence by way of 2-3':4'-dimethoxyphenyl-4-thiazolymethylmalonic acid (+H<sub>2</sub>O), m. p. 141° (ethyl ester, b. p. 251—255°/2—3 mm.), β-2-3':4'-dimethoxyphenyl-4-thiazolylpropionic acid, m. p. 94° (ethyl ester, b. p. 220—223°/3 mm., m. p. 69°; hydrazide, m. p. 162°; azide, m. p. 77—78°), and *s*-di-(β-2-3':4'-dimethoxyphenyl-4-thiazolylethyl)carbamide, m. p. 165—166°, into β-2-3':4'-dimethoxyphenyl-4-thiazolylethylamine, b. p. 210—212°/4 mm. (dihydrochloride, m. p. 225—227°; phthaloyl derivative, m. p. 143—144°). The corresponding dihydroxy-amine has not been obtained pure. H. BURTON.

**Constitution of dauricine.** H. KONDO and Z. MARITA (Ber., 1930, 63, [B], 2420—2423).—Dauricine is converted by ethyl bromide in presence of methylalcoholic potassium hydroxide into ethyldauricine ethobromide, decomp. 136—139° [corresponding chloroplatinate, (C<sub>23</sub>H<sub>32</sub>O<sub>3</sub>NCl)<sub>2</sub>PtCl<sub>4</sub>, decomp. 215—218°], transformed by boiling 20% potassium hydroxide into α-ethyldauricine-ethylmethine, [α]<sub>D</sub><sup>20</sup> ± 0° in acetone, from which the methiodide, C<sub>23</sub>H<sub>31</sub>O<sub>3</sub>N.MeI, decomp. 162—165°, is obtained. Degradation of the methiodide affords dimethylethylamine and de-*N*-ethyldauricine, oxidised by permanganate in acetone to 2-ethoxydiphenyl ether 3:4'-dicarboxylic acid. The constitution I is therefore rendered probable for dauricine. Redetermination of the mol. wt. of the base in camphor



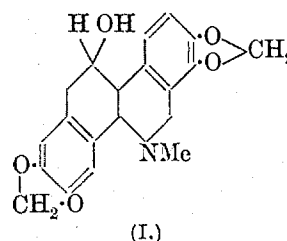
confirms the simple formula (cf. Faltis, this vol., 774). 2-Methoxydiphenyl ether 3:4'-dicarboxylic acid (cf. Späth, A., 1929, 1319) is demethylated to 2-hydroxydiphenyl ether 3:4'-dicarboxylic acid, m. p. 232°,

which with methyl alcohol and ethyl bromide gives 2-ethoxydiphenyl ether 3:4'-dicarboxylic acid, m. p. 276—277°. H. WREN.

[Yohimbe alkaloids. VI. Two further subsidiary alkaloids of yohimbine.] R. LILLIG (Ber., 1930, 63, [B], 2680).—A reply to Hahn and Schuch (this vol., 1194). The author confirms his observation (Merck's Jahresber., 1928) that crystals of α-yohimbine from 95% ethyl alcohol have the composition C<sub>21</sub>H<sub>26</sub>O<sub>3</sub>N<sub>2</sub>.EtOH.H<sub>2</sub>O. The divergent results are due to the use of methyl alcohol as solvent.

H. WREN.

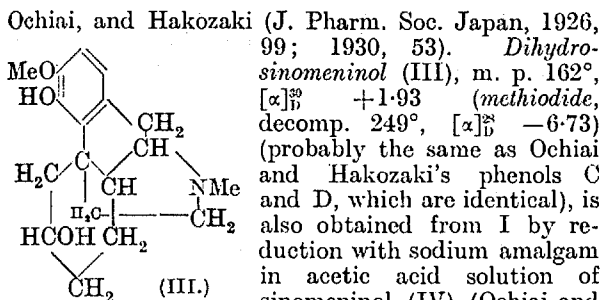
**Constitution of chelidonine.** F. VON BRUCHHAUSEN and H. W. BERSCH (Ber., 1930, 63, [B], 2520—2527).—Theoretical considerations together with the



likeness of protopine to chelidonine lead the authors to propose the constitution I for the latter alkaloid. This constitution is not in harmony with the oxidation of chelidoninemethene to hydrastic and 4:5-methylenedioxy-2-dimethylaminomethylbenzoic acids recorded by Schwarz (Diss., Marburg, 1928). Re-examination of the last-named acid shows it to be 3:4-methylenedioxy-2-dimethylaminomethylbenzoic acid.

Cryptopine is converted through the *iso*-chloride into anhydrocryptopine, which is catalytically reduced, essentially in the vinyl side-chain, in presence of palladised charcoal to the non-crystalline allodihydroanhydrocryptopine [methiodide, C<sub>22</sub>H<sub>26</sub>O<sub>4</sub>Ni, m. p. 233° (corr., decomp.)]. Treatment of the last-named substance with sodium amalgam in faintly acid solution causes saturation of the stilbene double linking, thus giving the non-crystalline tetrahydroanhydrocryptopine [methiodide, C<sub>22</sub>H<sub>28</sub>O<sub>4</sub>Ni, m. p. 222° (corr., decomp.)]. When methylated and boiled with alkali hydroxide the tetrahydro-compound de-*N*-methyltetrahydroanhydrocryptopine, C<sub>22</sub>H<sub>27</sub>O<sub>4</sub>N, m. p. 99° (corr.), oxidised by permanganate in acetone to 4:5-dimethoxy-2-ethylbenzoic acid, m. p. 146° (corr.), and 3:4-methylenedioxy-2-dimethylaminomethylbenzoic acid, m. p. 191° (identical with the acid of Schwarz), is obtained. The acid is prepared in better yield by ozonisation of the de-*N*-methyl compound. Its structure is confirmed further by its methylation and subsequent Emde degradation to 3:4-methylenedioxy-1-methylbenzoic acid, m. p. 215°. H. WREN.

**Sinomenine and disinomenine.** XIX. Reduction of sinomenine and dihydrosinomenine with sodium amalgam. K. GOTO and S. MITSUI (Bull. Chem. Soc. Japan, 1930, 5, 282—290).—Reduction of dihydrosinomenine (I) (A., 1926, 1160) by sodium amalgam equivalent to 4H gives, besides dihydrosinomeninol, a mixture, m. p. 144° (decomp. 149°), of demethoxydihydrosinomenine (this vol., 230) and demethoxydihydrosinomeninol (II), inseparable by physical means; this mixture on further reduction affords the latter, decomp. 143° (methiodide, m. p. 280°), thus confirming the observations of Kondo,



Hakoziaki's phenol F); the last-named results from the reduction of sinomenine by sodium amalgam in acetic acid solution.

A table of the colour reactions of II, III, and IV is given. R. CHILD.

**Arsenation of aromatic aldehydes.** A. B. SCOTT and C. S. HAMILTON (J. Amer. Chem. Soc., 1930, 52, 4122—4128).—3-Nitro-4-aminobenzaldehyde is converted by the Bart reaction into impure 3-nitrobenzaldehyde-4-arsinic acid (47% yield), which softens and darkens at 155° and then decomposes gradually (*p*-nitrophenylhydrazone, decomp. 260—270°; *β*-naphthylhydrazone, decomp. 235—245° after darkening at 210°; semicarbazone, decomp. about 250° after darkening at about 220°, reduced by ferrous chloride and alkali to 3-aminobenzaldehydesemicarbazone-4-arsinic acid). Benzaldehyde-*p*-nitrophenylhydrazone-3-arsinic acid, m. p. 200—210° (decomp.), is obtained when *m*-aminobenzaldehyde is subjected to the Bart reaction and the product treated with *p*-nitrophenylhydrazine. Oxidation of *p*-tolylarsinic acid with chromic oxide in presence of acetic acid, anhydride, and sulphuric acid at 0—10° affords the diacetate of benzaldehyde-4-arsinic acid (*p*-nitrophenylhydrazone). The reduction of arsinic acids to arsenobenzene derivatives by hypophosphorous acid serves as a qualitative test for the presence of the arsinic acid group; the arsenobenzene is precipitated.

H. BURTON.

***β*-Chlorovinylarsines.** W. L. LEWIS and H. W. STIEGLER (J. Amer. Chem. Soc., 1930, 52, 4164).—The compounds previously described (A., 1925, i, 1470) as 6-*β*-chlorovinylphenarsazine and 7-*β*-chlorovinyl-7:12-dihydrobenzophenarsazine are 10-chloro-5:10-dihydrophenarsazine and 7-chloro-7:12-dihydrobenzophenarsazine, respectively [as shown by Burton and Gibson (A., 1926, 419)]. H. BURTON.

**Constitution and properties of 10-chloro-5:10-dihydrophenarsazine and some derivatives.** C. S. GIBSON, J. D. A. JOHNSON, and D. C. VINING (Rec. trav. chim., 1930, 49, 1006—1035).—A résumé of previous work is given and priority is claimed for the views re-expressed by Kappelmeyer (this vol., 354). His view that 10-chloro-*N*-methyl-5:10-dihydrophenarsazine exists is criticised. The constitution of the molecular compounds formed from 10-chloro-5:10-dihydrophenarsazine and the common organic solvents is discussed, and a structural formula for the compound formed from carbon tetrachloride and 10-chloro-5:10-dihydrophenarsazine presented. The evidence in favour of a transannellar linking formula for some dihydrophenarsazine derivatives is reviewed.

It is considered that two factors will favour the preservation of the "true dihydrophenarsazine type" as distinct from the transannellar linking structure, viz., the replacement of the imino-hydrogen atom by an acyl group, or the presence of a suitable donor group in the 4-position in the dihydrophenarsazine nucleus, which restricts the motion of the imino-hydrogen atom by chelation. Lists are given of those secondary aromatic amines which do and do not condense with arsenious chloride, and assuming the possibility of formation of a preliminary additive compound only in certain cases, an explanation of the mechanism of, and factors underlying, condensation is advanced. The reduction of 2:4-dinitrodiphenylamine-6'-arsinic acid, m. p. 223—225° (decomp.) after softening (ammonium, calcium, barium, magnesium, and heavy metal salts), to 2:4-dinitrodiphenylamine-6'-dichloroarsine, m. p. 151—152°, is in agreement with previous work. Diphenylchloroarsine does not (?) react with ethyl sodiomalonate, and the formation of 10-chloro-5:10-dihydrophenarsazine is shown to be a reversible reaction.

The interpretation by Razubaiew (A., 1929, 585, 834) of his observations on the action of formic acid on phenarsazine derivatives, is shown to be at variance with modern views on valency, and an alternative explanation founded on the following experimental evidence is advanced. 10-Formyl-5:10-dihydrophenarsazine is converted on heating into a substance, (I)  $C_{24}H_{20}ON_2As_2$ . 10:10'-Oxybis-(5:10-dihydrophenarsazine) on treatment with hot formic acid yields a deep crimson-coloured solution from which after several days a dark reddish-brown substance (II)  $C_{22}H_{22}O_2N_2As$ , m. p. 320° (decomp.), slowly separates. When heated in air, this loses formic acid and a substance (III) of the same composition as, but not identical with, 10:10'-bis-(5:10-dihydrophenarsazine) is obtained. On hydrolysis, II furnishes 10:10'-oxybis-(5:10-dihydrophenarsazine) if aerial oxidation takes place, but a new "reduced" oxy-compound,  $C_{24}H_{20}ON_2As_2$ , identical with I if air be excluded. If III is dissolved in boiling formic acid and the crimson solution kept for several days, the colour of the solution fades and a scarlet substance (IV) gradually separates. These results are in quantitative agreement with those obtained by Razubaiew, but since I, II, and III dissolve in cold formic acid with the immediate formation of a crimson coloration (I and III reverting to II), the explanation of Razubaiew involving a meriquinonoid formula for the reduction product of 10-chloro-5:10-dihydrophenarsazine is considered unnecessary.

An improved method of preparation of *m*-bromophenylarsinic acid, m. p. 180—181° (calcium salt) (cf. Barber, A., 1929, 1471), is detailed, and the following are described: 4-hydroxydiphenylamine-6'-arsinic acid, darkens at 188°, blackens at 194°, and decomposes at 197—198°; a substance  $NHPh \cdot C_6H_4 \cdot NH_2 \cdot AsCl_2 \cdot 2HCl$  (?), m. p. 155—157°; *m*-bromophenyldichloroarsine, m. p. 8—10°, b. p. 165°/18 mm.; 10-fluoro-5:10-dihydrophenarsazine acetate,  $[NH(C_6H_4)_2AsF_3]_3 \cdot AcOH$ , darkens at 250—280°, decomp. 285—287°; a molecular compound of 10-iodo-5:10-dihydrophenarsazine and benzene; 10-thiocyano-5:10-dihydrophenarsazine, m. p. 238—240°

(indef.); 10-aceto-5:10-dihydrophenarsazine picrate, m. p. 170—174°; 10-trichloroaceto-5:10-dihydrophenarsazine, m. p. 159—160°; 10:10'-sulphatobis-(5:10-dihydrophenarsazine), red and yellow forms; both blacken at 280°, decomp. 290—295°; and 10:10'-oxalatobis-(5:10-dihydrophenarsazine) acetate,  $\{[NH(C_6H_4)_2AsO \cdot OC \cdot]_2 \cdot AcOH, decomp. 295—300^\circ$ .

Phenyldichloroarsine is dearsenicated when treated with aluminium chloride and chloroacetyl chloride in carbon disulphide, phenacyl chloride being formed.

J. D. A. JOHNSON.

**Valency-chemical investigation of metal alkyls of the third group of the periodic system. Subsidiary valency phenomena of aluminium aryls.** E. KRAUSE and P. DITTMAR (Ber., 1930, 63, [B], 2401—2407).—Aluminium tri-*p*-tolyl monoetherate, m. p. 125°, is prepared by the action of aluminium on mercury di-*p*-tolyl in complete absence of air (apparatus described). Expulsion of ether by heating necessitates the use of a temperature so high that the product is partly resinified. Aluminium tri-*p*-tolyl is therefore prepared from aluminium and mercury di-*p*-tolyl in presence of benzene. The ammoniate,  $Al(C_6H_4Me)_3 \cdot NH_3$ , softening at about 120°, is obtained from the etherate and ammonia in ether. Aluminium triphenyl, obtained in the same manner as the tri-*p*-tolyl, gives an ammoniate,  $AlPh_3 \cdot NH_3$ , m. p. 112° (decomp.). Aluminium tri-*p*-tolyl appears to be associated in freezing or boiling benzene, whereas its etherate (and that of aluminium triphenyl) has normal mol. wt.

H. WREN.

**Organic germanium derivatives. IV. Germanium diphenyl and octaphenylgermanoprop-ane.** C. A. KRAUS and C. L. BROWN (J. Amer. Chem. Soc., 1930, 52, 4031—4035).—Diphenylgermanium dichloride is not ammonolysed in ethylamine solution. The dichloride is reduced by lithium in ethylamine to a product which is probably a complex containing the diphenylgermanium group and ethylamine. Reduction of the dichloride with sodium in boiling xylene in an atmosphere of nitrogen (cf. Morgan and Drew, A., 1925, i, 1197) affords 10—20% of the theoretical amount of germanium diphenyl, probably  $(GePh_2)_4$ , m. p. 294—295° (corr.), and resinous material. When the diphenyl is treated with sodium in liquid ammonia disodium diphenylgermanide is produced. Treatment of this with ammonium bromide gives a viscous liquid. Diphenylgermanium dichloride (1 mol.) and sodium triphenylgermanide (2 mols.) react in warm benzene yielding octaphenylgermanoprop-ane [octaphenyltrigermane],  $Ge_3Ph_8$ , m. p. 247—248° (corr.), which when treated with bromine in carbon tetrachloride gives triphenylgermanium bromide, diphenylgermanium dibromide, and unchanged material; the Ge-Ge linking is less stable to bromine than the Ge-Ph linking.

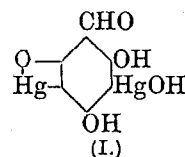
H. BURTON.

**Mercury derivatives of acetamidocresols.** A. PROSKOURIAKOFF and R. J. TITHERINGTON (J. Amer. Chem. Soc., 1930, 52, 3978—3984).—Aminocresols are conveniently prepared by reduction of nitrocresols with sodium hyposulphite in boiling 3% sodium hydroxide solution, and acetylated by acetic anhydride in presence of water. Treatment of 5-acetamido-*o*-

cresol dissolved in dilute sodium hydroxide with a solution of mercuric acetate in 15% acetic acid affords the 4:6-diacetoxymercuri-derivative, darkening and decomp. about 210°. Similarly, 6-acetamido-*m*-cresol, m. p. 171° [free base, m. p. 162° (decomp.)], gives the 2:4-diacetoxymercuri-derivative, m. p. 178° (decomp.), whilst 4-acetamido-*m*-cresol, m. p. 130° (lit. 125°), furnishes the 2:6-diacetoxymercuri-derivative, which when heated darkens and gradually decomposes. Mercuration of 6-acetamido-*o*-cresol, m. p. 78—79° (free base, m. p. 89°), even with an excess of mercuric acetate, affords the 4-acetoxymercuri-derivative, m. p. 122°. All the above mercurated cresols are soluble in dilute alkali.

H. BURTON.

**Mercuration of some polyhydroxybenzaldehydes and their monomethyl ethers.** T. A. HENRY and T. M. SHARP (J.C.S., 1930, 2279—2289).—Interaction of resorcyaldehyde with mercuric acetate in alcohol affords 3:5-diacetoxymercuri-2:4-dihydroxybenzaldehyde, m. p. above 300°, yielding by the usual method the 3:5-dichloromercuri-derivative, decomp. 260° (darkens 240°), converted by bromine in acetic acid into 3:5-dibromoresorcyaldehyde, m. p. 204°, and by iodine into 3:5-diiodoresorcyaldehyde, m. p. 168°. Methylation of the foregoing dibromo-compound gives the known 3:5-dibromo-2-hydroxy-4-methoxy- (Rao, Srikantia, and Iyengar, A., 1929, 1071) and 3:5-dibromo-4-hydroxy-2-methoxybenzaldehydes (Lindemann and Forth, A., 1924, i, 181), together with 3:5-dibromo-2:4-dimethoxybenzaldehyde, m. p. 101—102°. 2:3-, 2:5- (Gentisaldehyde), and 3:4-dihydroxybenzaldehyde are mercurated similarly, but the pure mercury compounds are not isolable, as they undergo intramolecular oxidation with deposition of metallic mercury or mercurous acetate. Phloroglucinaldehyde yields a compound which is probably I.

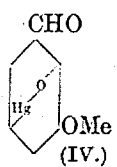


The monomethyl ethers mercurate less readily than the parent substances and give rise to monomercuri-derivatives in which the mercury occupies the *o*-position to the hydroxyl group when this is free, and the *p*-position when it is occupied (cf. J.C.S., 1922, 121, 1055; 1924, 125, 1049; A., 1926, 1162). The mercury compound of vanillin (Paolini, A., 1921, i, 902) is converted into 5-bromovanillin (Dakin, Amer. Chem. J., 1909, 42, 493); Paolini's iodovanillin is thus the 5-derivative. *iso*Vanillin affords 2-acetoxymercuriisovanillin, m. p. above 300° (corresponding chloromercuri-compound, m. p. 255—256°), converted through the bromomercuri-compound into 2-bromoisovanillin, m. p. 211—212° [identical with Pauly's supposed 6-bromoisovanillin (A., 1916, i, 150)], the constitution of which follows from its methylation (2-bromoveratraldehyde, m. p. 80°) and oxidation to 2-bromoveratric acid, m. p. 201—202° (methyl ester, m. p. 46°) (Zincke and Francke, A., 1897, i, 58). Bromination of isovanillin (Pauly, loc. cit.) yields, besides the above 2-bromo-compound, 6-bromoisovanillin, m. p. 112—114°, methylated to 6-bromoveratraldehyde, m. p. 150—151° (Pschorr, A., 1912, i, 775, gives m. p. 149—150°), and the latter oxidised to 6-bromoveratric acid, m. p. 185° (methyl ester, m. p.



81—82°) (Zincke and Francke, *loc. cit.*, give m. p. 183—184° and 88—89°). 3-Acetoxymercuri-2-hydroxy-4-methoxybenzaldehyde (II), m. p. 159—160° [from 2-hydroxy-4-methoxybenzaldehyde (Ott and Nauen, A., 1922, i, 555)], is converted through the bromomercuri-compound into 3-bromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 119—121° (*phenylhydrazones*, m. p. 166—167°), the constitution of which follows from its bromination to the above-mentioned 3 : 5-dibromo-2-hydroxy-4-methoxybenzaldehyde and its non-identity with 5-bromo-2-hydroxy-4-methoxybenzaldehyde, m. p. 120—121° (Rao and others, *loc. cit.*). 3-Chloromercuri-2-hydroxy-5-methoxybenzaldehyde (III), m. p. 242—243°, on treatment with bromine, gives 3-bromo-2-hydroxy-5-methoxybenzaldehyde, m. p. 110—111° (Rubenstein, J.C.S., 1925, 127, 2000, gives m. p. 107°). The compound from *o*-vanillin is probably 2 : 5-anhydro-5-hydroxymercuri-2-hydroxy-3-methoxybenzaldehyde (IV), although a dimeric formula is not

excluded; replacement of the hydroxymercuri-group by bromine leads to 5-bromo-2-hydroxy-3-methoxybenzaldehyde (Davies, J.C.S., 1923, 123, 1586, 2847). Bactericidal tests on the sodium salts of II, III, and IV (cf. A., 1925, i, 1006) show that the minimum concentrations required to kill *B. typhosus*, Rawlings, in 5 min. are 0.025, 0.0025, and 0.004%, respectively. R. CHILD.



**Tertiary arylalkylphosphines.** I. I. K. JACKSON, W. C. DAVIES, and W. J. JONES (J.C.S., 1930, 2298—2301).—From *p*-ethylphenyldichlorophosphine (Michaelis, A., 1897, i, 48, 146) and the appropriate magnesium alkyl bromide are obtained : *p*-ethylphenyldi-*n*-propylphosphine, b. p. 157°/21 mm.,  $d_4^{25}$  0.9147 (dibromide, an oil), -di-*n*-butylphosphine, b. p. 176°/15 mm.,  $d_4^{25}$  0.9042 (dibromide, a viscous liquid), and -di-*n*-amylphosphine, b. p. 201°/18 mm.,  $d_4^{25}$  0.9022 (mercurichloride, m. p. 95°). The other mercurichlorides and all three methiodides are non-crystalline. *p*-Ethylphenylmethyldi-*n*-propylphosphonium hydroxide (from the methiodide and silver oxide) (not purified) reacts alkaline and precipitates hydroxides from solutions of salts of the heavy metals (corresponding chloroplatinate, m. p. 195°); *p*-ethylphenylmethyldi-*n*-amylphosphonium chloroplatinate does not melt sharply.

Interaction of anisoyldichlorophosphine (improved preparation described), b. p. 150°/18 mm.,  $d_4^{25}$  1.331 (Michaelis, *loc. cit.*, gives about 130°/12—15 mm. and 1.0764), with Grignard reagents leads to : anisoyl-di-*n*-propylphosphine, b. p. 165°/17 mm.,  $d_4^{25}$  0.9738 (dibromide, a viscous liquid; mercurichloride, m. p. 134°; methiodide, m. p. 60°), -di-*n*-butylphosphine, b. p. 190°/16 mm.,  $d_4^{25}$  0.9600 [methiodide, m. p. 86°; anisoylmethyldi-*n*-butylphosphonium chloroplatinate (from the methiodide through the quaternary hydroxide), m. p. 196°], and -di-*n*-amylphosphine, b. p. 202°/18 mm.,  $d_4^{25}$  0.9382 (dibromide, m. p. about 85°; mercurichloride, m. p. 114°; methiodide, an oil; methochloroplatinate, m. p. 153°).

Data are given for the molecular refractivities of the foregoing phosphines and attention is directed to the optical exaltation produced by the linking of the phenyl group to phosphorus. R. CHILD.

**Reaction of organo-mercury compounds with salts of bivalent tin as a method for the preparation of organo-tin compounds.** A. N. NESMEJANOV and K. A. KOZESCHKOV (Ber., 1930, 63, [B], 2496—2504).—In absolute acetone, mercury diphenyl, dibenzyl, di-*p*-tolyl, di- $\alpha$ - and di- $\beta$ -naphthyl react with stannous chloride or bromide according to the scheme  $\text{HgR}_2 + \text{SnX}_2 = \text{R}_2\text{SnX}_2 + \text{Hg}$  (I). Except in the case of the first two compounds, the reaction in absolute alcohol follows more or less completely the course  $\text{HgR}_2 + \text{SnX}_2 + 2\text{EtOH} = 2\text{R}\cdot\text{H} + \text{Hg} + (\text{OEt})_2\text{SnX}_2$  (II). Reaction occurs rapidly with aryl compounds, slowly and complicated by side reactions with mercury diethyl. Freshly-prepared mercury dibenzyl resembles closely the aryl compounds. An aged specimen behaves similarly to mercury diethyl and only partly recovers its activity when recrystallised. Mercury aryl chlorides react with stannous chloride in acetone according to the scheme  $2\text{R}\cdot\text{HgCl} + 2\text{SnCl}_2 = \text{R}_2\text{SnCl}_2 + 2\text{Hg} + \text{SnCl}_4$  (III). If R is a radical which behaves according to II the change  $\text{R}\cdot\text{HgCl} + \text{SnCl}_2 + \text{EtOH} = \text{R}\cdot\text{H} + \text{Hg} + \text{OEt}\cdot\text{SnCl}_2$  occurs in ethyl alcohol. With mercury organic bromide and stannous bromide, mercurous bromide is precipitated. Mercury methyl and ethyl chlorides react slowly and not at all respectively with stannous chloride. Reactivity of the stannous salts is intimately connected with their solubility in the medium employed; stannous fluoride, iodide, and sulphate are almost inactive, whereas the thiocyanate reacts readily but yields products very liable to resinification.

The following data appear to be new : tin di-*p*-tolyl dibromide, m. p. 74°; tin di- $\alpha$ -naphthyl dichloride, m. p. 137—137.5°; tin di- $\beta$ -naphthyl dichloride, m. p. 110—111°, and dibromide, m. p. 114—114.5°; tin diethyl dichloride, m. p. 82—84°; phenylstannonic acid,  $\text{Ph}\cdot\text{SnO}\cdot\text{OH}$  (solubility data). H. WREN.

**Constitution of soluble proteins as reversible dissociable systems of components.** S. P. L. SØRENSEN (Kolloid-Z., 1930, 53, 102—124).—A critical review of the literature on the structure of proteins and of organic substances of high mol. wt.

E. S. HEDGES

**Constitution and electrochemical behaviour of proteins.** W. PAULI (Kolloid-Z., 1930, 53, 51—61).—A résumé of recent researches on the subject.

E. S. HEDGES.

**Constitution of proteins and polypeptides.** E. ABDEERHALDEN and H. BROCKMANN (Biochem. Z., 1930, 225, 386—408).—In order to throw light on the constitutions of polypeptides and proteins, free carboxyl groups in these are caused to react with benzylamine and free amino-groups with phenylcarbimide, and the products are hydrolysed by acid. The hydantoin of the amino-acid of which the amino-group reacted with phenylcarbimide is liberated and the remaining portion of the polypeptide, after further treatment with benzylamine, is hydrolysed, the amino-acid of which the carboxyl group reacted with benzylamine being set free. By suitable application of this process of combination of free amino-groups with phenylcarbimide polypeptides may be broken down step by step into their constituent amino-acids. The following are amongst the compounds examined : dl-leucylbenzyl-

amine, m. p. 56—57°, and its phenylcarbimide derivative, m. p. 209—210°; *glycylbenzylamine* (picrate, m. p. 188.5°); *dl- $\alpha$ -bromoisohexanilide*, m. p. 115°; *dl-leucylaniline*, m. p. 59—60°; *dl- $\alpha$ -bromohexoyl-dl-leucylglycine*, m. p. 163—164°; *dl-norleucyl-dl-leucylglycine*, m. p. 258°, and its phenylcarbimide derivative; 2:4-dinitroanilide of *dl- $\alpha$ -bromoisohexanoic acid*, m. p. 57°; *dl- $\alpha$ -bromoisohexoylisoamylamine*, b. p. 160—161°/10 mm.; *dl-leucylisoamylamine*, b. p. 167—170°/13 mm.; *dl- $\alpha$ -bromoisohexoyldiphenylamine*, m. p. 62°; *dl-leucyldiphenylamine*; the phenylcarbimide derivative of *dl-alanylglycyl-dl-leucine*; *dl-leucylglycylbenzylamine* (phenylcarbimide derivative, m. p. 187°) and the phenylcarbimide derivative of *glycyl-dl-leucylbenzylamine*. (All m. p. given are corrected.)

W. MCCARTNEY.

**Glutathione: preparation and properties of the thermostable oxidation-reduction system.** G. E. VLADIMIROV, M. J. GALVIALO, and K. A. MAKAROVA (Russ. J. Physiol., 1930, 13, 499—524).—Reduced glutathione or cysteine is oxidised by iodine to the disulphide form. This reaction forms the basis of an iodometric titration of the thiol groups in thermostable muscle preparations. Brewers' yeast is not a suitable source of glutathione. P. G. MARSHALL.

**Resistance to hydrolysis of benzoyl and halogenobenzoyl groups united to oxygen and to nitrogen in amino-acids and peptides.** E. ABDERHALDEN and H. BROCKMANN (Biochem. Z., 1930, 225, 426—440).—Observation of the alkaline hydrolysis of benzoyl and *p*-halogenobenzoyl derivatives of amino-acids and of amino-acid anhydrides shows that the resistance to hydrolysis of these groups is not affected when the acids (or anhydrides) form parts of the molecule of a peptide. The compounds examined included the following: *di-p-chlorobenzoyl-l-tyrosine*, m. p. 213—214°; *di-p-bromobenzoyl-l-tyrosine*, m. p. 227—229° (corr.); *dibenzoyl-dl-leucyl-l-tyrosine*; *dibenzoyl-glycyl-l-tyrosine*; *tribenzoyl-l-tyrosyl-l-tyrosine*, m. p. 160—185°; *dibenzoyl-l-tyrosine anhydride*, m. p. 293°, and *N-benzoyl-dl-leucyl-dl-serine*, m. p. 179° (corr.). Benzoylated fibroins from silk were also investigated. Dibenzoylcolamine has m. p. 90° (corr.).

W. MCCARTNEY.

**Denaturation of proteins by carbamide.** W. RAMSDEN (Nature, 1930, 126, 685).—The rate of denaturation of approximately isoelectric egg-albumin by carbamide has a negative temperature coefficient.

L. S. THEOBALD.

**Phase-rule studies on the proteins. IV. Quinquevalent nitrogen in organic compounds. III.** W. D. BANCROFT and C. E. BARNETT (J. Physical Chem., 1930, 34, 1930—1946).—The addition of hydrogen chloride by compounds containing three atoms of nitrogen is discussed (cf. this vol., 861).

L. S. THEOBALD.

**Action of dilute formaldehyde solution on proteins and protein derivatives.** M. FREEMAN (Austral. J. Exp. Biol., 1930, 7, 117—124).—The action of 0.5% formaldehyde solution at 37° on native and denatured proteins, proteoses, peptones, and tryptic digests has been investigated. Formaldehyde precipitates a portion of a proteose mixture and more from the primary than from the secondary proteoses. The

precipitate resembles a metaprotein. In all cases the amino-nitrogen content decreases whilst the optical rotations of the peptone and tryptic digest solutions increase.

F. O. HOWITT.

**Biochemistry of sulphur. IV. Colorimetric determination of cystine in casein by means of the  $\beta$ -naphthoquinone reaction.** M. X. SULLIVAN. **V. Cystine content of conphaseolin and phaseolin, the  $\alpha$ - and  $\beta$ -globulins of the navy bean.** M. X. SULLIVAN and D. B. JONES. **VII. Cystine content of purified proteins.** M. X. SULLIVAN and W. C. HESS (U.S. Pub. Health Rep. Suppl., 1929, 1930, Nos. 78, 82, 86).—IV. Casein is hydrolysed with 20% hydrochloric acid and the amount of cystine in the hydrolysate determined by Sullivan's method (cf. this vol., 488). The slight loss of cystine during hydrolysis is due not to racemisation but to losses in the decolorisation process. Humin formation during hydrolysis is best reduced by addition of titanous chloride, with subsequent aëration to convert cystine into cystine.

VI. Conphaseolin (cf. A., 1923, i, 493), the  $\alpha$ -globulin of *Phaseolus vulgaris*, contains more than 1% of cystine, whilst phaseolin, the  $\beta$ -globulin, contains little if any cystine. The  $\beta$ -globulins of the mung, adzuki, and Lima beans when pure contain little if any cystine, whilst the corresponding  $\alpha$ -globulins contain 0.5—1.35% of cystine.

VII. The cystine contents of the hydrolysates of 23 proteins have been determined by the methods of Sullivan, Okuda (cf. A., 1926, 190), and of Folin and Looney (cf. A., 1922, ii, 539), and for 14 proteins by the Folin-Marenzi method (cf. A., 1929, 1093). The Sullivan and Okuda determinations are in fair agreement. Whilst occasionally the Folin-Looney method agrees, it generally gives higher values; the Folin-Marenzi method gives still higher values. The Sullivan reaction is specific to the sulphur linking occurring in cysteine and cystine. C. C. N. VASS.

**Determination of carbon and hydrogen.** E. STANSFIELD and J. W. SUTHERLAND (Canad. J. Res., 1930, 3, 318—321).—Modifications in the ordinary apparatus are described.

H. BURTON.

**Use of copper tubes in determination of elements in organic compounds.** N. KLATSCHIN (Z. anal. Chem., 1930, 82, 133—144).—In combustions of organic substances copper tubes have many advantages over the usual glass tubes. With suitable modifications, satisfactory results may be obtained even with such substances as carbon disulphide and benzene rich in sulphur.

R. CUTHILL.

**Nitro-nitrogen determination by Kjeldahl's method in aromatic compounds.** M. WEIZMANN, J. YOFE, and B. KIRZON (Z. physiol. Chem., 1930, 192, 70—72).—The nitro-compound is reduced with fuming sulphuric acid and zinc in the cold during several hours, the mixture is heated gently for 5—6 hrs. in presence of copper and potassium sulphates, and the usual procedure is then followed.

J. H. BIRKINSHAW.

**Determination of amino-acids by physico-chemical methods.** H. LEY and B. ARENDS (Z. physiol. Chem., 1930, 192, 131—144).—The copper

salts of the amino-acids show characteristic absorption curves. The monoamino-acid complexes show a maximum at about  $\lambda$  620. Beer's law holds except at extreme dilutions; the molar extinctions ( $\epsilon$ ) of glycine for the wave-lengths 578 and 546 are 35.1 and 21.8 and for alanine 47 and 31.5, respectively. Neutral alkali salts have little effect on the absorption, but strongly dissociated copper salts lower the extinction considerably. The amounts of individual amino-acids in a mixture can be determined by absorption measurements. J. H. BIRKINSHAW.

**Colorimetric determination of aniline.** A. V. PAMFILOV and M. V. ALEKSEEVA (J. Appl. Chem., Russia, 1930, 3, 285—289).—Minaev's method (J. Soc. Chem. Ind., Russia, 1927, 4, 840) is criticised.

#### CHEMICAL ABSTRACTS.

**Action of ferric chloride on *o*-, *m*-, and *p*-toluidine.** W. H. PATTERSON (J.C.S., 1930, 2401).—When treated with hydrochloric acid followed by ferric chloride the above toluidines give, respectively, a bluish-green precipitate (purple reflex), a brown colour followed by a similar precipitate, and an intense plum-red colour only. The reactions are given by mixtures of the three toluidines. J. W. BAKER.

**Anthraquinone derivatives as base precipitants.** W. ZIMMERMANN (Z. physiol. Chem., 1930, 192, 124—130; cf. this vol., 1170).—Alizarindisulphonic acid precipitates guanidine from aqueous solution as the salt (AB), m. p. 259°; anthrarufindisulphonic acid precipitates creatinine as the salt (AB<sub>2</sub>), m. p. 333° (decomp.), and creatine as the salt (AB<sub>2</sub>), decomp. 310°. Purpurinmonosulphonic acid precipitates lysine as the salt (A<sub>2</sub>B), decomp. 249°, and putrescine as the salt (A<sub>2</sub>B), m. p. 258° (decomp.). The above salts are crystalline. J. H. BIRKINSHAW.

**Colour reactions of eugenol and clove oil.** H. SZANCER (Bull. Sci. pharmacol., 1929, 36, 611—613; Chem. Zentr., 1930, i, 3222).—The colour with ferric chloride changes more rapidly from blue through green to yellow with clove oil than with eugenol. If an alcoholic solution is floated on to concentrated sulphuric acid, eugenol gives a dark red and the oil an orange-red ring, both being bounded by a yellow and a violet ring. When shaken the former becomes dark cherry-red, whilst the latter becomes turbid and of the colour of red beet. If 5 c.c. of a solution of vanillin (0.5 g.) in alcohol (10 c.c.) and concentrated hydrochloric acid (90 c.c.) are shaken with a few drops of the liquid under examination, eugenol gives a dark orange and clove oil a dark red coloration.

A. A. ELDRIDGE.

**Determination of the acetyl group in acetylated derivatives of polyhydric phenols: conductometric determination.** C. TORRES, A. S. CAPUCHINO, and L. SOCIAS (Anal. Fis. Quím., 1930, 28, 694—705).—The acetylated polyhydric phenols are so readily oxidised in alkaline solution, with the formation of deeply coloured products, that it is impossible to employ the ordinary indicators for their determination. Methods based on the distillation and decomposition of the ethyl acetate formed by hydrolysis by sulphuric acid in presence of ethyl alcohol lead always to low results. Accurate determinations of

pyrocatechol diacetate may be made by hydrolysing the compound in dilute acid solution and titrating conductometrically with sodium hydroxide solution: three definite breaks occur in the titration curve, corresponding with sulphuric and acetic acids and the free pyrocatechol. H. F. GILLBE.

**Reactions with sodium nitroprusside.** T. PAVOLINI (Boll. Chim. Farm., 1930, 69, 713—722).—Of aldehydes and ketones of the terpene group, carvone, pulegone, ionone, and citral give, with sodium nitroprusside in alcoholic solution, intense red colorations, whereas camphor, fenchone, menthone, and citronellal yield no such coloration but gradual precipitation of yellow sodium nitropentacyanide, Na<sub>4</sub>Fe(NO<sub>2</sub>)(CN)<sub>5</sub>. Thus, a negative reaction is obtained with compounds containing either no double linkings or only one at a distance from the carbonyl group. The reaction hence furnishes aid in determining the presence and position of a double linking. The violet coloration given by pyrrole or indole with sodium nitroprusside in presence of excess of potassium hydroxide is not given by 2- or 3-methylindole, oxindole, dioxindole, carbazole, acridine, diphenylamine, pyridine, quinoline, benzimidazole, furan, or thiophen, the reaction being due solely to the grouping  $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{C} \\ \text{NH} \cdot \text{C} \end{smallmatrix}$ .

The reaction given with sodium nitroprusside in alkaline solution by various cyclic dinitro-compounds with the nitro-groups preferably in the *meta*-position, such as *m*-dinitrobenzene and 1:5- and 1:8-dinitronaphthalenes, is not very well defined and is not obtained with *o*-, *m*-, or *p*-nitrophenol, trinitrophenol, or *o*-nitrobenzaldehyde; in alcoholic solution, trinitrotoluene yields an intense violet-red coloration only on addition of potassium hydroxide. With nitroprusside and alkali, a violet-red coloration is given by alcoholic solutions of thiocarbamide, diphenylthiocarbamide, *o*-phenylenethiocarbamide, or, less rapidly, thiosiamine, but not by potassium or ammonium thiocyanate or ethyl sulphide. Under similar conditions, pyrocatechol and resorcinol give intense green colorations, and quinol, pyrogallol, phloroglucinol, and hydroxyquinol, brownish-green colorations, becoming greenish-blue on acidification with acetic acid.

T. H. POPE.

**Pauly diazo-reaction.** E. GEBAUER-FÜLNEGG (Z. physiol. Chem., 1930, 191, 222—224).—By coupling glyoxaline derivatives or tyrosine with non-sulphonated diazotised aromatic bases, distinctive colours soluble in certain organic solvents are obtained. Thus tyrosine and histidine may be differentiated by coupling with diazotised *p*-nitroaniline and extraction of the coloured product with butyl alcohol.

J. H. BIRKINSHAW.

**Colorimetric determination of alkaloids.** C. A. ROJAHN and R. SEIFERT (Arch. Pharm., 1930, 268, 499—520).—The author has examined the possibility of determining strychnine, quinine, emetine, and cinchonine by precipitation with a standard alkaloid reagent, the amount of which (*a*) in the precipitate or (*b*) in the filtrate is subsequently determined colorimetrically. Strychnine and cinchonine are satisfactorily precipitated by picric acid, which may be determined as ammonium picrate, but not as iso-

purpuric acid. The picrates of emetine and quinine are more soluble, and good results are obtained only under closely-defined conditions. Precipitation with silicotungstic acid and determination of tungsten by the method of Travers (A., 1918, ii, 176) gives good results with strychnine, emetine, and cinchonine and less favourable results with quinine. Correct values for the tungsten in phosphotungstates can be obtained by Travers' method only when standard concentrations of hydrochloric acid and titanous chloride are maintained. Under these conditions all four alkaloids may be determined with this reagent. Strychnine and

emetine may be precipitated by Mayer's reagent, the mercury being determined as the colloidal sulphide, but quinine and cinchonine give amorphous precipitates which cannot be washed satisfactorily. None of the alkaloids gives good results with Dragendorff's reagent. Ferrocyanic acid is applicable to the determination of strychnine, the ferrocyanide ion being determined as copper ferrocyanide in presence of gum. The results are in general accurate within 1–2% and, especially when only small quantities of alkaloid are present, are frequently superior to those obtained by volumetric methods. H. E. F. NOTTON.

## Biochemistry.

**Quantitative analysis for blood.** M. WAGENAAR (Pharm. Weekblad, 1930, 67, 1093–1100).—The methods hitherto proposed are described, and the difficulties and sources of error involved are discussed. The influence of age, history, and presence of other organic material may be eliminated by separate determination of total nitrogen and total iron: 30 mg. of nitrogen and 0.5 mg. of iron correspond with 1 g. of blood. The ratio is constant for human blood, but varies for blood from domestic animals.

S. I. LEVY.

**Oxygen and carbon dioxide content of venous blood.** W. G. LENNOX and E. LEONHARDT (Arch. Int. Med., 1930, 46, 630–636).—Figures are given for blood from various accessible veins in man as determined by the method of Van Slyke (A., 1927, 880). For the respective venous bloods, compared with that of the cubital, the gaseous content of the femoral is the same, whilst the internal jugular shows a less reduced and the external jugular a more reduced condition. The respiratory quotient, determined by application of the method of Doisy and Beckmann (A., 1923, i, 164), has values of 0.84 and 0.9 for cubital and internal jugular venous blood, respectively.

F. O. HOWITT.

**Changes in the exchange of material between blood and tissues effected by over-ventilation in normal and pathological conditions of the tissues.** K. KIMURA (Tohoku J. Exp. Med., 1930, 15, 199–235).—During over-ventilation (in dogs) the blood-oxygen saturation is increased and there is an excess of oxygen in the tissues; the blood-carbon dioxide, -oxygen capacity, -haemoglobin, serum-protein, and -sodium chloride are decreased. In cantharidin or uranium poisoning the changes are slower in appearing and in disappearing.

CHEMICAL ABSTRACTS.

**Photo-electrometric determination of haemoglobin.** A. H. SANFORD and C. SHEARD (J. Lab. Clin. Med., 1930, 15, 483–489).

CHEMICAL ABSTRACTS.

**Effect of carbon monoxide, illuminating gas, and automobile exhaust gas on the fragility of red blood-cells.** M. R. MAYERS, H. RIVKIN, and F. KRASNOW (J. Ind. Hyg., 1930, 12, 300–305).—The fragility of red blood-cells was determined by observing the degree of haemolysis in blood samples after admixture with sodium chloride solutions varying from

0.25 to 0.60%. Treatment of the blood with illuminating gas or automobile exhaust gas increased the fragility. This effect was not obtained by treatment with pure carbon monoxide. The haemolysing action of the gases was not due to a change in the hydrogen-ion concentration of the blood. G. F. MARRIAN.

**Influence of bilirubin on the number of red corpuscles in blood.** F. BENCSIK, A. GÁSPÁR, F. VERZÁR, and A. ZIH (Biochem. Z., 1930, 225, 278–285; cf. Verzár and Zih, A., 1929, 467).—Administration of bilirubin has the same effect on the number of red corpuscles in the blood in mice and rats as it has in rabbits. Very small doses cause increases which can be maintained for months; larger doses cause decreases. These changes are not accompanied by changes in the refractometric value of the serum. The view that bilirubin is an important regulator of the number of red corpuscles in the blood is thus confirmed. W. MCCARTNEY.

**Permeability of leucocytes for ions.** W. FLEISCHMANN (Pflüger's Archiv, 1929, 223, 47–55; Chem. Zentr., 1930, i, 2916).—The cell-wall of leucocytes (horse) is impermeable to magnesium, calcium, and barium ions, but permeable to anions. Cellular respiration and phagocytosis are sometimes similarly, sometimes differently, affected by salts.

A. A. ELDRIDGE.

**Enumeration of blood platelets.** I. OLEF (Arch. Int. Med., 1930, 46, 585–596).—Using a 2% solution of sodium metaphosphate in physiological saline as a preserving fluid, the number of platelets in human blood is found by comparison with that of the erythrocytes determined by direct count.

F. O. HOWITT.

**Variations in catalase and anticatalase of human blood under physiological conditions.** E. D. GAGARINA (Zhur. exp. Biol. Med., 1929, 12, 329–333).—Variation of blood-catalase during the day is parallel with that of haemoglobin. The menstrual cycle, but not digestion, affects the blood-catalase.

CHEMICAL ABSTRACTS.

**Critical temperature of serum: depolarisation factor and hydration of serum molecules.** P. L. DU NOÛY (Science, 1930, 72, 224–225).—The depolarisation factor of the light scattered by serum begins to increase, as do viscosity and rotatory power, after a certain temperature, viz., 57° for normal horse

serum, is reached. The increase, at first slow, becomes more rapid and is continuous and regular even after the gel state is reached. Hydration is the main factor and a quantitative explanation is afforded by the hypothesis that the water molecules can penetrate inside the large molecular structure of the protein and change the relative position of the groups. When the critical temperature is reached the kinetic energy of the water molecules is of the same order as the forces binding the external groups of the protein, and penetration commences. L. S. THEOBALD.

**Cell for measuring specific conductivity of blood-serum.** W. R. ASHBY (Biochem. J., 1930, 24, 1557—1559).—The cell contains two large flat electrodes close together but separated by an insulating plate with a small hole in the middle. Only 1 c.c. of serum is required for the determination. It has a coefficient of variation of 0.53% and is free from polarisation. S. S. ZILVA.

**Globulins and albumins of serum.** B. LUSTIG (Biochem. Z., 1930, 225, 247—263).—By fractional precipitation with ammonium sulphate solutions according to the method of Freund and Joachim (A., 1903, ii, 87) followed by dialysis and by treatment with dilute solutions of sodium chloride, carbonate, and hydroxide, the proteins of ox-serum were divided into three albumin, four euglobulin, and four pseudoglobulin fractions. These fractions, which differed greatly in amount, were examined as regards their limits of precipitation with ammonium sulphate solutions, temperatures of coagulation by heat, and nitrogen content. The contents of amino- and carboxyl groups were also determined as were the ratios total N :  $\text{CO}_2\text{H}$  ("carboxyl index"),  $\text{NH}_2$  : total N ("amino-index"), and  $\text{NH}_2$  :  $\text{CO}_2\text{H}$  (cf. Obermayer and Willheim, A., 1912, ii, 399; 1913, i, 668). Since, in the various fractions, both the properties examined and these ratios (with the possible exception of the last) exhibit great differences it is concluded that the serum actually contains many proteins. W. MCCARTNEY.

**Daily variation of the sulphur and tryptophan content of human serum-proteins.** K. LANG (Arch. exp. Path. Pharm., 1930, 154, 342—353).—The globulin:albumin ratio of blood-serum from patients suffering from various diseases usually increases during the course of the day, the total protein content tending to decrease. The sulphur and tryptophan contents vary somewhat irregularly, but the former tends to increase in the course of the day. W. O. KERMACK.

**Arteriovenous difference in blood-sugar content.** B. Y. GLASSBERG (Arch. Int. Med., 1930, 46, 605—609).—The difference in sugar content of venous and capillary blood [identical with that of arterial blood according to Foster (A., 1923, i, 503)] after ingestion of 100 g. of dextrose was investigated in normal and diabetic persons with a view to its utilisation in clinical diagnosis of abnormal carbohydrate metabolism. The figures given by the method of Somogyi (A., 1929, 1096) showed such a wide variation (2—60 mg. per 100 c.c.) that no diagnostic significance could be attached to them. F. O. HOWITT.

**Relations between blood-sugar and -fat in experiments with sugar loading.** G. D. OBRATZOV and M. KALLINIKOVA (Zhur. exp. Biol. Med., 1929, 12, 301—305).—On feeding sucrose (0.3 g. per kg.) a rise in blood-sugar may or may not be accompanied by a corresponding fall in blood-fat.

CHEMICAL ABSTRACTS.

**Lævulose of the blood and lymph.** K. KOZURA (Tohoku J. Exp. Med., 1930, 15, 398—418).—The blood-lævulose of rabbits is 7.2, of dogs 7.2, and of pigs 4.6 mg. per 100 c.c. Oral ingestion doubles the value and increases the blood-dextrose. Adrenaline does not mobilise lævulose. The animal can synthesise glycogen from lævulose.

CHEMICAL ABSTRACTS.

**Radiometric micro-determination of [blood-] sugar.** R. EHRENBURG (Biochem. Z., 1930, 226, 250—252).—When the method of Hagedorn and Jensen is so modified that the residual ferricyanide is measured radiometrically numerous determinations of sugar can be made using 0.1 c.c. of blood. A table with the help of which results can be calculated is given (cf. A., 1929, 1258). W. MCCARTNEY.

**Manometric determination of blood-sugar.** A. FUJITA and K. OKAMOTO (Biochem. Z., 1930, 225, 368—385).—The sugar content of 1 c.c. of blood is determined manometrically by a modification of Van Slyke and Hawkins' method (A., 1928, 1358) combined with the procedure of Warburg, changes of level thirteen times as great as those produced in the process of Van Slyke and Hawkins being obtained. A concentrated phosphate buffer solution is used in preference to a carbonate solution. W. MCCARTNEY.

**Colorimetric determination of calcium with 0.1 c.c. of blood.** S. YOSHIMATSU (Tohoku J. Exp. Med., 1930, 15, 355—362).—The calcium and magnesium are precipitated from the protein-free filtrate with 8-hydroxyquinoline, the calcium compound being redissolved in boiling ammoniacal ammonium chloride solution and determined colorimetrically. W. MCCARTNEY.

CHEMICAL ABSTRACTS.

**Calcium content of the serum of cattle with special reference to the influence of the sexual organs.** W. FREI and M. A. EMMERSON (Biochem. Z., 1930, 226, 355—380).—The calcium content of the serum of cattle in various stages of growth and of sexual condition as well as in certain pathological conditions has been examined. It is higher in female calves than in male and in calves than in adult cattle. In cows it is higher in oestrus than in interoestrus and in pregnancy than in the non-pregnant state. Castration lowers it in males but raises it in females. When the animals are suffering from cystic degeneration of the follicles in the ovary, it is increased, the fluid from the cysts having a higher content of calcium than has the serum. Injection of "progynone" reduces it, whilst that of "sistomensin" or of extract of the anterior lobe of the pituitary gland raises it. The significance of these results is discussed. W. MCCARTNEY.

**Determination of magnesium in blood.** F. EICHHOLTZ and R. BERG (Biochem. Z., 1930, 225, 352—357).—Since solutions of 8-hydroxyquinoline are unstable in presence of oxidising agents and are

catalytically decomposed by copper, zinc, or gold, Yoshimatsu's modification (Tohoku J. Exp. Med., 1929, 14, No. 1) of Berg's method (A., 1928, 39) for the determination of magnesium in blood must be accordingly altered. Precipitation of the magnesium-hydroxyquinoline compound should be initiated by scratching with a rod of glass of a certain composition.

W. MCCARTNEY.

**Determination of inorganic phosphate in serum and cerebrospinal fluid.** C. LOWENBERG and M. R. MATTICE (J. Lab. Clin. Med., 1930, 15, 598—600).—The determination is made by Benedict and Theis' method on the supernatant liquid after precipitation of calcium. CHEMICAL ABSTRACTS.

**Preparation and antigenic properties of carbon monoxide-haemoglobin.** A. K. BOOR and L. HEKTOEN (J. Infect. Dis., 1930, 46, 1—11).—Carbon monoxide-haemoglobin, prepared by saturating oxy-haemoglobin with carbon monoxide and crystallising the product from alcohol, is antigenic and mainly species-specific. CHEMICAL ABSTRACTS.

**Examination of the precipitate from haemoglobin and anti-haemoglobin serum and the nature of antibodies.** F. BREINL and F. HAURWITZ (Z. physiol. Chem., 1930, 192, 45—57).—The precipitate produced by haemoglobin and anti-haemoglobin serum contains 2—8% of lipins, 5—10% of salts, and an organic residue containing C 50.7, H 7.4, N 17.7%, figures typical of a protein. The protein resembles the globulin of serum, since it gives on hydrolysis about the same amount of tyrosine, cystine, and arginine. At low haemoglobin concentrations (1 in 1000 to 1 in 200,000) the precipitate contains 6—11%, at higher concentrations up to 24% of the antigen. The lipins of the precipitate resemble those precipitated with the globulins from serum; they contain neither cholesteryl phosphatides nor cerebrosides, are probably carried down mechanically, and therefore are without significance.

J. H. BIRKINSHAW.

**Protein-antibody system.** M. HEIDELBERGER and F. E. KENDALL (Science, 1930, 72, 252—253).—The precipitin reaction between a true antigen and its antibody is essentially the same as a typical inorganic precipitation. Data obtained with the antigen *R*-salt-azobenzidine-azo-cgg-albumin are recorded.

L. S. THEOBALD.

**Amount of circulating precipitin following the injection of a soluble antigen.** M. HEIDELBERGER and F. E. KENDALL (Science, 1930, 72, 253).—Data on the amounts of precipitable protein obtainable after the injection of rabbits with small doses of the antigen *R*-salt-azobenzidine-azo-cgg-albumin favour the view that the antigen plays no part in building up the antibody complex.

L. S. THEOBALD.

**Action of ultra-violet light on complement, amboceptor, agglutinin, the Wassermann reaction, and the precipitinogenic property of the serum.** A. HASKÓ (Biochem. Z., 1930, 226, 462—481).—The specific properties of the complement, the antibodies of Wassermann-positive sera, the amboceptor and agglutinin, serum-precipitinogen, and

bacillary protein are all diminished or destroyed by ultra-violet radiation. H. W. DUDLEY.

**Systemic effect of X-rays. I. Blood changes in dogs following exposure to filtered X-rays of short wave-length.** E. A. POHLE, E. L. SEVERINGHAUS, and L. DAVY (Amer. J. Roentgenol., 1930, 23, 291—298).—Changes in the blood-haemoglobin, -non-protein-nitrogen, -uric acid, -sodium chloride, and -cholesterol were not observed.

CHEMICAL ABSTRACTS.

**Biophysical origin of the law of ionic antagonism.** A. P. KONIKOV (Zhur. exp. Biol. Med., 1929, 12, 342—350).—The antagonism depends on the presence of a membrane containing lipin and of a potential in the cell surface. In specific haemolysis the antagonism is observed only when there is a combination of potassium or sodium salts with salts of cobalt, nickel, and manganese.

CHEMICAL ABSTRACTS.

**Chemical nature of the chondriome.** A. GIROUD (Protoplasma, 1929, 7, 72—98).—Protein was found in the chondriome of intestinal cells of *Ascaris canis*. The thiol group, where encountered, seems to be somewhat intimately connected with the chondriome, although the nitroprusside test is also given by the hyaloplasm.

CHEMICAL ABSTRACTS.

**Constituents of liver of aquatic animals. II. Nitrogenous compounds of the liver of the bonito, *Katsuwonus vagans*, Lesson.** K. YOSHIMURA and K. NISHIDA (J. Agric. Chem. Soc. Japan, 1930, 6, 118—125).—The liver contained: water 75.19, crude protein 18.65, protein 6.03, crude fat 3.28, crude ash 1.29, total nitrogen 2.984, protein-nitrogen 0.966, water-soluble non-protein-nitrogen 2.018%. The distribution of the nitrogen was determined.

CHEMICAL ABSTRACTS.

**New sterol in human brain.** I. H. PAGE and E. MÜLLER (Naturwiss., 1930, 18, 868).—The mother-liquor from the extraction of cholesterol from brains by the acetone process furnished, by further extraction, a new sterol,  $C_{25}H_{44}O$ , the *acetyl* derivative of which has m. p.  $105^{\circ}$ ,  $[\alpha]_D^{25} -25.17^{\circ}$ . The free sterol obtained by the action of sodium ethoxide on the acetate derivative had no definite m. p., and  $[\alpha]_D^{25} -18.95^{\circ}$ . It shows no maxima in the absorption spectrum above  $240\mu$ .

A. J. MEE.

**Determination of glutathione content of normal and pathological tissues.** T. KAMIYA (Nagaoya J. Med. Sci., 1928, 3, 25—44).—Comparative values for animal and vegetable tissues and organs are recorded. In plants the glutathione content increased in proportion to the chlorophyll.

CHEMICAL ABSTRACTS.

**Relation between glutathione content and growth of animals.** T. KAMIYA (Nagaoya J. Med. Sci., 1928, 3, 74—84).—The relation for silkworms, bees, and frogs differs from that for mammals.

CHEMICAL ABSTRACTS.

[Action of] proteolytic enzymes on [the protein of] Egyptian mummies (about 3000 years old) and mammoths (30,000—100,000 years old). O. STEPPUHN and X. UTKINA-LJUBOVZOVA (Biochem. Z., 1930, 226, 237—242).—Intracellular proteolytic



enzymes digest the proteins of preserved tissues of great age as readily as the protein of fresh tissue (cf. this vol., 956).

P. W. CLUTTERBUCK.

**Lipase of the tonsils.** T. MOTAI (Nagaoya J. Med. Sci., 1928, 3, 51—73).—Dogs' (2—3 months old) tonsils contain an active lipase with optimum  $pH$  7.8—8.4 which is resistant to quinine but sensitive to sodium fluoride and atoxyl. CHEMICAL ABSTRACTS.

**Biological significance and distribution of glycogen in the pregnant uterus of the bat.** I. Placenta, umbilical cord, and amnion. II. Yolk-sac and mesometrium of the uterus. M. KADIMURA (Keijo J. Med., 1930, 1, 288—315, 316—346).—I. Considerable amounts of glycogen are present in the blood-vessels of the embryonic placenta, but none in those of the mother. The umbilical cord also contains glycogen, although not in the early stages of pregnancy, and the amnion shows the presence of glycogen in considerable quantities. Glycogen of the placenta serves as a nutrient for the foetus from the beginning to the middle of pregnancy, and thereafter is laid down as a reserve in the muscle-glycogen.

II. Similar functions are ascribed to the glycogen of the yolk sac epithelium and mesometrium of the uterus, which, however, disappears shortly before birth.

P. G. MARSHALL.

**Specificity of the colour reactions of Dische for the purine- and pyrimidine-nucleosides of thymonucleic acid.** Z. DISCHE (Z. physiol. Chem., 1930, 192, 58—60).—The comments of Angermann and Bielschovsky (this vol., 1464) are discussed.

J. H. BIRKINSHAW.

**Artificial synthesis of bones and teeth. I. Preparation of glycine hexol salt and glycine phosphatocalcium carbonate.** T. GASSMANN (Z. physiol. Chem., 1930, 192, 61—69).—Glycine in presence of natural ice-water, when exposed to the air, combines with calcium oxide to form the glycine hexol salt. The latter, when treated with ammonium orthophosphate or with glucosephosphoric acid at 38—40°, yields glycine phosphatocalcium carbonate. By careful ignition of the latter the corresponding phosphatocalcium carbonate, giving apatite with barium chloride, is obtained. In the glycine complexes the glycine is a constituent part of the molecule not removable by water. The complexes are represented as follows:  $[Ca\{(OH)_2Ca\}_3CO_3 \cdot NH_2 \cdot CH_2 \cdot CO_2H] \rightarrow [Ca:::(O \cdot PO_3Ca)_2Ca\}_3CO_3 \cdot NH_2 \cdot CH_2 \cdot CO_2H]$ .

J. H. BIRKINSHAW.

**Spectrographic analysis of animal tissues.** H. M. FOX and H. RAMAGE (Nature, 1930, 126, 682).—Spectrograms have been obtained of animal tissues by the method previously described (A., 1929, 527). Iron and copper were invariably found and are probably universal constituents of protoplasm. Manganese is widely distributed in molluscs, whilst nickel, cobalt, lead, silver, cadmium, lithium (widespread), rubidium, and strontium (widespread) were detected in many tissues. Cesium and barium were not found. Calcium fluoride was identified in the body-wall of *Archidorus tuberculata* only. L. S. THEOBALD.

**Fasting gastric secretion.** F. RICCI (Arch. Farm. sperim., 1930, 51, 55—63).—The amount of

secretion and the content of hydrochloric acid have been determined in 70 cases, and the diagnostic value of the results is discussed. The administration of a test meal is not generally essential.

R. K. CALLOW.

**Unsaponifiable fraction of bile lipins.** E. P. HAÜSSLER and E. BRAUCHLI (Helv. Chim. Acta, 1930, 13, 908—915).—Extraction of ox bile with ether or benzene gives 0.1—0.3% of "fat," which after dissolution in ether, precipitation of coloured material by light petroleum, and evaporation of the remaining solution is hydrolysed by alcoholic potassium hydroxide in an atmosphere of nitrogen. The unsaponifiable matter (about 10% of the "fat") is separated by fractional crystallisation into cholesterol, a compound (I),  $C_{26}H_{42}O_4$  or  $C_{27}H_{44}O_4$ , m. p. 194—195°,  $[\alpha]_D^{20}$  —22° in chloroform (acetate, m. p. 169—170°), a substance (II), m. p. 217—218°, and a compound (III),  $C_{27}H_{42}O_4$  (or 44), m. p. 255—257°,  $[\alpha]_D^{20}$  —66° in chloroform (diacetate, m. p. 231—232°,  $[\alpha]_D^{20}$  —51° in benzene). The primary isolation of I is as an additive compound, m. p. 172—173°,  $[\alpha]_D^{20}$  —32.5° in chloroform, with cholesterol. Separation of this into its constituents is effected either by precipitation with digitonin or by benzoylation, separation of the cholesteryl benzoate, and hydrolysis of the product precipitated from the mother-liquors by water. The Liebermann-Burchard reaction is given by I and III, but not by II. None of the compounds gives the Rosenheim, Tortelli-Jaffe, Carr and Price, or Pettenkofer reactions; they have no aëstrus-producing action (cf. Gsell-Busse, A., 1929, 475).

H. BURTON.

**Changes in alkaline reserve and sugar content of bile under the influence of different physiological stimuli.** I. Food. V. M. KARATYGIN and A. I. HEFTER (Zhur. exp. Biol. Med., 1929, 13, 43—52).—The alkaline reserve of the bile of the fasting animal is 0—80 vol.-%. Dextrose, caseinogen, peptone, and Liebig's extract favour acidosis, and fats alkalosis. Bile-sugar is increased by carbohydrates, proteins, and extractives, and diminished by fat.

CHEMICAL ABSTRACTS.

**Primary tryptic action in the pancreas, biliary duct, and liver.** K. HOESCH (Z. klin. Med., 1929, 110, 735—747; Chem. Zentr., 1930, i, 2906).—Normal bile contains no trypsin activator. The presence of trypsin in the biliary duct is due to the presence of bacteria.

A. A. ELDRIDGE.

**Venom of the snake *Pseudechis Australis*.** C. H. KELLAWAY and D. F. THOMSON (Austral. J. Exp. Biol., 1930, 7, 125—133, 134—150).—The venom possesses powerful hæmolytic and anticoagulant actions, causes a transitory fall in blood-pressure in the rabbit, and in a concentration of 1:10,000 stops the beat of the isolated rabbit auricle in about 1 hr.

F. O. HOWITT.

**Structure of silk fibroin.** II. E. ABDERHALDEN and H. BROCKMANN (Biochem. Z., 1930, 226, 209—220).—When silk fibroin is benzoylated by means of benzoyl chloride in pyridine, the product shows a greater amount of readily, and the same amount of difficultly, hydrolysable benzoyl than that obtained by benzoylation in aqueous solution. Benzoylation also occurs on heating the fibroin with

benzoic anhydride in pyridine. Tussah silk is insoluble in concentrated lithium bromide solution (cf. A., 1929, 1473) and is only feebly attacked by benzoyl chloride in pyridine. Methylation of silk fibroin with diazomethane for a short time gives a product the methoxyl content of which corresponds with the tyrosine content of the fibroin, and for a longer time gives a constant methoxyl content. The hydroxyl content of the fibroin calculated from the exhaustively methylated product corresponds with that calculated from the benzoyl content. Fibroin dispersed in water is attacked by dog's gastric juice and by trypsin, but not by erepsin. Erepsin further degrades the products obtained by the action of pepsin. By the action of trypsin most of the tyrosine is separated and by the action of trypsin and erepsin half of the fibroin is converted into dialysable products.

P. W. CLUTTERBUCK.

**Waxy substance of cocoon silk fibres.** O. MASAMI (Bull. Agric. Chem. Soc. Japan, 1928, 4, 123—125).—The ether-soluble wax, containing orange pigments, has m. p. about 65° and contains C 77.9, H 13.2, O 8.9%. The unsaponifiable substance (63%) contains 82% of higher alcohols and 18% of hydrocarbons; it has m. p. 84° and contains C 81.6, H 14.6, O 3.8%. Hentriacontane, ceryl and myricyl alcohols, but not sterol, are present; the insoluble fatty acid is mainly melissic with some stearic and palmitic acids, whilst the soluble fatty acids have mol. wt. 140.

CHEMICAL ABSTRACTS.

**Relation between reeling process of the cocoon and physico-chemical properties of the aqueous colloidal solution of sericin.** H. KANEKO and M. MIYASAKA (Bull. Sericult. Japan, 1930, 3, 2—3).—The sericin of silk cocoons has been examined as to its solubility in hot water and the stability, viscosity, surface tension, osmotic pressure, specific electric conductivity, and degree of turbidity of its colloidal solutions. Increased ease of reeling appears to be correlated with lower solubility in hot water, higher stability of colloidal solutions, lower surface tension, greater conductivity, greater osmotic pressure, and greater turbidity.

W. O. KERMACK.

**Coagulation of liquid silk stored in the silk gland of silk-worm.** M. HIRASAWA (Bull. Sericult. Japan, 1930, 3, 6—7).—The liquid silk coagulates in two stages. Semi-coagulated silk which has undergone the first stage of coagulation may be stretched without breaking to about six times the length of the original silk gland, whereupon the second stage of coagulation occurs. The optimum reaction for the occurrence of the first stage is  $pH$  1.2—3.8 and the coagulating action of a saturated solution of sodium hydrogen sulphate is probably due partly to its reaction and partly to its dehydrating effect.

W. O. KERMACK.

**Detection of acetone in urine in presence of acetoacetic acid.** H. KAISER and E. WETZEL (Süddeut. Apoth.-Ztg., 1930, 70, 108—109; Chem. Zentr., 1930, i, 3220).—The acetone is evaporated into a drop of a solution of *p*-nitrophenylhydrazine in acetic acid, the hydrazone being detected microscopically. Acetone is differentiated from acetaldehyde by the use of the *m*-compound. A. A. ELDRIDGE.

**Micro-determination of sugar in urine.** E. PROS (Klin. Woch., 1930, 9, 500—501; Chem. Zentr., 1930, i, 3220).—Ammonium thiocyanate is added, whereby cuprous oxide is converted into the stable thiocyanate, and the disappearance of the blue cuprammonium complex serves as an indication of the end-point. A. A. ELDRIDGE.

**Undetermined carbon and sugar-carbon of normal urine.** P. FLEURY and P. AMBERT (J. Pharm. Chim., 1930, [viii], 12, 350—364).—After treatment of the urine with acid mercuric nitrate, the sugars are precipitated at 4° with a copper sulphate-barium hydroxide solution. The total carbon, nitrogen, urea, mercury-reducing value (cf. Fleury and Marque, A., 1929, 948), and copper-reducing value (cf. Fleury and Boutot, A., 1922, ii, 879) of the precipitated complex and the filtrate are determined before and after hydrolysis. One quarter of the total carbon left after treatment with mercuric nitrate is precipitated as the unstable cupro-barium precipitate, 75% of which reduces potassium iodomercurate, which is approximately twice the amount as determined by the copper-reducing method. The osazones, m. p. 160—175°, prepared from the cupro-barium precipitate resemble glycosazone (cf. Grimbert and Bernier, A., 1910, ii, 163), show no change on hydrolysis, and are identical with those obtained from urine after treatment with mercuric nitrate. The solutions obtained from the cupro-barium precipitates are optically inactive, their copper-reducing fraction consisting entirely of aldoses. C. C. N. VASS.

**Influence of feeding on certain acids in the faeces of infants. IV. Effect of an excess of lactose in breast milk and in whole cow's milk on the excretion of volatile acids and of lactic acid.** J. R. GERSTLEY, C. C. WANG, and A. A. WOOD (Amer. J. Dis. Children, 1930, 39, 729—735).—The addition of lactose (3%) to whole cow's milk causes an increase in the output of volatile acids and lactic acid and in the total titratable acidity, whilst the addition of 12% of lactose causes little change.

CHEMICAL ABSTRACTS.

**Citric acid content of the urine in acidosis and alkalosis.** O. ÖSTBERG (Biochem. Z., 1930, 226, 162—163).—The mean urinary citric acid of 200 persons was 0.2—1.0 g. per day. Subnormal values were obtained in diabetes and experimental acidosis and considerably increased values (up to 2.23 g. per day) after administration of sodium hydrogen carbonate. P. W. CLUTTERBUCK.

**Disturbance of lactic acid synthesis in adrenalectomised animals.** E. HAYASAKA (Tohoku J. Exp. Med., 1930, 14, 359—384).—Acidosis, increased basal metabolism, and impaired resynthesis of lactic acid to dextrose are corrected by prolonged infusion of adrenaline. CHEMICAL ABSTRACTS.

**Determination of the net volume of precipitated proteins in albuminuria.** K. INOUE (J. Biochem. Japan, 1930, 12, 7—25).—When the proteins are precipitated with Esbach's, Tsuchiya's, or Sueyoshi's reagent and centrifuged,  $V_t = t/(a + bt)$ , where  $V_t$  is the volume and  $t$  the time. The conversion of the values obtained into percentages is discussed.

CHEMICAL ABSTRACTS.

**Liquid and dry milk as anæmia-producing diets.** G. C. SUPPLEE, O. D. DOW, G. E. FLANIGAN, and O. J. KAHLBERG (*J. Nutrition*, 1930, 2, 451—469).—Addition of inorganic iron and copper does not protect rats from anæmia caused by a milk diet. Dried milk containing an increased quantity of iron arising from the cylinders had protective properties. The xanthate method for the determination of copper in milk is preferred.

CHEMICAL ABSTRACTS.

**Distribution of amino-acids in blood in anæmias.** A. SIMON (*Arch. exp. Path. Pharm.*, 1930, 154, 239—246).—The red blood-corpuscles of human patients suffering from various types of anæmia have a high amino-nitrogen content and the ratio of the concentration of amino-nitrogen in the corpuscles to that in the plasma is unusually large. During blood regeneration the corpuscle-amino-nitrogen and the ratio both tend to fall.

W. O. KERMACK.

**Cancer antigen.** Z. KOŁODZIEJSKA and W. HALBER (*Biochem. Z.*, 1930, 225, 464—477).—The substance which occurs in alcoholic extracts of cancerous tumours and reacts with sera from persons suffering from cancer and with that from pregnant women, combining with a complement, is found in the fraction containing the fatty acids.

W. MCCARTNEY.

**Chemotherapy of transplanted and spontaneous tumours.** P. ZADIK (*Z. Krebsforsch.*, 1930, 30, 473—481; *Chem. Zentr.*, 1930, i, 2924).—Chiefly negative results are recorded; the use of isamin-blue and of bismuth preparations, however, gave good results.

A. A. ELDRIDGE.

**Chemical measurement of carcinolysis.** R. WILLHEIM and K. STERN (*Biochem. Z.*, 1930, 226, 315—324).—During cytotoxicity there are liberated from the cells fat-like substances which develop a characteristic colour with aqueous solution of neutral-red. A description is given of a colorimetric process, based on this fact, for measuring the extent of carcinolysis.

W. MCCARTNEY.

**Mitogenetic radiation from the blood and urine of healthy and diseased persons.** W. W. SIEBERT (*Biochem. Z.*, 1930, 226, 253—256).—The mitogenetic power possessed by the blood of healthy persons is found also in their urine, but is usually absent from the blood and urine of persons suffering from various diseases (cf. Gurwitsch and Salkind, *A.*, 1929, 1330).

W. MCCARTNEY.

**Importance of mitogenetic radiation from human blood in diagnosis of carcinoma.** H. GESENIUS (*Biochem. Z.*, 1930, 226, 257—272; cf. preceding abstract and this vol., 1620).—The results obtained by Gurwitsch and Salkind and by Siebert have been confirmed by the method previously described.

W. MCCARTNEY.

**Dextrose tolerance in infants and young children.** A. B. MACLEAN and R. C. SULLIVAN (*Amer. J. Dis. Children*, 1929, 37, 1146—1160).—The dextrose tolerance of normal infants is greater than that of normal adults. The effect of pathological conditions is recorded.

CHEMICAL ABSTRACTS.

**Carbohydrate tolerance in infants and young children with celiac disease.** A. B. MACLEAN

and R. C. SULLIVAN (*Amer. J. Dis. Children*, 1929, 38, 16—25).—An increased dextrose tolerance is observed.

CHEMICAL ABSTRACTS.

(a) Influence of insulin on the characteristics of the blood, the velocity of sedimentation of erythrocytes, and the times of hæmorrhage and of coagulation. (b) Experimental glycaemia in diabetes mellitus during insulin therapy. G. LEGA (*Arch. Farm. sperim.*, 1930, 51, 1—23, 33—40).—(a) Diabetic patients show low values for the erythrocyte count and blood-hæmoglobin, a high leucocyte count, a slightly increased bleeding time, and distinctly increased times of coagulation and of sedimentation of the erythrocytes. Dietetic treatment affects only the erythrocyte count and blood-hæmoglobin beneficially. Under insulin treatment all the characteristics change in the direction of normal values.

(b) Observations of the blood-sugar curve after oral administration of dextrose show a progressive diminution of the intensity and duration of hyperglycaemia after insulin therapy.

R. K. CALLOW.

**Uricæmia in diabetes mellitus.** R. ALFREDO (*Arch. Farm. sperim.*, 1930, 51, 34—48).—Endogenous hyperuricæmia is generally found in diabetic patients, and the intensity and duration of hyperuricæmia provoked by administration of purines are increased. The connexion of this metabolic defect with defective carbohydrate metabolism is discussed.

R. K. CALLOW.

**Cholesterol content of normal and eclamptic placenta.** H. GOLDHAMMER (*Biochem. Z.*, 1930, 226, 401—403).—On the average the normal placenta contains 0.91% of its dry weight of cholesterol and the eclamptic 0.65%.

W. MCCARTNEY.

**Liesegang phenomenon in gall-stones.** J. E. SWEET (*Coll. Symp. Ann.*, 1929, 7, 249—258).—Liesegang rings, due to the diffusion of bilirubin, have been observed.

CHEMICAL ABSTRACTS.

**Respiratory metabolism in infancy and childhood. XI. Respiratory exchange in marasmus; effect of muscular activity.** J. R. WILSON, S. Z. LEVINE, and M. KELLY (*Amer. J. Dis. Children*, 1930, 39, 736—746).

CHEMICAL ABSTRACTS.

**Milk of cows in nymphomania.** E. MAYR and K. WURSTER (*Milchwirt. Forsch.*, 1930, 9, 335—338; *Chem. Zentr.*, 1930, i, 1869).—The milk had an unpleasant taste and odour; the density was normal, but the fat content high (4.9%). The actual and potential acidities and the refraction of the serum were increased, whilst the electrical conductivity was low.

A. A. ELDRIDGE.

**Plasma-proteins in relation to blood hydration. IV. Malnutrition and the serum-proteins.** F. S. BRUCKMAN, L. M. D'ESOP, and J. P. PETERS. V. Serum-proteins and malnutritional or cachetic oedema. F. S. BRUCKMAN and J. P. PETERS (*J. Clin. Invest.*, 1930, 8, 577—590, 591—595).—IV. The serum-albumin is subnormal in malnutrition not complicated by anhydramia.

V. Oedema develops when the serum-albumin is less than 3%.

CHEMICAL ABSTRACTS.

(a) State of the calcium in blood-serum of normal dogs and of parathyroidectomised dogs. (b) Amount of diffusible calcium in serum of normal and of parathyroidectomised dogs. (c) Effect of parathyroidectomy on rate of settling of red blood-corpuscles. A. VON BEZNÁK (Biochem. Z., 1930, 225, 295—304, 305—311, 312—317).—

(a) In the serum of dogs suffering from tetany as a result of removal of the parathyroid glands the amounts both of total calcium and of calcium which can be removed by adsorption on powdered bone are lower than those from normal dogs, the magnitude of the decrease being possibly related to the severity of the symptoms. The decrease may be a consequence of reduced formation of a negatively charged complex which holds calcium compounds in solution.

(b) Since the total calcium content of the lymph from the thoracic duct of normal dogs and of dogs from which the parathyroid glands have been removed is almost the same as that of their blood-serum it follows that the total calcium of the serum is diffusible and, since the proportion of calcium which can be removed by adsorption from both fluids is the same, the physico-chemical condition of the calcium in both must also be the same.

(c) The rate of settling of the red blood-corpuscles of rabbits and dogs is increased by removal of the parathyroid glands. The increase may be related to an accompanying decrease in the amount of the negatively charged calcium complex present in the blood.

W. MCCARTNEY.

**Determination of calcium in pus.** M. BEBER and S. S. PINTO (J. Lab. Clin. Med., 1930, 15, 693—695).—The material is digested with nitric acid and concentrated hydrogen peroxide solution; after removal of most of the nitric acid the solution is neutralised and diluted to 4 c.c., Kramer and Tisdall's method then being employed.

CHEMICAL ABSTRACTS.

**Cholesterol and phosphorus-containing lipins in the blood during experimental rabies.** D. ZUVERKALOV and I. GOLDENBERG (Biochem. Z., 1930, 226, 278—285).—In rabbits suffering from experimental rabies the cholesterol content of the blood increases in the early stages of the disease, but the increase may be a result rather of the accompanying derangement of the water supply in the organism than directly of the infection itself. Throughout the whole course of the disease the amount of phosphorus-containing lipin in the blood increases (cf. A., 1929, 1482).

W. MCCARTNEY.

**Blood-lactic acid in renal insufficiency.** R. ALFREDO (Arch. Farm. sperim., 1930, 51, 141—144).—Lactic acid is not present in the blood-plasma in cases of partial renal insufficiency, but is found when this insufficiency is absolute.

T. H. POPE.

**Pathogenesis of thrombosis.** B. STUBER and K. LANG (Arch. exp. Path. Pharm., 1930, 154, 22—40).—Thrombosis is due mainly to a retardation of blood movement, local or general, and a change in the chemical and physico-chemical characteristics of the corpuscles and plasma. Thus there is an increased acidity of the blood due to increase in the carbon dioxide content and a reduction in the electric charge

of the platelets. These changes in some cases followed soon after a mere change in the blood movement as studied in artificial vascular constriction, so that this retardation is the deciding factor. The actual relationship of these factors to thrombosis is discussed.

F. O. HOWITT.

**Influence of "germanin" on the blood-coagulation system: its application in thrombosis.** B. STUBER and K. LANG (Arch. exp. Path. Pharm., 1930, 154, 41—49).—The effect of intravenous injection of "germanin" (Bayer 205) on the blood-constituents is studied. The reaction is displaced to the alkaline side and the proportion of albumin in the blood-proteins increased. At the same time the number of thrombocytes is diminished and their charge increased, so that their coagulation is rendered difficult. On these experimental grounds, "germanin" is recommended in cases of thrombosis and thrombophlebitis.

F. O. HOWITT.

**Influence of intravenous sugar injection on the blood-coagulation system with special reference to the pathogenesis of thrombosis.** B. STUBER and K. LANG (Arch. exp. Path. Pharm., 1930, 154, 50—58).—An examination of the blood of normal individuals and those suffering from diseases of the circulatory system was made following injection of hypertonic dextrose solution. The blood-calcium, -lactic acid, and -protein appreciably alter, the fibrinogen-globulin fraction increases, and there is always an acceleration in the rate of blood-coagulation. Simultaneously the number of thrombocytes increases, whilst their electric charge decreases. The significance of these changes in the origin of thrombosis is discussed.

F. O. HOWITT.

**Blood chemistry of acute trypanosome infection.** R. W. LINTON (J. Exp. Med., 1930, 52, 103—111).—In infection with *Trypanosoma equiperdum* the carbon dioxide capacity of the serum is lowered, the blood-non-protein-nitrogen and uric acid are increased in the terminal stages, the cholesterol is unchanged, the lecithin increased, and the liver-glycogen diminished. The blood-sugar is at first unchanged.

CHEMICAL ABSTRACTS.

**Xanthæmia and xanthosis (carotenæmia).** W. C. BOECK and W. M. YATER (J. Lab. Clin. Med., 1929, 14, 1129—1143).—The relative amount of lipochrome pigments present in the blood-plasma may be estimated from the lipochrome index, for the determination of which a light petroleum extract of the blood-plasma is compared colorimetrically with a standard solution of potassium dichromate. Yellow pigmentation of the skin characteristic of xanthosis is associated with a low concentration of serum-bilirubin and a high icterus index; that accompanying jaundice is associated with a high concentration of serum-bilirubin and a low lipochrome index.

CHEMICAL ABSTRACTS.

**Oxidation-reduction potentials of living cells and their significance.** E. AUBEL (Z. angew. Chem., 1930, 43, 939—943).—A critical review of methods and results.

E. S. HEDGES.

**Mechanism of biological oxidation and function of the suprarenal gland.** A. S. GYÖRGYI

(Science, 1930, 72, 125—126).—Vegetable tissues which discolour on injury contain hexuronic acid, which is a strong reducing agent. In the cabbage this acid plays a central rôle in normal respiration, being rapidly oxidised by an enzyme, hexoxidase, and then reduced. The suprarenal cortex is now shown to contain hexuronic acid. The acid inhibits pigment formation in all systems in which a melanoid pigment is formed by oxidation of a phenol; it does not prolong life. The medulla contains besides adrenaline a strong reducing agent which is analogous to, but apparently not identical with, hexuronic acid.

L. S. THEOBALD.

**So-called specific-dynamic action of foods.**

II. Influence of carbohydrates on the oxygen consumption of isolated cells. Z. HORN and G. ÓNODY. III. Influence of blood-serum on the oxygen consumption of erythrocytes. IV. Influence of hormones on the respiration of cells. Z. HORN (Biochem. Z., 1930, 226, 286—296, 297—307, 308—314; cf. A., 1929, 1109).—II. The oxygen consumption of goose erythrocytes suspended in a physiological salt solution is increased by addition of dextrose, lævulose, or galactose. Although the increase tends to be greater as the concentration of sugar increases no regular proportionality is observed.

III. Very small amounts of goose-serum as well as of that from the dog, the rabbit, and man increase the oxygen consumption of goose erythrocytes, the increases being proportional to the quantity of serum used. Several substances, some dialysable some not so, are responsible for the increases.

IV. Neither thyroxine nor insulin is responsible for the increased oxygen consumption of goose erythrocytes to which blood-serum has been added.

W. MCCARTNEY.

**Oxygen consumption in tissues of rats fed on a diet poor in cystine.** A. D. MARENZI and N. C. LACLAU (Semana Méd., 1930, I, 1208).—A deficiency in cystine causes a decrease in the oxygen consumption, the glutathione content, and the oxido-reducing power of the tissues.

CHEMICAL ABSTRACTS.

**Influence of salts of potassium, calcium, strontium, barium, and magnesium on respiration of isolated kidney tissue.** J. LEIBOWITZ (Biochem. Z., 1930, 226, 338—354; cf. this vol., 949).—The respiration of isolated kidney tissue in Ringer's solution and in similar solutions in which the calcium is replaced by barium, strontium, or magnesium has been investigated by Warburg's methods. These metals are interchangeable, but magnesium chloride, added in very small quantities to Ringer's solution, greatly stimulates the respiration, although it inhibits this when added in larger quantities. The hydrogen-ion concentration of the solutions (at least between  $p_H$  6.9 and 7.8) had no specific effect on the respiration.

W. MCCARTNEY.

**Oxygen consumption of nerve during activity.** R. W. GERARD (Science, 1930, 72, 195—196).—The conclusions of Winterstein (*ibid.*, 71, 641) are criticised.

L. S. THEOBALD.

**Movement of ions in gelatin gels and in the nerve substance.** VI. Thickness and nature of the semipermeable membranes of irritable

tissue. Calculation of length of path of ions in the first phase of stimulation. V. V. EFIMOV (Biochem. Z., 1930, 226, 129—132).—The distance travelled by the hydroxyl ion under the influence of an electric impulse in causing the stimulation of a nerve is calculated as  $7.6 \times 10^{-7}$  cm. and corresponds with the diameter of the hæmoglobin or starch molecule (cf. this vol., 809).

P. W. CLUTTERBUCK.

**Internal condition of the lamprey (*Petromyzon marinus*). Its variations as a function of those of the environment.** FONTAINE (Compt. rend., 1930, 191, 680—682).—When lampreys are kept in an environment containing varying amounts of sodium chloride (as sea-water), the concentration of the chloride in the serum increases with rise in concentration of the external medium. The ratio of the osmotic pressure due to the chloride to the total osmotic pressure remains constant or decreases, indicating that substances other than sodium chloride pass into the blood.

H. BURTON.

**Alteration of the internal condition of potamic fish during reproduction.** FONTAINE (Compt. rend., 1930, 191, 736—737).—The chloride content of the serum of the common shad and lamprey diminishes during the spawning season; the ratio osmotic pressure due to chloride : total osmotic pressure also decreases.

H. BURTON.

**Effect of varying amounts of menhaden oil on the composition of the body-fat of the white rat. Storage of highly unsaturated fatty acids.** J. B. BROWN and S. G. MORRIS (J. Nutrition, 1930, 2, 509—515).—Diets containing 5—30% of menhaden oil result in the deposition of 9.7—17.2% of highly unsaturated acids. The amount of highly unsaturated fatty acids in the depot fat was always higher than that of the diet.

CHEMICAL ABSTRACTS.

**Physiological behaviour of glyceryl trimargarate.** D. L. R. MOORE, M. BRECKENRIDGE, and H. C. KOSER (J. Lab. Clin. Med., 1928, 14, 201—208).—Ingestion of the synthetic fat increased the excretion of ammonia, acetone substances, and organic acids.

CHEMICAL ABSTRACTS.

**Relation between fat and carbohydrate metabolism.** II. Relation between neutral fat, ketone substances, lactic acid, and sugar after splenectomy. Z. M. DINERSTEIN and S. G. GENES (Zhur. exp. Biol. Med., 1929, 11, 11—17).—Fat loading of splenectomised dogs causes hyperlipæmia, hyperketonæmia, and hyperglycæmia. The normal reciprocal relationship between the blood-ketone and lactic acid is more pronounced in splenectomised animals.

CHEMICAL ABSTRACTS.

**Free energy of dextrose and tripalmitin.** H. BORSOOK and H. M. WINEGARDEN (Proc. Nat. Acad. Sci. 1930, 16, 559—573).—The theoretical maximum work,  $W_R = -\Delta F + \Delta(PV)$ , obtainable by oxidation, under physiological conditions, of dextrose and tripalmitin is respectively 101 and 98% of the heat of combustion. To produce tripalmitin from dextrose requires energy from other sources equal to 20% of the energy change in the combustion of tripalmitin. These results are discussed with reference to the relative efficiencies as fuel and as

sources of muscular work of fats and dextrose as deduced from recent experimental results. It is concluded that there is probably little difference in the efficiency of utilisation of the two materials.

C. A. SILBERRAD.

**Production of acetaldehyde in the liver.** I. A. BORNSTEIN and H. MAYER. II. **Carbohydrates and related substances as aldehyde producers.** A. BORNSTEIN and R. PANTKE. III. **Production in the absence of bacteria.** H. GLOBIG and R. PANTKE (Biochem. Z., 1930, 225, 318—320, 321—325, 326—329).—I. Although the results obtained by Neuberg and Gottschalk (A., 1924, i, 785; 1925, i, 199) using guinea-pigs' livers have been confirmed, it has been found that, in the case of the dog, acetaldehyde is produced in glycogen-free livers only when certain substances (ethyl alcohol or glycogen but not dextrose or dextrose plus insulin) are added to them.

II. When glycogen along with certain other substances, such as amino-acids, carbohydrates, and alcohols (including substances such as dextrose which by themselves lead to no production of acetaldehyde), is added to liver preparations the amount of acetaldehyde produced exceeds, often very greatly, the sum of the amounts produced when glycogen and the other substance are added separately.

III. The production of acetaldehyde in liver preparations to which certain substances have been added is not a result of bacterial action.

W. MCCARTNEY.

**Behaviour of Sudan III when fed with carbohydrate.** E. H. MACARTHUR (Science, 1930, 72, 14).—Rats fed with maize starch, rice starch, dextrin, lactose, or sucrose each mixed with Sudan III deposit fatty tissue coloured by the dye. The excreta are also pink to red in colour.

L. S. THEOBALD.

**Glycogen metabolism.** W. D. BANCROFT and G. BANCROFT (Proc. Nat. Acad. Sci., 1930, 16, 651—657).—A discussion of the glycogen-lactic acid metabolism in muscle.

F. O. HOWITT.

**Fate of infused sugar with particular reference to the sugar affinity of the tissue cells.** VI. **Lactacidogen, lactic acid, and inositol in muscle after injection of sugar.** K. SATO, K. UEDA, and T. KUROKAWA (Tohoku J. Exp. Med., 1929, 14, 335—340).—No change was observed after injection of dextrose.

CHEMICAL ABSTRACTS.

**Time relationships of the resynthesis of lactic acid after muscular work.** K. KIMURA and K. KATO (Tohoku J. Exp. Med., 1930, 14, 569—579).—In experiments with the dog's gastrocnemius muscle the increased oxygen consumption, blood flow, and venous lactic acid became normal after 5 min., rising again in 20 min., and thereafter gradually becoming normal. The blood-sugar showed insignificant fluctuations.

CHEMICAL ABSTRACTS.

**Changes of the osmotic pressure of muscle in fatigue and rigor.** O. MEYERHOF (Biochem. Z., 1930, 226, 1—15).—A thermo-electric method for determination of changes of f. p. of muscle in fatigue and rigor is described. In prolonged fatigue and rigor the measured depression of f. p. is about 30% greater than would be expected from the known products of hydrolysis.

P. W. CLUTTERBUCK.

**Muscle contraction.** J. K. PARNAS (Naturwiss., 1930, 18, 916).—The fact observed by Mozolovski and Mann that frog muscle which has been poisoned by iodoacetic acid develops more ammonia after repeated stimulation than muscle which has not been treated with iodoacetic acid cannot be interpreted to show that the formation of ammonia is a primary chemical process of muscle contraction. The increase in ammonia content is found to develop some hours after the stimulation has been applied.

E. S. HEDGES.

**Production of ammonia by surviving kidney tissue.** II. **Possible precursors of urinary ammonia.** B. E. HOLMES and A. PATEY (Biochem. J., 1930, 24, 1564—1571).—There is present in the rat kidney an ammonia-producing system which acts aerobically; its optimum activity is at  $p_H$  5.2 or lower and is much reduced or even inhibited by dextrose. Ammonia production is much decreased in uranium nephritis when ammonia excretion is low. The possibility of adenylic acid or urea being the precursor of the ammonia is discussed. Adenylic acid may possibly be the precursor. Histidine and asparagine are not deaminated by surviving kidney tissue; tyramine gives a higher yield of ammonia in the presence of dextrose than in its absence. Aspartic acid and lysine both show considerable deamination at  $p_H$  7.3 and the deamination of lysine is much reduced by dextrose. Urea is formed by kidney tissue in air at  $p_H$  7.3.

S. S. ZILVA.

**Cyanic acid as an intermediate product in amino-acid metabolism.** A. BORNSTEIN and R. PANTKE (Biochem. Z., 1930, 225, 330—335).—Cyanic acid is not formed during the degradation of amino-acids in the animal organism, where also conversion of the acid into urea occurs only to a slight extent, if at all.

W. MCCARTNEY.

**Fate of choline in the organism.** I. H. PAGE and E. SCHMIDT (Z. physiol. Chem., 1930, 191, 262—272).—The average choline content of serum is 3 mg. per litre but is subject to wide variations. When choline was added to active serum some of the choline disappeared, the amount disappearing being proportional to the concentration and the time of action. This decrease was not observed in serum previously heated to 56°. Addition of choline to liver press-juice or extracts of liver powder produced an irregular decrease which cannot be accounted for by enzyme action since the amount was the same after varying periods of time.

J. H. BIRKINSHAW.

**Protein optimum for pregnant sows.** F. HÜRTER (Landw. Jahrb., 1930, 72, 459—479).—The protein metabolism of pregnant sows and the optimum starch value of the ration were examined. The normal protein ration need not be increased during pregnancy and in the first half of the period should be reduced.

A. G. POLLARD.

**Comparative value of different food-proteins for reproduction and lactation in the rat.** I. **Beef muscle, liver, and kidney.** M. M. CLAYTON and M. J. CUMMINGS (J. Nutrition, 1930, 2, 491—507).—Cod-liver oil and lard have an unfavourable effect on reproduction. With an adequate supply of vitamin-E, kidney-protein ranked first, liver



second, and muscle third as sources of protein for reproduction.

## CHEMICAL ABSTRACTS

**Dietary requirements for fertility and lactation. XXII. Milk-fat.** B. SURE and A. BEACH (J. Nutrition, 1930, 2, 485—489).—A study of the effect of the increase of small quantities of butter-fat in a ration satisfactory for growth but not adequate for lactation of rats.

## CHEMICAL ABSTRACTS.

**Relative value of plant and animal by-products as feed for brook-trout and the basic nutritional requirements of trout.** J. W. TITCOMB, E. W. COBB, M. F. CROWELL, and C. M. McCAY (Trans. Amer. Fish Soc., 1930, 126—145).—Cooked starch and dextrin are utilised more effectively than raw starch; soya-bean meal is of little, but cottonseed meal of high, value. Comparative studies on raw organs show that only lungs are adequate for the growth and maintenance of trout.

## CHEMICAL ABSTRACTS.

**Influence of infusoria on the digestion of ruminants.** A. VERENINOV, M. VINOGRADOV, T. VINOGRADOV, and M. DIAKOV (Biochem. Z., 1930, 226, 387—394).—The presence of infusoria in the first stomach of ruminants does not favour the digestion of any part of the food which they consume.

W. McCARTNEY.

**Oxidation of benzene in the isolated liver of warm- and cold-blooded animals.** TSCHERNIKOV, I. D. GADASKIN, and I. I. GUREVITSCH (Arch. exp. Path. Pharm., 1930, 154, 222—227).—The isolated liver of the cat, rabbit, or frog when perfused with a solution containing benzene is capable of converting it into phenol. The phenol is obtained from the liver of warm-blooded animals partly free and partly conjugated. Hepatectomised frogs live for about 24—48 hrs. and these animals when poisoned with benzene continue to convert it into phenol. It therefore appears that in frogs and presumably also in warm-blooded animals, the liver is not the only place in which oxidation of benzene takes place.

W. O. KERMACK.

**Physiology of glands. CXXI. Influence of "thymocrescin" on growth.** L. ASHER and W. W. NOWINSKI (Biochem. Z., 1930, 226, 415—428).—Extraction with water of the residue from successive extractions of the thymus of the calf with acetone and ether yields a water-soluble substance ("thymocrescin") which, when subcutaneously administered to rats in daily doses of 20 mg., counteracts for 14 days the loss of weight in the animals caused by lack of vitamins in the food consumed and is even able, while such food only is consumed, to produce increase in weight. The substance is not lipid-soluble.

W. McCARTNEY.

**Physiology of glands. CXXII. Iron metabolism in normal and splenectomised guinea-pigs living in low-pressure atmospheres.** L. ASHER and R. KALBERMATTEN (Biochem. Z., 1930, 226, 429—440).—The amount of iron excreted daily by guinea-pigs increases if they are kept in a vessel in which the atmospheric pressure is reduced to 300—350 mm. If the spleens of the animals are removed and they are caused to live under this pres-

sure, a further increase, which may either persist or slowly disappear, is observed in the amount of iron excreted. It is concluded that the spleen is an organ involved in iron metabolism and that the compensatory processes which begin when the spleen is removed can be restricted by reduction of the pressure under which animals live.

W. McCARTNEY.

**Physiology of glands. CXXIII. Exchange of electrolytes between tissues and blood under the influence of specific diuretics.** L. ASHER and W. RIESEN (Biochem. Z., 1930, 226, 441—456).—By measurement according to the methods of Kohlrausch of the conductivity of solutions with which frogs, suitably prepared, had been perfused it has been shown that when a specific diuretic is added to the solutions their electrolyte content increases on perfusion. In denervated frogs the increase is halved. These results support the view that the predominating factors of the regulation, under physiological conditions, of the activity of the kidneys are the changes which the tissues produce in the blood and the capability of the kidneys to react to these changes.

W. McCARTNEY.

**Effect of low-calcium, high-magnesium diets on growth and metabolism of calves.** C. F. HUFFMANN, C. S. ROBINSON, O. B. WINTER, and R. E. LARSON (J. Nutrition, 1930, 2, 471—483).—When added to a diet low in calcium, magnesium phosphate is not detrimental to cows, and the carbonate is beneficial. The magnesium carbonate was eliminated chiefly with the faeces. The phosphate is more effective than the carbonate in increasing the storage of magnesium.

## CHEMICAL ABSTRACTS.

**Minimum requirement of calcium and phosphorus in children.** C. C. WANG, R. KERN, and M. KAUCHER (Amer. J. Dis. Children, 1930, 39, 768—773).—The minimum requirements of calcium and phosphoric oxides are, respectively, 0.032 and 0.079 g. per kg. of body-weight per day.

## CHEMICAL ABSTRACTS.

**Mineral metabolism in infancy. II. Utilisation of mineral elements in human milk.** S. V. TELFER (Glasgow Med. J., 1930, 33, 10—20).—All of the elements are retained by the infant in the proportion in which they are present in the milk, the retention being approximately 60% of the intake.

## CHEMICAL ABSTRACTS.

**Manganese in relation to nutrition.** M. B. RICHARDS (Biochem. J., 1930, 24, 1572—1590).—There are wide differences in the manganese content of the reproductive organs in different plants. There is, however, little difference in the content between the male and female organs of the same plant. There is a marked increase in total manganese as the seed of the lupin grows to maturity. Samples of food-stuff from different sources show in general approximately the same content of manganese. The manganese content of a number of animal organs has been determined. Manganese is invariably present in the reproductive organs and there is a steady increase of it in the developing egg. The manganese content of the organs is constant even when large amounts of manganese salts are added to the diet. S. S. ZILVA.

**Storage of iodine in the thyroid gland.** W. KLEIN, G. PFEIFFER, and G. HERMANN (Biochem. Z., 1930, 225, 344—351).—Experiments on dogs to which iodine in various forms was administered showed that the accumulation of iodine in the thyroid glands is much greater when the iodine is in organic combination than when it is given as potassium iodide.

W. MCCARTNEY.

**Parenteral resorption. V. Resorption of trypan-blue from the subcutaneous connective tissue.** O. OKUNEV (Biochem. Z., 1930, 226, 147—156).—Although the concentration of trypan-blue in the blood never attains as high a value with subcutaneous as with intraperitoneal injection, the resorption curves are similar in type, pointing to a similarity in the physiological processes in the two cases. Local changes of blood and lymph circulation as caused by the application of heat, cold, adrenaline, and mustard plaster have a profound influence on the rate of resorption. Resorption of trypan-blue is accelerated in the early, and retarded in the later, stages of inflammation caused by injection of turpentine oil.

P. W. CLUTTERBUCK.

**Parenteral resorption of colloids. III.** M. MURATA (Biochem. Z., 1930, 226, 457—461; cf. A., 1929, 345).—The diastase content of the blood-serum of rabbits is increased by intravenous administration of the enzyme, but no increase is observed when the administration is intraperitoneal or subcutaneous.

W. MCCARTNEY.

**Physiological significance of hydrotropy.** F. VERZÁR and A. VON KÚTHY (Biochem. Z., 1930, 225, 267—277; cf. A., 1929, 466, 1194; Neuberg, A., 1916, ii, 555).—The bile acids and other hydrotropic substances can confer water-solubility, not only on fatty acids, but also on other otherwise insoluble substances such as quinoline, camphor, diphenylamine, and cholesterol, and these when so dissolved are often present in diffusible form. Hydrotropic substances may exhibit specificity in regard to the materials on which they confer solubility. It has been shown that many animal organs contain hydrotropic substances other than or in addition to bile acids and the consequences of this are indicated.

W. MCCARTNEY.

**Influence of bile on resorption.** H. LANGECKER (Arch. exp. Path. Pharm., 1930, 154, 1—21).—The presence of sodium glycocholate impairs the precipitating action of tannin and of alcohol on haemoglobin, hinders the crystallisation of *m*-aminobenzoic acid, and affects the relationship of particle size to the colour range of Congo-red. Adsorption of methylene-blue, morphine, adrenaline, etc. by charcoal and of methylene-blue by erythrocytes is hindered by the presence of bile acids, which also decrease the combining capacity of rabbit serum with pilocarpine and increase the permeability of frog skin.

F. O. HOWITT.

**Influence of bile acids on calcium metabolism.** T. SEKITOO (J. Biochem., Japan, 1930, 12, 59—69).—The hypercalcæmic effect of bile acids is removed by splanchnicotomy. The oral administration of bile acids has no effect on the blood-calcium of rabbits the vagus of which had been cut in the abdomen.

CHEMICAL ABSTRACTS.

**Significance of saturated sterols in the organism.** I. R. SCHÖNHEIMER, H. VON BEHRING, R. HUMMEL, and L. SCHINDEL. II. Quantitative separation of unsaturated and saturated sterols. III. Detection and identification of dihydrocholesterol as impurity in body-cholesterol. R. SCHÖNHEIMER. IV. Saturated sterol content of the sterols from various organs. R. SCHÖNHEIMER, H. VON BEHRING, and R. HUMMEL. V. Can saturated sterols be resorbed? H. VON BEHRING and R. SCHÖNHEIMER. VI. Excretion of saturated sterols. R. SCHÖNHEIMER and H. VON BEHRING (Z. physiol. Chem., 1930, 192, 73—76, 77—86, 86—93, 93—96, 97—102, 102—111).—I. Introductory.

II. The separation depends on the fact that cholesterol dibromide is not precipitated by digitonin. An alcoholic solution of bromine is added to the mixture of sterols in cooled alcoholic solution until the solution assumes a light yellow colour. The precipitated dibromide is removed by filtration and a digitonin solution added together with further small amounts of bromine to maintain the yellow colour. After 48 hrs. in the dark the digitonide is separated, washed, dried, and weighed. The method is able to detect less than 1% of dihydrocholesterol in cholesterol.

III. Commercial cholesterol is purified by conversion into the dibromide and subsequent debromination by boiling with sodium iodide in alcohol. A repetition of the process followed by recrystallisation from alcohol gives a pure product. The saturated sterol present in cholesterol from gall-stones was isolated as the digitonide and the latter was decomposed with boiling xylene. The product was further purified by boiling with xylene and sodium, followed by precipitation as the digitonide. The latter with xylene yielded pure dihydrocholesterol, m. p. 140.5°. The mother-liquor from the digitonin formed a syrup from which crystals of  $\alpha$ -cholestanol were obtained. Coprosterol was not detected in any sample of crude cholesterol out of several examined.

IV. The quantity of saturated sterols in the total sterols of various human and animal organs varied from 1 to 5%, the highest value being obtained with the sterols of the atherosclerotic aorta. In plants the proportion of saturated sterols is considerably higher (5—25%).

V. The total unsaponifiable fraction from mice fed on coprosterol or dihydrocholesterol showed no increase in saturated sterols over that from control animals on normal diet. The normal value for mice (8—10%) is higher than that obtained from other animal material.

The fluid from the thoracic duct of dogs fed on saturated sterols, dihydrocholesterol, or coprosterol contained no saturated sterols. On the other hand, cholesterol was present even when the food contained no sterols, showing that the lymph-cholesterol arises in part from the cholesterol discharged into the intestines.

VI. The total sterol of human faeces contains about 90% of saturated sterol. In order to investigate a possible source of this saturated sterol, the large intestine of a dog was closed at its upper end and its

secretion collected by frequent washing over a period of 2 months. The unsaponifiable matter of this material contained about 60% of saturated sterol, chiefly dihydrocholesterol. No coprosterol was detected. In dermoid cysts of ovaries a varying but high proportion of saturated sterols was observed.

J. H. BIRKINSHAW.

**Ester resorption.** R. SCHÖNHEIMER and R. HUMMEL (Z. physiol. Chem., 1930, 192, 114—116).—Small amounts of cholesteryl oxalate fed to mice with deoxycholic acid to promote resorption were completely hydrolysed before resorption, since the hydrolysed liver extract contained no oxalic acid. The latter substance was present in the urine.

J. H. BIRKINSHAW.

**Specificity of the resorption of sterols, depending on their constitution.** R. SCHÖNHEIMER, H. VON BEHRENG, and R. HUMMEL (Z. physiol. Chem., 1930, 192, 117—123).—Various sterols (cholesterol, sitosterol, stigmasterol, brassicasterol, *allo*cholesterol, *isocholesterol*) together with gallic acid to promote resorption were fed to mice. Only cholesterol and to some extent *allo*cholesterol increased the sterol content of the liver. In experiments with  $\epsilon$ -cholestanol and  $\psi$ -coprosterol, neither sterol was recovered from the eviscerated animals.

J. H. BIRKINSHAW

**Pharmacology of [d-]gluconic acid. Effect of free acids on the organism.** I, II, III. S. HERMANN (Arch. exp. Path. Pharm., 1930, 154, 143—160, 161—174, 175—192).—The following studies were made on a number of the more common organic and inorganic acids.

I. The toxicity (in rabbits) increases with increasing hydrogen-ion concentration, but for a definite  $pH$  value it depends on the acid used. Decreasing concentration results in higher relative toxicity, although equimolecular solutions are not equal in toxicity values. The toxicity depends on the ease of combustion in the organism as well as on the resulting change in osmotic pressure.

II. Under identical conditions one and the same acid produces hæmatin formation at different rates in different species of animals. The formation is dependent neither on the hydrogen-ion concentration nor on the molecular concentration of the acid used. In hæmolysed blood, however, it is dependent on the former but independent of the latter. Hæmatin formation in difibrinated non-hæmolysed blood is directly related to the permeability and lipin-solubility of the acid concerned. In this respect gluconic acid shows little effect and hence has a low lipin-solubility.

III. Intravenous injection of most of the acids investigated into normal and morphinised dogs affects the blood-pressure and respiration. Gluconic acid does not significantly change the blood-calcium in rabbits and dogs, but causes changes in the urinary and faecal calcium. Parenteral introduction of gluconic acid increases the serum-calcium. The calcium mobilisation due to gluconic acid is demonstrated by prevention of mustard-oil chemosis on the rabbit eye and by the increase in tolerance towards the lethal dose of citric acid. Excretion of the acid in the urine follows both parenteral and enteral administration of gluconic acid. F. O. HOWITT.

**Physiological action of xanthophyll.** P. KARRER, H. VON EULER, and M. RYDBOM (Helv. Chim. Acta, 1930, 13, 1059—1062; cf. A., 1929, 1343).—Feeding of xanthophyll (0.03 mg. per day) to chickens causes little or no growth; the animals are ultimately poisoned. Xanthophyll stearate does not promote growth. H. BURTON.

**Effect of phenol and some of its derivatives on muscle action.** T. HASEGAWA (Arch. exp. Path. Pharm., 1930, 154, 103—114).—The intensities of narcosis induced by phenol, *o*- and *m*-cresol, compared by the time taken to produce total narcosis in a surviving frog gastrocnemius, are in the ratio of 1:2.5:1.7, respectively. Dihydric phenols have a negligible and trihydric phenols a very weak narcotic action. The polyhydric phenol ethers show no narcosis. Thymol and  $\beta$ -naphthol produce a strong contraction of the muscle, the narcotic effect failing totally and the contraction passing over more or less rapidly to a rigor, presumably due to protein coagulation. Aminophenol and sodium phenolsulphonate are without action, whilst benzene itself produces reversible narcosis and contraction. F. O. HOWITT.

**Buck-wheat poisoning.** H. E. W. LUTZ and G. SCHMID (Biochem. Z., 1930, 226, 67—96).—Buck-wheat chlorophyll as extracted by ether from the seeds is not the pathogenic factor in buck-wheat poisoning, but the water-soluble portion of the alcoholic extract of the leaves, blooms, and seeds causes acute symptoms in guinea-pigs. The skin symptoms are accompanied by an increased sensitivity to light, due to a sensitising substance present in the alcoholic extract of the blooms. The injury of the central nervous system without accompanying skin symptoms which is obtained after feeding fresh flowering buck-wheat, buck-wheat bran, or after oral administration of the alcoholic extract of the green plants is also produced by intracardial injection of the water-soluble portion of the alcoholic extract. No evidence could be obtained for an increase of sensitivity due to insufficient nutrition and lack of vitamin-B. P. W. CLUTTERBUCK.

**Panax ginseng.** I. N. SUGIHARA. II. Starvation and the toxicity of drugs in rats fed on *Panax ginseng*. III and IV. Toxicity of convulsive and paralytic poisons in rats fed on *Panax ginseng*. N. SUGIHARA and P. MIN (Keijo J. Med., 1930, 1, 347—408).—I. A review.

II. The root of *Panax ginseng* is heated with 3 parts of water at 100° for 10 hrs. and filtered, the filtrate being used directly. After feeding for 4 weeks on millet and water or *Panax* extract, rats were starved, and death occurred in 10 or 12 days, according as they received water or extract. By morphine injections in rats receiving extract the appearance of curvature of the tail was postponed and that of convulsions and death hastened. The reverse takes place with strychnine. With curare no difference was observed between the rats receiving extract and the controls. Symptoms of irritability appear sooner in rats injected with cocaine.

III. 0.1% Picrotoxin, 1.0% caffeine, 50% camphor in olive oil, and 10% sodium salicylate produce, in suitable doses, a more rapid effect in rats receiving extract than in the controls.

IV. The effect of *Panax* extract is antagonistic to that of chloral hydrate, urethane, ethyl alcohol, and veronal.

P. G. MARSHALL.

**Poisonous principle of *Coriaria japonica*, A. Gray.** II. T. KARIYONE and T. SATO (J. Pharm. Soc. Japan, 1930, 50, 659—660).—Coriamyrtin and tutin possess similar chemical and physical properties and have the same physiological effect on animals.

CHEMICAL ABSTRACTS.

**Action of photodynamic substances on carbohydrate metabolism.** G. MONASTERIO (Arch. Farm. sperim., 1930, 51, 111—124).—Trypaflavine has greater toxicity for the dog than for the rabbit, both hyper- and hypo-glycaemia appearing in the dog when very small doses are administered; the action is attenuated by antiphotodynamic substances (resorcinol). No matter how or in what doses it is given, eosin causes no modification of the blood-sugar, but it exerts a marked influence on the reactivity of the rabbit to adrenaline, sugar, or insulin. Acridine-orange always produces hyperglycaemia, but the action is irregular. The blood-sugar is affected irregularly by acridine-yellow or acridine-red, slightly by "flavacid," and not at all by "rivanol."

T. H. POPE.

**Neutralisation of the toxicity of various poisons by thorium-X.** AVERSENQ, JALOUSTRE, and MAURIN (Compt. rend., 1930, 191, 734—736).—Prior injection of thorium-X into guinea-pigs before a fatal dose of sparteine sulphate causes survival; the toxic symptoms are also alleviated. The toxic actions of picrotoxin on fish and kephir, of potassium cyanide on fish, and of tetanus toxin on guinea-pigs are diminished by thorium-X.

H. BURTON.

**Pharmacology of the Hofmeister series.** O. EICHLER (Arch. exp. Path. Pharm., 1930, 154, 59—102).—The following responses occurring after administration of chloride, iodide, and thiocyanate anions by means of their sodium compounds were observed in frogs: toxicity, excretion following injection into the abdominal lymph sac, distribution of the anions under investigation in the main tissues of the body, ill-effects and distribution of lactic acid in the muscle. The data resulting from these observations are discussed on a mathematical basis with regard to a parallelism to the Hofmeister series.

F. O. HOWITT.

**Influence of colloidal silver on metabolism as shown by urinary constituents.** S. UEGAKI (Japan. J. Exp. Med., 1930, 8, 3—19).—Intravenous injection of colloidal silver into rabbits increases the urinary amino-acids and purine bases, particularly allantoin, and decreases the urea. The neutral sulphate is increased to a relatively greater extent than the total sulphate. The results indicate abnormal destruction of protein (especially of nucleoprotein), disturbance of liver function, and impairment of oxidative processes.

CHEMICAL ABSTRACTS.

**[Detection of] mercury oxycyanide poisoning.** A. SARTORI (Chem.-Ztg., 1930, 54, 813—814).—A *post-mortem* examination was made (2½ months after death) of the decomposed organs in a suspected case of poisoning by mercury oxycyanide: no cyanogen could be detected, but mercury was clearly indicated

by the Ludwig and Jannasch test (Chem.-Ztg., 1924, 48, 141).

E. LEWKOWITSCH.

**Action of certain carbohydrates on the toxicity of potassium cyanide.** P. MORETTI and G. MUSCOLINO (Arch. Farm. sperim., 1930, 51, 135—140).—Experiments with pigeons show that the toxic properties of potassium cyanide (1 g.) are annulled if the salt is incubated at 37° for 24 hrs. with a solution containing 15 g. of dextrose, galactose, laevulose, maltose, or lactose. Sucrose, gum, and dextrin produce no such effect, but starch has a slight action.

T. H. POPE.

**Pharmacology of "salyrgan." V. Behaviour of mercury in the organism after administration of salyrgan.** Salyrgan nephritis in rabbits. K. O. MÖLLER (Arch. exp. Path. Pharm., 1930, 154, 263—279).—After intravenous injection of salyrgan to dogs or rabbits, the mercury is rapidly excreted by the kidneys, about 40% in the first hour and 70—80% in the first 24 hrs. During the first hour the urine contains up to 90 mg. of mercury per 100 c.c. in the case of dogs and up to 370 mg. in the case of rabbits. A tubular nephritis is produced by salyrgan in rabbits with an acid as well as with an alkaline urine. During the first hour after administration to a dog only 3.5% of the mercury is excreted in the bile and 1% by the wall of the intestine; 3 days after the last administration to a dog only small quantities are found in the body, chiefly in the kidneys and liver.

W. O. KERMACK.

**Apparent multiplicity of respiratory enzymes.** R. P. COOK, J. B. S. HALDANE, and L. W. MAPSON (Naturwiss., 1930, 18, 848).—Lactic and succinic acids are almost completely oxidised by *Bacillus coli*, but after treatment with toluene a suspension of this organism converts them into pyruvic and fumaric acids, respectively. These two reactions have been studied at  $p_H$  7.5 in a Barcroft manometer at 17° in presence of different oxygen-carbon monoxide mixtures in order to determine the relative affinity of the respiratory enzymes for these gases. A similar experiment has been made with formic acid at  $p_H$  6.3. The mean values of  $K$  (the ratio of the affinities for oxygen and carbon monoxide) are 12.5 and 3.83 for lactic and formic acids, respectively; succinic acid gives the same value as formic. The enzyme-carbon monoxide compounds are almost insensitive to light. It appears that there are at least two respiratory enzymes, the one connected with lactic acid dehydrogenase, the other with formic acid dehydrogenase. Since the oxidation of formic acid is more easily arrested by hydrocyanic acid than is the oxidation of succinic acid, there are probably three different enzymes.

W. R. ANGUS.

**Thermolability of enzymes. I. Behaviour towards heat of extracts of peroxidase purified by ultrafiltration.** A. BACH and B. WILENSKY (Biochem. Z., 1930, 226, 482—488).—Extracts of peroxidase from horse-radish when freed as completely as possible from non-colloidal constituents by ultrafiltration are much more stable towards heat (100°) than are the original extracts. The purified extracts also, when they regain activity which is lost on heating, do so much more rapidly and to a greater extent

than do the others. The extent to which activity is regenerated decreases with the time of heating and reaches a maximum at 40% of the original activity within about 2 hrs. Regeneration of activity proceeds best at  $p_H$  6.8 and is only slightly influenced by the presence of salts. Purified extracts are completely and irreversibly inactivated by heating for 5 hrs. at 100°.

W. McCARTNEY.

**Biological oxidation-reduction potentials. System succinate-fumarate-succinodehydrogenase.** J. LEHMANN (Skand. Arch. Physiol., 1930, 58, 173—312; Chem. Zentr., 1930, i, 3195).—The preparation of succinodehydrogenase free from fumarase is described. The system on addition of methylene-blue or thionine gives definite electrode potentials; it does not do so in the absence of indicators. The values are independent of the nature of the indicator, the concentration of the constituents, and the noble metal used.

A. A. ELDRIDGE.

**Enzyme actions of larvæ of the silk-worm, *Bombyx mori*.** S. MATSUMURA (Bull. Sericult. Japan, 1930, 3, 10—15).—The diastatic activity of the digestive juice of the silk-worm fluctuates during growth, being feeble after the fourth moult and gradually becoming stronger until the full growth of the fifth stage is reached. The juice of the male is more active than that of the female. The activity is reduced when the health of the worm is impaired. European races of silk-worm show little or no amylase activity, whilst most of the Japanese monovoltine races exhibit it strongly. When the races are crossed, these two characters, weak diastase and strong diastase activity, behave as a simple Mendelian couple, the strong activity being dominant. Similar results were obtained with respect to the diastase activity of the body-fluid of the silk-worm. The catalase activity of the body fluid varies during growth and that of the male exceeds that of the female. The catalase activity of the body-fluid of various races shows interesting differences and the genetic behaviour has been investigated. Some experimental results are also given regarding the oxidase activity of the body-fluid.

W. O. KERMACK.

**Enzymic synthesis of higher dextrins.** S. NISHIMURA (Biochem. Z., 1930, 225, 264—266; cf. this vol., 1218).—The enzyme obtained from yeast causes polymerisation of achroodextrin. The polymeride resembles the substances derived from the degradation of starch by the action of amylase.

W. McCARTNEY.

**Synthesis of a hydrocarbon chain by means of enzymes. II. Carboligase.** A. STEPANOV and A. KUSIN (Ber., 1930, 63, [B], 2473—2476; cf. this vol., 957).—The precipitates obtained by the addition of alcohol and acetone or of alcohol to yeast maceration juice have little and no activity respectively in the synthesis of acetylmethylcarbinol from pyruvic acid. Ammonium sulphate gives minimal amounts of sufficiently active products. Adsorption with aluminium hydroxide if followed by rapid desiccation of the material in a vacuum gives in good yield a sufficiently active product which maintains its efficiency during 4 months. Formation of acetyl-

methylcarbinol from pyruvic acid can be detected at 0°, proceeds most readily at 25—35°, and ceases above 60°. Short preheating of the preparation greatly impairs its efficiency for synthesis, but no marked decrease of its carboxylase activity is observed below 50°. Chloroform almost completely inhibits carboligase action without greatly affecting carboxylase activity.

H. WREN.

**Carbamide formation in the animal body. I. Introduction.** S. SALASKIN. II. Carbamide formation in surviving organs and in their press-juice. S. SALASKIN and L. SOLOVIEV (Z. physiol. Chem., 1930, 192, 25—27, 28—44).—I. The general lines of projected experiments are indicated.

II. The whole of the carbamide formed in the autolysis of liver-pulp and probably of other organs is produced at the expense of the arginine-arginase system under ordinary conditions. Carbamide formation is rapid at first, but falls quickly. The decline is due either to a decrease in proteolysis or to greater difficulty in removing the residual arginine from the protein molecule.

J. H. BIRKINSHAW.

**Intermediary metabolism of histidine. II.** S. EDLBACHER and J. KRAUS (Z. physiol. Chem., 1930, 191, 225—242; cf. A., 1926, 1171).—Histidase, found only in liver extracts, has a  $p_H$  optimum at 8—9. It decomposes *l*-histidine into 1 mol. of formic acid, and 2 mols. of ammonia. It is partly purified by adsorption on aluminium hydroxide and kaolin followed by subsequent elution. Dialysis appears to induce a separation into components which are less active separately than combined. Histidase does not attack *d*-histidine, glyoxaline, iminazoly-lactic acid, iminazolyethylamine, or methylhistidine and probably neither carnosine nor histidine methyl ester.

J. H. BIRKINSHAW.

**Enzymic degradation of histidine.** F. KAUFFMANN and E. MISLOWITZER (Biochem. Z., 1930, 226, 325—337).—Experiments with livers from dogs, cats, rabbits, and guinea-pigs showed that there is no reason for supposing that the mechanism of the enzymic decomposition of histidine differs from that of other amino-acids, and the results of Edlbacher (A., 1926, 1171) could not be confirmed.

W. McCARTNEY.

**Hydrolysis of benzoyl derivatives of amino-acids by histozyme.** T. So (J. Biochem., Japan, 1930, 12, 107—131).—The benzoyl derivatives of monoamino-monocarboxylic acids are hydrolysed by the enzyme from pig's, dog's, or chicken's kidney, muscle, or liver. When a second amino-group is introduced the benzoyl derivative is attacked only by the kidney enzyme, but when a carboxyl group is introduced the benzoyl group is resistant to the action of the enzyme; a carboxylamido-group confers lability. Dibenzoyltyrosine is hydrolysed by the enzyme of pig's muscle, but not by that of the pig's kidney or the tissues of other animals.

CHEMICAL ABSTRACTS.

**Erepsin.** H. H. OELKERS (Biochem. Z., 1930, 226, 185—194).—Calcium and magnesium chlorides retard in a concentration of 0.003M and completely inhibit in 0.5M solution the hydrolysis of alanyl-glycine by intestinal erepsin at  $p_H$  7.8. Sodium fluoride (0.001—

0.1*M*) and ammonium thiocyanate (0.0008—0.021*M*) have no influence at  $p_H$  7.8. Addition of *l*-, *d*-, and *dl*-alanine and glycine considerably decreases the velocity of hydrolysis. P. W. CLUTTERBUCK.

**Nature of proteases. VI. Relation between buffering capacity and power of digestion of various pepsin preparations.** A. N. ADOVA and J. A. SMORODINCEV (Z. physiol. Chem., 1930, 191, 193—199; cf. this vol., 1065).—The hydrolytic activity of various pepsin preparations ran parallel with their buffering capacity. J. H. BIRKINSHAW.

**Method of titrating proteolytic enzymes.** F. L. GATES (Science, 1930, 72, 147—148).—The relative densities of a photographic film before and after exposure to the enzyme solution are read against a suspension of the same gelatin-silver emulsion in a Duboscq colorimeter or by means of a photometer.

L. S. THEOBALD.

**Determination of the action of pepsin.** M. MATSUYAMA and H. NAKAMURA (Bull. Agric. Chem. Soc. Japan, 1928, 4, 116—122).—For dilute solutions  $k=x/t^{\frac{1}{2}}$ , and for larger quantities of enzyme  $k=x/t^{\frac{1}{3}}$ , where  $k$  is the reaction constant,  $x$  the quantity of protein (egg-white) digested, and  $t$  the reaction time. The pepsin action,  $E/g.$  of preparation, has values of  $E$  as follows: 1 hr.,  $(100k/1.9724)^2$ ; 2—3 hrs.,  $(100k/2.5351)^{100/38}$ . CHEMICAL ABSTRACTS.

**Enzymic hydrolysis of lecithin.** H. KING, E. J. KING, and I. H. PAGE (Z. physiol. Chem., 1930, 191, 243—250).—Lecithin is hydrolysed by various tissue extracts with liberation of phosphoric acid at a  $p_H$  optimum of 7.4—7.6. The extent of the hydrolysis is greatly affected by the concentrations both of enzyme and substrate. Bone and liver extracts have little, kidney and intestinal extracts considerable, hydrolytic power. J. H. BIRKINSHAW.

**Extent of fermentation and the oxidation quotient of yeast.** O. MEYERHOF and K. IWASAKI (Biochem. Z., 1930, 226, 16—31).—The effect of Euler's "Z" factor on the fermentation of living yeast in nitrogen and oxygen is investigated. Optimal concentrations cause an increase of anaërobic fermentation with *S. Ludwigii* of 100—200% and with pressed yeast of 100%. Its effect is still noticeable when diluted 1000 times. The oxidation quotient of the fermentation is simultaneously increased, but the amount of respiration remains the same. The action increases with rise of temperature, is scarcely detectable at 10°, and is independent of the sugar concentration.

P. W. CLUTTERBUCK.

**Yeast fermentation. Validity of the Arndt-Schulz rule.** H. DANNENBERG (Arch. exp. Path. Pharm., 1930, 154, 211—221).—The presence of small quantities of quinine hydrochloride (up to 1/400), phenol (up to 1/1000), or mercuric chloride (up to 1/100,000) had no favourable action on the growth of yeast. The experiments fail to confirm the Arndt-Schulz rule according to which toxic substances in small concentration stimulate cell activity.

W. O. KERMACK.

**Influence of catalytic elements on alcoholic fermentation. II.** M. ROSENBLATT and A. MARCH (Biochem. Z., 1930, 226, 404—414; cf. A., 1926,

641).—The influences of nickel, cobalt, and iron on alcoholic fermentation in the presence of yeast and of a nutrient medium resemble that of manganese, all the metals at low concentrations having a stimulating effect. Higher concentrations, especially of nickel and cobalt, have an inhibitory effect and there are very great differences between the metals as regards the concentrations at which the effect is first observed, especially since this is also dependent on the origin of the yeast used. With respect to inhibitory action the metals may be arranged in the descending series, nickel, cobalt, iron, manganese. When any two of the metals manganese, cobalt, nickel are present simultaneously they act independently. When no nutrient medium is present the stimulating effect is never observed, the concentrations of metal in the presence of which fermentation can still proceed are much greater, and the metals, with respect to their inhibitory effect, now form the descending series, nickel, iron, cobalt and manganese (equal), nickel being much more toxic than cobalt and ferric iron much more toxic than ferrous. The results are analogous to those obtained in the examination of the influence of metals on acetic fermentation (cf. A., 1929, 1108). W. MCCARTNEY.

**Acidity optimum of yeast hexosediphosphatase.** Z. I. KERTESZ (J. Amer. Chem. Soc., 1930, 52, 4117—4119).—The maximum amount of inorganic phosphate liberated when dry bottom yeast (1.5 g.) acts on a mixture of an aqueous 4% solution of sodium hexosediphosphate (2.5 c.c.), water (2.5 c.c.), and (citric acid) buffer solution (5.0 c.c.) is at  $p_H$  6.5.

H. BURTON.

**Metabolic effects of mitogenetic irradiation.** H. GESENIUS (Biochem. Z., 1930, 225, 358—367; cf. A., 1929, 1340).—The metabolism of *Saccharomyces ellipsoideus* after exposure to mitogenetic radiation from yeast cultures and from blood has been examined by Warburg's methods and it has been found that the irradiation affects the fermentative and respiratory processes of the cells and leads to a deficit in the amount of energy liberated. The fermentative power of yeast maceration juice is restricted as a consequence of the irradiation. W. MCCARTNEY.

**Hydrogen-ion concentration in the interior of the cells of *Fusarium lini*, B., and of yeast.** S. MAHDIHASSON (Biochem. Z., 1930, 226, 202—208).—The  $p_H$  of the interior of cells of a top yeast and of *F. lini*, B., are shown by the micro-injection method to be 5.9—6 and 6—6.1, respectively, corresponding with the  $p_H$  of optimal enzymic activity (6.0). P. W. CLUTTERBUCK.

**Action of certain moulds on solutions of aldoses. I.** A. ANGELETTI and C. F. CERRUTI (Annali Chim. Appl., 1930, 20, 424—433).—Although the yield of *d*-gluconic acid formed by *Penicillium luteum purpurogenum*, st. 2 A. 3, may exceed 60% of the amount of sugar present, the yields obtained with *P. luteum*, Wehmer, and *P. purpurogenum* (Fléoroff), Stoll, grown in solutions containing dextrose and inorganic salts are only 15.5 and 1.21%, respectively, after 20 days; no other acid was found. *d*-Mannose solutions inoculated with the *P. luteum* and the *P.*



*purpurogenum* developed a slight acidity during 20 days, but no *d*-mannonic acid could be separated. With the *P. luteum purpurogenum*, however, the yield of *d*-mannonic acid reached 9.35% (on the sugar) in 20 days, no other acid being detected. No acid product was obtained from *d*-galactose by the action of any one of the three organisms. T. H. POPE.

**Synthetic nutrient solutions for *Ustilago zeae*.** E. R. RANKER (J. Agric. Res., 1930, 41, 435—443).—The organism causing smut in maize may be grown in a solution containing 0.3 g. of potassium sulphate, 0.1 g. each of ammonium nitrate, calcium chloride, and magnesium phosphate, and 10 g. of dextrose per litre of solution, which needs no adjustment for reaction. The addition of 1.5% of agar gives a satisfactory solid medium. E. HOLMES.

**Respiratory catalysts of the disease-producing bacteria.** A. LOCKE and E. R. MAIN (J. Infect. Dis., 1930, 46, 393—404).—Copper appears to be a necessary constituent of cells and tissues accustomed to survive periods of oxygen hunger. The production of diphtheria toxin can be partly inhibited by reduction of the proportion of ionic copper in the culture medium. It is suggested that bacterial toxins may owe their poisonous properties to the presence of a substance containing copper.

#### CHEMICAL ABSTRACTS.

**Chemistry of bacteria and the development of a practical technique for the chemical analysis of cells.** T. B. JOHNSON (Coll. Symp. Ann., 1929, 7, 223—232).—An outline of recent work on tuberculosis.

#### CHEMICAL ABSTRACTS.

**Comparative colorimetric determination of  $p_{\text{H}}$  in [bacteriological] media.** E. REMY (Zentr. Bakt. Par., 1930, I, 115, 391—395; Chem. Zentr., 1930, i, 2931).—Determinations with two-colour indicators gave results in good agreement with those made electrometrically. The accuracy of the Bjerrum-Arrhenius and Hellige universal colorimeters was  $\pm 0.025$ , and of the Hellige comparator 0.05.

A. A. ELDRIDGE.

**Do bacteria contain sterols?** H. VON BEHRING (Z. physiol. Chem., 1930, 192, 112—113).—No trace of sterol was found in cultures of *B. coli* and of the diphtheria bacillus when grown on peptone agar.

J. H. BIRKINSHAW.

**Pyruvic acid in bacterial metabolism: detection and determination of pyruvic acid.** R. P. COOK (Biochem. J., 1930, 24, 1526—1537).—Pyruvic acid is produced in the aerobic oxidation by *B. coli* of various substrates. It is not decarboxylated by the organism and is broken down to a mixture of formic and acetic acids.

S. S. ZILVA.

**Comparison of dehydrogenations produced by *B. coli communis* in presence of oxygen and methylene-blue.** R. P. COOK (Biochem. J., 1930, 24, 1538—1550).—In toluene-treated organisms the oxygen-activating mechanism is not affected by the treatment, nor are the oxidations which are due to the formic, lactic, and succinic dehydrogenases. The secondary oxidative processes are, however, eliminated by toluene treatment. The velocities of oxidation by methylene-blue and oxygen for lower temperatures

in the case of formate and lactate are nearly equal. Above a certain temperature the velocity of oxygen reduction does not increase. In the dehydrogenation of succinate there is a considerable difference between the velocities of oxidation by oxygen and methylene-blue. There is a competitive action of oxalate and malonate for the lactic and succinic dehydrogenase mechanisms respectively for the oxygen acceptor system. S. S. ZILVA.

**Growth of anaerobes in bile media containing malachite-green and brilliant-green.** C. F. POE and N. F. WITT (J. Amer. Water Works' Assoc., 1930, 22, 1365—1373).—A concentration of these dyes greater than 1:100,000 is ample to inhibit the growth of most anaerobes in lactose broth. *B. welchii* type II, however, required at least 1:20,000 to prevent gas formation. The inhibitive power of dyes in lactose broth decreases as the percentage of bile increases. A dye concentration of 1:20,000 in the case of brilliant-green and 1:30,000 in the case of malachite-green is sufficient to inhibit the growth of most anaerobes in a 5% bile medium. C. JEPSON.

**Arbutase content of *B. mycoides*.** H. GLINKA-TSCHERNORUTZKY (Biochem. Z., 1930, 226, 62—66).—*B. mycoides* sown on a medium containing arbutin hydrolyses it to quinol and dextrose. Arbutase cannot be separated from the bacterial cells by the methods usually employed for intracellular enzymes. P. W. CLUTTERBUCK.

**Gluconic acid fermentation. I. *Bacterium hoshigaki* var. *rosea*. II. Production of  $\alpha$ -ketogluconic acid. III. *B. induratum* var. *hoshigaki*.** T. TAKAHASHI and Y. ASAI (J. Agric. Chem. Soc. Japan, 1930, 6, 223—241, 407—412, 526—537).—I. The organism isolated from dried persimmon forms a red pigment; three others are also new.

II. The acid is produced by three varieties mentioned from dextrose.

III. One species was particularly active in the productive of gluconic acid from dextrose.

CHEMICAL ABSTRACTS.

**Acetone fermentation. *Bacillus maceiras*.** J. P. ZACHAROV (Zentr. Bakt. Par., 1930, II, 80, 205—218; Chem. Zentr., 1930, i, 2910).—A morphological and physiological study. Pure cultures produce no butyl alcohol. The cell walls of yeast and potato are attacked or dissolved. The formation of acetone is an anaerobic process, acetaldehyde being formed intermediately. A. A. ELDRIDGE.

**Nitrogen circulation. II. Proteolytic power of micro-organisms.** A. JANKE and H. HOLZER (Biochem. Z., 1930, 226, 243—249; cf. A., 1929, 1493).—The distinction between liquefiers and non-liquefiers previously observed is found to hold also for the following organisms: *B. prodigiosum*, Ehrenberg, *Streptococcus lactis* (Lister), Löhnis, *Saccharomyces cerevisiae*, Hansen, distiller's yeast, strain XII, *Willia anomala*, Hansen, *Klaeckera apiculata* (Hansen), Janke, *Mycoderma vini*, Desmazières, *Aspergillus niger*, van Tieghem, *Fusarium*, E 13 Holzer-Janke. It seems that the same enzyme acts in both cases: as an exoenzyme, and hence always, in the case of the liquefiers, and as an endoenzyme, and hence only

after the cell walls are damaged, in that of the non-liquefiers.

W. MCCARTNEY.

**Fixation of nitrogen by bacteria.** K. IWASAKI (Biochem. Z., 1930, 226, 32—46).—Increased respiration of cultures of *Azotobacter chroococcum* (Lingby) in air always corresponds with a division of the bacteria, whilst nitrogen fixation without division proceeds with constant respiration. At low tensions of oxygen, division is inhibited and nitrogen fixation favoured. In presence of humin substances the rate of growth and increase of respiration are greatly augmented. The action has an induction period of several hours and is independent of the humin concentrations, but its duration is proportional to the humin content. Humin is concerned with the assimilation and not the fixation of nitrogen.

P. W. CLUTTERBUCK.

**Denitrification in inorganic media.** M. V. TIULPANOVA-MOSEVICH (Ark. biol. nauk, 1930, 30, 203—214).—Denitrification by *Thiobacterium denitrificans* is normal in inorganic media comprising sulphur, nitrates, and carbonates or organic sources of carbon. The organism is a facultative anaërobe. During denitrification the reaction of the medium becomes alkaline. The sulphur is oxidised to sulphate.

CHEMICAL ABSTRACTS.

**Oxidation of sulphur and thiosulphate by thionic acid bacteria.** I. P. LANGE-POZDEEVA (Ark. biol. nauk, 1930, 30, 189—201).—Thiosulphate is oxidised by *Thiobacterium Beijerinckii* more readily than sulphur; the process is arrested when  $p_H$  5.2—5.7 is reached. Three types of oxidation are differentiated: (a) by *T. thio-oxidans*, in acid solution, when the oxidation of sulphur predominates, (b) by Trautwein strains, in alkaline medium, when thiosulphate is abundantly oxidised without production of sulphur, and (c) by *T. Beijerinckii*, Saslavsky strain, and *T. thioparus*, in alkaline medium, when thiosulphate is oxidised more readily than sulphur and always with the production of free sulphur. The final products are chiefly sulphates.

CHEMICAL ABSTRACTS.

**Effect of salts on obligate halophilic thionic acid bacteria.** A. SASLAVSKY and N. HARZSTEIN (Zentr. Bakt. Par., 1930, II, 80, 165—169; Chem. Zentr., 1930, i, 2910).—The effect of sodium chloride is partly specific and partly due to an increase in the osmotic pressure.

A. A. ELDRIDGE.

**Carbohydrate fermentation, nitrogen metabolism, and catalase production by variants of *B. anthracis*.** W. J. NUNGESTER (J. Infect. Dis., 1929, 45, 214—224).—Quantitative differences were observed for various strains in respect of proteolytic activity and ability to decompose hydrogen peroxide.

CHEMICAL ABSTRACTS.

**Metabolism of the *Brucella* group in synthetic media.** C. E. ZOBELL and K. F. MEYER (Science, 1930, 72, 176).—Cystine is an essential nitrogen source, whilst asparagine in combination with cystine enhances multiplication. Sodium or ammonium citrate is a suitable source of carbon and cultures of recently isolated strains can be obtained provided that sodium carbonate and potassium dihydrogen phosphate are mixed to give  $p_H$  7.0. Iron (20 parts per million) has a stimulating effect and glycerol

(2%) enhances growth in all types of *Brucella*. The addition of well-washed agar (0.2%) accelerates multiplication, but larger amounts diminish growth until at 1.5% of agar it is completely inhibited.

L. S. THEOBALD.

**Utilisation metabolism of proteus bacilli.** M. SELIGMANN (Z. Bakt. Par., 1930, I, 115, 346—358; Chem. Zentr., 1930, i, 2909).—Ammonium chloride can function as the sole source of nitrogen for *B. proteus anindologenes* and *indologenes*; propionic, lactic, malic, succinic, or citric acids, alcohol, glycerol, mannitol, arabinose, dextrose, lævulose, sucrose, lactose, or maltose may act as a source of carbon, whilst alanine, leucine, or sodium aspartate can act as a source of carbon and nitrogen. *B. vulgare anindolicum* can assimilate maltose and sucrose.

A. A. ELDRIDGE.

**Influence of the composition of the medium on the biological properties of micro-organisms.** N. A. DMITREVSKEYA and M. F. CHEBOTAREVICH (Arch. biol. nauk, 1930, 30, 215—224).—A study of the effects of the addition of sugars on the behaviour of various types of *B. typhi*.

CHEMICAL ABSTRACTS.

**Hydrolysis of sodium hippurate.** I. GILBERT and M. FROBISHER, jun. (Bull. Johns Hopkins Hosp., 1930, 47, 55—60).—Gram-negative, aerobic, non-spore-forming rods (except *B. aërogenes* and *B. bronchisepticus*), and anaërobes, have no action on sodium hippurate, which is hydrolysed by staphylococci.

CHEMICAL ABSTRACTS.

**Type-specific substance distinct from the specific carbohydrate in pneumococcus type I.** J. F. ENDERS (J. Exp. Med., 1930, 52, 235—252).—The substance, which resists peptic digestion, may be a haptene.

CHEMICAL ABSTRACTS.

**Specific action of a bacterial enzyme on pneumococcus type III.** O. T. AVERY and R. DUBOS (Science, 1930, 72, 151—152).—A soluble principle which is able to decompose the specific capsular polysaccharide of pneumococcus type III has been extracted from a bacillus isolated from the soil of the cranberry bogs of New Jersey. The rate and amount of decomposition appear to be quantitatively related to the concentration of the specific active principle which is destroyed at 60—65°. The active principle has specific protective, prophylactic, and curative effects on mice infected with pneumococcus type III.

L. S. THEOBALD.

**Oxidation-reduction potentials of pneumococcus cultures.** I. L. F. HEWITT (Biochem. J., 1930, 24, 1551—1556).—The oxidation-reduction potential-time curves are similar to those obtained with hæmolytic streptococci, but differ from those obtained with diphtheria bacilli and staphylococci. Peroxide is formed readily by pneumococci which are not able easily to maintain intense reducing conditions in the presence of an abundant oxygen supply. The general effect of different culture media has been studied.

S. S. ZILVA.

**Specific effect of bile salts on pneumococci and on pneumococcus pneumonia.** E. E. ZIEGLER (Arch. Int. Med., 1930, 46, 644—656).—The lysis of

pneumococci by bile salts, which can take place in dilutions as low as 1:25,000, occurs in presence of serum, but at a much slower rate and is five times as fast as the corresponding hæmolysis. Pneumococci exposed to human serum are unchanged in their lysis by bile salts, which also do not interfere with the agglutinin action of specific sera on the cocci.

F. O. HOWITT.

**Methylic antigen [of tubercle bacilli].** L. NÈGRE and A. BOQUET (Ann. Inst. Pasteur, 1930, 45, 415—432).—Antigen, prepared by a preliminary extraction of the fatty envelopes of tubercle bacilli by acetone and ether followed by extraction with methyl alcohol, exerts a satisfactory action in experimental tuberculosis.

F. O. HOWITT.

**Decomposition of fat by tubercle bacilli.** A. SEDYKH (Ark. biol. nauk, 1930, 30, 71—81).—Human tubercle bacilli utilise animal and vegetable fats, lanolin, beeswax, and spermaceti. The utilisation is accompanied by partial fission and by saturation of unsaturated acids. CHEMICAL ABSTRACTS.

**Changes in blood-dextrose and -inorganic phosphates after intravenous injection of paratyphoid-B filtrate into depancreatized dogs.** M. L. MENTEN and H. A. KIPP (J. Infect. Dis., 1930, 46, 267—274).—Normal dogs show a temporary rise in blood-sugar and -inorganic phosphate; with large doses fatal hypoglycæmia follows. In depancreatized dogs the rise in blood-phosphate is accompanied by early hypoglycæmia.

CHEMICAL ABSTRACTS.

**Toxin produced by *B. paratyphosus-B* (Aertrycke type).** M. L. MENTEN and C. G. KING (J. Infect. Dis., 1930, 46, 275—278).—The toxic fraction, precipitated by acetic acid, contained no phosphorus or sulphur; on hydrolysis it afforded a carbohydrate. The fraction precipitated by ammonium sulphate had no hyperglycæmic action.

CHEMICAL ABSTRACTS.

**Toxin of the gas-gangrene bacillus. I.** A. EBEL (Biochem. Z., 1930, 225, 336—343).—Methods of obtaining highly active preparations of the toxin of *B. phlegm. emphy.*, Fränkel, are described. The substance is dialysable and soluble in alcohol and can be precipitated by mercury salts or by phosphotungstic acid, but not by lead salts. It loses its activity when treated with dilute acid.

W. MCCARTNEY.

**Purification and concentration of scarlet-fever toxin.** L. E. SHINN (J. Infect. Dis., 1930, 46, 76—83).—Alcohol and acetic acid are employed for precipitation and concentration, and susceptible human skin for standardisation.

CHEMICAL ABSTRACTS.

**Effect of short electric waves on diphtheria toxin independent of the heat factor.** R. R. MELLON, W. T. SZYMANOWSKI, and R. A. HICKS (Science, 1930, 72, 174—175).—Diphtheria toxin is attenuated by exposure to waves of 1.9 m. and  $158 \times 10^6$  cycles per sec., but negative results were obtained in attempts to sterilise milk or to destroy bacteria.

L. S. THEOBALD.

**Hormone of the adrenal cortex.** F. A. HARTMAN and K. A. BROWNELL (Science, 1930, 72, 76).—A concentrated extract of the hormone, cortin, is best

prepared by extracting the cortex with ether, distilling the ether in a vacuum, extracting the residue with 80% alcohol, distilling the alcohol, and dissolving the residue in water.

L. S. THEOBALD.

**Origin of adrenaline.** J. E. ABELOUS and R. ARGAUD (Compt. rend. Soc. Biol., 1930, 103, 129—130; Chem. Zentr., 1930, i, 1956).—Adrenaline is formed in the cortex, and not in the medulla, of the adrenals.

A. A. ELDRIDGE.

**Determination of adrenaline in the blood.** A. M. PETRUNKIN and M. L. PETRUNKIN (Ark. biol. nauk, 1930, 30, 225—230).—The proteins are removed from oxalated blood with hydrochloric acid and ammonium sulphate; iodine is added to the filtrate and the excess titrated after 75 min. with thiosulphate, the residual pink colour being used (after intensification by addition of potassium cyanide) for the colorimetric determination. CHEMICAL ABSTRACTS.

**Antagonism of adrenaline and insulin on the regulation of blood-sugar in adrenalectomised dogs.** F. MEYTHALER and R. CARIO (Arch. exp. Path. Pharm., 1930, 154, 193—202).—When dextrose is injected into the pancreaticoduodenal artery of an adrenalectomised dog there is an immediate fall of the blood-sugar just as in the case of a normal animal, whilst if the injection is into a peripheral artery a marked rise in blood-sugar occurs for a short period. This supports the view that dextrose itself is the hormone which activates the outflow of insulin from the pancreas. Injection of adrenaline into the pancreaticoduodenal artery of an adrenalectomised dog produced no definite fall in blood-sugar.

W. O. KERMACK.

**Liver-sugar. I. Action of adrenaline and insulin on the liberation of sugar by the liver and its glycogen content.** H. MOLITOR and L. POLLAK (Arch. exp. Path. Pharm., 1930, 154, 280—300).—Experiments on anaesthetised rabbits and dogs in which the liver had been made accessible by previous operation show that the administration of adrenaline caused an increased liberation of sugar from the liver and a decrease in liver-glycogen. After injection of insulin inhibition of liberation of sugar by the liver is demonstrable within 10 min. The carbohydrate content of the liver remains constant or decreases, the decrease being apparently due to consumption in liver metabolism.

W. O. KERMACK.

**Variation of agglutination titre caused by insulin. I, II.** M. NOZAKI (Keijo J. Med., 1930, 1, 248—277, 278—287).—When rabbits, immunised with typhoid bacilli, are injected with insulin, a rise in the agglutination titre occurs, although no such rise occurs on the addition of insulin to immunised serum *in vitro*. This rise is dependent on the functioning of the reticulo-endothelial system and the presence of the thymus and suprarenal glands, but is unaffected by extirpation of the thyroid, parathyroid, pancreas, and ovary. Removal of the testes causes a fall in the agglutination titre. The increase of titre caused by pilocarpine is not dependent on any of the organs producing internal secretions. Transplantation of a thymus in a rabbit, in which the rise in titre due to

insulin had been abolished by extirpation of this gland, causes a reappearance of the rise. Similarly, transplantation of testis negatives the results of orchidectomy. It is not certain whether the parenchymal or interstitial cells are responsible for the lowering of agglutination titre. P. G. MARSHALL.

**Circulatory hormone. VI. Inactivation of callicrein.** H. KRAUT, E. K. FREY, and E. WERLE (*Z. physiol. Chem.*, 1930, **192**, 1—21; cf. this vol., 1069).—The inactivator of callicrein is present in extracts of the lymph glands, salivary glands, spleen, liver, and spinal chord of cattle, of the spleen of sheep and goats, and in human lymph. Certain differences between the action of organ extracts and that of blood are due to the presence of interfering substances in serum; the organ preparations contain the inactivator in a much purer state, and the inactivating power can be further increased by alcohol precipitation. Inactivation is at a maximum at  $p_H$  8—11; below  $p_H$  5 there is no appreciable action, and thus acidification reactivates inactivated callicrein. The inactivation is a time reaction, the velocity depending on the quantity of inactivator present. Equilibrium at the  $p_H$  optimum is in favour of the inactivated complex, but even with a large excess of inactivator a small amount of free callicrein is present. The inactivator is destroyed by kinase-free trypsin and is thus a polypeptide. J. H. BIRKINSHAW.

**Detoxicating hormone ["yakriton"] of the liver. XVI. Prophylactic effect of yakriton against ammonium carbonate convulsions.** H. MORISHATA. **XVII. Prophylactic effect of yakriton against phenol intoxication.** YASADA and A. SATO. **XVIII. Prophylactic effect of yakriton against subacute phosphorus poisoning.** K. ASAKURA and T. SATO. **XIX. Standardisation of yakriton.** A. SATO (*Tohoku J. Exp. Med.*, 1930, **14**, 167—175, 176—179, 180—186, 195—197).

#### CHEMICAL ABSTRACTS.

**Differentiation of thyroxine-iodine from inorganic iodine by membranes of the living organism.** W. LIPSCHITZ (*Klin. Woch.*, 1930, **9**, 642—644; *Chem. Zentr.*, 1930, **i**, 3204).—Fractionation by gland membranes of the blood-iodine takes place, the thyroxine being retained. Determination of the iodine in blood and in the gastric or parotid juice indicates the distribution of the iodine in blood.

A. A. ELDRIDGE.

**Influence of parenteral injection of cell substance of thyroid gland on blood-fat and -lipins. I. Cholesterol. II. Total fatty acid and lecithin.** S. SAKURAI (*Japan. J. Exp. Med.*, 1929, **7**, 449—464, 465—480).—The injection of the cell emulsion of the thyroid gland causes hyperfunction of the thyroid and a decrease in blood-cholesterol, although frequent injections result in the reverse effect. Parallel results were obtained for total fatty acid and lecithin.

#### CHEMICAL ABSTRACTS.

**Distribution of bromine in the organism. II. Action of thyroid and pituitary on distribution of bromine.** M. A. B. TOXOPÉUS (*Arch. exp. Path. Pharm.*, 1930, **154**, 247—253).—Extirpation of the thyroid from a dog or the administration of thyroid

gland or of the extract of the posterior lobe of the pituitary influences the distribution of bromine in the body after administration of potassium or sodium bromide by mouth. After administration of thyroid gland, the bromine accumulates in the skin and is scarcer in the muscle, whilst the blood and lungs, and less definitely the bones, are also enriched. In the thyroidectomised animals there is also a high skin and low muscle content of bromine, whilst the opposite occurs in the animals treated with pituitrin.

W. O. KERMACK.

**Effect of parathyroid extract on blood-phosphatase.** I. H. PAGE and M. RESIDE (*Biochem. Z.*, 1930, **226**, 273—277).—The activity of the phosphatase of the serum of dogs' blood is increased by administration of over-doses of parathyroid extract.

W. MCCARTNEY.

**Parathyroid hormone and calcium metabolism.** M. INABA (*J. Biochem.*, Japan, 1930, **12**, 35—58).—Subcutaneous, but not oral, administration of parathyroid hormone to rabbits causes hypercalcaemia. Intravenous injection of the hormone raises the blood-phosphorus. Of the substances tested only atropine and "pituglandol" increased the blood-calcium and -phosphorus.

#### CHEMICAL ABSTRACTS.

**Active substance in the follicular fluid of the ovary.** K. HIRANO (*Japan. J. Exp. Med.*, 1930, **8**, 21—38).—The active substance, which contains nitrogen, is soluble in water and in fat solvents and is adsorbed by fatty acids. It is not a fatty acid, lipin, amino-acid, primary amine, or purine base.

#### CHEMICAL ABSTRACTS.

**Preparation and properties of the gonad-stimulating hormone from urine of pregnancy.** F. DICKENS (*Biochem. J.*, 1930, **24**, 1507—1525).—The hormone is precipitated without loss of activity from aqueous solution by complete saturation with ammonium sulphate, by alcohol or acetone, by colloidal ferric hydroxide or tannic acid, but not by trichloroacetic, sulphosalicylic, or picric acid. Aqueous solutions containing up to 1000 mouse units per c.c. have been prepared and the injection of 0.02—0.006 mg. of the material produced the characteristic changes. The hormone passes only very slowly through parchment, but more rapidly through collodion. It is inactivated by boiling and by the action of acids or alkalis. It is not rapidly destroyed by trypsin or pepsin, although prolonged treatment causes inactivation. Concentrated solutions give a faint but definite biuret reaction; Millon's, glyoxylic acid, and Molisch's tests are positive. Injection of the hormone into immature mice and rats leads to precocious sexual maturity. In the female the formation of corpora lutea and of hæmorrhagic follicles in the ovary is observed and in the male great enlargement of the seminal vesicles. It is active by mouth when administered in high doses. The hormone is without action on castrated animals and on the growth rate of normal rats. Injection over a long period does not cause any appreciable change in the blood-cholesterol or -urea contents.

S. S. ZILVA.

**Relation of carotene content to the vitamin-A activity of different plant materials.** H. VON

EULER, V. DEMOLE, P. KARRER, and O. WALKER (Helv. Chim. Acta, 1930, 13, 1078—1083).—The carotene and xanthophyll contents of the ether-soluble unsaponifiable matter of the extractives of the dry leaves of spinach, beech (*Fagus sylvatica*), *Lolium perenne* (mixed with other grasses), lettuce (*Lactuca sativa*), nettle (*Urtica dioica*), the flowers of *Caltha palustris*, and maize grain have been determined; they vary from 1.9 to 22.8 mg. and 2.3 to 41.2 mg. per g. of extract, respectively. The vitamin-A activity of the unsaponifiable matter runs parallel to the carotene content. Lycopene, physaliene, and phaeophytin have no vitamin-A activity.

H. BURTON.

**Vitamin-A and carotene.** N. S. CAPPER (Nature, 1930, 126, 685).—Carotene functions as a precursor of vitamin-A in fowls.

L. S. THEOBALD.

**Derangement of resorption due to lack of vitamin-B.** G. GÁL (Biochem. Z., 1930, 225, 286—294).—In rats suffering from lack of vitamin-B the resorption of dextrose is reduced to one third, that of protein to one half, of the corresponding resorption in healthy rats. Resorption can be restored to normal by administration of the vitamin.

W. MCCARTNEY.

**Irradiated ergosterol and calcium-free diet: effect on calcium and phosphorus metabolism.** E. WATCHORN (Biochem. J., 1930, 24, 1560—1563).—Calcium and phosphorus retention in rats on Steenbock's rachitogenic diet is decreased by excessive doses of irradiated ergosterol. Both the urinary and the faecal phosphorus are increased. The faecal phosphorus but not the calcium is also increased in comparison with the intake. On a similar basal diet but calcium-free and richer in phosphorus irradiated ergosterol does not affect the phosphorus metabolism, but causes elimination of calcium by the kidney.

S. S. ZILVA.

**Experimental rickets. III. Isolation of ergosterol from brewer's yeast and activation of ergosterol by means of ultra-violet light.** S. IZUME, Y. YOSHIMARU, and I. KOMATSUBARA (Rept. Lab. S. Manchuria Rly., 1929, 18—21).—Yeast-fat was prepared from dried brewer's yeast by extraction with hot alcohol followed by ether. Lecithin and phosphatides were removed by adding an excess of acetone, and after filtration the solution was evaporated and the residue saponified with potassium hydroxide. Unsaponifiable matter was removed by Takahashi's method (cf. J. Chem. Soc. Japan, 1922, 43, 828) and the crude ergosterol purified by acetylation and hydrolysis. The material had m. p. 160—161°. Yeast-fat had no antirachitic potency, but it was rendered highly active by ultra-violet irradiation. The product of highest activity exhibited an absorption band of maximum intensity in the region 247.2  $m\mu$  (cf. Morton and others, A., 1927, 948). The band 311—260  $m\mu$  is the most efficient in the activation of ergosterol.

H. J. DOWDEN.

**Vitamins and refining of olive oil.** L. MARGAILAN (Compt. rend., 1930, 191, 725—727).—Rats fed on a diet supplemented by crude olive oil show better growth than those supplied with the refined oil. The

absence of vitamins in olive oil is due to the refining process.

H. BURTON.

**Permeability of cells of *Tradescantia virginica* and of *Allium cepa*.** R. BOUILLENNE (Bull. Acad. roy. Belg., 1930, [v], 16, 1027—1047).—The plasmolysis of cells of *Tradescantia virginica* and *Allium cepa* by potassium nitrate, potassium chloride, sodium chloride, and ammonium chloride, in solutions of  $pH$  7 and concentrations 0.13—1.0N, has been investigated, also the velocity of penetration by ammonium salts of fatty acids.

C. W. GIBBY.

**Osmosis in vegetable cells. Apparatus for measuring the speed of penetration of salt solutions into vegetable protoplasm.** R. BOUILLENNE (Bull. Acad. roy. Belg., 1930, [v], 16, 1017—1026).—An apparatus for the optical projection of the movement of cells during deplasmolysis is described.

C. W. GIBBY.

**Daily course of photosynthesis with plants of Central Asia.** C. P. KOSTYTSHEV and E. K. KARDOSYOEVA (Bull. Acad. Sci. U.S.S.R., 1930, 467—498).—Measurements of photosynthesis, both during short exposures and for the whole day, in Central Asia give results higher than any previously noted. Cultivated plants in wet regions work fairly regularly throughout the whole of the day, very large quantities of organic matter being accumulated; particularly high yields are obtained with grasses. Xerophytes show very wide variations in the daily course of photosynthesis, the yield being sometimes very high and sometimes quite low. Owing to the minimal leaf-surface development, the formation of organic substance for the whole plant is less than for cultivated plants in wet districts. Plants of the Karakumska sandy desert exhibit varying behaviour as regards photosynthesis, all of them, with the exception of *Aristida pennata*, liberating considerable quantities of carbon dioxide during the afternoon.

T. H. POPE.

**Influence of atmospheric fertilising on plants.** E. N. BAZYRINA and V. A. TSCHESNOKOV (Bull. Acad. Sci. U.S.S.R., 1930, 513—524).—Atmospheric fertilisation directly increases the daily output of photosynthesis, but no proportionality exists between the concentration of the carbon dioxide and the energy of photosynthesis. The mechanism of the action of atmospheric fertilisation on the daily photosynthetic production may vary. Thus, with the onion, the percentage increase of this production is the greater the more intensely the plant works under normal conditions. With beans, however, increase in the content of carbon dioxide in the air merely supplements the insufficiency in the amount of assimilated matter, its action being the more pronounced when the plant works the more feebly under natural conditions.

T. H. POPE.

**Evacuation of assimilated material from leaves.** V. A. TSCHESNOKOV and E. N. BAZYRINA (Bull. Acad. Sci. U.S.S.R., 1930, 499—511).—Evacuation of photosynthetic products by leaves is sometimes not observed during the night and when it does occur it proceeds irregularly. Sachs' method (A., 1885, 289) determines, not true evacuation, but some magnitude

connected with the excess of assimilated material in the leaves; it is hence regarded as unsuitable for investigating the diurnal evacuation. The method proposed by the authors is based on a parallel determination of the increase of the dry matter during photosynthesis, and results obtained in this way with the potato are sensibly constant for different plants. The daily evacuation proceeds differently with the two plants examined, the potato and the pea. With the former, evacuation takes place mainly during the night and does not occur when photosynthesis is most energetic; with the pea, on the other hand, evacuation is most marked when photosynthesis is at its maximum. Since the potato accumulates mostly insoluble, and the pea exclusively soluble, carbon in its leaves, a connexion between the form of the stored material and the character of the evacuation seems probable. T. H. POPE.

**Relation of total nitrogen to regeneration in the willow.** P. A. DAVIES (Science, 1930, 72, 277).—In *Salix nigra*, shoots develop in the area of highest total nitrogen (per g. dry weight) whilst roots are not confined to that of lowest total nitrogen but may appear along the entire cutting. L. S. THEOBALD.

**Rôle of ammonia in the synthesis of proteins in higher plants.** J. BJÖRKSTÉN and I. HIMBERG (Biochem. Z., 1930, 225, 441—446).—The amount of ammonia produced from urea by leaves from wheat seedlings is independent of the concentration of the urea present, but is increased if the leaves are first narcotised. No urease was detected in the preparations of the leaves. Although acetamide and butyramide are as effective as sources of nitrogen for the synthesis of proteins as is urea, no ammonia is produced from these amides by the leaves even after narcosis. It is concluded that ammonia plays no important direct part in the synthesis of proteins in higher plants, and a possible method of formation of proteins from amides and pyruvic acid is suggested. W. MCCARTNEY.

**Nitrogen metabolism in the leaves of *Vitis* and *Rheum*.** H. L. NEWBY and W. H. PEARSALL (Proc. Leeds Phil. Soc., 1930, 2, 81—85).—The total, water-soluble, and -insoluble nitrogen contents of the fresh leaves of the vine (*Vitis vinifera*) and rhubarb (*Rheum rhabarbaricum*) are studied. The ratio of protein to soluble nitrogen changes with the age of the leaf and increases in cut leaves dried by exposure to the air. These changes are correlated with fluctuations in the acidity of the first aqueous extract. F. O. HOWITT.

**Cambial activity and seasonal starch content in sycamore (*Acer pseudoplatanus*).** G. COCKERHAM (Proc. Leeds Phil. Soc., 1930, 2, 64—80).—Comparative determinations of the starch content at various points on the tree were made over the course of a year. Two maxima and two minima occur, the former in late winter and at leaf-fall and the latter in early winter and just after bud-break. The direction of starch formation and disappearance is given and a tentative correlation between fluctuations in starch content and seasonal changes in cambial activity is advanced. F. O. HOWITT.

**Colorimetric micro-reactions of the glutenogenic proteins and cellulosic gels of wheat grain.** P. BRÛÈRE (Compt. rend., 1930, 191, 792—794).—Treatment of a section of the grain with a 0.05% solution of bromocresol-green in alcohol causes the protein material to be coloured blue. The colorations with bromocresol-purple show that the periphery is less acidic than the nucleus. Superposition of phenosafranine causes the cellulosic gels to be coloured orange or red. H. BURTON.

**General occurrence of alkaloids in *Buxaceae*.** E. MARTIN-SANS (Compt. rend., 1930, 191, 625—626).—The occurrence of alkaloids (usually situated in morphologically distinct secretory cells) in nine species of *Buxaceae* has been demonstrated microchemically; no alkaloid was detected in *Daphniphyllum macropodium*, which is possibly not to be included among the *Buxaceae*. R. CHILD.

**Quinic acid as metabolic product in the young shoots of *Picea excelsa*.** A. KIESEL (Planta, 1928, 6, 519—525; Chem. Zentr., 1930, i, 3197).—The quinic acid amounted to 10% of the dry weight. Its formation may take place according to the equation  $C_6H_{12}O_6 + HCHO - H_2O = C_7H_{12}O_6$ .

A. A. ELDRIDGE.  
**Chemistry of halophytes.** II. J. ZELLNER and E. ZIKMUNDA (Monatsh., 1930, 56, 197—199; cf. A.; 1927, 387).—The ethereal extract of *Salicornia herbacea*, L., contains semi-solid material (1.29%; all percentages are of the dry material), the unsaponifiable matter of which contains an alcohol, m. p. 64°, similar to ceryl alcohol, and a sterol; the saponifiable fraction contains resin and fatty acids. The aqueous extract (39.28%) contains tannin (3.51%), betaine, reducing sugars (0.76%), polysaccharides (12.89%), free acids (as KOH) (0.73%), from which oxalic acid is isolated, and ash (20.75%). The dry plant also contains total nitrogen (1.41%), protein-nitrogen (0.89%), crude fibre (20.74%), pentosans (19.32%), methylpentosans (1.29%), and ash (23.14%). A complete analysis of the ash from *Lepidium crassifolium*, L., is given. H. BURTON.

**Detection of saponin in plants with "blood gelatin."** R. FISCHER (Monatsh., 1930, 56, 282—316).—A method is described (cf. Pharm. Monatsh., 1928, 9, I) for the detection of saponin which involves treatment of a plant section with a solution of gelatin containing a few drops of defibrinated ox-blood ("blood gelatin"); the gelatin used is clarified by treatment with egg-albumin in M/30-phosphate buffer containing sodium chloride, and the solutions are made up in phosphate buffers and then sterilised. The presence of saponin in the plant is denoted by the appearance of a transparent, blood-corpuscle-free zone in the gelatin owing to hæmolysis, which is often discernible only under the microscope. The method is applicable to drugs.

[With J. THIELE.]—The effect of hydrogen ion concentration of the "blood gelatin" on hæmolysis is studied. Thus, *Radix saponariae* shows slight hæmolysis at  $p_H$  7.4 and 8.4, but at  $p_H$  10 and especially 6.1 hæmolysis is more pronounced (cf. Kofler and Lázár, A., 1928, 318). Spinach leaves and *R. senega* show a sudden fall in their hæmolytic action when



the  $p_H$  of the "blood gelatin" rises. Other examples are quoted.

In many cases, the hæmolytic action of the saponin-containing plant is abolished when the section is warmed with an ethereal, alcoholic, or ethereal-alcoholic solution of cholesterol, probably owing to combination of the saponin and cholesterol. This occurs in the plant cells and the complex formed is non-hæmolytic. The complex is, however, decomposed by boiling xylene and the hæmolytic activity of the original preparation restored. Various examples are quoted.

[With H. SCHROPP.]—The above method is applied to 43 varieties of *Caryophyllaceæ*; various parts of the plants are examined.

[With H. NEWESELY.]—The hæmolytic activity of 97 species of *Caryophyllaceæ* and 13 *Solanaceæ* is studied.

H. BURTON.

Presence of a polyhydric alcohol in seeds of *Castanea vesca*. F. TRAETTA-MOSCA and M. VENEZIA (Annali Chim. Appl., 1930, 20, 445—448).—This compound, termed *castagnitol*,  $C_8H_{18}O_7 + H_2O$ , m. p.  $164^\circ$ , is optically inactive and does not reduce Fehling's solution or ammoniacal silver nitrate solution. It forms a *hepta-acetyl* derivative, m. p.  $121^\circ$ , and an *iodide*, b. p.  $160$ — $162^\circ$ . When oxidised with either nitric acid or bromine it gives a compound which forms a *phenylhydrazone*  $C_8H_{14}O_5(N_2HPh)_2$ , m. p.  $195^\circ$ .

T. H. POPE.

Plant colouring matters. XXVII. Colouring matter of sea-buckthorn berries (*Hippophaë rhamnoides*). P. KARRER and H. WEHRLI (Helv. Chim. Acta, 1930, 13, 1104—1105).—The berries (6 kg.) are crushed, dehydrated with 90% alcohol, dried, and extracted with ether. Hydrolysis of the extracted oil (63 g.) with 8.5% alcoholic potassium hydroxide affords an unsaponifiable fraction from which is isolated 0.1—0.2 g. of zeaxanthin.

H. BURTON.

Active constituent of "Hsi-sin" (*Rhizoma asari Sieboldi*). T. KONDÔ (Keijo J. Med., 1930, 1, 223—247).—By steam-distillation 3.07% of the essential oil, ( $d_{15}^{20}$  1.0113), is obtained. This was fractionated at ordinary pressure into five fractions with  $d$  0.9233—1.0506. From the products of oxidation veratric acid was isolated, in greatest yield from the fraction of b. p.  $245$ — $252^\circ$ . The toxic properties of the oil are described.

P. G. MARSHALL.

Chemistry of higher fungi. XXI. *Polyporus sulfureus*, L., and *Lentinus squamosus*, Schroet. J. ZELLNER and E. ZIEKMUNDA (Monatsh., 1930, 56, 200—203).—The light petroleum extract of *P. sulfureus* contains a small amount of a sterol-like substance, m. p.  $265^\circ$  (decomp.), which does not, however, give any sterol reactions. The fat extracted, after separation of the above substance, has acid value 92.0, saponification value 173.1, and iodine value (Margosches) 58.4; the unsaponifiable matter (25.16%) contains ergosterol, fungisterol, and a cerebrin-like substance, m. p.  $112$ — $114^\circ$ , similar to that isolated from *P. betulinus* (A., 1913, i, 573). Oxidation of the saponifiable material with potassium permanganate gives palmitic, stearic, and dihydroxy-

stearic acids. The ethereal extract of the fungus contains fumaric acid; the unsaponifiable fraction of the water-insoluble extracted material contains the above sterols. Potassium hydrogen oxalate and mannitol, but not mycose, are extracted from the fungus by alcohol.

The water-soluble portion of the material extracted from *L. squamosus*, Schroet. (*L. lepideus*, Bull.), by alcohol contains mannitol, dextrose, and choline. Hydrolysis of the polysaccharides isolated from the aqueous extract of the fungus with dilute hydrochloric acid gives dextrose as the sole product.

H. BURTON.

Compound of sterol nature from the sepals of the sunflower. L. ZECHMEISTER and P. TUZSON (Z. physiol. Chem., 1930, 192, 22—24).—The benzene extract of the sepals of the sunflower yields a substance,  $C_{21}H_{36}O_2$ , m. p.  $243^\circ$  (corr.),  $[\alpha]_D^{20} +40.4^\circ$ , behaving as unsaturated towards bromine and permanganate. The oxidation product obtained with chromic anhydride in acetic acid furnishes a *semicarbazone*, m. p.  $263^\circ$  (corr.), and a *phenylhydrazone*, m. p. about  $210^\circ$ .

J. H. BIRKINSHAW.

Plant chemistry. XXII. Chemistry of barks. VII. N. FRÖSCHL, J. ZELLNER, and E. ZIEKMUNDA (Monatsh., 1930, 56, 204—211).—The residue from the light petroleum extract of the bark of the black mulberry (*Morus nigra*, L.) is hydrolysed with alcoholic alkali hydroxide, the alcohol evaporated, and the resultant product separated into (a) ether-soluble, (b) aqueous hydrolysate, and (c) an insoluble precipitate (sodium myristate). The following substances are isolated: (a) phytosterol and ceryl alcohol; (b) stearic, myristic, and unsaturated acids (oxidised by potassium permanganate to sativic acid and an unidentified substance, m. p.  $162$ — $163^\circ$ ). Hydrolysis of the small amount of material extracted by ether gives ceryl alcohol and resin acids. The alcoholic extract of the bark contains phlobaphens, and water-soluble tannin and reducing sugars.

The light petroleum extract of the grey alder (*Alnus incana*, L.) contains protalunin, m. p.  $236^\circ$ , in addition to alnulin and alniresinol (cf. A., 1924, i, 814). The residue, after separation of these substances, gives on hydrolysis pure alniresinol, m. p.  $194$ — $195^\circ$ ,  $[\alpha] +33.39^\circ$  (cf. *loc. cit.*; A., 1926, 1281), resin acids, and small amounts of fatty acids. Hydrolysis of the ethereal extract of the light-petroleum-extracted bark furnishes resin acids, phlobaphens, and alnulin, m. p.  $260^\circ$  (acetyl derivative, m. p.  $293^\circ$ ) (cf. *loc. cit.*). Protalunin occurs in green, grey, and black alder. Alniresinol is found in the first two, whilst alnulin is extracted only from the last two varieties.

H. BURTON.

Characteristics of vegetable oils. J. B. MCNAIR (Field. Mus. Nat. Hist. Pub., 1930, No. 276, Bot. Ser. 9, No. 2, 47—68).—A study of the relation of the characteristics of vegetable oils to the habitat of the plants.

CHEMICAL ABSTRACTS.

Cyanogenetic glucosides in Australian plants. II. (A.) *Eremophila maculata*. H. FINNEMORE and C. B. COX. (B.) Presence of enzymes in fodder plants as a factor in the poisoning of stock. [With S. K. REICHARD] (J. Proc. Roy. Soc. N.S. Wales,

1929, 63, 172—182).—From the air-dried leaves of the fuchsia, *E. maculata*, prunasin has been obtained in a yield of 8.8%.

Neither *E. maculata* nor *Heterodendron olaeifolium*, which also contains a large amount of a cyanogenetic glucoside, contains cyanogenetic enzymes. In native grasses enzymes capable of hydrolysing prunasin and sambunigrin are more abundantly distributed than those which attack amygdalin. The unripe pods of *Acacia suaveolens* and *A. Georgina* decompose prunasin more rapidly than sambunigrin, whilst amygdalin is not attacked.

T. H. MORTON.

**Chemistry of digitalis seed.** S. H. CULTER (Amer. J. Pharm., 1930, 102, 545—547).—The amber-coloured fatty oil (31.4% yield; 1.86% of unsaponifiable matter) obtained from digitalis seeds contains linoleic acid, but the presence of oleic acid could not be proved. The fatty acid isolated from the dibromide forms an insoluble potassium soap and does not give a positive colour test for oleic acid.

E. H. SHARPLES.

**Chemistry of *Aegle marmelos* (the Indian Bel).** B. B. L. DIXSITT and S. DUTT (J. Indian Chem. Soc., 1930, 7, 759—764).—The roots, bark, leaves, fruit, and seeds of *A. marmelos* have been extracted with various solvents. The products isolated are an "active principle" from the fruit, termed *marmelosin*, m. p. 103°, and an oil from the seeds (11.94%), having  $d_{20}^{20}$  0.914, saponification value 195.2, Hehner value 91.3, and iodine value 126.1.

R. CHILD.

**Quantitative extraction and separation of the plastid pigments of tobacco.** P. D. PETERSON (Plant Physiol., 1930, 5, 257—261).—A modified method for the separation of carotene and xanthophyll of plant pigments is described; the formation of emulsions is avoided. The use of light petroleum instead of ether increases the formation of emulsions and affords low and erratic yields of xanthophyll. The altered green pigment was isolated.

CHEMICAL ABSTRACTS.

**Polyphenols of tobacco.** A. SCHMUK (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 7—13).—From the precipitate formed by addition of basic lead acetate to the aqueous extract of unfermented tobacco (Tyk-Kulak), a substance may be isolated which dissolves readily in water, exhibits tanning properties, and gives an intense green coloration with ferric chloride. It does not reduce Fehling's solution, but yields a reducing methylpentose (rhamnose) on acid hydrolysis, which takes place only with difficulty. The substance is apparently a glucoside, another of its components being a depside, containing both caffeic and quinic acids. Treatment with alkali hydroxide solution yields protocathechuic acid.

T. H. POPE.

**Inositol in tobacco.** A. SCHMUK (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 15—18).—The aqueous extract of fermented tobacco (Tyk-Kulak) contains a considerable proportion of inositol, and this may play a part in the biochemical processes resulting in the formation of nicotine and may serve

to explain the presence in the nicotine molecule of a six-membered ring, which is absent from the protein molecule. When tobacco seeds are treated with dilute mineral acid and the resulting solution is precipitated with alkali, phytin is obtained to the extent of 7—10% on the dry matter of the seeds.

T. H. POPE.

**Acids of tobacco. II.** A. SCHMUK and PIATNICKI (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 19—26).—The ethereal extract of fermented tobacco (Samsun) contains citric, caffeic, and probably chlorogenic acids. Although the presence of quinic acid has been observed by various authors, it could not be detected and it may form one of the components of chlorogenic acid.

T. H. POPE.

**Content of formic acid in tobacco.** A. SCHMUK and S. KASCHIRIN (U.S.S.R. State Inst. Tobacco Ind., Bull. 69, 1930, 29—32).—Using a modification of Fincke's method for determining formic acid (A., 1913, ii, 636), it is found that this acid is present in both fermented and unfermented tobaccos to the extent of 0.02—0.17%. Tobaccos of high and low grades contain rather more than those of medium quality. Fermented tobaccos are richer in the acid than unfermented ones, the proportion increasing with the energy of the fermentation process. Both formic acid and its salts diminish the strength of flavour of tobacco.

T. H. POPE.

**Influence of the degree of pulverisation and weight of samples on quantitative analyses, especially of plant-tissues.** R. C. MALHOTRA (Ind. Eng. Chem. [Anal.], 1930, 2, 398—401).—Analyses of various samples of plant-tissues, varying in fineness from 30- to 130-mesh, show that lower percentages, especially of hemicelluloses, pentosans, starch, and sugars, are obtained with the coarser powders, and that the most uniform results are obtained by using 60-mesh samples. The weight of sample recommended is 3—4 g., larger or smaller samples yielding low percentages.

H. F. GILLBE.

**Micro-determination of iodine.** J. F. REITH (Biochem. Z., 1930, 224, 223—241).—Various methods for micro-determination of iodine are critically reviewed and it is shown that, although Fellenberg's method gives good results for iodine in aqueous solutions of salts, it is subject to considerable error when applied to organic substances. The author's improved method (A., 1929, 337, 414, 1410) is simplified and supplemented. With this method, loss of iodine is greatly decreased but not completely avoided.

P. W. CLUTTERBUCK.

**Treatment of extracts for toxicological examination.** P. CHERAMY and F. LAGARCE (J. Pharm. Chim., 1930, [viii], 12, 366).—The addition of a 10% solution of barium chloride, until no further precipitation occurs, to the aqueous extract after removal of the alcohol yields a liquid which can be readily extracted with volatile solvents. The precipitate does not remove any ureides.

C. C. N. VASS.